BIODIESEL

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Keywords: biodiesel, fatty acid methyl esters, transesterification, methanol, diesel, alternative fuels

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Summary

The last few years have seen an increase in the interest in using new fuels that have improved ecological characteristics over conventional ones when burned or spilled into the environment. One of the most successful has been the introduction of biodiesel, a fuel made of using a chemically catalysed transesterification of vegetable oils or animal fats. Numerous advantages are attached to this fuel which make its use desirable, although it is still relatively expensive to manufacture with respect to petroleum diesel. However, a host of test runs have been carried out on vehicle fleets around the world, and legislation has been extended to such vehicles to make their use more widespread. The general success of the programs has only been tempered by the fact that its full potential impact on conventional diesel–fuelled vehicles is still limited, due principally to the availability of the necessary raw materials.

1. Introduction

The twentieth century has seen many advances in various technological fields, with the most popularized ones including the Apollo moon program, the computer industry, and engineering feats such as the Hoover Dam. However, these accomplishments would not have been possible without oil, whether as a power source or a raw material for the manufacture of plastics. Oil is the golden fluid of our age, it has given us the power we need to drive the turbines for electricity generation, the plastics used in our cars, chairs, appliances, and clothes, to name but a few. But one feature we associate even more with oil than any other is perhaps the automobile, a symbol of the freedom of individual travel, based on the internal combustion engine, itself an old concept. Despite this romanticized ideal, the human race has risked much to accommodate its whims. The pollution created by cars has become infamous in its own right, with issues of sulphur, lead, nitrogen oxides and particle emissions becoming commonplace and being raised with increasing alarm as time goes on. Despite increased efficiencies, cars still produce the daily "city smog" attributed to numerous cities around the world, including Los Angeles, New Delhi, and Bangkok. Health issues have been raised concomitantly as evidence has mounted for lead poisoning and a dramatic increase in the numbers of asthma sufferers has occurred. The West has been at the forefront in phasing out leaded petrol and using catalytic converters on cars that use unleaded fuel. Most of the domestic car market uses petrol, but a significant portion use diesel fuel, as do lorries, farm, and most large transport vehicles. The diesel engine is more efficient than the petrol one, but sluggish performance previously attributed to these engines made them less popular than petrol–driven cars. However, after several well–publicized environmental catastrophes and the subsequent rise in the political clout of the "green parties", solutions for the pollution–potential of all major oil derivative–using vehicles has been sought. One obvious aspect that has been examined is car fuel.

Petrol cars have undergone numerous pollution–decreasing upgrades over time, although at least one is now undergoing reversal. The removal of lead from petrol was a first step, with engines modified to cope without the lubricating effect of the additive. Numerous US initiatives have used gasohol, a petrol–ethanol blend aimed at essentially oxygenating the petrol to ensure more complete combustion. Unfortunately these two compounds tend to separate over time, leading to the introduction of MTBE (methyl *tert*–butyl ether). The advent of the Clean Air Act in the US mandated the use of certain prescribed oxygenate levels, however MTBE has recently fallen from favor, with Congress currently considering amending the Act while the Californian state government is also repealing its own stringent MTBE additive legislation. Formerly seen as a powerful answer to the combustion problem, MTBE has been found to be leaking from storage tanks into the ground water. Although the leaks themselves are to blame, the fact that they are unlikely to be stopped and that MTBE is considerably more miscible with water than petrol added to re-evaluated toxicity data has promised the MTBE era to be a short one.

Another approach has been that seen in Brazil, where the two world oil crises had a devastating impact. As a result, agriculture was geared to the growing and harvesting of sugar cane, which was subsequently fermented and distilled to make ethanol. Cars originally drove on petrol–ethanol blends but were later made to drive on pure ethanol (see also chapter *Production of Alcohol for Fuel and Organic Acids*). However, as the market price of oil became depressed again, ethanol–fuelled cars became more expensive than their petrol–fuelled counterparts, leading to a reversal of fortunes for the industry. The result has recently been the re–emergence of blended fuel cars on the roads of Brazil. However, apart from this single vast country and economy adopting what may be felt to be radical measures to combat not pollution but a much more powerful enemy, the cost of world oil, no other good alternatives exist. Any candidate would have to not only possess the technical, safety, and financial requirements that would be under consideration, but also practicality. Any fuel or oxygenate would need to be able to be produced in the quantities required, and require little or no car engine modifications to be economically viable. The unsuitability of either ethanol or MTBE has led to an uncertain future for oxygenated fuels and the environments that suffer their pollution.

However, there is one automotive fuel whose success has given cause for optimism. Diesel–fuelled cars, often labeled as the villains in the car industry, have had a different option presented to them in the form of biodiesel. This has now taken the general form of fatty acid methyl esters made directly from plant oils. These compounds are relatively simple to manufacture and have now generated a proven track record in the industry. The obstacles that exist are primarily political, rather than technological, presenting an envious position for the scientist but not necessarily governments.

2. The Approaches

When the idea of biodiesel first emerged, a number of options were examined for the manufacture of such a fuel. The criteria that emerged were several; the fuel had to be simple to manufacture, cheap, safe, and require little or no change to existing diesel engines. The first attempts were made with the obvious first choice of readily–available potential fuels: vegetable oils . Their direct use in diesel engines has been attempted, however their high viscosity was found to lead to poor flow and atomization characteristics within the engines. Although clearly an attractive option from a financial standpoint, they were been found to solidify at intermediate temperatures, which was impractical if they were to be used at low ambient temperatures found in temperate climates. (Palm oil starts to solidify at temperatures below 30 °C). Oil blends containing over 20 percent plant oil mixed with conventional diesel fuel resulted in erratic engine operation with characteristic deposits forming on the fuel injectors, so higher proportions are impractical. Furthermore, the cetane number for most plant oils is between 35 and 40, that is, short of the 45 necessary for diesel engines. In addition, plant oils have heat contents approximately 10 percent lower than Grade No. 2–D diesel fuel. Research has identified four possible approaches towards solving these problems.

Dilution (fuel blending) encompasses the mixing of Grade No 2–D diesel fuel with plant oil. It has been found that a solution of up to 20 percent plant oil (safflower seed oil) in diesel fuel can be tolerated by diesel engines without significant problems. However, their applicability in diesel engines over a long period of time is in some doubt, and the inherent problem of viscosity is not solved but rather reduced. To compound the problem, plant oils and diesel fuel have been shown to separate after time. This is a problem that has already been highlighted in the storage of gasohol, and, short of ensuring proper mixing during storage (which would be prohibitively expensive), this cannot be viewed as a solution. Poorly mixed components would cause engine failure and therefore be economically unviable.

Microemulsification requires the blending of diesel fuel with short chain alcohols aided by ionic or non–ionic amphiphiles. A microemulsion can be defined as a colloidal equilibrium dispersion of optically isotropic fluid microstructures with dimensions generally in the 1 to 150 nm range, formed spontaneously from two normally immiscible liquids and one or more amphiphiles. Essentially, emulsifiers are used to blend together certain components that would normally not mix. A common example of their use would be the common household detergents that are able to dissolve fats or oils in water, allowing cleaning to take place. Studies have found that satisfactory mixing of methanol with triolein was achieved with a 4:1 molar ratio of 2–octanol and polyoxyethylene(4)lauryl ether. The viscosity achieved lay within the range of 2–D diesel fuel, however the heating value was lower due to the alcohol content of the emulsion. Furthermore, there are doubts as to the financial feasibility on a large scale.

Another option that was examined was pyrolysis , which is sometimes referred to as thermal cracking. It is a process that breaks apart the triglyceride molecule using heat and a catalyst. These procedures, requiring high temperatures (300–500 °C) and catalysts, have been evaluated. It was noted that the degree of saturation played a role in the yield of hydrocarbon obtained; higher degrees of saturation led to higher yields of hydrocarbon free of oxygen groups. Catalysis using Al_2O_3 was found to minimize aromatic and unsaturated products. Soybean oil has been subjected to pyrolysis, yielding 31 percent alkanes (of which 75 percent were similar to those found in No. 2–D diesel fuel) and 28 percent alkenes by weight. Reactors have been designed that included hydrotreatment (removal of oxygen), hydrogenation, and pyrolysis in their systems. Up to 80 percent of feedstocks were converted to diesel fuel. Unfortunately, these relatively low yields, in conjunction with the costs and conditions required for their production, make this option unattractive.

Transesterification of plant oils to their corresponding methyl esters and glycerol addresses the issue of viscosity directly. Viscosity values for palm kernel oil and its corresponding methyl ester are 66.3 and 7.93 centipose, respectively; No. 2 diesel has a value of 3.80 centipose at 21 °C. This makes the potential use of the methyl (or ethyl) ester attractive, especially since the difference in the heating value of plant oils and their corresponding methyl (or ethyl) esters is negligible, with these values being about 10 percent lower than that for No. 2 diesel fuel. Furthermore, ethanol (see also chapter *Production of Alcohol for Fuel and Organic Solvents*) is widely available from biomass, and methanol from coal and natural gas.

Transesterification has become the preferred method for the synthesis of fatty acid methyl esters, compounds that have chemical characteristics similar to those of conventional diesel fuel in terms of combustion within modern diesel engines, provided that the reacted oils have the correct carbon chain length. Such oils include soybean, canola, and industrial rapeseed oils; for instance, the crop of choice in Europe has been rapeseed. Advantages of biodiesel over petroleum–derived diesel fuel include sulfur and aromatic contents so low as to be considered absent. Furthermore, diesel engines need not be modified to run on biodiesel, and emissions testing shows lower production of carbon monoxide, unburned hydrocarbons, and particulate matter than in the case of diesel produced from petroleum. These environmental considerations are of major importance to urban areas suffering from poor air quality, such as Los Angeles or Denver. Two other advantages exist: the vegetable matter remaining after oil extraction can be used as feed for livestock; and a valuable by–product of the transesterification reaction, glycerol, can be isolated and sold separately.

Once the transesterified fatty acids have been made, another previous option becomes a possibility again, their blending with conventional diesel fuel. This allows some of the favorable environmental aspects to be maintained while keeping production costs low. This blended fuel, also referred to as B20 as it is a 20 percent blend of biodiesel with petroleum diesel, has led the way in many developmental projects, some of which will be discussed below.

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Biographical Sketch

Ariel Louwrier was awarded his PhD in Biochemistry at the University of Kent (UK) in 1993 before moving to the USA to complete postdoctoral work on a Biodiesel–related project in non–aqueous enzymology at the Massachusetts Institute of Technology. He then returned to the UK, and is now the Technical Manager of Advanced Biotechnologies Ltd., a molecular biology reagents and plastics company. He has published widely and maintains his interest in alternative fuels.