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Biodiesel: History of Plant Based Oil Usage and Modern Innovations

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Abstract. The history of biodiesel dates back to mid-19th century when transesterification of vegetable oils was discovered. It took another half century for the world to realize its potential as fuel. Through the 20th century, two World wars and other regional turmoil increased the quest for energy security among nations. This chapter presents the history of biodiesels from the perspective of its development from vegetable oils, and animal fats. Usage of biodiesel and straight vegetable oil before World war, and how the energy crises sparked the intense development of these fuels around the globe towards the end of 20th century.

Keywords. Biodiesel, Biofuels, Vegetable oils, Transesterification, Energy policy, Food or Fuel.

INTRODUCTION

Modern society relies heavily on fossil fuel-based engines to achieve various tasks and work.[1] The rate of consumption of fossil fuels over the last two centuries has increased dramatically. A valuable alternative to diesel and related fossil fuels is Biodiesel: a liquid fuel derived from fats and oils of plants, animals, and other sources. Biodiesel can be produced from pure vegetable oil, algal cultures, oils from animal fats, tallow, grease, and waste cooking oil.[2]

The term vegetable oil covers a number of oil sources, such as nuts, seeds, vegetables and other plants.

This chapter will discuss the history of biodiesel, from conception and development to industrial scale production. Also detailed here is the historical use of plant oils and their adaptation to biodiesel. Over the past century, the global political climate, war, socio-economic conditions, government policies and various other factors have shaped the development and use of biodiesel. Generally, diesel is a C8 to C25 hydrocarbon mixture produced from the distillation of crude oil. Chemically, the term Biodiesel signifies mono-alkyl esters of fatty acids from oils and fats.[3] Although utilized since the late nineteenth century, the term Biodiesel wasn't used in the mainstream until the 1980s. In 1984, the word "Bio-Diesel" appeared in Power Farming magazine out of Sydney, Australia. The term has become more common in the literature subsequently. With the exception of a few non-technical reports, most articles use the term "biodiesel" without the hyphenation.

The definition of biodiesel in the present day is often confusing. With US regulations differentiating biodiesel and Biomass Based Biodiesel, the EU regulatory requirements are based on meeting the standards outlined in the definition of biodiesel. Biodiesel's fuel quality is measured by ASTM (USA) and designated as D6751 and in Europe (EU is EN 14214).[2] The qualities that define a biodiesel are completion of the transesterification reaction, complete removal of the catalyst, removal of glycerin, sulfur content, trace amounts of alcohol, and any free fatty acids present.[4]

The U.S. Department of Energy defines "biodiesel" as "renewable, biodegradable fuel manufactured from vegetable oils, animal fats of recycled restaurant grease. It is a liquid fuel often referred to as B100 or neat biodiesel in its pure form".[5]

The process of obtaining fuel from fat is an ancient one. Several civilizations have used Straight Vegetable Oil (SVO) and oils derived from animal fat and other sources for fuels.[6] In the seventeenth and eighteenth century, whale oil was used as a major fuel source throughout Europe and the US. In 1853, E. Duffy and J. Patrick reported transesterification of oils.[7]

Transesterification is a process of using triglycerides in the presence of a base or acid to chemically break the molecule and produce methyl or ethyl esters of the fatty acids.[8] This was not utilized for production of biodiesel until 1937 however, when a Belgium engineer patented the use of this process for producing fuels. Several countries explored the opportunity to use vegetable oils as fuels for diesel engines, as it gave some self-sufficiency to countries that had access to oil producing crops and other feedstock materials.[9]

Modern day demands for alternative energy and fuel sources is high. SVO usage in biofuels has increased over the 20th century globally, with major producers such as the European Union, South East Asia and the Americas.[10] Biodiesel can be produced from a variety of feedstocks, including edible and non-edible oils. Different countries utilize different plant based oils, but more than 95% of the world's biodiesel comes from edible oils. The popularity of some non-edible oils as feedstock is growing however, with easy to grow plants like Jatropha[11]. Multiple studies have been conducted on the use of biodiesel versus SVO outlining the cost-benefit to the consumer and the type of engine.[10–12] The use and production of SVO and biodiesels from edible oils has been shown to improve not only emissions and renewability, but can help local economies that are producing these fuels.[12]

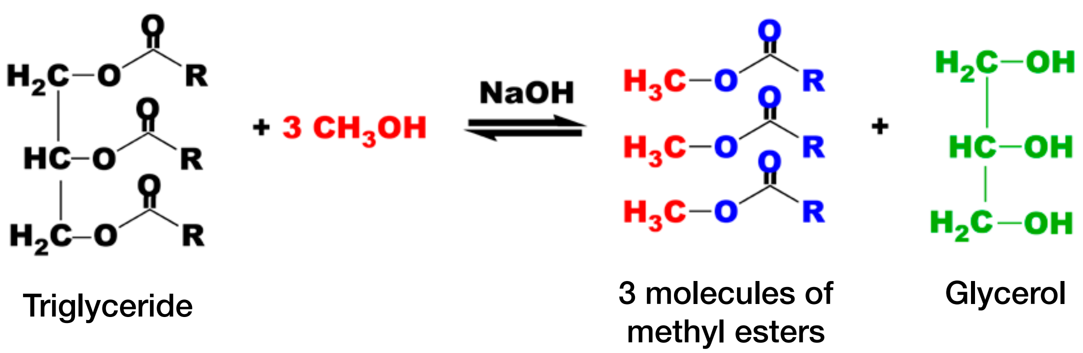
The use of biofuels and the evolution of biodiesel can be separated into four time periods:

1) Use of Straight Vegetable Oils (SVO) as a lamp fuel from times before antiquity to the mid-19th century; 2) The use of SVOs in internal combustion engines and esterification of SVOs to produce biodiesel during the 1930s and 40s 3) as replacement for petroleum during oil shortages in the 1970s; and 4) Present day need for alternative fuels including global energy needs, and sustainable agriculture and environmental impacts.

CHEMISTRY OF BIODIESEL TRANSESTERIFICATION OF OILS

In 1853, Irish chemists Patrick and Duffy reported transesterification of oils (**Scheme 1**).

Transesterification is an important reaction in industry, not only for biodiesel, but is crucial for the production of numerous household products, soaps and detergents. All biodiesel around the globe is produced through this process.[3,13,14] Triglycerides are molecules with a glycerol molecule head group and three fatty



Scheme 1. Transesterification of triglycerides with methanol.

acids attached to the three hydroxyl groups. In general, characteristics of the fat are determined by the chemical nature of the fatty acids attached to the glycerol. Vegetable and nut oils contain mostly triacyl glycerols or triglycerides, which is why they are often the precursors for biodiesels.[15]

When triacyl glycerols (triglyceride) are combined with a base and an alcohol (eg. methanol), they produce methyl esters of fatty acids and the byproduct glycerol. This class of reaction is known as transesterification.[8]

The previous scheme shows the chemical process for fatty acid methyl esters- biodiesel production. The reaction between the triglyceride and the alcohol is a reversible reaction, so the alcohol must be added in excess to ensure complete conversation of the reactants.[16] It was not until 1937, when Georges Chavanne patented the production of fuel through this process, that the utility of bio-diesel was realized.[2]

PRODUCTION AND PROPERTIES OF BIODIESEL

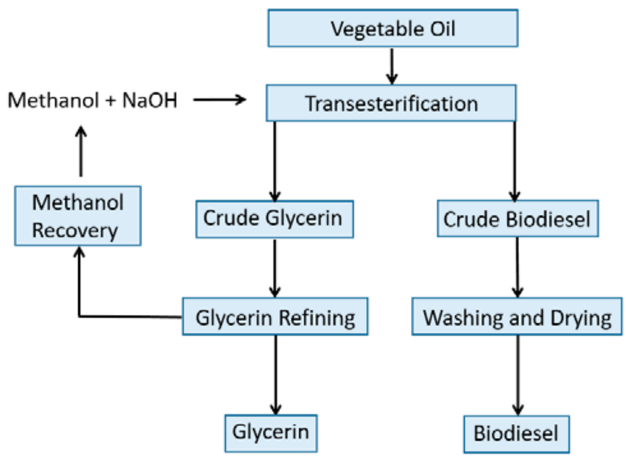
Biodiesel is produced from moisture-free vegetable oil. The oil is pre-heated to 60°C and sodium methoxide in methanol is added in a closed reactor. The reaction usually takes about two hours for completion.

The alcohol reacts with the fatty acids to form the mono-alkyl ester, the glycerol by-product of the reaction deposits on the bottom of the reactor due to its density and is removed. Industrial scale production of biodiesel is described in **Scheme 2**.

In most production, methanol or ethanol is the alcohol used (methanol produces methyl esters, ethanol produces ethyl esters) and is base catalyzed by either potassium or sodium hydroxide. Potassium hydroxide is more suitable for the ethyl ester biodiesel production, but either base can be used for methyl ester production.[14,16–18]

Various research has been performed over the years on enhancing the chemical stability of biodiesel. As they are derived from fatty acids, the oxidative stability has always been of concern.[19] This has been addressed mainly by modifying the fatty acid composition of the feedstock oil. Usually polyunsaturated fatty acids are avoided in the production of biodiesel. Literature reports suggest that carbon chain-lengths up to C16 and C18 show good oxidative stability. In permitted situations, the biodiesel produced will be fractionally distilled to separate saturated and unsaturated fractions.[20,21] Other than a transesterification reaction, the alternate two ways to produce biodiesel include: hydro processing or deoxygenation and microemulsion or co-solvent blending. The biodiesel production facility at Amsterdam (**Figure 1**) in Netherlands, producing 150,000 tons of biodiesel annually along with 50,000 tons of pharma grade glycerin.[22]

Biodiesel is bio-renewable in all aspects: the feedstock, the product and the byproducts are all renewable. For this reason, it is often termed as carbon neutral. Properties of biodiesel such as biodegradability and its high flash points makes it safer in the event of crash or spills. The present technology enables the production of biodiesel from any plant or animal derived oil. However as discussed above, some oils produce benefits upon conversion to biodiesel compared to others.[8,23] Around the globe various vegetable oils and other fat sources have been used as feedstock materials for years. Ultimately there was a need for suitable starting material that provides a high-quality lipid for transesterification and subsequent biodiesel product. The source material is composed of triglycerides, which contain three long



Scheme 2. Schematic representation of Biodiesel production process from vegetable oil.

Figure 1. Biodiesel Production facility at Port Amsterdam.

Table 1. Fatty acid composition of common oils and fats.

Fat or Oil	12:0	14:0	16:0	18:0	18:1	18:2	18:3	20:0	20:1	22:1
Soybean		.	8	5	25	55	11			
Corn		2	10	4	19-49	34-62	.			
Peanut		.	9	2-3	50-65	20-30	.			
Olive		.	10	2-3	73-84	10-12	.			
Cottonseed		0-2	23	1-2	23-35	40-50	.			
Butter		7-10	25	10-13	28-31	1-2.5	.2-.5			
Lard		1-2	30	12-18	40-50	7-13	0-1			
Tallow		3-6	26	20-25	37-43	2-3	.			
Linseed Oil		.	6	2-4	25-40	35-40	25-60			
Pongamina Pinnata		2	6	8	45-71	11-18		4	11	5
Coconut Oil	45-53	17-21	10	2-4	5-10	1-3	.			
Palm oil	.	.	44	5	39	10	.			
Palm kernel oil	48	16	8	.	15	3	.			

strings of fatty acids attached to a glycerin molecule. The fatty acids can differ in their length and degree of unsaturation. The overall fatty acid content differs in each oil source material.[15] **Table 1** shows the percentage composition of fatty acids in common oils used for biodiesel production.

The nomenclature of fatty acid is as follows, the number on the left represents the number of carbon atoms and the number after the colon represents the number of double bonds in the fatty acids. Based on the number of carbon atoms and number of double bonds, each fatty acid has different freezing point, ability to polymerize and overall energy content.[24] The fatty acid composition can also affect important physical properties of biodiesel such as viscosity (fluidity), ignition point and caking at low temperatures. Degree of unsaturation also effects the performance of biodiesel produced from vegetable oils.[22,25,26] The overall saturation levels of many biodiesel oils are given in **Table 2**.

Oils with maximum amounts of saturated fat content yield biodiesel that has a lower gel point. Biodiesels derived from oils with more unsaturation oxidize sooner than oils with less unsaturation. For example, biodiesel derived from walnut oil, poppy oil and linseed oil degrades relatively quickly.[25] Currently, biodiesels derived from cooking oils perform well comparatively to other source materials. Most of these oils contain one or two double bonds per fatty acid. This gives optimum shelf life for the biodiesel as well as desired properties.[15,26] Based on the performance, canola oil is reported to perform well when converted to biodiesel. Historically this has increased the cost of canola oil in the US market. Olive oil has also been an option for producing biodiesel. The advantage of canola oil is it is genetically modifiable to produce increased amount of polyunsaturated rather than saturated content. Hydrogenated vegetable oils have not been significant in biodiesel production as they yield a fuel with undesired qualities. Used cooking oils, especially the ones with high free fatty acids are attractive for biodiesel production.[13,22,23,27,28]

Waste Vegetable Oil (WVO), which is high in free fatty acids cannot be converted into biodiesel in the most preferred method of production: the base catalyzed. The use of base results in conversion of the free fatty acids to soaps. The acid catalyzed esterification process is better suited to WVO. The soaps formed as impurities from oils with high free fatty acid content during biodiesel conversion, can lead to accumulation of water due to the hygroscopic nature. This results in biodiesel with more water content than normal and an undesirable product.[16,29] The viscosities of SVOs are an order of magnitude higher than that of the biodiesels derived from them. The derivatives of SVO, methyl and ethyl esters also have different viscosities. Various biodiesel producing countries resort to methanol as the alcohol partner in transesterification, due to the low cost of methanol.[30] The viscosity of biodiesel is similar to petroleum diesel, in cases where biodiesel is mixed with petroleum diesel the lubricity of the fuel is increased.[8,26] Biodiesel and petroleum-based fuels are highly miscible and are available and utilized around the world in many markets. Biodiesel can be used as such in present day modified diesel engine vehicles (B100). Blends of 20% biodiesel with 80% petroleum diesel (B20) are used in unmodified diesel engines. Some drawbacks occur with the use of biodiesel, it will degrade natural rubber parts in vehicles manufactured

Table 2. Fatty acid nature (saturation) level in common oils and fats.

Oil	Saturated	Monounsat.	Polyunsat.
Butter	63%	26%	4%
Canola oil	7%	62%	31%
Coconut oil	90%	6%	2%
Camelina Oil	10%	33%	54%
Chufa oil	20%	67%	12%
Corn Oil	13%	24%	59%
Olive oil	14%	73%	11%
Soybean oil	16%	23%	58%
Peanut oil	17%	46%	32%
Cottonseed Oil	26%	18%	52%
Chicken Fat	30%	45%	21%
Lard	39%	45%	11%
Palm Oil	49%	37%	9%
Palm Kernal Oil	81%	11%	2%
Sunflower oil	10%	20%	66%
Safflower Oil	7%	14%	79%

* Note- The values are averaged. Actual values may vary based on the region of growth, genetic modification made, and method of extraction.

before 1992 and emissions of nitrogen oxide and ozone precursors are higher than in petroleum diesel. However, there are many benefits, the use of biodiesel has been found to breakdown the residues and deposits in fuel lines. Biodiesel burns cleanly with 80% less CO_2 emissions and 100% less sulfur dioxide than regular diesel. The octane number, measure of fuel's ignition quality for biodiesel is 100, for petroleum diesel it is 40. The energy content of biodiesel (average) is 35MJ per liter, close to petroleum diesel at 38.3MJ per liter.[31]

The US Federal Trade commission distinguishes biodiesel based on the starting material. Although it is not in the scope of the current report to discuss in detail regarding the differences and similarities between biodiesel and Biomass-Based Diesel (BBD). It is important to distinguish between the two.[32] The Federal Trade Commission defines BBD as "a diesel fuel substitute produced from non-petroleum renewable resources that meets the registration requirements for fuels and fuel additive established by the environmental protection agency under 42 U.S.C. 7545, and includes fuel derived from animal wastes, including poultry fats and poultry wastes and other wastes materials, or from municipal solid waste and sludge's and oils derived from wastewater and treatment of wastewater, except that the term does not include biodiesel". Whereas Biodiesel is simply defined as "the mono alkyl esters of long chain fatty acids derived from plant or animal matter that meet the ASTM standard D6751 requirement and registration requirements for fuel and fuel additive". [31–33]

Scheme 1 and **2** clearly shows that during the production of biodiesel, glycerol is produced as a byproduct. With the global increase in production of biodiesel, there has been an increase in crude glycerol production. For every 9 kilograms of biodiesel, about 1 kilogram of glycerol is produced as by-product. Although glycerol is a valuable material to produce industrial chemicals, intermediates, cosmetics and polymers, purifying this amount of crude glycerol poses a challenging problem from a sustainability standpoint. The average consumption of glycerol in the US in the past decade was 200 million kg. The amount of glycerol entering the US market was 20 billion kg in 2010. Since the early 2000s, methods for converting glycerol into other useful products have been explored. One approach is to convert glycerol to ethanol, CO_2 and hydrogen using *E.Coli*. In work from 2005, Dharmadi et al. reported the use of *E.Coli* to consume glycerol resulted in 75% theoretical yield ethanol. One drawback to this process is that it produced more than 50% carbon dioxide.

HISTORICAL USE OF VEGETABLE OILS

Plant and seed oils have documented use as far back as 1500 BCE. Oils and fats were not only historically used for light and heat fuel, but Ancient Egyptians used perfumed oils for beauty routines, religious ceremonies and medicine as well. Additionally, these oils have long been part of the food supply. Recent archeological work has shown that as early as 6000 BCE olive oil was being extracted for a food source in Galilee, Israel.[34,35]

Cultivation of olive trees dates to 3500 BCE in the eastern Mediterranean. Ancient Greeks utilized olive oil for food, religious ceremonies, fuel for oil lamps, and medicinal treatments. It was one of the regions chief exports and continues to be a commodity in modern Italy and Greece. Other ancient civilizations also utilized plant and natural oils in similar ways.[36]

The use of castor oil was extensive in ancient Egypt and is documented in the Ebers papyrus. The historic text outlines the use of multiple parts of the plant and extracted oil for headache, respiration, digestion, skin treatments, and hair growth. The oil was also used for fuel and ceremonies. Almond oil mixtures for skin and anti-aging treatments are also described in the Smith papyrus.[37,38]

Early Greece was also a consumer of plant oils, Herodotus recorded the use of castor oil for lamp light, and as a hair and skin treatment. The Greek expanded on the Egyptian knowledge of medicine that influenced care until the middle ages. The Greek physician Hippocrates recommended the use of olive oil for sports injuries and to warm the body[39]. As international exploration continued the varied uses of these oils spread to China and India. These societies also utilized plant oils for fuel, beauty, medicine and religious ceremonies.[38]

Linseed, or flax oil was used for waterproof clothing, luggage, carriages and shelter fabric in the 18th century, as documented by Louis Franquet, a French explorer. "They (Canadians) name prelart a large and heavy cloth, oil-painted in red, […] to keep oneself from the rain" Louis Franquet, 1752.[40] Canvas or linen was boiled with a combination of oil and paint in order to achieve the waterproofing.[41] Oilcloth remained popular through the late 1950s, until rubberized and plasticized fabrics became more available. In the 1870s, Procter and Gamble endeavored to make individually sized bars of soap to sell. In order to achieve this, they revolutionized the use of palm and coconut oil rather than animal fat for soap. Around this time, the US cotton industry was producing tons of oil as byproduct from the industrial process. Consumption of the cottonseed oil eventually led to production at such high rates, that this byproduct was later industrialized and converted to a food product that is now highly consumed in the US.[42,43]

During the late 19th and early 20th centuries, the use of natural medicinal oils fell out of favor due to growing advances in synthetic pharmaceutical chemistry.[44] In recent history, there has been a renewed interest in natural, plant and essential oils for their use as homeopathic remedies and Eastern-based medicine. For example, a recent study tested the efficacy of lemongrass, pine and clove oil compared to DEET. These oils were found to be up to 98% as effective as the common insecticide.[45] As with ancient times, modern use of these plant oils includes food, beauty and medicinal purposes. They are also still used for heat and lamp oil in developing countries and in generators during emergencies.

During the mid-nineteenth these plant oils were being utilized as fuel for combustion engines. Diesel, Otto and other inventors of the time designed engines that would run off pure oil, mixed petroleum and plant oils or other combinations of fuels.[14] Biodiesel is also an effective cleanup solvent for petroleum based oil spills, as shown in lab tests with simulated shorelines.[46] Modern day awareness for the environment have re-invigorated international policies encouraging the use of alternative fuels like plant-based biodiesel.

THE TRANSITION TO A FUEL: NINETEENTH CENTURY UTILIZATION OF THE INTERNAL COMBUSTION ENGINE AND CHOICE OF FUELS

Internal Combustion engines played a crucial role in shaping up the development and use of biodiesel. Prior to the invention of the diesel engine there were many attempts throughout the seventeenth century to develop an internal combustion engine.[47] Historian Lyle Cummins recorded the detailed history of these attempts in his book. In 1893, Rudolf Diesel, a German engineer (**Figure 2**) wrote an essay on theory and construction of a heat motor. Historical reports indicate the first biofuel powered vehicle is Diesel's oil powered 10 iron cylinder with a flywheel in the base. This ran on peanut oil for the first time in Augsburg, Germany on August 10th, 1893.[48] Diesel had a strong desire to develop alternatives to conventional fuel engines.[49] In 1912, a year before his death, he gave a speech in which he mentioned that, "the use of vegetable oils for engine fuels may seem insignificant today, but such oils may become, in the course of time, as important as petroleum and the coal-tar products of the present time."

In the following years he filed a patent for his design. At the time of Diesel's invention, steam engines were common, even with a relatively low efficiency at only about 10%. Diesel's invention came as a breakthrough during this era. In his internal-combustion engine design, the combustion of the fuel and the piston movement occurred through an isothermal reaction. Although revolutionary to the field, the initial models of Diesel's engine were bulky and could not be moved easily, so were not ideal for automobiles or trains.[47,48]

Throughout the time that Diesel was working on his engine, other engines with alternative fuel sources were being developed despite low gasoline prices. Alcohol fueled engines, coal gas, kerosene and gasoline engines were all advanced during this time. Kerosene was of particular interest, as the byproduct of gasoline fractionation, but multiple alternative sources were being utilized and explored at this time.[2,3,13,50] These other alternative combustion engines were capable of running on different fuels and fuel mixtures. Prior to Diesel's invention, in 1860, German engineer Nicholas August Otto developed an engine utilizing ethanol. Just like vegetable oil used for burning lamps in eighteenth and nineteenth century Europe, ethanol lamps or spirit lamps were also common. Hence, Otto conceptualized an engine burning ethanol as fuel. With funding from Eugen Langen, owner of a sugar refining company, they launched the Otto & Langen company which produced stationary piston engines in the 1870s. These engines were powered

Figure 2. Early portrait of Rudolf Diesel.

by coal gas. Later in the1880s, he came out with a four-stroke "Otto-cycle" engine that used gasoline.[47,50]

In 1900, at the Paris Exhibition, the French Otto Company had four diesel engines including one from Diesel's own son Eugen Diesel. Out of the five engines, one engine ran entirely on peanut oil; although not many of the visitors realized this according to Diesel.[51] He mentions that, "*the engine was built for petroleum (mineral oil) and was used for the plant oil without any change. In this case also the consumption experiments resulted in heat utilization identical to petroleum*". The French Government did take notice of the engine running on peanut oil. Diesel notes that the French had interests in testing the efficiency of Arachide (earthnut or in this case peanut oil). The availability of large quantities of ground nuts and other sources of vegetable oils in the French African colonies prompted the French government to encourage the cultivation of these food sources.[47,50] Thus, using these vegetable oils as possible fuel source in engines. From an engineer's perspective, this was made possible mainly because diesel engines developed around 1900s had complex injection system to accommodate various fuels. From kerosene, coal dust, oils and petroleum mixtures early diesel engines ran on various fuels.

The major implementation of Diesel's internal combustion engine (or diesel engine) did not start until almost two decades after Diesel's patent expired in 1908. Numerous varieties of diesel engines were introduced, to the extent that Diesel felt he was not accredited properly for his invention. Even though in histories of biodiesel, the first use of a bio-fueled engine is mistakenly attributed to Rudolf Diesel in 1900 at the World Expo in Paris. While it is true that there was an engine displayed at World's expo that ran completely on peanut oil, it was demonstrated by Nicolas Otto.[47,48]

Diesel engines quickly gained attention in early the 20th century due to their power, reliability and fuel economy. Numerous versions of Rudolf Diesel's engine were developed within a short span during this time. From Diesel's statements and speeches, it is evident that he envisioned the use of reliable SVOs to assist the fuel power of developing and underdeveloped nations such as African and Asian countries where petroleum-based fuels did not reach. Diesel had interest in creating an efficient engine.[47,52] From his book *Die Entstehung des Dieselmotors* (translation: The Emergence of the Diesel Engine) in his own words he mentions his motivation, "*the desire to realize the ideal Carnot process determined my existence*". Rudolf Diesel died in 1913, before his vision of developing efficient engines that could utilize SVOs was realized. During the decade following Diesel's death, the petroleum industry developed a by-product that was able to power the modified diesel engine, they termed it "diesel fuel". It was around this time that the industry shifted towards petroleum-based fuels and the focus on alternative fuels was lost. Diesel engine manufacturers of the 1920s altered engines to better suit low viscosity fuels rather than the viscous fuels such as SVO or biodiesel. August 10, the day Rudolf Diesel demonstrated his internal combustion engine using SVO is presently observed as International Biodiesel day.[31,47]

The fluidity of SVOs creates problems in present day diesel engines that are made to run on less viscous diesel. Preheated peanut oil, animal fat and other oils have been successfully used to power diesel engines, but this requires modifications to the engine.[53] When the shortage of petroleum-based fuels occurred in 1970's, the existing engines were only able to run specifically on diesel and issues occurred when other fuels were attempted. Petroleum industries have monopolized the automobile industry, as they have been able to produce fuels at much lower costs compared to biomass derived fuels. This has resulted in a century of added pollution and increased carbon emissions from the use of petroleum fuels. The research, infrastructure and technological advancements of biomass-based fuels such as biodiesel were suppressed for many decades due to the monopoly of petroleum-based fuels.[54]

WORLD WARS AND THE EFFECT ON DEVELOPMENT

During World War II, the demand for biofuels increased, as importing petroleum-based fuels was becoming difficult. Germany was experiencing a fuel shortage, which led to another phase in alternative fuel engine development. Mixing gasoline with alcohol derived from potatoes came into practice.[55] Following Germany, the UK implemented the use of mixing grain alcohol with gasoline. At the same time, Brazil prohibited the export of cottonseed oil so that it could be utilized as a substitute for diesel. In China, Tung oil and other SVOs were used to produce a fuel similar in performance to kerosene.[50]

American automobile entrepreneur Henry Ford also had great interests in alternative fuels. His interest and the fact that up to World War II, soybean crops in the US were mainly used for oil production, he developed the "soybean car" in 1941. During World War II, Ford built a single experimental soybean car, but due to the war activities it never saw the production line. The Soybean car weighed 2,000 pounds; 1,000 pounds lighter than other cars in production in 1941. After World War II, the development of the soybean car did not resume.[56]

After World War I and II, America, France and the UK had the advantage of access to petroleum-based fuels, resulting in the common saying "they floated to victory on a wave of oil". Germany had become self-sufficient in ethanol-based fuels as early as 1910, as ethanol production was a major part of their economy.[57] In 1942, Germany reached a peak in synthetic fuel production at 1.7 billion liters from coal. In the same year, Germany produced 267 million liters of fuel grade ethanol from potatoes. In sum, Germany made 54% of their fuels from non-petroleum-based sources.[58]

The war in the western hemisphere created different pressures in India and China. Since much of the fuel was imported by the allied nations, it sparked an interest in substitutes for petroleum-based fuels in these areas. Vegetable oils were not readily available due to the large populations of these countries, which were dependent on the land. One crop that proved viable as an alternative fuel source however, was sugar cane. Molasses from sugar cane was used as raw material for alcohol production. In China, Benzonite, a mixture of 55% ethanol, 40% benzene and 5% kerosene was sold after World War I. Sugarcane plants demand huge volumes of water for growth, hence India and China slowly made their shift away from sugarcane bioethanol to alternative plant based biodiesel.[59] The plantations moved to cheaper and drought resistant crops such as Jatropha. There are also reports that indicate that the use of biodiesel produced from peanuts, tea leaves, tung, cotton seed and cabbage seed was implemented during this time.[53]

Despite all of international advancements in the biodiesel industry, when peace returned to much of the world, the oil prices from the middle east region dropped again reducing the demand for alternative fuel research.[13]

THE RISE AND FALL OF BIODIESEL INNOVATION, HOW THE GLOBAL MARKET SHAPED THE INDUSTRY FROM THE 1950S THROUGH 1970S

The 1950s was a prosperous time for the US, and petroleum-based fuel was readily available. In the 30 years following the end of World War II, consumption of oil on the global scale had grown six times[60]. At this time the US was a top producer of soybean oil and Europe produced large amounts of canola oil. Although demand for biodiesel was low, these crops determined the type of biodiesel that would be developed and used in these countries. In 1951, US researchers reported the efficient use of cotton seed oil as diesel fuel.[61]

In the 1970s, the unstable political situation of the Middle East shook the global availability of petroleum fuel. This lack of supply propelled countries to search for alternate fuel sources once again. In the US and Europe, a major consumer of petroleum fuel was agricultural machinery and heavy vehicles.[52,57] From the period of 1973 to 1979, a serious supply deficit occurred all around the globe due to the growing conflict in the Middle East. The OPEC (Oil Producing and Exporting Countries) nations reduced the supply of fuels to non-OPEC nations, which increased the motivation to develop biodiesel. A second energy crisis occurred in October 1978, when Iranian oil refineries were attacked, effectively shutting down five percent of the world's oil exports. The conflict lasted until January 1979, increasing the cost per barrel twice in a time span of six months.[32]

The oil crisis of the 1970s primarily impacted the United States. On October 6th, 1973, Egypt, Saudi Arabia and other Arabian countries attacked Israel in an attempt to regain lost land from the 1967 war. US aids were flown to Israel on October 17th, but on the same day Arab oil ministers met in Kuwait and signed an agreement for an oil embargo against the United States and its allies. The agreement pledged to reduce oil production by five percent every month, which had immediate effects on the US oil market. The price of crude oil went up by four times. After these conflicts were resolved, the supply of petroleum-based fuels was restored. Diesel production and the improvement of supply chain infrastructure increased the accessibility of petroleum fuels. With these shifts in petroleum fuel availability, the concept of biodiesel research, development and production was not actively pursued and fell by the wayside once again.[51]

The twenty first century has seen a bigger push for alternatives to petroleum based fuels as growing concerns over climate change, carbon emissions and sustainability push politics towards subsidies and incentives for the biofuel industry.[62] Biodiesel initiatives around the globe have been implemented in which blends of diesel and biodiesel are sanctioned.[63] However, using SVO as a diesel engine fuel hasn't experienced the same uptick. Multiple studies have reviewed the usage of SVO in diesel and combustion engines with overall mixed conclusions about engine performance.[12,64] While the future of biodiesel and SVO as alternative fuel sources is promising, there are still many challenges to overcome.

BIODIESEL PRODUCTION GLOBALLY, INTERNATIONAL ENERGY POLICY AND REGULATIONS: SHAPING THE HISTORY OF BIODIESEL

US

In the United States, biodiesel programs rapidly developed and commercialized after 1980. It was difficult for the advancement of biodiesel to gain traction, as US oil industries propagated myths about alternative fuels.[65] Some of which espoused that ethanol is an inferior fuel, which creates technical issues, and that blending biodiesel and gasoline creates inferior quality fuel that doesn't have the same power output as petroleum-diesel. In addition, the US automobile industry historically backed the oil industry claims. On the other hand, the farming industry which relied heavily on diesel for heavy equipment operations, supported biodiesel production. During the 1980s, the Brazilian Alcohol expansion program worked with the Nebraska Corn Products Utilization committee to initiate road tests with corn ethanol to prove that the efficiency and power claims were completely true.[66]

Following the Second World War, the United States faced a shortage of petroleum-based fuels for a short time. This inspired the start of the "Dual Fuel" project, at Ohio State University (Columbus, OH).[67] Extensive exploration was carried out on cottonseed oil, corn oil and various blended oils as a substitute diesel fuel. Although the use of vegetable oils has resulted in satisfactory performance with engines, the power output consistently remained lower than conventional petrol engines.

After the oil crisis of the 1970s, in 1978 US President Jimmy Carter created a 25-million-dollar program called 'Aquatic Species Program' to investigate high-oil from algae, focusing on biodiesel production. In 1980, he signed another bill giving a $0.54 per gallon ethanol tax incentive. This legislation sealed the developmental path of the US biofuel and biodiesel programs. The US biodiesel industry slowed to a crawl in the 1990s, due to lower costs of petroleum-based fuels.[51,55] Despite this, in 1996 Pacific Biodiesel, the nation's first biodiesel plant was established on the island of Maui, Hawaii. It focused on recycling cooking oil into biodiesel. This plant, through its waste conversion to biodiesel, produced over 49,000 liters of biodiesel per day as of 2016 and was certified as a "Sustainable plant" that same year.[54]

Legislation in the US regarding biofuels started in the early 1990s in an effort to reduce market demands for foreign oil. The Energy Policy Act of 1992 was one of the pieces of legislature aimed at increasing research on biofuels and how federal programs should be constructed to increase biofuel implementation. It was the first time that requirements were put on the Department of Energy to increase biofuel utilization in their own vehicle fleets and to collect data on the efficiency, use and supply of biofuels and environmental effects of biofuels.[68]

Oil prices rose following the events of 9/11/2001, which again renewed interest in biodiesel production ventures. The Energy Policy Act of 2005 introduced a biodiesel tax credit which allowed blended fuel producers to claim a one-dollar credit per gallon. It also expanded research and development of alternative fuels to include expanded agricultural supplies of biofuel and additional bio-power energy systems.[69] This furthered the production and growth of the biodiesel industry. In the same year, Minnesota became the first state to make it mandatory for all diesel fuels sold in the state to have a minimum of 2% biodiesel.

Additional legislation in 2007, 2008 and 2009 to help liberate the US market from dependence on foreign oil and crashes in commodities were put in place via presidential order, and stimulus packages from congress. These laws helped protect troubled assets and gave tax credits to biodiesel and incentivize environmentally friendly energy practices.[70] These policies helped grow the biofuel industry in the US, providing innovation and furthered the reach and implementation of these alternatives.

The use of biodiesel in the continental United States has increased over the past decade. In 2017, the US produced 7.38 billion liters of biodiesel and imported 1.1 billion liters.[71] Biodiesel has been increasingly used as the fuel of choice for university and college campus transportations across the US. Biodiesel is biodegradable, nontoxic, and has significantly fewer emissions than petroleum-based diesel when burned. This makes it the fuel of choice in delicate eco-systems. In 1995, Yellowstone National Park launched the “Truck-in-the Park” project in collaboration with the University of Idaho and several other partners. The project featured a pick-up truck with a direct injected diesel engine that ran on canola ethyl ester. When an engine check was performed at 92,000 miles, the impact of emissions was far less than that of a regular diesel engine. Over the next decade, the National Park system started using solely biodiesel blends and by 2006 had completely converted to these blended fuels. As of 2016, a total of 163,000 liters of blended biodiesel had been consumed by trucks, graders, front-end loaders and other heavy vehicles utilized in the parks. This has reduced the carbon and sulfur dioxide emissions and particulate matter released into the air. Other pilot programs were introduced which utilized biodiesel for public transportation infrastructure, such as community buses and heavy equipment. The US made a pledge of achieving production of 120 metric tons of biofuels by 2022.[72]

Europe

Much of the present-day European biodiesel industry was developed in the 1980s. The fuel crisis that hit the US hard in the 1970s was also a detriment to supplies in Europe. In Europe and South Africa, pioneering work on biodiesel was conducted by researchers such as Martin Mittelbach who advanced the production processes and the storage stability of biodiesels.[73,74] This propelled the development of the biodiesel industry into the 1990s.

In 1990, France launched a program named “Diester” aimed at the production of biodiesel from rapeseed oil.[75] Specifically, the methyl ester derivative of rapeseed oil was sold as biodiesel in France, Austria, Germany, Sweden, Italy, Belgium, Hungary and the Czech Republic around 1988. Germany established specific criteria for rapeseed biodiesel to be sold using standards based on the density, viscosity, iodine value and residual catalyst.[57,65]

The European Union proposed a 90% tax reduction for biodiesel in 1997, leading to an increase in the production of biodiesel. The estimated amount produced was 660,000 tons per year in the following years. As of 2005, worldwide biodiesel production crossed 4.1 billion liters with the EU being the largest producer. The European legislation has had requirements in place since 2008 for the use and expansion of biofuel which has led to the production of over 10.6 billion liters of biodiesel as of 2017. Their work will continue into the 2020s, with directives to ban palm oil and increase energy efficiency in public transport and consumption.[76]

India, China and Southeast Asia

Shortly after World War II, India gained independence. In 1948, nine million liters of alcohol was produced for fuel and two million liters of alcohol blended fuel was used. Although there was a dire need for alternate fuels, the issue of “food vs fuel” prevented the use of grains for oil production. Hence, the expansion of biodiesel did not occur in these regions until after 1980. Since alcohol was also produced from sugar cane wastes, the Indian Alcohol Act of 1948 mandated the use of 20% alcohol blending in fuels.[77] This law was repealed in 2000, but an ethanol blending program was mandated in 2002. Unfortunately, it has been impossible to enforce this ethanol blended biofuel due to lack of supply and bureaucracy delays.[67]

In 1990, India established biodiesel production with a goal of reducing imported oil and improving energy security. Due to the vast amount of non-agricultural land available, the drought resistant Jatropha plant was chosen for biodiesel production. In 2003, the Indian government launched the National Biodiesel Mission in order to improve technology and extraction of biodiesel and to allocate land and the implementation of the industrialization of Jatropha to biofuel.[78] In 2011 and 2012, India’s total biodiesel production was projected to grow to 3.6 million tons. Although economic development has made automobiles affordable for much of the population in India, it comes hand in hand with pollution, increased greenhouse gases and total carbon emissions.

In the Philippines the first use of biofuel dates to 1914, when alcohol was used as an engine fuel on Calamba Sugar Estate, an American-operated sugar plantation. On August 22nd 1922, The Philippine Motor Alcohol Corporation was founded, with a goal of experimenting with and producing alternative fuels. During World War II, ethanol production stumbled in the Philippines, but soon regained momentum and reached 30 million liters by 1950[79]. Again, the years to come provided cheap oil availability, and alternative fuel sources were abandoned. A Philippine representative spoke at the United Nations on this issue stating that *“the use of blended motor fuel was abandoned, for the simple reason that the gasoline interests fought hard to kill it. After such a very sad experience, we fully realize that proper legislation similar to that in India should be adopted in the Philippines”.*

Many Asian countries faced the dilemma of increasing availability of cheap Middle East petroleum-based fuels versus their alternative fuel programs. Due to this inexpensive, readily available petroleum fuel and lack of sustainability for the programs, biofuel initiatives were abandoned in these regions after the 1950s.

In 2006, the Philippines established a biofuel usage mandate that required 5% ethanol blended gasoline distribution. In 2007 legislation regarding biofuel use and consumption was enacted, the first of its kind in Southeast Asia.[80] Ethanol production in the region has continued to increase over the past ten years to current day. Nine percent ethanol blended fuel is the current standard in the country, with an aim of 20% ethanol by 2020, which isn't projected to succeed. Biodiesel production and consumption has stayed stagnant since 2009 at a 2.5% blend rate.

Brazil

Brazil made several efforts in 1931 to encourage the use of alternative fuels like ethanol, this trend continued and eventually lead to the nation's efforts in the field of biodiesel production. In 1933, Brazil established Instituto do Assucar e do Alcool for sugarcane ethanol production. During the global oil crisis in the 1970s, Brazil pushed the production of ethanol blended fuel as well as vehicles which required it. Legislation for the reduction in sales tax for the use of pure alcohol fuels and blended fuels was introduced. This set the stage for Brazil to be one of the global leaders in production and innovation in the biofuel and biodiesel industry. Brazil is the only country where the production of biofuel is profitable without tax incentives and subsidies.[81]

In 2005, based on the success of their ethanol biofuel, Brazil invested in biodiesel with legislation requiring replacement of two percent of the petroleum diesel and an increase over the next seven years to five percent. The feedstock material for biodiesel in Brazil is soy beans. Brazil also uses palm and castor beans as well. Unfortunately, the development of biodiesel production has come at the cost of the rain forests of Brazil. At the urging of the Brazilian government, drier regions of the country are encouraged to use other sources: like Jathropha in India.[65,67,82]

Biodiesel production in Brazil is projected to reach 4 billion liters. Unlike ethanol biofuel, Brazil's biodiesel production is not profitable for the country and like the rest of the international markets, requires subsidies and tax incentives. These government supports have helped maintain biodiesel production and demand, especially for local farmers and the region where the feedstock is produced.[83]

Other Biodiesel programs

In 1932, 30 industrial nations introduced tax incentives for an ethanol-petroleum fuel blending program. From these 30 nations only a few graduated to establishing sustainable methods for biodiesel production.[53]

Argentina was one of the pioneer nations to utilize biofuel from oils for diesel engines. The first diesel engine was imported to Argentina in 1916. The same year, R.J. Gutierrez of Buenos Aires University tested castor oil on the engine. Biofuel is produced in Argentina from soybeans, and despite a mandate in 2010 for five percent blended fuel, most of their biofuel is exported and isn't supported through tax reimbursements.[84]

Cuba and Panama have been able to produce 20% ethanol mixed gasoline since 1922. This is in part due to the fact that raw ethanol was cheaper than gasoline. Unfortunately, these nations efforts towards ethanol were not matched in their biodiesel efforts. Failure to subsidize biodiesel production, and political obstacles historically prevented these nations from cultivating biofuel production and consumption.[67]

Canada has gotten on board with the biofuel movement, the Canadian Renewable Fuels Association promotes the use of ethanol and biodiesel. In 2008, the production of ethanol for use as a biofuel was incentivized through the EcoEnergy for Biofuels Program. This tax reimbursement was decreased annually however, and there are few trade protections on biofuel as compared to the international market. This has resulted in the cost of blended biodiesel in Canada being 10 cents higher than the cost of petroleum diesel.[84]

BIODIESEL AN ETHICAL DILEMMA? FOOD V. FUEL AND THE ECOLOGICAL IMPACTS

In countries where fossil fuels are not available, biodiesel was found to be a practical and sustainable means to meet the fuel demands. Although numerous crops and plants have been added to the list of feedstocks for biodiesel production, it is important to realize that crops abundant in a specific region are likely needed for food supply rather than biodiesel demands.[85]

Currently, only a fraction of biodiesel comes from waste products. The majority of the biodiesel is produced from sources such as seed and other vegetable oil. This in combination with the production of other biofuels such as corn-ethanol has sparked a controversy of 'food vs fuel'. The diversion in the use of the crops from fuel purposes has added pressure to food prices. In 2007, this issue was raised at the UN Food and Agricultural Organization, with some reporters calling the use of food sources as fuel a "crime against humanity". [1] This 'feed, food and fuel' debate has raised serious question about the impact of biofuels such as biodiesel on climate change, sustainability and biodiversity.[86] Since the early 2000s, when this debate began, studies have shown differing results supporting opposing sides of the food or fuel argument: depending on how the studies are carried out and the statistical analysis methods utilized.

In addition to strains on the food supply, growing non-food biofuel feedstock can also have ecological and environmental implications. Clearing of forest lands to grow fuel in addition to rising food demands results in higher amounts of carbon dioxide being released into the atmosphere.[87] Presently, sugar cane is the largest cultivated crop along with soybean, palm and Jatropha for biofuel production. Palm oil is the infamous biodiesel crop held responsible for destroying large areas of tropical rain forests in the Amazon.[88] The growth of plants and trees for biodiesel production in South America has presented a large ecological concern. Although the growth of the biodiesel industry in countries such as Brazil will benefit the economy and lessen the dependence on fossil fuels, the land abuse has created environmental problems that reach beyond pollution caused by fossil fuel usage. Millennia-old rain forests continue to be destroyed since the push for biodiesel production in the 1980s. Palm oil is the most infamous source for biodiesel, as rain forest clear cutting in order to grow this crop has recently been publicized. For the same reason, rainforests in Indonesia and Malaysia are being destroyed and raising further concerns of sustainability.[89]

Despite the great risk to amazon forests, there is an argument that well planned palm oil use can replace pastureland and reduce the global threat on the extinction of rainforests. Compared to any biofuel, palm oil yields the highest amount of fuel per hectare. Brazil introduced a biofuels policy where 80% of the palm plantations land should count towards forest area. Following Brazil's example, smaller countries like Colombia and Ecuador are also growing the size of their palm plantations. These developing nations argue that palm plantations create more jobs compared to soy or cattle farming while sustaining biodiesel production.[90]

CONCLUSION: WHAT DOES THE FUTURE HOLD FOR BIODIESEL?

Biodiesel's inception started with the discovery of transesterification of vegetable oils. German engineer Rudolf Diesel envisioned the efficient use of vegetable oils in his engines and was also well ahead of his time in his foresight into the challenges and potentials of renewable sources. In his 1912 book he talks about alternative power sources, *"In any case, they make it certain that motor-power can still be produced from the heat of the sun, which is always available for agricultural purposes, even when all our natural stores of solid and liquid fuels are exhausted"*.[51]

There is no recorded history of the use of mono alkyl esters of fatty acids from vegetable oils as fuels documented in the literature until George Chavanne's patent in 1937. Although not a major producer of the feedstock oil crops, countries like France, Belgium, and the UK showed great interests in biodiesel manufactured from vegetable and plant oil. This interest was primarily based on the availability of the raw materials from their colonies. As the global political environment changed, priorities and energy policies changed. Interest and investment into biofuel research and production ebbed and flowed depending on the global market until it gained real traction in the early 1970s when the industrial process for the production of biodiesel was developed. In 1977 Brazilian scientist Expedito Parente patented the production. It was over a decade later when the first commercial biodiesel plant started production in Austria in 1989.[47,48,50]

The success of the biofuel industry has always hinged on geography, political climate, economics of the feedstock material and regional regulations. Countries must navigate these obstacles in order to grow their alternative energy programs. The global petroleum fuel market has historically been the driving force behind nations' quest for energy security and the subsequent use of biodiesel and alternative fuels.

In order to drive the development and production of biofuels, petroleum-based fuels have historically needed to be scarce in the market, only recently have the challenges facing humanity been motivational for this industry. Challenges like species extinction, ecosystem collapse and resource sustainability have sparked debates on climate change, energy policy and food rights. Many of these debates are aimed at constructing an optimal and sustainable energy system. Biodiesel is a good candidate to lessen the world's reliance on fossil fuels and increase energy safety, with its clean emission profile. However, with minimal subsidies allocated to biodiesel and the long argued "food v. fuel" argument, the future of biodiesel will become increasingly unstable. Production of biodiesel will rely on an ideal situation where the world is able to produce renewable feedstocks such as plants and vegetables to meet the worlds food supply and keep the cost of biodiesel competitive to fossil fuels. Unlocking the potentials of renewable energy is not a choice but a need for the future generations to survive and sustain.

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