

ALTERNATIVE FUELS FROM BIOMASS SOURCES



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Licensing

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1: WHY ALTERNATIVE FUELS FROM BIOMASS?

1.1: Why Biofuels?

1.2: Increasing Energy Demand

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1.1: Why Biofuels?

Part of the purpose of the course is to help you to understand why biofuels are needed and how to make them, at the current state-of-the-art.

Why biofuels? To look at the situation a little more broadly, the question then becomes: why alternative fuels?

As **climate change** becomes an issue of ever-stronger concern in the world, stronger efforts are being devoted to tackling this issue. The International Energy Agency (IEA) has recently proposed the 2 °C scenario (2DS) as a way to handle the climate change issue. The 2DS has become a largely used quote for many policymakers and scientists. The 2DS scenario requires that carbon dioxide (CO₂) emissions in 2060 should be reduced by 70% in comparison to the 2014 level. The transport sector plays an important role to achieve this goal considering that the transportation sector is responsible for about 23% of total CO₂ emissions. Although electricity has been considered as a promising option for reducing CO₂ emissions in transportation (Yabe, Shinoda, Seki, Tanaka, & Akisawa, 2012), transport biofuel is estimated to be the key alternative energy in the transport sector (Ahlgren, Börjesson Hagberg, & Grahn, 2017). The share of biofuels in total transportation-fuel consumption by 2060 is predicted to be 31%, followed by electricity at 27% based on the mobility model results of IEA for the 2DS. Biofuels production must be increased by a factor of 10 to achieve this goal (Oh, Hwang, Kim, Kim, & Lee, 2018). In addition to the need for climate change adaptation, the **increasing concerns over energy security** is another main driver for the policy-makers belonging to the Organisation for Economic Co-operation and Development (OECD) to promote the production of renewable energy (Ho, Ngo, & Guo, 2014). Last but not least, **world energy demand will continue increasing**. The world energy demand was 5.5×10^{20} J in 2010. The studies predict an increase of a factor of 1.6 to reach a value of 8.6×10^{20} J in 2040. The bioenergy delivery potential of the world's total land area excluding cropland, infrastructure, wilderness, and denser forests is estimated at 190×10^{18} J yr⁻¹, 35% of the current global energy demand (Guo, Song, & Buhain, 2015).

A circle with 3 sections containing: Energy demand with an arrow leading 2 climate change then energy security & back to Energy Demand

Fig 1.1: Three main reasons to promote sustainable biofuel production and usage. Credit: Dr. Hilal Ezgi Toraman

In short, there are three main reasons to develop biofuels (Fig 1.1):

1. to meet the needs of increasing energy demand;
2. dependence on foreign fuel sources can be problematic, depending on US domestic fuel production;
3. to reduce greenhouse gas (GHG) emissions.

We will explore each of these reasons in more depth in the following sections.

References

Ahlgren, E. O., Börjesson Hagberg, M., & Grahn, M. (2017). Transport biofuels in global energy-economy modeling—a review of comprehensive energy systems assessment approaches. *Gcb Bioenergy*, 9(7), 1168-1180.

Guo, M. X., Song, W. P., & Buhain, J. (2015). Bioenergy and biofuels: History, status, and perspective. *Renewable & Sustainable Energy Reviews*, 42, 712-725. doi:10.1016/j.rser.2014.10.013

Ho, D. P., Ngo, H. H., & Guo, W. (2014). A mini review on renewable sources for biofuel. *Bioresource Technology*, 169, 742-749. doi:10.1016/j.biortech.2014.07.022

Oh, Y. K., Hwang, K. R., Kim, C., Kim, J. R., & Lee, J. S. (2018). Recent developments and key barriers to advanced biofuels: A short review. *Bioresource Technology*, 257, 320-333. doi:10.1016/j.biortech.2018.02.089

Yabe, K., Shinoda, Y., Seki, T., Tanaka, H., & Akisawa, A. (2012). Market penetration speed and effects on CO₂ reduction of electric vehicles and plug-in hybrid electric vehicles in Japan. *Energy Policy*, 45, 529-540.

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1.2: Increasing Energy Demand

The energy needs of most of the developed countries in the western world are increasing at a modest level. However, in underdeveloped countries, where the economy is booming, energy demands are increasing dramatically, e.g., in China and India. Figure 1.2 shows the gross domestic product (GDP) growth rate of the countries of the world in 2009. Most of the growth occurred in Asia. Africa and South America experienced some growth in areas, while the US did not experience much growth. However, if many of the third world countries were to dramatically increase their standard of living, there are estimates that worldwide energy consumption would double (the world uses ~13 TW). But where would that energy come from, particularly since there aren't huge stockpiles of crude oil sitting around? Petroleum cannot supply it all, and neither can natural gas or coal.

world map showing GDP growth rate as described in the text above

Credit: [GunnMap](#) via Wikimedia Commons

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1.3: Problematic Dependence on Foreign Fuel Sources

1.3 Problematic Dependence on Foreign Fuel Sources

The US is highly dependent on crude oil to produce fuels for transportation. Figure 1.3 shows how the transportation sector is almost all oil-based, and the other sources barely make a dent in the hold petroleum has. Up until the last few years, the US has been highly dependent on foreign sources of oil. The US was the world's largest petroleum **consumer** (EIA, 2012), but was third in crude oil **production**. Over half of the material that is imported into the US comes from the Western hemisphere (North, South, and Central America, and the Caribbean), but we also import 29% from Persian Gulf countries (Bahrain, Iraq, Kuwait, Saudi Arabia, and the United Arab Emirates). The top 5 sources of net crude oil and petroleum **imports** include: 1) Canada, 28%, 2) Saudi Arabia, 13%, 3) Mexico, 10%, 4) Venezuela, 9%, and 5) Russia, 5%. According to CNN Money, the US is behind Russia and Saudi Arabia in oil production for the first three months of 2016. See the following link for further information: [World's Top Oil Producers](#). However, this situation recently changed and the US became the world's largest oil producer in 2018 for the first time since 1973. See the following link for further information: [America is now the world's largest oil producer](#).

chart showing allocation of energy sources according to sector in US, see text description in link below

Figure 1.3: Allocation of energy sources by sector in the US (Quadrillion Btus)

[Click here for a text description of Figure 1.3](#)

Allocation of Energy Sources in the US: Transportation Sector

Allocation of Energy Sources in Quadrillion Btus'

Petroleum: 24.8

Natural Gas: 0.8

Coal: 0.0

Renewable: 1.1

Nuclear: 0.0

Allocation of Energy Sources in the US: Industrial Sector

Allocation of Energy Sources in Quadrillion Btus'

Petroleum: 8.0

Natural Gas: 8.9

Coal: 1.4

Renewable: 0.2

Nuclear: 2.3

Allocation of Energy Sources in the US: R&C Sector

Allocation of Energy Sources in Quadrillion Btus'

Petroleum: 1.5

Natural Gas: 7.2

Coal: 0.1

Renewable: 0.8

Nuclear: 0.0

Allocation of Energy Sources in the US: Electricity Sector

Allocation of Energy Sources in Quadrillion Btus'

Petroleum: 0.4

Natural Gas: 9.1

Coal: 15.6

Renewable: 4.6

Nuclear: 8.0

Credit: Based on [EIA Annual Energy Review, 2012](#)

So, while oil is fairly available currently, there is extensive potentially explosive turmoil in many petroleum-producing regions of the world, and, in several places, the US's relationship with some oil-producing countries is strained. China and India are now aggressive and voracious players in world petroleum markets because of high economic growth (as pointed out in the previous section). Saudi Arabia production is likely "maxed out," and domestic oil production peaked in 1970. While the US dependence on imported oil has declined after peaking in 2005, it is clear that if any one of the large producers decides to withhold oil, it could cause a shortage of fuel in the US and would cause the prices to skyrocket from an already high price (depending on the type of crude oil, the price of oil is currently 100–100–106/bbl) (see [U.S. Energy Information Administration website](#)). Figure 1.4 is a graphic showing the price level of oil from 1970 until recently (adjusted for inflation using the headline CPI). As you can see, there has been significant volatility in the price of oil in the last ~50 years. One of the first spikes came in 1974 when OPEC became more organized and withheld selling oil to the US. It was a true crisis at that point, with gasoline shortages causing long lines and fights at gas stations, with people filling up only on certain days depending on their license plates. It had a high spike in 1980, but a significant low in 1986. When the price of oil hit a significant low in 1998, the government took steps to lower the tax burden on oil companies. But when the prices went back up, the law remained in place, and currently, oil companies do not have to pay taxes on produced oil. When the reduced tax burden went into place in the late 90s, it made sense, but oil companies have

continued to convince Congress with lobbyists that it should stay that way. What do you think?

history of crude oil prices. See text alternative below

Figure 1.4: Crude Oil Price History Chart. Oil price level back to 1970, adjusted for inflation using the headline CPI.

[Click here for a text description of Figure 1.4](#)

Graph of WTI Crude Oil price between 1945 and 2015. The most important years are described in text above image. The general trends are as follows in \$/gallon (all numbers are approximate):

1950: \$28

1960: \$25

1970: \$19

1972: \$50

1980: \$118

1986: \$28

1990: \$64

1998: \$15

2000: \$44

2006: \$140

2010: \$110

2015: \$40

Credit: [Macrotrends](#)

Processing of oil into useable fuels has also increased. At one point in 2015, the price of gasoline nationwide stayed at >\$3.50/gal, *but then, the price has dropped down to as low as \$2.00/gal*. As we will discuss in a later lesson, there are several aspects that contribute to the price of gasoline. Figure 1.5a is a graphic that shows the price volatility for gasoline from December 2005 - December 2015, and Figure 1.5b shows a breakdown of what goes into the price of gasoline. Figures 1.6a and 1.6b are similar graphics, but for diesel.

Average Gas Price over 120 Months. See text alternative below

Figure 1.5a: Gasoline prices over a 10 year period. As can be seen in the graphic, the range in gasoline prices has been from \$1.43-4.10 per gallon. The lowest price in December 2008 was \$1.43, but the high was \$4.10 in June 2008. Most of the price changes have been less dramatic with many lesser peaks and valleys over the 10 year period.

[Click here for a text description of Figure 1.5a](#)

120 Month Average Retail Price per gallon of Regular Gas in the US. Data from 12/10/05 to 12/10/15. General Trends are as follows (all numbers are visual approximations):

8/2006: \$2.97
12/2006: \$2.10
4/2007: \$3.15
5/2008: \$4.10
1/2009: \$1.59
5/2009: \$2.59
10/2010: \$2.84
5/2011: \$4.00
2/2012: \$3.90
6/2012: \$3.35
3/2013: \$3.85
11/2013: \$3.20
7/2014: \$3.60
4/2015: \$2.40
12/2014: \$2.00

Credit: [GasBuddy](#)

Gas price breakdown, 10/2015. Price: 2.29 Taxes= 20%, Distribution & Marketing= 19%, Refining= 15%, Crude Oil= 47%

Figure 1.5b: The breakdown of gasoline prices for October 2015. Retail Price=\$2.29/gallon.

Credit: By US DOE EIA (Gasoline and Diesel Fuel Update) [Public domain], via Wikimedia Common

chart showing allocation of energy sources according to sector in US, see text description in link below

Figure 1.6a: Diesel prices over a 20 year period. As can be seen in the graphic, the range in diesel prices has been from \$1.10-4.60 per gallon. The lowest price in December 2008 was \$2.05, but the high was \$4.60 in June 2008. Most of the price changes have been less dramatic with many lesser peaks and valleys over the 10 year period. The current price range of diesel is ~\$2.50-2.80 per gallon.

[Click here for a text description of Figure 1.6a](#)

Diesel Price per Gallon in the US from 1994 to 2015. General Trends are as follows (all numbers are visual approximations).

3/1994 – 3/1999: ~\$1.20

9/2000: \$1.70

3/2002: \$1.20

3/2003: \$1.70

9/2005: \$3.20

9/2006: \$3.20

3/2008: \$4.60

3/2009: \$2.20

3/2010: \$3.00

3/2011-3/2014: \$4.00

3/2015: \$2.80

Credit: [U.S Energy Information Administration](#)

Diesel price breakdown, 10/2015. Price: 2.52 Taxes= 21%, Distribution & Marketing= 19%, Refining= 18%, Crude Oil= 43%

Figure 1.6b: The breakdown of diesel prices for October 2015. Retail Price=\$2.52/gallon.

Credit: By US DOE EIA (Gasoline and Diesel Fuel Update) [Public domain], via Wikimedia Commons

Natural gas prices have been volatile over recent years. As you can see in Figure 1.7, the production of natural gas and oil has expanded in the USA; so, the price went up in recent years, but lately, it has been going down.

Figure 1.7: Natural gas price trend from 2009 until 2020. Natural gas price is in \$ per MMBtu.

[Click here for a text description of Figure 1.7](#)

Natural Gas Price (\$/MMBtu) between 2009 and 2020. General Trends are as follows (approximations):

2009: 5.24

Mid 2009: 3.8

2010: 5.83

Mid 2010: 4.8

2011: 4.49

Mid 2011: 4.8

2012: 2.67

Mid 2012: 2.46

2013: 3.33

Mid 2013: 3.83

2014: 4.71

Mid 2014: 4.59

2015: 2.99

Mid 2015: 2.78

2016: 2.28

Mid 2016: 2.59

2017: 3.3

Mid 2017: 2.98

2018: 3.87

Mid 2018: 2.97

2019: 3.11

Mid 2019: 2.4

2020: 2.02

Mid 2020: 1.63

Credit: [U.S. Energy Information Administration \(open source data\)](#)

And even though coal isn't the "popular" fuel currently, almost 40% of electricity generation comes from coal. Power plants began switching to natural gas in the last few years because it was quite inexpensive in 2012, and there is a common belief that natural gas would put less carbon in the atmosphere than coal because of the molecular ratio of hydrogen to carbon (natural gas, CH₄, 4:1; petroleum, CH₂, 2:1; and coal, CH, 2:1). However, there are also issues with natural gas that we will discuss in another section. Figure 1.8 shows the price variation in coal over recent years. When the price of oil increased in 2010, so did the price of coal. However, as natural gas prices went down, so did prices for coal. The price of coal per short ton was \$40.00 in 2016. However, the price of coal typically has a range depending on the use of it (higher quality coal is used to make a carbon material called coke, a material that is used in the manufacturing of various metal materials). Lower priced coal tends to be coal that has more "bad actors" such as sulfur and nitrogen (we will discuss in another lesson) or higher water content or lower energy content.

Thermal Coal CAPP prices between 2010 and 2015. See text alternative below

Figure 1.8: Price of coal (thermal coal refers to coal used for power plants) from 2010-2015. The price of coal has ranged from **\$83/ton in Feb 2011 to \$41/ton in October 2015. Currently, the price of coal is ~\$40 per ton.**
[Click Here for a text description of Figure 1.8](#)

Thermal Coal CAPP Price (\$/ton) between Jan 2010 and Oct 2015. General Trends are as follows (all numbers are visual approximations):

1/2010: \$68/ton

2/2011: \$83/ton

4/2012: \$58/ton

6/2013: \$54/ton

9/2015: \$60/ton

10/2015: \$41/ton

Credit: InfoMine.com

In recent years, petroleum became less available and more expensive, and replacement alternative fuels emerged because the economics were beginning to become more favorable. However, due to lower demand and high petroleum supply, prices drastically dropped and may affect the development of alternative fuels. There is one factor that will most likely reverse this trend; energy demands will continue to increase worldwide. For future transportation fuel needs, most likely a liquid fuel will be necessary, and no one source will be able to replace petroleum. Figure 1.9 shows the breakdown of how much of the world's energy consumption is supplied by various materials, with fossil fuels use in 2011 constituting 83%. The EIA predicts that in 2040, fossil fuel use will only decrease to 78%, even with a doubling of biomass use. If significant changes are going to happen with reducing fossil fuel usage, then a major transformation will need to happen.

graph showing world energy consumption, see text description in link below

Figure 1.9: World energy consumption for 2011 and projected for 2040. The pie graphs predict that fossil fuels, coal, petroleum, and natural gas, will continue to dominate world consumption even until 2040, with slight increases in the use of biomass and other renewables.
[Click here for a text description of Figure 1.9](#)

Text Version of Two Pie Charts showing Energy Consumption in 2011 and Projected Energy Consumption in 2040

Year	Petroleum	Natural Gas	Coal	Nuclear	Hydropower	Biomass	Other Renewables
2011	37%	26%	20%	8%	3%	4%	2%
2040	31%	28%	19%	9%	3%	7%	3%

Credit: Institute for Energy Research

1.4: Reduction of Greenhouse Gas (GHG) Emission

1.4 Reduction of Greenhouse Gas (GHG) Emission

There is a scientific consensus that greenhouse gas (GHG) production is increasing, which has led to climate change and several other environmental concerns. As much as oil companies and conservative think tanks don't want this to be true, it is, and much of the severe weather that has been occurring worldwide is due to climate change issues. There is a significant amount of evidence to substantiate the existence of climate change and the overall warming of the earth. The change in climate is due to the Greenhouse Effect; it is a natural effect, caused by CO₂ and water vapor naturally present in the atmosphere. The focus for debate (scientific and political) has been on whether there is also an anthropogenic greenhouse effect causing further climate change. Carbon dioxide (CO₂) is not the only greenhouse gas (methane, CH₄ is another potent GHG; will be discussed further in upcoming sections), but most of the debate focuses on it. And it is thought that the dramatic increase in CO₂ in the atmosphere is due to burning fossil fuels.

The world is highly dependent on fossil fuels; the US is also highly dependent on fossil fuels. As we saw in Figure 1.9, in 2011, only 17% of the fuel consumed was non-fossil fuel based, and that consumption is projected to be 21% in 2040. And about half of that is renewables.

There is a mountain of evidence indicating that the planet is warming. Figure 1.10 shows a graphic depicting CO₂ levels plotted with change in average global temperatures from 1880-2010. The change has been most dramatic in the last 30 years.

Plot of global temperature and CO₂ concentration. Described in text above and in caption

Figure 1.10: Plot of global temperature and CO₂ concentration from 1880-2010. The graph shows the global temperature (56.9-58.4 °F) and the rise in CO₂ concentration (260-400 ppm) from 1880 through 2010. The dramatic increase in both occurred from 1940 through now, the time period where great economic growth meant increasing fossil fuel use.

Credit: [NOAA/ Global Climate Change Indicators](#)

In the Arctic and Antarctic regions, the ice pack and glaciers are melting, and at an even faster rate than originally anticipated. Scientists have found that increasing atmospheric temperatures are not the only cause of this; the melting is causing water currents to shift and move warmer water around the poles, so that melting is happening underneath the ice pack. Figure 1.11a shows the change in the ice pack from 1984 to 2012 for the Arctic, while Figure 1.11b shows the changes in sea level, globally, from 1993-2012.

Try This

Visit [Earth Observatory\(link is external\)](#) to try an interactive tool that allows you to manipulate images to show dramatic changes in ice pack.

Changes in polar ice cap around greenland between 1984 & 2012. In 1984 ice was over double and touched alaska & canada. In 2012 it does not

Figure 1.11a: Changes in polar ice cap from 1984 to 2012, please the significant reduction of ice in 2012

Credit: [NASA Earth Observatory](#)

Sea level rise globally. No change to slight lower on Pacific coast of the Americas. Everywhere else rose. Large rise in south pacific.

Figure 1.11b: Globals Sea level rise between Jan 1993 and Dec 2012.

Credit: [NOAA/NESDIS/STAR](#)

Another problem could stem from the increased production of natural gas. Natural gas consists primarily of methane. Sources

include petroleum and natural gas production systems, landfills, coal mining, animal manure, and fermentation of natural systems. Methane has 25 times the global warming potential of CO₂. Figure 1.12 shows the total GHG percentages from various sources. However, Figure 1.13 shows the emissions of various GHG emissions from 1990-2014. The EPA points out that overall emissions of CH₄ have been reduced by 11% from 1990-2012. However, an article published in Nature (Yvon-Durocher, March 2014) suggests that there may be an unexpected consequence of warming temperatures; global warming can increase the amount of methane evolved from natural ecosystems. So, it remains to be seen what impacts can happen that have not been included in climate change models.

Emission 2014 pie chart: Electricity 30%, Transportation 26%, Industry 21%, Commercial & Residential 12%, Agriculture 9%.

Figure 1.12: All emission estimates from the Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990-2014.

Credit: [EPA](#)

(1990-2014) Emissions in metric tons of CO₂ equivalents. CO₂ = ~7,000, Methane = 1,200, Nitrogen = 500, Fluorinated gases = 200

Figure 1.13: Levels of various greenhouse gas emissions from 1990 until 2014. Carbon dioxide (CO₂) and methane (CH₄) emissions in the United States dominate the gases emitted, but keep in mind the increased effect of methane, nitrous oxide, and fluorinated gases have a much greater effect per ton than carbon dioxide does. Between 1990 and 2014, emissions increased from sources associated with agricultural activities, while emissions decreased from sources associated with the exploration and production of natural gas and petroleum products.

Credit: [EPA](#)

There are several possible responses to abate CO₂ and CH₄: 1) do nothing; 2) reduce CO₂ and CH₄ prudently; 3) drastically reduce energy use; and 4) move to a carbon-free society. The easiest, but quite possibly the most damaging in the long run, is to do nothing - currently, there are some nations that are pushing to at least increase conservation. The use of hybrids has actually decreased our use of gasoline, as the increase in Corporate Average Fuel Economy (CAFE) standards has had an impact. However, prudent measures to reduce GHG will most likely not be enough to make a huge impact. Therefore, the use of biofuels could have great potential for reducing the impact of CO₂ and CH₄, if done well. However, some actions in South America have shown that if switching to biofuel growth is not handled well, a greater problem can be created. Some rainforest areas were removed from South America to clear land for producing biofuels, but the rainforests that were removed were burned, putting an excessive amount of CO₂ in the atmosphere. Rainforests have grown over long periods of time, so there was a lot of carbon stored in them - they were also places where exotic animals, plants, and insects lived, so the burning endangered the wildlife species in the rainforests. One thing to always keep in mind: whenever an action is taken in our atmosphere, there is the possibility of a negative consequence that one cannot foresee.

1.5: Assignments

1.5 Assignments

Homework #1

For this homework, you will read two selections and compose an essay.

1. Please read the following selections. Both can be accessed via **Library Resources**.
 - "Chapter 10: Biofuels." *Renewable Energies*. Ed. Jean-Claude Sabonnadiere. Hoboken, NJ: ISTE Ltd/John Wiley & Sons, 2009.
 - "Introduction: An Overview of Biofuels and Production Technologies." *Handbook of Biofuels Production: Processes and Technologies*. Ed. Rafael Luque, Juan Campelo, and James Clark. Oxford: Woodhead Pub., 2011.
2. Write an essay addressing these two questions:
 - Question #1: According to these two papers, what is one main advantage of the use of biofuels?
 - Question #2: According to these two papers, what is one main disadvantage of the use of biofuels?

Some notes on the format:

- Approximate length - 2 pages, double-spaced, 1" margins, 12 point font, name at the top.
- The essay should incorporate answers to both questions.
- Use [APA\(link is external\)](#) citation format.
- Use as filename **your user ID_HW1 (i.e., ceb7_HW1)**.
- Upload it to the **Homework #1 Dropbox**.

(12 points)

Discussion #1

Post a response that includes 2 statements (not your entire essay, but statements) from your Homework #1 essay addressing questions #1 and #2. Take some time to review others' responses. Then respond to at least one other person's post. Grades will reflect critical thinking in your input and responses. Don't just take what you read at face value; think about what is written.

(5 points)

1.6: Summary and Final Tasks

1.6 Summary and Final Tasks

Summary

This lesson was about how using biofuels can benefit society. We looked at increasing energy demands around the world, how economically dependent we are on foreign sources of fuel, and how we don't have much control over what the prices for our fuels will be. We also explored how the growth in GHG emissions is a vital environmental concern and discussed how, without the use of biofuels, we cannot achieve significant reductions in GHG.

References

"U.S. Energy Information Administration - EIA - Independent Statistics and Analysis." [EIA's Energy in Brief: How Dependent Are We on Foreign Oil?\(link is external\)](#) Web. 8 May 2014.

["Greenhouse Gas Emissions: Greenhouse Gases Overview."\(link is external\)](#) EPA. Environmental Protection Agency. Web. 27 May 2014.

Yvon-Durocher, G., Allen, A.P., Bastviken, D., Conrad, R., Gudas, C., St-Pierre, A., Thanh-Duc, N., del Giorgio, P.A., "Methane fluxes show consistent temperature dependence across microbial to ecosystem scales," *Nature*, 507, 488-491, 3/21/2014.

Reminder - Complete all of the Lesson 1 tasks!

You have reached the end of Lesson 1! Double-check the Road Map on the Lesson 1 *Overview* page to make sure you have completed all of the activities listed there before you begin Lesson 2.

Questions?

If there is anything in the lesson materials that you would like to comment on, or don't quite understand, please post your thoughts and/or questions to our *Throughout the Course Questions & Comments* discussion forum and/or set up an appointment for office hour& between 10:00 am-12:00 pm on Thursdays. The discussion forum is checked regularly (Monday through Friday). While you are there, feel free to post responses to your classmates if you are able to help.

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2: EXISTING FOSSIL FUEL TECHNOLOGIES FOR TRANSPORTATION

2.1: Chemistry Tutorial

2.2: Refining of Petroleum into Fuels

2.3: Jet Engines

2.4: Diesel Engines

2.5: Assignments

2.6: Summary and Final Tasks

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2.1: Chemistry Tutorial

2.1 Chemistry Tutorial

The chemical compounds that are important for understanding most of the chemistry in this course are *organic* - that means that the compounds primarily contain carbon, hydrogen, and oxygen atoms (also sulfur and nitrogen). They can also be called hydrocarbons. The basic structures that we will be discussing in this course are called: 1) alkane (aka aliphatic), 2) branched alkane, 3) cycloalkane, 4) alkenes (double-bonds), 5) aromatic, 6) hydroaromatic, and 7) alcohols. First, I will show the atoms and how they are connected using the element abbreviation and lines as bonds, and then I will show abbreviated structural representations.

1. Alkane - atoms are lined up. For stick representation, each corner represents a CH₂ group, and each end represents a CH₃ group.

Name	Atoms and Bonds
Heptane (7 C atoms)	Straight Line of 7 C's connected to each other. The connected to it and all the others ha

2. Branched Alkane - still an alkane, but instead of a straight line, the carbons are branched off of each other.

Name	Atoms and Bonds
Isobutane (4 C atoms)	Straight line of 3 Cs. The two end C's have 3 H's att has one H and one branch with a CH
Isopentane (5 C atoms)	Straight line of 4 Cs. The 2 end C's have 3H's attach Cs has 1 H and 1 branch with a CH ₃ group, the

3. Cycloalkanes - again, still an alkane, but forms a ring compound.

Name	Atoms and Bonds
Cyclohexane (6 C atoms)	hexagon with a CH ₂ at every ve

4. Alkenes - alkanes that contain a double bond.

Name	Atoms and Bonds
Pentene (5 C atoms)	line of 4 Cs connected by single lines (bond) and a f (double bond)

5. Aromatic - hydrocarbon ring compound with single and double bonds, significant differences in properties.

Name	Atoms and Bonds
Benzene (6 C atoms)	hexagon with CH on every vertice. Every other edge lines)

6. Hydroaromatics - hydrocarbon ring compound with an aromatic and an alkane in one molecule.

Name	Atoms and Bonds
1,2,3,4-tetrahydronaphthalene, aka tetralin (10 C atoms)	hexagon with alternating double bonded : single bonded side to a hexagon v

7. Alcohols - hydrocarbon with -OH functional group.

Name	Atoms and Bonds
Butanol (4 C atoms)	Line of 4 Cs in a row. The first C has 3Hs the last 3 have final C also has an -OH connect
Ethanol (2 C atoms)	A CH ₃ connected to a CH ₂ connected

The following table shows common hydrocarbons and their properties. It is important to know the properties of various hydrocarbons so that we can separate them and make chemical changes to them. This is a very brief overview - we will not yet be going into significant depth as to why the differences in chemicals affect the properties.

Table 2.1: List of Common Hydrocarbons and Properties

Name	Number of C Atoms	Molecular Formula	bp (°C),
Methane	1	CH ₄	-161.5
Ethane	2	C ₂ H ₆	-88.6
Propane	3	C ₃ H ₈	-42.1
Butane	4	C ₄ H ₁₀	-0.5
Pentane	5	C ₅ H ₁₂	36.1
Hexane	6	C ₆ H ₁₄	68.7
Heptane	7	C ₇ H ₁₆	98.4
Octane	8	C ₈ H ₁₈	125.7
Nonane	9	C ₉ H ₂₀	150.8
Decane	10	C ₁₀ H ₂₂	174.1
Tetradecane	14	C ₁₄ H ₃₀	253.5
Hexadecane	16	C ₁₆ H ₃₄	287
Heptadecane	17	C ₁₇ H ₃₆	303
Eicosane	20	C ₂₀ H ₄₂	343
Cyclohexane	6	C ₆ H ₁₂	81
Cyclopentane	5	C ₅ H ₁₀	49
Ethanol	2	C ₂ H ₆ O	78
Butanol	4	C ₄ H ₁₀ O	118
Pentene	5	C ₅ H ₁₀	30
Hexene	6	C ₆ H ₁₂	63
Benzene	6	C ₆ H ₆	80.1

Name	Number of C Atoms	Molecular Formula	bp (°C),
Naphthalene	10	C ₁₀ H ₈	218
1,2,3,4-Tetrahydronaphthalene	10	C ₁₀ H ₁₂	207

2.2: Refining of Petroleum into Fuels

2.2 Refining of Petroleum into Fuels

Much of the content in this particular section is based on information from Harold H. Schobert, Energy and Society: An Introduction, 2002, Taylor & Francis: New York, Chapters 19-24.

The following figure is a *simplified* flow diagram of a refinery. Since it looks relatively complicated, the diagram will be broken into pieces for better understanding.

see text description below

Figure 2.1: Simple flow diagram of an oil refinery. Crude oil is the first process, and it breaks the products down into LPG, straight-run gasoline, naphtha/kerosene/diesel, fuel oil, and resid. LPG is used in the alkylation process to add carbons; straight-run gasoline is processed in a catalytic reformer to change to a branched-chain alkane; naphtha/kerosene/diesel is hydrotreated and dewaxed; fuel oil is catalytically cracked to make more gasoline, and resid is thermally cracked to make more gasoline.

[Click Here for a text description of figure 2.1](#)

This is a simple flow diagram of crude oil refinery.

Crude oil enters and goes to distillation.

From distillation:

LPG (gases) goes through alkylation to become O.N. 100 Motor Fuel Alkylate which can go on to become gasoline

Straight-run gasoline goes through catalytic reforming to become O.N. 95 Reformate which can go on to become gasoline

Naphtha, Kerosene and Diesel all go through Hydrotreating and then dewaxing to become either treated Kerosene, Diesel (low sulfur) or lubricating oils.

Fuel Oil goes through a catalytic cracker to become O/N 90-95 Gasoline

Resid goes through Thermal Cracking to become either Carbon, Asphalt or O.N. 75 Gasoline.

Credit: Dr. Caroline B. Clifford

Distillation

We will start with the first step in all refineries: distillation. Essentially, distillation is a process that heats the crude oil and separates it into fractions. It is the most important process of a refinery. Crude oil is heated, vaporized, fed into a column that has plates in it, and the materials are separated based on the boiling point. Figure 2.2 shows the first stage of the refinery. It indicates that as the liquids are separated, the top end materials are gases and lighter liquids, but as you go down the column, the products have a higher boiling point, the molecular size gets bigger, the flow of the materials gets thicker (i.e., increasing viscosity), and the sulfur (S) content typically stays with the heavier materials. Notice we are not using the chemical names, but the common mixture of chemicals. Gasoline represents the carbon range of ~ C5-C8, naphtha/kerosene (aka jet fuel) C8-C12, diesel C10-C15, etc. As we discuss the refinery, we will also discuss important properties of each fuel.

The most important product in the refinery is gasoline. Consumer demand requires that 45-50 barrels per 100 barrels of crude oil processed are gasoline. The issues for consumers are, then: 1) quality suitability of gasoline and 2) quantity suitability. The engine that was developed to use gasoline is known as the Otto engine. It contains a four-stroke piston (and engines typically have 4-8 pistons). The first stroke is the intake stroke - a valve opens, allows a certain amount of gasoline and air, and the piston moves down. The second stroke is the compression stroke - the piston moves up and valves close so that the gasoline and air that came

in the piston during the first stroke are compressed. The third stroke happens because the spark plug ignites the gasoline/air mixture, pushing the piston down. The fourth stroke is the exhaust stroke, where the exhaust valve opens and the piston moves back up. Figure 2.3 shows the steps. There is a good animation in [How Stuff Works](#) (Brain, Marshall. 'How Car Engines Work' 05 April 2000. HowStuffWorks.com).

see text description below

Figure 2.2: Trends for products of the initial distillation

[Click Here for a text description of figure 2.2](#)

The products that come out of distillation are gases, gasoline, naphtha, kerosene, diesel, heating oils and resid. In that order boiling point increases, molecular size increases, viscosity increases and usually the sulfur content increase.

Credit: Dr. Caroline B. Clifford

Four strokes of Otto gasoline engine, see text description in link below

Figure 2.3a: Four strokes of Otto gasoline engine

[Click Here for a text description of figure 2.3](#)

Figure 2.3a: Four strokes of Otto gasoline engine

1. Intake stroke. Piston moves down. Intake valve open.
2. Compression stroke. Piston moves up. Valves closed.
3. Power stroke. Piston moves down. Valves closed.
4. Exhaust stroke. Piston moves up. Exhaust valve opens.

Credit: Dr. Caroline B. Clifford

You'll notice the x and the y on strokes 1 and 2. The ratio of x/y is known as the compression ratio (CR). This is a key design feature of an automobile engine. Typically, the higher the CR, the more powerful the engine is and the higher the top speed. The "action" is in the ignition or power stroke. The pressure in the cylinder is determined by 1) pressure at the moment of ignition (determined by CR) and 2) a further increase in pressure at the instant of ignition. At higher pressures with the CR, the more likely the pressure will cause autoignition (or spontaneous ignition), which can cause "knocking" in the engine - the higher the CR, the more likely the engine will knock. This is where fuel quality comes in.

For gasoline engines, the CR can be adjusted to the fuel rating to prevent knocking; this fuel quality is known as "octane" number. Remember the straight-chain alkanes in the chemistry tutorial? The straight-chain alkanes are prone to knocking. The branched alkanes are not. The octane number is defined as 1) heptane - octane number equal to 0, and 2) 2,2,4-trimethylpentane - octane number equal to 100 (this is also known as "octane"). See Figure 2.3b below for the chemical structures of heptane and octane for octane number. Modern car engines require an 87, 89, or 93-94 octane number. However, when processing crude oil, even a high-quality crude oil, we can only produce from distillation yield of 20% with an octane number of 50. This is why crude oil needs to be processed, to produce gasoline at 50% yield with an octane number of 87-94.

chemical structure of heptane, octane # of zero

chemical structure of octane, octane number = 100

Figure 2.3b: Chemical structures of heptane and "octane" for octane number reference. Heptane is seven carbons attached in a straight chain configuration, while "octane" is eight carbons with branching.

Credit: Dr. Caroline B. Clifford

Other ways to improve the octane number:

1. Add aromatics. Aromatics have an octane number (ON) greater than 100. They can be deliberately blended into gasoline to improve ON. However, many aromatic compounds are suspected carcinogens, so there are regulatory limits on the aromatic content in gasoline.
2. Another approach to increasing ON is to add alcohol groups. Methanol and ethanol are typical alcohols that can be added to

fuel. ON is ~110. They can be used as blends with racing cars (known as "alky").

But even with these compounds, distillation will not produce enough gasoline with a high enough ON. So other processes are needed.

"Cracking" Processes

Thermal cracking

One way to improve gasoline yield is to break the bigger molecules into smaller molecules - molecules that boil in the gasoline range. One way to do this is with "thermal cracking." Carbon Petroleum Dubbs was one of the inventors of a successful thermal cracking process (see Figure 2.4). The process produces more gasoline, but the ON was still only ~70-73, so the quality was not adequate.

Catalytic cracking

Eugene Houdry developed another process; in the late 1930s, he discovered that thermal cracking performed in the presence of clay minerals would increase the reaction rate (i.e., make it faster) and produce molecules that had a higher ON, ~100. The clay does not become part of the gasoline - it just provides an active surface for cracking and changing the shape of molecules. The clay is known as a "catalyst," which is a substance that changes the course of a chemical reaction without being consumed. This process is called "catalytic cracking" (see Figure 2.4). Figure 2.4 shows the reactants and products for reducing the hexadecane molecule using both reactions. Catalytic cracking is the second most important process of a refinery, next to distillation. This process enables the production of ~45% gasoline with higher ON.

dubbs process produces straight chain carbons (low O.N) and Hourdy's process produces branch chain carbons (high O.N)

Figure 2.4: Reaction of $C_{16}H_{34}$ using A) Dubb's process, thermal cracking and B) Houdry's process, catalytic cracking, and the products from each reaction (smaller molecules).

Credit: Dr. Caroline B. Clifford

Figure 2.5 is the refining schematic with the additional processing added.

refining schematic with added processes for catalytic cracking (O.N = 100) and thermal cracking (O.N = 70-73)

Figure 2.5: Refining schematic with added processes for catalytic and thermal cracking.

Credit: Dr. Caroline B. Clifford

There are also tradeoffs when refineries make decisions as to the amount of each product they make. The quality of gasoline changes from summer to winter, as well as with gasoline demand. Prices that affect the quality of gasoline include 1) price of crude oil, 2) supply/demand of gasoline, 3) local, state, and federal taxes and 4) distribution of fuel (i.e., the cost of transporting fuel to various locations). Figure 2.6 shows a schematic of how these contribute to the cost of gasoline.

described in caption and the text above

Figure 2.6: The schematic shows how the cost of crude oil, the cost of refining, the cost of distribution and marketing, and the cost of taxes contribute to the overall cost of gasoline in October 2015. The breakdown of gasoline prices for October 2015, Retail Price = \$2.29/gallon.

Taxes = 20%, Distribution & Marketing = 19%, Refining = 15%, Crude Oil = 47%.

Credit: By US DOE EIA (Gasoline and Diesel Fuel Update) [Public domain], via Wikimedia Commons

Additional Processes

Alkylation

The alkylation process takes the small molecules produced during distillation and cracking and adds them to medium-sized molecules. They are typically added in a branched way in order to boost ON. An example of adding methane and ethane to butane is shown in Figure 2.7.

adding small molecules to medium-sized molecules to boost ON by adding carbons and branch chains

Figure 2.7: Example of adding small molecules to medium-sized molecules in order to boost ON.

Credit: Dr. Caroline B. Clifford

Catalytic Reforming

A molecule may be of the correct number of carbon atoms, but need a configuration that will either boost ON or make another product. The example in Figure 2.8 shows how reforming n-octane can produce 3,4-dimethyl hexane.

Moving carbons around on a straight chain carbon molecule to add branches and increase ON

Figure 2.8: Example of catalytic reforming, moving atoms on the molecule to produce higher ON fuel.

Credit: Dr. Caroline B. Clifford

So, let's add these two new processes to our schematic in order to see how they fit into the refinery, and how this can change the ON of gasoline. Figure 2.9 shows the additions, as well as adding in the middle distillate fraction names. Typically, naphtha and kerosene, which can also be sold as these products, are the products that make up jet fuels. So, our next topic will cover how jet engines are different from gasoline engines and use different fuel.

see text description below

Figure 2.9: Refining of crude oil into gasoline with additional processes of alkylation and catalytic reforming.

[Click Here for a text description of figure 2.9](#)

This is a simple flow diagram of crude oil refinery.

Crude oil enters and goes to distillation.

From distillation:

LPG (gases) goes through alkylation to become O.N. 100 Motor Fuel Alkylate which can go on to become gasoline

Straight-run gasoline goes through catalytic reforming to become O.N. 95 Reformate which can go on to become gasoline

Naphtha, Kerosene and Diesel become jet fuels.

Fuel Oil goes through a catalytic cracker to become O.N 90-95 Gasoline

Resid goes through Thermal Cracking to O.N. 75 Gasoline.

Credit: Dr. Caroline B. Clifford

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2.3: Jet Engines

2.3 Jet Engines

The first aircraft used engines similar to the Otto four-stroke cycle, reciprocating piston engines. The Wright flyer was an aircraft with this type of engine. During WWII, powerful 16-cylinder, high compression ratio reciprocating engines were developed. However, the military was interested in developing engines that would make airplanes go faster, higher, and farther - this was to reduce the length of flights and provide better international communication. In order to achieve high-speed flight, a dilemma ensued: 1) the atmosphere thins at high altitudes, offering less air resistance to a plane which could lead to higher speeds, but 2) in "thinner" air, it is more difficult to get combustion air into the conventional piston engine. The modern jet engine was developed as part of a term paper by Frank Whittle while at the British Royal Air Force College, covering the fundamental principles of jet propulsion aircraft.

The jet engine begins with a "burner can," where jet fuel is injected and combusted in high-pressure air. The combustion produces a stream of high temperature, high-pressure gases (see Figure 2.10a). If more power is required, two to four-burner cans can be included, and the high temperature, high-pressure combustion gases operate a turbine (more about turbines for electricity generation in the lesson on electricity). Figure 2.10b depicts these additions. In Figure 2.10c, a containment vessel is put around the burner cans; the gases that exit the turbine pass through a nozzle. The gases exiting the nozzle provide thrust for the airplane. Figure 2.10d shows the completed engine - the high-pressure air comes from the air compressor, which is operated by the turbine.

burner can elements: compressed air enters one side, burner nozzle on the top and high temperature combustion gases come out the other side

Figure 2.10a: The elements of a "burner can."

Credit: Dr. Caroline B. Clifford

Combining two burner cans and adding a turbine where the high temperature combustion gases exit

Figure 2.10b: Combining two-burner cans and adding a turbine.

Credit: Dr. Caroline B. Clifford

A containment vessel is put around the burner cans... see caption for description

Figure 2.10c: A containment vessel is put around the burner cans, and the gases that exit the turbine pass through a nozzle - the gases exiting the nozzle provide thrust.

Credit: Dr. Caroline B. Clifford

Air compressor is placed inside containment unit before the burner cans

Figure 2.10d: The high pressure for the burner cans comes from the air compressor. The role of the turbine is to operate the air compressor.

Credit: Dr. Caroline B. Clifford

There are variations on a simplistic jet engine: 1) the fan jet (turbofan), 2) the prop jet (turboprop), and 3) the turboshaft. The fan jet has a large fan in front of the engine to help provide air to the air compressor. It is a little slower than a turbojet but more fuel-efficient. This is the type favored for civilian transport aircraft. The prop jet uses the mechanical work of the turbine to operate a propeller. These types of engines are typically used for commuter aircraft. The turboshaft is a gas turbine engine that uses all of the output of the turbine to turn the blades, without jet exhaust. Helicopters, tanks, and hovercrafts use these types of engines. So, what is the fuel for jets?

Jet Fuel

Conventional jet fuel is composed primarily of straight-run kerosene (straight-chain carbons and accompanying hydrogen, bigger molecules than gasoline). However, there are some purification steps that are needed to ensure that the fuel behaves in jet

engines.

The first step is the removal of sulfur. When sulfur is burned, it forms sulfur oxide compounds, such as sulfur dioxide (SO₂) and sulfur trioxide (SO₃). Because there are multiple sulfur oxide compounds, they are abbreviated into one chemical formula of SO_x. These compounds, when combined with water, form acid rain (more on this in the next lesson on coal for electricity generation). Sulfur compounds are corrosive to fuel systems and have noxious odors. Sulfur is removed by reacting it with hydrogen and a metal catalyst; the processes are known as hydrogen desulfurization processes (HDS) and produce H₂S (hydrogen sulfide), which is then reacted to solid sulfur.

Another problem that can occur with jet fuel is if it contains too much aromatic compound content. A small amount is actually necessary to lubricate gaskets and O-rings. However, aromatics are suspected carcinogens, and in combustion, aromatics are precursors to smoke and soot. Too much aromatic content can cause problems such as 1) poor aesthetics, 2) carcinogens, and 3) tracking of military aircraft. The way to remove aromatic compounds is the same as for removing sulfur; the aromatic compound is reacted with hydrogen and a metal catalyst to add hydrogen to the aromatic ring. The resulting compounds are heteroaromatics and cycloalkanes.

Another problem that can occur in the middle distillate fractions can occur if the fuel contains waxes. Waxes are higher molecular weight alkane hydrocarbons that can be dissolved in kerosene. At the very cold temperatures at high altitudes, wax can either separate as a solid phase or cause the fuel to freeze and cause plugging in the fuel lines. This can also cause a problem called low-temperature viscosity. Viscosity is a measurement of the flow of a fluid; the thicker the fluid gets (and flow is reduced), the higher the viscosity. While the fuel isn't frozen, it is flowing slower and could cause problems for the engine. Again, the reason for the increase in viscosity is similar to having waxes in the kerosene; high viscosity is caused by bigger molecules within the fuel. The way to improve jet fuel properties is to remove the larger molecules. This is called dewaxing.

The last problem we will discuss has to do with nitrogen. Jet fuels do not typically contain nitrogen, but when combusting fuel using air (which contains primarily nitrogen), nitrogen oxide compounds can form, shown as a formula NO_x. Because jet engines burn fuels at high temperatures, thermal NO_x is a problem. NO_x will contribute to acid rain. If there is any nitrogen in the fuel, it would be removed during the removal of sulfur.

A refinery will make ~10% of its product as jet fuel. The Air Force uses 10% of that fuel, so about 1% of refinery output is for military jet fuel. Figure 2.11 shows the additional processes just discussed in our schematic.

Primary processes that are typical in a petroleum refinery. See text description below

Figure 2.11: Primary processes that are typical in a petroleum refinery. Refer to Figure 2.1 for more details.
[Click for a text alternative for figure 2.11](#)

This is a simple flow diagram of crude oil refinery.

Crude oil enters and goes to distillation.

From distillation:

LPG (gases) goes through alkylation to become O.N. 100 Motor Fuel Alkylate which can go on to become gasoline

Straight-run gasoline goes through catalytic reforming to become O.N. 95 Reformate which can go on to become gasoline

Naphtha, Kerosene and Diesel all go through Hydrotreating and then dewaxing to become either treated Kerosene, Diesel (low sulfur) or lubricating oils.

Fuel Oil goes through a catalytic cracker to become O/N 90-95 Gasoline

Resid goes through Thermal Cracking to become either Carbon, Asphalt or O.N. 75 Gasoline.

Credit: Dr. Caroline B. Clifford

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2.4: Diesel Engines

2.4 Diesel Engines

Rudolf Diesel first developed Diesel engines in the 19th century. He did so because he wanted to develop an engine that was more efficient than an Otto engine and that could use poorer quality fuel than gasoline. The Diesel engine also operates on a four-stroke cycle, but there are some important differences. Diesel engines have a high compression ratio (CR)- a small Diesel engine has a CR of 13:1, while a high-performance Otto engine has a CR of 10:1. Upon the compression stroke (stroke 2), there is a high increase in temperature and pressure. In the third stroke, fuel is injected and ignites because of the high temperature and pressure of the compressed air. You can see an animation of this at [How Stuff Works](#) (Brain, Marshall. 'How Diesel Engines Work' 01 April 2000. HowStuffWorks.com). Diesel engines use fuel more efficiently; and under comparable conditions, a Diesel engine will always get better fuel efficiency than a gasoline Otto engine. Essentially, Diesel engines operate by knocking. The continuous knocking has two consequences: 1) a Diesel engine must be more sturdily built than a gasoline engine, so it is heavier and has a longer life - 300,000-350,000 miles before major engine service, and 2) fuel standards are "backwards" from that of gasoline; we want fuel to knock.

Cost of crude oil diagram, see caption

Figure 2.12: The schematic shows how the cost of crude oil, the cost of refining, the cost of distribution and marketing, and the cost of taxes contribute to the overall cost of diesel in October 2015. The breakdown of diesel prices for October 2015, Retail Price = \$2.52/gallon. Taxes = 21%, Distribution & Marketing = 19%, Refining = 18%, Crude Oil = 43%.

Credit: by US DOE EIA (Gasoline and Diesel Fuel Update) [Public domain], via Wikimedia Commons

Diesel Fuel

Diesel fuel has a much higher boiling range than gasoline. The molecules are larger than gasoline, and the octane scale cannot be used as a guide. The scale that is used for diesel fuel is called the cetane number. The compound, cetane, or hexadecane, $C_{16}H_{34}$, is the standard where the cetane number is 100. For the cetane number 0 (the other end of the scale), the chemical compound used is methylnaphthalene, an aromatic compound that doesn't knock. Most diesel fuels will have cetane numbers of 40-55, with the value in Europe on the higher end and the value in the US at the lower end of that range. In a refinery, diesel fuels are processed in the same fashion as jet fuels, using hydrogenation reactions to remove sulfur and nitrogen and reacting aromatics to hydroaromatics and cycloalkanes. Dewaxing also must be done to improve viscosity and low-temperature problems, particularly in colder climates. Therefore, Figure 2.11 applies to diesel fuel as well as jet fuel. Except in airplanes, Diesel engines dominate internal combustion engine applications. They are standard for large trucks; dominate railways in North America and other countries; are common in buses; and are adapted in small cars and trucks, particularly in Europe.

intake and compression stroke of piston: intake stroke piston moves down (air only); compression stroke piston moves up valves closed

Figure 2.12a: For a Diesel engine, the compression ratio (x/y) is higher and only air is injected in the first stroke, so only air is compressed in the second stroke, and to a higher pressure and temperature than with an Otto engine.

Credit: Dr. Caroline B. Clifford

ignition and exhaust strokes of pistons: ignition piston moves down valves closed; exhaust stroke piston moves up exhaust valve opens

Figure 2.12b: Fuel is injected in the third stroke at high pressure and temperature, which is what makes ignition occur. There are no spark plugs in a Diesel engine.

Credit: Dr. Caroline B. Clifford

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2.5: Assignments

2.5 Assignments

Homework #2

Complete **Homework #2**. It contains six questions that pertain to the Lesson 2 course material.

(10 points)

Discussion #2

Please read the following selections. Both can be accessed via **Library Resources**. Then answer the questions that follow in your discussion post.

For this discussion, you should read the following:

- Bryce, Robert. *Power Hungry: The Myths of 'green' Energy and the Real Fuels of the Future*. New York, NY: PublicAffairs, 2010. Print. (Chapters 1-3) (**Library Resources**)
- Laughlin, Robert B. *Powering the Future: How We Will (Eventually) Solve the Energy Crisis and Fuel the Civilization of Tomorrow*. New York: Basic, 2011. Print. (**Chapter 7**) (**Library Resources**)

After reading the two selections, answer the following questions in your discussion forum post:

1. What does Bryce (*Power Hungry*), think of the use of biofuels?
2. What does Laughlin (*Powering the Future*) think will be the best source of biofuel production and why?

In your posts, make at least one point agreeing with the author and one point disagreeing with the author. After posting your response, **please comment on at least one other person's response**. Discussion grades will be based on content, not just that you completed the assignment.

(5 points)

2.6: Summary and Final Tasks

2.6 Summary and Final Tasks

Summary

This lesson was a very brief overview - there are entire classes based on this one lecture. In this lesson, we discussed the different transportation engines for vehicles, the fuels used for these vehicles, and how the fuels are produced from a refinery. Gasoline is the lighter fuel used in typical automobile engines, while diesel fuel is used in Diesel engines. Diesel engines get better fuel mileage than gasoline engines - gasoline is lighter than diesel. Here in the US, the primary fuel produced is gasoline (~45-50%).

Reminder - Complete all of the Lesson 2 tasks!

You have reached the end of Lesson 2! Double-check the Road Map on the Lesson 2 *Overview* page to make sure you have completed all of the activities listed there before you begin Lesson 3.

Questions?

If there is anything in the lesson materials that you would like to comment on, or don't quite understand, please post your thoughts and/or questions to our Throughout the Course Questions & Comments discussion forum. The discussion forum will be checked regularly. While you are there, feel free to post responses to your classmates if you are able to help. The assistant will hold regular office hours to provide help for EGEE 439 students. Office hours are by appointment on Thursdays: 10:00-12:00 in the office or via Zoom. Please contact the assistant of the course to set up a time for the office hour the previous Sunday until 11:59 pm.

3: ELECTRICITY GENERATION 101

3.1: Basics of Electricity Production from Steam Turbines

3.2: Production of Steam – Plant Design

3.3: Production of Steam - Fuel

3.4: Plant End Systems

3.5: Assignments

3.6: Summary and Final Tasks

3.1: Basics of Electricity Production from Steam Turbines

3.1 Basics of Electricity Production from Steam Turbines

History

There were several people who tried to use steam pressure to produce some sort of mechanical energy, but they were not really able to accomplish this (including Watt, 1769; von Kempelen, 1784; Trevithick, early 1800s). The first steam turbine was developed by De Laval in the 1870s - his device was used to separate cream from milk. However, Charles Parsons was the first to use steam as the working fluid for electricity generation.

Mechanics

The overall goal is to move an electric generator in a circular fashion, which can be done with a turbine. In order for a turbine to be driven, a working fluid must be used. Water can be used for driving a turbine for electricity - it is known as hydroelectricity. Figure 3.1a shows the schematic of a water wheel and how it works, and Figure 3.1b shows a picture of a modern turbine. A turbine uses the force of water (and windmills work on this principle too) to turn a wheel (or turbine). The turning turbine can be used to move something else, like something that will grind wheat into flour.

Schematic of water turning a water wheel. Wheel turns clockwise, water flows right to left

Figure 3.1a: Schematic of water turning a water wheel. The water is the working fluid to turn the wheel, which is also known as a turbine.

Credit: top-alternative-energy-sources.com

wheel being turned by water pouring in from above

Credit: Permaculturing in Portugal Blog

A working fluid must meet certain criteria. It must be:

- cheap;
- available, or able to be produced in large quantities;
- reasonably safe and environmentally friendly.

One of the few substances that meets this criteria is water. However, since we don't have unlimited waterfalls to produce hydroelectricity, the next best thing is "gaseous water," or steam. And to produce electricity, we want the turbine to turn very fast, and the way to do that is with high-pressure steam.

The way to produce high-pressure steam is based on Boyle's Law: For a fixed quantity of gas held at a constant temperature, pressure times the volume equals a constant ($P \cdot V = \text{constant}$). For this application, Boyle's Law becomes important when combined with the work of Charles and Gay-Lussac, where volume is proportional to temperature. Therefore, for a fixed quantity of gas at constant pressure, then $P \cdot V = (\text{constant}) \cdot T$. If the volume is held constant, and temperature increases, then the pressure will increase as well. The key to producing high-pressure steam is to produce high-temperature steam. If high-pressure and high-temperature steam is fed to a turbine, the steam is allowed to expand across the turbine, and the volume increases. During expansion, as the volume increases, the pressure drops, which in turn causes the temperature to drop. Figure 3.2a is a schematic that summarizes how the steam plays a role in the turbine.

Schematic of how the steam plays a role in the turbine. Described in well in caption

Figure 3.2a: Schematic of high temperature, high-pressure steam as the working fluid for a turbine. As the steam goes across the turbine, the volume of the water increases and the temperature and pressure drop; the steam is then condensed to water and is used again in the process.

Credit: Dr. Caroline B. Clifford

The same schematic as above, but a generator is attached to the turbine. Caption describes well

Figure 3.2b: The same schematic, but with a generator attached to the turbine. As the turbine turns, the generator turns, which then generates electricity.

Credit: Dr. Caroline B. Clifford

When the turbine is connected to a generator, then electricity is produced. A generator is a coil of wire that is spun very quickly around a set of magnets. So, if we add a generator to the turbine.... (see Figure 3.2b) As seen in Figure 3.1, water can be used to turn a turbine, which then turns the generator for electricity. An example of a hydroelectric plant is the one at Hoover Dam in Nevada (see Figure 3.3).

Hoover Dam at night

Figure 3.3: Hoover Dam at night.

Credit: Bureau of Reclamation, Andrew Pernick, Photographer

Almost 99% of our electricity comes from generators. In the past, 12-15% of electricity was produced by hydroelectric facilities, but that number has gone down to 6-9%. Hydroelectricity is limited by location (waterfalls), therefore electricity has to come from another source. The remaining 85-94% comes from electricity plants in which steam is used as the working fluid in the turbine. So, how do we do this as cheaply and reliably as we can? Steam is the working fluid that is used, so now we'll go into how we do this.

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3.2: Production of Steam – Plant Design

3.2 Production of Steam – Plant Design

A typical modern medium to medium-large electricity plant may have a steam flow rate in excess of 3 million pounds per hour (lb/h). For comparison, the rate of steam that has to be generated would be equivalent to burning 20 gallons of gasoline (one car) 5-6 times per second. The factors that affect how steam is boiled are 1) heat transfer rate and 2) heat release rate. Think about a kettle of water heating to boiling on a stove. The more of the kettle that rests on the burner, the faster it will boil (heat transfer rate). The higher the heat is turned up, the faster the water boils (heat release rate).

Heat transfer can be affected in three ways 1) *conduction* – direct contact of an object with the source of heat; 2) *convection* – heat carried by currents of fluid; and 3) *radiation* – heat that is transmitted by electromagnetic radiation from glowing objects. In our case, the heat to produce steam is made available by burning fuel. That heat must somehow be transferred to the water or steam. The rate at which heat can be transferred depends on:

- the nature of the material through which heat is transferred;
- its thickness;
- the difference in temperature across the material (losses);
- the total area across which the heat is being transferred.

Increasing the surface area is the most effective way to do this. A way to increase surface area is to transfer the heat through smaller tubes. Doing this will reduce the need to make the boiler bigger and bigger – and if you think about a pot of water boiling, the more water you put in a pan, the longer it takes to boil it keeping the surface area constant.

The first evolutionary step in boilers was the fire-tube boiler. Heated gases are in the tubes, and water and steam are in a big tank; the entire tank is under pressure. The problem with using this design was that if the tank burst, it created a major explosion. This design provides a significantly more heat-transfer surface area than the corresponding flat plate boiler. Fire tube boilers are useful in industrial heating and in very small (by today's standards) electric plants. "Rolling fire tube boilers" were successful for 150 years as steam locomotives. However, the steady growth in electricity demand and the consequent increase in plant size and necessary steam rate meant that eventually not even the fire tube boiler could keep up.

This led to the next evolutionary design step, which was the water tube (or steam tube) boiler. This is the present state-of-the-art design. Depending on the fuel used and the necessary steam rate, a modern water tube boiler is 10-20 stories tall. The design changed so that the water/steam is in tubes within the boiler with hot gases surrounding the tubes.

For More Information

Visit howstuffworks.com for some [additional diagrams of steam engines](#).

3.3: Production of Steam - Fuel

3.3 Production of Steam - Fuel

The fuel that has been used as a primary source for electricity for several years is coal. It has not been the only source but has been beneficial to the electricity industry because:

1. coal has been the cheapest fuel, on \$ per million Btu basis; natural gas has been strongly competitive primarily in recent years;
2. at one time (recent), 60% of U.S. electricity was generated in coal-fired plants. Now ~40% from coal;
3. approximately 80% of U.S. coal production is burned in electric plants.

However, the main reason we are considering switching away from coal is *burning coal is one of the most challenging environmental problems*.

For purposes of the course, we consider steam generation from coal as steam generation from biomass; both fuels are fairly similar.

We want a high heat release rate, which is tied to the burning rate of fuel. Since coal is a solid fuel, it won't burn quickly if it is in chunks. So, the way to increase the burning rate is to increase the surface area of the coal; the way to increase the surface area is to pulverize the coal into very small particles. However, when the coal particles are small in size (something like flour), it makes it difficult to handle. It is hard to shovel something that is like dust or to support it on a grate. Instead, it is actually blown into the boiler unit with a current of air, which is called pulverized-coal firing or suspension firing. This is now the standard for electric power generation, abbreviated PC-fired water-tube boiler. Burning the coal produces heat; the heat is used to boil the water to steam; the steam moves across the turbine to move it; and the turbine turns the generator to produce electricity (see Figure 3.4). Through this sequence of transformations, the chemical potential energy of fuel (coal in this case) is converted to high-potential, high-voltage electricity for distribution to consumers. If you consider the net efficiency from the coal pile to the end of the plant, the plant efficiency is ~33%. Plants built more recently can be in the middle-high 30s range, while older plants may be in the mid-20s.

coal-fired power plant operates on RANKINE cycle; described above (pump, boiler, turbine, generator, condenser)

Figure 3.4: Schematic and outline of the steps to transform coal in boiler to electricity. See the text below for description.

Credit: Dr. Caroline B. Clifford

Figure 3.4 above is an illustration of a coal-fired power plant that operates on a RANKINE cycle. A Rankine steam cycle is the way most steam plants operate (the most ideal way to operate an engine is the Carnot cycle; the Rankine cycle is a modified version of the Carnot cycle.)

The following steps are involved:

1. Water is pumped at constant entropy to State 2 and into boiler.
2. Liquid is heated at constant pressure State 3 (saturated steam).
3. Steam expands at constant entropy through the turbine to State 4.
4. Constant pressure transfer of heat in condenser.
5. The turbine turns the engine to produce electricity.

For More Information

The following links provide some background information if you are interested:

- [Rankine cycle](#)
- [Carnot cycle](#)
- [Entropy](#)

The way to determine the efficiency is to look at the efficiency across each part of the plant. Losses can occur at each step of the process (see Figure 3.4). For a PC-fired modern power plant, assume operation at 2500 psi, with a steam temperature of 540°C, then the overall efficiency is 34%. Losses at each part include 1 & 2) heat losses in pipes and from the friction of the pump (efficiency of 92%); 3) heat losses and friction in the turbine (efficiency of 44%); 4) heat losses as the steam condenses back to water (efficiency of 85%), and 5) very little loss of efficiency from generator (efficiency of 99%). For every three rail cars of coal used to generate electricity, two cars of coal are lost to waste heat.

Figure 3.5 is an overall schematic of a power plant. The next sections will discuss several of the components.

schematic of coal-fired power plant as described in text above, showing water supply, coal supply, boiler, steam line, turbine, generator, condenser, transmission lines, and transformer)

Figure 3.5: Schematic of the coal-fired plant. See subsequent text and figures for a detailed description of what a coal-fired power plant entails.

Credit: [Principles of General Chemistry\(link is external\)Creative Commons BY-NC-SA 3.0](#)

Feeding Units

This is the front end of the plant. The materials that will be fed to the plant must be made into small particles in order to increase the surface area; for coal, it must be crushed to a certain size (less than 100 micrometers). We will discuss biomass preparation when we get to the discussion on the combustion of biomass. The front end of the coal delivery system includes a coal hopper (like a funnel in some ways) and a conveyor belt. Coal is typically sprayed into the boiler with air for better mixing of the two reactants.

Plant Boiler

The boiler has what is called a water wall inside - the water wall is a series of tubes welded together where the water flows. The "box" around the tubes is the boiler itself and is typically 10-20 stories high. The coal and air are sprayed into multiple burners. Figure 3.6a is an example of the water tubes inside a boiler, and Figure 3.6b shows the large scale of a boiler unit.

water tubes inside a boiler (called a water wall)

Figure 3.6a: Water tubes inside a boiler, known as a water wall.

Credit: [State of Delaware](#)

Outside view of boiler in power plant

Figure 3.6b: Outside view of boiler in power plant - note scale of it.

Credit: [e . mercado via flickr CC BY 2.0](#)

Burners Inside Boiler

There are typically multiple burners along the bottom of the boiler. It is a way to increase the area of heat being generated.

Burners in a boiler, blue flames pictured

Figure 3.7: Burners in a boiler.

Credit: [University of Salford Press Office via flickr CC BY 2.0](#)

Plant Turbines

In a coal-fired power plant, the turbines are significantly more sophisticated than the turbine we saw for a waterwheel or for wind.

Figure 3.8a shows the turbine - it actually has multiple stages on it in order to increase the efficiency.

technicians installing large turbine in power plant

Figure 3.8a: Actual turbine being installed for power plant facility.

Credit: [Turbine: from Wikipedia.org](#)

schematic of steam turning a turbine, as described in text above: steam enters, the turbine blades change the direction of the steam 90 degrees to where the steam outlet is

Figure 3.8b: Schematic of how steam turns the turbine.

Credit: [Geothermal Education Office](#)

Plant Generators

In order to generate electricity, the turbine is connected to a generator. A generator is a device of coiled wires that turn around a magnet - the action of the wires turning around the magnet generates electricity. Figure 3.9a shows the turbine in the previous figure connected to a generator, and Figure 3.9b shows the inside of the power plant generator and the enormous size that it is.

steam turning turbine connected to generator as described in text above; turbine is connected to a generator (wire coil and magnetic field generating electricity)

Figure 3.9a: Schematic of how steam turns the turbine and how it's connected to a generator.

Credit: [Geothermal Education Office](#)

man sitting beside power plant generator

Figure 3.9b: Inside of the power plant generator, showing the enormous size that it is.

Credit: [cleveland.com](#)

Interaction of Condenser and Cooling Water Facilities

Steam exits the turbine and is condensed back to water. Typically the condenser is a heat exchanger that uses a natural water source as working fluid. Many power plants are located along rivers or on lakes in order to have a place to return and reuse water. Condensate is returned to the boiler. Water must be extremely pure in order to avoid corrosion in boiler tubes and/or turbine blades; the purity standards may be stricter than for drinking water.

The condenser heat is transferred from the steam (including heat & condensation) to condenser water; therefore, the water leaving the condenser will be hot or warm. If the water is dumped directly into a water source while hot, it will alter the microclimate and local ecology. This is called thermal pollution. Often, cooling towers are used to cool condenser effluent before returning it to the water source. Figure 3.10a shows a schematic of how the condenser interacts with a reservoir and cooling tower, and Figure 3.10b is a picture of a cooling tower at a power plant.

steam flow and condensing water flow complex as described in text above

Figure 3.10a: Steam flow and condensing water flow complex, including cooling loop with tower and reservoir.

Credit: Dr. Caroline B. Clifford

steam coming out of two cooling towers

Figure 3.10b: Picture of cooling towers at powerplant.

Credit: [Jiří Sedláček, Wikimedia Commons](#)

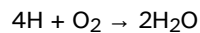
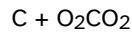
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3.4: Plant End Systems

3.4 Plant End Systems

At the end of the power plant facility, flue gases from the burning of fuel will come out of the stack. However, to meet mandated emission standards, there will be units to help reduce the "bad" emitters.

The primary combustion products come from carbon and hydrogen and are shown in the reaction equations below:



Carbon dioxide and water are formed. But they are not the only products of combustion.

Coal also has sulfur, nitrogen, and minerals that go through the combustion process. Sulfur turns into sulfur dioxide and trioxide, also known as SO_x . Nitrogen in coal can form NO , N_2O , and NO_2 , also known as NO_x (fuel NO_x). NO_x can also form from the nitrogen in air when the temperature in the boiler is high (thermal NO_x). Minerals that go through combustion are called ash and are the oxygenated compounds of the minerals in coal. If you have ever burned wood in a fireplace or at a campsite, you have seen the ash that remains.

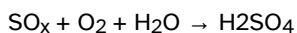
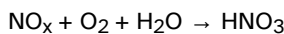
The constituents can be summarized in a mnemonic: NO CASH. Every product of combustion, other than water, has been implicated in an environmental problem of some sort. Table 3.1 shows a summary of NO CASH:

Table 3.1: Summary of NO CASH

Acronym	Coal Components
N	Nitrogen
O	Oxygen
C	Carbon
A	Minerals
S	Sulfur
H	Hydrogen

Coal Components - Environmental Issues

One of the worst environmental consequences that can occur is when NO_x and SO_x are released in the atmosphere and eventually converted into the corresponding acids:



Both nitric and sulfuric acids are very soluble in water. They will eventually fall to the earth either as acid precipitation (acid rain or snow) or as deposits.

acid rain production see text description below the image

Figure 3.11a: Depiction of acid rain and acid deposition from man-made and natural sources.

[Click Here for a text alternative to figure 3.11a](#)

The simplified schematic shows how the deposition of pollutants and acid rain occurs from natural and man-made sources. Man-made sources, depicted as a power plant, release pollutants like SO₂ and NO_x into the air. Natural sources, depicted as erupting volcano, release pollutants like NO_x into the air. In the atmosphere, these pollutants can become gaseous pollutants or particulate pollutants. Dry deposition of these pollutants can bring them back to the surface of the earth. Or the gaseous and particulate pollutants can become cloud water and precipitation pollutants which then rain down (wet deposition) as acid rain.

Credit: [EPA](#)

In many parts of the US, rainfall is 10 times as acidic as rain falling in unpolluted areas. In some locations, or on some occasions, it can be 100 times more acidic. Numerous environmental and health problems are related to acid rain, including the following:

- Acid rainfall accumulates in streams and lakes, so fewer and fewer aquatic species can reproduce or survive. Water areas can become biologically "dead."
- Acid rain in the soil can leach key nutrients out of the soil.
- Acid rain can affect trees, especially on mountain tops. The type of rainfall that can be particularly damaging is a fine mist of acid rain.
- Whole forests can be wiped out if the damage is extensive enough, including entire ecosystems of plants and some animals.
- Acid rain or deposition can be corrosive. It can attack marble, limestone, etc. Historic buildings, monuments, and statues have been defaced by acid deposition.
- Human health can be affected by acid rain. Humans can inhale a mist of dilute acids, which can irritate the respiratory tract, which, in turn, exacerbates chronic respiratory illnesses. The elderly and infants are at greatest risk.

Head sculpture on a doorway. Because of acid rain the features are undistinguishable

Figure 3.11b: Evidence of acid rain erosion; the statue on the wall has been eroded over time.

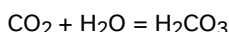
Credit: [mafleen](#) via Flickr

Degree of Acidity in an Aqueous Solution - pH Scale

Here are some key facts about pH:

- pH = 7 is perfectly neutral
- pH < 7 is acidic
- pH > 7 is basic (alkaline)
- smaller the number = more acidic the solution
- for each 1 unit change in pH, there is a ten-fold change in acidity
- a solution with pH=5 is 10 times more acidic than pH=6; pH=4 is 100 times more acidic than pH = 6

Natural rainfall is mildly acidic because carbon dioxide in the air (CO₂) is moderately acidic and soluble in water.



(carbonic acid, pH=5-6)

So, acid rain is defined as rainfall having a pH < 5.6.

When coal is burned in the absence of control equipment, smoke is generated. Smoke is a mixture of fly ash particles and unburned char. On a day of high humidity, the smoke particles act as points to condense moisture from the air. When coal has high sulfur content, you also have SO_x emissions. Under these conditions, the dispersion of sulfuric acid droplets occur, and when

associated with the particles of smoke:

SMOKE + FOG = SMOG

There have been sulfuric acid smog events that have killed people - in Donora, PA (1947), in New York City (1966), and in London (1952). In most industrialized nations, this is no longer a problem, as regulations have reduced the smoke and sulfur emissions at power plants and there is now little domestic use of coal.

Clean-up Strategies

There are several options for cleaning up the bad emissions:

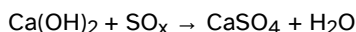
1. Do nothing. (Use a tall stack to disperse pollutants: the solution to pollution is dilution.)
2. Remove or reduce sulfur and nitrogen in fuel feedstock before it is burned (precombustion). This includes sulfur, nitrogen, and minerals.
3. Allow the SO_x , NO_x , and RO_x to form in the boiler, but capture them before they can be emitted into the environment. These are called post-combustion strategies.

The "do nothing" strategy is illegal in the US. The Clean Air Act of 1977 and amendments to the Clean Air Act of 1990 have changed the air environment in the US. However, this is still a problem in the former Soviet Bloc, China, and third world nations.

Precombustion strategies can be approached in the following ways. One way is to switch to cleaner fuel, such as natural gas. In order to do so, however, extensive changes may need to be made to the burners and boilers. Another way is to switch to a cleaner form of coal. Most low sulfur coals are in the western US and have to be transported to the east. These coals tend to have a lower heating value, which leads to more expensive operating costs related to the need to purchase more coal. Finally, impurities can be removed from coal; this can be done by removing minerals that contain sulfur or nitrogen, such as pyrite (FeS). However, some S and N are chemically bonded to the organic portion of coal itself and cannot be removed. Petroleum and natural gas can also have sulfur associated with it. For petroleum products, as discussed in Lesson 2, hydrogen is used to react with sulfur to form hydrogen sulfide (H_2S). H_2S can be captured from natural gas as well; H_2S can be converted into solid sulfur and sold to the chemical industry.

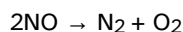
There are also post-combustion strategies for removing impurities. Most of the ash that forms during combustion drops to the bottom of a boiler (~80%) and can be removed for disposal back into the mine. However, up to 20% is carried out of the boiler through the flue gas and is known as fly ash (and can be called particulate matter). Fly ash can also cause health problems. A tiny particle of ash can get lodged in narrow air passages of the lungs. If the body cannot remove it by coating it with mucus and expelling it, then the body will try to seal it off with scar tissue. Solid particulate matter can be handled in two ways: the fly ash can be caught in gigantic fabric filter bags (like a vacuum cleaner bag), which is called the baghouse (see Figure 3.12a and 3.12b). The particles can also be given an electric charge. At high electric potentials, the charged particles are attracted to the electrode of opposite charge; the device used to do this is called an electrostatic precipitator (ESP) (see Figure 3.13).

We can also remove SO_x in the flue gas. The SO_x can dissolve in water to form an acid, which can then be neutralized by reacting it with a base. The cheapest and most available base is lime or limestone, which reacts:



Calcium sulfate (CaSO_4) is an insoluble precipitate; the SO_x wasn't destroyed; we just convert it from a gas to an easier to handle solid. The technology for the removal of SO_x is called flue gas desulfurization (FGD). The hardware is called a scrubber (see Figure 3.14). The SO_x scrubbers are effective, as they capture 97% of the emitted sulfur. The CaSO_4 produced is called scrubber sludge and is either put back in the mine or sold as gypsum to make drywall.

The hardest pollutant to deal with is NO_x . A scrubber does not work for NO_x control because nitrate salts are water-insoluble. To limit the production of thermal NO_x , low-temperature burners produce less NO_x or they use staged combustion so that the temperatures will be low enough to allow the reverse reaction:



Flue gas NO_x can be treated with ammonia:



All of the technologies discussed work. All add costs to producing power (a scrubber will add ~33% to the capital cost of a plant as well as operating costs). Coal cleaning adds \$2-3 per ton of coal to the coal cost. And hydrotreating diesel and heating oil add 5-7¢/gal to the cost of the fuels. And these costs are passed on to the consumer.

Outside of a power plant. Images shows Two tall skinny towers

Figure 3.12a: The unit will contain a cloth bag inside to capture particulate matter.

Credit: [America's Power via flickr\(link is external\)](#)CC BY 2.0

image of the inside of a vacuum cleaner. Has a fabric bag to catch all the dust and dirt coming in from the hose

Figure 3.12b: A baghouse operates much like a bag inside of a vacuum cleaner.

Credit: By Albin Olsson (Own work) [[GFDL](#) or [CC-BY-3.0](#)], via Wikimedia Commons

schematic of electrostatic precipitator; See text description below for details

Figure 3.13: Schematic of an electrostatic precipitator. The outside of the unit will look much like the picture of a baghouse (Figure 3.12a) but it functions very differently inside.

[Click Here for a text alternative to Figure 3.13](#)

This is a schematic of an electrostatic precipitator. There is a chamber that is attached to a high voltage power supply, rappers on one side and hoppers on the other. Inside the chamber are a series of metal collection plates. Particulate laden flue gas enters through a port, flows across the metal collection plates and clean gas exits and goes to the smokestack.

Credit: [Powerspan Corp.](#)

scrubbers at power plant: image shows 4 large round towers in a row

Credit: [power-eng.com](#)

3.5: Assignments

3.5 Assignments

Homework #3

1. Search for a news or opinion article related to biofuels, energy sustainability, or energy security. Provide a URL link to the article you select.
2. Write a paragraph summarizing the most important details of the article.
3. Select at least one item from the article and **research it on your own**, in order to establish if what was included is factual. Write another 1-2 paragraphs providing details as to whether the information from the article can be backed up with actual data or not. Include your sources. The format should be:
 - Approximate length – 2 pages, double-spaced, 1" margins, 12 point font, name at the top
 - Title and URL link for the article you select should be included
 - **For Citation and Reference Style**, You will use the [APA citation style](#).
 - Use as filename **your user ID_HW3 (i.e., ceb7_HW3)**
 - Upload it to the **Homework #3 Dropbox**.

(12 points)

Discussion #3

Post a response that includes an opening statement on the article you picked for the homework above. Take some time to review others' responses. Then respond to at least one other person's post. One thing you can comment on is if the article was written from a particular bias. You may need to look up some additional information to determine if there is a bias, such as additional factual information or the background of the person doing the reporting.

(5 points)

Exam #1

This week you will complete Exam #1.

3.6: Summary and Final Tasks

3.6 Summary and Final Tasks

Summary

There are two aspects to remember from this lesson. First, the way electricity is generated is by steam boiler plants. Every power plant contains a way to introduce the fuel to the boiler; a boiler to heat steam to high temperature and pressure; and steam which turns the turbine, which turns the generator for electricity. Other parts of the power plant include a water cycle to condense the steam and then reheat it. There are also several systems in place to reduce the “bad” emissions that come out with the flue gas. We did not discuss the issues with CO₂ emissions, what problems are caused by CO₂, and how we might mitigate CO₂ emissions, as that could be one lesson on its own. By using biomass, we mitigate CO₂ use, and that will be discussed in a future lesson.

Many different fuels can be used to generate heat for making steam. The most common way here in the US is by coal, although plants have been switching to natural gas due to the low cost of natural gas currently. Coal, along with all fossil fuels, has issues with emissions. This lesson detailed the emissions from coal and how we deal with them in boilers for power plants.

Reminder - Complete all of the Lesson 3 tasks!

You have reached the end of Lesson 3! Double-check the Road Map on the Lesson 3 *Overview* page to make sure you have completed all of the activities listed there before you begin Lesson 4.

Questions?

If there is anything in the lesson materials that you would like to comment on, or don't quite understand, please post your thoughts and/or questions to our Throughout the Course Questions & Comments discussion forum and/or set up an appointment for office hour between 10:00 am-12:00 pm on Thursdays. Discussion forum is checked regularly (Monday through Friday). While you are there, feel free to post responses to your classmates if you are able to help.

4: USE OF BIOMASS IN THERMAL TECHNOLOGIES

4.1: Wood

4.2: Biomass

4.3: Gasification

4.4: Assignments

4.5: Summary and Final Tasks

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4.1: Wood

4.1 Wood

History of Burning Wood

Wood has been used as a source of energy for thousands of years (the first known use of fire was determined when archeologists made discoveries of humans living 400,000 years ago), and wood was the obvious source to make fire. In the Americas, in 1637, the people of Boston suffered from the scarcity of wood. It became America's first energy crisis after less than one century of settlement. During the late 1700s, Benjamin Franklin invented a cast iron stove for indoor use. It held heat in the room after the fire burned out. However, it had a design flaw in that it had no way to pull in air, so fires went out quickly. So David R. Rittenhouse added a chimney and exhaust pipe to improve upon it.

Burning Wood

First, we will look at where energy is stored in materials, starting with the methane molecule. The combustion of methane is exothermic (releases heat as the reaction proceeds), but the reaction must be initiated before it will sustain itself with the continued availability of methane and oxygen. The formula below shows the reaction in a stoichiometric format:

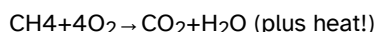


Figure 4.1 shows the same reactants and products, but with the bonds before reaction and after reaction, on a molecular/atomic level. The number of atoms in each molecule doesn't change, but how they are arranged and connected does. The only real change is how the atoms are linked - these are the chemical bonds. Since ENERGY comes out of a burning system, then it must mean that more energy is stored in 4 C-H bonds and 2 O-O bonds than in 4 H-O and two C-O bonds. **The ENERGY released during chemical combustion comes from ENERGY stored in chemical bonds of fuel & oxygen.**

methane and oxygen reaction showing bond connections before and after reaction - see text description below image

Figure 4.1: 1 Methane and 2 oxygen reaction showing bond connections before and after the combustion reaction.

[Click here for a text description of what is occurring in the reaction](#)

Reactants: Methane will react with two oxygen molecules. All of the four hydrogens in methane are connected to a single carbon atom by 4 single bonds. The oxygen molecules are each two oxygen atoms connected by a double bond.

During combustion, the atoms rearrange and form new bonds.

Products: The carbon atom connects to 2 oxygen atoms with a double bond between the carbon and each oxygen to produce one carbon dioxide molecule. Additionally, each of the other remaining oxygen atoms forms 2 single bonds to 2 of the remaining hydrogen atoms to form a water molecule. The net products of the reaction are 1 CO₂ molecule and 2H₂O molecules.

We now know the reaction chemistry of methane combustion, but wood is a much more complex material than methane. Wood contains up to 50% water. Water in the wood will reduce the heating value of the wood, and if the wood is very wet, it will lead to a smoky fire. The main components of wood (we will cover this in more depth in a later lesson) are cellulose (what paper is made from) and lignin (the part of a tree that makes it have a sturdy structure). In order to start a fire, you typically must ignite a material that burns easily to begin heating the wood (this can be newspaper or a "fire starter"). The components begin to decompose from the heat (therefore we are not technically "burning" yet), which produces vapors and char. The vapors are called "volatiles" and the char is composed of carbon and ash. The volatiles are what actually begins to burn, producing a flame. The carbon-rich char produces glowing embers or "coals," which are needed to keep the fire sustained. Wood does not typically contain sulfur, so no sulfur oxides (or SO_x) are produced.

There can be problems with burning wood. The smoke comes from particulates that did not burn or only partially burned that can

pollute the atmosphere, and typically come from resins in the trees. It isn't an issue when one or two people are burning wood, but when thousands of people burn wood in fireplaces. In State College, Pennsylvania, in the winter, one can see smoke in the air from fireplaces. Wood fires in fireplaces can also deposit soot and creosote in the chimneys, which if not cleaned periodically, can ignite. Burning wood (or really most things) will produce an ash material (minerals in wood and coal that react with air under combustion conditions); the ash must be disposed of. Wood smoke also contains a variety of chemicals that can be carcinogenic.

Now let's begin discussing different biomass sources, how we measure different properties of different biomasses, and how to determine the atomic composition of biomass.

4.2: Biomass

4.2 Biomass

There are four types of biomass resources that can be utilized: 1) agricultural residues, 2) energy crops, 3) forestry residues, and 4) processing wastes. Examples of different sources are listed below:

Agricultural Residues:

- Corn stover
- Wheat straw
- Rice straw
- Soybean stalk

Energy Crops:

- Switch grass
- Sweet sorghum
- Sugar canes
- Algae
- Cattail
- Duckweed

Forestry Residues:

- Saw dust
- Woody chips

Processing wastes:

- Food processing wastes
- Animal wastes
- Municipal solid wastes

As already mentioned, most biomass is at least partially composed of three components: cellulose, hemicellulose, and lignin. Figure 4.2a shows a diagram of lignocellulose, and Figure 4.2b shows the biomass broken down into the three parts. There will be significantly more discussion on biomass composition in future lessons. Cellulose is a crystalline polymer of ring molecules (6 carbons) with OH and COOH groups (in Figure 4.2a, cellulose is the straight green lines; in Figure 4.2b, the green molecule). Hemicellulose is similar, but has ring molecules with 5 and 6 carbons, and is amorphous in structures, as depicted in Figure 4.2a by the black squiggly line; Figure 4.2b shows how it is around the cellulose and more detail of the molecular structure. Lignin is the material that holds it all together and is the light blue line in Figure 4.2a; it is in red in 4.2b.

Looks like a sandwich. Lignin is the outer bread layer. Inside are flat rows of cellulose & inside squiggles labeled hemicellulose

Figure 4.2a: Diagram of lignocellulose.

Credit: [Lignocellulose.jpg: from MicrobeWiki](#)

Images of the complex chemical structures of hemicellulose, cellulose and lignin

Figure 4.2b: Chemistry of biomass broken into parts.

Credit: [Lignocellulose_structure.png: from MicrobeWiki](#)

How To Determine Properties of Biomass

There are four common ways to measure the properties of any carbon product, which will also be used for biomass: 1) proximate analysis, 2) ultimate analysis, 3) heat of combustion, and 4) ash analysis.

Proximate analysis

Proximate analysis is a broad measurement to determine the moisture content (M), volatile matter content (VM), fixed carbon content (FC), and the ash content. These are all done on a mass basis, typically, and are done in what is called a proximate analyzer – the analyzer just measures the mass loss at certain temperatures. Moisture is driven off at ~105-110°C (just above the boiling point of water); it represents physically bound water only. Volatile matter is driven off in an inert atmosphere at 950°C, using a slow heating rate. The ash content is determined by taking the remaining material (after VM loss) and burning it at above 700°C in oxygen. The fixed carbon is then determined by difference: $FC = 100 - M - \text{Ash} - VM$.

The following is an example of proximate analysis of lignin, which is part of wood and/or grasses, primarily:

- Moisture (wt%): 5.34
- Ash (wt%): 14.05
- Volatile Matter (wt%): 60.86
- $FC = 100 - M(\%) - A(\%) - VM(\%)$ $FC = 100 - 5.34 - 14.05 - 60.86 = 19.75$

Sometimes the moisture content will be removed from the VM and ash contents, on a dry basis:

- $FC = 100 - M(\%) - A(\% \text{ dry}) - VM(\% \text{ dry})$ $FC = 100 - 5.34 - 14.05 - 60.86 = 19.75$
- $FC = 100 - 14.05 - 60.86 = 25.09$

Ultimate analysis

Ultimate analysis is more specific in that it analyzes the elemental composition of the organic portion of materials. The compositions of carbon (C), hydrogen (H), nitrogen (N), sulfur (S), and oxygen (O) are determined on a mass percent basis, and can be converted to an atomic basis. In some cases, chlorine (Cl) will also be analyzed. There are instruments that are designed to measure only the C H N mass percent and then another to measure S percent; the instrument combusts the material and measures the products of combustion. The following is an example problem for determining the molecular atomic composition of biomass when being provided with an ultimate analysis. Oxygen is usually determined by difference. Water can skew the hydrogen results and must be accounted for.

Your Turn

Problem 1:

The ultimate analysis shows that the C, H, O, N and S contents of a biomass material are 51.9%, 5.5%, 41.5%, 0.8% and 0.3% on a dry basis. What is the chemical formula of this biomass? How many kilograms of air are required to completely combust 1 kg of this biomass? The results are shown below.

The following examples are of the calculation of Problem 1, the chemical formula of biomass, when given mass percent on a dry basis. If you know the elemental mass percent of the sample, you can divide by the molecular weight to determine the atomic value of each element. The values in the table are then divided by the atomic number of carbon to normalize the molecule. So, for every carbon, you have 1.26 atoms of hydrogen, 0.6 atoms of oxygen, etc.

Table 4.1: Problem 1 Calculations

Mass%(1/MW)=x	Values
$C = 51.9 \left(\frac{1}{12.011} \right)$	$\left(\frac{4.32}{4.32} \right) = 1$
$H = 5.5 \left(\frac{1}{1.0079} \right)$	$\left(\frac{5.46}{4.32} \right) = 1.260$

Mass%(1/MW)=x	Values
O=41.05 ($\frac{1}{15.9994}$)	($\frac{2.59}{4.32}$)=0.600
N=0.8 ($\frac{1}{14.0067}$)	($\frac{0.06}{4.32}$)=0.013
S=0.3 ($\frac{1}{32.06}$)	($\frac{0.01}{4.32}$)=0.002

Heat of combustion

The heat of combustion can be measured directly using a bomb calorimeter. This instrument is used to measure the calorific value per mass (calorie/gram or Btu/lb). It can also be estimated using different formulas that calculate it based on either ultimate or proximate analysis. A common type of calorimeter is the isoperibol calorimeter, which will contain the heat inside the jacket but will accommodate the change in temperature of the water in the bucket; see Figure 4.3 for a schematic. A sample is placed in a crucible that is put inside of a reactor with high-pressure oxygen. The sample is connected to a fuse and electrical leads that will ignite the sample, all contained within the reactor (sometimes called a bomb calorimeter). The water temperature in the bucket is measured before and after ignition, and with all the other parts calibrated, the specific heat of water and the change in temperature are used to determine the heat of combustion.

schematic of isoperibol calorimeter, see text description below

Figure 4.3: Schematic of isoperibol calorimeter.

Click Here for a text alternative to the above image

This is schematic of an isoperibol calorimeter. There is a crucible containing a sample. Both sit inside a reactor. The reactor itself is in a bucket with water that has an insulating jacket on the outside, including the top. Sticking into the water is a stirrer and a thermometer. The reaction is started by an ignition source connected to the reactor.

Credit: © Penn State University, is licensed under [CC BY-NC-SA 4.0](#)

The heating value is determined in a bomb calorimeter. Heating values are reported on both wet and dry fuel bases. For the high heating value (HHV), the value can be determined by normalizing out the moisture in a liquid form. For the low heating value (LHV), a portion of the heat of combustion is used to evaporate the moisture.

Ash analysis

The minerals in the material, once combusted, turn to ash. The ash can be analyzed for specific compounds that will contain oxygen, such as CaO, K₂O, Na₂O, MgO, SiO₂, Fe₂O₃, P₂O₅, SO₃, and Cl. The original minerals can also be measured. Once the mineral or ash is isolated, it often must be dissolved in various acids and then analyzed. There is other instrumentation available, but the analysis is quite complicated and not often done.

Bulk density is also determined for biomass as a property. It is typically determined by measuring the weight of material per unit volume. It is usually determined on a dry weight basis (moisture free) or on an as-received basis with moisture content available. For biomass, the low values (grain straws and shavings) are 150-200 kg/m³ (0.15-0.20 g/cm³), and high values (solid wood) are 600-900 kg/m³ (0.60-0.90 g/cm³). The heating value and bulk density are used to determine the energy density. Figure 4.4 shows a comparison of various biomass sources to fossil fuel sources on an energy density mass basis.

Energy density of several materials on a mass basis

Figure 4.4: Energy density of several materials on a mass basis, comparing fossil fuels to biomass fuels.

Credit: Bruce Miller, Sr. Research Associate, EMS Energy Institute, PSU

Many of the fuel characteristics we have been discussing need to be known for proper use of biomass in combustion, gasification, and other reaction chemistry.

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4.3: Gasification

4.3 Gasification

Now, we will go into gasification and compare it to combustion. Gasification is a process that produces syngas, a gaseous mixture of CO, CO₂, H₂, and CH₄, from carbonaceous materials at high temperatures (750 – 1100°C). Gasification is a partial oxidation process; reaction takes place with a limited amount of oxygen. The overall process is endothermic (requires heat to keep the reaction going), so it requires either the simultaneous burning of part of the fuel or the delivery of an external source of heat to drive the process.

Historically, gasification was used in the early 1800s to produce lighting, in London, England (1807) and Baltimore, Maryland (1816). It was manufactured from the gasification of coal. Gasification of coal, combined with Fischer-Tropsch synthesis was one method that was used during WWII to produce liquid fuel for Germany because they did not have access to oil for fuel. It has also been used to convert coal and heavy oil into hydrogen for the production of ammonia and urea-based fertilizer. As a process, it continues to be used in South Africa as a source for liquid fuels (gasification followed by Fischer-Tropsch synthesis).

Gasification typically takes place at temperatures from 750-1100°C. It will break apart biomass (or any carbon material), and usually, an oxidizing agent is added in insufficient quantities. The products are typically gas under these conditions, and the product slate will vary depending on the oxidizing agent. The products are typically hydrogen, carbon monoxide, carbon dioxide, and methane. There may also be some liquid products depending on the conditions used. Gasification and combustion have some similarities; Figure 4.5 shows the variation in products between gasification and combustion. Table 4.2 shows a comparison of the conditions.

Combustion produces, CO₂, H₂O, NO_x, SO_x, & Ash versus gasification which produces CO, H₂, N₂, H₂S & inert aggregates

Figure 4.5: Diagram showing the different products of Combustion and Gasification from carbon, hydrogen, nitrogen and sulfur.

Credit: Dr. Caroline B. Clifford

Table 4.2: Comparison of Combustion versus Gasification

Specification	Combustion	Gasification
Oxygen Use	Uses excess	Uses limited
Process Type	Exothermic	Endothermic
Product	Heat	Gas

Zones of Gasification

There are several zones that the carbon material passes through as it proceeds through the gasifier: 1) drying, 2) pyrolysis, 3) combustion, and 4) reduction. The schematic in Figure 4.6 shows the zones and the products that typically occur during that part of the process. First, we will discuss what happens in each zone. We will also be looking at different gasifier designs to show these zones change depending on the design, and each design has advantages and disadvantages.

The drying process is essential to remove surface water, and the “product” is water. Water can be removed by filtration or evaporation, or a combination of both. Typically, waste heat is used to do the evaporation.

general schematic of different regions in gasifier, see text description below

Figure 4.6: General schematic of different regions in a gasifier.

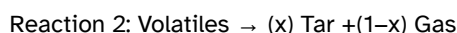
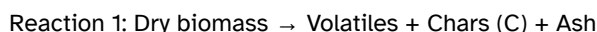
[Click here for a text alternative of figure 4.6](#)

Diagram showing different regions and products in a gasifier. Heat is applied to the entire system, oxidizing agents such as air, O₂, H₂O, and CO₂ enter from the bottom and biomass enters from the top.

The biomass first goes through drying which removes water. It then goes through pyrolysis which produces char, tar and methane. From pyrolysis the biomass can go to reduction or combustion which produces carbon dioxide and water. If the biomass goes through combustion it also then goes to reduction which produces hydrogen gas and carbon monoxide.

Credit: Dr. Caroline B. Clifford

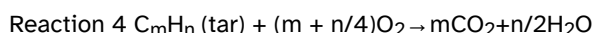
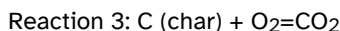
Pyrolysis is typically the next zone. If you look at it as a reaction:



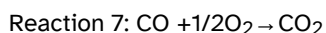
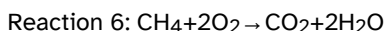
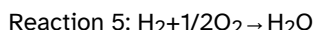
where x is the mass fraction of tars in the volatiles. Volatile gases are released from the dry biomass at temperatures ranging up to about 700°C. These gases are non-condensable vapors such as CH₄, CO, CO₂ and H₂ and condensable vapor of tar at the ambient temperature. The solid residues are char and ash. A typical method to test how well a biomass material will pyrolyze is thermogravimetric analysis; it is similar to the proximate analysis. However, the heating rate and oxidizing agent can be varied, and the instrument can be used to determine the optimum temperature of pyrolysis.

Gasification Process and Chemistry: Combustion and Reduction

A limited amount of oxidizing agent is used during gasification to partially oxidize the pyrolysis products of char (C), tar and gas to form a gaseous mixture of syngas mainly containing CO, H₂, CH₄ and CO₂. Common gasifying agents are: air, O₂, H₂O and CO₂. If air or oxygen is used as a gasifying agent, partial combustion of biomass can supply heat for the endothermic reactions.



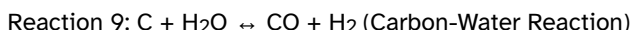
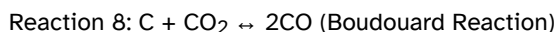
Combustion of gases:



The equivalence ratio (ER) is the ratio of O₂ required for gasification, to O₂ required for full combustion of biomass. The value of ER is usually 0.2 - 0.4. At too high ER values, excess air causes unnecessary combustion of biomass and dilutes the syngas. At too low ER values, the partial combustion of biomass does not provide enough oxygen and heat for gasification.

There are several reactions that can take place in the reduction zone. There are three possible types of reactions: 1) solid-gas reactions, 2) tar-gas reactions, and 3) gas-gas reactions. Essentially, H₂O and CO₂ are used as gasifying agents to increase the H₂ and CO yields. The double-sided arrow represents that these reactions are reversible depending on the conditions used.

Solid-gas reactions include:



Reaction 10: $C + 2H_2 \leftrightarrow CH_4$ (Hydrogenation Reaction)

Tar-gas reactions include:

Reaction 11: $C_mH_n(\text{tar}) + mH_2O \leftrightarrow (m+n/2)H_2 + mCO$ (Tar Steam Reforming Reaction)

Reaction 12: $C_mH_n(\text{tar}) + mCO_2 \leftrightarrow n/2H_2 + 2mCO$ (Tar Dry Reforming Reaction)

Gas-gas reactions include:

Reaction 13: $CO + H_2O \leftrightarrow CO_2 + H_2$ (Water-Gas Shift Reaction)

Reaction 14: $CO + 3H_2 \leftrightarrow CH_4 + H_2O$ (Methanation)

The reactions can be affected by reaction equilibrium and kinetics. For a long reaction time: 1) chemical equilibrium is attained, 2) products are limited to CO, CO₂, H₂, and CH₄, and 3) low temperatures and high pressures favor the formation of CH₄, whereas high temperatures and low pressures favor the formation of H₂ and CO. For a short reaction time: 1) chemical equilibrium is not attained, 2) products contain light hydrocarbons as well as up to 10 wt% heavy hydrocarbons (tar), and 3) steam injection and catalysts can shift the products toward lower molecular weight compounds.

Gasifier Designs

There are several types of gasifier designs: 1) updraft, 2) downdraft, 3) cross downdraft, 4) fluidized bed, and 5) plasma. The first type of gasifier is the **updraft** (Figure 4.7) design. The advantages include that it is a simple design and is not sensitive to fuel selection. However, disadvantages include a long start-up time, production of high concentrations of tar, and general lack of suitability for modern heat and power systems.

The **downdraft** gasifier (Figure 4.8) is similar, but the air enters in the middle of the unit and gases flow down and out. The oxidation and reduction zones change places. Advantages to this design include low tar production, low power requirements, a quicker response time, and a short start up time. However, it has a more complex design, fuel can be fouled with slag, and it cannot be scaled up beyond 400 kg/h.

updraft design gasifier, see text description below

Figure 4.7: Updraft design gasifier.

[Click here for a text alternative of figure 4.7](#)

Schematic of an Updraft Gasifier. The diagram looks like a cylinder with oxidizing gas entering at the bottom and flowing up and out at the top. There are 5 layered zones in the gasifier. Starting at the bottom there is the ash zone, the oxidation zone, the reduction zone, the pyrolysis zone and the drying zone.

Credit: Dr. Caroline B. Clifford

downdraft design gasifier, see text description below

Figure 4.8: Downdraft design gasifier.

[Click here for a text alternative of figure 4.8](#)

Schematic of a downdraft gasifier. The diagram again looks like a cylinder and again has 5 layered zones. From the bottom up they are, the ash pit, the reduction zone, the oxidation zone, the pyrolysis zone, the drying zone. The air enters in the middle of the gasifier at the oxidation zone and the air flows down and comes out the bottom as product gas.

Credit: Dr. Caroline B. Clifford

The **crossdraft** design gasifier is shown in Figure 4.9. Similar to the downdraft, it has a quicker response time and has a short start up time; it is also complex in design, cannot use high mineral containing fuels, and fuel can be contaminated with slag from ash.

A **fluidized bed** design gasifier is shown in Figure 4.10. The action of this gasifier is similar to how water might boil, except the air (or other gas) flows through the fines (the sample and sand) at temperature, creating a bubbling effect similar to boiling. Because of this action, it has the advantages of greater fuel flexibility, better control, and is quick in response to changes. But because of these advantages, these types of gasifiers have a higher capital cost, a higher power requirement, and must be operated on high particulate loading.

crossdraft design gasifier, see text description below

Figure 4.9: Crossdraft design gasifier.

[Click here for a text alternative of figure 4.9](#)

Schematic of a crossdraft gasifier. This gasifier again looks like a cylinder and has all 5 of the zones the previous 2 did. However, instead of layers, the zones look more like a bullseye. Air enters halfway up the cylinder in the very center which is the oxidation zone. Around the oxidation zone is the reduction zone and outside that is the pyrolysis zone. The drying zone is around them all. The ash pit is still a layer at the very bottom. Product gas comes out at the same level the air initially came in.

Credit: Dr. Caroline B. Clifford

fluidized bed design gasifier, see text description below

Figure 4.10: Fluidized bed design gasifier.

[Click here for a text alternative of figure 4.10](#)

Schematic of a fluidized bed design gasifier. This gasifier looks like a cylindrical capsule where air, oxygen or steam enters from the bottom. Near the bottom there is distributor plate. The fluidized bed with the fuel sits on top of the plate and at the bottom of the fluidized bed there is an exit for the ash. There is a mechanism to recirculate the fines near the top of the fluidized bed. To exit, the gas flows through a cyclone and out the top of the gasifier.

Credit: [FAO](#). Accessed March 28, 2014.

One of the new design gasifiers is a **plasma** gasifier design. Plasma gasification uses extremely high temperatures in an oxygen-starved environment to decompose waste material into small molecules and atoms, so that the compounds formed are very simple and form a syngas with H_2 , CO and H_2O . This type of unit functions very differently, as electricity is fed to a torch that has two electrodes – when functioning, the electrodes create an arc. Inert gas is passed through the arc, and, as this occurs, the gas heats to temperatures as high as 3,000 °C (Credit: [Westinghouse Plasma Corporation](#)). The advantages of such units include: 1) process versatility, 2) superior emission characteristics, 3) no secondary treatment of byproducts, 4) valuable byproducts, 5) enhanced process control, 6) volume reduction of material fed, and 6) small plant size. Units such as these are more expensive and scaling up is still in the research stage. These types of units are most commonly used for municipal waste sludge.

plasma design gasifier, see text description below

Figure 4.11: Plasma design gasifier.

[Click here for a text alternative of figure 4.11](#)

Schematic of a plasma design gasifier. This looks like a funnel with a lid. About halfway up there is a waste inlet. Below that there is an inlet for air or oxygen and near the bottom there are plasma torches. The syngas exits from an outlet at the top and slag and recovered metals are collected from an outlet at the bottom.

Credit: [Westinghouse Plasma Corporation](#)

General information on gasification

So what products are made, what advantages are there to using various oxidizing sources, how are the byproducts removed, and how is efficiency improved? Besides syngas, other products are made depending on the design. As stated previously, the syngas is composed of H_2 , CO, CO_2 , H_2O , and CH_4 . Depending on the design, differing amounts of tar and char can also be made. For

example, for steam fluidized gasification of wood sawdust at atmospheric pressure and 775°C, 80% of the carbon will be made into syngas, 4% of the carbon will produce tar, and 16% will produce char (Herguido J, Corella J, Gonzalez-Saiz J. Ind Eng Chem Res 1992; 31: 1274-82.)

There are multiple uses for syngas, for making hydrocarbon fuels, for producing particular chemicals, and for burning as a fuel; therefore, syngas has a heating value. The heating value can be calculated by the volumetric fraction and the higher heating values (HHV) of gas components, which is shown in this equation:

$$\text{HHV}_{\text{gas}} = V_{\text{CO}} (\text{HHV}_{\text{CO}}) + V_{\text{CO}_2} (\text{HHV}_{\text{CO}_2}) + V_{\text{CH}_4} (\text{HHV}_{\text{CH}_4}) \\ + V_{\text{H}_2} (\text{HHV}_{\text{H}_2}) + V_{\text{H}_2\text{O}} (\text{HHV}_{\text{H}_2\text{O}}) + V_{\text{N}_2} (\text{HHV}_{\text{N}_2})$$

where:

$$\text{HHV}_{\text{CO}} = 12.68 \text{ MJ/Nm}^3$$

$$\text{HHV}_{\text{CO}_2} = 0.00 \text{ MJ/Nm}^3$$

$$\text{HHV}_{\text{CH}_4} = 38.78 \text{ MJ/Nm}^3$$

$$\text{HHV}_{\text{H}_2} = 12.81 \text{ MJ/Nm}^3$$

$$\text{HHV}_{\text{H}_2\text{O}} = 2.01 \text{ MJ/Nm}^3$$

$$\text{HHV}_{\text{N}_2} = 0.00 \text{ MJ/Nm}^3$$

A problem based on this equation and HHVs will be included in the homework.

Other factors are determined for optimal gasification. **Thermal efficiency** is the conversion of the chemical energy of solid fuels into chemical energy and sensible heat of gaseous products. For high temperature/high pressure gasifiers, the efficiency is high, ~90%. For typical biomass gasifiers, the efficiency is reduced to 70-80% efficiency. **Cold gas efficiency** is the conversion of chemical energy of solid fuel to chemical energy of gaseous products; for typical biomass gasifiers, the efficiency is 50-60%.

There are several processing factors that can affect different aspects of gasification. Table 4.3 shows the main advantages and technical challenges for different gasifying agents. Steam and carbon dioxide as oxidizing agents are advantageous in making a high heating value syngas with more hydrogen and carbon monoxide than other gases, but also require external heating sources and catalytic tar reformation.

Table 4.3: Advantages and technical challenges of different gasifying agents. (Wang, LJ, Well, CL, Jones, DD and Hanna, MA. 2008. *Biomass and Bioenergy*, 32:573-581.)

Gasifying Agent	Main Advantages
Air	Partial combustion for heat supply of gasification. Moderate char and tar content.
Steam	High heating value syngas (10-15 MJ/Nm³) H₂-rich syngas (i.e., >50% by volume)

Gasifying Agent	Main Advantages
Carbon dioxide	High heating value syngas High H ₂ /CO and low CO ₂ in syngas

Basic design features can also affect the performance of a gasifier. Table 4.4 shows the effect of fixed bed versus a fluidized bed and differences in temperature, pressure, and equivalence ratio. Fixed/moving beds are simpler in design and favorable on a small scale economically, but fluidized bed reactors have a higher productivity and low byproduct generation. The rest of the table shows how increased temperature can also favor carbon conversion and the HHV of the syngas, while increased pressure helps with producing a high pressure syngas without compression to higher pressures downstream.

Table 4.4: Effect of bed design and differences in operating parameters on gasifier operation. (Wang, L.J, Weller, CL, Jones, DD and Hanna, MA. 2008. *Biomass and Bioenergy*, 32: 573-581.)

Bed Design	Main Advantages	Main Technical Challenges
Fixed/moving bed	Simple and reliable design Favorable economics on a small scale	Long residence time Non-uniform temperature distribution in gasifiers High char and/or tar contents Low cold gas efficiency Low productivity (i.e., ~5 GJ/m ² h)
Fluidized bed	Short residence time High productivity (i.e., 20-30 GJ/m ² h) Uniform temperature distribution in gasifiers Low char and/or tar contents High cold gas efficiency Reduced ash-related problems	High particulate dust in syngas Favorable economics on a medium to large scale
Increase of temperature	Decreased tar and char content Decreased methane in syngas Increased carbon conversion Increased heating value of syngas	Decreased energy efficiency Increased ash-related problems

Bed Design	Main Advantages	Main Technical Challenges
Increase of pressure	Low tar and char content No costly syngas compression required for downstream utilization of syngas	Limited design and operational experience Higher cost of gasifier at small scale
Increase of ER (Equivalence Ratio)	Low tar and char content	Decreased heating value of syngas

Product Cleaning

The main thing that has to be done to clean the syngas is to remove char and tar. The **char** is typically in particulate form, so the particulates can be removed in a way similar to what was described in the power plant facility. Typically for gasifiers, the method of particulate filtration includes gas cyclones (removal of particulate matter larger than 5 μm). Additional filtration can be done using ceramic candle filters or moving bed granular filters.

Tars are typically heavy liquids. In some cases, the tars are removed by scrubbing the gas stream with a fine mist of water or oil; this method is inexpensive but also inefficient. Tars can also be converted to low molecular weight compounds by “cracking” into CO and H_2 (these are typically the desired gases for syngas). This is done at high temperature (1000°C) or with the use of a catalyst at $600\text{--}800^\circ\text{C}$. Tars can also be “reformed” to CO and H_2 , which can be converted into alcohols, alkanes, and other useful products. This is done with steam and is called steam reforming of tar; the reaction conditions are at a temperature of $\sim 250^\circ\text{C}$ and pressure of 30–55 atm. The reaction is shown below, and is the same reaction as that shown in reaction 11:

Tar steam reforming reaction:



Steam reforming has advantages. It is generally a safer operation since there isn’t any oxygen in the feed gases, and it produces a higher H_2/CO ratio syngas product than most alternatives. The main disadvantage is a lower thermal efficiency, as heat must be added indirectly because the reaction is endothermic.

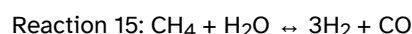
Syngas Utilization

As stated earlier, syngas has multiple uses. Syngas can be used to generate heat and power, and can even be used to turn a turbine in some engineering designs. Syngas can also be used as the synthesis gas for Fischer-Tropsch fuel production, synthesis of methanol and dimethyl ether (DME), fermentation for production of biobased products, and production of hydrogen.

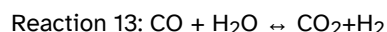
So, how is syngas utilized in **heat and power generation**? Syngas can be used in pulverized coal combustion systems; it helps the coal to ignite and to prevent plugging of the coal feeding system. Biomass gasification can ease ash-related problems. This is because the gasification temperature is lower than in combustion, and once gasified, can supply clean syngas to the combustor. Adding a gasifier to a combustion system helps in utilization of a variety of biomass sources with large variations in properties. Once the syngas has been cleaned, it can be fed to gas engines, fuel cells or gas turbines for power generation.

Syngas may also be used to produce hydrogen. When biomass is gasified, a mixture of H_2 , CO , CH_4 , and CO_2 is produced. Further reaction to hydrogen can be done using water reforming and water-gas shift reactions:

Water reforming reaction for CH_4 to H_2 :



Water-gas shift reaction for CO to H_2 (as shown earlier):

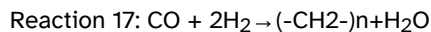


Carbon dioxide may also be removed, as it is typically an undesirable component. One method to keep it from going into the

atmosphere is to do chemical adsorption:

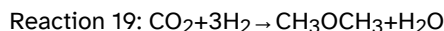
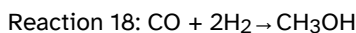


Syngas can also be utilized for Fischer-Tropsch synthesis of hydrocarbon fuels. Variable chain length hydrocarbons can be produced via a gas mixture of CO and H₂ using the Fischer-Tropsch method. The reaction for this is:

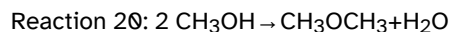


In order for the reaction to take place, the ratio should be close to 2:1, so gases generated via gasification may have to be adjusted to fit this ratio. Inert gases also need to be reduced, such as CO₂ and contaminants such as H₂S, as the contaminants may lower catalyst activity.

Methanol and dimethyl ether can also be produced from syngas. The reactions are:



Dimethyl ether (DME) can be made from methanol:



Syngas can also be fermented to produce bio-based products. This will be discussed in detail in a later lesson.

4.4: Assignments

4.4 Assignments

Homework #4

Download and complete **Homework #4**. It contains four questions that pertain to the Lesson 4 course material. Be sure to show your work! When you are finished, upload your completed assignment to the **Homework #4 Dropbox**. Use the following naming convention for your assignment: **your user ID_HW4 (i.e., ceb7_HW4)**.

(12 points)

Discussion #4

Answer the following questions in your discussion forum post:

- What is causing the change to the price of natural gas?
- How have oil prices changed over the last year?
- How might this affect the price of biofuels, or utilization of biofuels?
- What can be done to minimize the volatility in fuel prices, or can anything be done?

After posting your response, **please comment on at least one other person's response**. Discussion grades will be based on content, not just that you completed the assignment. Grades will reflect critical thinking and effort in your input and responses.

(5 points)

4.5: Summary and Final Tasks

4.5 Summary and Final Tasks

Summary

There are several potential crops that can be utilized for combustion and gasification. These include energy crops, crop residues, forest residues, and process wastes. These can be utilized in both combustion processes and gasification processes. For gasification, we looked at several factors: 1) gasification process and chemistry, 2) gasifier design and operation, 3) syngas cleaning, and 4) syngas utilization to make a variety of products. Biobased energy and chemical products discussed in the lesson include: 1) heat and power, 2) hydrogen, 3) F-T hydrocarbon fuels, 3) alcohols, and 4) biochemical and biopolymers.

References

Schobert, H.H., *Energy and Society: An Introduction*, 2002, Taylor & Francis: New York, Ch. 4-6.

Wang, L., Biological Engineering, North Carolina A&T University, BEEMS Module C1, Biomass Gasification, sponsored by USDA Higher Education Challenger Program, 2009-38411-19761, PI on project Li, Yebo.

Reminder - Complete all of the Lesson 4 tasks!

You have reached the end of Lesson 4! Double-check the Road Map on the Lesson 4 *Overview* page to make sure you have completed all of the activities listed there before you begin Lesson 5.

Questions?

If there is anything in the lesson materials that you would like to comment on, or don't quite understand, please post your thoughts and/or questions to our *Throughout the Course Questions & Comments* discussion forum. I will check that discussion forum daily (Monday through Friday). While you are there, feel free to post responses to your classmates if you are able to help.

5: BIOMASS PYROLYSIS AND PRETREATMENT

5.1: Biomass Pyrolysis

5.2: Biomass Carbohydrate Tutorial

5.3: Pretreatment of Lignocellulosic Biomass

5.3a: Size Reduction

5.3b: Low pH Methods

5.3c: Neutral pH pretreatment

5.3d: High pH (Alkaline)

5.3e: Organic Solvation Processes

5.3f: Ionic Liquids

5.3g: Biological Pretreatment

5.3h: Summary

5.4: Assignments

5.5: Summary and Final Tasks

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5.1: Biomass Pyrolysis

5.1 Biomass Pyrolysis

Figure 5.1 shows a graphic of the four methods of thermochemical conversion of biomass, with pyrolysis highlighted. We just went over combustion and gasification, and we'll cover direct liquefaction later on in the semester.

Thermal conversion of biomass can happen through combustion, gasification, pyrolysis or hydrothermal liquefaction \

Figure 5.1: Thermochemical routes for the conversion of biomass

Credit: Dr. Hilal Ezgi Toraman

There are differences in each of the thermal processes. For combustion, the material is in an oxygen-rich atmosphere, at a very high operating temperature, with heat as the targeted output. Gasification takes place in an oxygen-lean atmosphere, with a high operating temperature, and gaseous products being the main target (syngas production in most cases). Direct liquefaction (particularly hydrothermal processing) occurs in a non-oxidative atmosphere, where biomass is fed into a unit as an aqueous slurry at lower temperatures, and bio-crude in liquid form is the product.

So, what is pyrolysis? There are several definitions depending on the source, but essentially it is a thermochemical process, conducted at 400-600°C in the absence of oxygen. The process produces gases, bio-oil, and a char, and as noted in Lesson 4, is one of the first steps in gasification or combustion. The composition of the primary products made will depend on the temperature, pressure, and heating rate of the process.

There are advantages, both economical and environmental, to doing pyrolysis. They are:

- utilization of renewable resources through a carbon neutral route – *environmental potential*;
- utilization of waste materials such as lumber processing waste (barks, sawdust, forest thinnings, etc.), agricultural residues (straws, manure, etc.) – *economic potential*;
- self-sustaining energy – *economic potential*;
- conversion of low energy in biomass into high energy density liquid fuels – *environmental & economic potentials*;
- potential to produce chemicals from bio-based resources – *environmental & economic potentials*.

Pyrolysis was initially utilized to produce charcoal. In indigenous cultures in South America, the material was ignited and then covered with soil to reduce the oxygen available to the material – it left a high carbon material that could stabilize and enrich the soil to add nutrients ([Discussion of applications of pyrolysis], (n.d.), Retrieved from MagnumGroup.org). It has also been used as a lighter and less volatile source of heat for cooking (i.e., “charcoal” grills) in countries where electricity is not widely available and people use fuel such as this to cook with or heat their homes (Schobert, H.H., *Energy, and Society: An Introduction*, 2002, Taylor & Francis: New York). Not only is there a solid product, such as charcoal, liquid products can also be produced depending on the starting material and conditions used. Historically, methanol was produced from the pyrolysis of wood.

This process for pyrolysis can also be called torrefaction. Torrefaction is typically done at relatively low pyrolysis temperatures (200-300°C) in the absence of oxygen. The feed material is heated up slowly, at less than 50°C/min, and is done over a period of hours to days – this way the volatiles are released and carbon maintains a rigid structure. In the first stage, water, which is a component that can inhibit the calorific value of a fuel, is lost. This is followed by a loss of CO, CO₂, H₂, and CH₄, in low quantities. By doing this, approximately 70% of the mass is retained with 90% of the energy content. The solid material is hydrophobic (little attraction to water) and can be stored for a long period of time.

Classification of pyrolysis methods

There are three types of pyrolysis: 1) conventional/slow pyrolysis, 2) fast pyrolysis, and 3) ultra-fast/flash pyrolysis. Table 5.1 and Figure 5.2 summarize how each method differs in temperature, residence time, heating rate, and products made.

As mentioned earlier, slow pyrolysis is typically used to modify the solid material, minimizing the oil produced. Fast pyrolysis and ultra-fast (flash) pyrolysis maximize the gases and oil produced.

Fast pyrolysis is a rapid thermal decomposition of carbonaceous materials in the absence of oxygen in moderate to high heating rates. It is the most common of the methods, both in research and in practical use. The major product is bio-oil. Pyrolysis is an endothermic process. Along with the information listed in Table 5.1, the feedstock must be dry; of smaller particles (< 3 mm); and typically done at atmospheric temperature with rapid quenching of the products. The yields of the products are: liquid condensates – 30-60%; gases (CO, H₂, CH₄, CO₂, and light hydrocarbons) – 15-35%; and char – 10-15%.

Ultra-fast, or flash pyrolysis is an extremely rapid thermal decomposition pyrolysis, with a high heating rate. The main products are gases and bio-oil. Heating rates can vary from 100-10,000° C/s and residence times are short in duration. The yields of the products are: liquid condensate ~10-20%; gases – 60-80%; and char – 10-15%.

Table 5.1: Classification of pyrolysis methods with differences in temperature, residence time, heating rate, and major products.

Method	Temperature (°C)	Residence Time
Conventional/slow pyrolysis	Med-high 400-500	Long 5-30 min
Fast pyrolysis	Med-high 400-650	Short 0.5-2 s
Ultra-fast/flash pyrolysis	High 700-1000	Very short < 0.5 s

Chart of different pyrolysis conditions and the effect on product distribution. See text description below

Figure 5.2: Figure summarizing different pyrolysis conditions and the effect on product distribution.

[Click for a text alternative of figure 5.2](#)

Effect on product distribution of different pyrolysis conditions. All values are visual approximations based on the image

Heating rate	Time	Temperature (°C)	Char
Slow (<10 ³ W/m ²)	1000s	~500°C	25%
Medium (>10 ⁴ W/m ²)	100s	~500°C	17%
Fast (>10 ⁵ W/m ²)	1s	~500°C	15%
Flash (>10 ⁶ W/m ²)	0.01s	~500°C	10%
Slow (<10 ³ W/m ²)	1000s	~1000°C	40%
Medium (>10 ⁴ W/m ²)	100s	~1000°C	20%
Fast (>10 ⁵ W/m ²)	1s	~1000°C	15%
Flash (>10 ⁶ W/m ²)	0.01s	~1000°C	0%

Credit: (Created based on Xavier DEGLISE, Emeritus Professor at University Henri Poincaré, France. 2006 BEEMS Module C2, Brian He.)

Bio-oil Product Properties

Crude bio-oils are different from petroleum crude oils. Both can be dark and tarry with an odor, but crude bio-oils are not miscible with petro-oils. Bio-oils have high water content (20-30%); their density is heavier than water (1.10-1.25 g/mL); their heating value is ~5600-7700 Btu/lb (13-18 MJ/kg). Bio-oils have high oxygen content (35-50%), which causes high acidity (pH as low

as ~2). Bio-oils are also viscous (20-1000 cp @ 40°C) and have high solid residues (up to 40%). These oils are also oxidatively unstable, so the oils can polymerize, agglomerate, or have oxidative reactions occurring in situ which lead to increased viscosity and volatility. The values in Table 5.2 compare the properties of bio-oil to a petroleum-based heavy fuel oil.

Table 5.2: Typical properties of wood pyrolysis bio-oil and heavy fuel oil.

Physical Property	Bio-oil
Moisture Content	15-30
pH	2.5
Specific gravity	1.2
Elemental composition (wt%)	-
C	54-58
H	5.5-7.0
O	35-40
N	0-0.2
Ash	0-0.2
HHV, MJ/kg	16-19
Viscosity (cp, @50°C)	40-100
Solids (wt %)	0.2-1
Distillation residue (wt%)	Up to 50

(Czemik, S. and Bridgewater, A.V., 2004. *Overview of Applications of Biomass Fast Pyrolysis*, Energy Fuels **18**, 590-598).

Process Considerations

Several components are necessary for any pyrolysis unit, outside of the pyrolyzer itself. The units and how they are connected are shown in Figure 5.3.

general components of pyrolysis process. See text below image for pertinent info.

Figure 5.3: General components to a process for pyrolysis.

Credit: Dr. Caroline B. Clifford

The goal of the process is to produce bio-oil from the pyrolyzer. The bio-oil that's generated has potential as a transportation fuel after upgrading and fractionation. Some can be used for making specialty chemicals as well, especially ring-structure compounds that could be used for adhesives. The gases that are produced contain combustible components, so the gases are used to generate heat. A bio-char is produced as well. Biochar can be used as a soil amendment that improves the quality of the soil, sequesters carbon, or can even be used as a carbon material as a catalyst support or activated carbon. There will also be a mineral-based material called ash once it's been processed. Typically, the ash must be contained.

The next units to be considered are separation units. Char is solid, so it is typically separated using a cyclone or baghouse. It can be used as a catalyst for further decomposition into gases because the mineral inherent in the char as well as the carbon can catalyze the gasification reactions. The liquids and gases must also be separated. Usually, the liquids and gases must be cooled in order to separate the condensable liquids from the non-condensable gases. The liquids are then fractionated and will most likely be treated further to improve the stability of the liquids. At times, the liquid portion may plug due to heavier components. The non-condensable gases need to be cleaned of any trace amounts of liquids and can be reused if needed.

The next considerations are the heat sources for the unit. Hot flue gas is used to dry the feed. As the flue gas contains combustible gases, they can be partially combusted to provide heat. Any char that is left over is burned as a major supply of heat. And, biomass can be partially burned as another major source of heat.

Another important process to consider is the means of heat transfer. Much of it is indirect, through metal walls and tube and shell units. Direct heat transfer has to do with char and biomass burning. And in the fluidized bed unit, the carrier (most often sand) brings in the heat, as the carrier is heated externally and recycled to provide heat to the pyrolyzer.

Types of Pyrolyzers

So, what types of pyrolyzers are used? The more common types are fluidized-bed pyrolyzers. Figures 5.4a and 5.4b show schematics of two different types. The advantages of using fluid-beds are uniform temperature and good heat transfer; high bio-oil yield of up to 75%; a medium level of complexity in construction and operation; and ease of scaling up. The disadvantages of fluid-beds are the requirement of small particle sizes; a large quantity of inert gases; and high operating costs. The unit is shown in Figure 5.4b, the circulating fluid bed pyrolyzer, (CFB), has similar advantages, although medium-sized particle sizes for feed are used. Disadvantages include a large quantity of heat carriers (i.e., sand); more complex operation, and high operating costs.

Fluid-bed with electrostatic precipitator, see text description below

Figure 5.4a: Fluid-bed with electrostatic precipitator.

[Click here for a text alternative of figure 5.4a](#)

Schematic of a fluid-bed with electrostatic precipitator. The carrier gas enters the fluid-bed that has an intake feed. The gas then goes through a cyclone and the char and ash is removed as a product or taken to the char burner. The gas then passes through the quencher and the heavier fraction is removed as bio-oil, it then passes to the condenser where the lighter fraction is condensed as bio-oil and the non-condensable are taken to the boiler or the burner. Any gases created at the burner are used as a carrier gas.

Credit: BEEMS

Fluidized-bed with circulating heat carrier, see text description below

Figure 5.4b: Fluidized-bed with circulating heat carrier (circulating fluid-bed (CFB) pyrolyzers).

[Click here for a text alternative of figure 5.4b](#)

Schematic of a fluid-bed with circulating heat carrier (circulating fluid-bed (CFB) pyrolyzers). The carrier gas enters the bottom of fluid-bed through a pyrolyzer. The fluid bed also has an intake feed halfway up. The gas then goes through a cyclone and the char and heat carriers are removed and taken to a burner. The heat carriers (sand) are returned to the fluid bed/pyrolyzer. The ash is removed and flue gas is taken to the heating unit. The gases that come out of the cyclone then pass through the quencher and the heavier fraction is removed as bio-oil, it is then passed to the condenser where the lighter fraction is condensed as bio-oil and the non-condensable are taken to the boiler or the burner. Any gases created at the burner are used as a carrier gas.

Credit: BEEMS

Two other types of pyrolyzers are the rotating cone (Figure 5.5a) and the Auger (Figure 5.5b) pyrolyzers. The rotating cone creates a swirling movement of particles through a g-force. This type of pyrolyzer is compact, has a relatively simple construction and operation, and has a low heat carrier/sand requirement. However, it has a limited capacity, requires feed to be fine particles, and is difficult to scale up. Auger pyrolyzers are also compact, simple in construction, and easy to operate; they function at a lower process temperature as well (400 °C). The disadvantages of Auger pyrolyzers include long residence times, lower bio-oil yields, high char yield, and limits in scaling up due to heat transfer limits.

Rotating cone pyrolyzer, see text description below

Figure 5.5a: Rotating cone pyrolyzer.

[Click here for a text alternative of figure 5.5a](#)

Schematic of a rotating cone pyrolyzer. The cone has feed at the bottom and heat is applied to the outside walls of the cone. A motor spins the cone and the gas/condensables come out the top as does the char/ash.

Credit: BEEMS

Auger pyrolyzer , see text description below

Figure 5.5b: Auger pyrolyzer

[Click here for a text alternative of figure 5.5b](#)

Schematic of an Auger pyrolyzer. The diagram looks like a cylinder with a corkscrew inside. A motor is attached to the rotating corkscrew. The walls of the cylinder are heated and one end there is a feed. On the other end, there are outtake ports for condensables to come out the tops and char/ash to come out the bottom.

Credit: BEEMS

Bio-Oil Upgrading

As noted earlier, bio-oil has issues and must be upgraded, which means essentially processed to remove the problems. These problems include high acid content (which is corrosive), high water content, and high instability both oxidatively and thermally (which can cause unwanted solids formation).

The oils must be treated physically and chemically. Physical treatments include the removal of char via filtration and emulsification of hydrocarbons for stability. Bio-oils are also fractionated, but not before chemical treatments are done. The chemical treatments include esterification (a reaction with alcohol to form esters – this will be covered in detail when discussing biodiesel production); catalytic de-oxygenation/hydrogenation to remove oxygen and double bonds; thermal cracking for more volatile components; physical extraction; and syngas production/gasification.

Catalytic de-oxygenation/hydrogenation takes place. A catalyst is used along with hydrogen gas; specialty catalysts are used, such as sulfides and oxides of nickel, cobalt, and molybdenum. Hydrogenation is commonly used in petroleum refining for the removal of sulfur and nitrogen from crude oil and to hydrogenate the products where double bonds may have formed in processing. Catalytic processes are separate processes and use specific equipment to perform the upgrading. One problem can be that there may be components of bio-oil that may be toxic to catalysts.

Esterification reacts to the corrosive acids in bio-oils with alcohol to form esters. An ester is shown below in Figure 5.6. A discussion of the esterification reaction will be discussed in the biodiesel lesson.

Y shape with C at the center. One branch has a double bond O, one has a R and the other has an OR'

Figure 5.6: A general chemical formula of an ester compound, where R and R' can be any type of hydrocarbon. The R group is attached to the C=O and is the acidic part of the molecule, while the R' group is attached to the O and is the alcoholic part of the molecule.

Credit: [Ester-general: from Wikimedia Commons](#)

Bio-oil can also be thermally cracked and/or made into syngas through gasification. Please refer to Lesson 2 for the thermal cracking discussion and Lesson 4 for the gasification discussion. One other process that can be utilized is physical extraction, although extraction takes place due to the affinity of some of the compounds to a particular fluid. One example is the extraction of phenols. Phenols can be extracted using a sodium solution such as sodium hydroxide in water; the phenolic compounds are attracted to the sodium solution, while the less oxygenated compounds will stay in the organic solution. Again, this will be discussed in more detail in later lessons. Figure 5.7 shows a schematic of a typical processing unit to upgrade bio-oil.

Schematic of typical processing unit to upgrade bio-oil, see text description below

Figure 5.7: Schematic of a typical processing unit to upgrade bio-oil.

[Click for a text alternative of figure 5.7](#)

Schematic of a typical processing unit to upgrade bio-oil. Crude bio-oil and auxiliary chemicals enter the pre-reactor which does things such as de-acidify or esterify. From the pre-reactor the crude bio-oil goes to the separator. The aqueous fraction is removed and goes to the solubles recovery unit. The organic fraction goes to the reactor where hydrogen gas is pumped in to do hydrogenation and deoxygenation. The gases are removed to an hydrogen scrubber which cleans and separates the gases. The hydrogen gas is recycled. The bio-oil then goes to a distillation column. The heavy fraction is fuel oil candidate and could be cracked for lighter components. The medium fraction can become kerosene or a diesel candidate. The lightest fraction can become a gasoline candidate.

Credit: BEEMS

Biomass Pretreatment

Current methods of generating biofuels are primarily from starch or grain, and starch hydrolysis is fairly straightforward. However, because the starch feedstocks are typically food-based, the goal is to develop technologies to produce ethanol from cellulose; cellulose is obtained from lignocellulosic biomass sources and must be pretreated before breaking down into ethanol. Figure 5.8 is a schematic of the differences in processing for starch (current) and cellulose (emerging). Before we go any further, we will have a short tutorial on the various components of lignocellulosic biomass.

schematic of the differences in processing for starch (current) and cellulose (emerging), see text description below

Figure 5.8: Schematic of processing differences for cellulose and starch.

[Click for a text alternative of figure 5.8](#)

Schematic of processing differences for cellulose and starch. For starch or grain, it goes through starch hydrolysis and then the fermentation of glucose to recover the final product. The final products are food products, animal feed, ethanol and chemicals.

For cellulose (lignocellulosic biomass) it must go through a pretreatment before entering cellulose hydrolysis and then the fermentation of carbon 5 and 6 sugars to recover the final products. The final products are food products, animal feed, ethanol and chemicals. Any lignin residue goes through thermochemical conversion to become heat and power, and fuels and chemicals: pyrolysis oil and synthesis gas.

Credit: Source: The National Renewable Energy Laboratory (NREL)

5.2: Biomass Carbohydrate Tutorial

5.2 Biomass Carbohydrate Tutorial

When the word carbohydrate is used, I typically think of the carbohydrates in food. Carbohydrates are the sugars and complex units composed of sugars. This section will describe each.

Sugars are also called saccharides. Monomer units are single units of sugars called monosaccharides. Dimer units are double units of sugars called disaccharides. Polymers contain multiple units of monomers and dimers and are called polysaccharides.

So, what are typical **monosaccharides**? They are made up of a molecule that is in a ring structure with carbons and oxygen. Figure 5.9a shows the structure of **glucose**; it is made up of $C_6H_{12}O_6$. Glucose is distinguished by its structure: five carbons in the ring with one oxygen; CH_2OH attached to a carbon; and OH and H groups attached to the other carbons. This sugar is known as blood sugar and is an immediate source of energy for cellular respiration. Figure 5.9b shows **galactose** next to glucose, and we can see that galactose is almost like glucose, except on the No. 4 carbon the OH and H are an isomer and just slightly different (highlighted in red on the galactose molecule). Galactose is a sugar monomer in milk and yogurt. Figure 5.9c shows **fructose**; while it still has a similar chemical formula as glucose ($C_6H_{12}O_5$), it is a five-membered ring with carbons and oxygens, but two CH_2OH groups. This is a sugar found in honey and fruits.

Glucose structure with carbons numbered

Figure 5.9a: Glucose structure with carbons numbered.

Credit: Palaeos.com

Galactose structure next to glucose to highlight the main difference in the structures (H and OH are flipped on C4)

Figure 5.9b: Galactose structure next to glucose to highlight the main difference in the structures.

Credit: Palaeos.com

Fructose structure.

Figure 5.9c: Fructose structure.

Credit: Palaeos.com

We also have **disaccharides** as sugars in food. Disaccharides are dimers of the monomers we just discussed and are shown below. One of the most common disaccharides is **sucrose**, which is common table sugar and is shown in Figure 5.10a. It is a dimer of glucose and fructose. Another common sugar dimer is **lactose**. It is the major sugar in milk and a dimer of galactose and glucose (see Figure 5.10b). **Maltose** (5.10c) is also a sugar dimer but is a product of starch digestion. It is a dimer made up of glucose and glucose. In the next section, we will discuss what starch and cellulose are composed of in order to see why maltose is a product of starch digestion.

Sucrose (glucose + fructose) chemical structure.

Figure 5.10a: Sucrose (glucose + fructose) chemical structure.

Credit: World of Molecules

Lactose (galactose + glucose)

Figure 5.10b: Lactose (galactose + glucose).

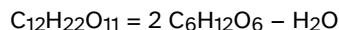
Credit: Optushome.com

Maltose (glucose + glucose) chemical structure
 Figure 5.10c: Maltose (glucose + glucose) chemical structure.

Credit: [Maltose Haworth: from Wikimedia Commons](#)

Carbohydrate structure

All carbohydrate polymers are monomers that connect with what is called a **glycosidic bond**. For example, sucrose is a dimer of glucose and fructose. In order for the bond to form, there is a loss of H and OH. So, another way to show this is:



And as dimers can form, polymers will form and are called **polysaccharides**. Typical polysaccharides include 1) glycogen, 2) starch, and 3) cellulose. **Glycogen** is a molecule in which animals store glucose by polymerizing glucose, as shown in Figure 5.11.

Macromolecule: large spiral of sugar molecules. bond level: straight chains of sugars & some branching off other sugar chains

Figure 5.11: Glycogen as a) macromolecule and at b) the bond level.

Credit: [Glico](#)

Starches are similar to glycogen, with a little bit different structure. Starch is composed of two polymeric molecules, amylose and amylopectin. The structures of both are shown in Figure 5.12a and 5.12b.

Amylose, the part of starch that is not branched. alpha-1,4-glycosidic linkages

Figure 5.12a: Amylose, the part of starch that is not branched.

Credit: [Marshall.edu](#)

Amylopectin, the part of starch that is branched, alpha 1,6-glycosidic bond makes the branch

Figure 5.12b: Amylopectin, the part of starch that is branched.

Credit: [nutritionalbiochem.blogspot.com](#)

About 20% of starch is made up of amylose and is a straight-chain that forms into a helical shape with α -1,4 glycosidic bonds and the rest of the starch is amylopectin, which is branched with α -1,4, and α -1,6 glycosidic bonds. Figure 5.13 shows the structure of cellulose. **Cellulose** is a major molecule in the plant world; it is also the single most abundant molecule in the biosphere. It is a polymer of glucose and has connectors of the glucose molecule that are different from starch; the linkages are β -1,4 glycosidic bonds. The polymer of cellulose is such that it can form tight hydrogen bonds with oxygen, so it is more rigid and crystalline than starch molecules. The rigidity makes it difficult to break down.

Cellulose structure

Figure 5.13: Cellulose structure. The glycosidic bonds are β -1,4 linkages.

Credit: Z.H. Gao, J.Y. Gu, X-M. Wang, Z.G. Li, X.D. Bai, (2005) "FTIR and XPS study of the reaction of phenyl isocyanate and cellulose with different moisture contents," *Pigment & Resin Technology*, Vol. 34 Iss: 5, pp.282 - 289

5.3: Pretreatment of Lignocellulosic Biomass

When the word carbohydrate is used, I typically think of the carbohydrates in food. Carbohydrates are the sugars and complex units composed of sugars. This section will describe each.

Sugars are also called saccharides. Monomer units are single units of sugars called monosaccharides. Dimer units are double units of sugars called disaccharides. Polymers contain multiple units of monomers and dimers and are called polysaccharides.

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Glucose structure with carbons numbered

Figure 5.9a: Glucose structure with carbons numbered.

Credit: Palaeos.com

Galactose structure next to glucose to highlight the main difference in the structures.

Figure 5.9b: Galactose structure next to glucose to highlight the main difference in the structures.

Credit: Palaeos.com

Fructose structure.

Figure 5.9c: Fructose structure.

Credit: Palaeos.com

We also have **disaccharides** as sugars in food. Disaccharides are dimers of the monomers we just discussed and are shown below. One of the most common disaccharides is **sucrose**, which is common table sugar and is shown in Figure 5.10a. It is a dimer of glucose and fructose. Another common sugar dimer is **lactose**. It is the major sugar in milk and a dimer of galactose and glucose (see Figure 5.10b). **Maltose** (5.10c) is also a sugar dimer, but is a product of starch digestion. It is a dimer made up of glucose and glucose. In the next section, we will discuss what starch and cellulose are composed of in order to see why maltose is a product of starch digestion.

Sucrose (glucose + fructose) chemical structure

Figure 5.10a: Sucrose (glucose + fructose) chemical structure.

Credit: World of Molecules

Lactose (galactose + glucose)

Figure 5.10b: Lactose (galactose + glucose).

Credit: Optushome.com

Maltose (glucose + glucose) chemical structure

Figure 5.10c: Maltose (glucose + glucose) chemical structure.

Credit: Maltose Haworth: from Wikimedia Commons

Carbohydrate structure

All carbohydrate polymers are monomers that connect with what is called a **glycosidic bond**. For example, sucrose is a dimer of glucose and fructose. In order for the bond to form, there is a loss of H and OH. So, another way to show this is:



There is a wide variety of sources for lignocellulosic biomass, which includes agricultural waste (i.e., corn stover), forest waste from furniture and home construction, municipal solid waste and energy crops. They all look very different, but all are composed of cellulose, hemicellulose, lignin, and other minor compounds. Figure 5.14a shows switchgrass (with parts magnified to emphasize different parts of the plant structure). Once you get down to the microfibril structure, you can see the components of the microfibril, which includes lignin on the outside layer, hemicellulose on the next layer, and finally, cellulose. Because of the structure, the lignocellulose is difficult to break down, which is known as recalcitrance. In order to get to the cellulose, the cell wall has to be opened up, the lignin has to be removed or separated from the hemicellulose and cellulose, and then the cellulose, crystalline in nature, has to be broken down. All these steps are resistant to microbial attack, so pretreatment methods are used to break it apart. In other words, biomass recalcitrance requires pretreatment.

Plant cells have cell walls which are a layered mesh of microfibrils, microfibrils are made of crystalline cellulose

Figure 5.14a: Switchgrass, to plant cells, to mesh of microfibrils, to microfibril structure, to crystalline cellulose to a cellulose molecule.

Credit: Rosa Estela Quiroz-Castañeda and Jorge Luis Folch-Mallol (2013). Hydrolysis of Biomass Mediated by Cellulases for the Production of Sugars, Sustainable Degradation of Lignocellulosic Biomass - Techniques, Applications and Commercialization, Dr. Anuj Chandel (Ed.)

Another Perspective

You can access the following online journal article to see another illustration of lignocellulose, but with the lignin component included (Fig. 1):

- [Wyman, Charles E., and Bin Yang. "Cellulosic Biomass Could Help Meet California's Transportation Fuel Needs." *California Agriculture* 63.4 \(2009\): 185-90\(link is external\).](#)

Pretreatment is the most costly step; however, the only process step more expensive than pretreatment is no pretreatment. Without pretreatment, yields are low and drive up all other costs, more than the amount saved without pretreatment. Increased yields with pretreatment reduces all other unit costs. Figure 5.15 shows a schematic of the role pretreatment plays. Pretreatment, depending on the method, will separate the lignin, the hemicellulose, and the cellulose. Figure 5.15 shows how these break apart. Part of the lignin and the hemicellulose are dissolved in liquid during hydrolysis, and part of the lignin and the cellulose are left as a solid residue. There is partial breakdown of the polymeric molecules, and the cellulose is now more accessible to microbial attack.

Diagram of pretreatment: biomass breaks into liquid hydrolysate (lignin and hemicellulose) and solid residue (lignin and cellulose)

Figure 5.15: The role of pretreatment in breaking apart parts of biomass.

Credit: BEEMS

Pretreatment is costly and affects both upstream and downstream processes. On the upstream side, it can affect how the biomass is collected or harvested, as well as the comminution of the biomass. Downstream of pretreatment, the enzyme production can be affected, which in turn will affect the enzymatic hydrolysis and sugar fermentation. Pretreatment can also affect hydrolysate conditioning and hydrolysate fermentation. The products made and the eventual final processing also will be affected by pretreatment. However, it is more costly to not do pretreatment.

There are two different types of pretreatment. Physical effects disrupt the higher-order structure and increase surface area and chemical/enzyme penetration into plant cell walls, and include mechanical size reduction and fiber liberation. Chemical effects include solubilization, depolymerization, and breaking of crosslinks between macromolecules. The individual components can "swell," depending on the organic solvent or acid used. Lignin can be "redistributed" into a solution, and lignin and carbohydrates can be depolymerized or modified chemically.

The following pretreatment technologies will be discussed in more depth: 1) size reduction, 2) low pH method, 3) neutral pH method, 4) high pH method, 5) organic solvent separation, 6) ionic liquid separation, and 7) biological treatments.

This page titled [5.3: Pretreatment of Lignocellulosic Biomass](#) is shared under a [CC BY-NC-SA 4.0](#) license and was authored, remixed, and/or curated by [Hilal Ezgi Toraman \(John A. Dutton: e-Education Institute\)](#) via [source content](#) that was edited to the style and standards of the LibreTexts platform.

5.3a: Size Reduction

5.3a Size Reduction

Size reduction is also known as comminution. Decreasing particle size of biomass improves accessibility to plant cell wall carbohydrates for chemical and biochemical depolymerization. It can also increase the bulk density for storage and transportation. There is a cost of energy when using mechanical size reduction. For example, 20-40 kWh/metric tons are needed to reduce the size of hardwood chips to coarse particles of 0.6-2.0 mm in size, and kWhs typically have a cost of anywhere from \$0.04-0.10 per kWh. To reduce the size of particles to a fine size (0.15-0.30 mm), 100-200 kWh/ton is required.

There are multiple methods used to reduce the size of particles, and the method used will depend on whether the sample is dry or wet. There are hammer mills (a repetitive hammering of sample), knife mills (a rotating knife slices the sample), and ball mills (the sample is put into a container with metal balls and rolled). Sometimes the sample has to be shredded and dried before using some of these techniques.

Samples can also be “densified.” Samples can be mixed with some sort of binder (to keep the materials together, like a glue) and pushed into shape, or pelletized. This increases the bulk density (i.e., from 80-150 kg/m³ for straw or 200 kg/m³ for sawdust to 600-700 kg/m³ after densification). This can lower transportation costs, reduce the storage volume, and make handling easier. After densification, the materials usually have lower moisture content.

pile of tan pellets

Figure 5.15a: Pelletized biomass.

Credit: [Marcus Kauffman](#) via Flickr

5.3b: Low pH Methods

5.3b Low pH Methods

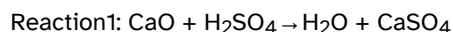
The mechanism for low pH treatments is the hydrolysis of hemicellulose. Hydrolysis is a reaction with water, where acid is added to the water to accelerate the reaction time. Several acids can be used, including dilute sulfuric acid (H₂SO₄), gaseous sulfur dioxide (SO₂), hydrochloric acid (HCl), phosphoric acid (H₃PO₄), and oxalic acid (C₂H₂O₄). Because it is a reaction, the key parameters affecting it include temperature, time, acid concentration, and moisture content of the biomass. The following reactions can take place: hemicellulose can be solubilized, lignin can be separated, acetyl groups are removed, and the surface of the biomass becomes more accessible. As an example (Figure 5.16), the α-1,4 bond is broken by the water and acid to yield two glucose units. An enzyme, amylase, can also promote the reaction. The addition of acid and elevated temperature increases the rate of reaction.

Hydrolysis reaction creating two glucose molecules, from a disaccharide. see caption and surrounding text

Credit: BEEMS Module B1

Not only is acid used to facilitate hydrolysis, but acid-catalyzed dehydration of sugars can form furans, which can break down into organic acids such as formic acid and levulinic acid. These compounds can be toxic to the enzymes that are used in sugar fermentation. So after reaction, the residual acid must be neutralized, and inhibitors formed or released during pretreatment must be reduced. Two methods are to use calcium oxide (also known as overliming) or ammonium hydroxide.

Calcium oxide is cheap, forms gypsum during the process, and has a loss of sugar of ~10%, with the necessity of by-product removal and disposal. The reaction is shown below in Reaction 1



The advantage of using ammonium hydroxide is that less sugar is lost and less waste is generated, but the cost is higher. The reaction is shown below in Reaction 2.

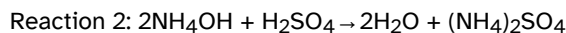


Figure 5.17a and 5.17b show process diagrams of typical configurations and reaction conditions for sulfuric acid and SO₂.

Schematic of sulfuric acid pretreatment process, see text description below

Figure 5.17a: Schematic of sulfuric acid pretreatment process.*

[Click here for a text alternative to figure 5.17a](#)

Schematic of sulfuric acid pretreatment process. Biomass is added to dilute sulfuric acid, called acid impregnation (0.5 – 5.0% H₂SO₄) it then goes to dilute acid pretreatment around (140-200 C). This pretreatment can take seconds to hours. It then becomes a slurry which goes into neutralization conditioning. The solids go to enzymatic hydrolysis where hexose sugars and solid residue (lignin) are separated. The liquids from the neutralization condition go to acid post-hydrolysis. The slurry can also go to solid/liquid separation. The solid products of this separation go to neutralization condition and the liquids go to acid post-hydrolysis. Acid post-hydrolysis yields pentose sugars.

Credit: BEEMS Module B1

Schematic of sulfur dioxide pretreatment process

Figure 5.17b: Schematic of sulfur dioxide pretreatment process.*

[Click here for a text alternative to figure 5.17b](#)

Schematic of sulfur dioxide pretreatment process. Biomass with water undergoes biomass humidification (50%-70% M.C.) and then it undergoes SO₂ impregnation (1-5%) and finally a steam explosion (180-210 C). This pretreatment can take seconds to minutes. It then becomes a slurry which goes into neutralization conditioning. The solids go to enzymatic hydrolysis where hexose sugars and solid residue are separated. The liquids from the neutralization conditioning go to acid post-hydrolysis. The slurry can also go to solid/liquid separation. The solid products of this separation go to neutralization conditioning and the liquids go to acid post-hydrolysis. Acid post-hydrolysis yields pentose sugars.

Credit: BEEMS Module B1

5.3c: Neutral pH pretreatment

5.3c Neutral pH Pretreatment

Pretreatment can also take place in neutral pH water. There are two pathways that can occur. One is when acidic compounds are released from acetylated hemicellulose, mainly acetic acid. This is also called **autohydrolysis**. Water can also dissociate as the temperature and pressure increases to near the supercritical point (approximately 374°C, 3200 psi), into H⁺ and OH⁻, and as this happens, the water behaves like an acid/base system. It is done in water without added chemicals, either in **liquid hot water, steam explosion, or water near the supercritical point**. The key parameters are time, temperature, and moisture content, and the effects are similar to low pH methods. A schematic for liquid hot water processing is shown in Figure 5.18.

Liquid hot water process flow diagram

Figure 5.18: Liquid hot water process flow diagram*.

[Click here for a text alternative of Figure 5.18](#)

Schematic of liquid hot water process flow diagram. Biomass is added to water and sent to liquid H₂O pretreatment (180-210 °C). Pretreatment can take seconds to hours. It then becomes a slurry which goes into water wash conditioning. The solids go to enzymatic hydrolysis where hexose sugars and solid residue (lignin) is separated. The liquids from the water wash conditioning go to acid post-hydrolysis. The slurry can also go to solid/liquid separation. The solid products of this separation go to water wash conditioning and the liquids go to acid post-hydrolysis. Acid post-hydrolysis yields pentose sugars.

Credit: BEEMS Module B1

One process, developed by Inbicon, is a counter-current multi-stage hot water pretreatment process. There is a pilot-scale unit at Skærbæk, Denmark. It is a three-stage process using hot water (hydrothermal) at 80°C, 160-200 °C, and 190-230°C. After the first stage, liquid composed C5-molasses (sugar) is taken out of the process, which is used for animal feed. After the third stage, the fiber fraction contains cellulose and lignin. Bioethanol and a solid fuel for heat and power are produced when using enzymes, yeast, and fermentation. Figure 5.19 shows the before and after pretreatment of wheat straw (the raw wheat straw and the cellulosic-lignin portion).

Pretreatment of wheat straw, before: volumous and yellow, after: compact and brown

Figure 5.19: Pretreatment of wheat straw, before and after.

Credit: BEEMS Module B1

The next pretreatment processes to discuss are at high pH. The high pH removes the lignin portion of biomass through the breaking of ether linkages (R-O-R') that hold aromatic phenolic compounds together; ring opening can also take place. It is a depolymerization process. There are several processes and bases used, including: lime, calcium carbonate, potassium hydroxide, sodium hydroxide, and aqueous ammonia. Key parameters include temperature, reaction time, concentration of base, moisture of the feed material, as well as oxidizing agents. The effects include removal of most of the lignin, some removal of hemicellulose, and removal of acetyl links between lignin and hemicellulose.

Lignin is most prominent in grasses and woody biomass. It composes 6-35% of lignocellulosic biomass, depending on the type of grass or wood. Lignin is comprised of crosslinked, branched, monoaromatic units with methoxy and propyl alcohol functional groups. These are shown in Figure 5.20a. Figure 5.20b shows a model of a lignin molecule and how the aromatic monomers are linked together.

chemical structures of p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol

Figure 5.20a: Aromatic monomer alcohols of building blocks for lignin.

Credit: Bembenic, Meredith, "The chemistry of subcritical water reactions of a hardwood derived lignin and lignin model compounds with nitrogen, hydrogen, carbon monoxide and carbon dioxide," PhD Thesis, PSU, 2011

Chemical structure of lignin representative molecule, Alder model

Figure 5.20b: Alder model of lignin representative molecule.

Credit: Bembenic, Meredith, "The chemistry of subcritical water reactions of a hardwood derived lignin and lignin model compounds with nitrogen, hydrogen, carbon monoxide and carbon dioxide," PhD Thesis, PSU, 2011

5.3d: High pH (Alkaline)

5.3d High pH (Alkaline) Pretreatment

There are two possible outcomes for the chemistry behind the high pH treatment: 1) one is essentially a degradation reaction that liberates lignin fragments and leads to lignin dissolution, and 2) the other is condensation reactions that increase the molecular size of lignin fragments and result in lignin precipitation. As you can see, lignin is a complicated molecule, with a variety of linkages, so reactions are complicated due to lignin complexity. Addition of oxidizing agents greatly improves delignification.

There are multiple processes that have been developed for this type of treatment. Figure 5.21 shows the lime pretreatment process flow diagram. The pretreatment can be done under various conditions, such as oxidative and non-oxidative conditions, short term high temperature (100-200°C, 1-6 h), and long term low temperature (25-65°C, 1-8 weeks). Figure 5.22 shows the soaking in aqueous ammonia (SAA) process flow diagram.

Lime pretreatment process flow diagram as described in the text

Figure 5.21: Lime pretreatment process flow diagram*.

[Click here for a text alternative to Figure 5.21](#)

Schematic of the Lime pretreatment process. Biomass enters a lime pretreatment with lime and oxygen gas. The temperatures and time of this process vary. There is about 1g of $\text{Ca}(\text{OH})_2$ per 1g of biomass the oxygen gas is at 100psi. After pretreatment, the biomass becomes a slurry that goes into water wash conditioning. The solids go to enzymatic hydrolysis where hexose sugars and solid residue (lignin) is separated. The liquids from the water wash conditioning go to acid post-hydrolysis. The slurry can also go to solid/liquid separation. The solid products of this separation go to water wash conditioning and the liquids go to acid post-hydrolysis. Acid post-hydrolysis yields pentose sugars.

Credit: BEEMS

Soaking in aqueous ammonia (SAA) process flow diagram

Figure 5.22: Soaking in aqueous ammonia (SAA) process flow diagram*.

[Click here for a text alternative to Figure 5.22](#)

Schematic of soaking in aqueous ammonia (SAA) process. Biomass is soaked in aqueous ammonia at 120-180 C. This pretreatment can take minutes to hours. The biomass then goes to post washing with water and counter-current leaching. The solids go to enzymatic hydrolysis where hexose sugars and the solid residue is separated. The liquids go to acid post-hydrolysis which removes the pentose sugars and lignin. This also removes the dilute NH_3 which is recycled.

Credit: BEEMS

One of the more developed high pH processes is the ammonia fiber expansion (AFEX) process. Lignocellulosic biomass is soaked in liquid ammonia (causing swelling) followed by the rapid release of pressure (causing expansion). Anhydrous liquid ammonia is used, and key parameters include temperature, residence time, ammonia concentration, and moisture content of the biomass. During this process, there is virtually no compositional change, but lignin is relocated, cellulose is decrystallized, and hemicellulose is depolymerized. This method increases the size and number of micropores in the cell wall to allow for greater accessibility of chemicals for the following stages of processing. A process schematic is shown in Figure 5.23.

AFEX process flow diagram

Figure 5.23: AFEX process flow diagram*.

[Click here for a text alternative to Figure 5.23](#)

Schematic of AFEX process. Biomass is added with ammonia to AFEX pretreatment (60-160 C). Pretreatment can take minutes to hours. The ammonia is recycled and the solids go to enzymatic hydrolysis where sugars and the solid residue is separated. Before enzymatic hydrolysis, there is an option post-washing step. The solids go into a water wash conditioning and then solid/liquid separation. The solids go into the enzymatic hydrolysis and the liquids go to acid post-hydrolysis which yields pentose sugars.

Credit: BEEMS

5.3e: Organic Solvation Processes

5.3e Organic Solvation Processes

The next process type is using an organic solvent, such as the Organosolv (OS) process or the Cellulose solvent- and Organic Solvent-based LIGNOCCELLULOSE Fractionation (COSLIF) process. For the OS pretreatment, the main mechanism involves the dissolution of lignin by organic solvent and then re-precipitation by adding an antisolvent, such as acidified water. This method was first introduced as a pulping method for papermaking. The organic solvents commonly used are acetone, ethanol, methanol, etc., in an aqueous solution of 20-60% water. Key parameters include temperature, residence time, chemical addition, and the water concentration. The effect is to: separate lignin from lignocellulosic biomass; solubilize hemicellulose; and increase pore size and surface area in the cell wall. Figure 5.24 shows a schematic of a process diagram for OS pretreatment.

Organosolv (OS) process flow diagram

Figure 5.24: Organosolv (OS) process flow diagram*.

[Click here for a text alternative of figure 5.24](#)

Schematic of Organosolv (OS) process. Biomass, water, 60% ethanol, and 1.25% H₂SO₄ undergo Organosolv pretreatment at 180 C for 60 minutes. After pretreatment it goes to filtration, the solids go to washing with water/ ethanol to remove the pulp (cellulose). The liquids head to lignin precipitation which separates the lignin and the water soluble sugars. Any remaining ethanol is recycled.

Credit: Pan et al., 2006. *Biotechnol Bioeng.* , 94: 851-61

Another organic solvent based process is cellulose-solvent and organic-solvent lignocellulose fractionation (COSLIF). For this process, an organic solvent is introduced to dissolve cellulose prior to Organosolv processing. Figure 5.25 shows a schematic of COSLIF processing.

Cellulose-solvent and organic-solvent lignocellulose fractionation (COSLIF) diagram

Figure 5.25a: Cellulose-solvent and organic-solvent lignocellulose fractionation (COSLIF) diagram and resulting effects.

[Click here for a text alternative of figure 5.25a](#)

Schematic of Cellulose-solvent and organic-solvent lignocellulose fractionation (COSLIF). The raw material enters the digester with H₃PO₄ at 50 C. It then goes to the precipitation tank where it is treated with acetone. The material then enters washer 1 where it is treated with acetone where the black liquor is removed and goes to the distiller. The remaining material enters washer 2 where it is treated with water and the light liquor is removed and goes to the flash tank. All remaining material goes to the hydrolysis tank (50 C) and glucose is removed.

Black liquor: In the distiller acetone, acetic acid, and H₃PO₄ are removed and low MW lignin is extracted.

Light Liquor: In the flash tank, CaCO₃ is added and acetone and H₃PO₄ are removed. Hemicellulose is extracted.

Credit: Zhang et al., 2007. *Biotechnol. Bioeng.*, 97: 214-223

2 photos showing before & after pretreatment. Before: under the microscope distinct fibers are visible. After: there are no distinct fibers

Figure 5.25b: Before and After COSLIF treatment.

Credit: Zhang et al., 2007. *Biotechnol. Bioeng.*, 97: 214-223

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5.3f: Ionic Liquids

5.3f Ionic Liquids

One of the more usual methods of pretreatment of biomass uses ionic liquids. Ionic liquids (ILs) are organic salts that usually melt below 100°C and are strong solvation agents. A common salt that we are all familiar with is table salt, sodium chloride, NaCl. If dissolved in water, it separates into the ions of Na⁺ and Cl⁻, but it is not an organic salt like ILs. It has interesting properties, including the fact that, depending on the IL, it can solubilize whole cellulosic biomass or selectively dissolve components, e.g., lignin and cellulose. It is relatively easy to separate the dissolvent component from the organic salt by using an anti-solvent such as water, methanol, or ethanol. When cellulose has been dissolved by organic liquid and then re-precipitated by an anti-solvent, cellulose is less crystalline and easier to break down. Unfortunately, this is still a costly method of pretreatment, as there is difficulty in recycling ILs, and the ILs can be toxic to the enzymes and microbes used in processing cellulose to ethanol. One such IL is known as EmimAc (1-ethyl-3-methylimidazolium acetate), and is able to completely solubilize both cellulose and lignin in switchgrass. Figure 5.26 shows the chemical structure of EmimAc and the change in cellulose after reprecipitation of it using an antisolvent (T = 120°C). Figure 5.27 shows a schematic of the process diagram.

EmimAc chemical structure and cellulose before and after IL pretreatment. Before: rod like structures. After: blob like

Figure 5.26: EmimAc chemical structure and cellulose before and after IL pretreatment.

Credit: Singh et al., 2009. Biotechnol. Bioeng., 104: 68-75

Schematic of IL (EmimAc) pretreatment flow diagram

Figure 5.27: Schematic of IL (EmimAc) pretreatment flow diagram.

[Click here for a text alternative to Figure 5.27](#)

Schematic of Ionic Liquid (EmimAc) pretreatment process. Biomass enters IL pretreatment (120-140 C) with EmimAC. This pretreatment takes hours. After pretreatment the products head to cellulose regeneration which washes the products with anti-solvents (water, acetone+ethanol). The cellulose is extracted, and the remaining products go into lignin precipitation which precipitates the lignin and recycles the anti-solvents and IL.

Credit: Singh et al., 2009. Biotechnol. Bioeng., 104: 68-75

5.3g: Biological Pretreatment

5.3g Biological Pretreatment

The last technology we will look at is biological pretreatment. Lignin is removed from lignocellulosic biomass through lignin-degrading microorganisms. Key parameters are temperature, cultivation time, nutrient addition, and selectivity on lignin. Some of the lignin-degrading enzymes include lignin peroxidase, manganese peroxidase, laccase, and xylanase. Advantages to using a system such as this include: no chemicals, mild conditions (ambient temperature and pressure), low energy and low capital outlay, and less enzyme use later on. However, pretreatments take days to weeks, loss of cellulose and hemicellulose, contaminants, and additional pretreatment for higher sugar yield.

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5.3h: Summary

5.3h Summary

Of the methods we've discussed, there are pretreatment options that lead the others (some under commercialization). The current leading pretreatment options include dilute acid, AFEX, liquid hot water, lime, and aqueous ammonia, with dilute acid and water, AFEX, and lime under commercialization. Figure 5.28 shows switchgrass before pretreatment and after several pretreatment options, i.e., AFEX, dilute acid, liquid hot water, lime, and soaking in aqueous ammonia (SAA).

Resulting Switchgrass Solids after Different Pretreatment Technologies

Figure 5.28: The Resulting Switchgrass Solids after Different Pretreatment Technologies.

[Click Here for a Text Alternative of Figure 5.28](#)

Control: mix of yellows and brown sticks

AFEX: dull brown sticks

Dil. Acid: red brown clumps

LHW: dark brown red sticks

Lime: yellow-brown clumps and sticks

SAA: light brown sticks

Credit: Donohoe et al., 2011. Bioresour. Technol.

To summarize the methods of pretreatment, Table 5.3 shows some of these pretreatment methods and the major and minor effects on lignocellulosic biomass. All methods (AFEX, dilute acid, lime, liquid hot water, soaking aqueous ammonia, and treatment with SO₂) have an effect on increasing surface area, removing hemicellulose, and altering lignin structure. Only AFEX, lime, and SAA pretreatment remove lignin, and AFEX and SAA decrystallize cellulose.

table showing Effects of Pretreatment of Biomass Recalcitrance

Table 5.3: Effects of Pretreatment of Biomass Recalcitrance.

[Click Here for a Text Alternative of Figure 5.28](#)

Effects of Pretreatments of Biomass Recalcitrance

Pretreatment	Increases Accessible Surface Area	Decrystallizes Cellulose	Removes Hemicellulose	Removes Lignin	Alters Lignin Structure
AFEX	Major Effect	Major Effect	Minor Effect	Major Effect	Major Effect
Dilute Acid	Major Effect		Major Effect		Major Effect
Lime	Major Effect	Not Determined	Minor Effect	Major Effect	Major Effect
Liquid H ₂ O	Major Effect	Not Determined	Major Effect		Minor Effect
SAA	Major Effect	Major Effect	Minor Effect	Major Effect	Major Effect
SO ₂	Major Effect		Major Effect		Minor Effect

Credit: Mosier et al., 2005. Bioresour. Technol., 96: 673-686

Table 5.4 shows the conditions for ideal pretreatment of lignocellulosic biomass for dilute acid, steam explosion, AFEX and liquid hot water.

Table 5.4: Comparison of Pretreatment Processes^a

Pretreatment Process	Dilute Acid	Steam Explosion
Reactive Fiber	Yes	Yes
Particle Size Reduction Required	Yes	No
Hydrolyzate Inhibitory	Yes	Yes
Pentose Recovery	Moderate	Low
Low Cost Materials of Construction	No	Yes
Production of Process Residues	Yes	No
Potential for Process Simplicity	Moderate	High
Effectiveness at Low Moisture Contents	Moderate	High

^a Modified from (86); AFEX ratings from Bruce Dale (personal communication).

^b For grasses, data for wood not available.

Credit: Lynd, 1996. Annual Rev. Energy Environ., 21: 403-465

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5.4: Assignments

5.4 Assignments

Homework #5

For this homework, you will read four selections and compose an essay.

1. Please read the following selections. The first three can be accessed via the links in the **Lesson 5 Module**. The Laughlin selection can be accessed via the **Library Resources**.
 - Wald, Matthew. "On the Horizon, Planes Powered by Plant Fuel." *New York Times* 17 Jan. 2012.
 - "Obama's Pitch on Energy." *New York Times* 14 Feb. 2012, The Opinion Pages sec.
 - Taylor, James. "Trump's Energy Policy: 10 Big Changes", Opinion Contributor, *Forbes* 26 December 2016.
 - Laughlin, Robert B. *Powering the Future: How We Will (Eventually) Solve the Energy Crisis and Fuel the Civilization of Tomorrow*. New York: Basic, 2011. Print. (**Chapter 3**)
2. Write a summary **of each article**, addressing these three questions:
 - Question #1: What is the perspective of the article?
 - Question #2: Do you agree/disagree with it?
 - Question #3: Explain why.

Some notes on the format:

- Approximate length – 1-1½ pages total (a paragraph for each article), double-spaced, 1" margins, 12-point font, name at the top.
- The essay should incorporate answers to all 3 questions for each article.
- Use footnotes to indicate which reading you are referring to (i.e., Wald, pg #).
- Use as filename **your user ID_HW5 (i.e., ceb7_HW5)**.
- Upload it to the **Homework #5 Assignment** in Lesson 5.

(12 points)

Discussion #5

Post a response in Discussion #5 that includes discussion of the following questions:

1. Do you think that jet fuel generated from biomass will make an impact on the jet fuel market?
2. What do you think about the proposed energy policy and suggestions about impacting the Big Oil companies?
3. What are the "jungle laws" that appear to be governing our energy policy currently?

Take some time to review others' responses. Then **respond to at least one other person's post**. Grades will reflect critical thinking in your input and responses.

(5 points)

Exam #2

This week you will complete Exam #2.

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5.5: Summary and Final Tasks

5.5 Summary and Final Tasks

Summary

Lesson 5 covered biomass pyrolysis and biomass pretreatment. Pyrolysis is a thermal treatment in the absence of oxygen and at lower temperature than gasification. The main products of interest are chars that are often used in combustion (with some of the undesirable components removed), and liquids that need to be processed further to remove oxygen functionality and add hydrogen.

The goal of pretreatment is to overcome biomass recalcitrance and improve conversion efficiency/economics. Mechanical size reduction is generally required. Several pretreatment technologies have been developed based on the use of different chemicals. They do the following:

- Low pH pretreatment: hemicellulose removal, acetyl removal, lignin solubilization and re-precipitation, increased surface area
- High pH pretreatment: lignin removal, acetyl removal, hemicellulose solubilization, increased surface area
- AFEX pretreatment: no-compositional changes, lignin alternation, cellulose decrystallization, increased surface area
- Organosolv and IL: fractionation of lignin from cellulose and hemicellulose, increased surface area

References

Schobert, H.H., *Energy and Society: An Introduction*, 2002, Taylor & Francis: New York, Ch. 4-6.

He, Brian, Department of Biological and Agricultural Engineering, University of Idaho, BEEMS Module C2, Biomass Pyrolysis, sponsored by USDA Higher Education Challenger Program, 2009-38411-19761, PI on project Li, Yebo.

Shi, Jian, Hodge, D.B., Pryor, S.W., Li, Yebo, Department of Food, Agricultural, and Biological Engineering, The Ohio State University, BEEMS Module B1, Pretreatment of Lignocellulosic Biomass, sponsored by USDA Higher Education Challenger Program, 2009-38411-19761, PI on project Li, Yebo.

Reminder - Complete all of the Lesson 5 tasks!

You have reached the end of Lesson 5! Double-check the Road Map on the Lesson 5 *Overview* page to make sure you have completed all of the activities listed there before you begin Lesson 6.

Questions?

If there is anything in the lesson materials that you would like to comment on, or don't quite understand, please post your thoughts and/or questions to our *Throughout the Course Questions & Comments* discussion forum. I will check that discussion forum daily (Monday through Friday). While you are there, feel free to post responses to your classmates if you are able to help.

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6: GENERAL ETHANOL PRODUCTION

6.1: Final Project (Biorefinery Project)

6.2: Biochemical Structural Aspects of Lignocellulosic Biomass

6.2a: Starch

6.2b: Cellulose

6.2c: Hemicellulose

6.2d: Lignin

6.3: Enzymatic Biochemistry and Processing

6.3a: The Reaction of Cellulose- Cellulolysis

6.3b: Composition of Enzymes

6.3c: Hemicellulases and Lignin-degrading Enzymes

6.4: Assignments

6.5: Summary and Final Tasks

6.1: Final Project (Biorefinery Project)

6.1 Final Project (Biorefinery Project)

The final project will be due at the end of the semester. Toward the end of the semester, the homework will be less, so you'll have ample opportunity to work on this. However, I am including the expectations now, so that you can begin to work on it.

Biomass Choice

You will be choosing a particular biomass to focus your report on. For the biomass you choose, you will need to **do a literature review on the biomass** and how and where it grows. Your requirements for location include 1) where it grows, 2) climate, 3) land area requirement, and 4) product markets near location. However, **you are not to make a choice that already exists in the marketplace**. This includes 1) sugarcane for ethanol production in Brazil and 2) corn for ethanol production in the Midwest of the USA. You need to put thought into what biomass you are interested in converting to fuels and chemicals, as well as where you want to locate your small facility. Most of all, choose biomass and location based on your particular interests, so as to make it interesting to you.

The literature review should consist of a list of at least ten resources that you have consulted from journals and websites of agencies such as IEA. If available, five of these sources should be from the last five years. Please use [APA style](#) for your references.

Location Choice and Method of Production

Once you have determined a biomass, choose a location based on previous information. Discuss your reasons for the choice of biomass, location, and desired products for production. Include a map of the area where you want to grow and market your product. You need to be aware of whether or not the biomass you choose can grow in the climate of the area you choose.

You will be choosing a method with which to convert your biomass into fuels. You are expected to include a schematic of the process units and a description of each process that will be necessary to do the biomass conversion; you should include what each process does and a little about the chemistry of each. Show the major chemical reactions that will take place in the process. Figures 6.1 and 6.2 show a process diagram and a chemical reaction so you have an idea of what I expect.

Schematic of sulfuric acid pretreatment process

Figure 6.1: Schematic of the sulfuric acid pretreatment process. This is a typical process schematic or diagram.

[Click here for a text alternative of Figure 6.1](#)

Schematic of the sulfuric acid pretreatment process. Biomass is added to dilute sulfuric acid, called acid impregnation (0.5 – 5.0% H₂SO₄) it then goes to dilute acid pretreatment around (140-200 C). This pretreatment can take seconds to hours. It then becomes a slurry which goes into neutralization conditioning. The solids go to enzymatic hydrolysis where hexose sugars and solid residue (lignin) are separated. The liquids from the neutralization condition go to acid post-hydrolysis. The slurry can also go to solid/liquid separation. The solid products of this separation go to neutralization condition and the liquids go to acid post-hydrolysis. Acid post-hydrolysis yields pentose sugars.

Credit: BEEMS Module B1

Reaction schematic of the reaction of lignin in subcritical water, see image caption, contact instructor if you need more assistance

Figure 6.2: Reaction schematic of the reaction of lignin in subcritical water (1. ether cleavage via hydrolysis, 2. cleavage of aldehyde/ketone and methoxy, rearrangement reaction with each other). This is a typical reaction depiction, although most likely more complex than what I expect you to include.

Credit: M. Bembenic and C. Clifford, Energy Fuels, 27 (11), 6681-6694, 2013

Market

The next section has to do with marketing your product. If you don't have somewhere to sell your product, it will sit in a warehouse, maybe degrade (spoil is a more common term), and you won't be making money on it. In the location you have chosen, is there a market for the product? If not, is there a location nearby where you can sell it? Discuss how you might market your products in the areas where you want to use biomass and sell products. How might you make the product you are selling appeal to the public? Due to the deregulation of electricity markets in various states, the prices of electricity will vary. Some companies charge more for renewable-based electricity, so they have to appeal to a particular market of people who are willing to spend more on renewable electricity.

Economics

We are going to assume that your process is going to be economic. However, any economic evidence that you can include that supports your process or indicates it would be a highly economical process will be beneficial to your paper. I would also like for you to include any research and development that must occur in order for the process to become viable and economic (i.e., what is the current research on this process?).

Other Factors

Discuss other factors that could affect the outcome of implementing a bio-refining facility. What laws, such as environmental laws, might be in place? What is the political climate of the community you have chosen? What is the national political climate related to the biomass processing you have chosen? Are there any tax incentives that would encourage your process to be implemented or the product to be sold? An example would be something like this: all airlines in the US are expected to include a certain percentage of renewables in the jet fuel they use. So, would your process make jet fuel, and how would you market it to airlines? Include other factors that could "make or break" the facility.

Format

The report should be 8-12 pages in length. This includes figures and tables. It should be in 12-point font with 1" margins. You can use line spacing from 1-2. It is to be clearly communicated in English, with proper grammar and as free from typographical errors as possible. You will lose points if your English writing is poor.

The following format should be followed:

- Cover Page – Title, Name, Course Info
- Introduction
- Body of Paper (see sections described above)
- Summary and Conclusions
- [APA citation style](#) for citations and references.

Grading Rubric:

- Outline 10 points
- Rough Draft 30 points
- Final Draft: 30 points
- Presentation: 30 points
- TOTAL: 100 points

Rubrics specific to each section of the final project are available in the submission dropboxes.

When submitting, please upload your final project to the **Final Project Submission Dropbox**. **Save it as a PDF** according to the following naming convention: **userID_FinalProject (i.e., ceb7_FinalProject)**.

Attention:

Please remember that by submitting your paper in Canvas, you affirm that the work submitted is yours and yours alone and that it has been completed in compliance with University policies governing Academic Integrity, which, as a Penn State student, are your responsibility to understand and follow. Your projects will be reviewed closely for unattributed material and may be uploaded the plagiarism detection service Turnitin.com to assure its originality. Academic dishonesty and lazy citation practices are not tolerated, and should you submit a paper that violates the Academic Integrity policies of the College and the University, be advised that the strictest penalties allowable by the University will be sought by your instructor. Please ask for help if you are concerned about proper citation.

Questions

If you have questions:

- Office hours are by appointment on Fridays: 15:30-17:30 via Zoom. Please contact the assistant of the course to set up a time for the office hour the previous Tuesday until 11:59 pm. Please provide the question(s) that you plan to ask during the office hour when you set up a time for the office hour.

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6.2: Biochemical Structural Aspects of Lignocellulosic Biomass

6.2 Biochemical Structural Aspects of Lignocellulosic Biomass

For Review

To begin this part of Lesson 6, review the **Biomass Carbohydrate Tutorial from the previous lesson**. It will be important to remember all of the terminology for carbohydrates.

So, at this point, we've talked a bit about what lignocellulosic biomass is composed of, what various carbohydrates are chemically, and how to pretreat various biomass sources. Now, we will discuss the use of enzymes in biomass conversion, particularly in cellulose conversion. I'll first introduce you to **cellulases**, and then we'll look at a model of enzymatic hydrolysis of cellulose, and enzymes for hemicellulose and lignin.

For cellulases, we'll discuss what they are, provide a brief history, look at **glycosyl hydrolases**, and, finally, cellulases.

The processing of cellulose in lignocellulosic biomass requires several steps (see Figure 6.3). We've discussed pretreatment, where cellulose, lignin, and hemicellulose are separated. Hemicellulose is broken down to xylose and other sugars, which can then be fermented to ethanol. Lignin is separated out and can be further processed or burned depending on the best economic outcome. The first step of processing is then on the cellulose.

process of producing ethanol from lignocellulosic biomass, see text description in link below

Figure 6.3: Preview to the process of producing ethanol from lignocellulosic biomass.

[Click for a text description of Figure 6.3.](#)

Producing Ethanol from lignocellulosic biomass:

Cellulose is pretreated so that hemicellulose is broken down to xylose, and other sugars are fermented to ethanol.
Lignin is separated and burned: energy exceeds processing requirements.

Cellulose goes through enzymatic hydrolysis to produce glucose, which then goes through fermentation to produce 5% ethanol, which is distilled to produce 100% ethanol.

Credit: Liao, BEEMS Module B2

Pretreatment helps to decrystallize cellulose. However, it must be further processed to break it down into glucose, as it is glucose (a sugar) that can be fermented to make ethanol, and the liquid product must be further processed to make a concentrated ethanol. So, we are focusing this lesson on enzymatic hydrolysis of starch and cellulose.

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6.2a: Starch

6.2a Starch

We briefly addressed what starch is in Lesson 5. Now, we'll go into a little more depth. In plants, starch has two components: **amylose** and **amylopectin**. Amylose is a straight-chain sugar polymer. Normal corn has 25% amylose, high amylose corn has 50-70% amylose, and waxy corn (maize) has less than 2%. The rest of the starch is composed of amylopectin. Its structure is branched and is most commonly the major part of starch. Animals contain something similar to amylopectin, called glycogen. The glycogen resides in the liver and muscles as granules.

You can visit howstuffworks.com to see a schematic of what amylopectin looks like in a granule (see '[How Play-Doh Works](#)') and then strands of the compound. Figure 6.4 shows some micrographs of starch as it begins to interact with water. When cooking with starch, you can make a gel from the polysaccharide. (A) This part of the figure shows polysaccharides (lines) packed into larger structures called starch granules; upon adding water, the starch granules swell and polysaccharides begin to diffuse out of the granules; heating these hydrated starch granules helps polysaccharide molecules diffuse out of the granules and form a tangled network. (B) This is an electron micrograph of intact potato starch granules. (C) This is an electron micrograph of a cooked flaxseed gum network.

See image caption. Starch granules before look like smooth beans. After they look like squiggly spaghetti

Figure 6.4: Formation of polysaccharide gels. (A) Polysaccharides (lines) are packed into larger structures called starch granules; upon adding water, the starch granules swell and polysaccharides begin to diffuse out of the granules; heating these hydrated starch granules helps polysaccharide molecules diffuse out of the granules and form a tangled network. (B) Electron micrograph of intact potato starch granules. (C) Electron micrograph of a cooked flaxseed gum network.

Credit: [Science and Food Blog](#)

Now, let's look at the starch components on a chemical structure basis. **Amylose** is a linear molecule with the α -1,4-glucosidic bond linkage. Upon viewing the molecule on a little larger scale, one can see it is helical. It becomes a colloidal dispersion in hot water. The average molecular weight of the molecule is 10,000-50,000 amu, and it averages 60-300 glucose units per molecule. Figure 6.5 depicts the chemical structure of amylose.

Amylopectin is branched, not linear, and is shown in Figure 6.6. It has α -1,4-glycosidic bonds and α -1,6-glycosidic bonds. The α -1,6-glycosidic branches occur for about 24-30 glucose units. It is insoluble compared to amylose. The average molecular weight is 300,000 amu, and it averages 1800 glucose units per molecule. Amylopectin is about 10 times the size of amylose.

amylose as described in the text, alpha 1-4-glycosidic bonds make it spiral

Figure 6.5: Chemical structure of amylose. Each monomer is connected by the α -1,4-glycosidic bond. When looking at a larger scale, the polymer is helical.

Credit: [Daily Kos](#) and [Amylose: from Wikipedia.org](#)

Chemical structure of amylopectin as described in the text, both alpha 1-4 and alpha 1-6 bonds. Straight branched molecule

Figure 6.6: Chemical structure of amylopectin. Each straight-chain monomer is connected by the α -1,4-glycosidic bond, while the branches are connected by an α -1,6-glycosidic bond.

Credit: [The Science of Nutrition Blog](#) and [Amylose: from Wikipedia.org](#)

6.2b: Cellulose

6.2b Cellulose

Cellulose is the most abundant polysaccharide, and it is also the most abundant biomass on earth. The linkages are slightly different from starch, called β -1,4-glycosidic linkages (see Figure 6.7C), as the bond is in a slightly different configuration or shape. As shown in Figure 6.7A and 6.7B, this bond causes the strands of cellulose to be straighter (not helical). The hydrogen on one polymer strand can interact with the OH on another strand; this interaction is known as a hydrogen bond (H-bond), although it isn't an actual bond, just a strong interaction. This is what contributes to the crystallinity of the molecule. *[Definition: the H-bond is not a bond like the C-H or C-O bonds are, i.e., they are not covalent bonds. However, there can be a strong interaction between hydrogen and oxygen, nitrogen or other electronegative atoms. It is one of the reasons that water has a higher boiling point than expected.]* The strands of cellulose form long fibers that are part of the plant structure (see Lesson 5 Figure 5.14). The average molecular weight is between 50,000 and 500,000, and the average number of glucose units is 300-2500.

cellulose structure shown under microscope, looks like long flat fibers criss crossing and as chemical structure

Figure 6.7a: Depiction of cellulose in different forms.

Credit: [The McGraw-Hill Companies](#)

chemical structure of cellulose and fibres. Fibres are stacked layers of cellulose. It has amorphous (not aligned) and crystalline areas

Figure 6.7b: Structure of cellulose - single chain and fibers.

Credit: [CHEMIK 2013, 67, 3, 242-249](#)

Table 6.1 shows a comparison of the two types of starch and cellulose. Cellulose forms elongated fibers that stretch out; it doesn't curl the way the amylose does (remember the helical structure) and doesn't branch and curl the way the amylopectin does. Because of its chemical structure, it forms a large network where H-bonds stabilize the strand itself, and also the cluster of strands that make up the fibers. The H-bond gives cellulose fibers several important structural features. It is incredibly tough. It is water-impermeable because of the H-bonds and thus excludes water. Table 6.1: Comparison of features of the two components of starch and cellulose.

Table 6.1: Comparison of features of the two components of starch and cellulose.

Type of polysaccharide	Starch (Amylopectin)	Starch (Amylose)
Types of linkages	• α-1,4-glycosidic • α-1,6-glycosidic	α -1,4-glycosidic
Function	Stores energy	Stores energy
Molecular weight (amu)	300,000	10,000-50,000
Size of glucose units	1800 glucose units	6-300 glucose uni

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6.2c: Hemicellulose

6.2c Hemicellulose

As seen in previous lessons, lignocellulosic biomass contains another component, hemicellulose. Rather than being a typical polymer where units repeat over and over again, hemicellulose is a heteropolymer. It has a random, amorphous structure with little strength. It has multiple sugar units rather than the one glucose unit we've seen for starch and cellulose, and the average number of sugar units is 500-3000 (glucose units with the starch and cellulose). The monomer units include: xylose, mannose, galactose, rhamnose, and arabinose units (see Figure 6.8 with a chemical structure of each). The various polymers of hemicellulose include: xylan, glucuronoxylan, arabinoxylan, glucomannan, and xyloglucan (see a couple of examples in Figures 6.9a and 6.9b).

monomer units and their chemical structures: xylose, mannose, galactose, rhamnose, and arabinose,

Figure 6.8: Monomer sugars found in hemicellulose.

Credit: Wikipedia page for each chemical, a) xylose wiki, b) mannose wiki, c) galactose wiki, d) rhamnose wiki, e) arabinose wiki

Example of polymers in hemicellulose (xylan)

Figure 6.9a: Example of polymers in hemicellulose (xylan).

Credit: [Xylan: from Wikimedia Commons](#)

Example of polymers in hemicellulose (arabinoxylan)

Figure 6.9b: Example of polymers in hemicellulose (arabinoxylan).

Credit: [Water Structure and Science Website](#)

6.2d: Lignin

6.2d Lignin

So, we've identified the chemical structures of starch, cellulose, and hemicellulose (see [Figure 6.3](#) to see how cellulose and hemicellulose are related.) Now we're going to take a look at what lignin is, chemically.

Vascular land plants make lignin in order to solve problems due to terrestrial lifestyles. Lignin helps to keep water from permeating the cell wall, which helps water conduction in the plant. Lignin adds support – it may help to “weld” cells together and provides stiffness for resistance against forces that cause bending, such as wind. Lignin also acts to prevent pathogens and why it is **recalcitrant** to degradation; it protects against fungal and bacterial pathogens (there is a discussion in Lesson 5 about recalcitrance). Lignin is comprised of crosslinked, branched aromatic monomers: p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol; their structures are shown in Figure 6.10a-c. Figures 6.10d and 6.10e show how these building blocks fit into the lignin structure. p-Coumaryl alcohol is a minor component of grass and forage type lignins. Coniferyl alcohol is the predominant lignin monomer found in softwoods (hence the name). Both coniferyl and sinapyl alcohols are the building blocks of hardwood lignin. Table 6.2 shows the differing amounts of lignin building blocks in the three types of lignocellulosic biomass sources.

Table 6.2: The amount of different building blocks in grasses, softwood, and hardwood.

Lignin Sources	Grasses	Softwood
p-coumaryl alcohol	10-25%	0.5-3.5%
coniferyl alcohol	25-50%	90-95%
sinapyl alcohol	25-50%	0-1%

Chemical structure for p-coumaryl alcohol

Figure 6.10a: Chemical structure for p-coumaryl alcohol.

Credit: [P-coumaryl alcohol: from The Board of Regents of the University of Wisconsin System](#)

Chemical structure for coniferyl alcohol

Figure 6.10b: Chemical structure for coniferyl alcohol.

Credit: [Coniferyl alcohol: from The Board of Regents of the University of Wisconsin System](#)

Chemical structure for sinapyl alcohol

Figure 6.10c: Chemical structure for sinapyl alcohol.

Credit: [Sinapyl alcohol: from The Board of Regents of the University of Wisconsin System](#)

Chemical structures for varieties of lignin

Figure 6.10d: Chemical structures for varieties of lignin.

Credit: <https://en.Wikipedia.org/wiki/Lignin>

Chemical structures for varieties of lignin

Figure 6.10e: Chemical structures for varieties of lignin.

Credit: [Lignin: from Wikimedia Commons](#)

There are several different materials that can be made from lignin, but most are not on a commercial scale. Table 6.3 shows the class of compounds that can be made from lignin and the types of products that come from that class of compounds. If an economic method can be developed for lignin depolymerization and chemical production, it would benefit biorefining of

lignocellulosic biomass.

Table 6.3: Low molecular chemicals and the products made from these types of chemicals.

Class of Compound	Product Example
Simple aromatics	Biphenyls, Benze
Hydroxylated aromatics	Phenol, Catechol
Aromatic Aldehydes	Vanillin, Syringal
Aromatic Acids and Diacids	Vanillic Acid
Aliphatic Acids	Polyesters
Alkanes	Cyclohexane

There are also high molecular weight compounds. These include carbon fibers, thermoplastic polymers, fillers for polymers, polyelectrolytes, and resins, which can be made into wood adhesives and wood preservatives.

6.3: Enzymatic Biochemistry and Processing

Starches are broken down by enzymes known as **amylases**; our saliva contains amylase, so this is how starches begin to be broken down in our body. Amylases have also been isolated and used to depolymerize starch for making alcohol, i.e., yeast for bread making and for alcohol manufacturing. Chemically, the amylase breaks the carbon-oxygen linkage on the chains (α -1,4-glucosidic bond and the α -1,6-glucosidic bond), which is known as hydrolysis. Once the glucose is formed, then fermentation can take place to break the glucose down into alcohols and CO_2 . The amylases were isolated and the hydrolysis of glucose began to be understood in the 1800s.

However, recall that cellulose linkages are β -1,4-glucosidic bonds. These bonds are much more difficult to break, and due to cellulose crystallinity, breaking cellulose down into glucose is even more difficult. It was only during WWII that enzymatic hydrolysis of cellulose was discovered. Instead of enzymes called amylases, the enzymes that degrade cellulose are called **cellulases**.

Cellulases are not a single enzyme. There are two main approaches to biological cellulose depolymerization: complexed and non-complexed systems. Each cellulase enzyme is composed of three main parts, and there are multiple synergies between enzymes.

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6.3a: The Reaction of Cellulose- Cellulolysis

6.3a The Reaction of Cellulose: Cellulolysis

Cellulolysis is essentially the hydrolysis of cellulose. If you recall from Lesson 5 (see Figure 5.16), in the low and high pH conditions, hydrolysis is a reaction that takes place with water, with the acid or base providing H^+ or OH^- to precipitate the reaction. Hydrolysis will break the β -1,4-glucosidic bonds, with water and enzymes to catalyze the reaction. Before discussing the reaction in more detail, let's look at the types of intermediate units that are made from cellulose. The main monomer that composes cellulose is glucose (Lesson 5, Figure 5.9a). When two glucose molecules are connected, it is known as cellobiose – one example of a cellobiose is maltose (Lesson 5, Figure 5.10b). When three glucose units are connected, it is called cellotriose – one example is β -D pyranose form. And four glucose units connected together are called cellotetraose. Each of these is shown below in Figure 6.11.

Glucose structure with carbons numbered.

Figure 6.11a: Glucose structure with carbons numbered.

Credit: Palaeos.com

Cellobiose, or maltose (glucose + glucose) chemical structure

Figure 6.11b: Cellobiose, or maltose (glucose + glucose) chemical structure.

Credit: Maltose Haworth: from Wikimedia Commons

Cellotriose in the β -D-pyranose form

Figure 6.11c: Cellotriose in the β -D-pyranose form.

Credit: Answers.com

Cellotetraose chemical structure

Figure 6.11d: Cellotetraose.

Credit: **Green Chem.**, 2012,14, 1284-1288

We've seen the types of intermediates, so now let's see the reaction types that are catalyzed by cellulose enzymes. The steps are shown in Figure 6.12.

1. Breaking of the noncovalent interactions present in the structure of the cellulose, breaking down the crystallinity in the cellulose to an amorphous strand. These types of enzymes are called **endocellulases**.
2. The next step is hydrolysis of the chain ends to break the polymer into smaller sugars. These types of enzymes are called **exocellulases**, and the products are typically cellobiose and cellotetraose.
3. Finally, the disaccharides and tetrasaccharides (cellobiose and cellotetraose) are hydrolyzed to form glucose, which are known as **β -glucosidases**.

Crystallized cellulose with endocellulase produces cellulose. Add exocellulase it produces cellobiose. Add Cellobiase & it produces glucose

Figure 6.12: Reaction sequence of cellulose with 1) endocellulase, 2) exocellulase, and 3) β -glucosidase.

Credit: Cellulase: from Wikipedia.org

Okay, now we have an idea of how the reaction proceeds. However, there are two types of cellulase systems: noncomplexed and complexed. A **noncomplexed** cellulase system is the aerobic degradation of cellulose (in oxygen). It is a mixture of extracellular cooperative enzymes. A **complexed** cellulase system is an anaerobic degradation (without oxygen) using a "cellulosome." The enzyme is a multiprotein complex anchored on the surface of the bacterium by non-catalytic proteins that serve to function

like the individual noncomplexed cellulases but is in one unit. Figure 6.13 shows a figure of how the two different systems act. However, before going into more detail, we are now going to discuss what the enzymes themselves are composed of. The reading by Lynd provides some explanation of how the noncomplexed versus the complexed systems work.

Hydrolysis schematic representation - see caption and text above

Figure 6.13: Schematic representation of the hydrolysis of amorphous and microcrystalline cellulose in A) noncomplexed and B) complexed cellulase systems.

Credit: Lynd et al., 2002

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6.3b: Composition of Enzymes

6.3b Composition of Enzymes

The first place to start is to describe the structure of a cellulase using typical terms in biochemistry. A modular cellobiohydrolase (CBH) has a few aspects in common; the common features include: 1) binder region of the protein, 2) catalytic region of the protein, and 3) a linker region that connects the binder and catalytic regions. Figure 6.14a shows a general diagram of the common features of a cellulase. The CBH is acting on the terminal end of a crystalline cellulosic substrate, where the cellulose binding domain (CBD) is imbedded in the cellulose chain, and the strand of cellulose is being digested by the enzyme catalyst domain to produce cellobiose. This type of enzyme is typical of exocellulases. Figure 6.14b shows a more realistic model, where the linker is attached to the surface of the cellulose.

One of the main differences between glycosyl hydrolases (a type of cellulase) and the other enzymes how the **catalytic domain functions**. There are three types: 1) pocket, 2) cleft, and 3) tunnel. *Pocket or crater* topology (Figure 15A) is optimal for the recognition of a saccharide non-reducing extremity and is encountered in monosaccharidases. Exopolysaccharidases are adapted to substrates having a large number of available chain ends, such as **starch**. On the other hand, these enzymes are not very efficient for fibrous substrates such as cellulose, which has almost no free chain ends. *Cleft or groove cellulase catalytic domains* are “open” structures (15B), which allow a random binding of several sugar units in polymeric substrates and is commonly found in endo-acting polysaccharidases such as endocellulases. *Tunnel* topology (Figure 6.15C) arises from the previous one when the protein evolves long loops that cover part of the cleft. Found so far only in CBH, the resulting tunnel enables a polysaccharide chain to be threaded through it. The red portions on each catalytic domain is supposed to be the carbohydrate being processed, although it is difficult to see in this picture.

CMH attacks crystalline cellulose It has a cellulose binder domain, linker region doing glycosylation & catalytic domain yielding cellobiose

Figure 6.14a: Biochemistry of cellulases – a modular cellobiohydrolase (CBH).

Credit: Himmel et al., *Cellulases: Structure, Function, and Applications*. In: *Handbook on Bioethanol: Production and Utilization*.

Model schematic of what cellulases look like

Figure 6.14b: Model schematic of what cellulases look like, showing a more realistic picture of the catalytic domain, binding module, and linker.

Credit: [National Renewable Energy Laboratory](#)

Catalytic Domains of Glycosyl Hydrolases – A) pocket, B) cleft, and C) tunnel, see text description in link below

Figure 6.15: Catalytic Domains of Glycosyl Hydrolases – A) pocket, B) cleft, and C) tunnel.

[Click for a text description of Figure 6.15](#)

Catalytic Domains of Glycosyl Hydrolases:

Pocket - glucomylase from *A. awamori*, Hydrolysis of amorphous polymers or dimers (e.g. starch and cellobiose)

Cleft - Endoglucanase (Cel6A) from *T. fusca* Hydrolysis of crystalline polymers (e.g. cellulose endoglucanases)

Tunnel - exoglucanase CHBII (Cel6A) from *T. reesei*, processive hydrolysis of crystalline polymers (e.g. exoglucanases)

Credit: Davies and Henrissat, 1995

The other main feature of these enzymes is the cellulose binding domain or module (CBD or CBM). Different CBDs target different sites on the surface of the cellulose; this part of the enzyme will recognize specific sites, help to bring the catalytic domain close to the cellulose, and pull the strand of cellulose molecule out of the sheet so the glycosidic bond is accessible.

So now, let's go back to noncomplexed versus complexed cellulase systems. Figure 6.16 is another comparison of noncomplexed

versus complexed cellulase systems, but this time, it focuses on the enzymes. Notice in Figure 6.16A, the little PacMan look-alike figures for enzymes. The enzymes are separate, but work in concert to break down the cellulose strands into cellobiose and glucose. Recall that this process is aerobic (in oxygen).

Now look at Figure 6.16B and the complexed system. The enzymes are attached to subunits that are attached to the bacterium cell wall. The products are the same, but recall that this system is anaerobic (without oxygen), and these enzymes all work together to produce cellobiose and glucose.

Noncomplexed versus complexed cellulase systems. Described in text above

Figure 6.16: Noncomplexed versus complexed cellulase systems, focusing on the enzymes and their differences in both systems.

*Credit: Khanok Ratanakhanokchai, Rattiya Waeonukul,
Patthra Pason, Chakrit Tachaapaikoon, Khin Lay Kyu,*

Kazuo Sakka, Akihiko Kosugi and Yutaka Mori (2013). Paenibacillus curdlanolyticus Strain B-6 Multienzyme Complex: A Novel System for Biomass Utilization, Biomass Now - Cultivation and Utilization, Dr. Miodrag Darko Matovic (Ed.), ISBN: 978-953-51-1106-1, InTech, DOI: [10.5772/51820](https://doi.org/10.5772/51820).

So, what are those subunits that are essentially the connectors in the enzyme? Figure 6.17 shows a schematic of the types. The cellulosome is designed for the efficient degradation of cellulose. A **scaffoldin subunit** has at least one cohesin modules that are connected to other types of functional modules. The CBM shown is a cellulose-binding module that helps the unit anchor to the cellulose. The **cohesin modules** are major building blocks within the scaffoldin; cohesins are responsible for organizing the cellulolytic subunits into the multi-enzyme complex. **Dockerin modules** anchor catalytic enzymes to the scaffoldin. The **catalytic subunits** contain dockerin modules; these serve to incorporate catalytic modules into the cellulosome complex. This is the architecture of the *C. thermocellum* cellulosome system. (Alber et al., CAZpedia, 2010). Within each cellulosome, there can be many different types of these building blocks. Figure 6.18 shows a block diagram of two different structures of *T. neapolitana* LamA and *Caldicellulosiruptor* strain Rt8B.4 ManA in a block diagram form. Due to the level of this class, we will not be going into any greater depth about these enzymes.

Cellulosome components for complexed enzyme, described in text above

Figure 6.17: Cellulosome components for a complexed enzyme.

Credit: [Cellusome: from CAZYpedia](#)

Modular structure of *T. neapolitana* LamA and *Caldicellulosiruptor* strain Rt8B.4 ManA. Shows peptides in their sequence

Figure 6.18: Modular structure of *T. neapolitana* LamA and *Caldicellulosiruptor* strain Rt8B.4 ManA.

Credit: Summa et al., Biochem. J., 2001

6.3c: Hemicellulases and Lignin-degrading Enzymes

6.3c Hemicellulases and Lignin-degrading Enzymes

Hemicellulases work on the hemicellulose polymer backbone and are similar to endoglucanases. Because of the side chain, “accessory enzymes” are included for side-chain activities. An example of hemicellulase activity on arabinoxylan and the places where bonds are broken by enzymes are shown (blue) in Figure 6.19. Figure 6.20 shows another example of how hemicellulose breaks down hemicellulose, a complex mixture of enzymes in order to degrade hemicellulose. The example depicted is cross-linked glucurono arabinoxylan.

The complex composition and structure of hemicellulose require multiple enzymes to break down the polymer into sugar monomers—primarily xylose, but other pentose and hexose sugars also are present in hemicelluloses. A variety of debranching enzymes (red) act on diverse side chains hanging off the xylan backbone (blue). These debranching enzymes include arabinofuranosidase, feruloyl esterase, acetylxytan esterase, and alpha-glucuronidase [Table 6.4 shows enzyme families for degrading the hemicellulose]...As the side chains are released, the xylan backbone is exposed and made more accessible to cleavage by xylanase. Beta-xylosidase cleaves xylobiose into two xylose monomers; this enzyme also can release xylose from the end of the xylan backbone or a xylo-oligosaccharide. (U.S. DOE, 2006)

Example of hemicellulase activity on arabinoxylan, showing bonds that are broken.

Figure 6.19: Example of hemicellulase activity on arabinoxylan, showing bonds that are broken. The hemicellulases are shown in blue.

Credit: [U.S. DOE. 2006. Breaking the Biologic Barriers to Cellulosic Ethanol](#)

enzymes for degrading hemicelluloses: xylanase, arabinofuransidase, feruloyl esterase, b-exlosidase, a-glucuronidase, acetylxytan esterase

Figure 6.20: Complex mixture of enzymes for degrading hemicelluloses. Instead of using chemical structures, this example uses abbreviations for different parts of the glucurono arabinoxylan so the connections can be observed more easily. The backbone is shown in blue, while the hemicellulases are shown in red.

Credit: [U.S. DOE. 2006. Breaking the Biologic Barriers to Cellulosic Ethanol](#)

Table 6.4: Enzyme families for degraded hemicelluloses, i.e., glycoside hydrolase (GH) and carbohydrate esterase (CE).

Enzyme	Enzyme Families
Endoxylanase	GH5, 8, 10, 11, 43
Beta-xylosidase	GH3, 39, 43, 52, 54
Alpha-L-arabinofuranosidase	GH3, 43, 51, 54, 62
Alpha-glucuronidase	GH4, 67
Alpha-galactosidase	GH4, 36
Acetylxytan esterase	CE1, 2, 3, 4, 5, 6, 7
Feruloyl esterase	CE1

Lignin-degrading enzymes are different from hemicellulases and cellulases. They are known as a group as oxidoreductases. Lignin degradation is an enzyme-mediated oxidation, involving the initial transfer of single electrons to the intact lignin (this would be a type of redox reaction or reduction-oxidation reaction). Electrons are transferred to other parts of the molecule in uncontrolled chain reactions, leading to the breakdown of the polymer. It is different from the carbohydrate hydrolysis because it is an oxidation reaction, and it requires oxidizing power (e.g., hydrogen peroxide, H₂O₂) to break the lignin down. In general, it is a significantly slower reaction than the hydrolysis of carbohydrates.

Examples of lignin-degrading enzymes include lignin peroxidase (aka ligninase), manganese peroxidase and laccase, which contain metal ions involved in the electron transfer. *Lignin peroxidase* (previously known as ligninase) is an iron-containing enzyme, which accepts two electrons from hydrogen peroxide (H_2O_2), then passes them as single electrons to the lignin molecule. *Manganese peroxidase* acts in a similar way to lignin peroxidase but oxidizes manganese (from H_2O_2) as an intermediate in the transfer of electrons to lignin. *Laccase* is a phenol oxidase, which directly oxidizes the lignin molecule (contains copper). There are also several hydrogen-peroxide generating enzymes (e.g., glucose oxidase), which generate H_2O_2 from glucose. ([The Microbial World](#) website)

If you are interested in learning about mechanisms of these enzymes, then visit [this website from the Department of Chemistry, University of Maine](#). There are several pages that discuss how each of the different types of enzymes works mechanistically.

Lesson 7 will discuss the process of ethanol production after the use of cellulases on cellulose.

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6.4: Assignments

6.4 Assignments

To Read

Please read Lynd, L. R., P. J. Weimer, W. H. Van Zyl, and I. S. Pretorius. "Microbial Cellulose Utilization: Fundamentals and Biotechnology." *Microbiology and Molecular Biology Reviews* 66.3 (2002): 511-15. This can be accessed via the **Library Resources**. You will need to use the information from this selection to complete Homework #2.

Homework #2

Download and complete **Homework #2**. It contains questions that pertain to the Lesson 6 course material. When you are finished, upload your completed assignment to the **Homework #2 Dropbox**. Use the following naming convention for your assignment: **your user ID_HW2 (i.e., ceb7_HW2)**.

(12 points)

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6.5: Summary and Final Tasks

6.5 Summary and Final Tasks

Summary

In Lesson 6.1, we went over the requirements for the final project. In a future lesson, you will be expected to choose your biomass and outline your project.

Lesson 6.2 provided an overview of lignocellulosic biomass structure in greater depth than the previous lesson did. The greater depth is needed in order to understand how the enzymes work. You are expected to understand what lignocellulosic biomass is and how the components can break apart (i.e., what the fragments are chemically).

Lesson 6.3 discussed the basic composition of enzymes, how cellulosic enzymes (cellulases) work, and how hemicellulosic and lignitic enzymes work. The homework provided a background of what you need to know for enzymes.

References

M. Bembenic and C.E.B. Clifford, "Subcritical water reactions of model compounds for a hardwood derived Organosolv lignin with nitrogen, hydrogen, carbon monoxide and carbon dioxide gases," *Energy Fuels*, 27 (11), 6681-6694, 2013.

David Hodge, Wei Liao, Scott Pryor, Yebo Li, *Enzymatic Conversion of Lignocellulosic Materials: BEEMS Module B2*, sponsored by USDA Higher Education Challenger Program 2009-38411-19761.

Lee Lynd, P.J. Weimer, W.H. van Zyl, I.S. Pretorius, "Microbial cellulose utilization: Fundamentals and biotechnology," *Microbiology and Molecular Biology Reviews*, 66 (3), 506-577, 2002.

Gideon Davies and Bernard Henrissat, "Structures and mechanisms of glycosyl hydrolases," *Structure*, 3, 853-859, 1995.

Alber, O., Dassa, B., and Bayer, E., "Cellulosome" within the [CAZpedia website](#), 2010, accessed June 5, 2014.

Summa, A., Gibbs, M.D., and Bergquist, P.L., "Identification of novel β -mannan- and β -glucan-binding modules: evidence for a superfamily of carbohydrate-binding modules," *Biochem. J.*, 356, 791-798, 2001.

U.S. DOE, [Breaking the Biological Barriers to Cellulosic Ethanol: A Joint Research Agenda](#). DOE/SC-0095, U.S. Department of Energy Office of Science and Office of Energy Efficiency and Renewable Energy, 2006.

Reminder - Complete all of the Lesson 6 tasks!

You have reached the end of Lesson 6! Double-check the Road Map on the Lesson 6 *Overview* page to make sure you have completed the activity listed there before you begin Lesson 7.

Questions?

If there is anything in the lesson materials that you would like to comment on, or don't quite understand, please post your thoughts and/or questions to our *Throughout the Course Questions & Comments* discussion forum and/or set up an appointment for office hour. While you are there, feel free to post responses to your classmates if you are able to help.

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7: PROCESSING TO PRODUCE ETHANOL AND BUTANOL FROM CARBOHYDRATES AND ENZYMES

7.1: Ethanol Production - General Information

7.2: Sugarcane Ethanol Production

7.3: Ethanol Production from Corn

7.3a: Composition of Corn and Yield of Ethanol from Corn

7.3b: How Corn is Processed to Make Ethanol

7.4: Butanol Production

7.5: Assignments

7.6: Summary and Final Tasks

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7.1: Ethanol Production - General Information

7.1 Ethanol Production - General Information

Back in Lesson 2, I included a chemistry tutorial on some of the basic constituents of fuels. In this lesson, we will be discussing the production of ethanol ($\text{CH}_3\text{-CH}_2\text{-OH}$) and butanol ($\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-OH}$) from starch and sugar. Ethanol, or ethyl alcohol, is a chemical that is volatile, colorless, and flammable. It can be produced from petroleum via chemical transformation of ethylene, but it can also be produced by fermentation of glucose, using yeast or other microorganisms; current fuel ethanol plants make ethanol via fermentation.

The basic formula for making ethanol from sugar glucose is as follows:



chemical structure of glucose

Figure 7.0 Chemical Structure of Glucose

Credit: [Wikiwand](#)

For fermentation, yeast is needed (other enzymes are used but yeast is most common), a sugar such as glucose is the carbon source, and anaerobic conditions (without oxygen) must be present. If you have aerobic (with oxygen) conditions, the sugar will be completely converted into CO_2 with little ethanol produced. Other nutrients include water, a nitrogen source, and micronutrients.

Here in the US, the current common method of ethanol fuel production comes from starches, such as corn, wheat, and potatoes. The starch is hydrolyzed into glucose before proceeding with the rest of the process. In Brazil, sucrose, or sugar in sugarcane is the most common feedstock. And in Europe, the most common feed is sugar beets. Cellulose is being used in developing methods, which includes wood, grasses, and crop residues. It is considered developing because converting the cellulose into glucose is more challenging than in starches and sugars.

The International Energy Agency (IEA) predicts that ethanol will constitute two-thirds of the global growth in conventional biofuels with biodiesel and hydrotreated vegetable oil accounting for the remaining part (2018-2023). Global ethanol production is estimated to increase by 14% from about 120 bln L in 2017 to approximately 131 bln L by 2027 (Figure 7.1). Brazil will accommodate fifty percent of this increase and will be used to fill in the domestic demand (OECD/FAO (2018), "OECD-FAO Agricultural Outlook").

picture

Figure 7.1: Development of the world ethanol market.
[Click here for a text alternative to Figure 7.1](#)

Development of the World Ethanol Market 2010-2027. All values are based on visual approximations

Year	World Ethanol Trade in Billions of Liters
2010	6
2011	10
2012	9
2013	8
2014	7
2015	7
2016	9
2017	10
2018	9
2019	9
2020	9
2021	9
2022	9
2023	9
2024	9
2025	9
2026	9
2027	9

Credit: OECD/FAO (2018), “OECD-FAO Agricultural Outlook”, OECD Agriculture statistics (database), <http://dx.doi.org/10.1787/agr-outl-data-en>

World production of ethanol-based by country is shown in Figure 7.2. The US produces the most ethanol worldwide (~57%), primarily from corn. Brazil is the next largest producer with 27%, primarily from sugarcane. Other countries, including Australia, Columbia, India, Peru, Cuba, Ethiopia, Vietnam, and Zimbabwe, are also beginning to produce ethanol from sugarcane.

pie chart of world ethanol production as described in the text

Figure 7.2: World ethanol production by country, in percent.

[Click here for a text alternative to Figure 7.2](#)

World Ethanol Production by Country

Country	Percent (%)
US	57%
Brazil	27%
Europe	6%
China	3%
India	2%
Canada	2%
Rest of the World	3%

Credit: [Renewable Fuels Association\(link is external\)](#)

Figure 7.3a shows the growth of sugarcane in the world, in tropical or temperate regions. Sugar beet production in Europe is the other source of sugar for ethanol. It is grown in more northern regions than sugarcane, primarily in Europe and a small amount in the US. Figure 7.3b shows the growth of sugar beets in the world.

world map showing sugarcane production concentrated in central & South America, india & some in Africa, and Southern Asia

Figure 7.3a: Sugarcane production around the world. The dark green represents the areas of greatest production.

Credit: [Sugarcane: from Wikipedia.org](#)

world map showing sugar beet production concentrated in Europe with some production in rural United States

Figure 7.3b: Sugar beet production around the world. The dark green represents the areas of greatest production.

Source: [Sugar beet: from Wikipedia.org](#)

7.2: Sugarcane Ethanol Production

7.2 Sugarcane Ethanol Production

Production of ethanol from corn will be discussed in the next section; this section will focus on sugarcane ethanol production. So, what needs to be done to get the sugar from sugarcane?

The first step is sugarcane harvesting. Much of the harvesting is done with manual labor, particularly in many tropical regions. Some harvesting is done mechanically. The material is then quickly transported by truck to reduce losses.

The cane is then cut and milled with water. This produces a juice with 10-15% solids from which the sucrose is extracted. The juice contains undesired organic compounds that could cause what is called sugar inversion (hydrolysis of sugar into fructose and glucose). This leads to the clarification step in order to prevent sugar inversion.

In the clarification step, the juice is heated to 115°C and treated with lime and sulfuric acid, which precipitates unwanted inorganics.

The next step for ethanol production is the fermentation step, where juice and molasses are mixed so that a 10-20% sucrose solution is obtained. The fermentation is exothermic; therefore, cooling is needed to keep the reaction under fermentation conditions. Yeast is added along with nutrients (nitrogen and trace elements) to keep yeast growing. Fermentation can take place in both batch and continuous reactors, though Brazil primarily uses continuous reactors.

Figure 7.4 shows a schematic of one process for ethanol production along with the option to produce refined sugar as well. Sugarcane contains the following: water (73-76%), soluble solids (10-16%), and dry fiber or bagasse (11-16%). It takes a series of physical and chemical processes that occur in 7 steps to make the two main products, ethanol and sugar.

Schematic of process of sugarcane to produce ethanol and sugar, see text description below

Figure 7.4: Schematic of process of sugarcane to produce ethanol and sugar.

[Click Here for a text alternative to Figure 7.4](#)

Here is a list of the seven stages of the sugar cane process, followed by a step-by-step explanation of the seven stages:

Stage 1: Extraction
Stage 2: Juice Treatment (leading to sugar)
Stage 3: Juice Treatment (leading to ethanol)
Stage 4: Multi Effect Evaporator
Stage 5: Crystallization, Drying
Stage 6: Fermentor
Stage 7: Ethanol Distillation
Explanation of the seven stages beginning with Sugar Cane:

Stage 1 (Extraction) results in juice [also produces bagasse]. Juice is sent on to two possible stages: Stage 2 (eventually leading to sugar) or Stage 3 (eventually leading to ethanol).

Stage 2 produces Treated Juice [also produces cake].

Stage 3 produces Treated Juice. Treated Juice from Stage 3 is sent on to Stage 6 (Fermentor), while Treated Juice from Stage 2 is sent on to Stage 4 (Multi Effect Evaporator).

The result of Stage 4 (Multi Effect Evaporator) is syrup [this stage also produces vapor]. This syrup is sent on in several possible directions.

Option 1. The syrup finishes at Stage 5 (Crystallization, Drying), where the syrup becomes sugar [or sub-products].

Option 2. The syrup passes through Stage 5 (Crystallization, Drying), where the syrup becomes molasses and then goes on to Stage 6 (Fermentor).

Option 3. The syrup goes directly to Stage 6 (Fermentor).

The result of Stage 6 (Fermentor) is wine. The wine is sent on to Stage 7.

The result of Stage 7 (Ethanol Distillation) is ethanol [this stage also produces sub-products].

So, why produce both sugar and ethanol? Both are commodity products, so the price and market of the product may dictate how much of each product to make. This is how Brazilian ethanol plants are configured. In order to have an economic process, all of the products, even the by-products, are utilized in some fashion.

As noted previously, one of the major by-products is the dry fiber of processing, also known as bagasse. Bagasse is also a by-product of sorghum stalk processing. Most commonly, bagasse is combusted to generate heat and power for processing. The advantage of burning the bagasse is lowering the need for external energy, which in turn also lowers the net carbon footprint and improves the net energy balance of the process. In corn processing, a co-product is made that can be used for animal feed, called distillers grains, but this material could also be burned to provide process heat and energy. Figure 7.5 shows a bagasse combustion facility. The main drawback to burning bagasse is its high water content; high water content reduces the energy output and is an issue for most biomass sources when compared to fossil fuels, which have a higher energy density and lower water content.

Bagasse (see Figure 7.6) can have other uses. The composition of bagasse is: 1) cellulose, 45-55%, 2) hemicellulose, 20-25%, 3) lignin, 18-24%, 4) minerals, 1-4%, and 5) waxes, < 1%. With the cellulose content, it can be used to produce paper and biodegradable paper products. It is typically carted on small trucks that look like they have “hair” growing out of them.

sugar mill

Figure 7.5: The Usina Santa Elisa sugar mill in Sertãozinho, Brazil. Bagasse, a by-product of sugar production, can be burned for energy or made into ethanol.

Credit: [Enerzine](#)

bagasse- looks like dried, tan husks

Figure 7.6: Bagasse.

Credit: ["Ribeira Principal-Distillerie II-Canne à sucre déchiquetée"](#) by Ji-Elle - Own work. via Wikimedia Commons [CC BY-SA 3.0](#)

Another crop that has some similarities to sugarcane is sorghum. Sorghum is a species of grass, with one type that is raised for grain and many other types that are used as fodder plants (animal feed). The plants are cultivated in warmer climates and are native to tropical and subtropical regions. Sorghum bicolor is a world crop that is used for food (as grain and in sorghum syrup or molasses), as animal feed, the production of alcoholic beverages, and biofuels. Most varieties of sorghum are drought- and heat-tolerant, even in arid regions, and are used as a food staple for poor and rural communities. Figure 7.7 shows a picture of a sorghum field.

sorghum plants: tons of round orange brown clusters on the top of a stalk

Figure 7.7: Sorghum growing in Mississippi.

Credit: [Mississippi State University Extension Service](#)

The US could use several alternative sugar sources to produce ethanol; it turns out corn is the least expensive and, therefore, the most profitable feed and method to produce ethanol. Table 7.1 shows a comparison of various feedstocks that could be used to make ethanol, comparing feedstock costs, production costs, and total costs. When you look at using sugar to make ethanol (from various sources), you can see processing costs are low, but feedstock prices are high. However, in Brazil, sugarcane feed costs are significantly lower than in other countries. Notice the data is from 2006.

Table 7.1: Summary of estimated ethanol production costs (\$/gal)^a (Credit: [USDA Rural Development](#))

Cost Item	Feedstock Costs ^b	Processing Costs
UC Corn wet milling	0.40	0.63
UC Corn dry milling	0.53	0.52
US Sugarcane	1.48	0.92
US Sugar beets	1.58	0.77
US Molasses ^c	0.91	0.36
US Raw Sugar ^c	3.12	0.36
US Refined Sugar ^c	3.61	0.36
Brazil Sugarcane ^d	0.30	0.51
EU Sugar beets ^d	0.97	1.92

a Excludes capital costs

b Feedstock costs for US corn wet and dry milling are net feedstock costs; feedstock for US sugarcane and sugar beets are gross feedstock costs

c Excludes transportation costs

d Average of published estimates

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7.3: Ethanol Production from Corn

7.3 Ethanol Production from Corn

The following pages will describe the process of ethanol production from corn.

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7.3a: Composition of Corn and Yield of Ethanol from Corn

7.3a Composition of Corn and Yield of Ethanol from Corn

As established in the previous section, corn has the least expensive total cost for ethanol production. So what part of the corn is used for ethanol? Primarily the corn kernel is used for ethanol production. Figure 7.8 shows the general composition of corn. It is a picture of **yellow dent** corn, which is commonly used for ethanol production. The **endosperm** is mostly composed of starch, the corn's energy storage, and protein for germination. It is the starch that is used for making fuel. The **pericarp** is the outer covering that protects the kernel and preserves the nutrients inside. The pericarp resists water and water vapor and protects against insects and microorganisms. The living organism in the kernel is the **germ**. It contains genetic information, enzymes, vitamins, and minerals, which help the kernels grow into a corn plant. About 25% of the germ is corn oil and is a valuable part of the kernel. The **tip cap** is where the kernel is attached to the cob, and water and nutrients flow through the tip cap. This part of the kernel is not covered by the pericarp.

corn kernel layers labeled as described in the text above. From outside in: Pericarp, endosperm, and germ. The tip cap is at the very bottom

Figure 7.8: Composition of a kernel of corn.

Starch is a polymer. It is made up of D-glucose units. Therefore, glucose components directly impact ethanol yields. The components of yellow dent corn are the following. It is primarily composed of starch, at 62%. The corn kernel is also composed of protein and fiber (19%), water (15%), and oil (4%). It can also contain traces of other constituents, but these are small relative to the main components. If you'll recall from Lesson 6, starch is composed of two different polymeric molecules: amylose and amylopectin. If you factor in these two carbons, the starch can be broken into these components: amylopectin is 50% of the yellow dent corn kernel (80% of the starch) and amylose is 12% of the kernel (20% of the starch).

One bushel of corn (56 lbs.) can provide several products. The one bushel can provide:

31.5 lbs. of starch

OR

33 lbs. of sweetener

OR

2.8 gal. of fuel ethanol

OR

22.4 lbs of PLA fiber, which is a starch-based polymer called polylactic acid

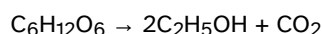
In addition, the corn will provide 13.5 lbs. of gluten feed (20% protein), 2.5 lbs. of gluten meal (60% protein), and 1.5 lbs. of corn oil. Based on this information, we can calculate the actual yield to the theoretical yield and determine the percent yield we can achieve for ethanol conversion. This is shown below:

1 bushel of corn:

56 lbs/bu x 62% starch = 34.7 lbs of starch/bu

34.7 lbs starch x 1.11 lbs glucose/lb starch = 38.5 lbs glucose/bu

The reaction of glucose to ethanol:



180g/mol 2*46 g/mol

38.5 lbs glucose x 92 lbs EtOH/180 lbs glucose = 19.7 lbs EtOH/bu

19.7 lbs EtOH x 1 gal EtOH/6.6 lbs = 3.0 gal EtOH/bu theoretical

100 x 2.8/3.0 = 93% yield of ethanol, typically

As discussed in Lesson 5 for pretreatment of lignocellulosic biomass, breaking down of glucose also requires hydrolysis. As water ionizes into H^+ and OH^- , it will break apart a molecule such as maltose into two glucose molecules. The reaction does not happen fast without either an enzyme (Lesson 6) or acid/heat (Lesson 5). Figure 7.9 shows the ratio of glucose monomer to the glucose subunit in starch. When starch is broken down, it is done so by adding the water molecule to form the glucose. This is where the value for lbs glucose/lb starch is derived for the calculation above.

maltose reacting in water to form two glucose molecules. Also shows molar masses and that there is 1.11g glucose/1g starch

Figure 7.9: Maltose reacting in water to form two glucose molecules.

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7.3b: How Corn is Processed to Make Ethanol

7.3b How Corn is Processed to Make Ethanol

The process of making corn into ethanol is a multistep process. The first step is to milling the corn. It can be done by dry milling or wet milling. Figures 7.10a and 7.10b show the process steps for each wet and dry milling. For wet milling, the corn kernels are broken down into starch, fiber, corn germ, and protein by heating in the sulfurous acid solution for 2 days. The starch is separated and can produce ethanol, corn syrup, or food-grade starch. As is noted in Figure 7.10a, the wet milling process also produces additional products including feed, corn oil, gluten meal, and gluten feed. Dry milling is a simpler process than wet milling, but it also produces fewer products. The main products of dry milling are ethanol, CO₂, and dried distiller grain with solubles (DDGS). Let's go through each of the steps in the dry grind process. The five steps are: 1) grinding, 2) cooking and liquefaction, 3) saccharification, 4) fermentation, and 5) distillation.

diagram of wet milling see text description below

Figure 7.10a: Wet Milling Process.

[Click here for a text alternative to figure 7.10a](#)

Schematic of The Wet Milling Process

First Corn is steeped. From steeping the corn the products are separated into:Starch/Gluten

The Starch/Gluten goes through a further step of separation and the starch is combined with all the other starch.

The wet gluten is then taken and dried to make dry 60% protein gluten meal

Starch

- The Starch goes through 3 separate processes
 - Drying to make starches
 - Fermentation to make ethanol chemical
- Syrup refining to make corn syrup, dextrose, and high fructose corn syrup

Corn Germ/Fiber go through grinding screening to yield

- Germ
 - goes through oil refining to become corn oil
- Fiber
 - Becomes feed product, wet feed

Credit: [Renewable Fuels Association](#)

diagram of the dry grind ethanol process, see text description below

Figure 7.10b: Dry grind ethanol process.

[Click here for a text alternative to figure 7.10b](#)

First corn is ground, cooked, liquefied and saccharified. From saccharification, it goes through fermentation which produces CO₂. After fermentation, it goes into distillation which produces ethanol. It is then centrifuged and evaporated which yields distillers grains with solubles.

Credit: Caroline Clifford

Grinding

For dry grinding corn, a **hammermill** or roller mill is used to do the grinding. Figure 7.11 is a schematic of a hammermill with

corn being put through it. The hammers are attached to rods that turn on a rotor. As the rotor turns, the feed (corn in this case) is hammered against the wall. A screen at the bottom allows particles that are small enough to leave the unit and keep in the larger particles to continue to be hammered until all the material is in the correct size range. The grinding helps to break the tough outer coatings of the corn kernel, which will increase the surface area of the starch. Once the corn is broken down, it is mixed/**slurried** with heated water to form a **mash** or **slurry**.

hammermill with parts labeled as described in the text: delivery device, hammers, rod, rotor, screen, take-away

Figure 7.11: Hammermill for dry grinding of corn.

Credit: [Feed Machinery](#)

Cooking and Liquefaction

Once the corn slurry (mash) is made, it goes through cooking and liquefaction. The cooking stage is also called **gelatinization**. Water interacts with the starch granules in the corn when the temperature is $>60^{\circ}\text{C}$ and forms a viscous suspension. Have you ever cooked with cornstarch to make thick gravy? Figure 7.12 shows a picture of starch mixed with water being poured into a heated sauce as it cooks. It will thicken with heat.

Corn starch mixed with water is being poured into a sauce mixture on a stove

Figure 7.12: Corn starch mixed with water is being poured into a sauce mixture; as it heats, it will thicken to form a sauce or gravy.

Credit: [I Want to Cook Blog](#)

The liquefaction step is actually partial hydrolysis that lowers the viscosity. It is essentially breaking up the longer starch chains into smaller chains. One way to measure this is to look at dextrose equivalents (DE), or a measure of the amount of reducing sugars present in a sugar product, relative to glucose, expressed as a percentage on a dry basis. Dextrose is also known as glucose, and dextrose equivalent is the number of bonds cleaved compared to the original number of bonds. The equation is:

$$\text{Equation 1: } 100 \times \frac{\text{number of bonds cleaved}}{\text{number of original bonds}}$$

Pure glucose (dextrose): DE = 100

Maltose: DE = 50

Starch: DE = 0

Dextrins: DE = 1 through 13

Dextrins are a group of low molecular weight carbohydrates produced by hydrolysis of starch or glycogen. Dextrins are mixtures of polymers of D-glucose units linked by α (1,4) or α (1,6) glycosidic bonds. Dextrins are used in glues and can be a crispness enhancer for food processing.

Maltodextrin: DE = 3 through 20

Maltodextrin is added to beer.

Recall that starch hydrolysis is where water reacts with the sugar to break the sugar down and form glucose. The water breaks into the H^+ and OH^- ions to interact with the starch as it breaks down.

In order to accomplish liquefaction, the reaction must take place under certain conditions. The pH of the mash is maintained in the range of 5.9-6.2, and ammonia and sulfuric acid are added to the tank to maintain the pH. About one-third of the required type of enzyme, α -amylase, can be added to the mash before jet cooking (2-7 minutes at $105\text{-}120^{\circ}\text{C}$) to improve the flowability of the mash. The jet cooking serves as a sterilization step to avoid bacterial contamination during the fermentation step later on. At this stage, shorter dextrins are produced but are not yet glucose.

Three types of processes can be utilized for liquefaction. Figure 7.13 shows the three options. Process 1 is where the α -amylase

is added and the material is incubated at 85-95°C. Process 2 has the mash in the jet cooker at 105-120°C for 2-7 minutes, then flows to a flash tank at 90°C. α -Amylase is added three hours later. The third option, Process 3, adds the α -amylase, the heats in the jet cooker at 150°C, followed by flow to the flash tank at 90°C and adding more α -amylase.

three options for liquefaction of corn mash, see text description below

Figure 7.13: The three option types for liquefaction processing of corn mash.

[Click here for a text alternative to figure 7.13](#)

Three processes

Process Type 1

α -amylase added; incubated at 85-95°C

Process Type 2

Jet cooker 105-120°C for 2-7 minutes

Flash Tank to 90°C; add α -amylase for 3 hours

Process Type 3

α -amylase added

Heating/Jet cooking @ 150°C

Flash tank to 90°C ; add more α -amylase

Credit: BEEMS Module B5

The α -amylase for liquefaction acts on the internal α (1,4) glycosidic bonds to yield dextrans and maltose (glucose dimers). A type of α -amylase exists in the saliva of humans; a different α -amylase is utilized by the pancreas. Figure 7.14a shows one type of α -amylase. The α -amylase works a little faster than the β -amylase, and the β -amylase works on the second α (1,4) glycosidic bond so that maltose is formed (see Figure 7.14b). β -amylase is part of the ripening process of fruit increasing the sweetness of fruit as it ripens.

protein structure of α -amylase

Figure 7.14a: Schematic of an α -amylase.

[Click here for a text alternative to figure 7.14a](#)

Coming

Credit: [Amylase: from Wikipedia.org](#)

protein structure of β -amylase

Figure 7.14b: Schematic of a β -amylase.

Credit: [Amylase: from Wikipedia.org](#)

Saccharification

The next step in the process of making ethanol is saccharification. Saccharification is the process of further hydrolysis to glucose monomers. A different enzyme is used, called a glucoamylase (also known by the longer name amyloglucosidase). It cleaves both the α (1,4) and α (1,6) glycosidic bonds from dextrin ends to form glucose. The optimum conditions are different from the previous step and are at a pH of 4.5 and a temperature of 55-65°C. Figure 7.14c shows a schematic of the glucoamylase, which is also called a γ -amylase. There are a wide variety of amylase enzymes available that are derived from bacteria and fungi. Table 7.2 shows different enzymes, their source, and the action of each.

protein structure of glucoamylase (aka a Y-amylase)
Figure 7.14c: Schematic of a glucoamylase (aka a Y-amylase).

Credit: [Global Healing Center](#)

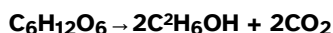
Table 7.2: Different enzymes used in starch depolymerization. (Credit: MF Chaplin and C. Bucke, *Enzyme Technology*, Cambridge University Press, 1990)

Enzyme	Source	Action
α-Amylase	<i>Bacillus amyloliquefaciens</i>	Only α-1,4-oligosaccharide links are cleaved to give α-dextrins and predominantly maltose (G2), G3, G6, and G7 oligosaccharides
	<i>B. licheniformis</i>	Only α-1,4-oligosaccharide links are cleaved to give α-dextrins and predominantly maltose, G3, G4, and G5 oligosaccharides
	<i>Aspergillus oryzae</i> , <i>A. niger</i>	Only α-1,4 oligosaccharide links are cleaved to give α-dextrins and predominantly maltose and G3 oligosaccharides
Saccharifying α-amylase	<i>B. subtilis</i> (<i>amyloliquefaciens</i>)	Only α-1,4-oligosaccharide links are cleaved to give α-dextrins with maltose, G3, G4 and up to 50% (w/w) glucose
β-Amylase	Malted barley	Only α-1,4-links are cleaved, from non-reducing ends, to give limit dextrins and b-maltose
Glucoamylase	<i>A. niger</i>	α-1,4 and α-1,6-links are cleaved, from the nonreducing ends, to give β-glucose
Pullulanase	<i>B. acidopullulyticus</i>	Only α-1,6-links are cleaved to give straight-chain maltodextrins

Some of the newer developed enzymes (granular starch hydrolyzing enzymes – GSHE) allow skipping the liquefaction stage by hydrolyzing starch at low temperatures with cooking. Advantages include: 1) reduced heat/energy, 2) reduced unit operation (reducing capital and operating costs), 3) reduced emissions, and 4) higher DDGS. They work by “coring” into starch granules directly without the water swelling/infusion. Disadvantages include: 1) enzymes cost more and 2) contamination risks.

Fermentation

The final chemical step in producing ethanol from the starch is fermentation. The chemical reaction of fermentation is where 1 mole of glucose yields 2 moles of ethanol and 2 moles of carbon dioxide. The reaction is shown in Equation 2 below:



To cause fermentation to take place, yeast is added. A common yeast to use is *saccharomyces cerevisiae*, which is a unicellular fungus. The reaction takes place at 30–32°C for 2–3 days in a batch process. Supplemental nitrogen is added as ammonium sulfate ((NH₄)₂SO₄) or urea. A protease can be used to convert proteins to amino acids to add as an additional yeast nutrient. Virginiamycin and penicillin are often used to prevent bacterial contamination. The carbon dioxide produced also lowers pH, which can reduce the contamination risk. Close to 90–95% of the glucose is converted to ethanol.

It is possible to do saccharification and fermentation in one step. It is called Simultaneous Saccharification and Fermentation (SSF), and both glucoamylase and yeast are added together. It is done at a lower temperature than saccharification (32–35°C), which slows the hydrolysis into glucose. As glucose is formed, it is fermented, which reduces enzyme product inhibition. It lowers initial glucose concentrations, lowers contamination risk, lowers energy requirements, and produces higher yields of ethanol. Because SSF is done in one unit, it can improve capital costs and save residence time.

Distillation and Increase of Ethanol Concentration

The last phase of ethanol production is the processing of ethanol to increase the ethanol concentration. Downstream from the fermenters, the ethanol concentration is 12–15% ethanol in water (which means you have 85–88% water in your solution!). **Distillation** was mentioned in an earlier lesson; crude oil must be distilled into various boiling fractions to separate the oil into useable products. Distillation is a process to separate components using heat and specially designed towers to keep the liquid flowing downward and the vapors being generated to flow upwards. Water boils at 100°C, while ethanol boils at 78°C. However,

because water and ethanol evaporate at a lower temperature than their boiling points, and because they both have OH functional groups that are attracted to each other, ethanol and water molecules are strongly bound to each other and form an azeotrope together. That just means that you cannot completely separate ethanol from water – the ethanol fraction will contain about 5% water and 95% ethanol when you get to the end of the distillation process. Figure 7.15 shows a schematic of a distillation unit. You don't want water in gasoline as you drive, because it prevents efficient combustion. Do you want water in your ethanol if you use it as a fuel?

Column with refluxing ethanol and a condenser to collect water out of the column

Figure 7.15: Distillation unit for increasing concentration of ethanol.

Credit: [Newcastle](#)

The answer is no, so you must use an additional method to remove all the water from ethanol. The method is called **dehydration**. The unit that is used is called a molecular sieve, and the material used in it is called zeolite. Under these conditions, the zeolite absorbs the water into it, but the ethanol will not go into the zeolite. They use what is called a pressure-swing adsorption unit. The unit is designed to run in two modes. At high pressure, the ethanol is dehydrated in Unit 1, and at low pressure, anhydrous ethanol is fed through to remove the water from Unit 2 (Figure 7.16a). When the zeolite sieve has absorbed all the water, Unit 1 is switched to become the low pressure regenerating bed, and Unit 2 becomes the high-pressure unit (Figure 7.16b). The residence time for the process is 3-10 minutes. The zeolite for this process is a highly ordered aluminosilicate with well-defined pore sizes that are formed into beads or included in a membrane. The zeolites attract both water and ethanol, but the pore sizes are too small to allow the ethanol to enter. As noted in Figure 7.17, the pore size of the zeolite membrane is 0.30 nm, while the size of the water molecule is 0.28 nm and the ethanol 0.44 nm. Depending on the type of unit, the membrane or beads can be regenerated using heat and vacuum, or by flowing the pure ethanol through the unit as well as described above.

Diagram of parts of EtOH distillation. see text description below

Figure 7.16a: The first unit is the dehydrator to remove water while the second unit is having the water removed.

[Click here for a text alternative to figure 7.16a](#)

The diagram shows 95% EtOH vapor from distillation going into Unit 1: a high pressure dehydrating bed. Out of that 60-85%, EtOH goes to the final product while 15-40% of the EtOH enters unit 2, a low-pressure vacuum regenerating bed. Out of this, the wet EtOH Vapor goes back to distillation.

Credit: *BEEMS Module B5*

Same diagram as previous except unit 1 is now the low pressure vacuum regenerating bed and unit 2 is the high pressure dehydrating bed

Figure 7.16b: The units switch places because the second bed of zeolite had the moisture removed and now acts as a dehydrator.

Credit: *BEEMS Module B5*

Diagram shows a zeolite membrane and says: Zeolite attracts water and ethanol but pore size limits ethanol absorption.

Figure 7.17: How the sieve works to keep water in and ethanol out.

Credit: *BEEMS Module B5*

So once we have fermented the material to ethanol, it goes through a series of processes to obtain the products in the form that we want them. Figure 7.18a is a schematic of product recovery, and Figure 7.18b shows the definitions of some of the terminology.

Product recovery diagram of ethanol and other products. See text description below

Figure 7.18a: Product recovery diagram of ethanol and other products.

[Click here for a text alternative to figure 7.18a](#)

Product recovery diagram of ethanol and other products. From fermentation, CO₂ is recovered along with Beer: 12-13% Ethanol. From there distillation occurs. This recovers 95% ethanol which goes through a molecular sieve to become 100% ethanol and goes into denatured ethanol storage with gasoline. From distillation whole stillage is also recovered. This goes into separation/centrifugation and yields thin stillage and WDG. The thin stillage is either recycled or it goes into the evaporator and becomes syrup. The WDG and syrup are combined to become WDGS. The WDGS goes into the dry and becomes DDGS.

Credit: BEEMS Module B5

Product separation/recovery terminology as described in the text. See text description below

Figure 7.18b: Product separation/recovery terminology.

[Click here for a text alternative to figure 7.18b](#)

The image defines terminology.

Whole Stillage (waste liquid from distillation) goes to centrifuge or filter presses.

Thin Stillage (liquid from centrifuge) is recycled or evaporated to make

Syrup (solubles) which are added to the

WDG (Wet distillers grains) which are then dried to make

DDGS (Distiller Dried Grains with Solubles)

Credit: BEEMS Module B5

To summarize, corn has 62% starch, 19% protein, 4% oil, and 15% water. If you look at the products on a dry basis (you don't look at the water like a product), 73% of the corn is starch and 27% is protein, fiber, and oil. For every bushel of corn, realistically you'll generate 2.8 gallons of ethanol, ~17 lbs of CO₂, and ~17 lbs of DDGS. We'll look at the economics of this process and a couple of other processes in a later lesson.

So, at this point, you can see how to generate ethanol from corn. If you want to generate ethanol from cellulose in plants, you have the information from Lesson 6 to generate glucose from cellulose (it is a more involved process), but once you have glucose, you can use the same end steps in ethanol production from fermentation of glucose. In the next section, we'll look at the production of another alcohol, butanol.

7.4: Butanol Production

7.4 Butanol Production

Another alcohol that can be generated from starch or cellulose is butanol, a four-carbon chain alcohol. There are usually two isomers: normal butanol (n-butanol) and iso-butanol. Their structures, along with ethanol, are shown below:

Table 7.3

Name	Atoms and Bonds
n-Butanol (4 C atoms)	butanol
Ethanol (2 C atoms)	ethanol
Isobutanol (4 C atoms)	atoms and bonds of isobutanol

There are some advantages of butanol when compared to ethanol:

1. It has a higher energy content than ethanol.
2. It is less hydrophilic than ethanol (less attracted to water).
3. It is more compatible with oil and its infrastructure.
4. It has a lower vapor pressure and higher flash point than ethanol (evaporates less easily).
5. It is less corrosive.
6. N-butanol works very well with diesel fuel.
7. Both n-butanol and iso-butanol have good fuel properties.

Table 7.4 shows a comparison of the energy content of various fuels in Btu/gal. The higher the value the more miles per gallon one can achieve; the Btu/gal value of butanol is close to the value of gasoline, and is higher than ethanol.

Table 7.4: Energy content of various fuels.

Fuel	Energy Content
Gasoline	114,800
Diesel fuel	140,000
Methanol	55,600
Ethanol	76,100
Butanol	110,000

Butanol production is also a fermentation process – we'll go over the differences in a little bit. There is a history regarding butanol production. It was known as the ABE process, or acetone, butanol, ethanol process. It was commercialized in 1918 using an enzyme named *Clostridium acetobutylicum* 824. Acetone was needed to produce Cordite, a smokeless powder used in propellants that contained nitroglycerin, gunpowder, and a petroleum product to hold it together – the acetone was used to gelatinize the material. In the 1930s, the butanol in the product was used to make butyl paints and lacquers. It has also been reported that Japanese fighter planes used butanol as fuel during WWII. The process of ABE fermentation was discontinued in the US during the early 1960s due to unfavorable economic conditions (made less expensively using petroleum). South Africa used the process into the 1980s, but then discontinued. There are reports that China had two commercial biobutanol plants in 2008, and currently, Brazil operates one biobutanol plant. There are three species of enzymes commonly used for butanol fermentation because they are some of the highest producers of butanol: *Clostridium acetobutylicum* 824, *Clostridium beijerinckii* P260, and *Clostridium beijerinckii* BA101. Figures 7.19a and 7.19b show micrographs of two of the fermentation enzymes used for butanol production.

Micrograph of *Clostridium beijerinckii* BA101, ovular bacteria

Figure 7.19a: Micrograph of *Clostridium beijerinckii* BA101.

Credit: [Joint Genome Institute](#)

Micrograph of *Clostridium acetobutylicum* 824, ovular bacteria

Figure 7.19b: Micrograph of *Clostridium acetobutylicum* 824.

Credit: [BacMap Genome Atlas](#)

As in the conversion of starch to ethanol, the plants must be processed in a similar way, so I won't repeat the five steps we just covered – we just use different enzymes, and end processing may be different because of the different chemicals produced. Starch must be hydrolyzed in acid before using the enzyme. And, as with using cellulose and hemicellulose as the starting material, it must first be pretreated to separate out the cellulose, then treated again to eventually produce glucose in order to make butanol from fermentation. Remember the glucose to ethanol reaction? Starch will produce the following products: 3 parts acetone (3 $\text{CH}_3\text{-CO-CH}_3$), 6 parts butanol (6 $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{OH}$), and 1 part ethanol (1 $\text{CH}_3\text{-CH}_2\text{-OH}$).

So, what feed materials are used for butanol production? Similar to what is used for ethanol production, which includes: 1) grains, including wheat straw, barley straw, and corn stover, 2) by-products from paper and sugar production, including waste paper, cotton woods, wood chips, corn fiber, and sugarcane bagasse, and 3) energy crops including switchgrass, reed canarygrass, and alfalfa. Table 7.5 shows the costs of various biomass sources.

Table 7.5: Prices of biomass sources for alcohol production.

Source	Price (\$/ton)
Wheat straw	24
Barley straw	26
Oat straw	32
Pea straw	44
Grass hay	50
Corn stover	50
Switchgrass	60
Corn	260 (varied fr

The price and the availability of feeds determine what might be used to produce various biofuels. The feeds most available in the US are corn stover (2.4×10^8 ton/year) and wheat straw (4.9×10^7 ton/year). Other biomass substrates include corn fiber, barley straw and corn fiber at $\sim 4\text{-}5 \times 10^6$ ton/year. Yields of butanol from corn and corn products by fermentation are shown in Table 7.6.

Table 7.6: Yields of ABE and as individual components from corn and corn products during fermentation by solventogenic *Clostridium* species.

Clostridium species.">

Fermentation Substrates			
Acetone (g/L)	3-7	3-7	3-7
Butanol (g/L)	7-20	7-20	7-19
Ethanol (g/L)	0.3-1	0.3-1	0.5-1.7
Total ABE (g/L)	14-26	14-26	14-27
ABE yield g/g	0.33-0.42	0.33-0.44	0.33-0.50

The solventogenic *Clostridium* species can metabolize both hexose and pentose sugars, which are released by cellulose and hemicellulose in wood and agricultural wastes; this is an advantage over other cultures used to produce biofuels. If all the residues available were converted into acetone-butanol (AB), the result would produce 22.1×10^9 gallons of AB. In 2009, 10.6×10^9 gallons of ethanol was produced, but that was only equivalent to 7.42×10^9 gallons of butanol on an equal energy basis.

There are several issues that are a challenge to producing AB in a traditional batch process: 1) product (butanol) concentration is low 13-20 g/L, 2) incomplete sugar utilization (<60 g/L), and 3) the process streams are large. These issues are due to severe product inhibition. Other issues include: 1) butanol glucose yield low, 22-26%, 2) butanol concentration in fermentation is low, 1.5%, 3) butanol concentration of 1% inhibits microbial cell growth, 4) butanol fermentation is in two phases, and 5) feedstock cost is high.

One of the more important considerations of butanol production is limiting the microbial inhibitory compounds. These compounds include some compounds related to lignin degradation, including syringaldehyde, coumaric acid, ferulic acid, and hydroxymethylfurfural.

As an example of one particular process, wheat straw was processed using a separate hydrolysis, fermentation, and recovery process. The following conditions were used: 1) wheat straw milled to 1-2 mm size particles, 2) dilute sulfuric acid (1% v/v) pretreatment at 160 C for 20 min., 3) mixture cooled to 45 C and hydrolyzed with cellulase, xylanase, and β -glucosidase enzymes for 72 h, followed by centrifugation and removal of sediments, 4) fermentation with *C. beijerinckii* P260 (fermentation gases CO₂ and H₂ were released to the environment, but could be captured, separated and used in other processes, and 5) butanol removed by distillation. For this particular process, the production of ABE was relatively high, with butanol and acetone being the major products. The reaction was done in a batch reactor and no treatment was used to remove inhibitor chemicals. Table 7.7 shows the process with wheat straw, barley straw, corn stover and switchgrass. Wheat straw did not need to be detoxified, but the others did. Detoxification can be done with adding lime (a weak base) or using a resin column to separate out the components.

A schematic diagram of acetone butanol ethanol (ABE) production see text description below

Figure 7.20: A schematic diagram of acetone butanol ethanol (ABE) production.

[Click for an alternative text description of figure 7.20](#)

ABE production. The wheat straw goes into milling and then into treatment where it is treated with H₂SO₄, BuOH and water. It then goes into hydrolysis with enzymes. Out of hydrolysis Lignin is removed and the rest of the product continues to fermentation. During fermentation CO₂ and H₂ are removed and after fermentation, the solids are removed. After that Acetone and ethanol are recovered.

Credit: Pryor, Scott; Li, Yebo; Liao, Wei; Hodge, David; "Sugar-based and Starch-based Ethanol," BEEMS Module B

So, what can be done to overcome butanol toxicity? What kind of downstream processing needs to be done to separate out the wanted components? The butanol level in the reactor has to be kept to a certain threshold in order to reduce toxicity to the culture and utilize all the sugar reactants.

First of all, these are the typical processing steps that must be utilized in some form for most refining units (the upstream processing includes pretreating the raw material, similar to what we discussed in Lesson 5): 1) sorting, 2) sieving, 3) comminution (size reduction by milling), 4) hydrolysis, and 5) sterilization. The next main stage is the bioreaction stage: metabolite biosynthesis and biotransformations. The final aspect of processing is downstream processing, and the methods used depend on the products made. To separate solids, filtration, precipitation, and centrifugation take place. Flocculation can also be done. To separate liquids, several processes can be done: 1) diffusion, 2) evaporation, 3) distillation, and 4) solvent-liquid extraction.

For butanol processing, there have been several processes developed to reduce the level of toxicity. These include: 1) simultaneous saccharification, fermentation, and recovery (SSF), 2) gas stripping (using N₂ and/or fermentation gases – CO₂ and H₂), 3) cell recycle, 4) pervaporation (combination process of permeation/evaporation using selective membranes), 5) vacuum fermentation, 6) liquid-liquid extraction, and 6) perstraction (combination of solvent extraction and membranes for permeation). The goal is to convert all the sugars to acetone and butanol, but remove the products as they are produced to decrease toxicity. We'll discuss more about liquid-liquid extraction (or solvent extraction) when we get to the lesson on biodiesel.

Table 7.7: AB production from detoxified agricultural residue hydrolysates.

Substrate	Before detoxification
-----------	-----------------------

Substrate	Before detoxification
Wheat straw	
ABE (g/L)	25.0-28.2
Productivity (g/L•h)	0.63-0.71
Barley straw	
ABE (g/L)	7.1
Productivity (g/L•h)	0.10
Corn stover	
ABE (g/L)	0.00
Productivity (g/L•h)	0.00
Switchgrass	
ABE (g/L)	1.5
Productivity (g/L•h)	<0.02

7.5: Assignments

7.5 Assignments

Reminder

Remember that your Final Project outline will be due October 25th. You can see the full Final Project Outline Assignment in the next lesson.

Discussion #1

Please read the following selections.

- Robison, D. (2012, March 19). Startup Converts Plastic To Oil, And Finds A Niche.
- Bourzac, K. (2009, July 9). Biofuel Plant Opens in Brazil.

Write a paragraph discussing how these articles relate to biomass production and sustainability.

After posting your response, **please comment on at least one other person's response**. Discussions will be reviewed, and grades will reflect critical thinking in your input and responses. Don't just take what you read at face value; think about what is written.

(5 points)

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7.6: Summary and Final Tasks

7.6 Summary and Final Tasks

Summary

This lesson continued from the previous lesson, but went into greater depth with the processing aspects of ethanol production. Starch and cellulose must first be converted into glucose before fermentation into ethanol and CO₂. Starch feedstocks include sugarcane in Brazil, sugarbeets in Europe, and corn in the US. In order to process corn, there are five steps: grinding, cooking and liquefaction, saccharification, fermentation, and distillation. Enzymes are needed in saccharification, and yeast is needed in fermentation. Cellulose to glucose requires some additional steps and enzymes in order to break the structure down, but once it gets to the glucose stage, all the processing is the same. Because the water in the ethanol must be removed for use as a fuel, the last steps include distillation and molecular sieve.

Butanol can be produced in a similar way, but acetone and ethanol also accompany butanol processing. Different enzymes are used. While the concentration of butanol is low when converting from feed materials, butanol has some advantages over using ethanol; it mixes better with gasoline and has a higher energy content.

References

Pryor, Scott; Li, Yebo; Liao, Wei; Hodge, David; "Sugar-based and Starch-based Ethanol," BEEMS Module B5, USDA Higher Education Challenger Program, 2009-38411-19761, 2009.

Bothast, R.J., Schilcher, M.A., Biotechnological processes for conversion of corn into ethanol, Appl. Microbiol. Biotechnol., 67, 19-25, 2005.

Reminder - Complete all of the tasks!

You have reached the end of this Lesson! Double-check the Road Map on the Lesson *Overview* page to make sure you have completed all of the activities listed there before you begin the next lesson.

Questions?

If there is anything in the lesson materials that you would like to comment on, or don't quite understand, please post your thoughts and/or questions to our Throughout the Course Questions & Comments discussion forum and/or set up an appointment for office hour. While you are there, feel free to post responses to your classmates if you are able to help.

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8: THERMOCHEMICAL METHODS TO PRODUCE BIOFUELS

8.1: Review of Refinery Processing and Chemical Structures for Jet Fuel and Diesel Fuel

8.2: Direction Liquefaction of Biomass

8.3: Bioprocessing to Make Jet Fuel

8.4: Natural Gas and Synthetic Natural Gas as Feedstocks for Liquid Fuels

8.5: Fischer-Tropsch Process to Generate Liquid Fuels

8.6: Assignments

8.7: Summary and Final Tasks

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8.1: Review of Refinery Processing and Chemical Structures for Jet Fuel and Diesel Fuel

8.1 Review of Refinery Processing and Chemical Structures for Jet Fuel and Diesel Fuel

Recall from Lesson 2 the general schematic of a refinery, shown here in Figure 8.1. Jet fuel is typically in the middle distillate range, also known as naphtha and kerosene. Diesel fuel is heavier (higher molecular weight and longer long-chain hydrocarbons). These fuels do not require as much processing because they can be obtained primarily from distillation of oil, but because of sulfur/oxygen/nitrogen functional groups and high molecular weight waxes, these fuels must have these components removed. They are hydrotreated (hydrogen is added, sulfur/oxygen/nitrogen are removed, and aromatics are made into cycloalkanes). Waxes are also separated out.

Primary processes that are typical in a petroleum refinery see text description below

Figure 8.1: Primary processes that are typical in a petroleum refinery.

[Click here for a text alternative of Figure 8.1](#)

This is a simple flow diagram of crude oil refinery.

Crude oil enters and goes to distillation.

From distillation:

LPG (gases) goes through alkylation to become O.N. 100 Motor Fuel Alkylate which can go on to become gasoline

Straight-run gasoline goes through catalytic reforming to become O.N. 95 Reformate which can go on to become gasoline

Naphtha, Kerosene and Diesel all go through Hydrotreating and then dewaxing to become either treated Kerosene, Diesel (low sulfur) or lubricating oils.

Fuel Oil goes through a catalytic cracker to become O/N 90-95 Gasoline

Resid goes through Thermal Cracking to become either Carbon, Asphalt or O.N. 75 Gasoline.

Credit: Dr. Caroline B. Clifford

The primary structure we want for jet fuel and diesel fuel is:

Alkane - atoms are lined up. For stick representation, each corner represents a CH₂ group, and each end represents a CH₃ group.

Name	Atoms and Bonds
Heptane (7 C atoms)	7 Cs connected in a line with 3Hs on each terminal C and 2 C

Cycloalkanes - again, still an alkane, but forms a ring compound.

Name	Atoms and Bonds
Cyclohexane (6 C atoms)	hexagon with CH ₂ on each vertice

Table 8.1 also shows a list of different chemicals and the properties of each. This table is mainly focused on those chemicals that would be in jet and diesel fuels.

Table 8.1: List of common hydrocarbons and properties

Name	Number of C Atoms	Molecular formula	bp (°C)
Decane	10	C ₁₀ H ₂₂	174.1
Tetradecane	14	C ₁₄ H ₃₀	253.5
Hexadecane	16	C ₁₆ H ₃₄	287
Heptadecane	17	C ₁₇ H ₃₆	303
Eicosane	20	C ₂₀ H ₄₂	343
Cyclohexane	6	C ₆ H ₁₂	81
Cyclopentane	5	C ₅ H ₁₀	49
Benzene	6	C ₆ H ₆	80.1
Naphthalene	10	C ₁₀ H ₈	218
Tetrahydronaphthalene(tetralin)	10	C ₁₀ H ₁₂	207
Decahydronaphthalene(decalin)	10	C ₁₀ H ₁₈	187,19

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8.2: Direction Liquefaction of Biomass

8.2 Direction Liquefaction of Biomass

Graphic of the 4 methods of thermochemical conversion of biomass: pyrolysis, gasification, combustion & direct liquefaction (highlighted)

Figure 8.2: Next thermochemical conversion method of biomass – direct liquefaction. (The fourth, combustion, is not really a thermochemical conversion of biomass).

Credit: Dr. Caroline B. Clifford

There are differences for each of the thermal processes, as described in Lesson 5. Here we focus on direct liquefaction. Direct liquefaction (particularly hydrothermal processing) occurs in a non-oxidative atmosphere, where the biomass is fed into a unit as an aqueous slurry at lower temperatures, with bio-crude in the liquid form being the product. The primary focus of these particular processes is to produce a liquid product that is a hydrocarbon with an atomic H:C ratio of ~2, and a boiling range of 170-280 °C.

Many of the processes developed are based on coal-to-liquids processing. The main purposes in taking coal and biomass into a liquid is to produce liquids, to remove some of the less desirable components (i.e., sulfur, oxygen, nitrogen, minerals), and to make a higher energy density material that will flow.

One of the primary processes to convert coal into liquids directly is through a combination of thermal decomposition and hydrogenation under pressure. There are several single and two-stage processes that have been developed but have not been made commercial in the US. However, China opened a commercial direct liquefaction plant partially based on US designs in 2008. Figure 8.3a shows the general schematic of the plant as well as the products they make in Figure 8.3b. Design considerations include: 1) temperatures of ~400-450°C, 2) hydrogenation catalysts, 3) hydrocarbon solvents that are similar to fuels, 4) naturally occurring aromatics in coal, 5) sulfur, nitrogen, minerals that must be removed in refining of the liquid. Biomass can be processed in a similar manner, but biomass has significantly more oxygen and less aromatic compounds and decomposes differently than coal. Other processes have been developed for biomass, that appear to do a better job of processing cellulose. One process is hydrothermal processing in pressurized water using an acid catalyst such as LaCl_3 at 250°C - we won't go into more detail here, but it is different from the direct liquefaction discussion in the next paragraph.

schedmatic of Direct coal liquefaction schematic from Shenhua plant in China

Figure 8.3a: Direct coal liquefaction schematic from Shenhua plant in China.

[Click Here for a text description of figure 8.3a](#)

Schematic of Direct Coal Liquefaction.

Air enters the system and goes through air separation. This produces N_2 and O_2 . N_2 goes towards coal preparation and O_2 going to gasification and purification.

The coal enters the system and goes to coal preparation. Follow preparation it can either go to gasification and then on to purification and liquefaction or upgrading. Or it can go into a coal slurry preparation process. This process requires a catalyst and a solvent. Following treatment, the slurry begins liquefaction, followed by separation. Following separation, the residue is removed, and the solvent is recycled. The rest of the product goes to upgrading where H_2 is introduced. From upgrading the coal goes to fractionation which yields gas, naptha, jet fuel, and diesel.

Credit: [Translated into English from Yuzhuo Zhang](#)

11 jars of different colored liquids on a table. Ranging from black to red to yellow to clear (final product)

Figure 8.3b: Intermediates and final products from Shenhua plant – the two on the right (Hydro-upgraded Diesel and Hydro-upgraded Naptha) are the final products.

Credit: [Cornerstone](#)

So, what are the differences with direct liquefaction of biomass? On the surface, it looks pretty much the same as the process for coal liquefaction. It is a thermochemical conversion process of organic material into liquid bio-crude and co-products. Depending on the process, it is usually conducted under moderate temperatures (300–400°C, lower than coal liquefaction) and pressures (10–20 MPa, similar or maybe a little higher with primarily hydrogen in coal to liquids) with added hydrogen or CO as a reducing agent. Unlike coal, the biomass is “wet”, or at least wetter than coal, and can be processed as an aqueous slurry. When processed as an aqueous slurry, the process is referred to in the literature as hydrothermal processing and can be subcritical to supercritical for water. Figure 8.4 shows the conditions for supercritical water; water behaves more like an acid/base system under these conditions. Thus, it can also be a catalyst. There is also a high solubility of organic material in water under these conditions. This mainly occurs along the liquid/vapor line. The basic reaction mechanisms can be described as:

1. depolymerization of biomass;
2. decomposition of biomass monomers by cleavage, dehydration, decarboxylation, and deamination;
3. recombination of reactive fragments.

Different types of biomasses react differently depending on the biomass source. Carbohydrates, such as cellulose, hemicellulose, and starch can decompose in hydrothermal water. The typical product formed under these conditions is glucose, and glucose can then be fermented to make alcohol or further degrade in water to make glycolaldehyde, glyceraldehyde, and dihydroxyacetone. The products made depend on the conditions: at temperatures, ~180°C, products are sugar monomers, but at higher temperatures, 360–420°C, the aldehyde, and acetone compounds are formed.

Water phase diagram. Supercritical fluid happens after approx. 400°C and 22 MPa

Figure 8.4: Conditions for water to be supercritical and subcritical on a phase diagram.

Credit: DOI: 10.1016/j.energy.2011.03.013

Lignin and fatty acids also decompose in hydrothermal water, but the products are very different because the substrate is different. For lignin, the products are similar to the building blocks for lignin, as shown in [Figure 5.20a of Lesson 5](#) (p-coumaryl, coniferyl, and sinapyl alcohols), although the functional groups vary depending on the hydrothermal conditions. Bembenic and Clifford used hydrothermal water at 365°C and ~13 MPa to form methoxy phenols, using different gases to change the product slate (hydrogen, carbon monoxide, carbon dioxide, and nitrogen). For lipid or triglyceride (fats and oils) reaction in hydrothermal water at 330–340°C and 13.1 MPa, the main products are the free fatty acids (HC – COOH) and glycerol (C₃H₈O₃). The free fatty acids can then be reacted to straight-chain hydrocarbons that can be used for diesel or jet fuel, although the temperature usually needs to be a little higher (400°C) for this to take place. Figure 8.5 shows the schematic of a hydrothermal water process to convert algae into liquid fuels, making use of heat from an integrated heat and power system. Flue gas from a power generation facility is used to grow algae. Algae is then harvested and concentrated in water. The algae are then reacted in a hydrothermal unit followed by catalytic hydrogenation to make the straight-chain hydrocarbon liquid fuels.

Schematic for hydrothermal liquefaction of algae for production of liquid fuels, see text description below

Figure 8.5: Schematic for hydrothermal liquefaction of algae for production of liquid fuels (diesel, jet fuel).

[Click Here for a text description of figure 8.5](#)

Schematic for hydrothermal liquefaction of algae. First, the algae are grown, flue gas enters along with water, nutrients and recycled CO₂. Evaporation occurs during this period. After growth, the next step is cell concentration/dewatering (settling, dissolved air flotation and centrifugation). Next is hydrothermal liquefaction (HTL) and the aqueous phase is removed. Finally, comes catalytic is hydrotreating and product fractionation. Here hydrogen gas from a hydrogen plant is added. This process yields hydrocarbon biofuels. In the diagram, all of these steps have double-headed arrows pointing to heat integration and power generation (catalytic hydrogasification (CHG) + Biogas Combustion).

Credit: [USDE OSTI](#)

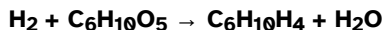
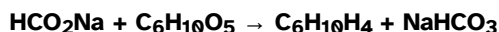
Many types of catalysts can be used, although it depends on the process stage in which catalysts are used and what feed material is used. In hydrothermal processing, the more common catalysts used are acid and base catalysts. Particle size for biomass needs to be fine, with a size of < 0.5 mm. The introduction of the feed into the reactor is also challenging, as it is fed into a high-pressure reactor. Some advantages of using this process for biomass: 1) it is possible to process feeds with high water content, as much as 90%, 2) it is possible to process many different types of waste materials, including MSW, food processing waste, and animal manure, and 3) the process serves the dual roles of waste treatment and renewable energy production.

Process parameters include solids content, temperature, pressure, residence time, and use of catalysts. Often simultaneous reactions are taking place, which makes the overall understanding of the reactions complicated. The types of reactions taking place include solubilization, depolymerization, decarboxylation, hydrogenation, condensation, and hydrogenolysis.

For one particular process, hydrothermal liquefaction requires the use of catalysts. One typical catalyst used is sodium carbonate combined with water and CO to produce sodium formate:



This dehydrates the hydroxyl groups to carbonyl compounds, then reduces the carbonyl group to an alcohol:



The formate and hydrogen can be regenerated and recycled. Other catalysts used that behave in a similar manner include K_2CO_3 , KOH, NaOH, and other bases. For simultaneous decomposition and hydrogenation, nickel (Ni) catalysts are used.

Similar to pyrolysis, the major product of this process is a liquid biocrude, which is a viscous dark tar or asphalt material. Up to 70% of the carbon is converted into biocrude; lighter products are obtained when different catalysts are used. Co-products include gases (CO_2 , CH_4 , and light hydrocarbons) as well as water-soluble materials. The liquid biofuel has a similar carbon to hydrogen ratio as in the original feedstock and is a complex mixture of aromatics, aromatic oligomers, and other hydrocarbons. In this process, the oxygen is reduced and is 10-20% less than typical pyrolysis oils, with a heating value higher than pyrolysis oils, 35-40 MJ/kg on a dry basis. However, the USDA has developed a pyrolysis process using recycled gases that produces a fairly light hydrocarbon with very little oxygen content. (Mullens et al.) I will discuss this more in the next section. Table 8.2 shows a comparison of biocrudes from various processes and feed materials. The quality of the biocrude shown from hydrothermal processing is for a heavy biocrude. Other processes will make a lighter material, but also produce more co-products that must be utilized as well.

Table 8.2: Comparison of biocrude from hydrothermal processing, bio-oil from fast pyrolysis, and heavy petroleum fuel.

Characteristic	Hydrothermal Bio-oil		Fast pyrolysis Bio-oil	
Water Content, wt%	3-5		15-25	
Insoluble solids, %	1		0.5-0.8	
HHV, MJ/kg	30		17	
Density, g/ml	1.10		1.23	
Viscosity, cp	3,000-17,000		10-150	
	Wet	Dry	Wet	Dry
Carbon, %	73.0	77.0	39.5	55.8
Hydrogen, %	8.0	7.8	7.5	6.1
Oxygen, %	16.0	13.0	52.6	37.9
Nitrogen, %	<0.1	<0.1	<0.1	<0.1
Sulfur, %	<0.05	<0.5	<0.05	<0.5
Ash, %	0.3-0.5	0.3-0.5	0.3-0.5	0.2-0.3

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8.3: Bioprocessing to Make Jet Fuel

8.3 Bioprocessing to Make Jet Fuel

Many researchers and scientists think that ground transportation will become increasingly dependent upon batteries, as in hybrids and electric vehicles. Reduction in fuel usage has been realized in the last 10 years, due to hybrid automobiles coming into the auto market. However, this is not a viable option for air travel, which will remain dependent on liquid fuel. Since more fuel will be available for aircrafts if less is used for vehicles, petroleum refineries should be able to keep up with demand. However, if there is a concern about emissions, especially the need to reduce CO₂, liquid jet fuels from biomass will by far be the best option. Jet fuel must also go through a qualification process and become certified for use depending on the source of the fuel and the type of jet engine. As discussed briefly in Lesson 2, jet fuel should have certain properties. Table 8.3 shows some of the ASTM qualifications for jet fuel that currently exist.

Table 8.3: Some jet fuel properties for certified military fuel JP-8.

	JP-8 spec limits, Min
Flash point, °C	38 (min.)
Viscosity, cSt, -20°C	--
Freezing point, °C	--
Smoke pt., mm	19 (min.)
Sulfur , wt%	--
Aromatics, %	--
Thermal stab.@ 260°C	--
Calorific value, Btu/lb	18,400
Hydrogen content	13.4
API gravity, 60°	37.0
FSII (DiEGME)	0.10
Conductivity pS/m	150

The Federal Aviation Administration has been working diligently to get some alternative fuels available in the market. The government has aspirational goals for American airlines to utilize alternative jet fuel, with the hope of 1 billion gallons of alternative jet fuel per year by the year 2018. Airlines will need to meet this requirement either by purchasing alternative jet fuel or finding viable methods to produce alternative jet fuel. The expectations for jet fuel are that it be primarily composed of long chain alkanes (although shorter carbon chain lengths than diesel fuel) with some cycloalkane and/or aromatic content for the necessary O-ring lubrication and other reasons.

There are several known biomass materials that could be utilized in the production of jet fuel. These include fats/oils, cellulose, woody biomass, and coal.

One of the primary sources is vegetable oil (this also includes algae oil and fats from production of meats). Vegetable oils contain long chain hydrocarbons connected by three carbons as esters. The fatty acid portion of the oil is easily converted into fatty acid methyl esters (FAMES) through transesterification to produce biodiesel. We will discuss biodiesel production for transesterification extensively in another lesson, but I will briefly discuss here why the FAA is interested in making jet fuel from fats and oils. Unfortunately, currently, FAMES are an issue for biojet fuel and requirements include a limit of 5 ppm, as the FAMES can cause corrosion, have a high freeze point, and are not compatible with materials in a jet engine. (Fremont, 2010) At present, biodiesel production is not always economic due to the high cost of oils and the method of production, and the ester must be removed for jet fuel.

Therefore, other methods are being evaluated to produce not only biodiesel, but also biojet fuel. These process methods include Hydroprocessed Esters and Fatty Acids (HEFA), Catalytic Hydrothermolysis, and Green Diesel. (Hileman and Stratton, 2014) Figure 8.6 shows a schematic of the process for HEFA. Jet fuel made from HEFA has been approved for use in airplanes because it has gone through the approval process. The following white paper, [Alternative fuels specification and testing](#), (Kramer, S., 2013, March 1, Retrieved December 16, 2014) includes a schematic of the approval process on page 4; as you can see, it is a thorough and complicated process, and it takes quite some time to get a particular type of fuel qualified.

There are others who want to explore the use of the fluid catalytic cracking (FCC) unit in a refinery to convert vegetable oils into jet fuel. Al-Sabawi et al. (CanmetENERGY) provided a review of various biomass products that have been processed at a lab scale in the FCC unit. They show that the main effect would be on the catalyst used and the lifetime of the catalyst. (Al-Sabawi, 2012)

Renewable jet process diagram for HEFA produced jet fuel.
Figure 8.6: Renewable jet process diagram for HEFA produced jet fuel.
[Click here for a text alternative to figure 8.6](#)

Natural Oils, Fats, and Greases are processed. First, they go into a hydrogen-rich environment and undergo deoxygenation. Water and CO₂ are removed during this step. From there the products go into another hydrogen-rich environment and undergo selective hydrocracking. Following hydrocracking, the products are separated. Any H₂ is recycled and the products become light fuels, green jet fuel, synthetic paraffinic Kerosene (SPK), and green diesel.

Credit: Dr. Caroline B. Clifford

Mullens and Boateng of the USDA have developed a process to produce pyrolysis oils of low oxygen content (data of properties of fuel in the previous section). (Mullens, 2013) The review paper by Al-Sabawi et al. also discusses the potential processing of pyrolysis oils in the FCC unit. The main requirement is the pyrolysis oils need to be low in oxygen, but additional information on the composition of the oil could tell us whether the FCC unit or another unit in a refinery would be best for processing.

Cellulosic sources for producing alternative jet fuel can be used. By use of gasification of biomass and Fischer-Tropsch processing, a good biojet fuel can be produced, although some additives need to be included to prevent some potential problems. There are also processes to produce medium chain length alcohols from cellulose, as methanol and ethanol do not have the energy density necessary to allow planes to fly long distances. One of the fuels that made it through the approval process is Synthetic Paraffinic Kerosene (SPK) made by Fischer-Tropsch synthesis. (Hileman and Stratton, 2014) It may also be possible to use by-products from the production of ethanol from corn (corn stover), sugar cane (bagasse), and paper production (tall oil). Westfall et al. (2008) and Liu et al. (2013) have also outlined other potential sources to produce fuels, with most processes including a catalytic deoxygenation aspect. (2008) The next section of this lesson will discuss Fischer-Tropsch and other chemical processes to make liquid fuels; it is an indirect method, as either natural gas or carbon materials that have been gasified must be used in these processes.

Additionally, there are some processes being developed for the production of alternative jet fuel from biomass-natural gas and biomass-coal. Researchers are working to develop processes at the demonstration scale for eventual commercialization. [Virent, along with Battelle in Ohio, have produced ReadiJet Fuel using a pilot scale facility. \(Conkle et al., 2012a, 2012b\)](#) Their paper includes a diagram of a schematic of their process (p. 3), a catalytic process to deoxygenate oils similar to the HEFA process. Liu et al. point out that jet fuel from natural gas has some advantages, especially the transportation aspect of fuels (2013). Jet fuel made from natural gas is made via steam reforming to CO and H₂, then use of the Fischer-Tropsch method to make long chain alkanes (see additional explanation toward the end of the lesson). The fuel is very clean (no sulfur and no aromatics) and can be a drop in replacement for petroleum-derived jet fuel - jet fuel made in this way has been thoroughly tested and the fuel has been qualified for use in military and commercial jet airliners so long as the alternative fuel composes less than 50% of the fuel mixture. Penn State and the Air Force have been involved with the production of a coal-based jet fuel (Balster et al., 2008) that could possibly be co-processed with some type of bio-oil, such as vegetable oil or low-oxygen pyrolysis oil. The potential for using the coal-based jet fuel lies in its high energy density, superior thermal properties, and few issues with lubricity. Table 8.4 shows how the fuel produced by Battelle/Air Force and PSU/Air Force meets some of the ASTM requirements; Battelle's fuel has been certified, but PSU's fuel has not completely met certification criteria. Recently, Penn State received DOE funding to expand the solvent extraction unit to a continuous reactor and will use solvent from Battelle's process to extract the coal - the goal is to incorporate coal into a biomass process in a more environmentally sound way than using other solvents. Figure 8.7 shows a schematic of the PSU unit. Elliot et al. (2013) at Pacific Northwest National Laboratory have developed a specific hydrothermal process to convert algal water slurries into organic hydrocarbons at subcritical water conditions (350 °C and 20 MPa pressure). The process also includes catalytic processes to remove oxygen, sulfur, and nitrogen, and the liquids generated are most likely of

fuel quality.

Table 8.4: Some jet fuel properties for certified military fuel JP-8 compared to fuel produced by PSU/Air Force and BETTELLE/Air Force
(Credit: Conkel et al. and Balster et al.)

	JP-8 spec limits, Min	JP-8 spec limits, Max.	JP-900 (actual) PSU/ Air Force	ReadiJet (actual) Battelle/ Air Force
Flash point, °C	38 (min.)		61	42
Viscosity, cSt, -20°C		8.0 (max.)	7.5	4.2
Freezing point, °C		-47 (max.)	-65	-44
Smoke pt., mm	19 (min.)		22	25
Sulfur, wt%		0.3 (max.)	0.0003	0.0
Aromatics, %		25 (max.)	1.9	10
Thermal stab.@260°C		25 mm (max.)	0	1
Calorific value, Btu/lb	18,400		18,401	18,659
Hydrogen content	13.4		13.2	
API gravity, 60°	37.0	51.0	31.1	44.5
FSII (DiEGME)*	0.10	0.15	0	0
conductivity pS/m*	150	600	0	0

*No additives were included in these fuels for these tests. Balster et al., Conkel et al.

PSU Solvent Extraction Unit - Large Laboratory Scale
Figure 8.7: PSU Solvent Extraction Unit - Large Laboratory Scale.
[Click here for a text alternative to figure 8.7](#)

This is a diagram of the PSU Solvent Extraction Unit. The diagram shows N₂ or H₂ gas at 100 psig being loaded into an extractor with a coal solvent (0.25 -1 kg/h). The extractor runs at 250-500°C. After the extractor, there is a settler at 200°C and any solids are removed for gasifying. Following the settler, there is a filter operating at 200°C, 100psig, 0.25-1kg/h. Any solids are removed for gasifying. After the filter, there is a liquids receiver and liquids for further upgrade are removed.

Credit: Dr. Caroline B. Clifford

8.4: Natural Gas and Synthetic Natural Gas as Feedstocks for Liquid Fuels

8.4 Natural Gas and Synthetic Natural Gas as Feedstocks for Liquid Fuels

In Lesson 4, we discussed gasification in depth. We also briefly discussed using syngas to make liquids. In Lesson 8, we will go into a little more depth. These types of processes are called indirect liquefaction.

The primary objective of gasification is to produce a syngas primarily composed of carbon monoxide (CO) and hydrogen (H₂). After gasification, the product needs to be cleaned to remove any liquids, and there are several reactions that can be done to change the H₂/CO ratio or to make different products. This is where we will start this lesson.

Figure 8.8 (a, b and c) shows the three different process phases that the gas must go through. The first phase (Figure 8a) is the gasifier and separation of gas, liquid, and solid products. The biomass is not pure carbon, and all the streams will contain a variety of other compounds that may not be wanted or may be harmful.

Solids are removed by a cyclone or an electrostatic precipitator. The particles are similar to what is seen in combustion – ungasified or partially gasified particles. Some mineral matter/ash can also be in the solids. A separator is used to remove the liquids, mainly tars and water that must be separated and processed for use. The water fraction can be used to react the organic compounds further, and the tars can be distilled and reacted further similar to the direct liquefaction processes we described in previous sections. In any case, the water must be treated before disposal.

1st phase - see text description below

Figure 8.8a: Gasification process to produce liquid products – the first phase is gasification and separation.

[Click here for a text alternative of Figure 8.8a](#)

Phase 1 of Gasification:

Coal is crushed, ground and sized in the presence of hydrogen. Next the prepared feed coal goes into the gasifier where there is steam from a boiler and lots of oxygen gas. Ash and slag are removed, and the remaining products go into tar separation where the raw gas is separated from the tar.

Credit: Dr. Caroline B. Clifford

The gases can also contain unwanted gases. Three gases that need to be removed from the gas phase are ammonia (NH₃), carbon dioxide (CO₂), and hydrogen sulfide (H₂S). They are corrosive and/or toxic and need to be removed. The acid gases (H₂S and CO₂) are called acid gases because they can dissolve in water and produce weak acids that can be corrosive to metals. There is a range of processes that can separate out the acid gases. One typical method to remove these harmful gases is called the Rectisol process (Figure 8.8b). Both H₂S and CO₂ are soluble in methanol, while H₂ and CO are not. In the simplified schematic in Figure 8.10b, there are two parts to the process, an absorber, and a regenerator. The raw gas goes into the absorber and comes into contact with the lean solution of methanol. The purified gas goes out the top, and the solution rich in unwanted absorbed gases goes to the regenerator – the acid gases are then separated out from the methanol so that a lean methanol solution comes out the bottom to be recycled for use in the absorber. The H₂S in the acid gas can be burned or reacted with SO₂ to form solid sulfur, which is used for making chemicals. The CO₂ goes out the stack but could also be captured if processes to capture it are put into place.

2nd phase - see text description below

Figure 8.8b: Gasification process to produce liquid products – the second phase is gas purification using the Rectisol process.

[Click here for a text alternative of Figure 8.8b](#)

Phase 2 of Gasification:

Raw Gas from phase one enters the absorber and the purified gas is removed. Then the remaining rich solution goes into the regenerator. Acid gas is separated in the regenerator and the remaining lean solution returns to the absorber

Credit: Dr. Caroline B. Clifford

The H₂/CO ratio may not be ideal for downstream synthesis reactions. Figure 8.8c shows a process to use the water-gas shift reaction to change the ratio of H₂/CO.

3rd phase - see text description below

Figure 8.8c: Gasification process to produce liquid products – the third phase after gas purification is the change in the ratio of H₂/CO.

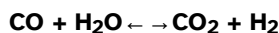
[Click here for a text alternative of Figure 8.8c](#)

Phase 3 of Gasification:

The purified gas and steam go to a WHS reactor. From there they enter a CO₂ scrubber which can send the gas to the regenerator to remove additional CO₂ after that the gas can return to the scrubber and with hydrogen gas proceed to synthesis.

Credit: Dr. Caroline B. Clifford

Ideally, the gas stream coming off the gasifier followed by a Rectisol unit could be reasonably pure H₂ and CO. The water-gas shift can change the ratio of H₂/CO. The reaction is shown below:



This would be the way to make less CO and more H₂, but the reaction can go in reverse to make more CO and less H₂ as well. From coal gasification, we want to shift it to the right as written. Advantages include:

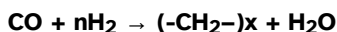
- that it's an equilibrium process;
- can shift reaction other direction by taking advantage of LeChatlier's Principle;
- with the same number of moles on both sides, the equilibrium position is independent of pressure – no requirement of compression or release of pressure of shift reactor;
- can be adapted to any operating pressure.

The major disadvantage of the water-gas shift reaction is it's a CO₂ factory! There only a few ways of separating CO₂, such as a monoethylamine (MEA) scrubber. You can separate the CO₂ to a 99% concentration, which would be ideal for CCS. Another thing to consider is we do not need to separate the entire gas stream and shift it; we only need to do enough to get the H₂/CO ratio where we want it to be. Once we get to this point, we can be ready to do some synthesis of liquids.

8.5: Fischer-Tropsch Process to Generate Liquid Fuels

8.5 Fischer-Tropsch Process to Generate Liquid Fuels

So, what can be done with synthesis gas? It can be burned and used in a gas turbine to heat exchange the heat to produce steam and operate a second turbine for electricity. The gas can be fed to a solid oxide fuel cell to generate electricity. We can also use synthesis gas to generate fuels, chemicals, and materials. In fact, the dominant application of synthesis gas from coal is the production of synthetic hydrocarbons for transportation fuels – Fischer Tropsch (FT) synthesis. This is what is primarily done in South Africa by the company Sasol and was also one of the methods used by the Germans in WWII to generate liquid fuels; in fact, direct liquefaction was the primary method used to produce liquid fuels in Germany in the 1940s. However, it is not the only gasification to liquids process. As noted in Lesson 4, the FT synthesis reaction can be presented by:



We are taking carbon atoms and building them up as alkanes, containing up to at least 20 carbon atoms. It is really a polymerization process, and it follows polymerization statistics. Figure 8.9 shows a typical polymerization statistical function. You will not obtain one single pure alkane from the FT process, and there will be a distribution of products. As with all chemical reactions, you will have reaction variables to adjust, such as temperature, pressure, residence, and addition of a catalyst. By skillful selection of variables (T, P, t, and catalyst), we can, in principle, make anything from methane to high molecular weight waxes. The intent is to maximize liquid transportation fuel production.

Number of atoms on x-axis, mass fraction on a log scale on y-axis. Slope is linear and negative.

Figure 8.9: Polymerization statistics for FT synthesis, where W_x is the weight fraction of compound with x atoms.

Credit: Dr. Caroline B. Clifford

The primary process for FT is the Synthol Process; the schematic is shown in Figure 8.10. The synthesis gas goes into the reactor at 2.2 MPa of pressure and 315–330°C. The product leaves the reactor where the catalyst is recovered, oils are removed by a hydrocarbon scrubber, and the tail gas recovered. The gas part is recycled, and the rest of the material is then distilled into gasoline, jet fuel, and diesel fractions. The Synthol reactor is a fluid bed reactor that uses an iron-based catalyst.

Schematic of Synthol process for FT liquids production see text description below

Figure 8.10: Schematic of Synthol process for FT liquids production.

[Click here for a text alternative of figure 8.10](#)

Schematic of Synthol Process for FT liquid production:

Synthesis gas enters the synthol reactor. From there it moves onto the catalyst recover. The gas can then return to the synthol reactor or proceed to the HC scrubber where heavy oil is introduced. Dissolved heavy oils are removed and everything else moves onto tall gas recovery. The tall gas is then recycled and everything else moves to distillation where it goes on to become gasoline, jet fuel and diesel.

Credit: Dr. Caroline B. Clifford

The liquids produced make very clean fuels. The product is near zero sulfur and low in aromatic compounds, and it is composed of mainly straight-chain alkanes. When considering the carbon-steam reaction, it is an endothermic reaction (the gasification, need to add heat). In this case, the reaction is “backward,” or going the other direction. Therefore, the FT synthesis reaction is an exothermic reaction. Because the reaction is exothermic, heat is generated, so Synthol reactors have internal cooling tubes with steam that when heated generate high-pressure steam that can be used in other processes.

FT diesel fuel is high-quality diesel fuel – we want to have linear alkanes, low aromatic content, and low sulfur. FT diesel fuel has all three aspects of diesel fuel that we want, and has a cetane number ≥ 70 – it is an ideal diesel fuel (recall that a good diesel fuel has a cetane number of 55).

Jet fuel made from FT synthesis makes a decent fuel. It is low in aromatic and sulfur content. **It is the first bio-based jet fuel that has been certified for use in aircraft and has been tested in blends with major airlines (Virgin).** However, for use in military jets, it must be blended because newer designs use the fuel as a coolant for electronics, as the fuel can have issues in these aircraft. For example, alkanes have the lowest density of various compound classes in jet fuel, so FT jet fuel has borderline volumetric density. Alkanes are also likely to undergo pyrolysis reactions at certain high temperatures, and if the fuel is used as a heat-exchange fluid to reduce the heat load, carbon formation can occur – this is mainly a problem for some of the newer military jet aircraft.

FT gasoline that comes straight off of the reaction is not great gasoline, as it has a low octane number. Recall that branched alkanes and aromatic compounds have higher octane numbers. Since FT compounds tend to be straight-chain alkanes, the isomerization is required, and an appropriate catalyst must be used for catalytic reforming.

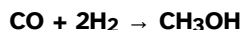
The primary location for gasification and FT synthesis is in South Africa – the gasoline being sold in South Africa has an octane number of 93. An integrated plant will also produce aromatics, waxes, liquid petroleum gas, alcohols, ketones, and phenols in addition to liquid hydrocarbon fuels. The reasoning behind marketing multiple products is because all the products will go up and down in price; when something goes up in price, you make more of it, when something goes down in price, you may make less. This is a way for plants to maximize their profits.

Methanol Production

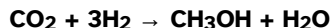
Synthesis gas can also be used to produce methanol, CH₃OH. The current technology for making methanol is fairly mature. Typically natural gas is used as the feedstock, which is steam reformed to make CO and hydrogen:



Then methanol is synthesized by the reaction:



However, another methanol synthesis reaction allows for CO₂ to be in the feed gas:



But because water and methanol are infinitely soluble, an additional step is required downstream to isolate methanol from water. Typical operating conditions in the methanol synthesis reactor are 5-10 MPa pressure, 250-270°C, using a copper/zinc catalyst. The reaction is extremely exothermic, so heat must be removed to keep the reaction under control. Similar to the FT reaction, the reactor has a shell and tube heat exchanger where the coolant is circulated through the shell, and catalyst particles are packed into the tubes where the reactant/product liquids flow. Figure 8.11 shows a schematic of the methanol synthesis process.

Feed and recycled gas go to the methanol synthesis reactor, then the methanol separator. Raw methanol is removed, other gases are recycled.

Figure 8.11: Schematic of the methanol synthesis process.

Credit: Dr. Caroline B. Clifford

So, what can methanol be used for? It is periodically used as a replacement for gasoline, particularly for racing fuel, as it has a high octane number. It has no sulfur in it, will produce almost no NO_x due to the low flame temperature and can be blended with gasoline.

There are also some disadvantages to using methanol as a fuel. It is infinitely miscible with water, it has health and safety issues, provides only half the volumetric energy density of gasoline, and may have compatibility issues with materials in some vehicles.

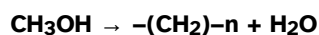
Enormous tonnages of methanol are produced and handled annually with excellent safety – but within the chemical process industry. However, if the general public is handling methanol, safety may be an issue, because methanol has toxic properties. Methanol is being seriously considered as the fuel of choice in the use of fuel cells. However, there is a process to make methanol directly into gasoline, so concerns about methanol aren't an issue then.

Methanol-To-Gasoline (MTG)

Methanol can be used to make a gasoline product. The process uses a special zeolite catalyst with pore size such that molecules up to C10 can get out of the catalyst. Larger molecules cannot be made with this process; therefore, a product is made with no carbon molecules greater than C10, which boils in the gasoline range. In this process, aromatics and branched-chain alkanes are made, which means the MTG process produces very high octane gasoline. Gasoline is the only product. In the reaction, methanol is converted into dimethyl ether (which can be a good diesel fuel) by the following reaction:



As the reaction progresses, the dimethyl ether is dehydrated further to the product hydrocarbons. The overall reaction is:



As with the other reactions we've looked at in this section of the lesson, the reaction is highly exothermic, so the reactor and process has to be designed to remove heat from the reaction to keep it under control. The conditions for this reaction are 330-400°C and 2.3 MPa. If one wanted to envision how a plant could incorporate all of these processes together, the following would be one scenario:

1. Add an MTG unit to existing natural gas-fed methanol plants (produce high octane gasoline).
2. Replace the natural gas units with coal and/or biomass gasification and gas conditioning.
3. Add parallel trains of Synthol reactors (produce high cetane diesel).
4. Add a third section, using a solid oxide fuel cell to generate electricity using synthesis gas as the feed material.

The plant then produces gasoline, diesel, and electricity.

8.6: Assignments

8.6 Assignments

Final Project Outline Assignment

Biomass Choice: Choose biomass to focus paper on.

This week, I am asking you to begin your biomass project. You will do a 1-2 page write-up, stating the information listed below. It can be an outline at this point but needs to have enough information so I can see what your project will be about and to see that you have begun to work on it.

1. Biomass Choice. **Reminder** - do not make choices that already exist in the marketplace. This includes sugar cane used to make ethanol in Brazil or corn used to make ethanol in the midwest of the USA.
2. Literature review on the biomass (at this point, this should consist of a list of resources that you have consulted - APA style, please!)
3. Requirements for location
 - Climate (i.e., tropical, subtropical, moderate,...)
 - Land area required or another type of facility to grow
4. Method of Production
5. Product markets around location
6. Economic Evidence
7. Other factors (environmental, political, tax issues, etc.)

Some notes on format:

- Approximate length - 2 pages, double-spaced, 1" margins, 12 point font, name at the top.
- The outline should include elements listed above.
- Use as filename **your user ID_Outline (i.e., ceb7_Outline)**.
- Upload it to the **Outline Dropbox**.

8.7: Summary and Final Tasks

8.7 Summary and Final Tasks

Summary

Lesson 8 covered thermochemical methods of converting biomass into fuels. These are the main methods being considered at this point; however, research continues on additional methods and what is included may not be a complete list. The main advantage of fermentation is that it is a natural process that does not require additional chemicals, but the main disadvantage to fermentation is the processes tend to be slow. All of the thermochemical processes require heat and some other process parameters that may make it more expensive – another lesson will discuss the economics behind all of the processes we've discussed for comparison.

We discussed both direct and indirect methods for making fuel from biomass. These methods are not just directed towards making ethanol. Many of these processes are used to make hydrocarbon fuels that limit the amount of oxygen in the product, as too much oxygen typically results in either causing the fuel to form unwanted "gums" or a corrosive environment that will cause problems in the units and storage containers. For jet fuels, oxygenated compounds will keep the fuel from being certified for use, so most of the methods presented make deoxygenated jet fuel. I would suggest continuing to monitor the news to see the progression in certification for additional bio-based fuels.

References

Al-Sabawi, M., Chen, J., Ng, S. "Fluid Catalytic Cracking of Biomass-Derived Oils and Their Blends with Petroleum Feedstocks: A Review," *Energy Fuels*, 26, 5355-5372, 2012.

Balster, L., Corporan, E., DeWitt, M., Edwards, J. T., Ervin, J.S., Graham, J.L., Lee, S-Y., Pal, S., Phelps, D.K., Rudnick, L.R., Santoro, R.J., Schobert, H.H., Shafer, L.M., Striebich, R.C., West, Z.J., Wilson, G.R., Woodward, R., Zabarnick, S. "Development of an advanced, thermally stable, coal-based jet fuel," *Fuel Processing Technology*, 89 (4), 364-378, 2008.

[CAPA Centre for Aviation](#), December 25, 2013, accessed June 17, 2014.

Conkle, H.N., Marcum, G.M., Griesenbrock, E.W., Edwards, E.W., Chauhan, S.P., Morris, Jr., R.W., Robota, H.J., Thomas, D.K., ["Development of Surrogates of Alternative Liquid Fuels Generated from Biomass."](#) 2012, accessed June 17, 2014.

Conkle, H.N., Griesenbrock, E.W., Robota, H.J., Morris, Jr., R.W., Coppola, E.N., ["Production of Unblended, "Drop-in," Renewable Jet Fuel."](#) 2012, accessed June 17, 2014.

Elliott, D.C., Hart, T.R., Schmidt, A.J., Neuenschwander, G.G., Rotness, L.J., Olarte, M.V., Zacher, A.H., Albrecht, A. O., Hallen, R.T., Holladay, J.E., "Process development for hydrothermal liquefaction of algae feedstocks in a continuous-flow reactor," *Algal Research-Biomass Biofuels and Bioproducts*, 2 (4), 445-454, 2013.

Fremont, M. "Jet Fuel Contamination with FAME- World Jet Fuel Supply," *Airbus FAST Magazine*, #46, August 2010, 8-13.

Kramer, S., ["Alternative Fuels: Specifications and Testing."](#) CAAFI: Research and Development Team White Paper Series: Specifications and Testing, 2011, accessed August 20, 2014.

Hileman, J.I., Stratton, R.W., "Alternative jet fuel feasibility," *Transport Policy*, article in press, 2014.

Liu, G. Yan, B., and Chen, G., "Technical review on jet fuel production," *Renewable and Sustainable Energy Reviews*, 25, 59-70, 2013.

Martinkus N, W. Shi, N. Lovrich, J. Pierce, P. Smith, and M. Wolcott. 2014. [Integrating biogeophysical and social assets into biomass-to-biofuel supply chain siting decisions](#), *Biomass and Bioenergy* 66 (2014) 410-418.

Mullen, C.A., Boateng, A., and Goldberg, N., "Production of Deoxygenated Biomass Fast Pyrolysis Oils via Product Gas Recycling," *Energy Fuels*, 27 (7), 3867-3874, 2013.

Westfall, P.J., Gardner, T.S., "Industrial fermentation of renewable diesel fuels," *Current Opinion in Biotechnology*, 22 (3), 344-350, 2011.

The World Bank. Health [Internet]. [Social capital: what is social capital?](#) c2012. [Cited 2012 Feb 13].

Reminder - Complete all of the Lesson 8 tasks!

You have reached the end of Lesson 8! Double-check the Road Map on the Lesson 8 *Overview* page to make sure you have completed all of the activities listed there before you begin Lesson 9.

Questions?

If there is anything in the lesson materials that you would like to comment on, or don't quite understand, please post your thoughts and/or questions to our Throughout the Course Questions & Comments discussion forum and/or set up an appointment for office hour. While you are there, feel free to post responses to your classmates if you are able to help.

9: BIODIESEL PRODUCTION

9.1: Terminology for Vegetable Oils and Animal Fats

9.2: The Reaction of Biodiesel- Transesterification

9.3: Various Processes Used to Make Biodiesel

9.4: Biodiesel Properties and Specifications

9.5: Assignments

9.6: Summary and Final Tasks

9.1: Terminology for Vegetable Oils and Animal Fats

9.1 Terminology for Vegetable Oils and Animal Fats

Fat is a generic term for lipids, a class of compounds in biochemistry. You would know them as greasy, solid materials found in animal tissues and in some plants – oils that are solids at room temperature.

Vegetable oil is the fat extracted from plant sources. We may be able to extract oil from other parts of a plant, but seeds are the main source of vegetable oil. Typically, vegetable oils are used in cooking and for industrial uses. Compared to water, oils and fats have a much higher boiling point. However, there are some plant oils that are not good for human consumption, as the oils from these types of seeds would require additional processing to remove unpleasant flavors or even toxic chemicals. These include rapeseed and cottonseed oil.

Animal fats come from different animals. Tallow is beef fat and lard is pork fat. There is also chicken fat, blubber (from whales), cod liver oil, and ghee (which is a butterfat). Animal fats tend to have more free fatty acids than vegetable oils do.

Chemically, fats and oils are also called “**triglycerides**.” They are esters of glycerol, with a varying blend of fatty acids. Figure 9.1 shows a generic diagram of the structure without using chemical formulas.

: A generic diagram of oils and fats; three fatty acids are shown connected to the glycerol
 Figure 9.1: A generic diagram of oils and fats; a free fatty acid is when the fatty acid separates from the glycerol.

Credit: BEEMS Module B4

So what is **glycerol**? It is also known as glycerin/glycerine. Other names for glycerol include: 1,2,3-propane-triol, 1,2,3-tri-hydroxy-propane, glyceritol, and glycol alcohol. It is a colorless, odorless, hygroscopic (i.e., will attract water), and sweet-tasting viscous liquid. Figure 9.2 shows the chemical structure in two different forms.

Chemical structure of glycerol, 3 carbon chain with 1 OH group attached to each carbon. 1 form all OH same side, 2nd middle OH opposite side

Figure 9.2: Chemical structure of glycerol.

Credit: BEEMS Module B4

So now we need to define what the fatty acids are. Essentially, fatty acids are long-chain hydrocarbons with a carboxylic acid. Figure 9.3a shows the generic chemical structure of a fatty acid with the carboxylic acid on it.

Central carbon atom double bonded to an oxygen atom, & bonded to an OH group & a long chain of hydrocarbons (designated R)
 Short hand=RCOOH

Figure 9.3a: Generic carboxylic acid chemical structure.

Credit: BEEMS Module B4

Figure 9.3b shows different fatty acid chemical structures. The chemical structures are shown as line chemical structures, where each point on the links is a carbon atom and the correct number of hydrogen atoms is dependent on whether there is a single or double bond. Fatty acids can be saturated (with hydrogen bonds) or unsaturated (with some double bonds between carbon atoms). Because of the metabolism of oilseed crops, naturally formed fatty acids contain even numbers of carbon atoms. In organic chemistry, carbon atoms have four pairs of electrons available to share with another carbon, hydrogen, or oxygen atom. Free fatty acids are not bound to glycerol or other molecules. They can be formed from the breakdown or hydrolysis of a triglyceride.

Steric acid	Palmitic acid	Oleic acid	Linoleic acid
$\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$	$\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$	$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$	$\text{CH}_3(\text{CH}_2)_4\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$
single carbon to carbon bonds.	single carbon to carbon bonds	18 total carbons, carbon to carbon bonds except a double bond between carbons 9-10	18 carbons, single carbon to carbon bonds except double bonds between carbons 9-10 and 12-13

Figure 9.3b: Other long-chain acids, such as steric, palmitic, oleic, and linoleic acids.

Credit: BEEMS Module B4

The fatty acids shown have slightly different properties. Palmitic acid is found in palm oil. Figure 9.4 shows the relationship of each fatty acid to its size and saturation. Palmitic and steric acids are saturated fatty acids, while oleic and linoleic acids are unsaturated with different amounts of double bonds. Figure 9.4 shows differing amounts of carbon atoms compared to the number of double bonds in the compound.

Palmitic & steric acid are saturated fatty acids. Oleic acid is monounsaturated and Linoleic acid is polyunsaturated

Figure 9.4: Series of fatty acids. The ratio represents the carbon atoms: double bonds in compound.

Credit: BEEMS Module B4

Figure 9.5a shows the part of the triglyceride that is a fatty acid and the part that is glycerol, including chemical structures this time. The chemical structure shown here is a saturated triglyceride.

Chemical structure of triglyceride, glycerol bonded to 3 fatty acid chains

Figure 9.5a: Chemical structure of triglyceride, pointing out fatty acid parts and glycerol part.

Credit: BEEMS Module B4

So, we've discussed what fats and oils are. Now, what is biodiesel? What is at least one definition? It is a diesel fuel that was generated from biomass. However, there are different types of biodiesel. The most commonly known type of biodiesel is a fuel comprised of mono-alkyl esters (typically methyl or ethyl esters) of long-chain fatty acids derived from vegetable oils or animal fats – this is according to ASTM D6551. An ASTM is a document that contains the standards for particular types of chemicals, particularly industrial materials. This is a wordy definition that doesn't really show us what it is chemically.

So when we talk about an **alkyl** group, it is a univalent radical containing only carbon and hydrogen atoms in a hydrocarbon chain, with a general atomic formula of $\text{C}_n\text{H}_{2n+1}$. Examples include:

Alkyl groups defined for methyl and ethyl groups. Methyl: CH_3 - Ethyl: CH_3CH_2 -

Figure 9.5b: Alkyl groups defined for methyl and ethyl groups.

Credit: BEEMS Module B4

Another term we need to know about is an **ester**. Esters are organic compounds where an alkyl group replaces a hydrogen atom in a carboxylic acid. For example, if the acid is acetic acid and the alkyl group is the methyl group, the resulting ester is called methyl acetate. The reaction of acetic acid with methanol will form methyl acetate and water; the reaction is shown below in Figure 9.6. An ester formed in this method is a condensation reaction; it is also known as esterification. These esters are also called carboxylate esters.

Reaction of acetic acid with methanol to form methyl acetate and water.

Figure 9.6: Reaction of acetic acid with methanol to form methyl acetate and water.

Credit: BEEMS Module B4

This is the basic reaction that helps to form biodiesel. Figure 9.7 shows the different parts of the chemical structure of the

biodiesel, the methyl ester fatty acid, or fatty acid methyl ester (FAME).

The chemical structure of the typical biodiesel, methyl ester fatty acid, or FAME. Methyl + ester+fatty acid

Figure 9.7: The chemical structure of the typical biodiesel, methyl ester fatty acid, or FAME.

Credit: BEEMS Module B4

So, at this point, let's make sure we know what we have been discussing. Biodiesel is a methyl (or ethyl) ester of a fatty acid. It is made from vegetable oil, but it is **not** vegetable oil. If we have 100% biodiesel, it is known as B100 – it is a vegetable oil that has been transesterified to make biodiesel. It must meet ASTM biodiesel standards to qualify for warranties and sell as biodiesel and qualify for any tax credits. Most often, it is blended with petroleum-based diesel. If it is B2, it has 2% biodiesel and 98% petroleum-based diesel. Other blends include: B5 (5% biodiesel), B20 (20% biodiesel), and B100 (100% biodiesel). We'll discuss why blends are used in the following section. And to be clear: sometimes vegetable oil is used in diesel engines, but it can cause performance problems and deteriorate engines over time. Sometimes, vegetable oil and alcohol are mixed together in emulsions, but that it is still not biodiesel, as it has different properties from biodiesel.

So, if straight vegetable oil (SVO) will run in a diesel engine, why not use it? Vegetable oil is significantly more viscous (gooey is a non-technical term) and has more poor combustion properties. It can cause: carbon deposits, poor lubrication within the engine, and engine wear, and it has cold starting problems. Vegetable oils have natural gums that can cause plugging in filters and fuel injectors. And for a diesel engine, the injection timing is thrown off and can cause engine knocking. There are ways to mitigate these issues, which include: 1) blend with petroleum-based diesel (usually < 20%), 2) preheat the oil, 3) make microemulsions with alcohols, 4) "crack" the vegetable oil, and 5) use the method of converting SVO into biodiesel using transesterification. Other methods are used as well, but for now, we'll focus on biodiesel from transesterification. Table 9.1 shows three properties of No. 2 diesel, biodiesel, and vegetable oil. As you can see, the main change is in the viscosity. No. 2 diesel and biodiesel have viscosities that are similar, but vegetable oils have much viscosity and can cause major problems in cold weather. This is the main reason for converting the SVO into biodiesel.

9.2: The Reaction of Biodiesel- Transesterification

9.2 The Reaction of Biodiesel: Transesterification

So, how do we make biodiesel?

The method being described here is for making FAMES biodiesel. The reaction is called transesterification, and the process takes place in four steps. The first step is to mix the alcohol for reaction with the catalyst, typically a strong base such as NaOH or KOH. The alcohol/catalyst is then reacted with the fatty acid so that the transesterification reaction takes place. Figure 8a shows the preparation of the catalyst with the alcohol, and Figure 8b shows the transesterification reaction.

Methanol and NaOH produces sodium ions, water and -OCH_3 . See link in caption for text description

Figure 9.8a: Formation of methoxide

[Click for a text description of Figure 9.8a.](#)

Methanol and base (NaOH in this case) is combined. NaOH Separates into ions in methanol. The -OH reacts with the H of methanol to make H_2O , leaving the -OCH_3 to react with the fatty acid. Both should be as dry as possible. Water production increases the side reaction of soap formation which is unwanted.

Credit: BEEMS Module B4

Triglycerides and methanol with the NaOH catalyst produces fatty seers and glycerin

Figure 9.8b: Chemistry of biodiesel production.

Credit: BEEMS Module B4

The catalyst is prepared by mixing methanol and a strong base such as sodium hydroxide or potassium hydroxide. During the preparation, the NaOH breaks into ions of Na^+ and OH^- . The OH^- abstracts the hydrogen from methanol to form water and leaves the CH_3O^- available for reaction. Methanol should be as dry as possible. When the OH^- ion reacts with H^+ ion, it reacts to form water. Water will increase the possibility of a side reaction with free fatty acids (fatty acids that are not triglycerides) to form soap, an unwanted reaction. Enzymatic processes can also be used (called lipases); alcohol is still needed and only replaces the catalyst. Lipases are slower than chemical catalysts, are high in cost, and produce low yields.

Once the catalyst is prepared, the triglyceride will react with 3 mols of methanol, so excess methanol has to be used in the reaction to ensure complete reaction. The three attached carbons with hydrogen react with OH^- ions and form glycerin, while the CH_3 group reacts with the free fatty acid to form the fatty acid methyl ester.

Figure 9.9 is a graphic of the necessary amounts of chemicals needed to make the reaction happen and the overall yield of biodiesel and glycerin. The amount of methanol added is almost double the required amount so the reaction goes to completion. With 100 lbs of fat and 16-20 lbs of alcohol (and 1 lb of catalyst), the reaction will produce 100 lbs of biodiesel and 10 lbs of glycerin. The reaction typically takes place at between 40-65°C. As the reaction temperature goes higher, the rate of reaction will increase, typically 1-2 hours at 60 °C versus 2-4 hours at 40°C. If the reaction is higher than 65°C, a pressure vessel is required because methanol will boil at 65°C. It also helps to increase the methanol to oil ratio. Doubling the ratio of 3 mols of alcohol to 6 mols will push the reaction to completion faster and more completely.

Conversion of fatty acid into biodiesel. as described in the text

Figure 9.9: Conversion of fatty acid into biodiesel. Note excess alcohol.

Credit: BEEMS Module B4

The following video shows a time-lapsed reaction of transesterification of vegetable oil into biodiesel. It also incorporates the steps after the reaction to separate out the biodiesel (9:44).

Making biodiesel

[Click here for a transcript of the making biodiesel video.](#)

MARK HALL: Hello. I'm Mark Hall of the Auburn University Extension Renewable Energy Specialist. We're doing several of these things on energy options that you can do, several pieces that, each piece of the puzzle, that you can contribute to our energy independence by making ethanol, making biodiesel, being more energy efficient in how you operate your home.

Today, we're going to talk about making biodiesel. And we have Lance Hall. Lance has been making biodiesel to run in his car. He bought a used Volkswagen off eBay and started making biodiesel. And he's liked it so much that he's bought a new diesel car. And he's been real successful doing this for a couple of years.

Before we bring Lance in, I'd like to thank my friend and coworker Walter Harris, the county agent coordinator in Madison County, for filming us today. Lance, come in and show us what you've been doing. And congratulations. You've been successful doing this.

I was talking to my daddy about my new job several years ago. And he said, well, Lance has been doing that for a long time. I said, what? I didn't know that. So Lance, show people how to make biodiesel.

LANCE HALL: OK. A lot of people know about the biodiesel. They've read the stories. They've done some research. But, yet, they still don't have enough confidence in their ability to actually make a batch. So I'm going to show you today on how to make a batch of biodiesel, just small scale, but it's easy.

OK. The first thing that we're going to do is start off with vegetable oil. Now, this will be 800 milliliters. And don't be confused between the milliliters and your normal units of measure. It's a simple conversion that anybody can do with a handheld calculator.

So we've got 800 milliliters here. Well, first thing we want to do is heat it. Now, don't be concerned about this fancy piece of equipment, either. The main element of this is to heat it any way that you can safely.

And these things here are magnetic stirrers. Again, don't be concerned with this. Just stir it while you're heating it to even things out. And we're going to heat this up to about 130 degrees Fahrenheit.

MARK HALL: Lance, tell them about where you get this equipment.

LANCE HALL: All of this equipment that I've got in my shop, all my lab stuff, eBay is a wonderful place to find a used lab supplies, lab glass. These are magnetic stirrer plates. These are really handy to have if you have the means to buy them. You don't have to have them, of course. But I like to use them.

And this is also an electronic scale that comes in handy when you start weighing out your catalyst, doing anything that you want to measure a precise weight. That's worth the money there. And that's going to take a little while, so--

MARK HALL: Lance, is there any other sites, internet sites that you would recommend for people that are interested in making biodiesel?

LANCE HALL: There are several sites out there. One of the most informative on what biodiesel is, where it's being used, is biodiesel.org. That's the National Biodiesel Board website, lots of good information there. It won't really tell you as much how to make it, but hopefully, this will be one of the more informative sites that you'll actually be able to see somebody make one, make a batch.

OK. As our oil is heating up, we have to mix up our methanol potassium hydroxide mixture. So safety is paramount with the use of methanol or the strong caustic lye potassium hydroxide. Methanol can cause blindness or death, and it can be absorbed through the skin. And the potassium hydroxide will burn your skin if it gets on you.

So here's what we're going to do. We're going to take our methanol and we're going to pour this into a container. Face shields are good, too.

We're going to use 175 milliliters of the methanol. That's roughly 20% of the 800 milliliters of oil. You usually want to use about a 20% methanol volume compared to the veggie oil volume.

OK. Our next ingredient is our potassium hydroxide. That's our lye. Now, we have to do a quick calculation on how much of this we need to mix with our methanol in order for the reaction to take place.

I've got a nice spreadsheet that I like to use. It's the Biodiesel-o-matic. You can usually find it online from different biodiesel websites. I'm going to pull that up.

OK. We want to use 7 grams of potassium hydroxide per each liter of veggie oil. So you take 7 divided by 0.8. And that gives you 6.4 grams.

Double bag this stuff, or it will absorb moisture. And that will kill your process.

So we're going to use our scale. We're going to zero the container. And then we're going to put 6.4 grams into it. Make sure you have your gloves on.

OK. That's our 6.4 grams. Close this immediately. Keep it double bagged. OK. Now, you're going to take your 6.4 grams of potassium hydroxide and put that into your 175 milliliters of methanol.

Again, you want to stir this. It's not necessary to heat it, though. Just stir. And stir this until at least the potassium hydroxide is completely dissolved into the methanol. You don't want to see any chunks of white potassium hydroxide flakes.

All right. Our potassium hydroxide is fully mixed into our methanol. We want to remove the stir bar. And then we're just going to slowly pour this into our oil as it's being stirred.

Again, you don't have to have fancy equipment. Just pour it in as you're stirring it manually. But the key is to do it slowly.

Figure 9.10 shows a schematic of the process for making biodiesel. Glycerol is formed and has to be separated from the biodiesel. Both glycerol and biodiesel need to have alcohol removed and recycled in the process. Water is added to both the biodiesel and glycerol to remove unwanted side products, particularly glycerol, that may remain in the biodiesel. The wash water is separated out similar to solvent extraction (it contains some glycerol), and the trace water is evaporated out of the biodiesel. Acid is added to the glycerol in order to provide neutralized glycerol.

Schematic of biodiesel process using transesterification. see long description below

Figure 9.10: Schematic of the biodiesel process using transesterification.

[Click here for a text alternative to Figure 9.10](#)

Schematic of the biodiesel process using transesterification:

Oil, alcohol, and a catalyst undergo transesterification. From there they are mixed methyl esters from which crude glycerol is removed. The crude glycerol goes into a separator under heat and a vacuum in which alcohol is removed. It then goes through a water wash and is neutralized with acid to produce neutralized glycerol. The other remaining mixed methyl esters from transesterification go into a different separator which removes any alcohol.

They then undergo an extraction using water and move into a second separator under heat and a vacuum that removes any water. This yields biodiesel.

Credit: BEEMS Module B4

As briefly discussed, the initial reactants used in the process should be as dry as possible. Water can react with the triglyceride to make free fatty acids and a diglyceride. It can also dissociate the sodium or potassium from the hydroxide, and the ions Na^+ and K^+ can react with the free fatty acid to form soap. Figure 9.11 shows how water can help to form a free fatty acid, and that free fatty acid can react with the Na^+ ion to form soap. The sodium that was being used for a catalyst is now bound with the fatty acid and unusable. It also complicates separation and recovery. All oils may naturally contain free fatty acids. The refined vegetable oil contains less than 1%, while crude vegetable oil has 3%, waste oil has 5%, and animal fat has 20%. Animal fats are a less desirable feedstock.

water + triglyceride can to form a free fatty acid, and that free fatty acid can react with the Na^+ ion to form soap

Figure 9.11: A. Side reaction of triglyceride with water. B. The formation of free fatty acid can react with alkali ions to form soap.

Credit: BEEMS Module B4

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9.3: Various Processes Used to Make Biodiesel

9.3 Various Processes Used to Make Biodiesel

Some of the processes used in making biodiesel are different from what we've discussed. The first of these processes we'll discuss is solvent extraction.

In the process of making biodiesel through transesterification, we noted that biodiesel and glycerol are the products, with some water formation and unwanted potential soap formation. So, the products are liquid, but they are also immiscible (do not dissolve in each other) and have differences in specific gravity. The specific gravity of the products is shown in Table 9.2.

Table 9.2: Specific gravity of products and unused reactants in biodiesel transesterification processing.

Material	Specific gravity
Glycerol (pure)	1.26
Glycerol (crude)	1.05
Biodiesel	0.88
Methanol	0.79

In batch processing, gravity separation is used, and the products remain in the reactor; the reactor then becomes a settler or decanter. Once the reaction is finished, the product mixture then sits without agitation. After 4-8 hours, the glycerol layer settles at the bottom (because it has higher gravity) and the biodiesel settles at the top. However, if a continuous flow facility is utilized, the products separate too slowly in a settler, so a centrifuge is used. A centrifuge will spin the liquids at a very high speed, which helps to promote density separation. Figure 9.12 shows a few different types of industrial centrifuges that can be used for biodiesel separation.

Various industrial size centrifuges for biodiesel separation, blue cylinder with white cone cap

Figure 9.12: Various industrial size centrifuges for biodiesel separation.

Credit: dolphinseparation.blog

One of the issues that can happen during separation is the forming of a layer containing water and soap, in between the glycerol and biodiesel. That will hinder the separation. Another issue is the glycerol contains 90% of the catalyst and 70% of the excess methanol. In other words, the glycerol fraction is kind of the "trashcan" layer of the process. The biodiesel layer also contains some contaminants, including soap, residual methanol, free glycerol, and residual catalyst. The catalyst in the biodiesel is extremely problematic if introduced into fuel systems. One way to improve the separation is through water washing with hot water, as the contaminants are soluble in water, but the biodiesel is not. Water washing will remove contaminants such as soap, residual methanol, free glycerol, and catalyst. The water should be softened (had ions removed) and be hot (both the biodiesel and water should be at 60°C). Thorough mixing with the wash water is needed so that all the contaminants can be removed, but the mixing intensity should also be controlled so that emulsions do not form between the biodiesel and water. Sometimes acid is added in the wash process to separate out the soaps. However, the last portion of washing needs to be acid free, so a step may need to be added to neutralize the glycerol.

There is more than one way to implement the washing process. For batch processes, two of the methods are: a) top spray and b) air bubbling (see Figure 9.13). For the top spray, a fine mist of water is sprayed top-down in a fine mist. The water droplets contact the biodiesel as the water flows down, separating out the impurities. The air bubbling is a method that uses air as a mobile phase. Air bubbles through a layer of water and carries water with it on the way up. As the air bubbles burst on the way up, water droplets are released and drop down on the biodiesel at the bottom, contacting the biodiesel and washing out impurities. It can be a relatively slow process; a combination of the two is also possible.

two of the methods for water washing are: a) top spray and b) air bubbling as described in the text

Figure 9.13: For batch processes, two of the methods for water washing are: a) top spray and b) air bubbling.

Credit: BEEMS Module B4

For continuous-flow processes, different equipment is used, which typically incorporates some sort of counter-current flow process. The lighter biodiesel is introduced at the bottom and the heavier water is introduced at the top, and as they flow the fluids contact each other so that the biodiesel at the top has impurities removed and the water flowing down out the bottom contains the contaminants. Figure 9.14 shows two types of counter-current units: a) counter-flow washing system and b) rotating disc extractor. Both units contain materials to increase the interaction between the water and biodiesel. For the counter-flow system, packing increases the interaction, while for the rotating disk extractor, disks rotate around as the fluid flows through. These types of equipment are typically used on an industrial scale and need precise mechanical design and process control; these units cost much more than the other type of system.

Two types of counter-current units: a) counter-flow washing system and b) rotating disc extractor

Figure 9.14: Two types of counter-current units: a) counter-flow washing system and b) rotating disc extractor.

Credit: BEEMS Module B4

The most problematic step in biodiesel production, however, is water washing. It requires heated, softened water, some method of wastewater treatment, and water/methanol separation. Methanol recovery from water is somewhat costly using methanol-water rectification. Water can also be removed by vacuum drying. One of the alternative methods for removing water is the use of absorbent materials such as magnesium silicate. One company that provides a process for doing this is Magnesol, which is produced by the Dallas Group. Once the magnesium silicate removes the water, it can be regenerated by heating it up and evaporating the water. Methanol must also be removed from the biodiesel; one method for doing this is flash vaporization of methanol.

So, which type of process should be used? Should it be a batch or continuous flow system? Smaller plants are typically batch (< 1 million gallons/yr). They do not require continuous operation 24 hours per day for 7 days a week. The batch system provides better flexibility and the process can be tuned based on particular feedstocks. However, in a commercial, industrial setting, most likely a continuous flow system will be used because of increased production and high-volume separation systems, which will increase the throughput. There is automation and process controls, but this also means higher capital costs and the use of trained personnel. It is feasible to have hybrid systems as well.

The primary byproduct is glycerin (aka glycerine, glycerol). It is a polyhydric alcohol, which is sometimes called a triol. The structure is shown in Figure 9.2. It is a colorless and odorless liquid, which is viscous (thick flowing) and sweet-tasting. It is non-toxic and water-soluble. Parameters to test quality are purity, color, and odor. Glycerol properties and chemical information are shown in Table 9.3.

Table 9.3: Chemical information and properties of glycerol. (Credit: BEEMS Module B4)

Chemical name	Propane-1,2,3
Chemical formula	$C_3H_5(OH)_3$
Molecular Weight, g/mol	92.09
Density, g/cm ³ @ 20°C	1.261
Viscosity, mPa.s, @ 20°C (93% w/ water)	1500 (400)
Melting point, °C (°F)	17.9 (64.2)
Boiling point, °C (°F)	290 - 297 (55)
Auto-ignition, °C (°F)	370(700)
Flash Point, °C (°F)	188 - 199 (370)
Food energy, kJ/g	18

There are several different applications that glycerol can be used for, including the manufacture of drugs, oral care, personal care, tobacco, and polymers. Medical and pharmaceutical preparations use glycerol as a means to improve smoothness, lubrication, and moisturize – it is used in cough syrups, expectorants, laxatives, and elixirs. It can also be substituted for alcohol, as a solvent that will create a therapeutic herbal extraction.

Glycerol can be used in many personal care items; it serves as an emollient, moisturizer, solvent and lubricant – it is used in toothpaste, mouthwashes, skincare products, shaving cream, hair care products, and soaps. Glycerol competes with sorbitol as an additive; glycerol has better taste and a higher solubility.

Since it can be used in medical and personal care products, glycerol can also be used in foods and beverages. It can be used as a solvent, moisturizer, and sweetener. It can be used as a solvent for flavors (vanilla) and food coloring. It is a softening agent for candy and cakes. It can be used as part of the casings for meats and cheeses. It is also used in the manufacture of shortening and margarine, filler for low-fat food, and thickening agent in liqueurs.

Glycerol is also used to make a variety of polymers, particularly polyether polyols. Polymers include flexible foams and rigid foams, alkyl resins (plastics) and cellophane, surface coatings and paints, and as a softener and plasticizer.

Unfortunately, there is already enough glycerol produced for the glycerol market. Glycerol consumption in traditional uses is 450 million lb/yr, and traditional capacity is 557 million lb/yr. If we produce glycerol from making biodiesel, it has the potential of producing 1900 million lb/yr. Therefore, we need to find a new market for glycerol or it will be wasted in some fashion.

There is research being done to find new uses for glycerol. This includes use in additional polymers as an intermediate, conversion to propylene glycol for antifreeze, production of hydrogen via gasification, as a boiler fuel (have to remove alkali), in an anaerobic digester supplement, and for algal fermentation to produce Omega-3 polyunsaturated fatty acids.

9.4: Biodiesel Properties and Specifications

9.4 Biodiesel Properties and Specifications

To ensure quality biodiesel, there are standards for testing the fuel properly to see that it meets specifications for use. ASTM (an international standards and testing group) has a method to legally define biodiesel for use in diesel engines, labeled ASTM D6751. Table 9.4 shows the test methods necessary for all the expected standards for biodiesel.

Table 9.4: Legal definition of biodiesel according to ASTM D6751
Credit: www.biodiesel.org

Property	ASTM Method	Limits
Ca & Mg, combined	EN 14538	5 max
Flash point	D 93	93 min
Alcohol Control	-	-
1. Methanol content	EN14110	0.2 max
2. Flash point	D 93	130 min
Water & Sediment	D2709	0.05 max
Kinematic Viscosity, 40°C	D445	1.9-6.0
Sulfated Ash	D874	0.02 max
Sulfur	-	-
S 15 Grade	D5453	0.0015 max (15)
S 500 Grade	D5453	0.05 max (500)
Copper Strip Corrosion	D130	No. 3 max
Cetane	D613	47 min
Cloud Point	D2500	report
Carbon Residue (100% sample)	D4530	0.05 max
Acid Number	D664	0.50 max
Free Glycerin	D6584	0.020 max
Total Glycerin	D6584	0.240 max
Phosphorus Content	D4951	0.001 max
Distillation, T90 AET	D1160	360 max
Sodium/Potassium, combined	EN 14538	5 max
Oxidation Stability	EN 14112	3 min
Cold Soak Filtration	Annex to D6751	360 max
For use in temperatures below -12 °C	Annex to D6751	200 max

There are advantages and disadvantages to using biodiesel compared to ultra-low sulfur diesel. It has a higher lubricity, low sulfur content, and low CO and hydrocarbon emissions. This makes it good to blend with diesel from petroleum to be able to achieve the

required specifications for ultra-low sulfur diesel, because ultra-low sulfur diesel has poor lubricity. But as discussed previously, biodiesel has poor cold weather properties. It really depends on the location; for instance, if using biodiesel in the upper Midwest, there could be problems in the winter.

As with all materials, production and quality of biodiesel is important. Most importantly, the transesterification reaction should reach completion for highest production and quality. Due to the nature of transesterification of triglycerides, a small amount of tri-, di-, and mono-glycerides remain. Figure 9.15 shows the changes in these compounds as the glycerides react to form biodiesel. Some terminology to be aware of: 1) **bound glycerol** is glycerol that has not been completely separated from the glyceride and is the sum of tri-, di-, and mono-glycerides and 2) **total glycerol** combines the bound glycerol with the free glycerol.

yield on y, time on x, Triglycerides fall fast Biodiesel rises rapidly & plateaus @ 90%, di & mono rise briefly @ start then fall 20

Figure 9.15: Conversion of glycerides to biodiesel showing intermediates.

Credit: BEEMS Module B4

Glycerol content in biodiesel must be as low as possible, as ASTM standards state. The biodiesel will not technically be “biodiesel” unless ASTM standards are met, which means being below the total glycerol specifications. High glycerol content can cause issues with high viscosity and may contribute to deposit formation and filter plugging. Crude glycerol is often a dark brown color and must be refined and purified before use elsewhere. In biodiesel preparation, brown layers will form, and, possibly, white flakes or sediments, formed from saturated mono-glycerides, that will fall to the bottom of the tank the biodiesel is being stored in.

Biodiesel is also a great solvent, better than petroleum-based diesel. It can loosen carbon deposits and varnishes that were deposited by petro-diesel and can cause fuel-filter plugging when switching over to biodiesel. Filters should be changed after the first 1,000 miles with biodiesel.

jar containing layers of light (top, biodiesel) and dark (bottom, glycerol with sediment) colored liquid

Figure 9.16: Example of biodiesel with crude glycerol and saturated mono-glyceride settled at the bottom.

Credit: [eXtension](#)

Another issue is cold weather properties for biodiesel. These properties include cloud point, pour point, and cold soak filtration. Biodiesel can form cloud points at a much higher temperature than petro-diesel, close to the freezing point. The cloud point is the temperature that crystals begin to form; it can cause the biodiesel to gel and flow slower than it should. Once the pour point is reached (basically completely frozen), the fuel cannot move. It depends on the normal temperature of the climate as to whether the fuel can be used or blended with petrodiesel. What can complicate it more is the saturated or unsaturated fatty acid content. High saturated fatty acid content can lead to higher fuel stability but higher pour points. High unsaturated acid content can lead to lower pour points but less stability for storing. Figure 9.17 shows a pour point comparison of biodiesels made from various oils (including fatty acid content) compared to petrodiesel. Petro-diesel pour points are significantly lower than biodiesels.

Pour point comparison. See text description below

Figure 9.17: Pour point comparison of biodiesels made from various oils (including fatty acid content) and No. 1 diesel fuel.

[Click here for a text alternative to Figure 9.17](#)

Pour Point Comparison of Biodiesels and the No. 1 diesel fuel. (No. 1 Diesel is neither methyl ester nor ethyl ester)

Biodiesel	Pour Point (Methyl Ester) °C	Pour Point (Ethyl Ester) °C	% Saturated Fatty Acids	% Monounsaturated Fatty Acids	% Polyunsaturated Fatty Acids
Canola	15	22	6%	62%	32%
Safflower	22	22	10%	20%	77%
Sunflower	24	28	11%	13%	69%
Soybean	25	30	15%	24%	61%
asdf	-45	-	-	-	-

Credit: Data from [The Biodiesel Handbook](#)

Cetane number is also an important property for diesel fuels. Cetane number measures the point that the fuel ignites under compression, and this is what we want for a diesel engine. The higher the cetane number, the greater the ease of ignition. Most petro-diesel fuels have a cetane number of 40-50 and meet the ASTM specification for ASTM D975. In general, most biodiesels have higher cetane numbers, 46-60 (some as high as 100) and meet the specifications for ASTM D6751. Because of the higher cetane numbers of biodiesel, the engine running on biodiesel will have an easier time starting and have low idle noise. Table 9.5 shows the heats of combustions for various fuels along with their cetane number.

Table 9.5: Various biodiesels and No. 2 diesel heats of combustion and cetane number (Credit: [National Biodiesel Education Program](#))

Fuel	Heat of Combustion (MJ/kg)
Methyl Ester (Soybean)	39.8
Ethyl Ester (Soybean)	40.0
Butyl Ester (Soybean)	40.7
Methyl Ester (Sunflower)	39.8
Methyl Ester (Peanut)	-
Methyl Ester (Rapeseed)	40.1
No. 2 Diesel	45.3

If full-strength biodiesel is used (i.e., B100), most engine warranties will not be covered. It will also require replacing rubber seals in older engines. Blends include B2, B10, and B20 (2%, 10%, and 20% biodiesel, respectively). Adding biodiesel as a blend with ultra-low sulfur should improve lubricity for ultra-low sulfur diesel fuel, which will improve engine wear. Emissions of hydrocarbons, CO, NO_x, and particulate matter are similar to petrodiesel fuels, although can be reduced in some cases.

Biodiesel is stored very similarly to petrodiesel. It is stored in clean, dark, and dry environments. It can be stored in aluminum, steel, fluorinated polyethylene, fluorinated polypropylene, and Teflon types of containers. It is best to avoid copper, brass, lead, tin, and zinc containers.

In another lesson, we will discuss the economics behind using biodiesel.

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9.5: Assignments

Homework (Quiz)

Watch the video on biodiesel production. It is in three parts, so watch all three parts. It will take less than 30 minutes and will give you a first-hand view of how biodiesel is made in a batch process.

Part 1

Biodiesel Production Demonstration

[Click here for a transcript of Biodiesel Production](#)

MARK HALL: Hello. I'm Mark Hall of the Auburn University Extension Renewable Energy Specialist. We're doing several of these things on energy options that you can do, several pieces that, each piece of the puzzle, that you can contribute to our energy independence by making ethanol, making biodiesel, being more energy efficient in how you operate your home.

Today, we're going to talk about making biodiesel. And we have Lance Hall. Lance has been making biodiesel to run in his car. He bought a used Volkswagen off eBay and started making biodiesel. And he's liked it so much that he's bought a new diesel car. And he's been real successful doing this for a couple of years.

Before we bring Lance in, I'd like to thank my friend and coworker Walter Harris, the county agent coordinator in Madison County, for filming us today. Lance, come in and show us what you've been doing. And congratulations. You've been successful doing this.

I was talking to my daddy about my new job several years ago. And he said, well, Lance has been doing that for a long time. I said, what? I didn't know that. So Lance, show people how to make biodiesel.

LANCE HALL: OK. A lot of people know about the biodiesel. They've read the stories. They've done some research. But, yet, they still don't have enough confidence in their ability to actually make a batch. So I'm going to show you today on how to make a batch of biodiesel, just small scale, but it's easy.

OK. The first thing that we're going to do is start off with vegetable oil. Now, this will be 800 milliliters. And don't be confused between the milliliters and your normal units of measure. It's a simple conversion that anybody can do with a handheld calculator.

So we've got 800 milliliters here. Well, first thing we want to do is heat it. Now, don't be concerned about this fancy piece of equipment, either. The main element of this is to heat it any way that you can safely.

And these things here are magnetic stirrers. Again, don't be concerned with this. Just stir it while you're heating it to even things out. And we're going to heat this up to about 130 degrees Fahrenheit.

MARK HALL: Lance, tell them about where you get this equipment.

LANCE HALL: All of this equipment that I've got in my shop, all my lab stuff, eBay is a wonderful place to find a used lab supplies, lab glass. These are magnetic stirrer plates. These are really handy to have if you have the means to buy them. You don't have to have them, of course. But I like to use them.

And this is also an electronic scale that comes in handy when you start weighing out your catalyst, doing anything that you want to measure a precise weight. That's worth the money there. And that's going to take a little while, so--

MARK HALL: Lance, is there any other sites, internet sites that you would recommend for people that are interested in making biodiesel?

LANCE HALL: There are several sites out there. One of the most informative on what biodiesel is, where it's being used, is biodiesel.org. That's the National Biodiesel Board website, lots of good information there. It won't really tell you as much how to make it, but hopefully, this will be one of the more informative sites that you'll actually be able to see somebody make one, make a batch.

OK. As our oil is heating up, we have to mix up our methanol potassium hydroxide mixture. So safety is paramount with the use of methanol or the strong caustic lye potassium hydroxide. Methanol can cause blindness or death, and it can be absorbed through the skin. And the potassium hydroxide will burn your skin if it gets on you.

So here's what we're going to do. We're going to take our methanol and we're going to pour this into a container. Face shields are good, too.

We're going to use 175 milliliters of the methanol. That's roughly 20% of the 800 milliliters of oil. You usually want to use about a 20% methanol volume compared to the veggie oil volume.

OK. Our next ingredient is our potassium hydroxide. That's our lye. Now, we have to do a quick calculation on how much of this we need to mix with our methanol in order for the reaction to take place.

I've got a nice spreadsheet that I like to use. It's the Biodiesel-o-matic. You can usually find it online from different biodiesel websites. I'm going to pull that up.

OK. We want to use 7 grams of potassium hydroxide per each liter of veggie oil. So you take 7 divided by 0.8. And that gives you 6.4 grams.

Double bag this stuff, or it will absorb moisture. And that will kill your process.

So we're going to use our scale. We're going to zero the container. And then we're going to put 6.4 grams into it. Make sure you have your gloves on.

OK. That's our 6.4 grams. Close this immediately. Keep it double bagged. OK. Now, you're going to take your 6.4 grams of potassium hydroxide and put that into your 175 milliliters of methanol.

Again, you want to stir this. It's not necessary to heat it, though. Just stir. And stir this until at least the potassium hydroxide is completely dissolved into the methanol. You don't want to see any chunks of white potassium hydroxide flakes.

All right. Our potassium hydroxide is fully mixed into our methanol. We want to remove the stir bar. And then we're just going to slowly pour this into our oil as it's being stirred.

Again, you don't have to have fancy equipment. Just pour it in as you're stirring it manually. But the key is to do it slowly.

Credit: [Alabama, A&M, & Auburn Universities Extension](#)

Part 2

Biodiesel Production Demonstration

[Click here for a transcript of Biodiesel Production](#)

PRESENTER: You always want to start with a much bigger container than for the amount of oil that you're going to make because you have to add another 20% to that with your methanol. This is a 1,000 milliliter container. So if I would've made a 1,000 milliliters, I would have overflowed it when I put in an extra 200 milliliters of the methanol. OK, we've added about half of our methanol. Let it stir. Then I'm going to add. Add some more.

You can tell when you need to add more. Once the color change goes from an opaque to a translucent. And then when we come back, it will be-- we'll show you how it separates.

OK. We're done with the first batch of bio-diesel. We're making bio-diesel with regular, unused oil. And as you

watch this will eventually go down. And it will be clear. And you'll have the separated layers.

So while we're waiting on that to separate out, most people that want to make bio-diesel want to make it out of recycled veggie oil from restaurants or cafes or whatever it may be. There's a few things we need to do before we start making that though. The most important thing you need when you're using with recycled veggie oil is the titrant solution. This is going to determine-- this is going to help us determine how much extra catalyst we need to neutralize the free fatty acids that are in the vegetable oil that are made during the cooking process.

So we're going to start on our scale over here in at least a one liter jar. I'm going to zero that out. We need one gram of our potassium hydroxide. Now we want to add 1,000 grams of water, which is extremely close to one liter, or 1,000 milliliters. So we're going to add that to our current jar. Oh, maybe. OK, there's our one liter of titrant solution. OK.

So we've made our solution. We're going to heat our 800 milliliters again because we're only using 1,000 milliliter bakers to 140 degrees like we did earlier. I'm going to wait while that heats up. Bio-diesel is messy. Be prepared to have all kinds of paper towels and soap and everything else to clean up. OK, while that's heating up, we're going to do the titration to determine how much we need to add.

So we're going to use this. This is a titration Burette. These can be found on eBay for really cheap, and they're really precise. So I recommend getting at least getting this. OK, we're going to take a small container. And then what we want to do is we want to measure out 10 milliliters of isopropyl alcohol. Also known as ISO-HEET. The regular HEET version is not isopropyl. We're going to get 10 milliliters. We've got milliliters of our isopropyl alcohol. Now we need one milliliter of the oil that we're about to make into bio-diesel.

And this is-- you can find these just about anywhere. These are turkey flavor injectors from any grocery store. Don't use them as turkey injectors once you make bio-diesel with them. Get the air out. And these are graduated in 1 milliliter so we want to move from one line to the next line. OK. Put the rest back. So we've got 10 milliliters of isopropyl alcohol and we've got 1 milliliter of our veggie oil in it. Now we need an indicator solution to know when the pH has changed to the appropriate level. So we'll put about four drops of a phenol saline solution. This can be purchased off of eBay. A couple little bottles go a long way.

And as with everything else, I have stir bar for this. And a bug. So we'll let the oil dissolve into the isopropyl alcohol. OK. Now we're going to use this. These are graduated in 0.1 milliliter increments. So it's very precise. So I'm going to run just briefly some distilled water though it just to wash out any contaminants. And then we're going to pour in our titrant solution, our 0.1 potassium hydroxide titrant solution. And we want to do this a couple of times to make sure that the water that may be left in this does not affect our readings.

OK. We've washed our titration duray with our titrant solution. Now what we're going to do is slowly add the titrant solution to our isopropyl alcohol and veggie oil mixture down here. The indicator solution that we put in at the phenol saline will turn a bright pink when we reach a certain pH, which is the pH that we want. So as soon as it turns pink and stays pink, that's when we stop.

Credit: [Alabama, A&M, & Auburn Universities Extension](#)

Part 3

Biodiesel Production Demonstration

[Click here for a transcript of Biodiesel Production](#)

LANCE HALL: OK you can see it's remaining pink, now. So that gives us about 4 milliliters of our solution went in to change this from a dull yellow to a pink.

So we're going to put this in our spreadsheet.

I'm using the spreadsheet. You can also make a worksheet that you just write your numbers down. And you use a standard calculator for.

So as we did before, we're going to use same jar. This time, we're going to put 9 grams of our potassium hydroxide.

OK, we've got our 9 grams. Now, we're going to add 175 milliliters of methanol.

OK, we're going to stir that up again.

All right, so we've got our methanol and potassium hydroxide mixture. And then, we're going to do the same thing, just add it slowly to our waste veggie oil, recycled veggie oil, however you want to say it. And you'll be able to know when you need add more by the color change.

I don't know if the camera can see it or not, but while you're looking right at through the top, you can tell when it turns translucent. And see how it lightened it up. It's not quite as clear.

All right, can tell how it's lightened up there, from adding some to it. That will turn to a darker translucent as it gets mixed in. OK, we're going to let that mix for a few minutes. And then, when we come back, we'll show you how it separated.

Just as a demonstration, this is a batch that I made, a larger batch, that I made a couple of weeks ago. And you can see how clear it actually gets after a little bit of time of settling. This is almost, if not just as, clear and the same color as the virgin veggie oil. So once you get your process down, you should be able to make just as high quality stuff with the waste veggie oil as you do with the virgin.

OK once you feel comfortable with your biodiesel-making technique, it's time to step up for a reactor. I've got five tanks in my system. This is a oil processing tank. When I first get my waste veggie oil, I pour it through a large strainer to catch all the big bits of French fries, and tater tots, and chicken nuggets, and everything else.

And I heat it up. So I can put it into my storage tank. I have to heat it because it's got another filter on the inside of this tank to filter even the smaller bits out. And it has to be heated up to go through that filter. So once we're done with it in storage, and we're ready to make a batch, it comes to this 60 gallon full drain inductor tank.

It's got a large lid on it. So I put my veggie oil in here. This tank is the methanol lye mixture tank. Only methanol and lye's ever in this tank. Once I figured out how much lye and methanol I need for my batch of oil, I mix it up in here. And then it's mixed in the pump and also heated. And it reacts in this tank.

And once it's done reacting, I will drain the glycerine off of the bottom using these series of valves. And then I'll do whatever means necessary to get the methanol and other nasties out of it. And once it's done, and I'm happy with it, it comes to this storage tank. And once it's in the storage tank, I can then put it in my tractor, car, whatever.

MARK HALL: Walter, Lance, thank you so much for showing us how to make biodiesel today. Wherever you live, you can make a difference in our nation's energy crisis. Please look and do what you can to lessen our dependence on foreign oil. Look at our website, and you'll see more opportunities to save renewable energy. For the Alabama Cooperative Extension system, this is Mark Hall.

Credit: [Alabama, A&M, & Auburn Universities Extension](#)

9.6: Summary and Final Tasks

9.6 Summary and Final Tasks

Summary

In this lesson, you've learned about how to make biodiesel from vegetable oils. You've had the opportunity to see how it is made and that it's fairly simple to make. You've been provided with information on properties and how biodiesel is typically used. In a future lesson, you will be provided with information on the economics behind biodiesel and ethanol, as well as determining how much energy it takes to make biodiesel, versus the amount of energy that is produced. The additional information is important to determining the use of, and best practices for making alternative fuels.

References

Scott W. Pryor ^{1*}, B. Brian H ², J.H. Van Gerpen ² 1. Department of Agricultural and Biosystems Engineering, North Dakota State University, 2. Department of Biological and Agricultural Engineering, University of Idaho BEEMS Module B4, Biodiesel, USDA Higher Education Challenger Program, 2009-38411-19761. Contact: Scott Pryor, Scott.Pryor@ndsu.edu

Reminder - Complete all of the Lesson 9 tasks!

You have reached the end of this Lesson! Double-check the Road Map on the Lesson *Overview* page to make sure you have completed all of the activities listed there before you begin the next Lesson.

Questions?

If there is anything in the lesson materials that you would like to comment on, or don't quite understand, please post your thoughts and/or questions to our Throughout the Course Questions & Comments discussion forum and/or set up an appointment for office hour. While you are there, feel free to post responses to your classmates if you are able to help.

10: ALGAE AS A SOURCE FOR FUELS

10.1: Introduction

10.2: What are Algae?

10.3: Algae Growth and Reaction Conditions

10.4: Design of Algae Farms

10.5: Algae Harvesting and Separation Technologies

10.6: Assignments

10.7: Summary and Final Tasks

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10.1: Introduction

10.1 Introduction

Algae are generated from sunlight, water, CO₂, and nutrients as well as algal cultures. There are more than 30,000 species of algae. One of the major factors in the use of algae to generate fuels is choosing the best species for oil generation and developing methods for removing the oil and making it into a fuel. Fuels that can be made from algae oil are biodiesel, n-alkane hydrocarbons, ethanol, methane, and hydrogen. Algae can also be used for soil conditioners and agrochemicals such as fertilizers and proteins as well as fine chemicals and bioactive substances such as polysaccharides, antioxidants, omega-3 and-6 fatty acids, proteins and enzymes.

There are currently several applications for algae including: 1) algin – a thickening agent for food processing (brown algae), 2) carrageenan – foods, puddings, ice cream, toothpaste (red algae), 3) iodine (brown algae), 4) agar – growth media in research (red algae), 5) as food (red and brown algae), 6) plant fertilizers, and 7) diatomaceous earth – used for filtering water, insulating, soundproofing. Table 10.1 shows some additional applications detailing the species, end product, origin, and main way to culture the algae.

Table 10.1: Current commercial applications of algae

Species	End Product	Origin
<i>Chlorella</i> spp.	Health food	Germany Indonesia Japan
<i>Spirulina</i> spp.	Health food	China, India Japan Thailand, USA
<i>Dunaliella salina</i>	β -carotene	Australia India
<i>Haematococcus pluvialis</i>	Astaxanthin	Israel USA
<i>Cryptocodinium cohnii</i>	DHA	USA
<i>Chaetoceros</i> spp. <i>Nannochloropsis</i> spp. <i>Navicula</i> spp. <i>Tetraselmis</i> spp. <i>Pavlova</i> spp.	Aquaculture feed	Throughout the world

The role of algae in the aqueous world is that they are the base of the aquatic food chain and are photosynthetic organisms. There is a symbiotic relationship between fungi and algae known as lichens. A lichen is a composite organism that emerges from algae or cyanobacteria living among filaments of a fungus in a mutually beneficial relationship. Their properties are plant-like, but lichens are not plants. Lichens help to cause the pigments of algae, reduce harmful amounts of sunlight, and kill bacteria. They can also serve as shelters, such as kelp forming underwater forests and red algae that form reefs.

Algae can have some negative impacts via *eutrophication*. Eutrophication is the ecosystem response to the addition of artificial or natural substances, mainly phosphates through detergents, fertilizers, or sewage to an aquatic system. It can also be caused by dense bloom of cyanobacteria or algae. These can cause impacts through 1) clogging of waterways, streams, and filters, 2) a decrease in water taste and quality, and 3) potential toxicification. Red tide is one event that can be caused by dinoflagellates.

So why make biofuels from algae? There are several reasons. Algae have high lipid content (up to 70%); they grow rapidly and will produce more lipids per area than other terrestrial plants (10-100 times). To grow algae, non-arable land (this can be thought of as land that is not typically used for farming) can be used along with saline or brackish water. Algae don't have the same competition with generating food or feed as other oil producing plants. One of the most amazing features is the use of CO₂ in growing algae; it helps grow algae significantly. It also provides nutrient (N, P) removal in agricultural and municipal wastewater. Table 10.2 shows

a comparison of annual oil yield from a variety of plants and algae. Even microalgae with lower lipids content (30%) will generate 50.00 m³/ha, significantly higher than palm oil. (Mata et al., 2010)

Table 10.2: Oil yields from various plants and microalgae.

Source	Annual oil y
Corn	0.14
Soybeans	0.45
Sunflower	0.95
Canola (Rape)	1.20
Jatropha	1.90
Palm	5.90
Microalgae (30% lipids)	59.00
Microalgae (50% lipids)	98.00
Microalgae (70% lipids)	140.00

10.2: What are Algae?

10.2 What are Algae?

Algae are eukaryotic organisms, which are organisms whose cells contain a nucleus and other structures (organelles) enclosed within membranes. They live in moist environments, mostly aquatic, and contain chlorophyll.

Algae are not terrestrial plants, which have 1) true roots, stems, and leaves, 2) vascular (conducting) tissues, such as xylem, and phloem, and 3) lack of non-reproductive cells in the reproductive structures. Algae are not cyanobacteria. Cyanobacteria are prokaryotes, which lack membrane-bound organelles and have a single circular chromosome. Figure 10.1a shows the cellular composition of blue-algae and 1b shows a micrograph of the cells. The cell has a wall with a gelatinous coat. Just beneath the cell wall is a plasma membrane. Within the cell, there are layers of phycobilisomes, photosynthetic lamellae, ribosomes, protein granules, and circular DNA known as nucleoids. These are typical components of growing plants - however, the component we are interested in are lipid droplets, which are oils that can be extracted from the algae.

diagram of cell structure of blue algae, see above text for important information. See link in caption for text description

Figure 10.1a: Cell structure of blue-algae.

[Click for a text description of Figure 10.1a.](#)

Cell Structure of blue-algae including liquid droplet, nucleoid (circular DNA), protein granule, ribosome, photosynthetic lamellae, phycobilisomes (cyanosomes), plasma membrane, cell wall, gelatinous coat

Credit: [TutorVista](#)

micrograph of blue-algae, blue circles with several green dots within them

Figure 10.1b: Micrograph of blue-algae.

Credit: [B.R. Speer](#)

Algae is composed of ~ 50% carbon, 10% nitrogen, and 2% phosphorus. Table 10.3 shows the composition of various algae looking at the percentages of protein, carbohydrates, lipids, and nucleic acid.

Table 10.3: Composition of algae – protein, carbohydrates, lipids, and nucleic acid.

Species	Protein	Carbohydrates
<i>Scenedesmus obliquus</i> (green alga)	50-56	10-17
<i>Scenedesmus quadricauda</i>	47	-
<i>Scenedesmus dimorphus</i>	8-18	21-52
<i>Chlamydomonas reinhardtii</i> (green alga)	48	17
<i>Chlorella vulgaris</i> (green alga)	51-58	12-17
<i>Chlorella pyrenoidosa</i>	57	26
<i>Spirogyra</i> sp.	6-20	33-64
<i>Dunaliella bioculata</i>	49	4
<i>Dunaliella salina</i>	57	32
<i>Euglena gracilis</i>	39-61	14-18
<i>Prymnesium parvum</i>	28-45	25-33
<i>Tetraselmis maculata</i>	52	15

Species	Protein	Carbohydrates
<i>Porphyridium cruentum</i> (red alga)	28-39	40-57

So what are the characteristics of algae?

1. Eukaryotic organisms:

As mentioned above, algae are eukaryotic organisms. The structure of a eukaryote (a typical plant cell) is shown in Figure 10.2a. Figure 10.2b shows the cell structure of a prokaryote, a bacterium, one of two groups of the prokaryotic life. Some do not consider the prokaryotes as true algae because they have a different structure, but most include these in the family of algae. There are labels for the different parts of the organisms, but I will not require you to know this information in detail - it is there so if you have a desire to look up more information, you can. Table 10.4 shows a comparison of both these types of cells.

Eukaryote schematic structure as described in the text. See link in caption for text description

Figure 10.2a: Eukaryote schematic structure.

[Click for a text description of Figure 10.2a.](#)

Eukaryotic Cell includes: A nucleus (Nuclear pore, nuclear envelope, nucleolus), rough endoplasmic reticulum, ribosomes, smooth endoplasmic reticulum, small membranous vesicles, filamentous cytoskeleton, plasmodesmata, plasma membrane, cell wall, chloroplast (thylakoid membrane, starch grain), vacuole (vacuole, tonoplast), mitochondrion (mitochondria), peroxisome, cytoplasm, golgi vesicles, golgi body (golgi apparatus)

Credit: [Eukaryote: from Wikipedia.com](#)

Prokaryote schematic structure. See link in caption for text description

Figure 10.2b: Prokaryote schematic structure.

[Click for a text description of Figure 10.2b.](#)

A Prokaryote cell contains: A nucleoid (circular DNA), Ribosomes, Plasmid, Cytoplasm, plasma membrane, Cell wall, Capsule, Pili, Bacterial flagellu

Credit: [Prokaryote: from Wikipedia.com](#)

Table 10.4: Comparison of eukaryotic cells and prokaryotic cells.

--	Eukaryotic cells
Size	Fairly large in size
Nuclear region	Nuclear materials surrounded by a membrane
Chromosome	More than one chromosome present
Membrane	Membrane-bound cell organelles are present

2. Live in moist environments

These organisms lack a waxy cuticle (the wax in terrestrial plants prevents water loss). There are a wide variety of growth environments for algae. The typical conditions for algae are moist, tropical regions and they can grow in marine and freshwater. Freshwater algae grow in animals, aquatic plants, farm dams, sewage, lakes, rivers, lagoons, snow, mud/sand, and soil.

3. Contain chlorophyll

Algae are mostly photosynthetic, like plants. They have five kinds of photosynthetic pigments (chlorophyll a, b, c, d, and f) and have many accessory pigments that are blue, red, brown, and gold. Chlorophyll is a green pigment found in almost all plant algae and cyanobacteria. It absorbs light and transfers light energy to ATP (adenosine triphosphate).

So how are algae classified?

Algae belong to the Protista kingdom. Figure 10.3 shows a schematic of where Protista fits with other classifications of Plantae, Animalia, Fungi, Eubacteria, and Archaeobacteria.

Algae can also be classified based on chlorophyll content. The first type is chromista. These types of algae contain chlorophylls a and c, and examples of the algae include brown algae (golden-brown algae), kelp, and diatoms. These materials are a division of *Phaeophyta*. These types have a habitat on rocky coasts in temperate zones or open seas (cold waters). The structure is multicellular and they can grow up to 50 m long.

kingdoms of life 3 initial branches. See link in caption for text description

Figure 10.3: Various kingdoms of life.

[Click for a text description of Figure 10.3.](#)

Eubacteria (unicellular, prokaryotic)

Archaeobacteria (unicellular, prokaryotic)

Protista (eukaryotic, unicellular and multicellular)

Plantae (multicellular, eukaryotic)

Animalia (multicellular, eukaryotic)

Fungi (multicellular, eukaryotic)

Credit: By Hull (Google) [Public domain], via Wikimedia Commons

A phylogenetic tree example with different organisms on different branches of a cartoon tree

Figure 10.4: A phylogenetic tree.

Credit: [Phylogenetic Tree from creationwiki.org](#)

Red algae are another type and contain chlorophyll a, such as marine algae (seaweed). These organisms are in the division of *Rhodophyta*, which has over 4000 species. These are some of the oldest eukaryotic organisms on Earth (there are 2 billion-year-old fossils). They are abundant in tropical, warm waters. They act as food and habitat for many marine species. The structure ranges from thin films to complex filamentous membranes. These algae have accessory pigments, and the phycobilins (red) mask chlorophyll a. Figure 10.5b shows various red algae. Dinoflagellates are unicellular protists, and these are associated with red tide and bioluminescence.

A pile of bright yellow kelp

Figure 10.5a: Kelp

Credit: BEEMS Module A3

Green algae contain chlorophylls a and b. They are in the division *Chlorophyta*. This is the largest and most diverse group of algae. It is found mostly in freshwaters and also on land (rocks, trees, and soil). The structures are single cells (*Micrasterias*), filamentous algae, colonies (*Volvox*), and leaf-like shape (*Thalli*). Terrestrial plants arose from a green algal ancestor. Both have the same photosynthetic pigments (chlorophyll a and b). Some green algae have a cell wall made of cellulose, similar to terrestrial plants. Figure 5c shows examples of green algae.

3 different algae's & magnifications, 1 looks like a branch, 1 is zoomed in to look like branches made of rectangles & 1 is brown dots

Figure 10.5b: Red algae photo- and micrographs.

Credit: BEEMS Module A3

Examples of green algae: Chlamydomonas, Volvox, Ulothrix, Frustuliella, Ulva, Hydrodictyon

Figure 10.5c: Examples of green algae.

Credit: BEEMS Module A3

10.3: Algae Growth and Reaction Conditions

10.3 Algae Growth and Reaction Conditions

There are two primary ways that algae reproduce. Some algae are unicellular and demonstrate the simplest possible life cycles (see Figure 10.6a). Note that there is a generative phase and a vegetative phase. During the generative phase, cysts are freed. The cysts open to form gametes and then form the zygote. From there, the vegetative phase occurs so the plant grows and new cysts can form. Most algae have two recognizable phases, sporophyte and gametophyte. Figure 10.6b shows a schematic of the two phases. The main difference is a male and female type is required to form the zygote. I will not be expecting you to know the details in depth, but want you to recognize there are differences.

life cycle of unicellular algae
Figure 10.6a: Life cycle of unicellular algae.
[Click for a text description](#)

The vegetative phase: zygote, stalk growth, whorl formation, cap formation, maximum cap

The generative phase: from the maximum cap to cyst formation, add secondary nuclei, free cysts with many nuclei, formation of gametes, to opening of cysts releasing gametes, the copulation which results in a zygote

Credit: [Photo-Atlas of living Dasycladales](#)

diagram of two phase regeneration of algae
Figure 10.6b: Two-phase regeneration of algae. This type requires a male and female to form the zygote.
[Click for a text description](#)

Diploid (2N) Zygote goes through mitosis to make a sporophyte, sporophyte undergoes mitosis to produce **haploid (1N) spores**. Spores undergo germination to make a young gametophyte. Mitosis results in mature male and female gametophytes. Mitosis produces egg and sperm which become a **diploid (2N) zygote** through fertilization

Credit: modification of work by Mariana Ruiz Villareal via [OpenStax](#)

Algae have a particular path of growth, beginning with a lag phase, and continuing on to an exponential phase, a linear phase, and stationary phase, and decline of death phase. Figure 10.7 shows a schematic of algal growth rate in a batch culture.

graph of growth of algae culture-Shaped like an “S” with an early exponential phase followed by a linear phase & finally a stationary phase

Figure 10.7: Growth of algae culture. The figure is similar to several online.

Credit: [fao.org](#)

There are several factors that influence the growth rate. The temperature will vary with algae species. The optimal temperature range for phytoplankton cultures is 20-30°C. If temperatures are higher than 35°C, it can be lethal for a number of algal species, especially green microalgae. Temperatures that are lower than 16°C will slow down the growth of algae.

Light also has an effect on the growth of algae: it must not be too strong or weak. In most algal growth cultivation, algae only need about 1/10 of direct sunlight. In most water systems, light only penetrates the top 7-10 cm of water. This is due to bulk algal biomass, which blocks light from reaching into deeper water.

Mixing is another factor that influences the growth of algae. Agitation or circulation is needed to mix algal cultures. An agitator is used for deep photo reactor systems. Paddle wheels are used for open pond systems. And pump circulation is used for a photo-tube system.

Of course, algae need nutrients and the proper pH to grow effectively. Autotrophic growth requires carbon, hydrogen, oxygen, nitrogen, phosphorous, sulfur, iron, and trace elements. The compositional formula of $C_{1.48}H_{1.83}N_{0.11}P_{0.01}$ can be used to calculate the minimum nutrient requirement. Under nutrient limiting conditions, growth is reduced significantly and lipid accumulation is triggered. Algae prefer a pH from neutral to alkaline.

There are particular steps for algal biodiesel production. Figure 10.8 shows the processing steps for algae production in biodiesel production. The first step is the cultivation of algae, which includes site selection, algal culture selection and process optimization. Process optimization includes design of the bioreactor and necessary components for algal cell growth (nutrients, light, and mass transfer). Once the algae grow to the necessary level, the algae are harvested. The biomass must first be processed in order to dewater, thicken, and dry the algae in order to extract the oil that will then be processed into biodiesel. The biomass process differs depending on the method of oil extraction and biodiesel production. You primarily learned about transesterification to make biodiesel in Lesson 9, but there are other processes being researched and developed.

steps in algal biodiesel production. see above text for description

Figure 10.8: Steps in algal biodiesel production.

[Click Here for a text alternative to Figure 10.8](#)

Steps in algal biodiesel production

The first step is algae and site selection. Then there is algae cultivation which receives light, water, CO_2 , and nutrients. (The algal culture, 0.02-0.06% Total suspended solids-TSS). The algal effluent (2-7% TSS) then goes to harvesting. The culture is recycled and the algal slurry (5-15% TSS) goes to biomass processing (dewatering, thickening, filtering, drying). The nutrients are recycled and the algal cake (15-30% TSS) goes into oil extraction (cell disruption and oil extractions). The lipids and free fatty acids then go to biodiesel production.

Credit: BEEMS Module A3

10.4: Design of Algae Farms

10.4 Design of Algae Farms

Site selection is an important area to investigate. The best areas to grow algae are areas with adequate sunlight year round, with tropical and subtropical climates. In the US, this includes the following states: Hawaii, California, Arizona, New Mexico, Texas, and Florida. This also means that the temperature will moderate year round. There also has to be adequate land availability (for open-pond systems) and close proximity to CO₂ (i.e., near a power plant or gasifier). To keep costs at a minimum, water and nutrients must be available at lower costs and manpower kept at reasonable rates.

There are two main types of culturing technologies: open systems and closed systems. Open systems include tanks, circular ponds, and raceway ponds. Closed systems include three different types: flat-plate, tubular, and vertical-column enclosed systems. Figure 10.9 shows several different examples of open and closed systems.

Open systems can be in natural waters or specifically engineered to grow algae. Natural water systems include algae growth in lakes, lagoons, and ponds, while the engineered systems are those described in the previous paragraph: tanks, circular ponds, and raceway ponds. Of course, there are going to be advantages and disadvantages of open systems. The main advantages are that open systems are simple in design, require low capital and operating costs, and are easy to construct and operate. However, disadvantages include: little control of culture conditions, significant evaporative losses, poor light utilization, expensive harvesting, use of a large land area, limited species of algae, problems with contamination, and low mass transfer rates. One of the more common designs is the raceway pond. It has existed since the 1950s and is a closed loop for recirculation channel for mass culture. The design includes a paddlewheel for mixing and recirculation, baffles to guide the flow at bends, and algal harvesting is done behind the paddlewheel. Cyanotech has a field of raceway ponds located in Kona, Hawaii, with a wide variety of algae.

Drawing: Paddlewheel pushes H₂O through a series of hairpin turns w/ baffles (semicircle gates) 2 guide H₂O Harvesting is done before paddlewheel

Figure 10.9a: Open system raceway design, schematic and picture.

Credit: Schematic: [Beranek-Collins, Adam G](#), Picture: [Mission 2014](#)

Round open tank design Large circular tanks with hanging lamps above Open tank designs Flat rectangular pools of water

Figure 10.9b: Open tank designs.

Credit: [Laboratory of Aquaculture & Artemia Reference Center/ Biomass and bioenergy](#)

tubular design: Green hairpin pipes stacked in tall columns. Flat plate design: Green vertical rectangles in a line, many rows Many rows

Figure 10.9c: Tubular and flat plate engineering designs.

Credit: [Chlorella blog/ ASU LightWorks](#)

So, what are some of the design features to keep in mind with algae systems? Algal systems are phototrophic, which means they need to obtain energy from sunlight to synthesize organic compounds. Therefore, the growth rate depends on: light intensity, temperature, and substrate concentration, as well as pH and species type.

There are also factors that affect how specific systems are designed. Open pond design is affected by factors including: the pond size, the mixing depth, paddle wheel design, and the carbonator. The carbonator is how the carbon is added to the algae - it can be done in a number of ways, including carbonaceous seed materials, but utilizing CO₂ from power systems (generated from combustion of carbon-based materials) is one of the more common for algae growth - it also mitigates generation of GHG. We

will not go into ways to design these systems, as that is above the level of this course.

There are also a variety of closed systems. One type of system is the photobioreactor (PBR). Advantages of a system such as this include: 1) compact design, 2) full control of environmental conditions, 3) minimal contamination, 4) high cell density, and 5) low evaporative losses. The disadvantages include: 1) high production costs, typically an order of magnitude higher than open ponds, 2) overheating, and 3) biofouling. A company that has systems such as this is Algatechnologies. They have a plant located in Kibbutz Ketura, Israel. Figure 10.10 shows a picture of the various algae they have growing in Israel.

algae growth in PBR units. Ride line looking pipes in a field
Figure 10.10: Algae growth in PBR units in Israel, at Algatechnologies.

Credit: [Haaretz](#)

There are three types of designs for the PBRs: flat plate, tubular, and vertical column. Advantages of the flat plate PBR include: 1) large surface area, 2) good light path, 3) good biomass productivity, and low O₂ build-up. However, the drawbacks include: 1) difficulty in scaling up, 2) difficulty in controlling temperature, and 3) algae wall growth. A flat plate PBR is shown in Figure 10.9c. For the tubular PBR, advantages include: 1) good biomass productivity, 2) good mass transfer, 3) good mixing and low shear stress, and 4) reduced photoinhibition and photooxidation. Tubular PBRs also have disadvantages: 1) gradients of pH, dissolved O₂ and CO₂ along the tubes, 2) O₂ build-up, 3) algae wall growth, 4) requirement of large land area, and 5) a decrease of illumination surface area upon scale-up. Figure 10.9c and Figure 10.10 are examples of tubular PBRs. Vertical column PBRs have different advantages and disadvantages. The positive features include: 1) high mass transfer, 2) good mixing and low shear stress, 3) low energy consumption, 4) high potential for scalability, 5) easy sterilization, and 6) reduced photoinhibition and photooxidation. The negative features are: 1) small illumination surface area, 2) need for sophisticated materials for construction, and 3) decrease of illumination surface area upon scale-up. Figure 10.11 shows a vertical column PBR.

vertical column PBR: small cylinders filled with green and topped with white foam

Figure 10.11: Continuous flow bubble vertical column PBR located in India as part of the National Institute of Ocean Technology.

Credit: [NIOT](#)

We can compare open and closed systems by looking at various parameters and providing general comparisons of these systems. Table 10.5 provides a list of parameters to compare for each type of system. Open systems tend to cost less, but process control is difficult and growth rate lower. Closed systems are a much higher cost, but control is much better and productivity is therefore higher.

Table 10.5: Comparison of open and closed systems for growth of algae.

Parameters	Open systems
Contamination	High
Process control	Difficult
Species control	Not possible
Mixing	Not uniform
Foot-print	Extremely high
Area/volume ratio	Low (5 to 10 m ⁻¹)
Capital cost	Low
Operation cost	Low
Water losses	Very high
Light utilization	Low
Productivity	Low
Biomass conc.	Low

Parameters	Open systems
Mass transfer	Low

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10.5: Algae Harvesting and Separation Technologies

10.5 Algae Harvesting and Separation Technologies

The following video is produced by Los Alamos National Laboratory in New Mexico. The video provides a nice overview of how algae are generated, how to harvest them, and the areas of research LANL are focusing on to improve various aspects of the process to make it more economical (3:12).

Turning Algae into Energy

[Click here for transcript of the Turning Algae into Energy video.](#)

RICHARD SAYRE: The upside of renewable fuels is that they're sustainable. They reduce the environmental impact, and they can help potentially mitigate climate change. We particularly like algae as biomass or bio fuel feedstock. Algae grow about two to 10 times faster than the best terrestrial crop plants.

They often will store oils as a energy reserve product. And oils that come out of these algae, we've found can be directly converted into fuels, using preexisting technologies.

JOSE OLIVARES: So the laboratory is interested in this area because we have a mission around energy security, providing new technologies for energy for the nation. The big problem, the big challenge is how to get that whole process to be economically and energetically efficient.

RICHARD SAYRE: To make algal biofuels economically viable, there are two very important factors that we have to improve, and that's the biomass productivity per unit land area or the yield. And the other very important factor that we need to improve is reducing the costs of harvesting the algae from the pond.

JOSE OLIVARES: The laboratory is actually developing some nice technologies in a number of different areas, transforming the algae so that it can produce more lipids, more biomass, overall better productivity, under better conditions.

PETER LAMMERS: You've seen how we transfer the algae from the lab from, colonies on a Petri dish to larger cultures. We bring them out here, adapt them to the outdoors and the sunshine. We begin to scale them up. Pretty soon, we'll have algae at hundreds of acres, if not thousands of acres.

RICHARD SAYRE: Another important concern is water, how much water are we going to use. And to address those issues, we're now focusing on developing heat tolerant strains of algae that can be grown in ponds that are covered with plastic to reduce the evaporation. We've figured out how to engineer algae so they can use light more efficiently than normal algae do. We've seen up to a two-fold increase in growth.

We've also figured out how to engineer algae to make more oil. So at the time that we want to harvest the algae, we'll induce the expression of a gene that will cause all of the algae to stick to each other, settle out of the pond and then we pick them up. Maybe the last reason why we like algae is that we can recycle the nutrients that are in waste waters.

PETER LAMMERS: Algae can do wastewater treatment better than conventional systems. So why not take an energy intensive expensive process and turn it into a energy generating system where you're getting clean water and liquid fuels as your two products, and do that in a way that generates revenue rather than consumes revenue.

Credit: [Los Alamos National Lab](#)

Algae are typically in a dilute concentration in water, and biomass recovery from a dilute medium accounts for 20-30% of the total production cost. Algae can be harvested using: 1) sedimentation (gravity settling), 2) membrane separation (micro/ultra filtration), 3) flocculation, 4) flotation, and 5) centrifugation.

Sedimentation is the initial phase of separating the algae from water. Once agitation is completed, the algae are allowed to

settle and densify. However, other methods most likely will also be required to achieve complete separation.

Membrane separation is a form of filtration. In the lab, a funnel is attached to a vacuum flask. The contents are poured out onto the filter on the funnel and allowed to dry some on the filter as the vacuum continues to be pulled. This method can be used to collect microalgae with low density, but is typically done on a small scale. But the main disadvantage is membrane fouling. There are three modifications: 1) reverse-flow vacuum, 2) direct vacuum with stirring blade above the filter, and 3) belt compression.

Flocculation is another technique. Flocculation is a method where something is added to the mixture of water and algae that causes the algae to “clump” together (or aggregate) and form colloids. Chemical flocculants include alum and ferric chloride. Chitosan is a biological flocculant, but has a fairly high cost. Autoflocculation is an introduction of CO₂ to an algal system to cause algae to flocculate on their own. Often flocculation is used in combination with a filter compressor as described in the last paragraph.

Froth floatation is another method for harvesting and separating algae from water. This is a technique that has been used in coal and ore cleaning technology for many years. It is based on density differences in materials. Typically air bubbles are incorporated into the unit. Sometimes an additional organic chemical or adjustment of pH will enhance separation. For algal systems, the algae will accumulate with the froth of bubbles at the top, and there is some way to collect or scrape the froth and algae from the top to separate it from the water. It is an expensive technology that, at this point, may be too expensive to use commercially. There is also the possibility of combining froth floatation with flocculation. For example, when alum is used as a flocculant for the algae, air is bubbled through to separate the flocculant by density. It can also be combined with a filter compressor.

One of the more commonly used machines is a **continuous-flow centrifuge**. It is efficient and collects both algae and other particles. However, it is more commonly used for production of value-added products from algae and not for fuel generation.

Along with these separation techniques, moisture needs to be removed from algae to improve the shelf-life. Algae are concentrated from water through a series of processes, including the separation process. The concentration of algae in the pond starts at about 0.10–0.15% (v/v). After flocculation and settling, the concentration is increased to 0.7%. Using a belt filter process, the concentration increases to 2% (v/v). Drying algae from 2% to 50% v/v requires almost 60% of the energy content of the algae, which is a costly factor of algae use.

Lipid Separation Technologies

This is an important aspect to the use of algae to generate fuels. It is likely also an expensive option. The algae cells have to be subjected to cell disruption for the release of the desired products. Physical methods include: 1) mechanical disruption (i.e., bead mills), 2) electric fields, 3) sonication, 4) osmotic shock, and 5) expeller press. There are also chemical and biological methods, including: 1) solvent extraction (single solvent, co-solvent, and direct reaction by transesterification), 2) supercritical fluids, and 3) enzymatic extraction.

Single solvent extraction is one of the more common methods. A solvent that is chemically similar to the lipids is used, such as hexane or petroleum ether (this is just a light petroleum-based solvent). This is a commercial process. Extraction takes place at elevated temperatures and pressure. Advantages include an increased rate of mass transfer and solvent accessibility and a reduced dielectric constant of immiscible solvent. The use of a co-solvent process is a little different. There are two criteria used to select a co-solvent. Selection should include: 1) a more polar co-solvent that disrupts the algae cell membrane, and 2) a second less polar co-solvent to better match the polarity of the lipids being extracted (alkanes can meet this criteria). There are several examples of co-solvent extraction. One method was developed by Bligh and Dyer in 1959. Alcohol and chloroform are the solvents, and the majority of the lipids dissolve into the chloroform phase. The interactions include water/methanol > methanol/chloroform > lipid/chloroform. Other combinations of co-solvents include: 1) hexane/isopropanol, 2) dimethyl sulfoxide (DMSO)/petroleum ether, and 3) hexane/ethanol.

Supercritical extraction is similar to solvent extraction. The main difference is that the solvent is maintained until certain pressure and temperature conditions are met, which change the solvent properties and helps extract the materials. It is often done on a smaller scale and may not be useful at an industrial level.

Enzymatic extraction is also similar to solvent extraction, except instead of a solvent, an enzyme is used to separate the materials.

As discussed in the biodiesel lesson (Lesson 9), the reaction of transesterification is often used to convert lipids into fatty ester methyl esters (FAMEs) using alcohol and a catalyst. The advantages of using this method are the high recovery of volatile medium

chain triglycerides, and the fact that antioxidants are not necessary to protect unsaturated lipids. There are other methods as well, as discussed near the end of the biodiesel lesson.

Direct Biofuel Production from Algae

Besides separating out the lipids to make diesel fuel, other fuels can be obtained from algae directly. These include alcohols such as ethanol and butanol, hydrogen, and methane.

Alcohols can be made from algae by heterotrophic (carbon nutrients from organic materials) fermentation of starch to alcohols, including ethanol and butanol. Marine algae used for this are *Chlorella vulgaris* and *Chlamydomonas perigranulata*. Procedures include starch accumulation via photosynthesis, subsequent anaerobic fermentation under dark conditions to produce alcohol, and alcohol extracted directly from the algal culture media. Hydrogen can also be produced directly from algae through photofermentation and dark fermentation. Methane can be produced by anaerobic conversion of algae. It can be coupled with other processes (using the residue after lipids are removed, for example). Challenges include high protein content of biomass, which can result in NH_3 inhibition and can be overcome by co-digestion with high carbon co-substrates. Figure 10.12 shows a schematic of different processes to convert algae, and the range of fuel products that can be made.

See text description below. Products are: Biogas, transportation fuels, hydrogen, methanol and ethanol, liquid hydrocarbon fuels

Figure 10.12: Fuel products from various processes of algae.

[Click here for a text alternative to Figure 10.12](#)

Algae

Gasification to syngas

- Fischer tropch to catalytic upgrading to liquid hydrocarbon fuels
 - Higher alcohol synthesis to MeOH, EtOH, etc
 - Hydrogen

Pyrolysis to liquid or vapor fuel to catalytic upgrading to transportation fuels: liquid or gas

Supercritical Fluids to liquid or vapor fuel to catalytic upgrading to transportation fuels: liquid or gas

Anaerobic digestion to biogas

Credit: BEEMS Module A3

10.6: Assignments

10.6 Assignments

Final Project Rough Draft

Please submit a rough draft of your final project by the specified due date in Canvas. To review, your project should include the following elements:

Format

The report should be 8-12 pages in length. This includes figures and tables. It should be in 12-point font with 1" margins. You can use line spacing from 1-2. It is to be written in English, with proper grammar and as free from typographical errors as possible. You will lose points if your English writing is poor.

The following format should be followed:

- Cover Page – Title, Name, Course Info
- Introduction
- Body of Paper:
 - Biomass choice
 - Literature review on the biomass (APA style, please!)
 - Requirements for location
 - Climate (i.e., tropical, subtropical, moderate,...)
 - Land area required or other type of facility to grow
 - Method of production
 - Product markets around location
 - Economic evidence
 - Other factors (environmental, political, tax issues, etc.)
- Summary and Conclusions
- References

Use as filename **your user ID_Draft (i.e., ceb7_Draft)**

Upload it to the **Rough Draft Dropbox**.

(20 points)

10.7: Summary and Final Tasks

10.7 Summary and Final Tasks

Summary

Algae are an excellent source of lipids for biodiesel production. They can grow under conditions that terrestrial plants cannot grow, in water, using CO₂ and waste materials. Pairing the proper species of algae with appropriate growing conditions will increase the amount oil produced with the algae. Discussion on the economics of algae production will be included in another lesson, in order to compare it to other sources of biodiesel. For now, I will note that production under highly controlled conditions can be expensive.

References

Mata et al. (2010) Renew. Sust. Energy Rev. 14: 217–232.

Liao, W. Khanal, S., Park, S.Y., Li, Y., BEEMS Module A3, Algae, USDA Higher Education Challenger Program 2009-38411-19761, 2009.

Reminder - Complete all of the Lesson 10 tasks!

You have reached the end of Lesson 10! Double-check the Road Map on the Lesson 10 *Overview* page to make sure you have completed all of the activities listed there before you begin Lesson 11.

Questions?

If there is anything in the lesson materials that you would like to comment on, or don't quite understand, please post your thoughts and/or questions to our Throughout the Course Questions & Comments discussion forum and/or set up an appointment for office hour. While you are there, feel free to post responses to your classmates if you are able to help.

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11: ECONOMICS OF BIOMASS PRODUCTION – ETHANOL, BUTANOL, AND BIODIESEL

- 11.1: Background for Economic Evaluation of Biofuel Use
- 11.2: Ethanol Production and Economics
- 11.3: Economics of Butanol Production
- 11.4: Economics of Biodiesel Production, Including Economics of Algae
- 11.5: Assignments
- 11.6: Summary and Final Tasks

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11.1: Background for Economic Evaluation of Biofuel Use

11.1 Background for Economic Evaluation of Biofuel Use

Essentially, I am a big proponent of the use of alternative fuels, as I believe they are necessary for our environment. However, to convince others of the environmental benefits, we must also have economic benefits. Use of biofuels in power generation must be competitive with coal and natural gas, and using alternative fuels in transportation must be economically competitive with petroleum refining of crude oil. The following section provides methods to evaluate economics of energy facilities.

There is a time value of money. The purchasing power of money is continuously declining, there is inflation, and investors want an increase in their investment beyond inflation. There are ways to track the time value of money, and this is done through the calculation of annual price indexes. The **Consumer Price Index (CPI)** is a measure of the overall cost of living, while the **Producer Price Index (PPI)** is a measure of cost of goods and other expenditures needed to stay in business. Table 1 shows the CPI and PPI for the USA and the CPI for the United Kingdom from 1997-2010.

Table 11.1: Consumer Price Index and Producer Price Index for the USA, and the Consumer Price Index for the United Kingdom. Source: US Bureau of Labor Statistics (2011) for USA data; UK National Statistics (2011).

Year	CPI, USA	PPI, USA
1997	87.4	95.5
1998	94.7	94.7
1999	96.7	96.4
2000	100.0	100.0
2001	102.8	102.0
2002	104.5	100.7
2003	106.9	103.8
2004	109.7	107.6
2005	113.4	112.8
2006	117.1	116.2
2007	120.4	120.7
2008	125.0	128.3
2009	124.6	125.1
2010	126.7	n/a

Indexed to Year 2000 = 100

Note: 2010 PPI value for US not available at time book went to press

Source for data as cited in Energy Systems Engineering: US Bureau of Labor Statistics (2011) for USA data; UK National Statistics (2011).

Example 11-1 Factor of CPI and PPI (from ESE book)

A particular model of car costs \$17,000 in 1998, and \$28,000 in 2005, given in current dollars for each year. How much are each of these values worth in constant 2002 dollars? Use the US CPI values from Table 1.

Values from the table are used to correct the constant 2002 dollars, for \$17,000 in 1998 dollars, and \$28,000 in 2005 dollars, respectively.

$$\$17,000 \times \frac{(104.5)}{(94.7)} = \$18,763$$

$$\$28,000 \times \frac{(104.5)}{(113.4)} = \$24,986$$

If energy projects are going to be funded, the costs and predicted earnings for these projects must be valued for a later date and compared to the option of keeping money in savings or investments. A method to include the actual cost of money in the future is **discounting**. In discounting, current funds are projected into the future, knowing that the money today is worth less in the future due to inflation. Other terms are also defined:

- Term of project: Planning horizon over which cash flow is assessed – typically the value of years N is divided over the project.
- Initial cost: One time expense at the beginning of first compounding period.
- Annuity: Annual increment of cash flow related to project – can be positive or negative.
- Salvage value: One time positive cash flow at end of planning horizon of project – due to sale of asset at actual condition at end.

Projects can be evaluated without discounting. We are not going to discuss discounting beyond this part because I don't want to spend too much time on discounting – we can look at energy projects without it. Discounting is also ignored for projects with short lifetimes. These shorter projects are evaluated with what is called a **simple payback**, and this is the method we'll focus on. The factors in the simple payback include:

- adding up all cash flows in and out of the project;
- this is known as **net present value (NPV)**;
- if NPV is positive, the project is financially viable;
- breakeven point – the year in which total annuities from the project surpass the initial costs.

There is also terminology for energy projects. One such value is called the **Capital Recovery Factor (CRF)**. This is applied to electricity generation. It is a measure used to evaluate the relationship between cash flow and investment cost. This can be applied to short-term investments (i.e., a project that takes place over 10 years or less).

Annual capital cost (ACC) can be determined from the following equation (1) and the CRF can be determined from ACC and NPV shown in equation (2):

(1) $ACC = \text{annuity} - NPV/N$, where NPV is the net present value and N is the number years.

(2) $CRF = ACC/NPV$

The Electric Power Research Institute (EPRI) recommends a maximum CRF value of 12%.

So, how can energy projects be evaluated in order to determine their financial viability? There are multiple ways – the most common is the **present worth method (PW)**. This method takes into account discounting of money. For the present worth method, all the elements of the financial analysis are discounted back to the present worth. This takes into account the positive and negative elements of cash flow summed up. If the NPV is positive, it would be a financially attractive project. In this method, a **minimum attractive rate of return (MARR)** would be chosen (kind of like an interest rate). Example 11-2 first looks at a simple payback NPV. While I do not expect you to know how to discount, I will expect you to know that it can affect the cost of a project, as suggested in the following example.

Example 11-2 Net Worth of a Plant (from ESE book)

A municipality is considering an investment in a small-scale energy system that will cost \$6.5 million to install, and then generate a new annuity of \$400,000/year for 25 years, with a salvage value at the end of \$1 million. Calculate the net worth of the project using a simple payback approach.

Annuity= +\$400,000 per year

N = 25 years

Salvage value = \$1,000,000

Installation cost = \$6,500,000

NPV = total value of annuities + salvage value – installation cost

$$NVP = (25 \cdot \$400,000) + \$1,000,000 - \$6,500,000 = \$4,500,000$$

This looks like the project is a good deal.

However, if discounting were to be included in this, there would be a factor to reduce the value of the annuities for the 25 years, so the salvage value would be reduced by a significant factor. These factors would be based on a parameter called the minimal attractive rate of return (MARR) – if the MARR is 5%, this project would not be viable.

Another parameter that can be used is the called the **benefit-cost ratio (B/C) method**. This is a method that is a ratio of all the benefits of the project to all of the costs. If the B/C ratio is greater than 1, the project is acceptable. When the B/C ratio is less than 1, the project is unacceptable. If the B/C value is close to 1, it may be necessary to reevaluate the project to see if minor changes would make it acceptable. The conventional B/C ratio equation is shown in equation (3).

(3) $B/C = \text{Total benefits} / (\text{Initial cost} + \text{Operating costs})$

Example 11-3 Benefit to Cost Ratio

Let's take the example in 11-2. In Part a, we'll calculate the B/C for the investment using the simple payback method. In Part b, we'll add in \$50,000/year in operating costs for 25 years.

1. Total benefits include:

Income (annuity over 25 years) $\$400,000 \times 25 = \$10,000,000$

Salvage \$1,000,000

Total costs = \$6,500,000

$$B/C = \frac{\text{Total benefits}}{\text{Total costs}} = \frac{\text{Annuity} + \text{Salvage}}{\text{Total costs}} = \frac{\$10,000,000 + \$1,000,000}{\$6,500,000}$$

$$B/C = 1.69$$

2. Now we'll add in the operating costs for 25 years

$25 \times \$50,000 = \$1,250,000$

$$B/C = \frac{\$11,000,000}{\$6,500,000 + \$1,250,000} = 1.42$$

So operating costs can influence the costs.

Discounting will also influence the costs, maybe to the point that the project would not be viable.

The last factor we will look at is the **Levelized Cost of Energy**. This is a method that incorporates the role of both the initial capital costs and ongoing costs. The levelized cost is determined per unit of energy output. Therefore, all the cost factors are combined into a cost-per-unit measure. We need a predicted average output of electricity in kWh and a sum of all the costs on an annual basis, divided by the annual output (see equation 4):

(4) $\text{Levelized cost} = (\text{Total annual cost}) / (\text{annual output})$

Total annual cost = annualized capital cost + operating cost + return on investment (ROI)

Annual output is in kWh

Example 11-4 Levelized Cost of Energy

So, now we'll continue with Example 11-3 and input the information into a formula to examine the Levelized Cost of Energy. This plant would produce 2.6 million kWh per year.

Income per year \$400,000

Salvage \$1,000,000

Total costs = \$6,500,000

\$50,000/year operating costs for 25 years

So, the first thing to do is to determine the overall costs on an annual basis – recall that we are not discounting at all, we are doing a simple payback method.

Costs on an annual basis

= Income/year – Operating Costs/Year + (Salvage – Initial costs) /25 years

= \$400,000 – \$50,000 + (\$1,000,000 – \$6,500,000)/25

= \$130,000 per year

Levelized costs = \$130,000/2.6 million kWh

= \$0.050/kWh

The average electric energy price in the US in 2004 for all types of customers was \$0.0762 – this has not changed drastically in the current year. Therefore, with a plant of this size, this would be competitive in the US.

Another aspect that needs to be considered is the direct costs versus external costs and benefits. Direct costs include capital repayment costs and operating costs. Operating costs include energy supply, labor, and maintenance costs. However, there are also external costs that are sometimes called overhead. These costs include health care and lost productivity due to pollution. Direct benefits include revenues from selling the product and services. External benefits include benefits to the local environment or the use of unusual energy technology, which could encourage visitors to the company.

Costs are important, but by using biofuels, we also expect a benefit to the environment. So, there have been interventions in energy investments for social aims. We expect the alternative form of energy to be “clean” energy. This means that there may be intervention in the marketplace because of the potential social benefit, which is typically done by government. Intervention by government can be on the local, state, and federal levels. Why do this? It is because we can't put a “value” on the social benefit, and it gives fledgling technologies a chance to grow in sales volume to allow for competition in the marketplace. For example, government subsidies were given to the production of ethanol from corn for many years, and now ethanol from corn in the US is the most viable method of ethanol production (data will be presented on this in the following section).

There is more than one method of intervention. One support mechanism is to support research and development (R&D). The support usually comes from the government, but industry may also participate so that they are not supporting the funding all on their own. Government can also support commercial installation and operating systems. This can be in the form of direct costs, tax credits, and interest rate buydown.

Most of our discussion so far has been on electricity systems. But how do we evaluate the production of biofuels and economic viability? There are two metrics that are used: 1) **net energy balance ratio** and 2) **life cycle assessment**. The net energy balance ratio is a metric to compare bioenergy systems. It is a ratio to compare energy available for consumption to the energy used to produce the fuel. So, for example, how might we look at ethanol? The energy carrier itself is ethanol. However, energy was consumed in order to grow, harvest, and process the corn in order to produce the ethanol. This is known as energy to produce. The ratio would look like this:

(5) NEB = Energy from fuel/ Energy to produce

If the NEB ratio is greater than 1, there is more energy available for consumption than is used to produce the biofuel. If the NEB

ratio is less than 1, then more energy is required to produce the fuel than is available in the fuel for consumption – which makes for an unattractive project. This is a good metric for debate, but it is not a parameter that can stand alone.

The other metric is **life cycle assessment (LCA)**. It is a method of product assessment that considers all aspects of the product's life cycle. One way to express this is a cradle-to-grave analysis. For biofuels in transportation, it could be plant/harvest-to-wheels. In the petroleum industry, it's known as well-to-wheels.

Example 11-5 Shows How the NEB and LCA are Determined

There are two farms that grow corn to produce ethanol. Farm A is 40.2 km from the ethanol plant. Farm A sells corn for \$289.36 per metric ton. Farm B is 160.0 km from the ethanol plant, and corn sells for \$284.02 per metric ton. Other information:

Truckload can carry 10.9 metric tons (500 bushels)

Truck emits 212.3 g CO₂eq/metric ton-km (310 g CO₂eq/ton-mile)

Plant needs 130.6 metric tons per year (6000 bushels/year)

Truck weighs 9.1 metric tons empty

Plants needs: 130.6 metric tons/year @ 10.9 metric tons

= 12 truckloads per year

For the two farms, examine the two farms – both for economics and GHG emissions.

Farm A

- Economic return
 - 130.6 metric tons/year (\$289.36)=\$37,800/year
- Transportation
 - 40.2km (12 trips/year) = 482.4km/year
- GHG
 - Empty truck: 482.4km/year (9.1 metric tons) (212.3 CO₂eq/metric ton-km) = 0.93 MgCO₂eq
 - Full truck: 482.4km/year (20 metric tons) (212.3 CO₂eq ton-km) = 2.05MgCO₂eq
 - Total 2.98 Mg CO₂eq

Farm B

- Economic return
 - 130.6 metric tons/year (\$248.02) = \$32,400/year
- Transportation
 - 160.9 km (12 trips/year) = 1930.8km/year
- GHG
 - Empty truck: 1930.8 km/year (9.1 metric tons) (212.3 CO₂eq/metric ton-km) = 3.72MgCO₂eq
 - Full truck: 1930.8 km/year(20 metric tons)(212.3CO₂eq ton-km) = 8.18MgCO₂eq
 - Total 11.90 Mg CO₂eq

As you can see, Farm A produces a better economic return. And it also puts out less CO₂eq as well, so Farm A is the better plant to provide raw material.

We also want to determine the fuel productivity per unit of cropland per year. This should be done before choosing a regional crop. Keep in mind that, depending on location, sunlight provides 100-250 W/m² – however, less than 1% is available in starches and oils as a raw material for conversion to fuel. Research has focused on conversion of lignocellulosic biomass (whole biomass) and utilization of the entire plant in order to produce fuel and/or value-added products – the economics improve under these conditions. Data on changes to the land must also be incorporated, especially if the land is being changed to sustain a large-scale biofuels program. For example, if a rainforest or peatland is removed to make space, the material from the land is typically burned, adding CO₂ to the atmosphere before even getting the system started.

So, what is the NEB ratio of ethanol? Early on in conversion of corn to ethanol, the ratio was positive, but not a very high ratio – 1.25. However, recent assessments show improved NEB of 1.9-2.3. And if the fuel used to run the plant that produces the ethanol is 50% biomass, the NEB is 2.8, almost 3. And you will see in the economics, production of ethanol is economical. The problem comes up when petroleum prices go down, such as in recent months; ethanol production is less economical.

So, what about the NEB ratio of biodiesel? When compared to the NEB of ethanol, in early stages of biofuel production, the NEB ratio of biodiesel was 1.9 when co-products are included. It is higher because biodiesel production requires reduced energy requirements during processing, mainly because less distillation is required. The one drawback to biodiesel production is the GHG contains N₂O, so use of biodiesel has ~60% of petrodiesel emissions instead of being neutral. Another issue for biodiesel is soybeans suffer as a crop due to lower yields per land area compared to corn. Example 11-6 shows the NEB ratio calculation of soybeans to biodiesel.

Example 11-6 Calculate the Ratio of Energy Available in the Resulting Biodiesel to the Total Energy Input

Does biodiesel provide more energy than it consumes?

- Each gallon of biodiesel requires 7.7 lbs. of soy as feedstock
- Acre yields ~452 lbs. soy
- Assume pure biodiesel
- Assume a gallon of biodiesel contains 117,000 Btu net

Farming Inputs

Input	Energy (1000 Btu)
Fuels	1025
Fertilizer	615
Embodied energy	205
All other	205

Plant inputs: Per 1000 lbs. of Soybeans

Input	Energy (1000 Btu)
Process heat & electricity	1784
Embodied energy	595
Transportation	297
All other	297

Solution:

- Energy in to produce biodiesel
 - 452 lbs. soy/acre $\frac{1 \text{ gal biodiesel}}{7.7 \text{ lbs soy}} = 58.7$
 - 452 lbs. soy/acre (2973) $\frac{1000 \text{ Btu}}{1000 \text{ lbs. soy}} = 1.34 \times 10^6 \text{ Btu/acre}$
 - $2.050 \times 10^6 \text{ Btu/acre} + 1.34 \times 10^6 \text{ Btu/acre} = 3.39 \times 10^6 \text{ Btu/acre}$
- Energy out from biodiesel produced
 - 117,000 Btu/gal (58.7 gal/acre) = $6.87 \times 10^6 \text{ Btu/acre}$
 - $\text{NEB} = \frac{6.87 \times 10^6 \text{ Btu/acre}}{3.39 \times 10^6 \text{ Btu/acre}}$
- = 2.02

This 2.02. A typical NEB for biodiesel production is ~1.9 to as high as 2.8.

So, are ethanol and biodiesel being consumed in our current fuel supply? Yes, they are, but partially because of an Environmental Protection Agency (EPA) mandate to use oxygenated fuel in a blend with gasoline and diesel fuel. Approximately 10% of the gasoline supply is ethanol, while in diesel, it's estimated that diesel sold contains ~5-6% biodiesel.

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11.2: Ethanol Production and Economics

11.2 Ethanol Production and Economics

The major feedstock for ethanol has been coarse grains (i.e., corn). Second-generation ethanol (from cellulosic biomass) is around ~7% of the total ethanol production. Figure 11.1 shows the global ethanol production by feedstock from 2007-2019.

graph of Global ethanol production by feedstock from 2007-2019 as described in the text

Figure 11.1: Global ethanol production by feedstock from 2007-2019.

[Click here for a text alternative to Figure 11.1](#)

Global Ethanol Production in billions of liters by Feedstock from 2007-2019. All values are visual approximations

Year	Coarse Grains	Wheat	Sugar Cane	Molasses	Sugar Beet	Biomass based (2nd Generation)	Roots and Tuber	Other Feed Stocks	Total
2007-2009	37	1	27	3	2	-	-	5	75
2010	50	2	30	2	3	-	-	6	93
2011	54	3	32	4	2	-	-	5	100
2012	56	4	35	4	2	-	-	6	107
2013	59	5	38	3	2	1	1	6	115
2014	61	6	43	3	2	2	1	6	124
2015	64	5	45	4	2	3	1	7	131
2016	65	6	47	5	2	4	1	7	143
2017	65	6	52	4	3	5	1	7	153
2018	66	6	53	4	3	8	1	8	149
2019	61	6	59	3	2	13	1	8	159

Credit: [The Crop Site](#)

In 2013, the world ethanol production came primarily from the US (corn), Brazil (sugarcane), and Europe (sugarbeets, wheat). Figure 11.2 shows ethanol production contributions, in millions of gallons, from all over the world. In addition to Brazil, ethanol production from sugarcane is also being done in Australia, Columbia, India, Peru, Cuba, Ethiopia, Vietnam, and Zimbabwe. In the US, ethanol from corn accounts for ~97% of the total ethanol production in the US.

Millions of gallons: US- 13300, Brazil-6267, Europe-1371, China-696, India-545, Canada-523, Rest-727

Figure 11.2: World ethanol production, millions of gallons, from various countries for 2013.

[Click here for a text alternative to Figure 11.2](#)

World Ethanol Production

Country	Millions of Gallons of Ethanol
US	13300
Brazil	6267
Europe	1371
China	696
India	545
Canada	523
Rest of the World	727

Credit: [RFA](#)

Table 11.2 shows a comparison of costs for first-generation ethanol feedstock along with their production costs. The data in this table is from 2006, but it gives you an idea of why ethanol is made from corn in the US: because it is less expensive and more profitable. However, as seen in the other charts, the use of sugar-based materials like sugarcane and sugarbeets is growing, as well as the use of cellulosic materials.

Table 11.2: Summary of 2006 Estimated Ethanol Production Costs in the U.S. (\$/gal)^a

Cost Item	Feedstock Costs ^b	Processing Costs
US Corn wet milling	0.40	0.63
US Corn dry milling	0.53	0.52
US Sugarcane	1.48	0.92
US Sugar beets	1.58	0.77
US Molasses ^c	0.91	0.36
US Raw Sugar ^c	3.12	0.36
US Refined Sugar ^c	3.61	0.36
Brazil Sugarcane ^d	0.30	0.51
EU Sugar Beets ^d	0.97	1.92

a Excludes capital costs

b Feedstock costs for US corn wet and dry milling are net feedstock costs; feedstock for US sugarcane and sugar beets are gross feedstock costs

c Excludes transportation costs

d Average of published estimates

Credit: rd.usda.gov

Figure 11.3 shows the overall process of making ethanol from corn. It also shows the additional products made from corn. If you recall from Lesson 7, DDGS is a grain that can be used to feed cattle. Corn oil is also produced for use. Typical yields of each product per bushel of corn are shown (2.8 gal of ethanol, 17 lbs. of CO₂, and 17 lbs. of DDGS).

Product distribution of corn, see text description in link below

Figure 11.3: Product distribution of corn.

[Click for a text description of Figure 11.3](#)

Corn Starch – 73% db

- **Ethanol--0.57 g/g (th)**
 - **(0.511 g/g glucose)**
 - **2.8 gal/bu**
 - **3.0 gal/bu (th)**
- **CO₂--0.54 g/g (th)**
 - **~17lbs/bu**
 - **18.9 lb/bu (th)**
- **Yeast**

Protein, fiber, oil – 27% db

- **DDGS**
 - **~17lbs/bu**

Credit: BEEMS Module B5

So, what are the ethanol revenue streams? Figure 11.4 shows that the revenue streams are ethanol, DDGS, and CO₂. The revenue streams are market driven; ethanol is the plant's most valuable product and typically generates 80% of the total revenue. The DDGS represents 15-20% of the revenue, and CO₂ represents a small amount of revenue. The revenue margins are tight, however, and sale of DDGS and CO₂ is probably essential for the plant to be profitable.

see long description

Figure 11.4: Ethanol revenue streams. The numbers at the top of each bar are the revenue \$ per bushel of corn. The values with the "@" are the values of how each product is sold.

[Click for a text description of Figure 11.4](#)

Ethanol Revenue Streams

Product	Revenue \$ per bushel of corn
Ethanol	4.05
Ethanol	5.40
Ethanol	6.75
DDGS	0.51
DDGS	1.02
DDGS	1.53
CO ₂	0.07

Credit: BEEMS Module B5

Figure 11.5 shows the volatility of the price of corn, the price of ethanol, and the price of gasoline. Notice the price of gasoline and the price of ethanol are highly correlated, at least since 2009. For example, in 2010, the price of gasoline and the price of ethanol were ~\$2.00 per gal. However, in recent months, with the price of oil going down significantly, expect that the profitability of ethanol will be less.

Chart of corn, ethanol, and gasoline prices from 2005-2011 as described in the text

Figure 11.5: Chart of corn, ethanol, and gasoline prices from 2005-2011.

Credit: [USDA ERS](#)

The major cost in producing ethanol from corn is the cost of the feedstock itself. Figure 11.6 shows the cost of feedstock is 55% of the expenses for the production of ethanol from corn, while energy is 21%, materials are 11%, and maintenance and personnel are 13%. If a bushel of corn sells for \$4/bu or more, then the percentage for the feedstock price goes to 65-75% of the expenses.

Dry grind ethanol case expenses (\$/gal) for 2005 as described in the text above

Figure 11.6: Dry grind ethanol case expenses (\$/gal) for 2005.

Credit: Shapouri, H., & Salassi, M. (2006). [The Economic Feasibility of Ethanol Production from Sugar in the United States](#).

Another issue with the production of ethanol is that water is used, and water is becoming less available. Water is used for gasoline production as well, but water use is a little higher for ethanol production (for gasoline, 2.5 gallons water per gallon of gasoline is used, while for ethanol it is 3 gallons of water per gallon of ethanol). The extra water use is due to growing the plants for harvest.

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11.3: Economics of Butanol Production

11.3 Economics of Butanol Production

Just as ethanol can be produced from corn, so, too, can butanol. The main disadvantage to butanol production is yields are significantly lower. But recall that the advantages include a better interaction of butanol with gasoline than ethanol as well as the higher energy content of butanol. If all of the available residues of the corn along with the corn are converted to acetone-butanol (AB), the result would be the production of 22.1×10^9 gallons of AB biofuel – this is a yearly amount. In 2009, 10.6×10^9 gallons of ethanol were produced from corn – this would be equivalent to 7.42×10^9 gallons of butanol on an equal energy basis. Recall that butanol production is accomplished in a similar fashion to ethanol production; it uses different enzymes. Figure 11.7 shows the schematic of wheat straw processing that was shown in Lesson 7. A description of the process and some information on production using wheat straw and other feedstocks can be found at the end of Lesson 7.

Wheat straw to milling to treatment to hydrolysis to fermentation to recovery to A&E and also BuOH and water to butanol. See link in caption for text description

Figure 11.7: A schematic diagram of acetone butanol ethanol (ABE) production from wheat straw.

[Click for a text description of Figure 11.7.](#)

Milling (wheat straw enters)

Treatment (input of H_2SO_4)

Hydrolysis (input of enzymes, output of lignin)

Fermentation (output of CO_2 and H_2 , and solids)

Recovery (distillation and more) (output of A&E, Butanol and water)

Credit: Nasib Qureshi, Adriano Pinto Mariano, Vijay Singh, Thaddeus Chukwuemeka Ezeji, "Biomass to Butanol," BEEMS Module B6

So, how much investment might be necessary to build a plant for butanol production? An extensive computer simulation was done to determine costs, payback time and return on investment – we will not discuss the details of the computer simulation because it is beyond the scope of this course. However, I will provide a summary of the study to give you an idea of the related costs. An estimate was done for producing butanol from wheat straw (BEEMS Module B6). The estimate was based on a plant size of 150×10^6 kg/year, or 48×10^6 gallons of butanol per year, and the following costs were determined:

- Equipment purchase cost $\$27.66 \times 10^6$
- Total plant direct cost (TPDC) $\$88.08 \times 10^6$
- Total plant indirect cost (TPIC) $\$52.85 \times 10^6$
- Total plant cost (TPC = TPDC + TPIC) $\$140.93 \times 10^6$
- Contractor's fee & contingency (CFC) $\$21.14 \times 10^6$
- Direct fixed capital cost (DFC = TPC+CFC) $\$162.06 \times 10^6$

It would take ~\$162 million to build a butanol plant that produces 48 million gallons of butanol. Operating costs must also be taken into consideration, which would be more than \$200,000,000. The major factors in the operating costs are utilities (59% of the costs) and raw materials (21%). With these costs in mind, it was estimated that for a grass roots plant, the butanol production cost would be \$1.37/kg, or \$4.28/gal. For an annexed plant the cost of butanol production would be lower, or \$0.82/kg, or \$2.55/gal. The researchers doing this work have been successful at producing AB from lignocellulosic substrates, though there are some challenges ahead. In conclusion, these are the overall estimates:

- Cost of production of butanol from WS is \$1.37/kg (distillative recovery)

- Return on investment is 19.87% and payback time is 5.03 years
- Expansion of an existing plant would result in production cost of \$1.07/kg (distillative recovery), and \$0.82/kg (membrane recovery)
- Utilities affect butanol production cost most

This kind of information may convince a venture capitalist to contribute to the building of a butanol plant, especially if payback is in 5 years and the return on investment is 19.87%. However, this was a computer simulation, and would have to be updated for current prices. That could alter the numbers.

11.4: Economics of Biodiesel Production, Including Economics of Algae

11.4 Economics of Biodiesel Production, Including Economics of Algae

One of the major feedstocks for biodiesel is soy oil or any other vegetable oil. Animal fats can also be used, but as pointed out in a previous lesson, animal fats can produce more by-products that cause issues (i.e., free fatty acids which can cause soap formation). [Jatropha](#) is another oil used for biodiesel production. Second-generation biodiesel can be produced from algae, and use of algae for biodiesel production is a growing market (Figure 11.8). The feedstock is the primary cost involved in producing biofuel. Haas et al (2006) estimate that the cost of oil is ~ 85% of the production costs, while Duncan (2003) estimates it to be ~80% of the production costs.

see text description below

Figure 11.8: Global biodiesel production by feedstock.

[Click here for a text alternative to Figure 11.8](#)

Global biodiesel Production in billions of liters by Feedstock from 2007-2019. All values are visual approximations

Year	Vegetable Oil	Nob Agricultural (animal fats)	Jatropha	Biomass-based (2nd Generation)	Total
2007-2009	13	1.75	.25	0	15
2010	18.5	2.25	.25	0	21
2011	20	2.5	.5	0	23
2012	21.25	3.5	.75	0	25.5
2013	22.75	3.25	1	0	27
2014	24.5	3.5	1.25	0	29.25
2015	26.75	3.25	1.5	0	31.5
2016	27.5	3.5	2.75	.25	34
2017	29	3.75	2.5	1	36.25
2018	29.75	3.75	2.5	1	36.25
2019	31	4	3	2.5	40.5

Credit: [The Crop Site](#)

Figures 11.9a and 11.9b show the challenges of the economics behind biodiesel production. Figure 11.9a shows the breakeven price of biodiesel plotted with the actual biodiesel price. Most years, the biodiesel price and breakeven price were the same. But in 2011 and 2013, the biodiesel sold at a higher price than the breakeven price, a good indicator for demand. In Figure 11.9b, we can see that in most years, the ULSD price was lower than biodiesel, by ~\$1 per gallon, but in late 2013 and 2014, the price was almost the same and the margin between the two were much closer. Again, this suggests a greater demand for biodiesel as well as the costs becoming closer to the processing of petrodiesel.

Rises in 2007-2008. Drops between 2008-2010 spikes in 2011 & 2013. Price & breakeven lines similar except in 2011 and 2013 -price is higher

Figure 11.9a: Weekly biodiesel price and breakeven price at Iowa plant, 2007-2014.

Credit: [OPIS](#)

ULSD & biodiesel follow similar fluctuations but biodiesel is roughly \$1+ more. Circle around 2014 - both prices are similar & declining

Figure 11.9b: Weekly wholesale ultra-low sulfur diesel (ULSD) and biodiesel price at Chicago, 2007-2014.

Credit: [OPIS](#)

Most of the information we are looking at is based on soy oil production, but as we have discussed in Lessons 9 and 10, biodiesel can be produced in ways other than transesterification and can be produced from other sources, such as algae. The reason for producing biodiesel using other methods would be to reduce the oxygenates from the biodiesel, mainly so the biodiesel could be used as jet fuel, as jet fuel cannot have oxygenates in it. The reason behind using algae is because of the advantages of 1) using land areas that would not be able to grow terrestrial plants, 2) the ability of algae to produce much greater amounts of oil per landmass than plants like soy, and 3) algae plants take in much greater amounts of CO₂ and could be located near a power plant to utilize emissions from the flue gases. However, as you will see from data in the following tables, the costs of oil from algae are still fairly high. One of the useful aspects of growing algae is it can be grown in water sources that can contain salt or some sediment - even though water usage may be high, some of the water may be separated out and used again.

The following data is from an overview review article on producing biodiesel from algae, from 2007. In Table 11.3, Chisti compared the production of biodiesel from PBR and an open raceway pond, to show differences in production.

Table 11.3: Comparison of Photobioreactor and Raceway Production Methods

Variable	Photobioreactor facility
Annual biomass production (kg)	100,000
Volumetric productivity (kg m ⁻³ d ⁻¹)	1.535
Areal productivity (kg m ⁻² d ⁻¹)	0.048 ^a 0.072 ^c
Biomass concentration in broth (kg m ⁻³)	4.00
Dilution rate (d ⁻¹)	0.384
Area needed (m ²)	5681
Oil yield (m ³ ha ⁻¹)	136.9 ^d 58.7 ^e
Annual CO ₂ consumption (kg)	183,333
System geometry	132 parallel tubes/unit; 80 m long tubes; 0.06 m tube
Number of units	6

^a Based on facility area.

^b Based on actual pond area.

^c Based on projected area of photobioreactor tubes.

^d Based on 70% by wt oil in biomass.

^e Based on 30% by wt oil in biomass.

Credit: Chisti, Y., Biotechnology Advances, 2007

As you can see, the PBR can produce more oil for a number of reasons, but costs associated with the PBR are higher. Chisti estimates the cost to produce algae oil on a scale of 10,000 tons at \$0.95 per pound. This particular article estimated that the cost of producing biodiesel from algae would range from \$10.60 – \$11.13 per gallon. The processing costs for palm oil would be ~\$0.53 per gallon, and the processing costs for soybean oil would be \$3.48 per gallon. A slightly more recent report, a project to estimate the price of biodiesel, indicates prices from \$10.66 per gallon to as high as \$19.16 depending on location and oil production. (Davis, R., et al., 2012) Yet another computer-simulated estimate provided by Richardson et al. shows a cost to produce algal oil at \$0.25 - \$1.61 per pound, not too far off of costs to produce soybean oil (\$0.35 - \$0.38 per pound) (Richardson et al., 2010). They also estimated the cost of biodiesel from algae oil to be \$2.35 per gallon, less than a gallon of ULSD. However, they may not be including algae harvesting costs in this estimate.

So, you can see that biodiesel from microalgae is a long way off from being a reality, yet it probably has a future if the costs can be brought down due to benefits.

So, how does biodiesel compare to ethanol as a fuel? Ethanol from corn has become big business here in the US. Figure 11.10a shows the production by county and plant locations for ethanol production from corn. We saw earlier in the lesson that ethanol from corn has a NEB ratio greater than 1 and is improving, and that production of ethanol from corn is the least expensive here in the US. The amount of ethanol produced in 2014 was 13 billion gallons per year and is a \$30 billion a year industry. It makes up 10% of the gasoline pool, although the government has mandated that the gasoline pool can utilize up to 10% ethanol, and companies get tax credits for using ethanol. Because of the high price of gasoline due to oil prices, demand for gasoline fell, and this has made it more difficult for ethanol producers to continue selling ethanol at the level that they had over the last several years. Recently, the EPA examined whether to raise the ethanol limit to 15%, but because of the drop in oil prices, the EPA has been reconsidering this and has not set levels for 2015. In the assignment section, you will read an article related to this so you can get a feel for what is facing the biofuels industry. Remember that by including ethanol in the gasoline pool, we reduce GHG emissions.

Figure 11.10b shows the location of biodiesel facilities in the US from 2007. If you would like to view a more recent map and location of facilities (2015), go to [Biodiesel Magazine](#). According to the most recent statistics, there are 145 biodiesel facilities in the US that provide more than 2.60 billion gallons of biodiesel per year (in 2010, the production of biodiesel was less than 0.4 billion gallons per year, which is an order of magnitude increase). Biodiesel makes up about 5-6% of the diesel fuel pool. Biodiesel plants tend to be smaller and more evenly distributed across the US than ethanol. You will also read an article related to biodiesel pricing. **RIN means renewable identification number** and **RFS stands for renewable fuel standard**.

Corn production and location of ethanol plants in US 2013. Most corn and ethanol plants in the northern Midwest

Figure 11.10a: Ethanol production from corn: Production by county and location of plants 2012.

Credit: [Virginia places](#)

US biodiesel production facilities, 2007. Most plants sit on the Eastern half of the United States, especially in the Great Lakes region

Figure 11.10b: US biodiesel production facilities, 2007.

Credit: [APEC](#)

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11.5: Assignments

11.5 Assignments

Discussion #2

Please read the following selections:

- Matthew Philips, "[Ethanol, Fighting for Its Life, Gets a Temporary Reprieve.](#)" Bloomberg Report, Nov. 24, 2014.
- Scott Irwin, "Understanding the behavior of biodiesel RINs prices," Ag Professional, Oct. 13, 2014.

After reading the selections, write a paragraph discussing how these articles relate to biomass production.

After posting your response, **please comment on at least one other person's response**. Discussions will be reviewed , and grades will reflect critical thinking in your input and responses. Don't just take what you read at face value; think about what is written.

(5 points)

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11.6: Summary and Final Tasks

11.6 Summary and Final Tasks

Summary

The economics of biofuels depends on the overall economic health of the country as well as what is going on in the fuel industry for fossil fuels. Biofuels have come a long way in becoming a part of US industry, but issues with gasoline and diesel prices, as well as government involvement, will continue to dictate the use of biofuels.

Are you beginning to grasp the complexity of the issues surrounding how the biofuel production industry will survive going forward? If it reduces the carbon footprint, isn't it worthwhile to continue to support biofuel production?

References

Vanek, F., Albright, L., and Angenent, L., "Energy Systems Engineering: Evaluation and Implementation", Second Edition, McGraw-Hill, 2012.

Pryor, Scott; Li, Yebo; Liao, Wei; Hodge, David; "Sugar-based and Starch-based Ethanol," BEEMS Module B5, USDA Higher Education Challenger Program, 2009-38411-19761, 2009.

Xiaodong Du and Lihong Lu McPhail, "Inside the Black Box: The Price Linkage and Transmission Between Energy and Agricultural Markets," Energy Journal, Vol. 33, No. 2, 2012, pp. 171-194.

Nasib Qureshi, Adriano Pinto Mariano, Vijay Singh, Thaddeus Chukwuemeka Ezeji, "Biomass to Butanol," BEEMS Module B6, USDA Higher Education Challenger Program, 2009-38411-19761, 2009.

Haas, M.J., McAloon, A.J., Yee, W.C., Foglia, T.A., "A process model to estimate biodiesel production costs," Bioresource Technology, 97, 671-678, 2006.

Duncan, J., "Costs of biodiesel production," Energy Efficiency and Conservation Authority Report, 2003.

Chisti, Y., "Biodiesel from microalgae: A research review," Biotechnology Advances, 25, 294-306, 2007.

Davis, R., et al., "Renewable diesel from algal lipids: An integrated baseline for costs, cost, emission and resource potential from a harmonized model," Technical Report, prepared for US DOE Energy Biomass Program, ANL/ESD/12; NREL/TP-5100; PNNL-21437, June 2012.

Richardson, J.W., Outlaw, J.L., and Allison, M., "The economics of microalgae," AgBioForum, 13 (2), 119-130, 2010.

Reminder - Complete all of the Lesson 11 tasks!

You have reached the end of this lesson! Double-check the Road Map on this lesson *Overview* page to make sure you have completed all of the activities listed there before you begin the next Lesson.

Questions?

If there is anything in the lesson materials that you would like to comment on, or don't quite understand, please post your thoughts and/or questions to our Throughout the Course Questions & Comments discussion forum and/or set up an appointment for office hour. While you are there, feel free to post responses to your classmates if you are able to help.

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12: ADDITIONAL PROCESSES FOR FUELS FROM BIOMASS

12.1: Anaerobic Digestion

12.2: Syngas Fermentation

12.3: Microbial Fuel Cells

12.4: Final Thoughts on the Use of Biomass for Fuel Generation

12.5: Assignments

12.6: Summary and Final Tasks

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12.1: Anaerobic Digestion

12.1 Anaerobic Digestion

Anaerobic digestion (AD) is a biological process that breaks down organic materials (feedstocks) in the absence of oxygen (anaerobic conditions) into methane (CH_4) and carbon dioxide (CO_2). It is a process that occurs naturally in bogs, lake sediments, oceans, and digestive tracts. Cows contain one of the most well known fermentation vats, the rumen, which is part of the stomach (in other animals as well). Fermentation takes place during digestion! Figure 12.1 shows a schematic of anaerobic digestion.

See text description below

Figure 12.1: Anaerobic digester process.

[Click here for a text alternative to Figure 12.1](#)

This is the anaerobic digester process. Organic materials (carbohydrates, proteins, fats, oils, etc) enter the cycle. The sugars, amino acids, and fatty acids become H_2 , CO_2 and organic acids. From there the digester effluents (residual solids and water) are removed. The digester yields CH_4 , CO_2 and H_2S which are removed as biogas.

Credit: Dr. Caroline E. Burgess Clifford

There are benefits to using an anaerobic digester, particularly when raising livestock. A biogas, which contains methane and hydrogen, will be produced that can be used as a fuel. From a waste treatment point of view, it reduces the volume and mass of the waste, as well as reduces organic content and biodegradability of waste so that the residual matter can be better used as soil amendment and fertilizer. There are also environmental benefits: 1) odors and emissions of greenhouse gases (i.e., methane) and volatile organic compounds are reduced, and 2) the digester will destroy pathogens in the waste.

So, what are the biological processes that occur during AD? The bacteria ferment and convert complex organic materials into acetate and hydrogen. There are four basic phases of anaerobic digestion, which is a synergistic process using anaerobic microorganisms: 1) hydrolysis, 2) acidogenesis, 3) acetogenesis, and 4) methanogenesis. Figure 12.2 shows the progression and types of products for each phase.

4 phases see text description below

Figure 12.2: Schematic of four phases of biogas production.

[Click here for a text alternative to Figure 12.2](#)

Four Phases of Biogas Production

Phase 1 – Hydrolysis

Complex Biopolymers (proteins, polysaccharide, fats/oils) in the presence of fermentative bacteria become broken down monomers and oligomers (sugars, amino acids, peptides)

Phase 2 – Acidogenesis

The broken-down monomers and oligomers in the presence of fermentative bacteria become propionate, butyrate, etc (short-chain volatile organic acids)

Phase 3 – Acetogenesis

The broken-down monomers and oligomers from phase 1, in the presence of fermentative bacteria, can also become acetate or $H_2 + CO_2$. The propionate and butyrate in the presence of Acetogens (H_2 producing or consuming) can also become acetate or $H_2 + CO_2$.

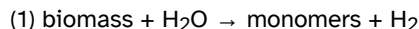
Phase 4 – Methanogenesis

$H_2 + CO_2$ in the presence of CO_2 reducing methanogens becomes $CH_4 + CO_2$. Acetate in the presence of acetoclastic methanogens can also become $CH_4 + CO_2$

Credit: BEEMS Module B7 - Anaerobic Digestion

Hydrolysis Biochemistry

We have talked about hydrolysis in earlier lessons. Hydrolysis is a reaction with water. Acid and base can be used to accelerate the reaction. However, this occurs in enzymes as well. Figure 12.3 shows the hydrolysis reaction, and how cellulose, starch, and simple sugars can be broken down by water and enzymes. In anaerobic digestion, the enzymes are exoenzymes (cellulosome, protease, etc.) from a number of bacteria, protozoa, and fungi (see Reaction 1).



(Sources: cellulose, starch, sugars, fats, oils) (Products: mono-sugars [glucose, xylose, etc.], fatty acids)

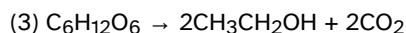
Hydrolysis reaction - described in text and caption

Figure 12.3: The α -1,4 bond is attacked by water so that the water splits into H^+ and OH^- and forms the two glucose molecules below the figure.

Credit: BEEMS Module B1

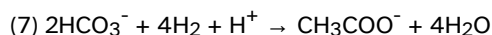
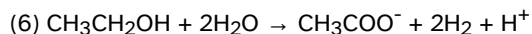
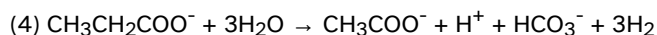
Acidogenesis Biochemistry

During acidogenesis, soluble monomers are converted into small organic compounds, such as short chain (volatile) acids (propionic, formic, lactic, butyric, succinic acids – see Reaction 2), ketones (glycerol, acetone), and alcohols (ethanol, methanol – see Reaction 3).



Acetogenesis Biochemistry

The acidogenesis intermediates are attacked by acetogenic bacteria; the products from acetogenesis include acetic acid, CO₂, and H₂. The reactions 4-7 shows the reactions that occur during acetogenesis:



Several bacteria contribute to acetogenesis, including:

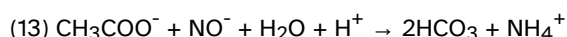
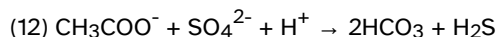
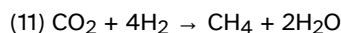
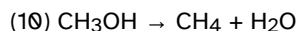
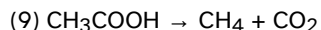
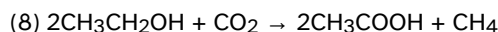
Syntrophobacter wolinii, propionate decomposer

Syntrophomonas wolfei, butyrate decomposer

Clostridium spp., *peptococcus anaerobes*, *lactobacillus*, and *actinomyces* are acid formers.

Methanogenesis Biochemistry

The last phase of anaerobic digestion is the methanogenesis phase. Several reactions take place using the intermediate products from the other phases, with the main product being methane. Reactions 8-13 show the common reactions that take place during methanogenesis:



Several bacterial contribute to methanogenesis, including:

Methanobacterium, *methanobacillus*, *methanococcus*, and *methanosarcina*, etc.

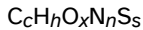
As you can see, the bacteria for anaerobic digestion are different from other enzymes for making biofuels, and could even be in our own stomachs!

Any kind of organic matter can be fed to an anaerobic digester, including manure and litter, food wastes, green wastes, plant biomass, and wastewater sludge. The materials that compose these feedstocks include polysaccharides, proteins, and fats/oils. Some of the organic materials degrade at a slow rate; hydrolysis of cellulose and hemicellulose is rate limiting. There are some organic materials that do not biodegrade: lignin, peptidoglycan, and membrane-associated proteins. The organic residues contain water and biomass composed of volatile solids and fixed solids (minerals or ash after combustion). And it's the volatile solids (VS) that can be non-biodegradable and biodegradable.

As we discussed regarding pretreatment of biomass for making of ethanol, efficiency of anaerobic digestion improves with pretreatment. Hydrolysis of cellulose and hemicellulose (phase 1 in AD) is improved with pretreatment because it overcomes biomass recalcitrance. As discussed in a previous lesson, pretreatment options include treatments with acids, alkalines, steam

explosion, size-reduction, etc. Common alkaline agents include: NaOH, Ca(OH)₂, and NH₃.

Theoretical methane yield (Y_{CH_4} , m³ STP/kg substrate converted) can be calculated from the elemental composition of a substrate:



$$Y_{CH_4} = \frac{22.4(\frac{c}{2} + \frac{h}{8} + \frac{x}{4} - \frac{3n}{8} - \frac{s}{4})}{12c + h + 16x + 14n + 16s}$$

Table 12.1 shows the substrate, a common elemental formula, and the theoretical methane yield for each.

Table 12.1: Theoretical methane yield (m³ STP/kg substrate converted) for several biomass sources (Credit: Frigon and Guiot, 2010)

Substrate	Elemental formula
Carbohydrates	(CH ₂ O) _n
Proteins	C ₁₀₆ H ₁₆₈ O ₃₄ N ₂₈ S
Fat	C ₈ H ₁₅ O
Plant biomass	C ₅ H ₉ O _{2.5} NS _{0.025}

Figure 12.4 shows the biogas yield for several different feedstocks in m³/ton. Be aware that after digestion, there is a biogas yield and the remainder of the digestion, known as digestate. The biogas typically contains 50-60% CH₄, with the rest primarily composed of CO₂ and other trace gases. The digestate contains fiber, nutrients, and water, and these can be used for compost, animal bedding, and composite boards. Figure 12.5 shows a schematic of the components of the digester.

see text description

Figure 12.4: Biogas yields (m³/ton) of different biomass feedstocks.
Click for text description of Figure 12.4

Biogas Yields (m³/ton) of Different Biomass Feedstocks:

- **Maize 200**
- **Grasses 110**
- **Mangel 75**
- **Used Fats 800**
- **Fatty Wastes 400**
- **Vegetable Oil 350**
- **Sewage Waste 80**
- **Distillery Waste 80**
 - **Dairy Waste 55**
- **Fruits & Vegetables 35**
 - **Poultry Manure 35**
 - **Cattle Manure 30**
 - **Pig Manure 25**

Credit: BEEMS Module B7 Anaerobic digestion

Schematic of an anaerobic digester facility and product output see text description

Figure 12.5: Schematic of an anaerobic digester facility and product output.

[Click for a text description of figure 12.5](#)

Farm leads to manure which goes to a digester. The products of the digester are separated into solids & liquids, and biogas. The biogas is stored in tanks and then is sent to a CHP unit. From there the energy is used to produce power, or heat to warm the farm or the digester. The solids and liquids go through de-watering and are used as bedding, compost or fertilizer

Credit: [Cornell Small Farms Program, Anerobic Digesters](#)

There are several factors that will affect anaerobic digestion. Different feedstocks will degrade at different rates and produce different amounts of methane (as seen in Figure 12.4 and Table 12.1). That depends on the biological degradability and methane potential, the carbon and nutrients available, and the moisture content of each feed material. As noted in Figure 4 and Table 12.1, fats contain the highest volatile solids and can generate the greatest amount of biogas. Solids take a longer time to digest than feedstocks that are soluble. Nutrients are also important. A suitable carbon to nitrogen ratio (C/N) is less than 30, and the carbon to phosphorous ratio (C/P) should be less than 50. For example, lignocellulosic biomass has a high C/N ratio, so nitrogen sources must be added. Nutrients also must be free of toxic components. Other factors that can influence digestion are the availability and location of feed materials (transportation costs involved here), logistics of how to get materials to certain sites, and if size reduction is going to be necessary.

Digester performance will also depend on the microbial population in the digester. This means maintaining adequate quantities of fermenting bacteria and methanogens. A recycled stream is used to take a portion of the liquid digestate as inoculum (material used for inoculation of feed materials). And depending on feeds, there may be an acclimation period to reach acceptable conditions.

There are also variations in the operational factors and environmental conditions of the digester. It is important to know the total solids (TS) and volatile solids (VS) in the feeds, the best retention times, and to provide mixing. Operational factors include the amount and strength type of feedstocks added to the digester. The operation also depends on maintaining the microorganism population and organic loading in reactors, whether operating in a batch or continuous reactor. Mixing is also an important factor in any reaction. The goal of mixing is to keep the microorganisms in close interaction with the feed and nutrients. Mixing also prevents the formation of a floating crust layer, which can reduce the amount of biogas percolating out of the slurry. Mixing will benefit the breakdown of volatile solids and increase biogas production, but keep in mind mixing adds energy cost, so this must be balanced. The types of mixing in this system include gas bubbling and/or mechanical mixing.

Environmental conditions include the temperature and pH of the reactor, as well as concentrations of materials, including the volatile fatty acids, ammonia, salt, and cationic ions. Different methanogens react in temperature ranges. The type of methanogens that produce the most biogas are thermophiles, but the digester must be operating between 40-70 °C. Methanogens also prefer neutral pH conditions (6.5-8.2). Accumulation of volatile fatty acids (VFAs) can cause the digestion to stop producing gas – this happens when too much digestible organic material is added, a toxic compound is added, or there is a sudden temperature change. Toxic materials include: 1) oxygen, 2) antibiotics, 3) cleaning chemicals, 4) inorganic acids, 5) alkali and alkaline earth salt toxicity, 6) heavy metals, 7) sulfides, and 8) ammonia. An additional reason for AD process failure has to do with the reaction within being out of balance. In particular, the rate of acid formation and methane production should be equal. This is done by maintaining definite ranges and ratios of the following: solids loading, alkalinity, temperature, pH, mixing, and controlling VFA formation. When the methanogen microorganisms cannot keep up with the fermenting bacteria, the digester becomes acidic – also known as “sour.”

An ambient temperature liquid phase AD reactor is called a covered lagoon. Advantages of the covered lagoon are the low cost, ease of construction, and control of odor control with manure storage. Disadvantages include difficult sludge removal and only seasonal production. However, there are several designs that have controlled temperature, and are typical to different types of reactors: 1) complete mixing, 2) plug flow, 3) sequencing batch, and 4) fixed film. Table 12.2 shows a comparison of the variables for each type of anaerobic digester configuration.

Table 12.2: Comparison of various types of anaerobic digester configurations (Credit: On-Farm Anaerobic Digester Operator Handbook. M.C. Gould and M.F. Crook. 2010. Modified by D.M. Kirk. January 2010.)

Characteristic	Covered Storage	Plug Flow Digester	Mixed Plug Flow Digester	Complete Mix Digester	Fixed Film Digester	Induced Blanket Digester	Two-Stage Digester
Digestion Vessel	Clay or synthetic lined storage	Rectangle tank in ground	Rectangle tank in ground	Round/square in/above ground tank	In/above ground tank	In/above ground tank	In/above ground tank
Level of technology	Low	Low	Medium	Medium	Medium	High	High
Added heat	No	Yes	Yes	Yes	Optional	Yes	Yes
Total solids	3-6%	11-13%	3-13%	3-10%	2-4%	<8%	~5%
Solids characteristics	Coarse	Coarse	Medium Coarse	Coarse	Fine	..	..
Retention time(days)	60+	15+	15+	15+	<4	3-5	10-13
Farm type	Dairy, Swine	Dairy, Swine	Dairy, Swine	Dairy	Dairy, Swine	Dairy, Swine	Dairy, Swine
Optimum location	All climates	All climates	All climates	All climates	Temperate/warm	All climates	All climates

12.2: Syngas Fermentation

12.2 Syngas Fermentation

There is an unusual process for liquids production from biomass: gasification followed by fermentation of gases into liquids. During gasification, the gases of CO, H₂, and CO₂ are formed (as we have learned in past lessons), but instead of using something like FT or MTG, this is formation of liquids fuels through a fermentation process using a microbial catalyst. Products are typically ethanol, acetone, and butanol. Gasification was discussed in depth in Lesson 4, but I will cover it briefly here to remind you of the various processing aspects. Gasification takes place at temperatures of 750-900°C under partial oxidation. It happens in the following steps: drying; pyrolysis in absence of O₂; gas-solid reactions to produce H₂, CO, and CH₄ from char; and gas-phase reactions that manage the amounts of H₂, CO, and CH₄. It is most often known as syngas, but if it contains N₂, then it is called producer gas. Syngas can be generated from any hydrocarbon feed. The main cost associated with gas-to-liquid technologies has to do with the syngas production, which is over half of the capital costs. Costs can be improved using improved thermal efficiency through better heat utilization and process integration and by decreasing capital costs.

There are advantages to using fermentation as part of liquids generation rather than using something like Fischer-Tropsch:

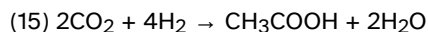
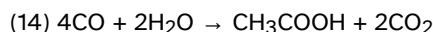
1. As with any gasification, it is independent of feedstock, and therefore, independent of biomass chemical composition.
2. Microorganisms are very specific to ethanol production, whereas with chemical catalysts, there are a wide range of reaction products.
3. No pretreatment is required as part of the biochemical platform.
4. Complete conversion of biomass is achieved, including lignin conversion. This can reduce the environmental impact of waste disposal.
5. Fermentation takes place at near ambient temperature and pressure, thus at a place where costs can be reduced significantly.
6. The requirement for CO/H₂ ratio is flexible.

Of course, there are disadvantages as well. These include:

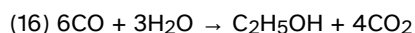
1. Gas-liquid mass transfer limitations.
2. Low ethanol productivity, usually related to low cell density.
3. Impurities in syngas generated from biomass.
4. Sensitivity of microorganisms to environmental conditions (pH, oxygen concentration, and redox potential).

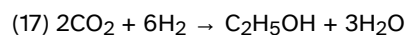
The microorganisms that are used for ethanol production from syngas are acetogens that can produce ethanol, acetic acid, and other products from CO and H₂ in the presence of CO₂. The organisms are: 1) *Clostridium* strain P11, 2) *Clostridium ljungdahlii*, 3) *Clostridium woodii*, 4) *Clostridium thermoaceticum*, and 5) *Clostridium carboxidivorans* P7. (Wilkens and Atiyeh, 2011) The bacteria are some of the same ones that occur during anaerobic digestion: acetogens and acidogens. I won't go into great detail about the biochemistry, as it is a little beyond the scope of this class. The acetogens utilize the reductive acetyl-CoA (or Wood-Ljungdahl) pathway to grow carbons and hydrogens on single carbon substrates such as CO and CO₂. *Clostridium* bacteria use H₂ or organic compounds as the electron source for the reduction of CO₂ to acetyl-CoA, which are further converted into acids and alcohols. The process proceeds in two phases: acidogenic and solventogenic phases. In the acidogenic phase, mainly acids are produced (i.e., acetic acid and butyric acid). In the solventogenic phase, mainly solvents are produced (i.e., alcohols such as ethanol and butanol). Reactions 14 and 15 show the reaction chemistry for acetic acid formation, and reactions 16 and 17 show the reaction chemistry for ethanol formation:

Acetic acid formation:



Ethanol formation:





In summation, gasification-fermentation alternative is a method for biofuel production utilizing syngas generated from gasification of biomass feedstocks. Because it is biologically based, it has the potential for reducing costs compared to other syngas to liquid technologies, but there are several challenges related to this technology. Challenges include low alcohol productivity, low syngas conversion efficiency, and limitations in gas-liquid mass transfer. These challenges must be solved if this technology is to become economically viable.

12.3: Microbial Fuel Cells

12.3 Microbial Fuel Cells

A microbial fuel cell is a bio-electro-chemical device that can convert chemical energy directly into electrical energy. But first, let's go over what a fuel cell is. A fuel cell is a battery of sorts. So, what is a battery? A battery is when two different types of metals are connected together through what is called an electrolyte. One metal is an anode, which is a metal that "wants" to give off electrons when under the right conditions. One metal is a cathode, which is a metal that "wants" to accept electrons when under the right conditions. When these two metals are in close proximity, and there is a fluid that will conduct the electrons (an electrolyte), then the flow of electrons from one metal to the other can occur. And we can capture that flow to extract electricity. Batteries that we use in remotes for televisions will eventually get used up and need to be replaced. This is an example of a **primary battery**. Figures 12.6a-12.6c show a generic cell, a stack of cells using zinc and copper, and a picture of a Voltaic cell as created by Alessandro Volta (inventor).

schematic of 1 cell of a battery: metal 1 anode on top of electrolyte, on top of metal 2 cathode. Electrons flow from metal 1 to 2

Figure 12.6a: Generic schematic of one cell of a battery.

Credit: Dr. Caroline B. Clifford

Stacks of elements composed of cation copper, electrolyte and anode zinc

Figure 12.6b: Stacks of cells in a battery, also called a voltaic pile.

Credit: [Wikipedia](#)

Voltaic pile as constructed by Alessandro Volta

Figure 12.6c: Voltaic pile as constructed by Alessandro Volta.

Credit: [Battery Facts](#)

We can also have **secondary batteries**, where the flow of electricity is established to provide electrical energy, but we can also apply electricity to the battery to reverse the flow of electrons and regenerate the life of the battery. While regenerated batteries don't last forever, you can definitely get your money's worth because you can regenerate them.

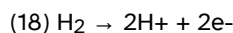
Fuel cells are also a sort of battery, but the materials are different and flow continuously to produce electricity. Figure 12.7 shows a generic fuel cell. As with a battery, it has an anode, cathode, and electrolyte. The anode typically uses hydrogen as the fuel, on the left side of the figure, and oxygen as the oxidant used in the cathode, on the right side of the figure. The electrolyte contains a fluid but also a membrane that removes the protons from the hydrogen, leaving the electrons to flow, and allows oxygen to accept the protons to form water. Typically, these cells are run on hydrogen and oxygen, but we get electrical energy out rather than heat from burning hydrogen and oxygen.

Generic schematic of fuel cell as described in the text

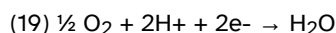
Figure 12.7: Generic schematic of fuel cell.

Credit: Dr. Caroline B. Clifford

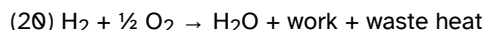
At the anode, hydrogen reacts as shown in reaction 18:



This is an oxidation reaction that produces protons and electrons at the anode. The protons then migrate through an acidic electrolyte, and the electrons travel through an external circuit. Both arrive at the cathode to react with the oxidant, oxygen, as shown in reaction 19:



This is the reduction reaction, where oxygen can be supplied purely or in air. Essentially, the total circuit is completed through the mass transfer of protons in the electrolyte and external electrical circuit. There will be a small amount of heat lost through the electrodes. The overall reaction is shown in reaction 20:



The water and waste heat are the by-products and must be removed on a continuous basis. An ideal voltage from this reaction is 1.22 volts, but less than that voltage will be realized. Other issues include use of fuel different from hydrogen (methanol, hydrocarbons, etc.) and the fact that fuel cells produce direct current (DC) when most applications require alternating current. This little bit of background has been provided so a short discussion on microbial fuel cells can be had.

We are not going to go into great depth on microbial fuel cells, as some of the biochemistry can be complex. I will provide you with some generic information on how a microbial fuel cell is set up. These are bio-electro-chemical devices, which convert chemical energy directly into electrical energy. As we have discussed before, there are some steps that need to occur. Cellulose is hydrolyzed into sugars, i.e., glucose. The sugars are fermented into short chain fatty acids, alcohols, hydrogen, and carbon dioxide. Finally, electricogenesis takes place, producing electricity, and carbon dioxide is carried through. Electricogenesis converts chemical energy to electrical energy by the catalytic reaction microorganisms. The anode is anaerobic, and the anode chamber contains microbes and feedstock. The fuel is oxidized by microorganisms, which generates CO_2 , electrons, and protons. The cathode is the aerobic chamber, and just like other fuel cells, a proton exchange membrane separates the two chambers and allows only protons (H^+ ions) to pass.

There are two types of microbial fuel cells (MFCs): mediator or mediator-less. The mediator type was demonstrated in the early 20th century and uses a mediator: a chemical that transfers electrons from the bacteria in the cell to the anode. Some of these chemicals include thionine, methyl viologen, methyl blue, humic acid, and neutral red. These chemicals are expensive and toxic. Mediator-less MFCs are a more recent development, from the 1970s. These types of cells have electrochemically active redox proteins such as cytochromes on their outer membrane that can transfer electrons directly to the anode. Some electrochemically active bacteria are *Shewanella putrefaciens* and *Aeromomas hydrophila*. Some bacteria have pili on the external membrane, which allows for electron production through the pili. They are beginning to find commercial use in the treatment of wastewater. I've included some YouTube videos explaining how the MFCs work. The first video is a brief but complete explanation of how an MFC works (2:03).

MudWatt Microbial Fuel Cell

[Click here for transcript of the MudWatt video.](#)

[MUSIC PLAYING]

PRESENTER: The MudWatt Microbial Fuel Cell is a bio electrical device that uses the natural metabolisms of microbes found within soil to produce electrical energy. Here's how it works.

The MudWatt is comprised of two graphite felt electrodes-- the anode and the cathode-- held within a durable airtight container. The piece of electronics on top is used for experimentation and also features an LED light which blinks using the power of the microbes within your soil. The user simply fills the MudWatt with wet soil, burying the anode while resting the cathode on top.

In this configuration, a healthy community of electricity generating microbes will develop on the surface of the anode in a matter of days. These bacteria have unique metabolic abilities which enable them to respire the sugars and nutrients within the soil and deposit electrons onto the anode as part of their natural metabolism. Protons and carbon dioxide are released into the soil as metabolic byproducts and diffuse toward the cathode.

Once transferred to the anode, the electron then travels through the electrode wire, through the MudWatt electronics to the cathode. While passing through the electronics, this electrical current will light the LED light on top, giving you a visual indication that your microbes are healthy and happy.

At the cathode, the electron interacts with oxygen in the air, as well as protons coming from the anode, to form water. The carbon dioxide originating from the anode is released into the air. The cycle continues, limited only by the availability of nutrients within the soil and oxygen within the air.

[MUSIC PLAYING]

Credit: KeegoTech

The next video is a little longer and goes into a little more depth of what was described above (7:23).

Microbial Fuel Cell

[Click here for transcript of the Microbial Fuel Cell video.](#)

[MUSIC PLAYING]

PRESENTER: Inspiration to build bio-electrochemical systems came from a discovery of certain microbes that live in soil. These bacteria swim up to the solid metal-- such as iron-- transfer electrons to the metal, dissolving it in process. This is similar to aerobic bacteria that transfer electrons to molecules of oxygen during respiration. The electron transfer generates electricity. To where there's electricity, there is power.

PRESENTER: To harvest the electricity, a bio-electrochemical fuel cell is used. This system consists of two compartments-- an anode compartment and a cathode compartment. These two compartments are separated by a membrane. A biofilm grows on the end of it.

[MUSIC PLAYING]

An organic feed stream, such as waste water, enters the fuel cell, where it is oxidized by the biofilm. Simultaneously, oxidized products leave the fuel cell. The oxidation of organics-- for instance, acetate-- produces electrons and protons. This half reaction releases a certain amount of energy.

Electrons are conducted over the wire while protons move through the membrane to the cathode to uphold electron neutrality. Oxygen is supplied to the cathode chamber. There accepts the electrons and reacts with the protons to form water. This half reaction also releases a certain amount of energy.

[MUSIC PLAYING]

The theoretical maximum energy gain is determined by combining both half reactions. However, resistances are found in multiple layers of the fuel cell.

[MUSIC PLAYING]

The ohmic losses are found in the electrical wire and in the proton transfer from the anode to the cathode. Concentration losses occur when the rate of mass transferred either to anode or cathode compartment limits the rate of product formation. Bacterial metabolic losses can be described by the amount of energy that is used by the microbes to grow.

The energy is harvested to form a proton gradient over the inner membrane. Activation losses are described by the capacity of the biofilm to transfer the electrons to the anode. Certain organisms can grow conductive nanowires-- called pili-- that directly interact with anode to transfer the electrons.

[MUSIC PLAYING]

[BIRDS CHIRPING]

PRESENTER: OK. Today, we're out in the wild. And we're looking for some sludge to power our bio-battery. I think this a nice spot. Ah, it's perfect.

PRESENTER: Another application of bio-electrochemical systems is the production of chemicals. In this case power must be applied to biofilm by external source. Electrons are produced by the oxidation of water. Now the biofilm grows on the cathode. The energy-rich electrons are used by organisms to fixate carbon dioxide.

[MUSIC PLAYING]

Carbon dioxide enters the cathode compartment and fuses to the cathode. There, to harvest energy from the electrons, CO₂ is fixed. And acetate is formed.

PRESENTER: All right. Let's have a look at our bio-battery. We buried the anode in our soil. Make sure there are no air bubbles in the soil. It has to be anaerobic. On top of the soil, we placed the cathode, which is in direct contact with the oxygen in the air.

Now let's look at another application of microbial fuel cell. Desalination can be achieved by inserting an extra compartment in between the anode and the cathode. A forward osmosis membrane is placed at the anode. This allows transport on both positively and negatively charged ions.

At the cathode, a cation exchange membrane is placed, which permits only transport of positively charged ions. Salt water is flowing through this compartment while negatively charged ions move to the anode, and positively charged ions moved to the cathode.

To finalize our bio-battery and to see the energy production, we have to connect the cathodes to the anodes. the electricity is stored in a transformer and used to power a LED light.

[MUSIC PLAYING]

Credit: [Sebastiaan de Bruin](#)

The next short video has Dr. Bruce Logan, a professor in the Civil Engineering Dept. at PSU providing a brief explanation on using these MFCs for wastewater treatment facilities (3:05).

Electrifying Wastewater

[Click here for transcript of the Electrifying Wastewater video.](#)

PRESENTER: Clean water and electricity are essential for everyday life. But to get one, we often need the other. We generate electricity to purify water. And in many parts of the world, we use water to create energy.

In the United States, an average of 5% of the electricity we produce goes towards powering our water infrastructure. But what if we could use wastewater for energy? As it turns out, a decades' old technology known as microbial fuel cells can help extract the energy and wastewater to produce electricity.

BRUCE LOGAN: A microbial fuel cell is a device where we use bacteria to directly produce electrical current from something as simple as waste water. Right now, we have wastewater treatment plants that consume electrical power. And we can imagine a time when these treatment plants are transformed into what we hope would be power plants.

PRESENTER: Deep in the sewers in wastewater treatment plants, there are billions of bacteria, or microbes, that break down organic matter to produce electrons. They surrender their electrons to oxygen molecules in exchange for energy. But in a microbial fuel cell, the electrons take a detour.

BRUCE LOGAN: This is a microbial fuel cell. It's really a very simple device. It's just a tube with electrodes on either side of that tube-- one which is sealed off, so the bacteria can't get at the oxygen, the other one which is exposed to oxygen.

The most important part of a microbial fuel cell are the microbes. The microbes grow on an electrode, which is oxygen free so that they send off those electrons to an electrode rather than oxygen. The electrons flow through a circuit, so we extract that electrical current as electrical power.

PRESENTER: To complete the circuit, the electrons end up on the other side of the tube and combine with oxygen. The theory is simple. But putting it into practice is not so easy.

BRUCE LOGAN: We initially thought that the greatest challenge would be the bacteria. But as it turns out, it's actually everything but the bacteria that we've had the greatest challenges with. We have systems the size of this cube and maybe a little bit bigger, but we really haven't gone out and built 1,000-liter systems or 10,000-liter systems. And that's an engineering challenge that we need to address next.

PRESENTER: Despite these challenges, Logan is optimistic about microbial fuel cells.

BRUCE LOGAN: I am really excited about microbial fuel cells and these different technologies because it creates a truly sustainable way to produce energy and power our water infrastructure.

PRESENTER: In other words, if microbial fuel cells deliver on their promise, wastewater will be waste no longer.

[MUSIC PLAYING]

Credit: [BytesizeScience](#)

And the last video, put together by Dr. Logan's group at PSU, shows how to construct three different types of MFCs (4:26).

Several Types of Microbial Fuel Cells

[Click here for transcript of the types of microbial fuel cells video.](#)

[MUSIC PLAYING]

PRESENTER: Here we have three different microbial fuel cell reactor architectures. In front we have cube reactors. This is a single bottle MFC reactor. And this is a double bottle reactor, also known as an H-type reactor.

[MUSIC PLAYING]

Here we have a cube reactor disassembled. I just want to be able to show you all the parts before I put them back into the reactor itself.

This is the body of the reactor. It's a lexan cube with a 28 milliliter volume anode chamber; two holes drilled in the top for refilling and emptying of substrate.

This is the cathode end plate, and this is the cathode. This is actually an air cathode made out of carbon cloth.

This side has the four diffusion layers of PTFE. This side has carbon black and platinum catalyst. This is the side that actually faces the interior of the MFC.

This is the other end plate. There's many different nanomaterials that can be used. In this example, we are using a carbon brush fiber anode.

Now I will demonstrate assembly of a cube reactor.

First place the cathode in, the platinum-- carbon black side facing in. We use gaskets to make sure that there is no leakage and good connection between the platinum side and the current collector, which is a titanium wire.

The cube reactor is held together just with all thread and wing nuts using compression to keep all the places in-- all the pieces in place.

So the front's done. Apply a gasket, O-ring; the end plate gets slid on.

There you have it-- a cube reactor.

[MUSIC PLAYING]

So here we have a single bottle reactor. This is very similar to the cube reactors. In this setup we have a brush anode as well as another air cathode.

Now I'll demonstrate how to assemble a bottle reactor. So this is just a standard media bottle with an arm attached to it. Once again, replace the cathode with the platinum and carbon black side facing into the reactor and the PTFE diffusion layer side facing towards the air.

So all we're doing is placing the cathode, current collector, O-ring-- this is just a cap that will be used for compression to keep the cathode in place-- using just a regular arm clamp. All that remains to be done is placing

of the brush anode into the bottle.

And that is a single bottle reactor.

[MUSIC PLAYING]

OK. Now I'll demonstrate the assembly of two bottle MFC reactor architecture, or an H-type reactor.

In this situation, the anode and cathode are both the same size, and we're using the same material for the anode and cathode, which is carbon paper.

And it's just been attached to a titanium wire as the current collector. And once again, this is being used as both the anode and the cathode.

In this situation, the cation exchange membrane is placed in between the two chambers.

Use a clamp. Tighten the clamp if necessary.

And you have a two-chamber microbial fuel cell reactor.

Credit: [MFC Technology](#)

MFCs can also be used in food processing plants and breweries, as well as being implanted as biomedical devices. There are technical challenges to MFCs. They have relatively low power densities, which means they don't generate much power. Therefore research continues to improve power densities. These devices have an incredible future, but still need more research to be commercialized at a large scale.

12.4: Final Thoughts on the Use of Biomass for Fuel Generation

12.4 Final Thoughts on the Use of Biomass for Fuel Generation

We have explored many uses of biomass to generate fuels, from use in electricity generation through combustion, to several conversion technologies to make ethanol, biodiesel, and fuels that are very similar to petroleum-based fuels like gasoline, jet fuel, and diesel fuel. I also wanted you to have the opportunity to see what is still being researched and what has been commercialized. While currently, due to the cost of crude oil being low, biofuels may not be as competitive economically, they show great benefit environmentally, especially when renewable methods are used to harvest and generate the fuels. You looked up several very interesting articles related to biofuel generation and use. Read articles on biofuels with a critical eye; you now know enough about biofuels so that you can be a more critical reader. I hope that you enjoyed the class.

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12.5: Assignments

12.5 Assignments

Final Project Reminder

Remember that your Final Project will be due at the specified time in Canvas.

Quiz#4

You will complete take home Quiz #4.

12.6: Summary and Final Tasks

12.6 Summary and Final Tasks

Summary

This last lesson covered topics that are practical, such as anaerobic digestion (it is part of digestion), and also topics that are more research-oriented, such as syngas fermentation and microbial fuel cells. The best application for anaerobic digestion is on farms, as a way to utilize waste from animals. Syngas fermentation could be a lower energy-intensive process that could make gasification/syngas fermentation less expensive than using FT synthesis. And, finally, microbial fuel cells are a unique fuel cell that can take advantage of bacteria to make electricity or clean up wastewater inexpensively.

References

Jian Shi¹, Ruihong Zhang², Wei Liao³, Conly L. Hansen⁴, Yebo Li^{1, *} 1. Department of Food, Agricultural, and Biological Engineering, The Ohio State University, 2. Department of Biological and Agricultural Engineering, University of California-Davis. 3. Department of Biosystems and Agricultural Engineering, Michigan State University, 4. Department of Nutrition and Food Sciences, Utah State University, BEEMS Module B7, Anaerobic Digestion, USDA Higher Education Challenger Program, 2009-38411-19761. Contact: Yebo Li, li.851@osu.edu

Frigon and Guiot, 2010, Biofuels, Bioproducts & Biorefining, 4, 447-458.

On-Farm Anaerobic Digester Operator Handbook. M.C. Gould and M.F. Crook. 2010. Modified by D.M. Kirk. January 2010.

Hasan K. Atiyeh, Department of Biosystems and Agricultural Engineering, Oklahoma State University, Syngas Fermentation, BEEMS Module N1, USDA Higher Education Challenger Program, 2009-38411-19761, Contact: Hasan K. Atiyeh, hasan.atiyeh@okstate.edu.

Wilkins and Atiyeh. Current Opinion in Biotechnology 2011, 22:326-330.

Reminder - Complete all of the Lesson 12 tasks!

You have reached the end of Lesson 12! Double-check the Road Map on the Lesson 12 *Overview* page to make sure you have completed all of the activities listed there.

Questions?

If there is anything in the lesson materials that you would like to comment on, or don't quite understand, please post your thoughts and/or questions to our Throughout the Course Questions & Comments discussion forum and/or set up an appointment for office hour. While you are there, feel free to post responses to your classmates if you are able to help.

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C

cellulases

6.3: Enzymatic Biochemistry and Processing

GLOSSARY

S

Sample Word 1 | Sample Definition 1

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