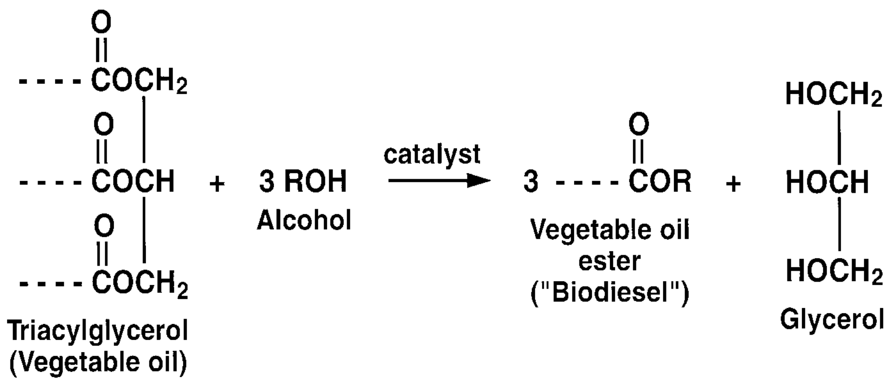

The transesterification reaction. Currently, the preferred alcohol is methanol (R = CH_3).

Historical perspectives on vegetable oil-based diesel fuels

R. Diesel

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Biodiesel, defined as monoalkyl esters of vegetable oils or animal fats (Scheme 1), is a promising alternative fuel for use in compression-ignition (diesel) engines and is being produced or used commercially in numerous countries around the world, including the United States, Austria, the Czech Republic, France, Germany, Italy, Malaysia, and Sweden.

It is generally known that vegetable oils were tested as diesel fuels well before the energy crises of the 1970s and early 1980s generated renewed interest in alternative fuels, but details on the first uses (until the early 1950s) are often unclear or presented inconsistently in the literature. Valuable insights into the use of vegetable oils and their derivatives as diesel fuels were achieved during that time, only to be rediscovered beginning in the late 1970s. This article will discuss the history of biodiesel or, more generally, that of vegetable oil-based diesel fuels and correlate it with current use. Most literature references used here were found through a *Chemical Abstracts* search or are listed in a publication summarizing literature prior to 1949 on fuels from agricultural sources (1). After the 1940s, literature on vegetable oil-based diesel fuels is very sparse until the late 1970s. Although discussed later in this article in more detail, two references (2,3) describing the first use of a fuel meeting the current definition of biodiesel are worth close examination.

THE ORIGINAL DEMONSTRATION

A relatively common literature statement on the early use of vegetable oils as diesel fuels is that Rudolf Diesel, the inventor of the engine that bears his name, tested "his" engine on peanut oil at the 1900 World's Fair in Paris, the Exposition Universalle. A biography of Diesel by Nitske and Wilson (4) often is cited as a source. On page 139 of that biography, the statement is made that "as the nineteenth century ended, it was obvious that the fate and scope of the internal-combustion engine were dependent on its fuel or fuels. At the Paris exposition of 1900, a Diesel engine, built by the French Otto Company, ran wholly on peanut oil. Apparently none of the onlookers was aware of this. The engine, built especially for that type of fuel, operated exactly like those powered by other oils."

Unfortunately, the bibliography in that biography (4) does not clarify where the authors obtained this information nor does it list references to certain articles by Diesel that will be discussed later in this paper. Thus, according to Nitske and Wilson, the peanut oil-powered diesel engine at the 1900 World's Fair in Paris was built specifically to use that fuel, which is not consistent with later statements by Diesel, as discussed below. Furthermore, that biography implies that it was not necessarily Diesel who conducted the demonstration and that he was not the source of the idea of using vegetable oils as fuel. This interpretation is corroborated by Diesel's later statements. The idea for using peanut oil appears to have originated instead within the French government, according to Diesel. However, Diesel conducted related tests in later years.

A *Chemical Abstracts* search yielded references to papers by Diesel in which he reflected on that event in 1900. Two references (5,6) related to a presentation Diesel made to the Institution of Mechanical Engineers (of Great Britain) in March 1912 (apparently in the last few years of his life, Diesel spent considerable time traveling to promote and to discuss his engine, according to the biography by Nitske and Wilson). In any case, Diesel states in those papers that *"at the Paris Exhibition in 1900 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, and worked so smoothly that only very 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 which can be easily cultivated there, because in this way the colonies could be supplied with power and industry from their own resources, without being compelled to buy and import coal or liquid fuel.*

"This question has not been further developed in France owing to changes in the Ministry, but the author resumed the trials a few months ago. It has been proved that Diesel engines can be worked on earth-nut oil without any difficulty, and the author is in a position to publish, on this occasion for the first time, reliable figures obtained by tests: Consumption of earth-nut oil, 240 grammes (0.53 lb.) per brake horsepower-hour; calorific power of the oil, 8600 calories (34,124 British thermal units) per kg, thus fully equal to tar oils; hydrogen 11.8 per cent. This oil is almost as effective as the natural mineral oils, and as it can also be used for lubricating oil, the whole work can be carried out with a single kind of oil produced directly on the spot. Thus this engine becomes a really independent engine for the tropics."

Diesel continued that (note the prescient concluding statement) *"similar successful experiments have also been made in St. Petersburg with castor oil; and animal oils, such as train-oil, have been used with excellent results. The fact that fat oils from vegetable sources can be used may seem insignificant today, but such oils may perhaps become in course of time of the same importance as some natural mineral oils and the tar products are now. Twelve years ago, the latter were not more developed than the fat oils are today, and yet how important they have since become. One cannot predict what part these oils will play in the Colonies in the future. 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."*

Diesel also wrote the book *Die Entstehung des Dieselmotors,* published by Verlag von Julius Spring, Berlin, in 1913, in which he referred to the use of peanut oil in a diesel engine at the Paris World's Fair in 1900. However, the statements in that book are considerably less detailed than those in the other two references (5,6).

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.

—Diesel

BACKGROUND AND SOURCES

The aforementioned background on using vegetable oils to provide European tropical colonies, especially those in Africa, with a certain degree of energy self-sufficiency can be found in the related literature throughout the 1940s. Palm oil was often considered as a source of diesel fuel in the "historic" studies, although the diversity of oils and fats as sources of diesel fuel, an important aspect again today, and striving for energy independence were reflected in other "historic" investigations. Belgium, France, and Italy particularly appear to have been interested in vegetable oil fuels at the time, although several British and German papers were published. Reports from other countries also reflect a theme of energy independence.

Vegetable oils also were used as emergency fuels and for other purposes during World War II. For example, Brazil prohibited the export of cottonseed oil in order to substitute it for imported diesel fuel (7). Reduced imports of liquid fuel were also reported in Argentina, necessitating the commercial exploitation of vegetable oils (8). China produced diesel fuel, lubricating oils, "gasoline," and "kerosene," the latter two by a cracking process, from tung and other vegetable oils (9,10). However, the exigencies of the war caused hasty installation of cracking plants based on fragmentary data (9). Researchers in India, prompted by the events of World War II, extended their investigations on ten vegetable oils for development as a domestic fuel (11). Work on vegetable oils as diesel fuel ceased in India when petroleum-based diesel fuel again became available plentifully at low cost (12). The Japanese battleship *Yamato* reportedly used edible refined soybean oil as bunker fuel (13).

Concerns about the rising use of petroleum fuels and the possibility of resultant fuel shortages in the United States in the years after World War II played a role in inspiring a "dual fuel" project at The Ohio State University (Columbus, Ohio), during which cottonseed oil (14) and corn oil (15), and blends thereof with conventional diesel fuel, were investigated.

Once again, energy security perspectives have become a significant driving force for the use of vegetable oil-based diesel fuels, although environmental aspects (mainly reduction of exhaust emissions) play a role at least as important as energy security. For example, in the United States, the Clean Air Act Amendments of 1990 and the Energy Policy Act of 1992 mandate the use of alternative, or "clean," fuels in regulated truck and bus fleets. Amendments to the Energy Policy Act enacted into law in 1998, which provide credits for biodiesel use (also in blends with conventional diesel fuel), are a major reason the use of biodiesel in the United States is increasing significantly.

In modern times, biodiesel is derived, or has been reported to be producible from, many different sources, including vegetable oils, animal fats, used frying oils, and even soapstock.

Generally, factors such as geography, climate, and economics determine which vegetable oil is of most interest for potential use in biodiesel fuels. Thus, in the United States, soybean oil is considered as a prime feedstock; in Europe, it is rapeseed (canola) oil; and in tropical countries, it is palm oil. As noted above, different feedstocks were investigated in the "historic" times. These included palm oil, soybean oil, cottonseed oil, castor oil, and somewhat less common oils, such as babassu (16), as well as nonvegetable sources such as industrial tallow (17) and even fish oils (18–21). Walton (22) summarized results on 20 vegetable oils (castor, grapeseed, maize, camelina, pumpkin seed, beechnut, rapeseed, lupin, pea, poppyseed, groundnut, hemp, linseed, chestnut, sunflower seed, palm, olive, soybean, cottonseed, and shea butter). He also pointed out (22) that "at the moment the source of supply of fuels is in a few hands, the operator has little or no control over prices or qualities, and it seems unfortunate that at this date, as with the petrol engine, the engine has to be designed to suit the fuel whereas, strictly speaking, the reverse should obtain—the fuel should be refined to meet the design of an ideal engine." More insights can be gained by consulting the references listed in this article.

Although environmental aspects played virtually no role in promoting the use of vegetable oils as fuel in "historic" times and no emissions studies were conducted, it is still worthwhile to note some allusions to this subject from that time.

- "In case further development of vegetable oils as fuel proves practicable, it will simplify the fuel problems of many tropical localities remote from mineral fuel, and where the use of wood entails much extra labor and other difficulties connected with the various heating capacities of the wood's use, to say nothing of the risk of indiscriminate deforestation" (23).
- "It might be advisable to mention, at this juncture, that, owing to the altered combustion characteristics, the exhaust with all these oils is invariably quite clean and the characteristic diesel knock is virtually eliminated" (22).
- Observations by other authors included: "invisible" or "slightly smoky" exhausts when running an

engine on palm oil (24); clearer exhaust gases (25); in the case of use of fish oils as diesel fuels, the exhaust was described as colorless and practically odorless (21).

The visual observations of yesterday have been confirmed in "modern" times for biodiesel fuel. Numerous recent studies have shown that most exhaust emissions are reduced when using biodiesel fuel.

Technical aspects

The kinematic viscosity of vegetable oils is about an order of magnitude greater than that of conventional, petroleum-derived diesel fuel. High viscosity causes poor atomization of the fuel in the engine's combustion chambers and ultimately results in operational problems, such as engine deposits. Since the renewal of interest during the late 1970s in vegetable oil-derived fuels, four possible solutions to the problem of high viscosity have been investigated: transesterification, pyrolysis, dilution with conventional petroleum-derived diesel fuel, and microemulsification (26).

Transesterification is the most common method and leads to monoalkyl esters of vegetable oils and fats, now called biodiesel when used for fuel purposes. Briefly, it consists of reacting the vegetable oil feedstock with an alcohol, usually methanol, in the presence of a catalyst, usually a base such as sodium or potassium hydroxide, to give the corresponding vegetable oil (usually methyl) esters. Methyl esters are the most common form of biodiesel, largely due to methanol being the least expensive alcohol.

Artificial "gasoline," "kerosene," and "diesel" were obtained in China from tung oil and other oils. Other oils that were used in such an approach included fish oils, linseed oil, castor oil, palm oil, and cottonseed oil.

The high viscosity of vegetable oils as a major cause of poor fuel atomization resulting in operational problems such as engine deposits was recognized early (24,26–28). Although engine modifications such as higher injection pressure were considered (27,29), reduction of the high viscosity of vegetable oils usually was achieved by heating the vegetable oil fuel (24,27). Often the engine was started on petrodiesel and, after a few minutes of operation, was then switched to the vegetable oil fuel, although a successful cold-start on high-acidity peanut oil was reported (30). Advanced injection timing was a technique also employed (31). Seddon (32) gives an interesting practical account about a truck that operated successfully on different vegetable oils using preheated fuel.

Pyrolysis, cracking, or other methods of decomposition of vegetable oils to yield fuels of varying nature is an approach that accounts for a significant amount of the literature in "historic" times. Artificial "gasoline," "kerosene," and "diesel" were obtained in China from tung oil (9) and other oils (10). Other oils that were used in such an approach included fish oils (16–18), linseed oil (33), castor oil (34), palm oil (35), and cottonseed oil (36).

The other approaches—microemulsification and dilution with petrodiesel—appear to have received little or no attention during the "historic" times of studies on vegetable oils as diesel fuel. However, the use of blends of conventional diesel fuel with cottonseed oil (14), corn oil (15), and linseed oil (18) has been described. Ilieff (37) used alcohol (ethanol) for improving the atomization and combustion of highly viscous castor oil.

Various other technical aspects, the effect of different kinds of vegetable oils relative to corrosion and lube oil dilution and contamination, etc. have been studied (38).

The first 'biodiesel'

Walton (22) recommended that "to get the utmost value from vegetable oils as fuel it is academically necessary to split off the triglycerides and to run on the residual fatty acid. Practical experiments have not yet been carried out with this; the problems are likely to be much more difficult when using free fatty acids than when using the oils straight from the crushing mill. It is obvious that the glycerides have no fuel value and in addition are likely, if anything, to cause an excess of carbon in comparison with gas oil."

Although Walton's statement points in the direction of what is now termed biodiesel by recommending the elimination of glycerol from the fuel, some remarkable work performed in Belgium and its former colony the Belgian Congo (known after its independence for a long time as Zaire) deserves more recognition than it has received. Indeed, it appears that Belgian patent 422,87, granted on Aug. 31, 1937, to G. Chavanne (of the University of Brussels), constitutes the first report on what is today known as biodiesel. It describes the use of ethyl esters of palm oil (although other oils and methyl esters are mentioned) as diesel fuel. These esters were obtained by acid-catalyzed transesterification of the oil (base catalysis is now more common). This work has been described in more detail (2).

Of particular interest is a related extensive report published in 1942 on the production and use of palm oil ethyl ester as fuel (3). That work described what was probably the first test of an urban bus operating on biodiesel. A bus fueled with palm oil ethyl ester served the commercial passenger line between Brussels and Louvain (Leuven) in the summer of 1938. Performance of the bus operating on that fuel reportedly was satisfactory. It was noted that the viscosity difference between the esters and conventional diesel fuel was considerably less than that between the parent oil and conventional diesel fuel. Also, the article pointed out that the esters are miscible with other fuels. That work also discussed what is probably the first cetane number (CN) testing (CN is a combustion-related diesel fuel quality index) of a biodiesel fuel. On page 52 of that report, CN of palm oil ethyl ester was reported as approximately 83 (relative to a high-quality standard with CN 70.5 and a low-quality standard of CN 18 and diesel fuels with CN of 50 and 57.5). Thus, those results agree with "modern" work reporting relatively high CN for such biodiesel fuels.

In more recent times, use of methyl esters of sunflower oil to reduce the viscosity of vegetable oil was reported at several technical conferences in 1980 and 1981 (39–41) and marks the beginning of the rediscovery and eventual commercialization of biodiesel.

A final thought should be given to the term "biodiesel" itself. A *Chemical Abstracts* search (using the "SciFinder" search engine with "biodiesel" as the key word) yielded first literature use of the term biodiesel in a Chinese paper published in 1988 (42). The next paper using that term appeared in 1991 (43) and from then on the use of the term "biodiesel" in the literature has expanded exponentially.

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The numbered references are available at the inform *portion (netlink: www.aocs.org/press/inform.htm) of the AOCS Internet page. Persons who have e-mail but do not have Internet access should send a request for references to inform@aocs.org. References also will be sent by fax upon a request to* inform *by fax (217-351-8091) or by mail (*inform*, P.O. Box 3489, Champaign, IL 61821-3489).*❑

To make a diesel vehicle able to cope with WVO, you essentially install a parallel fuel system with hardware that is resistant to the specific corrosive qualities of vegetable oil. This system also needs to be heated to keep the oilâ€™s viscosity low. Hereâ€™s the basic procedure, although some applications might require extra parts or steps. 1. Install a second tank for the veggie oil. The engine will start on diesel, and once warmed up, lines from the engineâ€™s cooling system provide heat to warm the WVO. (Local veg-oil mechanic Joe McEachern prefers to switch to a 205-degree engine thermostat fo Using vegetable oil as a fuel without paying fuel tax on it is considered tax evasion. â€¢ The U.S. Environmental Protection Agency (EPA) frowns on using vegetable oil in engines designed to burn diesel fuel because the emissions are not the same.Â Using vegetable oil instead of diesel fuel could quite likely affect the emissions from your car, Millett says. â€œAlso, a vehicle has to be modified to run on vegetable oil.â€ Jones says.Â In cold weather, the biologically-based diesel has to be mixed with conventional diesel because it has a tendency to coagulate at very low temperatures. Using waste vegetable oil requires a substantial initial investment, especially if like me one is mechanically inexperienced and must depend on others to do all the installation work. Hydrotreated Vegetable Oil (HVO) is a paraffinic bio-based liquid fuel originating from many kinds of vegetable oils, such as rapeseed, sunflower, soybean, and palm oil, as well as animal fats (Aatola et al., 2008). It can be used in conventional diesel engines, pure or blended with fossil diesel (petrodiesel). Although largely unproven, HVO substitutes directly petrodiesel or blend in any proportion with it, without modification of CI engines (Soo-Young, 2014). As it has been mentioned for biodiesel, vegetable feedstocks compete with food production. Therefore, alternative non-food oils such Biodiesel is a vegetable oil-based fuel that runs in diesel engines â€” cars, buses, trucks, construction equipment, boats, generators, and oil home heating units. Itâ€™s usually made from soy or canola oil, and can also be made from recycled fryer oil. You can blend it with regular diesel or run 100% biodiesel. What are the benefits of using Biodiesel? No Engine Conversions. Biodiesel runs in any conventional, unmodified diesel engine. No engine modifications are necessary to use biodiesel and there is no engine conversion. In other words, you just pour it into the fuel tank. Vegetable oil can be used as diesel fuel just as it is, without being converted to biodiesel. The downside is that straight vegetable oil (SVO) is much more viscous (thicker) than conventional diesel fuel or biodiesel, and it doesn't burn the same in the engine -- many studies have found that it can damage engines.Â The central problem in using vegetable oil as diesel fuel is that vegetable oil is much more viscous (thicker) than conventional diesel fuel (petro-diesel, DERV, "dino-diesel"). It's 11 to 17 times thicker.Â Recent comment at the British-based vegoil-diesel mailing list: "The often mentioned 3% mix of white spirit does nothing other than make you think your 'modified' fuel is doing no damage to your fuel pump." (Oct 2005).