



## Prospects of biodiesel for future energy security

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### ABSTRACT

The demand for petroleum is increasing with each passing day. This may be attributed to the limited resources of petroleum crude. In that case, it becomes utmost necessity to search for alternative fuels, which are renewable, and in that biodiesel emerges as a real solution. Because of diminishing petroleum reserves and the deleterious environmental consequences of exhaust gases from petroleum diesel, biodiesel has attracted attention during the past few years as a renewable and environmentally friendly fuel. Since it is made entirely from oils, it is renewable and biodegradable. Biodiesel is a cleaner burning fuel than diesel and a suitable replacement. It is made from non-toxic, biodegradable, renewable resources. It can be produced in many ways.

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### Introduction

Transesterification of a vegetable oil was conducted as early as 1853 by scientists E. Duffy and J. Patrick, many years before the first diesel engine became functional. Rudolf Diesel's prime model, a single 10 ft (3 m) iron cylinder with a flywheel at its base, ran on its own power for the first time in Augsburg, Germany, on 10 August 1893 running on nothing but peanut oil. In remembrance of this event, 10 August has been declared "International Biodiesel Day". It is often reported that Diesel designed his engine to run on peanut oil, but this is not the case. Diesel stated in his published papers, "at the Paris Exhibition in 1900 (*Exposition Universelle*) there was shown by the Otto Company a small Diesel engine, which, at the request of the French government ran on arachide (earth-nut or pea-nut) oil (see biodiesel), and worked so smoothly that only a few people were aware of it. The engine was constructed for using mineral oil, and was then worked on vegetable oil without any alterations being made. The French Government at the time thought of testing the applicability to power production of the Arachide, or earth-nut, which grows in considerable quantities in their African colonies, and can easily be cultivated there." Diesel himself later conducted related tests and appeared supportive of the idea.<sup>[21]</sup> In a 1912 speech Diesel said, "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."

Despite the widespread use of fossil petroleum-derived diesel fuels, interest in vegetable oils as fuels for internal combustion engines was reported in several countries during the 1920s and 1930s and later during World War II. Belgium, France, Italy, the United Kingdom, Portugal, Germany, Brazil, Argentina, Japan and China were reported to have tested and used vegetable oils as diesel fuels during this time. Some operational problems were reported due to the high viscosity of vegetable oils compared to petroleum diesel fuel, which results in poor atomization of the fuel in the fuel spray and often leads to deposits and coking of the injectors, combustion chamber and valves. Attempts to overcome these problems included heating

of the vegetable oil, blending it with petroleum-derived diesel fuel or ethanol, pyrolysis and cracking of the oils.

On 31 August 1937, G. Chavanne of the University of Brussels (Belgium) was granted a patent for a "Procedure for the transformation of vegetable oils for their uses as fuels" (fr. "*Procédé de Transformation d'Huiles Végétales en Vue de Leur Utilisation comme Carburants*") Belgian Patent 422,877. This patent described the alcoholysis (often referred to as transesterification) of vegetable oils using ethanol (and mentions methanol) in order to separate the fatty acids from the glycerol by replacing the glycerol with short linear alcohols. This appears to be the first account of the production of what is known as "biodiesel" today.<sup>[22]</sup>

Later, in 1977, Brazilian scientist Expedito Parente invented and submitted for patent, the first industrial process for the production of biodiesel.<sup>[23]</sup> This process is classified as biodiesel by international norms, conferring a "standardized identity and quality. No other proposed biofuel has been validated by the motor industry."<sup>[24]</sup> Currently, Parente's company Tecbio is working with Boeing and NASA to certify bioquerosene (bio-kerosene), another product produced and patented by the Brazilian scientist.<sup>[25]</sup>

Research into the use of transesterified sunflower oil, and refining it to diesel fuel standards, was initiated in South Africa in 1979. By 1983, the process for producing fuel-quality, engine-tested biodiesel was completed and published internationally.<sup>[26]</sup> An Austrian company, Gaskoks, obtained the technology from the South African Agricultural Engineers; the company erected the first biodiesel pilot plant in November 1987, and the first industrial-scale plant in April 1989 (with a capacity of 30,000 tons of rapeseed per annum).

Throughout the 1990s, plants were opened in many European countries, including the Czech Republic, Germany and Sweden. France launched local production of biodiesel fuel (referred to as *diester*) from rapeseed oil, which is mixed into regular diesel fuel at a level of 5%, and into the diesel fuel used by some captive fleets (e.g. public transportation) at a level of

30%. Renault, Peugeot and other manufacturers have certified truck engines for use with up to that level of partial biodiesel; experiments with 50% biodiesel are underway. During the same period, nations in other parts of the world also saw local production of biodiesel starting up: by 1998, the Austrian Biofuels Institute had identified 21 countries with commercial biodiesel projects. 100% Biodiesel is now available at many normal service stations across Europe.

In September 2005 Minnesota became the first U.S. state to mandate that all diesel fuel sold in the state contain part biodiesel, requiring a content of at least 2% biodiesel.<sup>[27]</sup>

In 2008, ASTM published new Biodiesel Blend Specifications Standards.<sup>[28]</sup>

### Properties

Biodiesel has better lubricating properties and much higher cetane ratings than today's lower sulfur diesel fuels. Biodiesel addition reduces fuel system wear,<sup>[29]</sup> and in low levels in high pressure systems increases the life of the fuel injection equipment that relies on the fuel for its lubrication. Depending on the engine, this might include high pressure injection pumps, pump injectors (also called *unit injectors*) and fuel injectors.

The calorific value of biodiesel is about 37.27 MJ/kg.<sup>[30]</sup> This is 9% lower than regular Number 2 petro diesel. Variations in biodiesel energy density are more dependent on the feedstock used than the production process. Still these variations are less than for petro diesel.<sup>[31]</sup> It has been claimed biodiesel gives better lubricity and more complete combustion thus increasing the engine energy output and partially compensating for the higher energy density of petro diesel.<sup>[32]</sup>

Biodiesel is a liquid which varies in color—between golden and dark brown—depending on the production feedstock. It is immiscible with water, has a high boiling point and low vapor pressure. \*The flash point of biodiesel (>130 °C, >266 °F)<sup>[33]</sup> is significantly higher than that of petroleum diesel (64 °C, 147 °F) or gasoline (−45 °C, −52 °F). Biodiesel has a density of ~ 0.88 g/cm<sup>3</sup>, higher than petro diesel (~ 0.85 g/cm<sup>3</sup>).

Biodiesel has virtually no sulfur content, and it is often used as an additive to Ultra-Low Sulphur Diesel (ULSD) fuel to aid with lubrication, as the sulfur compounds in petro diesel provide much of the lubricity.

### Material compatibility

- **Plastics:** High density polyethylene (HDPE) is compatible but polyvinyl chloride (PVC) is slowly degraded. Polystyrenes are dissolved on contact with biodiesel.
- **Metals:** Biodiesel has an effect on copper-based materials (e.g. brass), and it also affects zinc, tin, lead, and cast iron. Stainless steels (316 and 304) and aluminum are unaffected.
- **Rubber:** Biodiesel also affects types of natural rubbers found in some older engine components. Studies have also found that fluorinated elastomers (FKM) cured with peroxide and base-metal oxides can be degraded when biodiesel loses its stability caused by oxidation. Commonly used synthetic rubbers FKM-GBL-S and FKM- GF-S found in modern vehicles were found to handle biodiesel in all conditions.<sup>[34]</sup>

### Technical Standards

Biodiesel has a number of standards for its quality including European standard EN 14214, ASTM International D6751, and others.

### Low temperature gelling

When biodiesel is cooled below a certain point, some of the molecules aggregate and form crystals. The fuel starts to appear cloudy once the crystals become larger than one quarter of the

wavelengths of visible light - this is the cloud point (CP). As the fuel is cooled further these crystals become larger. The lowest temperature at which fuel can pass through a 45 micrometre filter is the cold filter plugging point (CFPP). As biodiesel is cooled further it will gel and then solidify. Within Europe, there are differences in the CFPP requirements between countries. This is reflected in the different national standards of those countries. The temperature at which pure (B100) biodiesel starts to gel, varies significantly and depends upon the mix of esters and therefore the feedstock oil used to produce the biodiesel. For example, biodiesel produced from low erucic acid varieties of canola seed (RME) starts to gel at approximately −10 °C (14 °F). Biodiesel produced from tallow tends to gel at around +16 °C (61 °F). There are a number of commercially available additives that will significantly lower the pour point and cold filter plugging point of pure biodiesel. Winter operation is also possible by blending biodiesel with other fuel oils including #2 low sulfurdiesel fuel and #1 diesel / kerosene.

Another approach to facilitate the use of biodiesel in cold conditions is by employing a second fuel tank for biodiesel in addition to the standard diesel fuel tank. The second fuel tank can be insulated and a heating coil using engine coolant is run through the tank. The fuel tanks can be switched over when the fuel is sufficiently warm. A similar method can be used to operate diesel vehicles using straight vegetable oil.

### Contamination by Water

Biodiesel may contain small but problematic quantities of water. Although it is not miscible with water, it is, like ethanol, hygroscopic (absorbs water at a molecular level).<sup>[35]</sup> One of the reasons biodiesel can absorb water is the persistence of mono and diglycerides left over from an incomplete reaction. These molecules can act as an emulsifier, allowing water to mix with the biodiesel. In addition, there may be water that is residual to processing or resulting from storage tank condensation. The presence of water is a problem because:

- Water reduces the heat of combustion of the bulk fuel. This means more smoke, harder starting, less power.
- Water causes corrosion of vital fuel system components: fuel pumps, injector pumps, fuel lines, etc.
- Water & microbes cause the paper element filters in the system to fail (rot), which in turn results in premature failure of the fuel pump due to ingestion of large particles.
- Water freezes to form ice crystals near 0 °C (32 °F). These crystals provide sites for nucleation and accelerate the gelling of the residual fuel.
- Water accelerates the growth of microbe colonies, which can plug up a fuel system. Biodiesel users who have heated fuel tanks therefore face a year-round microbe problem.
- Additionally, water can cause pitting in the pistons on a diesel engine.

Previously, the amount of water contaminating biodiesel has been difficult to measure by taking samples, since water and oil separate. However, it is now possible to measure the water content using water-in-oil sensors.

Water contamination is also a potential problem when using certain chemical catalysts involved in the production process, substantially reducing catalytic efficiency of base (high pH) catalysts such as potassium hydroxide. However, the supercritical methanol production methodology, whereby the transesterification process of oil feedstock and methanol is effectuated under high temperature and pressure, has been

shown to be largely unaffected by the presence of water contamination during the production phase.

#### Availability and Prices

Global biodiesel production reached 3.8 million tons in 2005. Approximately 85% of biodiesel production comes from the European Union. B99 and B100 generally cost more than petro diesel except where local governments provide a tax incentive or subsidy.

#### Production

Biodiesel is commonly produced by the transesterification of the vegetable oil or animal fat feedstock. There are several methods for carrying out this transesterification reaction including the common batch process, supercritical processes, ultrasonic methods, and even microwave methods.

Chemically, transesterified biodiesel comprises a mix of mono-alkyl esters of long chain fatty acids. The most common form uses methanol (converted to sodium methoxide) to produce methyl esters (commonly referred to as Fatty Acid Methyl Ester - FAME) as it is the cheapest alcohol available, though ethanol can be used to produce an ethyl ester (commonly referred to as Fatty Acid Ethyl Ester - FAEE) biodiesel and higher alcohols such as isopropanol and butanol have also been used. Using alcohols of higher molecular weights improves the cold flow properties of the resulting ester, at the cost of a less efficient transesterification reaction.

A lipid transesterification production process is used to convert the base oil to the desired esters. Any free fatty acids (FFAs) in the base oil are either converted to soap and removed from the process, or they are esterified (yielding more biodiesel) using an acidic catalyst. After this processing, unlike straight vegetable oil, biodiesel has combustion properties very similar to those of petroleum diesel, and can replace it in most current uses.

A by-product of the transesterification process is the production of glycerol. For every 1 tonne of biodiesel that is manufactured, 100 kg of glycerol are produced. Originally, there was a valuable market for the glycerol, which assisted the economics of the process as a whole. However, with the increase in global biodiesel production, the market price for this crude glycerol (containing 20% water and catalyst residues) has crashed. Research is being conducted globally to use this glycerol as a chemical building block.<sup>[38]</sup>

Usually this crude glycerol has to be purified, typically by performing vacuum distillation. This is rather energy intensive. The refined glycerol (98%+ purity) can then be utilized directly, or converted into other products. The following announcements were made in 2007: A joint venture of Ashland Inc. and Cargill announced plans to make propylene glycol in Europe from glycerol<sup>[39]</sup> and Dow Chemical announced similar plans for North America.<sup>[40]</sup> Dow also plans to build a plant in China to make epichlorhydrin from glycerol<sup>[41]</sup> Epichlorhydrin is a raw material forepoxy resins.

#### Production levels

In 2007, biodiesel production capacity was growing rapidly, with an average annual growth rate from 2002-06 of over 40%.<sup>[42]</sup> For the year 2006, the latest for which actual production figures could be obtained, total world biodiesel production was about 5-6 million tonnes, with 4.9 million tonnes processed in Europe (of which 2.7 million tonnes was from Germany) and most of the rest from the USA. In 2008 production in Europe alone had risen to 7.8 million tonnes.<sup>[43]</sup> In July 2009, a duty was added to American imported biodiesel in the European Union in

order to balance the competition from European, especially German producers.<sup>[44]</sup> <sup>[45]</sup> The capacity for 2008 in Europe totalled 16 million tonnes. This compares with a total demand for diesel in the US and Europe of approximately 490 million tonnes (147 billion gallons).<sup>[46]</sup> Total world production of vegetable oil for all purposes in 2005/06 was about 110 million tonnes, with about 34 million tonnes each of palm oil and soybean oil.<sup>[47]</sup>

#### Biodiesel feedstocks

A variety of oils can be used to produce biodiesel. These include:

- Virgin oil feedstock – rapeseed and soybean oils are most commonly used, soybean oil alone accounting for about ninety percent of all fuel stocks in the US. It also can be obtained from field pennycress and jatropha and other crops such as mustard, flax, sunflower, palm oil, coconut, hemp (see list of vegetable oils for biofuel for more information);
- Waste vegetable oil (WVO);
- Animal fats including tallow, lard, yellow grease, chicken fat,<sup>[48]</sup> and the by-products of the production of Omega-3 fatty acids from fish oil.
- Algae, which can be grown using waste materials such as sewage<sup>[49]</sup> and without displacing land currently used for food production.
- Oil from halophytes such as *Salicornia bigelovii*, which can be grown using saltwater in coastal areas where conventional crops cannot be grown, with yields equal to the yields of soybeans and other oilseeds grown using freshwater irrigation<sup>[50]</sup>

Many advocates suggest that waste vegetable oil is the best source of oil to produce biodiesel, but since the available supply is drastically less than the amount of petroleum-based fuel that is burned for transportation and home heating in the world; this local solution does not scale well.

#### Quantity of feedstocks required

Current worldwide production of vegetable oil and animal fat is not sufficient to replace liquid fossil fuel use. Furthermore, some object to the vast amount of farming and the resulting fertilization, pesticide use, and land use conversion that would be needed to produce the additional vegetable oil.

#### Yield

Feedstock yield efficiency per unit area affects the feasibility of ramping up production to the huge industrial levels required to power a significant percentage of vehicles.

Jatropha has been cited as a high-yield source of biodiesel but yields are highly dependent on climatic and soil conditions. The estimates at the low end put the yield at about 200 US gal/acre (1.5-2 tonnes per hectare) per crop; in more favorable climates two or more crops per year have been achieved.<sup>[62]</sup> It is grown in the Philippines, Mali and India, is drought-resistant, and can share space with other cash crops such as coffee, sugar, fruits and vegetables.<sup>[63]</sup> It is well-suited to semi-arid lands and can contribute to slow down desertification, according to its advocates.<sup>[64]</sup>

#### Efficiency and economic arguments

According to a study by Drs. Van Dyne and Raymer for the Tennessee Valley Authority, the average US farm consumes fuel at the rate of 82 litres per hectare (8.75 US gal/acre) of land to produce one crop. However, average crops of rapeseed produce oil at an average rate of 1,029 L/ha (110 US gal/acre), and high-yield rapeseed fields produce about 1,356 L/ha (145 US gal/acre). The ratio of input to output in these cases is roughly 1:12.5 and 1:16.5. Photosynthesis is known to have

an efficiency rate of about 3-6% of total solar radiation<sup>[65]</sup> and if the entire mass of a crop is utilized for energy production, the overall efficiency of this chain is currently about 1%<sup>[66]</sup> While this may compare unfavorably to solar cells combined with an electric drive train, biodiesel is less costly to deploy (solar cells cost approximately US\$1,000 per square meter) and transport (electric vehicles require batteries which currently have a much lower energy density than liquid fuels). A 2005 study found that biodiesel production using soybeans required 27% more fossil energy than the biodiesel produced and 118% more energy using sunflowers.<sup>[67]</sup>

Some typical yields		
Crop	Yield	
	L/ha	US gal/acre
Algae <sup>[n 1]</sup>	~3,000	~300, 1500-3000
Palm oil <sup>[n 4]</sup>	4752	508
Coconut	2151	230
Rapeseed <sup>[n 4]</sup>	954	102
Soy (Indiana) <sup>[59]</sup>	554-922	59.2-98.6
Peanut <sup>[n 4]</sup>	842	90
Sunflower <sup>[n 4]</sup>	767	82
1. ^ est.- see soy figures and DOE quote below. The larger estimates comes from the New York Times, "Colorado Company to Take Algae-Based Fuel to the Next Level," 11 Nov 2008, M.L. Wald 2. ^ Klass, Donald, "Biomass for Renewable Energy, Fuels, and Chemicals", page 341. Academic Press, 1998. 3. ^ Kitani, Osamu, "Volume V: Energy and Biomass Engineering, CIGR Handbook of Agricultural Engineering", Amer Society of Agricultural, 1999. 4. ^ a b c d "Biofuels: some numbers". Grist.org. Retrieved 2010-03-15.		

However, these statistics by themselves are not enough to show whether such a change makes economic sense. Additional factors must be taken into account, such as: the fuel equivalent of the energy required for processing, the yield of fuel from raw oil, the return on cultivating food, the effect biodiesel will have on food prices and the relative cost of biodiesel versus petrodiesel, water pollution from farm run-off, soil depletion, and the externalized costs of political and military interference in oil-producing countries intended to control the price of petrodiesel.

The debate over the energy balance of biodiesel is ongoing. Transitioning fully to biofuels could require immense tracts of land if traditional food crops are used (although non food crops can be utilized). The problem would be especially severe for nations with large economies, since energy consumption scales with economic output.<sup>[68]</sup>

If using only traditional food plants, most such nations do not have sufficient arable land to produce biofuel for the nation's vehicles. Nations with smaller economies (hence less energy consumption) and more arable land may be in better situations, although many regions cannot afford to divert land away from food production.

For third world countries, biodiesel sources that use marginal land could make more sense; e.g., honge oil nuts grown along roads or jatropha grown along rail lines.<sup>[69]</sup> In tropical regions, such as Malaysia and Indonesia, plants that produce palm oil are being planted at a rapid pace to supply growing biodiesel demand in Europe and other markets. Critics

argue that the removal of rainforest for palm plantations is not ecologically sound. It has been estimated in Germany that palm oil biodiesel has less than one third of the production costs of rapeseed biodiesel.<sup>[70]</sup> The direct source of the energy content of biodiesel is solar energy captured by plants during photosynthesis. Regarding the positive energy balance of biodiesel<sup>[citation needed]</sup>.

When straw was left in the field, biodiesel production was strongly energy positive, yielding 1 GJ biodiesel for every 0.561 GJ of energy input (a yield/cost ratio of 1.78). When straw was burned as fuel and oilseed rapemeal was used as a fertilizer, the yield/cost ratio for biodiesel production was even better (3.71). In other words, for every unit of energy input to produce biodiesel, the output was 3.71 units (the difference of 2.71 units would be from solar energy).

### Energy Security

One of the main drivers for adoption of biodiesel is energy security. This means that a nation's dependence on oil is reduced, and substituted with use of locally available sources, such as coal, gas, or renewable sources. Thus a country can benefit from adoption of biofuels, without a reduction in greenhouse gas emissions. While the total energy balance is debated, it is clear that the dependence on oil is reduced. One example is the energy used to manufacture fertilizers, which could come from a variety of sources other than petroleum. The US National Renewable Energy Laboratory (NREL) states that energy security is the number one driving force behind the US biofuels programme,<sup>[71]</sup> and a White House "Energy Security for the 21st Century" paper makes it clear that energy security is a major reason for promoting biodiesel.<sup>[72]</sup> The EU commission president, Jose Manuel Barroso, speaking at a recent EU biofuels conference, stressed that properly managed biofuels have the potential to reinforce the EU's security of supply through diversification of energy sources.<sup>[73]</sup>

### Environmental Effects

The surge of interest in biodiesels has highlighted a number of environmental effects associated with its use. These potentially include reductions in greenhouse gas emissions,<sup>[74]</sup> deforestation, pollution and the rate of biodegradation. According to the EPA's Renewable Fuel Standards Program Regulatory Impact Analysis, released in February 2010, biodiesel from soy oil results, on average, in a 57% reduction in greenhouse gases compared to fossil diesel, and biodiesel produced from waste grease results in an 86% reduction. See chapter 2.6 of the EPA report for more detailed information.

### Food, land and water vs. fuel

In some poor countries the rising price of vegetable oil is causing problems.<sup>[75]</sup> Some propose that fuel only be made from non-edible vegetable oils such as camelina, jatropha or seashore mallow which can thrive on marginal agricultural land where many trees and crops will not grow, or would produce only low yields.

Others argue that the problem is more fundamental. Farmers may switch from producing food crops to producing biofuel crops to make more money, even if the new crops are not edible. The law of supply and demand predicts that if fewer farmers are producing food the price of food will rise. It may take some time, as farmers can take some time to change which things they are growing, but increasing demand for first generation biofuels is likely to result in price increases for many kinds of food. Some have pointed out that there are poor farmers

and poor countries who are making more money because of the higher price of vegetable oil.

Biodiesel from sea algae would not necessarily displace terrestrial land currently used for food production and new algaculture jobs could be created.

#### Current research

There is ongoing research into finding more suitable crops and improving oil yield. Using the current yields, vast amounts of land and fresh water would be needed to produce enough oil to completely replace fossil fuel usage. It would require twice the land area of the US to be devoted to soybean production, or two-thirds to be devoted to rapeseed production, to meet current US heating and transportation needs.

Specially bred mustard varieties can produce reasonably high oil yields and are very useful in crop rotation with cereals, and have the added benefit that the meal leftover after the oil has been pressed out can act as an effective and biodegradable pesticide.

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