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Biodiesel Fuel

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GRADE B+

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'Biofuels' is a broad term that includes the lowest technology, older fuels as well as some of the newest, highest tech fuels. In contrast to "fossil fuels" that were created millions of years ago, biofuels are "contemporary" materials such as wood, charcoal, and crop and animal waste, all of which are in wide use today throughout the developing world, where they expose their users to highly elevated levels of indoor air pollution, and lead to hundreds of thousands of excess illnesses and deaths each year. In advanced societies, older biofuels, such as wood, have maintained a toe-hold in space heating applications, but the newer biofuels are used primarily in the transportation sector. This application has deep roots: the Ford Model T was a 'flex fueled' vehicle sold early in the last century, able to run on ethanol, which at that time was a farmproduced biofuel. In the intervening century, fossil fuels largely replaced biofuels in transportation applications. However, rising concerns about energy security and the environmental impacts of fossil fuel dependence has created a resurgence in interest in transportation biofuels.

Transportation-related biofuels can be divided into two broad categories: biodiesel, which can replace conventional fossil fuel-derived diesel fuel; and ethanol and related fuels that serve as substitutes for fossil fuel-derived gasoline. Use of these fuels sometimes requires varying degrees of blending with petroleum-based fuels, or engine modification, although some biofuels and many blends can be used as drop-in replacements for diesel or gasoline fuels. Currently

most gasoline fuels contain a small quantity of bio-ethanol, up to 10%, to increase oxygen content and hence octane rating, and to provide fleet-wide reductions of pollutants such as carbon monoxide. Biodiesel sales have been growing rapidly since 2005, but they currently account for less than 2% of diesel sales.

Production of, and emissions from, each biofuel is a complex topic of its own. Here we focus on biodiesel, and specifically, on the less-considered aspects of the environmental impacts of biodiesel fuel.

SOURCE OILS

Rising concerns surrounding energy security and the environmental impacts of fossil fuel dependence has created a resurgence in interest in transportation biofuels.

The future of biodiesel is promising for sources such as Jatropha, with high yields, relative lack of competition with food crops, and potential to contribute to sustainable development.

Biodiesel fuels can be divided into two groups: fuels certified by the appropriate standards organization (the American Society for Testing and Materials in the United States), and unprocessed fuels used directly with minimal modifications. Certified fuels have undergone "esterification" to create a product with similar characteristics as diesel fuels. This reduces the viscosity of the fuel to avoid flow and plugging problems. Any plant or animal oil can be converted into certified biodiesel, and biodiesel fuels have been produced from dozens of raw materials on small scales. These raw materials or source oils are also known as feedstocks.

Commercial production of biodiesel fuel currently uses primarily soy (North America and Brazil), canola or rapeseed (Europe and North America), and palm oil (South East Asia). Waste cooking oil and animal fats, known as yellow grease, are also increasingly recovered for biodiesel production. While some yellow grease would end up in a landfill, some would find other uses, such as an animal feed additive or a spray for roads to control dust. While the magnitudes of the advantages and disadvantages of first generation crop-based biodiesel fuels are currently hotly debated, they can clearly impact food production activities and potentially drive up food prices. Additionally, they create pressure to convert currently undeveloped land to agricultural production. Palm oil production in particular has already caused extensive deforestation in parts of S.E. Asia.

A number of alternative fuels have potential to circumvent or partly avoid the "food vs. fuel" debate. Primary among these are algae oil and a handful of tropical oil seeds such as Jatropha curcas or Pongamia pinnatta (karanja or honge nut). Jatropha, a small South American tree with oil-rich seeds,

Jatropha

was used in Portuguese colonies in the 1600's to produce lamp oil and medicine. It is grown widely in the tropics for its many desirable qualities. It requires little rain, grows in marginal soils, is not invasive, and lives for 50 years. Because animals do not graze on it, it is favored for fencing and shade. The oil of most varieties is not edible. Jatropha's potential as a source of oil for biodiesel and other applications such as soap is slowly being recognized, and it has a promising role in supplying both energy and revenue in the developing world. While there is substantial existing potential for its expansion into marginal lands, including along rail lines and abandoned agricultural land, like other agricultural crops, it may also encourage conversion of wild lands.

Algae are a promising nextgeneration biodiesel source, although commercialization is thought to be at least 5 to 10 years away.

Algae are another promising next-generation biodiesel source. Of the many thousands of algae species known, dozens have potential to produce high oil yields under a wide range of conditions. Algae can grow in saline and brackish water, use far less space than crop-based feedstocks, and unlike higher productivity species such as jatropha and oil palm, can be grown in northern climates. Much interest in algae arises from their potential to reduce carbon emissions from power plant and industrial stack gasses, a role for which they have little competition. This application may boost the cost-effectiveness of algae oil production; in addition to benefiting from elevated CO $_2$ concentrations in stack gasses, their processing can take advantage of waste heat to aid in drying the algae for harvest. This process may also earn emissions credits by consuming some of the CO $_2$ emissions.

About one billion dollars in research and investment funding has been committed to algae biofuel research in just the past two years in the United States. Even so, commercialization is thought to be at least 5 to 10 years away. San Diego is benefitting from the influx of investment. The city has been dubbed the "algae biofuel company capitol of the world", with at least eight companies actively working toward developing algae biodiesel and other biofuels for market, and an active and coordinated university research program.

SPACE AND LANDUSE

Soy and rapeseed are land-intensive, producing only 50- 100 gallons of biodiesel fuel per acre. At this yield, all of the agricultural land in the United States could produce only 40 – 80% of current US diesel fuel consumption. Waste oil clearly does not directly use land, but it has total potential to produce only about 0.25% of current US transportation diesel consumption. Less land intensive fuels are needed to provide a substantial fraction of current liquid fuel supply. Tropical crops such as palm and jatropha are about 5-10 and 1.5- 8 times, respectively, more

productive per hectare than soy. Algae has the potential to produce more biodiesel (or gasoline, jet fuel, etc.) per acre by factors of 8 to as high as 50 or more compared to soy, another reason it is the focus of so much research and development.

LIFE CYCLE ANALYSIS

Life cycle analysis aims to account for the impacts and fuel consumption associated with producing a product over its entire lifecycle, from its initial production through its final consumption or disposal. Several lifecycle analyses have been carried out for biodiesel fuel, with a range of conclusions. Calculations are usually based on the fossil fuel consumed to produce the biodiesel. While bioethanol calculations sometimes conclude more fossil fuel was consumed than bioethanol (and useful byproducts) produced, biodiesel production is uniformly associated with a net positive energy balance. Soy and rapeseed feedstocks generally have the lowest energy balance, estimated as producing 1.2- 3.6 energy units out per energy unit of fossil fuel consumed.

Not all of the energy accounted for is in the biodiesel product; some of it is in useful agricultural and industrial processing byproducts such as fodder and glycerin. Waste oil feedstock is, as expected, higher, at 5-6, and palm oil highest of all at 8-10 energy units out per energy unit of fossil fuel consumed. Life cycle analyses also still do not always account for two emerging factors in climate impacts. First, emissions of the strong greenhouse gas $\textsf{N}_{2}\textsf{O}$ can be associated with agricultural production of biofuels, particularly when nitrogen fertilizers are used. Second, with the exception of waste oils, and possibly algae, extensive implementation of alternative biodiesel sources will cause substantial conversion of currently undeveloped land into cropland, which can result in substantial release of carbon stored in wild land leaf litter and soil.

ARE BIODIESEL EMISSIONS CLEANER?

Biodiesel fuel has been touted as a much cleaner alternative to conventional diesel fuel. Here, we examine the state of the knowledge on this topic, considering oxides of nitrogen NO_x emissions, climate impact data, and toxicity. We emphasize this research is new, and currently incomplete.

Diesel exhaust particulate emissions have been designated as an air toxic by the state of California and the US Environmental Protection Agency. They also impact climate (below). Diesel combustion is characterized by relatively low emissions of pollutants such as carbon monoxide and volatile organic compounds, but exceptionally high emissions of NO_x and

particulate matter. NO_x is an essential precursor for photochemical production of urban ozone, which is both a respiratory irritant and a greenhouse gas. Particulate matter from combustion sources consists of tiny solid and liquid particles, smaller than about one hundredth of the diameter of a human hair. Particulate matter has both climate and health impacts.

Biodiesel will not be a "silver bullet" for clean air, although it may, on balance, offer modest improvements.

Diesel Engine Emissions

Test results for diesel engine emissions vary widely depending largely on 1) the specific engine (a function of both the original engine characteristics and subsequent maintenance and tuning) and 2) the power output (or load) of the engine. Biodiesel test results also depend strongly on the two factors above, but they additionally depend on the biodiesel blend, if any. Biodiesel can be mixed with conventional diesel in any ratio; "B5" refers to a blend with 5% biodiesel and 95%

Biodiesel Pump

conventional diesel, while B100 is pure biodiesel.

For some pollutant emission/engine combinations, changes in emissions are proportional to the amount of biodiesel in the blend, while other test results show similar emissions changes for all blends between 10% and 100% biodiesel. As a result of this complicated situation, emissions measurements have meaning only if they are compared to a control test using conventional diesel fuel. For most pollutants, it is possible to find results and analyses in the scientific literature that support many hypotheses, and the prevalence of unsupported general statements is much higher than would be accepted in more developed scientific fields.

Finally, it should be emphasized that biodiesel is generally tested and used as a "drop in" replacement for conventional diesel. This makes for an uneven playing field; if the engines had been designed specifically around biodiesel, the comparisons might be very different. Assuming the design parameters focused on engine efficiency and low emissions, biodiesel would likely look better.

Photochemical Smog Production Photochemical smog is a persistent problem in urban areas around the world. Characterized by high summertime ozone and particles, smog is worst in areas with intense sunlight, and meteorology that traps air near the ground. Photochemical smog arises from sunlightdriven reactions of volatile organic compounds (VOCs) and oxides of nitrogen (NO $_{\sf x}$). Diesel engines produce high levels of NO $_{\sf x}$ and particulate matter, but contribute little to total VOC emissions. NO_x emissions have been the target of regulations for decades, thus NO $_{\sf x}$ emissions from biodiesel are relatively well studied.

Because the production of biodiesel yields more fuel than the fossil fuel invested, and because it has lower black sooty emissions, biodiesel will be a boon to climate mitigation efforts.

The vast majority of studies indicate biodiesel produces slightly more NO_x, around 5-10%, than conventional diesel. As is the case with most other biodiesel tailpipe pollutants however, there are some engine/load combinations that are reported to produce equal or even lower NO $_{\sf x}$ emissions from biodiesel. While the typical increase in NO $_{\sf x}$ emissions is relatively small, it is large enough that widespread introduction of biodiesel could reverse a few years of hard-won improvements in urban air quality. Higher NO $_{\sf x}$ emissions result from biodiesel's higher oxygen content leading to higher combustion temperatures, which produce more NO_x. The problem can likely be addressed by adjusting parameters such as engine timing, but this may lead to increased emissions of carbon monoxide and particulate matter.

Climate Impacts: Miles Per Gallon vs. Miles Per Carbon 'Miles per gallon' is a basic property of vehicles, varying little from one gasoline blend to the next. Diesel fuel and the different biofuels, however, contain different amounts of carbon in each gallon, so a straight miles per gallon (mpg) comparison doesn't allow a fair comparison of greenhouse gas emissions. Conventional diesel fuel contains about 15% more carbon per gallon than gasoline. For example, if a diesel passenger car gets 10% better mpg than a gasoline car, it actually gets about 5% worse mileage on a carbon emissions basis. Because biodiesel contains some oxygen (diesel fuel contains no oxygen), it has somewhat less carbon per gallon. If biodiesel gets 10% better mpg, it will match gasoline in miles per carbon. There is an additional aspect of the diesel-to-gasoline comparison: climate impacts of black carbon and organic carbon particles, as discussed below.

Particulate Matter Climate Impacts Diesel particulate matter has components that can be either climate warming or climate cooling. Absorbing materials absorb both incoming sunlight and outgoing infrared light. Both of these effects lead to increases in the earth's surface temperature. In contrast, tiny clear or white droplets (water, organic carbon, sulfate) act to cool our planet, by reflecting some of the incoming sunlight back out to space. Diesel's sooty "black carbon" particles are believed to trap 5000 – 12,000 times more heat than carbon dioxide per unit weight, making black carbon particles a powerful potential contributor to greenhouse warming. Black carbon that falls on snow also enhances snow melting and can alter water supplies and enhance flooding. Organic carbon particles, on the other hand, cool the earth, as do sulfate particles. From

a purely climate point of view, emissions of black carbon is 'bad', while unburned fuel (or organic carbon) is 'good'.

Developments in the field of biodiesel fuel are moving rapidly and hold promise as one component of efforts to lessen our dependence on fossil fuels.

The ratio of particle emissions that heat the atmosphere vs. those that cool the atmosphere changes with engine power output. At high power output ("high load", for example when a truck is accelerating) diesels typically emit mostly black carbon, while at idle they produce mostly organic carbon. Because the black carbon component is so strongly warming, on balance diesel particle emissions are warming. Diesel emissions are believed to be responsible for about 20% of global black carbon particles in the atmosphere; the rest is largely attributed to burning of coal, and biomass in fires, cooking and heating. If biodiesels produce either less particulate matter or a lower ratio of black carbon-to-organic carbon, they will mitigate this impact.

The majority of studies indicate biodiesel fuel produces moderately less particulate matter than diesel, by 10- 50%. More dramatic is the change in particulate matter composition. The ratio of biodiesel black carbon-to-organic carbon is typically only 30-60% of the diesel black carbon-toorganic carbon ratio. When combined with the reduction in particulate matter mass, black carbon emissions from biodiesel may only be 20-40% of the diesel black carbon emissions, making for much "cooler" emissions from biodiesel fuel.

Toxicity Toxicity studies for biodiesel emissions are far from complete. Toxicity, like the biology of people, animals and their many diseases, is a broad and complex subject. A wide array of toxicity tests are available to probe the ability of materials to cause or enhance many different diseases. The tests assess different properties of potential toxins, so it is not surprising that biodiesel emissions appear to be less toxic than diesel emissions in some assays and more toxic in others. Given the inherent variability of the results, it is too early to tell if biodiesel from any particular feedstock will be more toxic than biodiesel from other feedstocks.

On the positive side, most (but not all) studies have shown lower toxicity for particulate matter (PM) emissions from biodiesel compared with PM emissions from diesel. The reduction in toxicity is modest however, in the 10-40% range. Average particle size (which affects lung deposition properties) is reported to increase modestly in some studies and decrease in others, so likely there is little influence from changes in particle size on particle toxicity.

On the other hand, several studies report the gas-phase and semi-volatile fractions of the emissions from biodiesel combustion may be more toxic than the same fraction from conventional diesel combustion. Semi-volatiles are organics that can be in either the gas or particle phases depending primarily on the

temperature. Volatile emissions from biodiesel, as expected, contain many more oxygenated compounds, including several carbonyls such as formaldehyde. Formaldehyde, a known air toxic, is highly elevated in biodiesel exhaust compared to diesel exhaust. Biodiesel fuel itself also appears to be moderately less toxic than diesel fuel, again by 10-40%. At this point, it is not clear if the lower or higher toxicity aspects of biodiesel emissions will dominate, but it is clear that from a toxicity point of view, biodiesel fuel is not a panacea.

It is important to note that emissions from combustion of unprocessed oils (raw feedstocks that have not been converted to biodiesel) exhibit highly elevated toxicity relative to conventional diesel, often by a factor of eight or more.

SUMMARY AND FUTURE OUTLOOK

Because the production of biodiesel generally yields more fuel than the fossil fuel invested, and because it has significantly lower black sooty emissions, biodiesel will be a boon to climate mitigation efforts. While a sizeable minority of toxicity assays indicate an increase in toxicity of biodiesel combustion products vs diesel combustion products, a larger number of studies indicate a modest decrease. An important caveat is that raw vegetable oils combusted without first converting to biodiesel generally test as much more toxic than conventional diesel combustion emissions. Biodiesel in most applications also modestly increases emissions of NO_x , which contributes to photochemical smog formation. Clearly, biodiesel will not be a "silver bullet" for clean air, although it may, on balance, offer modest improvements. The need for exhaust aftertreatment, and other programs aimed at reducing emissions, remains as great for biodiesel fuel as it is for diesel fuel.

The future of biodiesel fuels is particularly promising for sources such as jatropha, the tropical tree with high yields, relative lack of competition with food crops, and potential to contribute to sustainable development. Algae offer a uniquely desirable set of advantages, including very high per acre yields and the potential to "scrub" carbon dioxide from smoke stack gasses. Even though commercialization is years away, investment in its development is well placed.

In summary, developments in the field of biodiesel fuel are moving rapidly and hold promise as one component of efforts to lessen our dependence on fossil fuels.

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B+ Biofuels have potential to become a viable alternative to fossil fuels, and are on balance much better for mitigating climate change, and likely slightly less toxic than diesel fuel. Algae are the fuel source with highest potential to produce large quantities of fuel in reasonable land areas in North America; however their commercialization is still unproven. Additionally, the current huge flow of funding into biofuels research is likely to result in some inefficient investments.

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