Biofuels – Feasibility of Using Algae Biomass in ABE Process

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Submitted to:
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Abstract

The predominant forms of renewable biofuels consist of bioethanol and biodiesel. Bioethanol is made by fermenting corn while biodiesel is derived from algae. Biobutanol has been identified as being energetically favorable compared to Bioethanol because it is more stable and closely matches the properties of oil. This report determines the feasibility of using algae as a feedstock for the ABE process to create butanol and ethanol.

Authorship

Thomas Butler has researched and written this report.

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Chapter1: Introduction

Oil has been used since 347 A.D. and has been a critical energy resource since the 20th century (Clark, 2011) (Wall, 2013). Ethanol and butanol are renewable replacements to Crude Oil. Ethanol is a chemical primarily used in alcohol as well as a fuel additive for gasoline. Butanol is a chemical originally used as a solvent in a number of industrial chemical processes (Isobutanol, 2013). It is important to find replacements to crude oil because the demand for crude oil has increased over the past decades; there is a question of the availability of oil in the future.

Oil is not a renewable resource and its supply is limited. This is heavily debated but we have not hit peak production for oil, but the speed of production of oil is decreasing (U.S. Energy Information Administration, 2013, International Energy Statistics). When peak production is reached, from that point on, oil will never be produced at the same rate again (Institution of Mechanical Engineering, 2013). Because of peak production, we need other sources of fuel such as butanol and ethanol. Yet current methods of producing ethanol and butanol are not enough, therefore newer methods for producing butanol and ethanol need to be developed. One method that became commercially viable is fermenting cellulosic biomass or corn to produce ethanol (Renewable Fuels Association, 2013).Biomass has the important advantage over oil because it is a renewable resource.

This paper investigates the history of the production of butanol and ethanol from oil or alternatively by fermentation of biomass. This paper also investigates the possibility of using a non-traditional biomass source, namely algae, as an alternate source material.

Chapter 2: Background

2.1 Crude Oil

Crude oil is made by dead organisms buried under the earth exposed to heat and pressure for many years. A hole is drilled to the pocket of oil and is pumped from the ground using an oil well. It is then shipped to a refinery where it is then refined by fractional distillation. Fractional distillation separates crude oil based upon boiling point (Leffler, 1985). As shown in Figure 1, these separate and form fractions which are primarily used for fuel, but some fractions can be used for making chemicals or bitumen (asphalt) for roads and roofs.

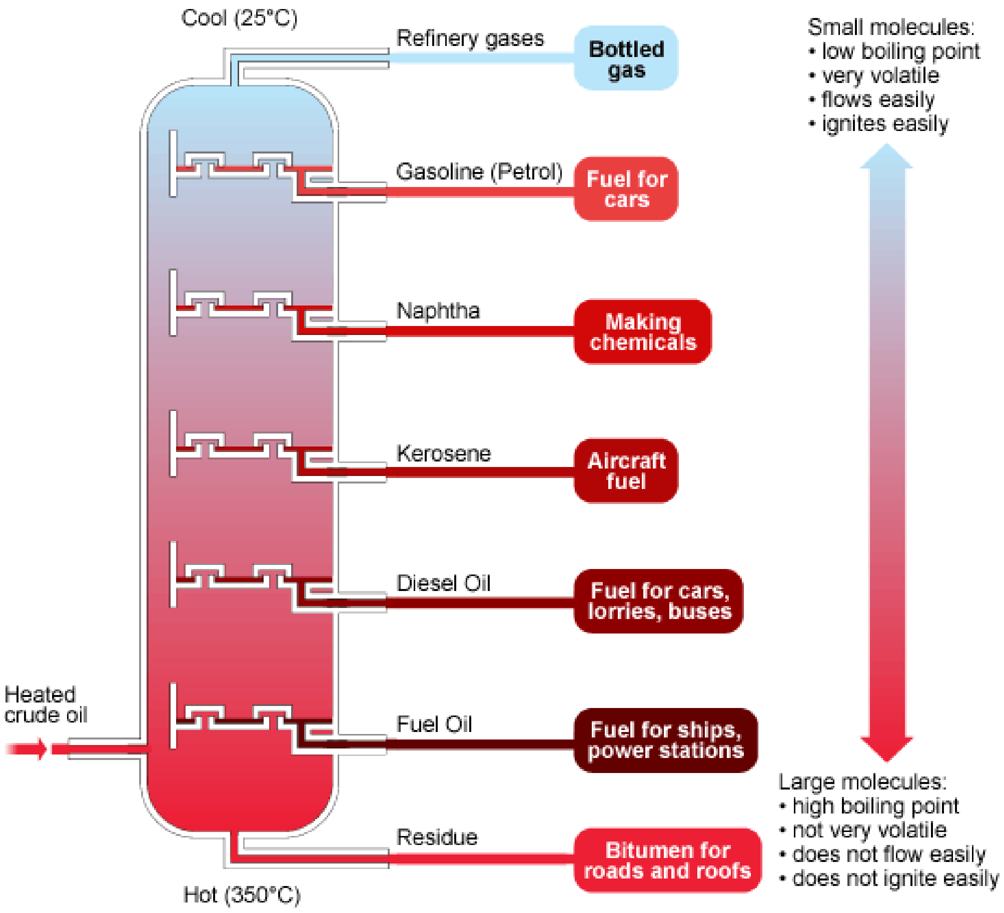


Figure 1: This is a picture of fractional distillation. Crude Oil is heated and separated into different parts via boiling point (BBC, 2013, Fuel from Crude Oil).

These different fractions can then make ethanol or butanol. Ethanol is made in multiple steps. First the fractions undergo cracking. Cracking is a process where larger hydrocarbons are broken down into alkanes, such as ethene (C_2H_4) and propene (C_3H_6). Cracking can be done by using heat alone or a catalyst with heat, however the larger the hydrocarbon the more energy required to break the hydrocarbon down. This means that the higher the boiling point of the fraction, the more energy required to crack it. After the hydrocarbons are cracked into ethene they are made into ethanol by high temperature, high pressure, and a catalyst of phosphoric acid. Figure 2 outlines the equation for converting ethene and steam into ethanol.

$$\text{Ethene + steam} \xrightarrow{\text{High Temperature, High Pressure}} \text{ethanol}$$

$$C_2H_4 + H_2O \xrightarrow{\text{High Temperature, High Pressure}} C_2H_5OH$$

Figure 2: This is the equation for making ethanol from ethene. (BBC, 2013, Polymers and ethanol from oil).

Butanol can be produced from any of the products in Figure 1 by hydrogenating butyraldehyde with a catalyst to form isobutanol and 1-butanol, different conformations of butanol (Figure 3). It is then purified to separate out the different conformations of butanol (Hernandez, 2001).

$$\text{Butyraldehyde +Hydrogen} \xrightarrow{\text{Catalyst}} \text{Butanol}$$

$$CH_3CH_2CH_2CHO + H_2 \xrightarrow{\text{Catalyst}} C_4H_9OH$$

Figure 3: This is the equation to make Butanol from Butyraldehyde

2.2 Biomass

Biomass is a biological material which is made from living or recently living material. Biomass is most often made from plants, but can be also made from animals or vegetables. Plant biomass typically is made from three different plant sources: virgin wood, energy crop and agricultural residues. **Virgin wood** is wood from the forest transported and burned for energy, it requires no processing. **Energy crop** is a crop grown in the most energy efficient manner to then harvested and either burned or turned into a fuel and then burned. Some examples of energy crops are vegetables which are turned into vegetable oil, which is then turned into biodiesel and sugar or starch which is fermented into bioethanol. **Agricultural residue** includes a wide variety of different sources, these are: arable crop residue (ex: straw, husks), animal manure, animal bedding, and unused/unwanted organic material. These can be dried and burned for energy. These can be dried by passive or active drying. Passive drying is done by leaving the biomass out in a low moisture environment over an extended period of time. Active drying is done by leaving in an area with unnaturally low moisture content in the air. It is preferable that there is good air circulation and the system is powered with solar power to reduce energy costs.

The most common energy sources inside of plant biomass are sucrose, starch, and lignocellulose. All of these are different parts found in plants and feed the bacteria creating the fuel. Sucrose and starches are just sugars. Sucrose is a disaccharide consisting of glucose and fructose while starch is a complex carbohydrate, a polysaccharide consisting of multiple glucose. Lignocellulose is the woody cell wall parts of a plant cell, made primarily of cellulose and lignin.

Normally using sugars, starches, and cellulose from plant biomass is not optimal because these are made for human/animal consumption. An alternative option is to use algae. Algae are also considered a biomass and its advantage is that it doesn’t compete with the food of our eco system like plant biomass. Besides if we keep using livestock feed to power us there will be less bacon and steaks for the human race.

2.3 Carbon Costs and Carbon Neutrality

The equation for carbon cost of a fuel's lifecycle is shown below in Figure 4. $CO_{2Emission}$ is the amount of carbon that is released when the fuel is burned. $CO_{2\ make}$ is the amount of carbon that is released or taken back when the fuel is completed. If the CO_{2Cost} is 0 then carbon neutrality is achieved. Carbon neutrality is important because high carbon costs negatively affect the atmosphere.

$$CO_{2Cost} = CO_{2E} + CO_{2\ make}$$

Figure 4: This is the equation to determine carbon cost during the lifecycle of a fuel.

For example the carbon cost for crude oil, is high because it is drilled from the ground, processed, and then burned. This converts carbon (oil) sequestered in the ground to CO_2 gas, which enters the atmosphere as a greenhouse gas. There is no carbon neutrality in this case because it always generates high amounts of CO_2. On the other hand, fermentation of plant biomass approaches carbon neutrality because plant materials capture the CO_2 in our atmosphere. As they are converted to butanol and ethanol, which are eventually burned, they release the CO_2 back into the atmosphere. The CO_2 essentially is captured and released so there is carbon neutrality and no net gain to the carbon costs. The plant biomass is made into fuel by fermenting the biomass by the Acetone-Butanol-Ethanol Process or ABE Process.

2.4 ABE Process

The Acetone-Butanol-Ethanol (or ABE) Process was created by Charles Weizmann (Weizmann, 1919). The process uses biological material to create acetone, ethanol, and butanol at a ratio of 30%, 60%, and 10%, respectively. The ABE Process involves fermenting sterilized biological material with *Clostridium acetobutylicum* at 35-36^{0}C for 58 hours, 5-10 hours of waiting for fermentation to begin and 48 hours for fermentation to end. The mixture is then distilled via fractal distillation (Weizmann, 1919) (ATCC, 2012, *Clostridium acetobutylicum* McCoy et al. emend. Keis et al. (ATCC® 824™)).

Some of the basic materials and equipment needed for the ABE process are:

- *Clostridium acetobutylicum* bacteria,
- Feedstock materials,
- Fermentation Reactor (to convert the sugars/starches to the ABE),
- Membrane separation equipment (to separate out the reacted and unreacted products after fermentation),
- Distillation equipment (to separate out acetone, butanol, and ethanol).

Chapter 3: Companies

There are several companies that are currently involved in butanol production.

Butamax is developing biobutanol by converting sugars into isobutanol using proprietary recombinant microorganisms and key enzymes. The plan is to develop biobutanol at a competitive price to ethanol. They are based in Wilmington, Delaware. This company is a joint effort between BP and DuPont.

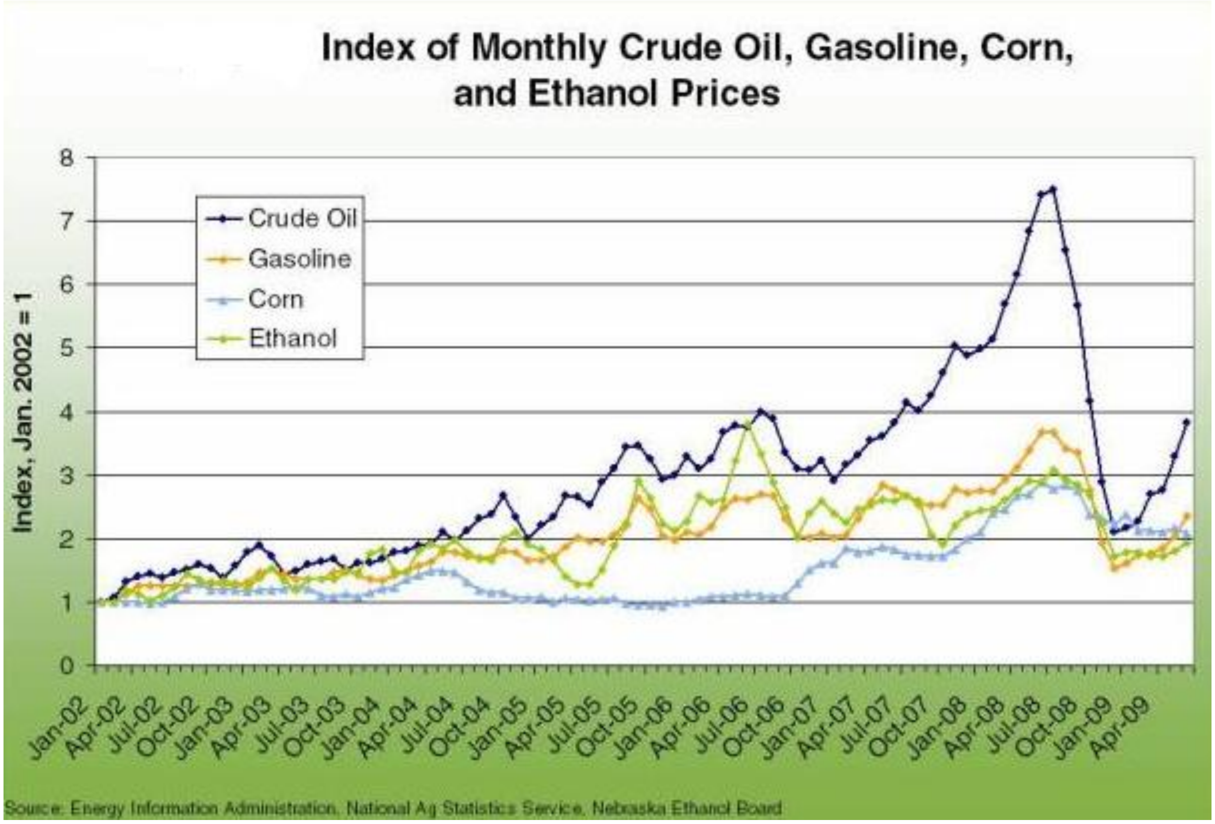
Gevo has developed a method to modify existing ethanol plants to produce isobutanol. They are using a proprietary yeast catalyst to convert sugar into isobutanol.

Green Biologics is making biobutanol from renewable feedstock using better strains of *Clostridia* and modified fermentation methods to optimize production. They are based in Abingdon, Oxfordshire, UK.

Chapter 4: Feasibility Study

4.1 Ethanol from Oil and Plant Biomass

First, we have to look at the current plant biomass to ethanol compared to oil. Corn is one of the major sources for plant biomass. Corn ethanol will only be examined here. Currently the ethanol market fluctuates and follows the price line for gasoline pretty closely as seen below in Figure 5.


Index of Monthly Crude Oil, Gasoline, Corn, and Ethanol Prices

Source: Energy Information Administration, National Ag Statistics Service, Nebraska Ethanol Board

Figure 5: This is a picture of monthly prices for Crude Oil, Gasoline, Corn and Ethanol (Wisner, 2009).

This means that we can determine that ethanol prices will follow gasoline prices and therefore will also follow crude oil prices. There is another factor to consider, since corn has other markets, namely food for humans and livestock, the price of corn will not follow the gasoline prices. So in order to determine if it is economically feasible to use corn to produce ethanol, to factors have to be considered, the price of oil, the price of corn and repaying debt (upfront costs), this is done below in Figure 6.

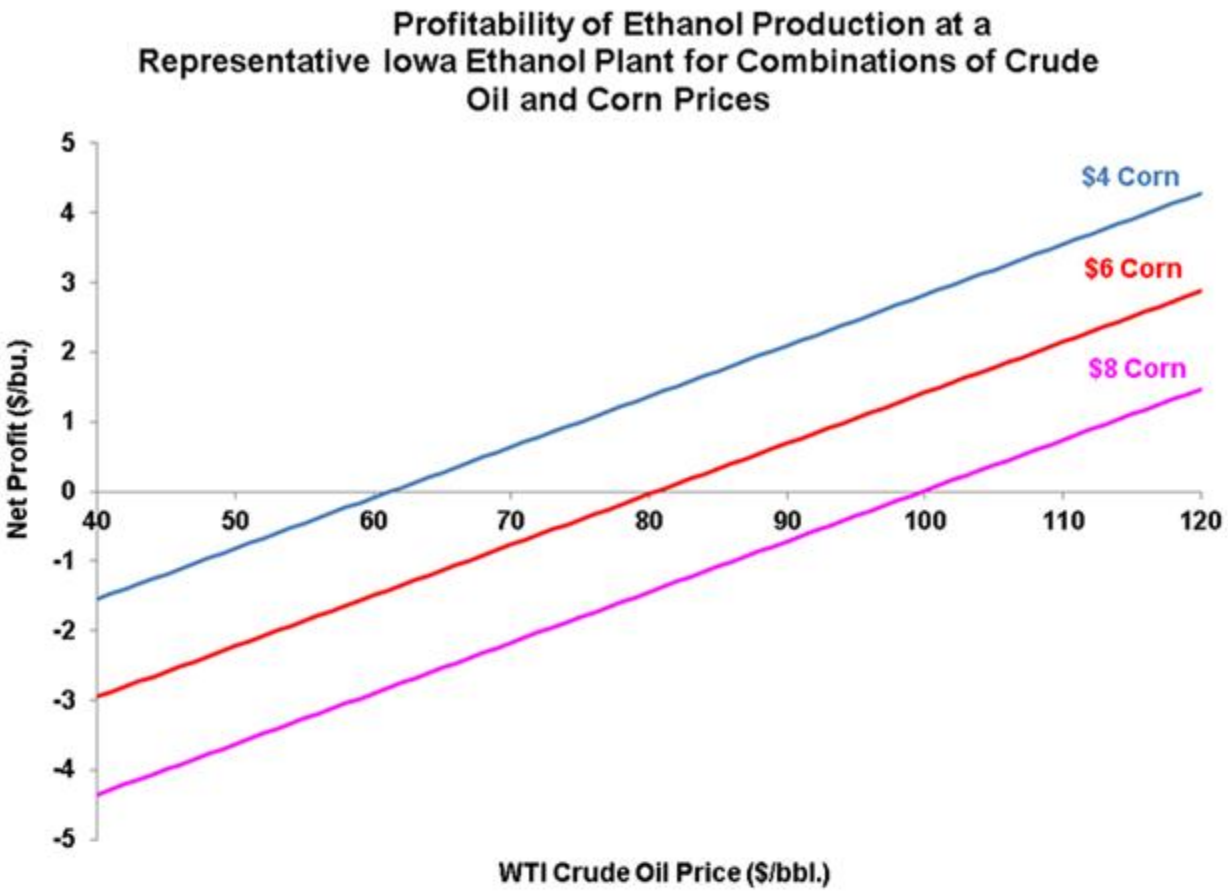


Figure 6: This is a picture of the profitability of corn ethanol at certain prices of corn per bushel to crude oil per barrel (Irwin, 2012).

As of 5/26/13 the price of a barrel of oil according to the WTI index is $93.87 and has stayed around that price since 2009 (WTI index, 2013). As of 5/26/13 the price of corn is $7.61 per bushel. This price point has some seasonal changes but has averaged out to this price since February 2011 (CME Group, 2013). This means that at current prices, this factory is sustaining a small loss. Figure 6 shows if a bushel of corn is $7.61 then the price of crude oil must be above $96.10 to make a profit.

This market is heavily dependent on the price of corn which is not in control of the industry since there are other competing interests. Currently it does not seem like this is an economically viable method to make ethanol unless the price of corn decreases or the price of oil increases.

4.2 Butanol from Oil and Plant Biomass

Using corn as feed stock for the ABE process, butanol can be produced at 1.50 gallons of butanol per bushel of corn (Wu, 2007). Currently butanol for laboratory supplies is priced at $134 per 4 liters or $126.81 per gallon (Fisher Scientific, 2013). This seems overpriced and it will be assumed that butanol can be priced at the price of crude oil. This price is $93.87 per barrel or $2.68 per gallon (WTI index, 2013). This means an estimate of using the ABE process to produce butanol from corn requires that corn be under $4.02 per bushel to break even.

This is not economically feasible, as stated above the price of corn has been around $7.61 per bushel since February 2011 (CME Group, 2013). This means unless the ABE process is improved or the price of butanol is above $5.07 per gallon, this is not a viable way to produce butanol. This estimate doesn’t include CO_2 sequestration or the upfront costs/loans.

4.3 Butanol from Algae Biomass

It is possible using algae as a feedstock for ABE process. The waste generated from algal biofuel plants can be used as the feedstock so there is not purchasing cost. Typically, algae of the genus Chlorella, Protococus, and Pleurococus, are used. Since they are single-celled, they double in mass every day with proper sunlight and $CO_{2,}$. In fact, each tank needs 1500 pounds of CO_2 daily, which is $75 a day in CO_2 sequestration according to the U.S. Department of Energy. This method produces about 6 gallons of butanol per each tank for each sunny day or for each ~1000 pounds of algae. If butanol is assumed to be $2.68 per gallon then this means the profit is roughly $16 per day from butanol, which doesn't include the carbon credits for eliminating CO_2 from the atmosphere. We estimate that the operating costs should be similar to these.

4.4 Feasibility and Problems of Ethanol/Butanol in Gas for Cars

Ethanol is currently be used as an additive to gasoline, it is put in at 10% or E10. E15 or 15% ethanol 85% gas can also be used by light duty vehicles that have a model year greater than 2001 (U.S. Energy Information Administration, 2013, How much ethanol is in gasoline and how does it affect fuel economy?). E85 or 51-83% ethanol in gasoline also exists, although a modified engine is required to use E85. Ethanol also holds less energy than gasoline so there is a decrease in gas mileage when using this fuel. It is however a higher octane fuel so there is an increase vehicle power and performance (U.S. Department of Energy, 2013). Ethanol absorbs water, which can be a problem because it can cause ethanol/gas mixtures to and if left untreated can cause corrosion to the car or clog parts of the engine (USA Fuel Service LLC, 2013).

Butanol can currently be blended into diesel at 40% and gasoline at 20% (Green Biologics, 2012, Biofuels). It is a much better choice for blending than ethanol, especially since it has a higher energy value than ethanol which is much closer to gasoline. Ethanol has an energy value of 76,100 BTU/Gal. Butanol has an energy value of 110,000 BTU/Gal. Gasoline has an energy value of 114,000 BTU/Gal (Green Biologics, 2012, biobutanol - fuel grade).

This only requires the upfront cost of building a factory to produce butanol. It seems that butanol is only a few years off from becoming a replacement for ethanol in gasoline.

4.5 Carbon Footprint of Biofuels

In the USA, carbon emissions are regulated and are required to be reduced by the government (Mathews, 2008). California is following a stricter base than the rest of the national requirements. Below is information on their plan to reduce CO_2 emissions (Table 1) and data on CO_2 emissions from other fuels (Table 2). This shows that all biofuels aren't carbon neutral; in fact often at best they are carbon neutral. However, there are carbon-negative biofuels, which reduce the amount of CO_2 in the atmosphere via CO_2 sequestration (Mathews, 2008). The only method to make carbon-negative biofuels is through CO_2 sequestration. Butanol does release more CO_2 than ethanol. This is obvious if one looks at the chemical formulas, Butanol is C_4H_9OH and ethanol is C_2H_5OH. This means if butanol is completely combusted, it releases 4 CO_2 molecules where as ethanol only releases 2. Unfortunately, there isn't enough data to determine which biomass is the best for carbon sequestration.

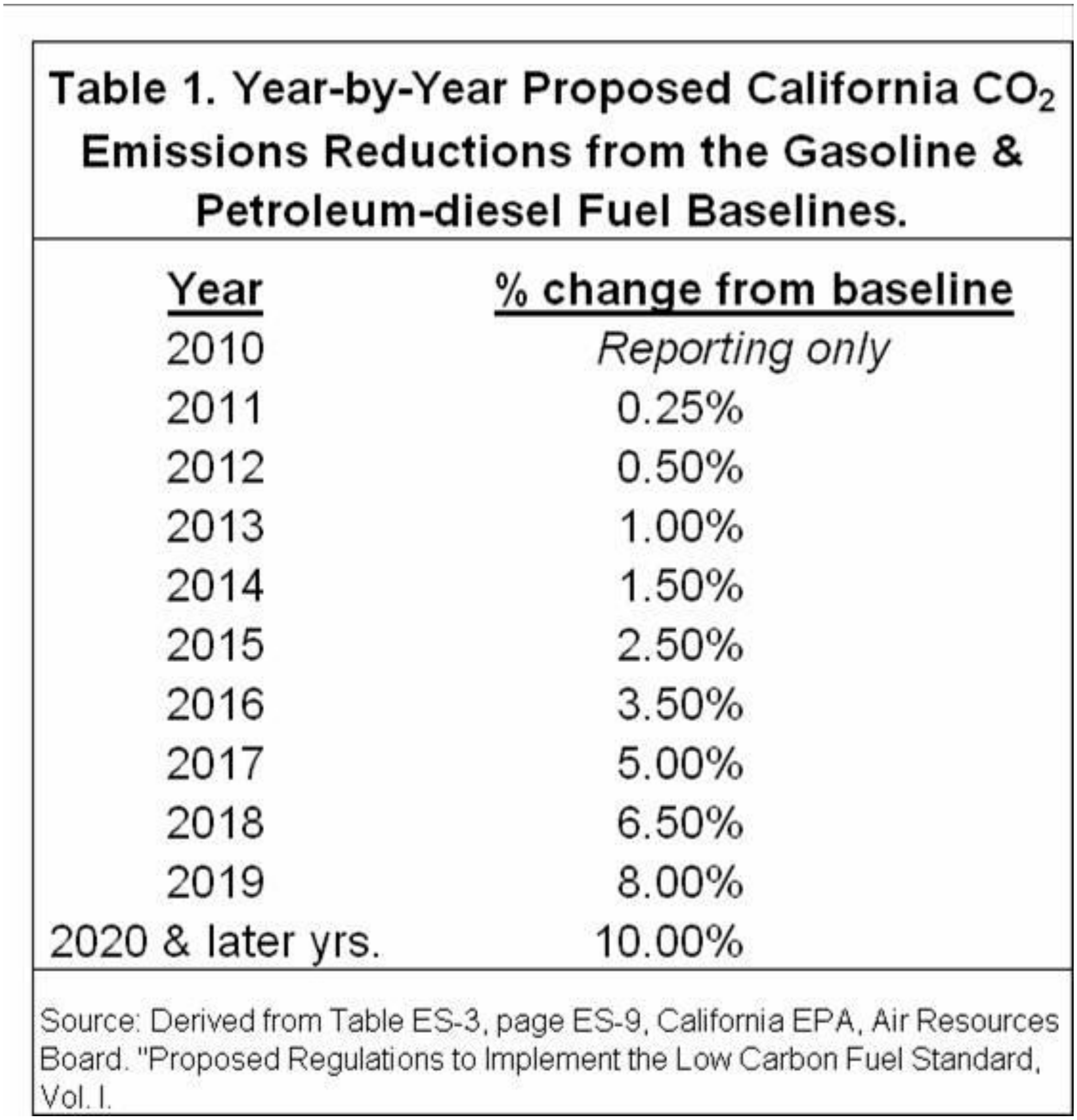


Table 1. Year-by-Year Proposed California CO_2 Emissions Reductions from the Gasoline & Petroleum-diesel Fuel Baselines.

Year	% change from baseline
2010	*Reporting only*
2011	0.25%
2012	0.50%
2013	1.00%
2014	1.50%
2015	2.50%
2016	3.50%
2017	5.00%
2018	6.50%
2019	8.00%
2020 & later yrs.	10.00%

Source: Derived from Table ES-3, page ES-9, California EPA, Air Resources Board. "Proposed Regulations to Implement the Low Carbon Fuel Standard, Vol. I.

Table 1: This is California's Plan to reduce CO_2 emissions by 2020 (Wisner, 2009, biofuels and greenhouse gas emissions…).

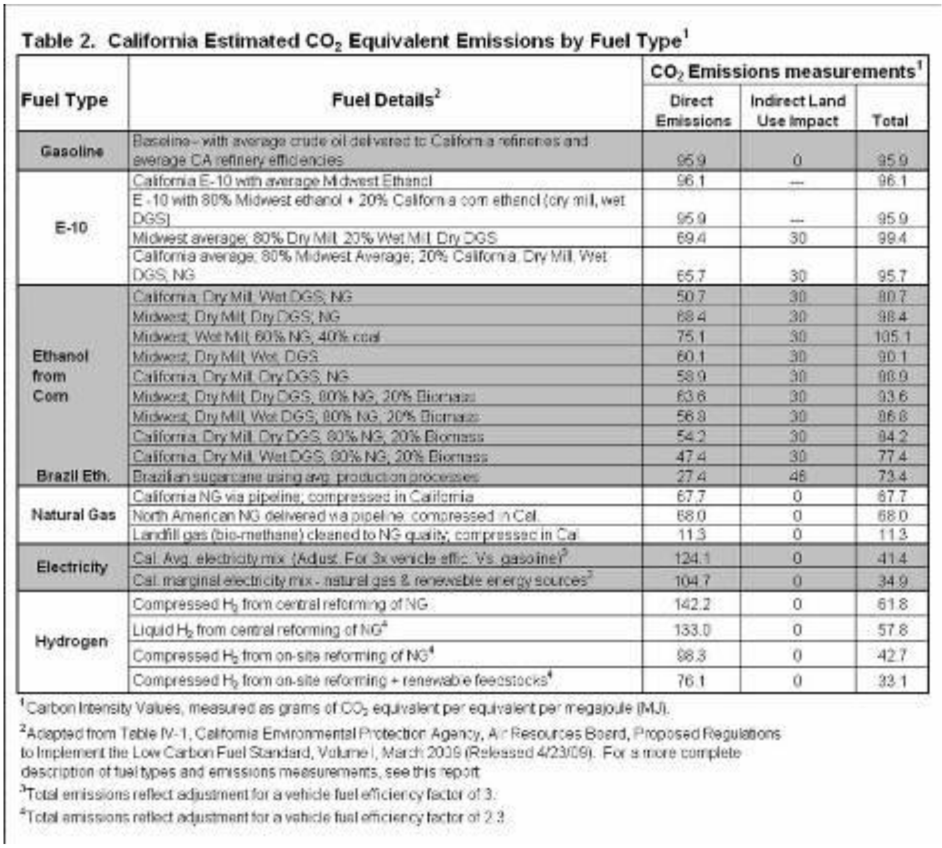


Table 2. California Estimated CO_2 Equivalent Emissions by Fuel Type[1]

Fuel Type	Fuel Details[2]	CO_2 Emissions measurements[1]		
		Direct Emissions	Indirect Land Use Impact	Total
Gasoline	Baseline - with average crude oil delivered to California refineries and average CA refinery efficiencies	95.9	0	95.9
E-10	California E-10 with average Midwest Ethanol	96.1	---	96.1
	E-10 with 80% Midwest ethanol + 20% California corn ethanol (dry mill, wet DGS)	95.9	---	95.9
	Midwest average; 80% Dry Mill; 20% Wet Mill; Dry DGS	69.4	30	99.4
	California average; 80% Midwest Average; 20% California; Dry Mill; Wet DGS; NG	65.7	30	95.7
Ethanol from Corn	California; Dry Mill; Wet DGS; NG	50.7	30	80.7
	Midwest; Dry Mill; Dry DGS; NG	68.4	30	98.4
	Midwest; Wet Mill; 60% NG; 40% coal	75.1	30	105.1
	Midwest; Dry Mill; Wet; DGS	60.1	30	90.1
	California; Dry Mill; Dry DGS; NG	58.9	30	88.9
	Midwest; Dry Mill; Dry DGS; 80% NG; 20% Biomass	63.6	30	93.6
	Midwest; Dry Mill; Wet DGS; 80% NG; 20% Biomass	56.8	30	86.8
	California; Dry Mill; Dry DGS; 80% NG; 20% Biomass	54.2	30	84.2
	California; Dry Mill; Wet DGS; 80% NG; 20% Biomass	47.4	30	77.4
Brazil Eth.	Brazilian sugarcane using avg. production processes	27.4	46	73.4
Natural Gas	California NG via pipeline; compressed in California	67.7	0	67.7
	North American NG delivered via pipeline; compressed in Cal.	68.0	0	68.0
	Landfill gas (bio-methane) cleaned to NG quality; compressed in Cal.	11.3	0	11.3
Electricity	Cal. Avg. electricity mix (Adjust. For 3x vehicle effic. Vs. gasoline)[3]	124.1	0	41.4
	Cal. marginal electricity mix - natural gas & renewable energy sources[3]	104.7	0	34.9
Hydrogen	Compressed H_2 from central reforming of NG	142.2	0	61.8
	Liquid H_2 from central reforming of NG[4]	133.0	0	57.8
	Compressed H_2 from on-site reforming of NG[4]	98.3	0	42.7
	Compressed H_2 from on-site reforming + renewable feedstocks[4]	76.1	0	33.1

[1] Carbon Intensity Values, measured as grams of CO_2 equivalent per equivalent per megajoule (MJ).

[2] Adapted from Table IV-1, California Environmental Protection Agency, Air Resources Board, Proposed Regulations to Implement the Low Carbon Fuel Standard, Volume I, March 2009 (Released 4/23/09). For a more complete description of fuel types and emissions measurements, see this report.

[3] Total emissions reflect adjustment for a vehicle fuel efficiency factor of 3.

[4] Total emissions reflect adjustment for a vehicle fuel efficiency factor of 2.3.

Table 2. This is California's estimation of which fuels have a CO_2 equivalent emissions compared to their current crude oil (Wisner, 2009, biofuels and greenhouse gas emissions…).

4.6 Algal Biofuels

Algae holds oil that can be squeezed out. This can be done by mechanical or chemical methods. These are often combined. For mechanical extraction there are two methods. The first mechanical method is an expeller press. First the algae is dried and then squeezed with an oil press. This can be with a screw, piston, etc; each strain of algae is different and different pressing applicators work better than others. The second mechanical method is ultrasonic-assisted extraction. This is where ultrasonic waves create cavitation bubbles which collapse near algae and break open the cell walls (Oilgae, 2013, Extraction of Algal Oil by Mechanical Methods). There are three different methods for chemical extraction. The first chemical method is hexane solvent method.

This is typically done after expeller pressing the algae. Hexane, Benzene or ether can be used to dissolve the algae oil into it. The pulp is filtered out and the solution is distilled. The second chemical method is soxhlet extraction. This method uses repeated washes in hexane or petroleum ether. The pulp is filtered out and the solution is distilled. The third chemical method is Supercritical Fluid Extraction. This method liquefies CO_2 by pressure and temperature to where CO_2 behaves like a liquid and gas. This is then used as a solvent to extract the oil (Oilgae, 2013, Extraction of Algal Oil by Chemical Methods).

Chapter 5: Implementation of Algae pulp to ABE process

Algae have had their oil harvested to be used as a biofuel and then the pulp that is taken out from the process is seen as waste. Why can't this waste be used to feed the ABE process? It is possible to use algae as a biomass which can be fed into the ABE process to produce butanol/ethanol. *Clostridium acetobutylicum* digests high sugar, starch, cellulose and lignin (Minton, 2013). Unfortunately not all of the algae waste will be useable since algae cell walls are not all made of cellulose or lignin so only certain algae strains will be ideal with this model (Sengbusch, 2004).

The algae waste can be placed as feedstock for *Clostridium acetobutylicum* at 36°C to be fermented for an undetermined about of time, shouldn't be longer than 1 week, but experimentation needs to be done to determine the time where *Clostridium acetobutylicum* stops creating butanol and ethanol. Then, the algae + *Clostridium acetobutylicum* mixture can be distilled and separated by fractal distillation.

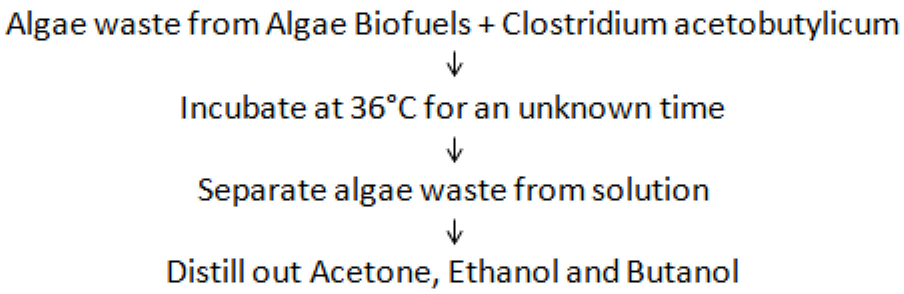


Figure 7: Plan to use the ABE process to make fuel from algae “waste.”

Chapter 6: Conclusion

There are two major benefits to using biomass over oil as a means for producing butanol and ethanol. Biomass is renewable and has a lower carbon cost than oil (possibly carbon negative depending on the method used to make the biomass). The traditional means for producing butanol and ethanol is using plant biomass and the ABE Fermentation process. However, by using algae biomass as a feed source in the ABE Fermentation process, you can have additional benefits. Most notably is that algae does not compete with sources for plant biomass (such as sugars and starches used by humans or animals) and that it is easier and faster to grow.

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