David Consiglio[1]

Biofuels, fossil energy ratio, and the future of energy production

[1] Southfield High School for the Arts and Technology, Southfield, MI 48033, USA, E-mail: davecons@gmail.com

Abstract:
Two hundred years ago, much of humanity's energy came from burning wood. As energy needs outstripped supplies, we began to burn fossil fuels. This transition allowed our civilization to modernize rapidly, but it came with heavy costs including climate change. Today, scientists and engineers are taking another look at *biofuels* as a source of energy to fuel our ever-increasing consumption.

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1 Introduction

If you turn on the news or read about current events, you will likely find many stories about climate change. Most of them read the same way:

> The world faces a crisis. Climate change is altering our planet in numerous and highly undesirable ways. Farmland is turning to desert, sea levels are rising, corals are bleaching, and storms may increase in severity and number. The main culprit is carbon dioxide that spews from our power plants and cars when they burn fossil fuels. The problems our planet faces will only worsen … that is, unless we do something to stop it.

So why don't we? Why don't we just stop polluting and reverse climate change?

In this chapter, you will learn about the basic chemistry and synthesis of biofuels, an alternative to fossil fuels. In addition, we will introduce the *fossil energy ratio*, or FER, a concept that makes it easier to understand alternative fuels and can point the way to improvements that can help make alternative energy a reality.

1.1 What are biofuels?

Biofuels were humanity's first supply of energy outside of our bodies. Beginning several hundred thousand years ago [1], humanity began to control and use fire. This innovation allowed humans to transform their world and way of living in ways no other animal ever had. Humans used fire to repel predators, drive prey, and stay warm. Over time, humans used fire to clear fields for planting, create metal from ore, and build our modern civilization.

Throughout this entire time period, humans burned *biofuels*. A biofuel is simply any organically-derived substance that can be burned to produce energy. The most commonly known biofuel is wood, but humans around the planet have used all sorts of biofuels, including animal dung, animal fat, and grasses.

But, biofuels had shortcomings. They were not always readily available. Furthermore, as civilization progressed toward industrialization, more and more fuel was needed to drive the machinery of modern life. Whole regions were deforested in the quest to provide biofuels for our growing industry.

1.2 The transition to fossil fuels

Around 200 years ago, humans started shifting from burning biofuels to burning *fossil fuels*. Fossil fuels are ancient biofuels that have been fossilized. The fossil fuels in use today are coal (primarily fossilized trees), oil (primarily fossilized microscopic sea creatures), and natural gas (primarily the gas formed by the partial

David Consiglio is the corresponding author.

decomposition of many organic materials). As industry grew, fossil fuels took on a greater role; today they account for over 80 % of energy production [2].

For decades, fossil fuels powered the industrialization of the world, but fossil fuels are not without problems. Most of the easily obtained fossil fuels are gone – they were the first to be mined and drilled for. More pressingly, the fossilized carbon in these fuels stored has been released into the atmosphere, significantly increasing the amount of carbon dioxide in our air. Direct measurements of CO_2 levels in the air have been measured directly since the 1950s, when levels were around 315 ppm. At the time of this writing, they are just over 400 ppm and steadily rising [3]. Higher CO_2 levels result in an increase in global temperatures [4].

The effects of this warming have, until recently, been relatively minor. But, as CO_2 levels have increased more dramatically, worrying changes have started happening. Land ice is melting at higher rates, leading to rising sea levels [5]. Storms and severe weather have increased in frequency and intensity [6]. CO_2 concentration in the oceans is rising, leading to ocean acidification and the destabilization of coral reef ecosystems [7].

These effects could get significantly worse: sea level rise alone could result in the forced relocation of nearly a billion people [8]. Scientists are looking for ways to reduce the rate of CO_2 emission and reduce, if not fully reverse, the effects of climate change brought about by the industrial age.

In my first year high school chemistry course, students participate in a project entitled “Saving Miami” [9]. The premise is simple: if humanity continues to burn fossil fuels at projected rates, sea level rise will submerge much of the greater Miami area – millions of people will lose their homes. Students choose from one of seven hypothetical “solutions” that sequester carbon dioxide. Stoichiometry plays a central role in the project as students have to perform multiple conversions to calculate the costs, land use, and time required to “save” Miami using each of these solutions. The project does not have a correct answer. Instead, students have to make value judgments to justify their choice. Additionally, students work extensively with scientific notation in order to handle the enormous numbers associated with carbon dioxide emission. Students write a scientific paper, present their work, and participate in interviews to demonstrate their mastery of the content. Along the way, they gain a new understanding of the vast scale of the problem that climate change poses to our planet.

1.3 Fossil carbon versus atmospheric carbon

After 200 years of decreasing importance, biofuels have emerged as a possible weapon in the fight against climate change. But how do biofuels work, and how can they reduce CO_2 emissions?

All combustion, whether of a fossil fuel or biofuel, proceeds via the following basic formula:

$$C_xH_yO_z + O_2 \Rightarrow CO_2 + H_2O$$

In this equation, $C_xH_yO_z$ represents any organic molecule. As you can see, CO_2 is produced regardless of the fuel being burned. So how can biofuels *reduce* CO_2 emissions?

All fuels derive their carbon from photosynthesis. In other words, the carbon in wood, coal, even animal dung, was once in the air. Plants absorbed carbon dioxide from the air and turned it into complex organic molecules. In some cases, animals ate these plants and further transformed the carbon-containing molecules.

Under most circumstances, this carbon would return to the air when the plant or animal died and decayed. So when we burn a biofuel, the carbon that is released was, until very recently, already in the air. If we burned nothing but biofuels, the amount of CO_2 in the air would remain relatively constant – plants would absorb CO_2 through photosynthesis, and we would return that CO_2 to the air through combustion.

But when we burn a fossil fuel, the CO_2 that is released was removed from the air millions of years ago. Ancient plants and animals were sometimes buried underground and fossilized. This removed the carbon from the atmosphere. When we burn a fossil fuel, this ancient CO_2 is returned to the air.

This is why biofuels have taken on renewed interest – they can be burned without significantly contributing to atmospheric CO_2 levels. But how are biofuels produced, and how can they replace existing fossil fuels?

2 Solid biofuels

Solid biofuels are used in a similar way to solid fossil fuels. Wood, grass, farm, or forestry wastes are typically burned as they are. This can be done in facilities similar to coal plants, and, in most cases, existing coal plants can be modified to allow the use of solid biofuels [10].

In some cases, solid biofuels must be processed before they are burned. The most common kind of processing is known as *densifying*, which refers to the process of compressing particulate biomass (such as sawdust) into logs or pellets for easier transportation and burning. Densified biomass is often bound using tree sap or other forestry waste – in this way, an additional waste product can be burned, increasing the energy output of a solid biofuel.

3 Liquid biofuels

Unlike solid biofuels, the chemistry of liquid biofuels is complex and varied. Liquid fuels are used almost exclusively for transportation, but unlike coal and natural gas power plants, gasoline and diesel engines are far less flexible in terms of the fuels they can burn [11]. In order to replace fossil fuels in cars and trucks, liquid biofuels must closely mimic gasoline or diesel fuel.

3.1 Gasoline substitutes

There are several liquid fuels that can stand in for petroleum-derived gasoline, but by far the most common is *ethanol*. Ethanol, the kind of alcohol that humans drink, is generally produced via fermentation of grain. This process is very similar to the production of alcohol for drinking and follows these basic steps:

1. Grain is harvested and processed to remove non-fermentable material like stalks and leaves.
2. The grain is ground into a powder.
3. Enzymes are added to break down complex sugars and starches to form simple sugars.
4. Yeast and water are added.
5. The yeast ferments the sugar in the grain to form alcohol via the following equation:

$$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$$
$$\text{Glucose} \rightarrow \text{Ethanol} + \text{Carbon Dioxide}$$

1. The resulting mixture, known as *industrial beer*, is distilled to remove most of the water.
2. The remaining water is removed using molecular sieves.
3. The ethanol is denatured, typically with gasoline, to render it undrinkable.
4. The CO_2 is captured and used for carbonating beverages.
5. The solid by-product is sold to farmers as animal feed.

In the United States, all gasoline engines must be capable of burning a gasoline mixture containing a small percentage of ethanol [12]. In recent years, FlexFuel vehicles have been produced that can burn up to 85 % ethanol. In some countries, 100 % ethanol vehicles have been manufactured.

3.2 Diesel substitutes

Diesel fuel substitute, known as *biodiesel*, is derived primarily from vegetable oil, but can be made from any oil or fat source, including used cooking oil. The most common process by which vegetable oil is transformed into biodiesel is known as *transesterification*. Vegetable oil consists of three long, fatty-acid chains connected to a glycerol backbone. In transesterification, these three fatty-acid chains are chemically removed and converted into methyl esters as shown in Figure 1.

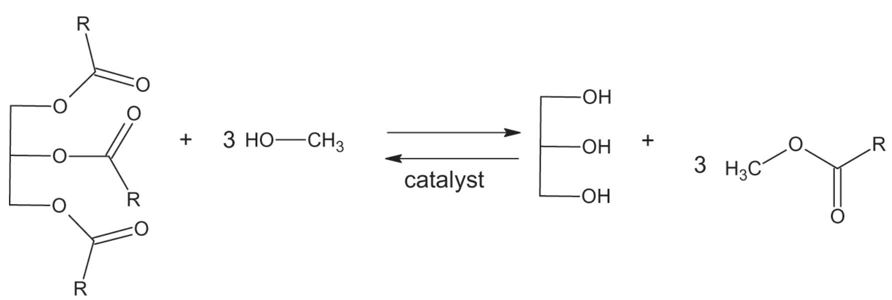

Figure 1: Transesterification.

The catalyst for this reaction is typically sodium or potassium hydroxide.

Biodiesel is very similar to petroleum-derived diesel fuel and the two fuels can be mixed in any ratio [13]. There are, however, two important differences regarding biodiesel:

1. Biodiesel is an excellent solvent that is capable of dissolving some fuel lines. Any vehicle that uses biodiesel must use fuel lines that are insoluble in biodiesel.
2. Biodiesel has a higher *cloud point* than petroleum-derived diesel [14]. Cloud point refers to the temperature at which the liquid becomes cloudy. At temperatures below the cloud point, biodiesel can become too viscous to flow easily into the engine. As a result, biodiesel is easier to use in warmer climates.

4 Gaseous biofuels

Many organic materials can be converted into methane using either chemical or biological processes [10]. This methane is often impure, containing significant quantities of carbon dioxide and other gases. This impure mixture can be burned as a lower-quality fuel, or purified and used in the existing natural gas infrastructure. In addition, other flammable gases can be produced from organic materials.

4.1 Biomethane and methane substitutes

Currently, there are two technologies that can be used to produce gaseous biofuels from solid or liquid biomass – digestion and gasification.

Digestion refers to the decomposition of solid or liquid biomass resulting in the production of methane. This process typically proceeds as follows:

$$C_{2x}H_yO_z \rightarrow xCO_2 + xCH_4$$

As you can see, this process does produce some CO_2 as a by-product, which reduces its impact on climate change.

Digestion is typically accomplished using anaerobic microorganisms that consume biomass and produce methane as a waste product. This process takes place at many landfills today, and in some cases the methane produced is used for power or heat generation.

Gasification involves drying and heating solid biomass to drive off water, and then hydrogen and oxygen, to make solid carbon called *char*. This char then reacts with water:

$$C + H_2O \rightarrow CO + H_2$$

This mixture of carbon monoxide and hydrogen gas is called *syngas* and can be burned in industrial power plants [15]. Syngas has a significant downside – carbon monoxide is highly toxic and must be used with extreme caution. It is not suitable for in-home use. Alternatively, the CO can be reacted with extra water to produce methane:

$$4CO + 2H_2O \rightleftharpoons CH_4 + 3CO_2$$

via a multistep process:

$$\begin{array}{rcl} CO + 3H_2 & \rightarrow & CH_4 + H_2O \\ +\ 3CO + 3H_2O & \rightarrow & 3CO_2 + 3H_2 \\ \hline 4CO + 2H_2O & \rightarrow & CH_4 + 3CO_2 \end{array}$$

In my high school AP Chemistry course, I use these reactions as an example of an industrially important reversible reaction that takes place in multiple steps. The equilibrium constant of the overall reaction is the product of the equilibrium constants of the component reactions. In this case, the overall reaction is highly desirable but has a low equilibrium constant. Students use this information to design reaction conditions that maximize the yield of the desired product, in this case methane.

5 Fuel energy ratio

Every biofuel has a *fuel energy ratio*. This is simply the amount of energy a fuel produces divided by the amount of fossil energy it took to make that fuel:

$$FER = \frac{E_{out}}{E_{in}}$$

If a fuel has a high FER, then that fuel takes very little fossil fuel to make a large amount of energy. In contrast, fuels with a low FER take more fossil fuel energy to make, and produce less energy. Even fossil fuels have an FER – it takes fossil fuel energy to extract fossil fuel energy from the ground.

Clearly, a high value of FER is desirable in a fuel. But, how are energy output and energy input calculated?

5.1 Energy output

Calculating the energy output of a fuel is a simple matter of burning a unit of the fuel and measuring the energy given off by that fuel. This can be done via *calorimetry*. In this process, fuel is combusted with pure oxygen in a device known as a bomb calorimeter. The bomb portion of the calorimeter is submerged in water. After the fuel is burned, the temperature of the water will increase, as will the temperature of the calorimeter itself. Calculating the energy released by the fuel (ΔH) is then the simple matter of multiplying the change in temperature (ΔT) by the heat capacity of the calorimeter/water combination (C_v):

$$\Delta H = C_v \Delta T$$

The heat can then be divided by the amount of fuel that was burned, which gives the *heat of combustion* (ΔH_c). Scientists will typically calculate this value in kJ/mol, but industrially the units tend to be more practical and specific to the country in question. For example, the U.S. Government uses Btu/gal to measure energy output from liquid fuels.

In the end, the units do not matter so long as we are consistent: FER is a unitless quantity and FER values for different fuels can be directly compared.

Some scientists include the energy output values for co-products and by-products. For example, when corn ethanol is produced, there are leftover stalks, leaves, and other plant products that cannot be used to produce ethanol [16]. However, these can be burned to produce energy; therefore, some scientists include the energy output of these products in their calculations. It is important to determine if this energy has been used in the FER calculation before directly comparing FER values.

5.2 Energy input

Unlike energy output, which is straightforward to calculate, energy input is more difficult to determine precisely. This is due to the fact that energy inputs come from four major sources:

1. The energy required to grow the fuel crop – this includes fertilizer, insecticides, and energy to run sprinklers and water pumps
2. The energy required to plant and harvest the crop – this includes fuel for plows, tractors, and combines
3. The energy required to transport the crop for processing – this includes fuel for trucks and trains
4. The energy required to process the crop into fuel – this includes electricity for the processing plant, necessary chemical inputs for the crop, and disposal of waste materials

As you can imagine, these numbers take a bit more work to calculate. The details of energy inputs can be a source of considerable variability in FER values, and there is difficulty in determining some of them accurately. There are a few details worth noting:

1. Crop yields have been increasing steadily for decades as better farming practices, pesticides, fertilizer, and genetically engineered crops have increased the productivity of many fuel crops.
2. Processing crops into fuels near the fields where the crops are grown can reduce the energy costs of crop transportation.
3. Improvements in processing have reduced the production of waste, and uses for waste have arisen, both of which have reduced energy inputs for waste disposal.

5.3 FER values

Below is a list of values of FER for various fuels [17–25]:

Electrical Generation	Energy Ratio	Transportation Fuel	Energy Ratio
Coal – U.S. average	9	Cellulosic ethanol	5.4
Unscrubbed Western coal	6	Biodiesel	3.2–5.5
Biomass direct combustion	6–13	Wheat straw ethanol	1.6
Biomass gasification	2–5	Corn ethanol	0.85 – 2.00
Scrubbed Western coal	2.5	Petroleum-derived diesel	0.84
Natural gas fired	2.3	Gasoline	0.74–0.91

[1] -

As you can see, there is a spectrum of FER values. Also, notice that FER is actually less than 1 for both diesel fuel and gasoline. This value results from the fact that while diesel fuel and gasoline emit a significant amount of energy when burned, extracting oil from the ground and refining that oil into diesel fuel or gasoline requires even more energy per unit. For comparison, consider that unrefined petroleum has a fuel energy ratio around 10. The net result is that both diesel fuel and gasoline produce less energy than was required to make them. In addition, many of the fuels have a range of FER values. This is due to the variability of production techniques, crop yields, and improvements in technology.

Coal has the highest energy ratio of any fuel currently used. This is due to the fact that coal is very abundant, relatively easy to mine, and simple to process. This makes replacing coal as a fuel more economically challenging than replacing gasoline and diesel fuel.

High school students often struggle with nuanced explanations. The high energy ratio of coal provides an opportunity to walk students through such an explanation. Coal truly is the cheapest fuel available – provided one ignores the cost of the pollution it produces. But if the cost of the pollution is considered, the relative value plummets. These two ways of looking at coal provide students with an insight into how facts and information can be skewed to support or refute various positions. By judging coal from the perspective of energy ratios (it is a wonderful fuel) and pollution (it is a terrible fuel), students can begin to step away from simplistic “good” and “bad” explanations and toward a deeper understanding of the challenges of modern life.

6 Problems with biofuels

Biofuels are not without their limitations. First among these is the staggering amount of fossil fuel used each year – far more than can be replaced using biofuels.

As an example, the United States harvested 86.6 million acres of corn in 2016 [26] at an average yield of around 170 bushels per acre [27]. Every bushel can produce around 2.8 gallons of ethanol [28]. The net result is that if we used all of the corn grown in the United States to make ethanol, we could produce around 41 billion gallons of ethanol annually.

While this may sound like an enormous number, the United States burned around 140 billion gallons of gasoline in 2015, more than three times this amount [29].

In addition, ethanol has a lower energy content per gallon than petroleum-derived gasoline does (roughly 50 % less, though mileage is typically around 75–80 % of what it would be with regular gasoline) [30]. Thus, it would require perhaps 180 or 190 billion gallons of ethanol to completely replace gasoline as a fuel for cars in the United States.

There is one more issue, and it is extremely pressing – a significant fraction of the corn grown gets eaten, either by animals or people. In fact, farming on this scale and then using all of the grain to produce ethanol would result in massive food shortages!

Biodiesel has similar problems. The United States used around 36 billion gallons of diesel for on-road transportation in 2014 [31]. This does not include fuel used by tractors, trains, and other off-road vehicles. In 2015, the United States. produced around nearly four billion bushels of soybeans, which could produce around six billion gallons of biodiesel [32]. This is sufficient to replace just 17 % of the on-road diesel used each year. And again, most of the soybean crop was used to produce food for animals and people.

Solid biofuels have different but still important limitations. Typically, the biomass being used as solid biofuels is inedible to people, and thus does not contribute to food shortage or higher food prices. For example, corn cobs, stalks, and other parts of the plant are not eaten but could be burned to produce energy.

The two main problems with using solid biomass in this way are fuel quality and transportation. The inedible parts of a plant are typically a low-quality fuel that does not produce much energy when burned. In addition, it is spread out over millions of acres of farmland, but would need to be collected and transported to a power plant in order to be utilized as a biofuel.

Gaseous biofuels suffer from the same transportation problem – the biomass needed to generate a flammable gas are not concentrated in one area. Additionally, producing a gas from biomass is a slow process and involves storing the biomass for long periods of time. Not all of the biomass will be converted to methane, leaving behind waste products. These must be disposed of, and the energy and cost for this disposal must be considered.

Perhaps my greatest challenge as a high school chemistry teacher is helping students who are required to take the course. The problems with biofuels can provide a connection point for these students. The disadvantages of biofuels are economic, cultural, and aesthetic in nature. By relating biofuel disadvantages to fields unrelated to chemistry, teachers can provide a feeling of inclusion to students whose interests may not be primarily scientific.

7 Potential for future improvements in biofuels

Existing biofuels cannot replace fossil fuels outright. So, why are people so interested? The answer lies in the prospect of making biofuels from other sources, specifically waste. Biofuels have already been made from turkey offal (the portions of turkey that are not eaten), sawdust, forestry waste, even used cooking oil. But, these sources are relatively small. There is a much larger source of waste that, if it could be used, would allow biofuels to take over a significant fraction of energy production: cellulose.

When ethanol is made from grain, an enormous amount of energy, water, fertilizer, pesticides, and other inputs have to be used to grow the crop (in the United States, this is almost always corn). Then, the crop is harvested, and only the corn kernels are used. The stalks, leaves, roots, and husks are all discarded. The primary solid constituent of these waste products is *cellulose*, a long-chain polymer formed from many sugar molecules.

Currently, the technology to produce ethanol from cellulose exists, but processing the cellulose into sugar requires a significant amount of energy and very specialized enzymes. These restrictions limit the use of cellulose as a feedstock for the production of ethanol. However, it is estimated that over a billion tons of cellulosic waste is available annually in the United States, sufficient to replace around one-third of transportation fuel in the United States. This does not include cardboard, paper, and packaging waste, which currently accounts for around 40 % of municipal waste. Using marginal land to grow crops rich in cellulose (such as grasses) could increase production still further, allowing ethanol to become the dominant transportation fuel in the United States.

Similar advancements are possible in the production of gaseous biofuels. Improved catalysts can increase the yield of combustible gases produced from solid waste products. Genetic engineering of microbes is also being investigated.

Many hurdles remain if biofuels are going to become a major source of future energy production. However, with continued research and investment, biofuels can be an increasingly important tool in the fight against climate change and a high quality, domestically produced fuel source that the United States can rely on for decades to come.

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