Final Report

Annex XXXIV: Biomass-Derived Diesel Fuels

Task 1: Analysis of Biodiesel Options

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Executive Summary

Biofuels are fuels that are made from biomass, and biomass can be defined as any plant related material that has captured energy of sun by photosynthesis. Biomass can be divided into three categories: woody biomass, non-woody biomass, and organic waste.

The word, biodiesel, refers to a fuel made from biomass that has properties similar to those of petroleum-based diesel fuels. More specifically though, in common use today, the word refers to a fuel that is a mixture of fatty acid alkyl esters and made from vegetable oils, animal fats, or recycled greases. However, today biodiesel produced by hydrotreatment oil and fats is already commercially available, and Biomass-to-Liquids (BTL) biodiesel produced by gasification is under heavy development.

Part A, Biodiesel – Fatty Acid Esters

Use of vegetable oils as motor fuels is not new. They were used during the oil shortages in the 1930s and 40s, and in the latter part of the 20th century attention in Europe and North America turned to the potential for replacement of petroleum diesel fuel with fuels derived from vegetable oils.

Biodiesel is made from oils in a process called transesterification. In this process the triglyceride oils in the vegetable oils, animal fats, or recycled greases are reacted with an alcohol (most commonly, methanol and to a lesser extent, ethanol), forming fatty acid alkyl esters (biodiesel) and glycerin. The process requires heat and the use of a strong base catalyst, e.g., sodium hydroxide or potassium hydroxide.

A typical biodiesel plant combining a pretreatment process and the transesterification process is illustrated in the schematic diagram, Figure ES-1 below:

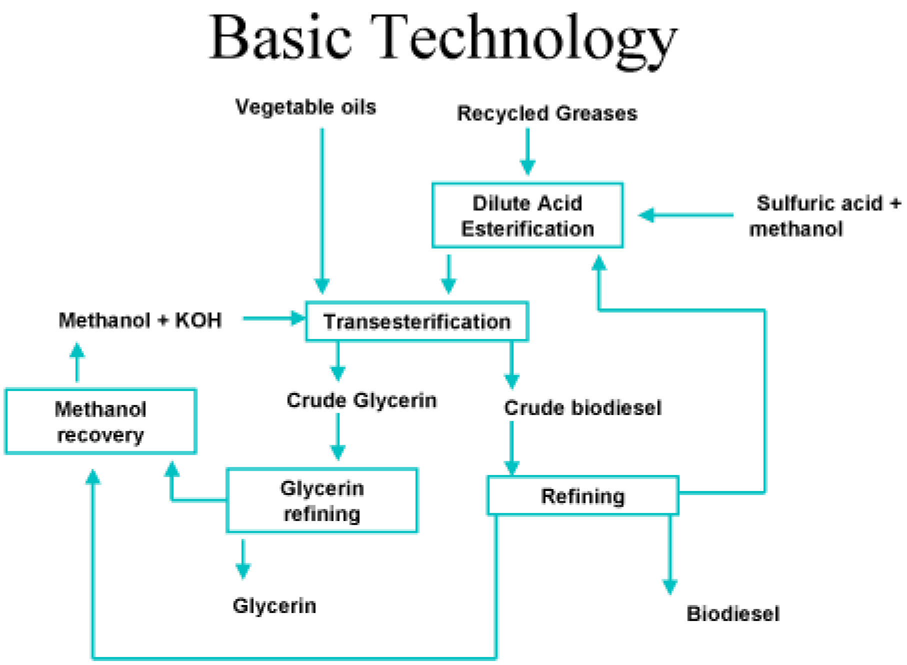
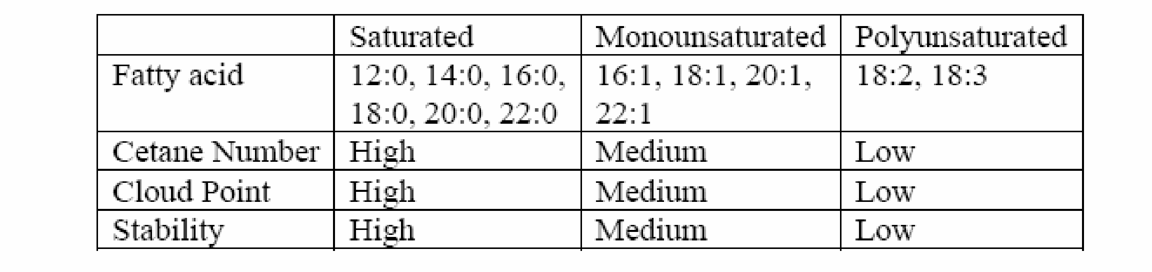


Figure ES-1 - Schematic Diagram of Typical Biodiesel Transesterification Plant (DOE Biomass Program)

The figure above represents the transesterification process when methanol is used as the alcohol in the process, and the product is a fatty acid <u>methyl</u> ester. In fact, the use of methanol is the most common production technique and the least expensive, but not the only one. Ethanol and higher alcohols such as isopropanol and butanol can also be used for the same purpose. So, for example, if ethanol is used instead of methanol, the product will be a fatty acid <u>ethyl</u> ester. The alcohols of higher molecular weight will produce biodiesel fuels with improved cold flow properties at the cost of a less efficient transesterification process.

Properties of vegetable oils vary widely, and those property differences in feedstocks can have profound effects on the properties of the finished biodiesel product, the fatty acid alkyl ester. Affected properties can cause large differences in performance in the areas of emissions (especially NOx), cetane number, cold flow properties, and stability. Property variations are directly related back to the degree of saturation (number of double bonds between carbon atoms) of the feedstock. Table ES-1 below shows three important properties of biodiesel, cetane number, cloud point, and stability, and the relation of those properties to the degree of saturation of the feedstock.

Table ES-1 - Variation of Finished Biodiesel Properties with Feedstock Composition (NREL 2006)



	Saturated	Monounsaturated	Polyunsaturated
Fatty acid	12:0, 14:0, 16:0, 18:0, 20:0, 22:0	16:1, 18:1, 20:1, 22:1	18:2, 18:3
Cetane Number	High	Medium	Low
Cloud Point	High	Medium	Low
Stability	High	Medium	Low

Biodiesel properties that can be affected by choice of feedstock include energy content, cold flow properties, cetane number, oxidative stability (shelf life), cleaning effect, and lubricity. Therefore, it is important to take account of these differences when choosing a feedstock for a transesterification facility, and the geographic and demographic features must be considered for the market in which the biodiesel use is intended. For example, a biodiesel fuel with poor cold flow properties should not be considered for use in high blend levels in any cold or winter climates.

Biodiesel fuel, whether in neat form or in blends with petroleum diesel fuel, generally have beneficial effects on engine emissions – effects which can vary with feedstock, engine technology, and the properties of the diesel fuel into which the biodiesel is blended. Many tests have been done over the past 10 to 15 years to document the effects of biodiesel on exhaust emissions. The U.S. Environmental Protection Agency did a thorough study of many of the reported results to generate a consensus of the average effects on emissions for different blend levels of biodiesel with regular diesel fuel. Their results are summarized in Figure ES-2 below.

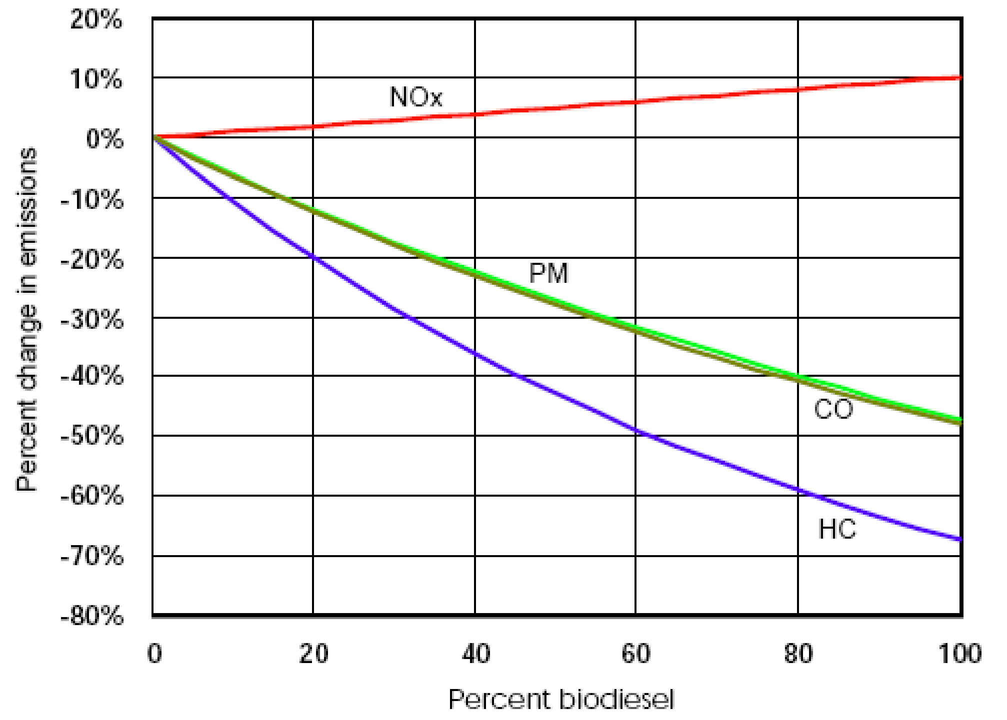


Figure ES-2 - Average Emissions Impacts of Biodiesel in Heavy-Duty Engines (EPA 2002)

The graph shows that typically particulate matter, carbon monoxide, and hydrocarbon emissions will be reduced with biodiesel blends, while nitrogen oxides (NOx) will be increased slightly. The increase in NOx emissions has been widely attributed to the fact that biodiesel contains oxygen, but the explanation is probably not that simple and might be very complex. Considerable work has been done to try to answer the NOx dilemma, and most recently it has been noted that the results indicating an increase in NOx with biodiesel have generally come from tests with older model diesel engines tested on engine dynamometers. More recent tests in the U.S. of current-technology engines in vehicles tested on chassis dynamometers have shown no increase or reductions of NOx with biodiesel.

Since biodiesel properties can be greatly affected by choice of feedstock, it follows that emissions from biodiesel blends can also be affected by choice of feedstock. Indeed they are, as illustrated in Figures ES-3 and ES-4 below.

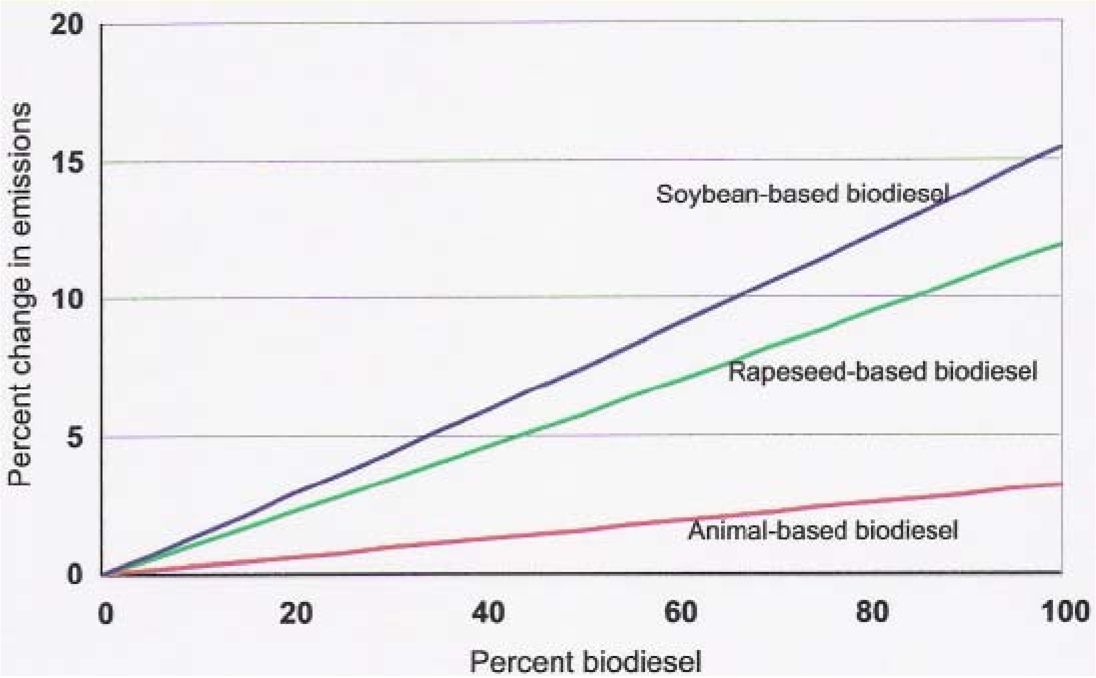


Figure ES-3 - Changes in NOx Emissions with Biodiesel Feedstock Selection (EPA 2002)

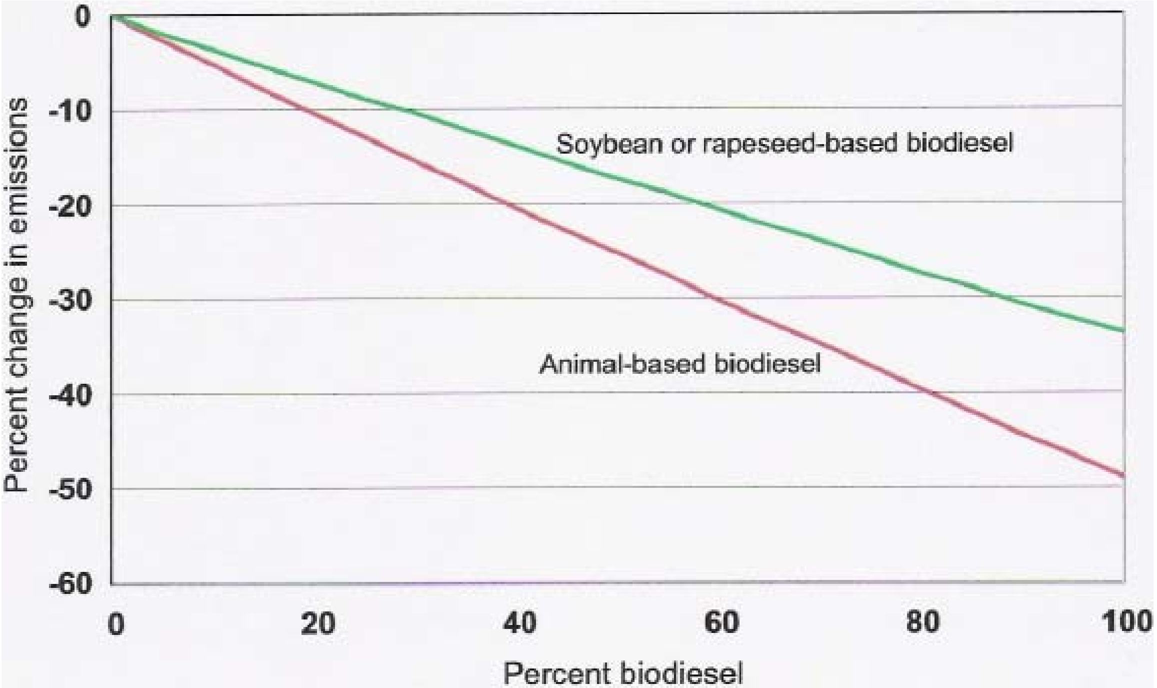


Figure ES-4 - Changes in PM Emissions with Biodiesel Feedstock Selection (EPA 2002)

In order for *any* fuel (including biodiesel) to be viable as an alternative fuel, it must meet certain criteria as follows:

- It should provide a net energy gain, not use more energy to produce the fuel than it provides itself
- It should provide environmental benefits
- It should be economically competitive
- It should be producible in sufficient quantities without impacting the availability or price of the same feedstocks to be used as food. Preferably, the feedstock would not compete with its use as food.

Life cycle analyses are required to determine whether a candidate alternative fuel meets these requirements, and a number of such analyses have been done for biodiesel. One of the more thorough of such analyses was done by the National Renewable Energy Laboratory (NREL) in the U.S. and reported in Sheehan (1998). With regard to emissions of carbon dioxide (CO_2), the NREL researchers found that all blend levels of soybean-based biodiesel with diesel fuel achieved reductions in CO_2 emissions compared to diesel fuel itself, as illustrated in Figure ES-5 below.

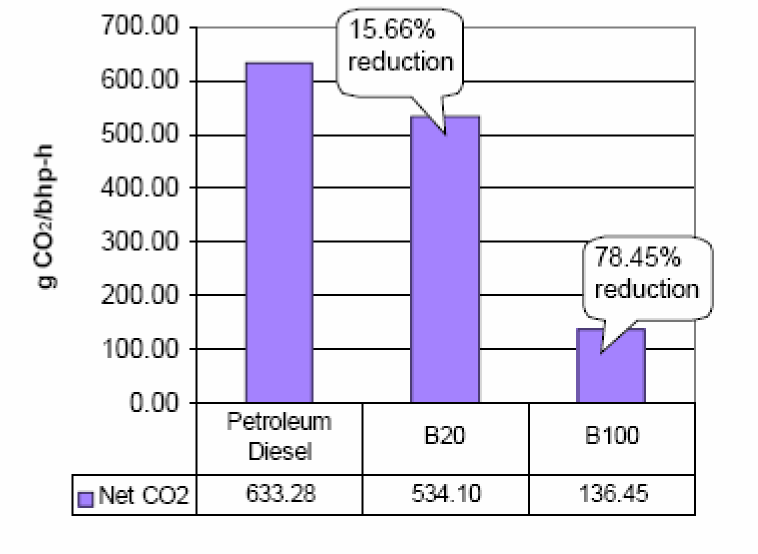
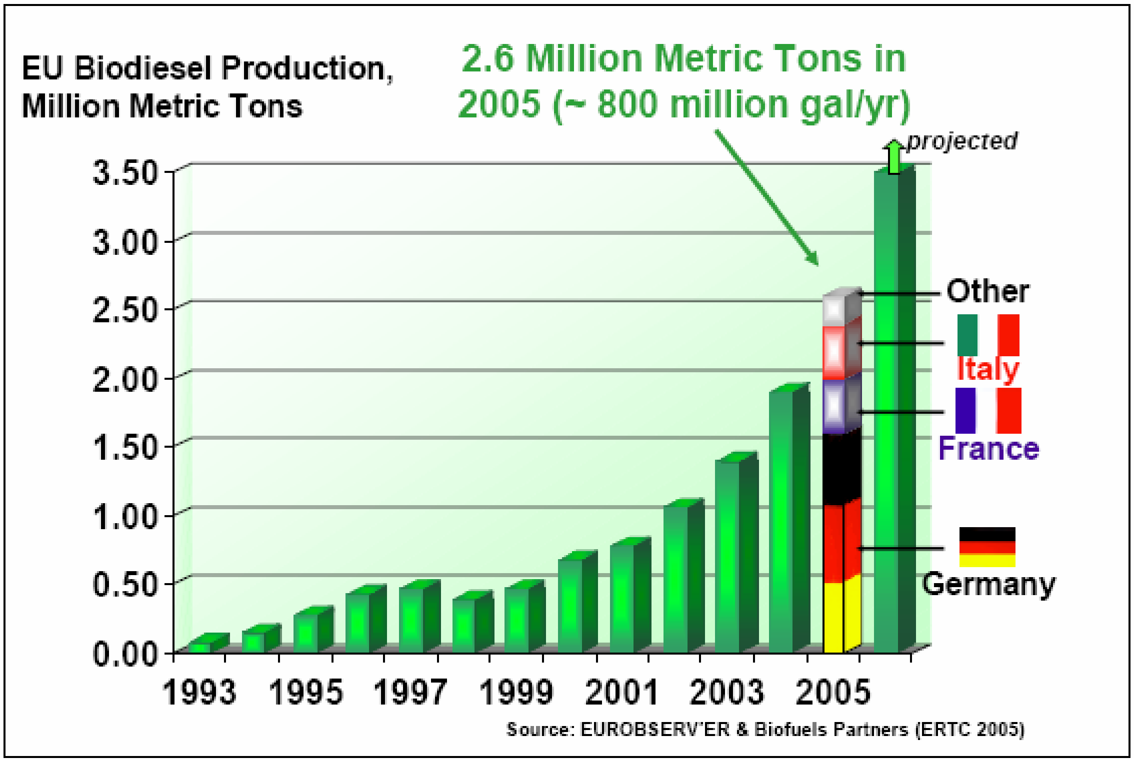


Figure ES-5 - Comparison of Life Cycle CO2 Emissions for Petroleum Diesel and Soy Biodiesel Blends (Sheehan et al 1998)

Production and consumption of biodiesel has soared in the last decade with Europe leading the way. The U.S. has made great progress in the last few years, and many other countries are enacting policies that will boost the use and consumption of biodiesel around the world. Figures ES-6 and ES-7 show the rise in biodiesel production in Europe and the U.S., respectively.



Source: EUROBSERV'ER & Biofuels Partners (ERTC 2005)

Figure - ES-6 - Biodiesel Production in the EU (Biofuels Center 2007)

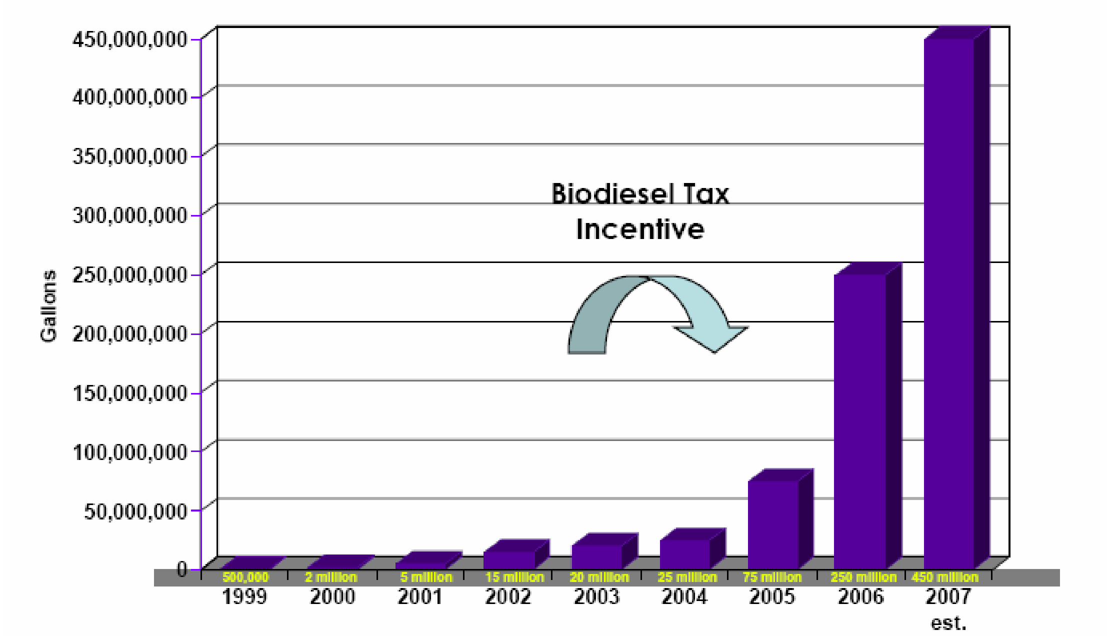


Figure ES-7 - U.S. Production of Biodiesel since 1999 (NBB 2007) (Note: 250 million gallons in the U.S. in <u>2006</u> equals about 830,000 metric tons, or about 32% of the EU production in <u>2005</u>)

While the demand for vegetable oils as fuels is soaring, worldwide pressure is being put on prices. The result is higher food prices, and one must consider the possibility that the competition for the same resources to be used as food or fuel will drive food prices up even more. In the U.S. there is a similar phenomenon occurring with ethanol from corn. Farmers are choosing to switch crops to grow more corn because it commands a higher price, and food prices in general are rising in the U.S. In turn, many farmers are not growing soybeans as a rotation crop with corn as they normally would because corn will garner a higher price in the market than soybeans. In conjunction with these phenomena there is also a growing demand worldwide for vegetable oils as food.

Promar International, an agriculture consulting group, has estimated the growth in vegetable oil use as fuel to the year 2012/2013. This projection is shown below in Figure ES-8 in terms of the global mix of oils as well as the distribution by geographic region. The EU will continue to be the major user of vegetable oils for fuel, but their proportion of the total will shrink from 90% in 2005 to about 60% in 2012. Rapeseed oil use will diminish from 70% in 2005 to less than 40% in 2012. At the same time, soy oil use will rise to about one third of the world use in 2012 (Promar 2005).

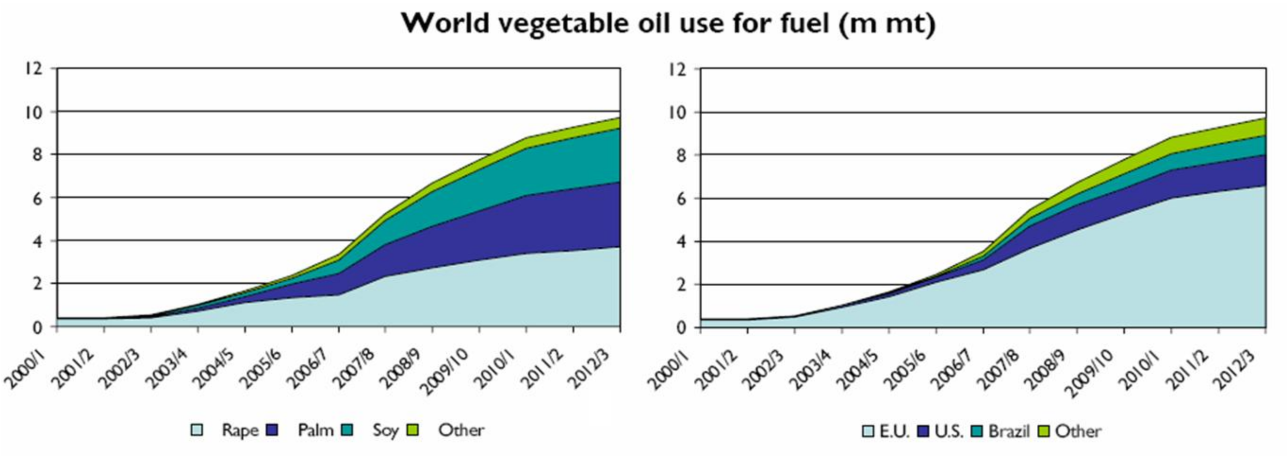


Figure ES-8 - World Vegetable Oil Use for Fuel to 2012/13 (Promar 2005)

Total vegetable oil demand for all uses will grow quite substantially, according to Promar's projections, shown in Figure ES-9 below.

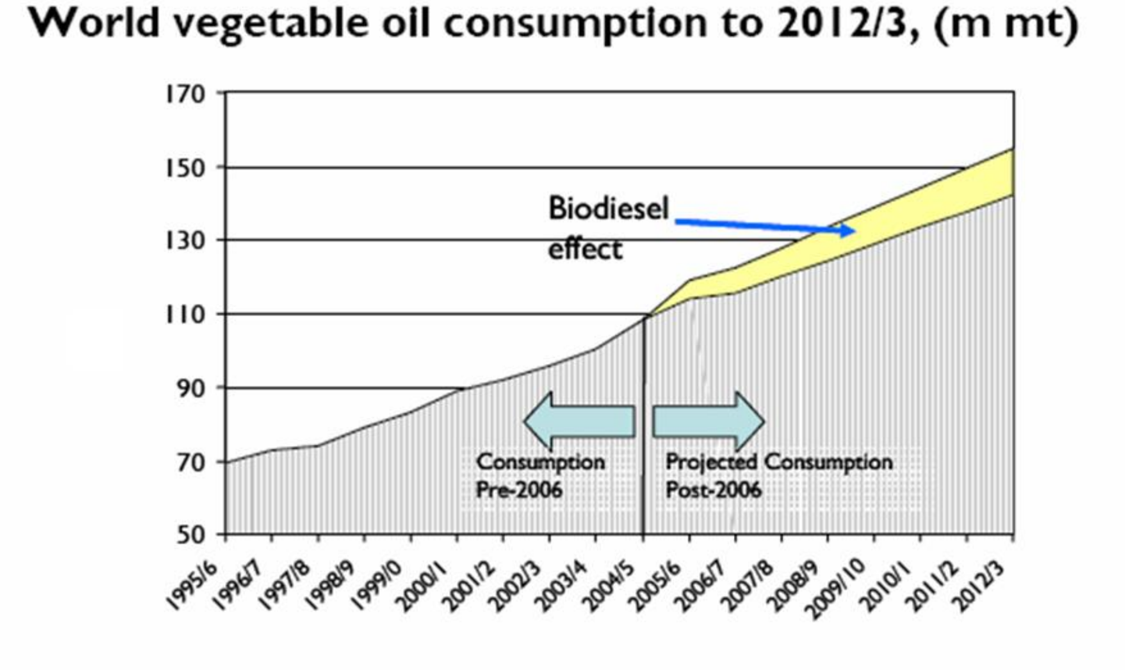


Figure ES-9 - World Vegetable Oil Consumption to 2012/13 (Promar 2005)

The projections also look at the import/export situation for vegetable oils for both the EU and the U.S. In the EU the main driver is the rapid growth in demand for vegetable oil for fuel. The EU is currently a net exporter of soybean and rapeseed oil, but in the future scenario the EU will become a net importer of soy, rape, sun, and palm oils. In the case of the U.S. the trade impacts are not as severe because of the greater ability of the U.S. to generate additional vegetable oil supplies through domestic production. For the four oils studied, the biofuels scenario shows net imports rising to 1 million metric tons as rape and palm oil imports increase and soybean oil exports decrease.

So, while production and demand for biodiesel from vegetable oils are soaring there is also increasing concern for the pressure that is going to be placed on future prices and availability of vegetable oils for food. Most researchers and policymakers believe that utilization of non-edible biomass in all forms will make for a more sustainable future for fuels to replace both gasoline and diesel fuel. One of the basic targets is to move from traditional biofuels, biodiesel and ethanol to the next generation of fuels based on non-edible feedstock.

The World Energy Outlook 2006 predicts that the usage of biofuels will rise from 20 Mtoe in 2005 to 92-147 Mtoe in 2030, and that biofuels will cover only modest share of 4-7% of world transport fuel demand in 2030. However, potential of biomass is estimated to be sufficient to cover a substantial share of world energy demand over the following decades. It is up to policies how much of this will be used in transport sector. The highest increase and usage of biofuels is expected in the U.S., and Europe will take the second place from Brazil.

PART B. BIODIESEL – ADVANCED OPTIONS

Lignocellulosic biomass represents the greatest part of the bioenergy potential, and thus the challenge today is to develop conversion technologies for this material. Solid biomass cannot be practically used as such for transportation. It needs to be converted to gaseous or liquid fuels. This can be done with a number of Biomass-to-Liquids (BTL) processes.

One benefit of the biomass-to-liquids (BTL) technologies is that the whole plant can be utilized, whereas production of traditional biofuels (FAME-type biodiesel and bioethanol), uses only parts of the plant. In addition, a variety of feedstocks can be used in the BTL process, meaning that production potential and efficiency is improved, and less land area under cultivation is needed than in traditional biofuel production. Also end-use properties of BTL biodiesel are improved when compared to traditional biodiesel.

These new "BTL" fuels are generally referred to as *2nd Generation Biofuels*, and they will be produced in *biorefineries*. The concept of biorefinery implies an integrated production of fuels, energy, and chemicals from biomass. This resembles oil refineries producing many fuels and products from crude oil. That is, a *biorefinery* is a unit delivering *multiproducts-from-biomass*. A biorefinery can be stand-alone or integrated in, for example, heat and power plants, pulp and paper mills, and oil refineries. Co-production of many different products and high-value chemicals means that synergetic benefits can be obtained regarding e.g. the energy balance, infrastructure and economy.

A number of different technologies can be used to convert biomass to fuels (Table ES-2). Diesel-type biofuel can be processed via gasification followed by a liquefaction step, such as the Fischer-Tropsch process. Pyrolysis of plants can produce bio-oil, a kind of bio-crude, which can be further processed to biodiesel. Catalytic depolymerization can be used to separate biodiesel from hydrocarbon wastes. Hydrotreatment of oils and fats into paraffins is also one option, and this process is already commercialized.

Table ES-2 - Different Technologies to Convert Biomass to Fuels

Process	Product	End-use
Natural oils →		
Esterification	Biodiesel (by-product glycerol)	Transport fuels
Hydrotreatment	Biobased diesel	Transport fuels
No processing	Oils	Food, energy
Biomass → syngas →		
Fischer-Tropsch	FT-fuels, ethanol, various other products, chemicals	Transport fuels and chemical industries
Methanol-to-liquids	Gasoline type fuels ("MTG" process)	Transport fuels and chemical industries
Syngas to alcohols, ethers	Methanol, ethanol etc.	Transport fuels and chemical industries
Water-shift	H_2	Fuel cells
No processing	Syngas	Power and heat
Biomass → pyrolysis oil →		
Hydroprocessing	Biobased fuels, other products	Feed to petroleum refinery, transport fuels and chemical industries
No processing	Pyrolysis oil	Power and heat, feed to syngas production
Biomass → sugars →		
Biochemical	Ethanol	Transport fuels and chemical industries
Anaerobic digestion	Methane (biogas)	Transport

From Biomass to Biofuels

The different technology pathways to "BTL" biodiesel are discussed in detail in Chapter 9, *"Biofuel Refineries – The Pathway to the Future?"* Here, only a short description of options is given.

Hydrotreatment

An intermediate pathway for using vegetable oils and fats, short of the full technology of a biorefinery but an advance over esterification, is to use hydrogenation of vegetable oils in conjunction with a petroleum refinery. It has many benefits over esterification of vegetable oils to FAME. Hydrotreatment can produce high-quality biobased diesel resembling F-T diesel from a variety of feedstocks. Several types of vegetable oils can be used, even non-food crops, as well as animal fats. In future, even algae and bacteria could be used. Hydrotreatment in a way decouples feedstock issue from end-use product quality.

Hydrotreated biobased diesel (HO) as well as BTL are hydrocarbon fuels in the same way as conventional diesel fuel. However, conventional diesel fuel contains a mix of different kinds of hydrocarbons, aromatic compounds, naphthenic compounds as well as paraffins, whereas hydrotreated biodiesel and BTL are paraffinic fuels. Paraffinic diesel has very high cetane number, excellent ignition properties, no sulfur, nitrogen nor aromatics. Both HO and BTL contain no oxygen. Storage stability of this fuel is good and water solubility is low. From a safety point of view paraffinic fuel is equivalent to conventional diesel fuel.

Hydrotreatment of different biobased feedstocks at oil refineries seems to be the fastest growing area to produce non-traditional biofuels. The first commercial, refinery-scale hydrotreatment process for vegetable oils and animal fats was developed by Neste Oil in Finland. The process is called NExBTL. The first NExBTL plant started production of 170,000 tons of neat biocomponent per year in the summer of 2007, and the second plant with equivalent capacity will open in 2008. An 800,000 t/a (tonnes per anum) plant is also slated for Singapore.

Properties of NExBTL, GTL (Gas-to-liquids), FAME, and diesel fuel are compared in Table ES-3 below. Note the superior cetane number, cloud point, and sulfur for the hydrotreated vegetable oil fuel product compared with FAME and diesel fuel.

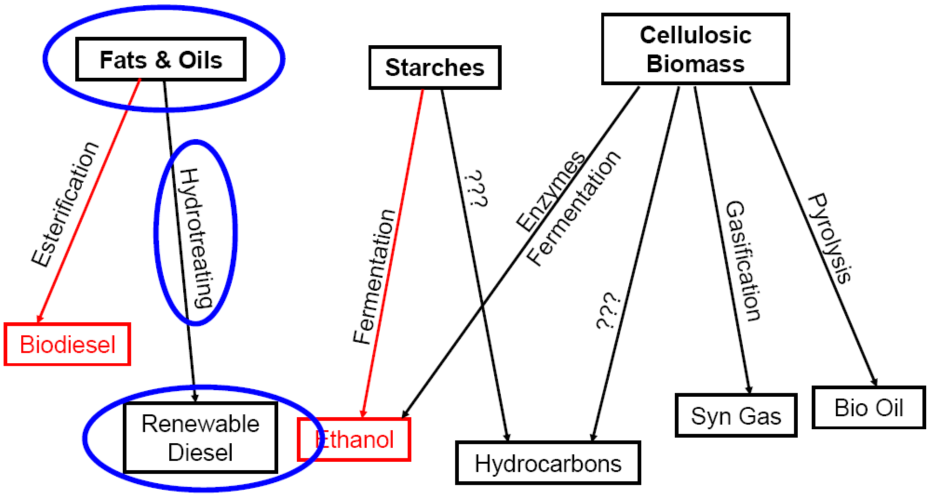


Figure ES-10 - Different Paths to Utilize Biobased Material, including hydrotreatment (Kaufmann 2007)

Table ES-3 - A Comparison of Diesel Fuel Properties. (Rantanen et al. 2005)

FUEL PROPERTIES *)	**NExBTL**	**GTL diesel**	**FAME (RME)**	**Diesel EN590/2005**
Density @15°C, kg/m^3	775...785	770....785	≈ 885	≈ 835
Viscosity @40°C, mm^2/s	2.9...3.5	3.2...4.5	≈ 4.5	≈ 3.5
Cetane number	84...99 **)	73...81	≈ 51	≈ 53
Distillation, 10 vol%, °C	260...270	≈ 260	≈ 340	≈ 200
Distillation, 90 vol%, °C	295...300	325...330	≈ 355	≈ 350
Cloud point, °C	- 5...- 30	0...- 25	≈ - 5	≈ - 5
Lower heating value, MJ/kg	≈ 44	≈ 44	≈ 38	≈ 43
Lower heating value, MJ/liter	≈ 34	≈ 34	≈ 34	≈ 36
Polyaromatics, wt%	0	0	0	≈ 4
Oxygen, wt%	0	0	≈ 11	0
Sulfur, mg/kg	≈ 0	< 10	< 10	< 10

Hydrotreatment of oils and fats is currently integrated into existing oil refineries. However, if the scale were sufficient to improve technical and economical feasibility, they could be designed as stand-alone plants.

Gasification/Liquefaction Path

The gasification results in syngas, a mixture of carbon monoxide (CO) and hydrogen (H_2), which can be converted to fuels and chemicals. Coal-to-liquids (CTL) and Gas-to-liquids (GTL) processes are already well-known technologies utilizing gasification/FT process. The Fischer-Tropsch process sets stringent requirements for gas cleanliness. In the case of biomass (BTL) effective cleaning methods are needed. These better methods are complicated and expensive. Overall, biomass is a more challenging feedstock for gasification than coal and natural gas. Gasification of mixtures of biomass and fossil feedstocks can help in this respect (XTL).

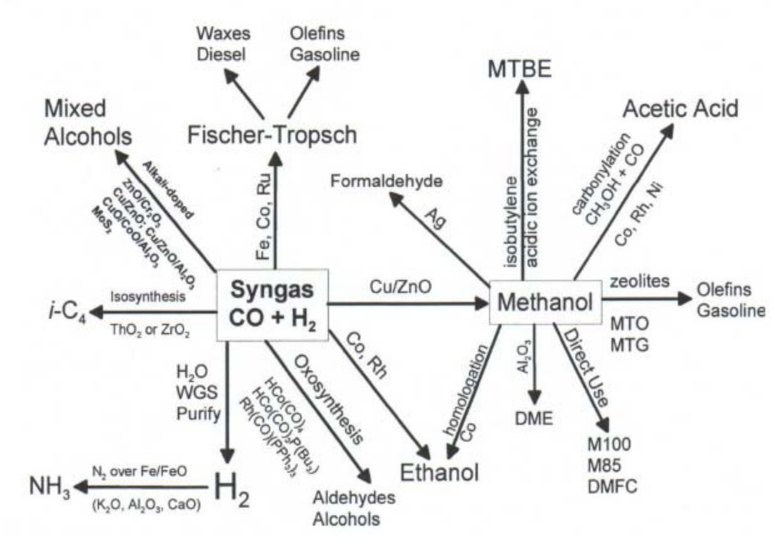


Figure ES-11 - Synthesis gas processes (Dayton 2007)

The first stand-alone biorefineries are also already being built. Fischer-Tropsch diesel (FTD) may be available within a few years depending on competition within energy sectors. FTD can use existing diesel infrastructure and this is one reason why the focus is on FTD in Germany and in Finland. In Germany, CHOREN in co-operation with Shell, Daimler, and VW is building a biorefinery in Freiburg. CHOREN has been running the first BTL pilot, and is expected to start the world's first commercial BTL-plant (Beta-Plant) at its Freiberg site in 2008. The next step will be an industrial-scale BTL plant with production of around 200,000 tons/year, which would operate around 2012. In Finland two consortiums, Neste-Stora Enso and UPM-Andritz/Carbona are planning demonstration plants.

A number of other activities are also under way. Activities include partnerships of MPM Technologies Inc. and Losonoco Inc.; and Chevron Corporation and Weyerhauser Company. These projects all utilize gasification of biomass and Fischer-Tropsch (FT) synthesis. However, there are also options other than Fischer-Tropsch for liquefaction of syngas.
The FT distillate fractions can be upgraded using conventional oil refinery processes, but tailored processes can maximize benefits.

Gasification technology enables usage of a wide variety of feedstocks, but there are also requirements for feedstock quality. The challenge is to develop in-plant pre-treatment to economically convert a wide range of feedstocks to be acceptable for gasification. However, generally speaking, gasification provides the most flexible technology regarding the feedstock.

Pyrolysis path

Pyrolysis of plants can produce bio-oil, a kind of bio-crude which can be further processed to biodiesel. Pyrolysis and gasification are related processes. Fast pyrolysis is used commercially for production of chemicals. Pyrolysis oil is a very challenging product, containing water, acids, and other difficult species, resulting in high oxygen content and high acid numbers. In addition, pyrolysis oil is not soluble with conventional hydrocarbon fuels. Pyrolysis oil cannot be used as such for engines. One benefit of fast pyrolysis is that it could be commercially feasible at small-scale for decentralized production. Partial upgrading of pyrolysis oil could make it suitable for conventional refineries. Development of feasible small-scale BTL technology would help with logistics and increase utilization of biomass feedstock.

Presently three pyrolysis paths are under study for biodiesel production (Figure ES-2):

- Direct conversion of biomass by catalytic hydrocracking into liquid transport fuel
- Production of pyrolysis liquid and the deoxygenation of the liquid or its fractions into oil refinery feed and i.e. into biodiesel
- Use of pyrolysis liquid as a pre-treatment step in biomass syngas production and biodiesel conversion

The U.S. Department of Energy (DOE) announced in April 2008 the issuance of a Funding Opportunity Announcement (FOA) for up to $7 million in federal funding over two years (FY 2008 – 2009) in advanced research and development in converting non-food based biomass to advance clean and affordable biofuels. Combined with private minimum cost share of 20 percent, up to $8.75 million would be invested in this research effort. (http://www.energy.gov/)

UOP (USA) is exploring the possibility to use pyrolysis oil or its fractions as a feedstock for refinery based hydroprocessing (Marker et al. 2005) to fuels~~.~~

In Europe, the EU-BIOCOUP (2006-2011) project aims at upgrading pyrolysis liquid or its fractions for refinery based hydroprocessing to fuels and chemicals (Figure ES-3).

Pyrolysis can also be used as a pre-treatment step in biodiesel production (Figure ES-4). One clear benefit is logistic. Small-scale fast pyrolysis plants may be located adjacent, like in forest areas or integrated with a pulp mill. Energy density of pyrolysis liquid is higher than that of solid biomass and when properly designed the transportation and storage of pyrolysis liquid is easier than that of solid fuel. Another advantage of liquid feed compared to solid one is its easier feeding. FZK (Germany) and Lurgi (Germany) are developing the Bioliq-process (Figure ES-4) where pyrolysis liquid is produced from straw in small decentralized plants, transported into a refinery where it is used as feedstock in synthesis gas production followed by conversion into biodiesel.

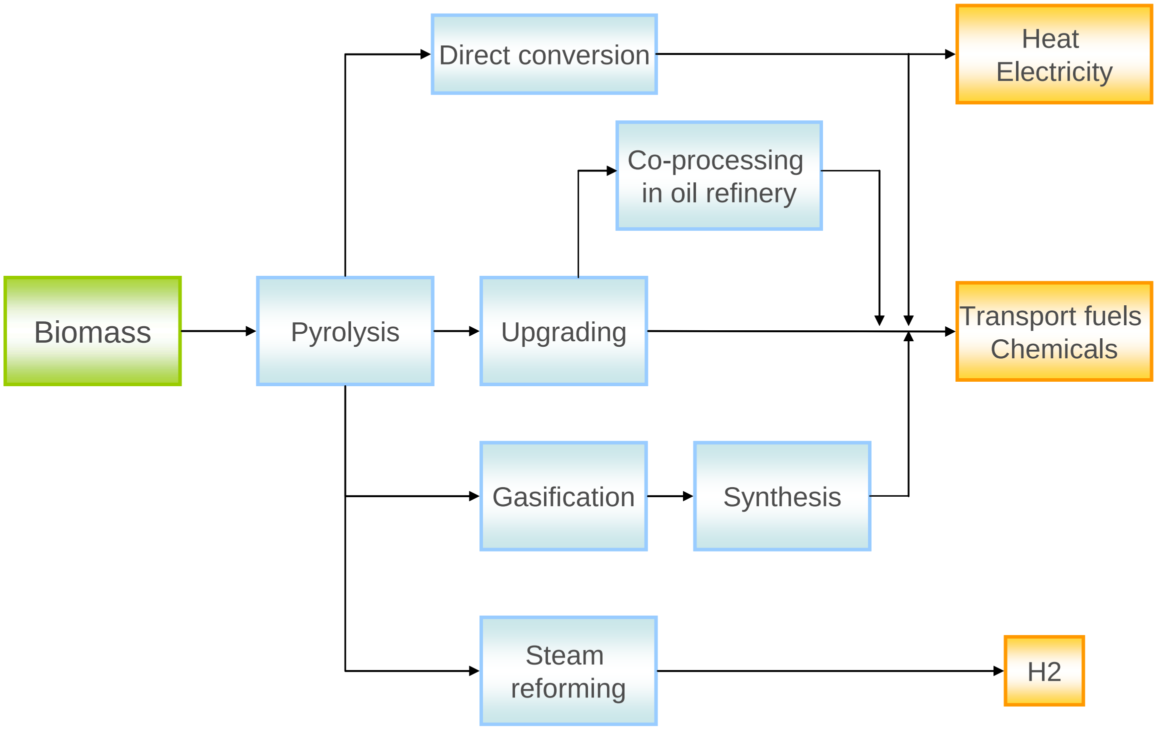


Figure ES-12 - Schematic illustration of utilisation pathways using pyrolysis (compiled according to Bridgwater 2007b, Marker et al. 2005 and Solantausta 2006)

Costs and sustainability issues

The major issues regarding costs are feedstock costs, process costs, land costs, labor costs, by-products, subsidies, and the role of competitive industries. Evaluation of costs for different biorefinery options is complicated task. Especially today there are many uncertainties regarding future feedstock prices and transportation costs.

Most biorefineries target a biofuel price of about US$1/gallon (below US$8/GJ). IEA estimates that the cost of BTL diesel from ligno-cellulose is currently more than $0.9 per liter of diesel equivalent, with a potential reduction to $0.7 - $0.8 per liter of diesel equivalent.

Hydrotreatment of oils and fats is an economically profitable concept, if low cost feedstock is available. Although the capital investment is slightly higher than in conventional biodiesel production, the premium quality and market value of the product may compensate the investment. The competitiveness is based on the superior quality of the end product, which is also widely preferred among vehicle manufacturers.

The costs for feedstock of diesel-type biofuels vary significantly between different regions. For example, straight vegetable oil produced in Asia (palm oil) is the cheapest, rapeseed oil produced in Europe the most expensive.

In a recent study fast pyrolysis was evaluated to a promising alternative in replacing fossil fuels in European Pulp & Paper Industry. The European P & P industry has a potential to build up to 50 pyrolyzers integrated to fluidized bed boilers. In the short-term, pyrolysis oil market is in fuel oil and natural gas replacement in lime kilns and boilers, while long-term RTD is focused on transportation fuels. The major challenge is to develop and demonstrate technical and economical feasibility of the concept and availability of woody biomass at competitive price. (Sipilä et al. 2007)

One major driving force for biofuels is the target to reduce greenhouse gas emissions. For the time being BTL is expensive, but could be a clean future option. Neste Oil has announced that life-cycle greenhouse gas emissions of NExBTL, hydrotreated biobased diesel fuel, are lower than for fossil diesel with the feedstocks evaluated. The calculations of lifecycle emissions are complicated, and many basic factors, like depreciation period used, can be questioned. One aspect concerns consideration of alternative options to use land/biomass. Generally, the benefit of using wood for electricity is substantially higher than using it for road fuels.

Sustainability issues will become ever more important when large-scale utilization of biomass will start. This will concern all new biomass options, and even new fossil resources. In 2007 sustainability of palm oil was discussed vividly, this is an example of sustainability problems, and the efforts to cope with them.

Comparison of Biodiesel Options

The primary biodiesel option has traditionally been FAME. Today, hydrotreatment of oils and fats provides a commercial alternative to FAME. Hydrotreatment of oils and fats is an efficient process, which produces a high-quality biodiesel from a large feedstock basis, even from non-food crops. However, the next generation BTL biodiesel will be the first option combining large-scale production from non-food feedstocks with high-quality biodiesel as product.

The next generation, BTL-type paraffinic biodiesel and hydrotreated biodiesel resemble each other as concerns end-use properties. A summary of the comparison of these fuels with FAME is as follows:

Table ES-4 - A Comparison of BTL-type and FAME-type biodiesel.

	BTL-type paraffinic fuels	FAME
Can be based on non-food crops	+	-
Simple, inexpensive production	-	+
Can be used as high concentration blends with diesel	+	-
Compatible with existing infrastructure and advanced diesel vehicles	+	-
Performance in engines/after-treatment devices (sulfur-free, low aromatics, no oxygen, high cetane, no engine oil dilution, no carryover of impurities)	+	-
Lubricity	-	+
Exhaust emissions, NOx reductions	+	-
Exhaust emissions, PM reductions	+	+
Handling and storage	+	-
Enables development of future engines/after-treatment devices	+	-

+ means benefit; - means drawback

In spite of the advantages listed above for next generation paraffinic BTL-type fuels, conventional biodiesel (FAME), being a low-toxicity product, will likely stay on the market far into the future. However, it can substitute for only a small fraction of diesel.

In general, barriers for biodiesel are related to costs, competition with food and other industries, arable land, regional markets, transport costs, poor agricultural practices in developing countries, water and fertilizer use, conversation of biodiversity, logistics, and distribution networks.

Nevertheless, the tremendous rise in production and use of fatty acid methyl esters as diesel fuel substitutes together with the large number of startup operations in hydrotreating vegetable oils and more general biorefineries all convey the message that biofuels are here to stay, and the future of biofuels seems assured. It will be important, though, to move away from the edible feedstocks for the future.

Integrated thermochemical platforms will probably take the lead in producing both gasoline and diesel range biofuels, serving as the first solution combining large-scale production and high-quality products. However, the potential for an early conflict between the fuel and the food industries may be underestimated, as well as sustainability problems.

Preface

This report illuminates the status of biodiesel fuels as replacements for a portion of the diesel fuel consumed worldwide. The report considers first today's "biodiesel" fuel, which typically is a fatty acid ester made from vegetable oils. The report then looks at the emergence of more advanced diesel replacement fuels – a 2nd generation biodiesel - made potentially from a more diverse range of biomass resources. This report has been produced as the final deliverable of the International Energy Agency's Advance Motor Fuels Implementing Agreement Annex XXXIV – Biomass-Derived Diesel Fuels: Subtask 1 – Analysis of Biodiesel Options.

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List of Abbreviations

ASTM	American Society for Testing and Materials
B100	100% biodiesel
B20	20% biodiesel blended with petro-diesel fuel
BTL	Biomass-to-liquid
CCS	Carbon Capture and Storage
CO	Carbon monoxide
CTL	Coal-to-liquid
DME	Dimethyl ether
DOE	Department of Energy (U.S.)
DTBP	di-tert-butyl-peroxide
EERE	Energy Efficiency and Renewable Energy (Division of U.S. DOE)
EHN	2-ethyl-hexyl-nitrate
EJ	Exajoules (10^{18} joules)
EPA	Environmental Protection Agency (U.S.)
EPACT	Energy Policy Act (U.S.)
FAME	Fatty Acid Methyl Ester
FFA	Free Fatty Acids
FOA	Funding Opportunity Announcement
FT	Fischer – Tropsch
FTD	Fischer – Tropsch Diesel fuel
GHG	Greenhouse Gases
GJ	Gigajoules
GTL	Gas-to-liquid
H/C	Hydrogen-to-Carbon ratio
HC	Hydrocarbon emissions
HO	Hydrotreated biobased diesel fuel
IGCC	Integrated Gasification Combined Cycle
Ktons	Thousands of tons
MSAT	Mobile Source Air Toxics
MTG	Methanol to gasoline
Mtons	Millions of tons
mtpa	Metric tons per anum
MW	Megawatts
MWh	Megawatts per hour
NBB	National Biodiesel Board (U.S.)
NOx	Nitrogen oxide emissions
NREL	National Renewable Energy Laboratory (U.S.)
PM	Particulate matter emissions
ppb	Parts per billion
ppm	Parts per million
REE	Rape Ethyl Ester
RME	Rape Methyl Ester
SME	Soy Methyl Ester
SoCab	South Coast Air Basin

TOE	Tons of oil equivalents
ULSD	Ultra-Low Sulfur Diesel
VOC	Volatile Organic Compounds
WEO	World Energy Outlook
XTL	Mixture of biomass with conventional fuel, e.g., biomass and coal

1 Introduction

Use of fatty acid esters (biodiesel, as they are commonly known today) as a substitute diesel fuel is on the rise around the world. Volumes of biodiesel used and produced are growing very rapidly from nearly zero in just the mid 1990s to several million metric tons per year currently. The outlook is very good for continued rapid growth in the market for fatty acid esters and hydrotreated oils and fats for at least the next decade. In addition, more advanced biodiesel options are expected from biorefineries.

Such a rosy outlook for biofuels is not without technical hurdles, though. Esters from vegetable oils face some serious technical barriers that either require special measures to accommodate the fuels or limit their practical use in some climates at some blend levels. Among these barriers are poor oxidative stability, incompatibility with some elastomers, low-temperature flow properties, higher NO_x emissions, and competition for the same resources that are used in the food industries.

When we talk of biodiesel fuels today, we are generally talking about fatty acid methyl esters, usually made in a transesterification process from vegetable oils, such as soy, rapeseed, sunflower, etc. These esterification plants are very efficient, with a very high percentage usage of the feedstock. They operate under fairly low temperatures and pressures, thus the product can be rather low in cost. The transesterification process is basically limited in feedstocks to using oils derived from vegetable, animal, and waste fats. And, the product is always an ester.

If we are to achieve greater impact of bio-derived fuels, we must utilize all varieties of biomass feedstocks and produce a broader slate of fuel choices, ranging from gasoline replacements to diesel replacements. Therefore, the world's attention is turning to concepts of more diverse manufacturing processes, and the notion of a flexible biorefinery is coming into being. A number of very promising biofuel production facilities are already up and running and producing high grade fuel products from biomass resources.

With all of the activity in this area, it is difficult for policy makers and researchers to stay abreast of the latest developments. Therefore, this annex was conceived as a means of illuminating in one report most of the developments and activities in the biodiesel arena and to make an assessment of the competing biodiesel production concepts with a view to characterizing the comparative advantages of the processes and the products.

The overall objective of the project has been to provide a better picture for the IEA-AMF of where the biodiesel industry is going in the future – how technical barriers will be overcome, what bio-derived fuels will replace significant quantities of diesel fuel, what will be the feedstocks for those fuels, and what will be the processes by which the fuels will be made. The technical task statements for the annex are listed below:

Task 1. Make a thorough review of the literature pertaining to the use of FAME as a diesel replacement fuel with a special emphasis on research results related to overcoming the technical barriers to the greater use of FAME in blend with diesel fuel. Assess the likelihood that reasonable solutions have been found or will be found to mitigate the major technical barriers, such as cold flow properties and NOx emissions from biodiesel blends. A summary of findings of this review will be included in the final report.

Task 2. Conduct an in-depth investigation into the new concepts being proposed for flexible biorefineries. This will include literature reviews, discussions with knowledgeable persons in the industries or laboratories from which the concepts are evolving, and thorough study of the concepts. The focus will be on understanding how broadly we can reasonably extend the range of biomass feedstocks as well as fuel products from the conceptual biorefineries in addition to thoroughly understanding the chemical and thermal processes required by the concepts. Results from this investigation will be summarized in the final report.

Task 3. Task 3 was planned to include a critical technical assessment of the various concepts for biorefineries, concentrating on analysis of energetics on the condition that five countries participate to the Annex. With four participating countries, Task 3 was limited to general view on feedstock availability, efficiency of production, logistics, and the influence on greenhouse gases. The target is to evaluate the most potential options to produce biodiesel from biomass giving the highest priority on sustainability of production.

This report is divided into two major sections: Part A. Biodiesel – Fatty Acid Esters; and Part B. Biodiesel – Advanced Options.

In Part A we discuss the rapidly growing market for biodiesel from fatty acid esters. We will cover the market, the manufacturing technology, fuel properties, emissions, life-cycle emissions, the conflict with food resources, technical specifications, national policies and incentives, and the potential future growth of the industry. These topics are covered in Chapters 2 through 8.

The emerging 2nd generation biodiesel fuels and processes are covered in Chapters 9 through 12. In these chapters we cover biofuel refineries, manufacturing process technologies, fuel properties and emissions, development and status of different biorefinery concepts, and cost and energy efficiencies.

2 Definition of Biodiesel and Biomass

2.1 Definitions

Biofuels are fuels that are made from biomass, and biomass can be defined as any plant related material that has captured energy of sun by photosynthesis. This report deals with (1) traditional biodiesel produced from oil plants, and (2) future biodiesel options.

The word, biodiesel, refers to a fuel made from biomass that has properties similar to those of petroleum-based diesel fuels. More specifically though, in common use today, the word refers to a fuel that is a mixture of fatty acid alkyl esters and made from vegetable oils, animal fats, or recycled greases. However, today biodiesel produced by hydrotreatment oil and fats is already commercially available, and Biomass-to-Liquids (BTL) biodiesel produced by gasification is under heavy development.

Feedstocks suitable for traditional biodiesel are very limited, as will be described in Part A "Biodiesel – Fatty Acid Esters" (essentially, the 1st generation of biodiesel fuels). Today, for all practical purposes only soy oil and rapeseed oil are used as feedstocks for biodiesel ester, even though other oil plants can be used as well. Since these vegetable oils are also used in great volumes in food production, then it seems inevitable that the competition for resources will be a big factor determining their use in transportation fuels. In the future, though, biodiesel processes will use a wide variety of feedstocks from oil plants to cellulosic feedstocks, or mixtures of different feedstocks, and these uses of the resources will not compete with their use in the food industries. Today's hydrotreatment process supports wider selection of suitable feedstocks liked with better end-use properties than esterification for traditional biodiesel. However, only BTL will solve large-scale production from inedible feedstocks.

This chapter describes what the word "biomass" implies and the potential for biomass. These issues set borderlines for the future development of biodiesel. A special chapter is devoted to vegetable oils and feedstocks for the traditional biodiesel (fatty acid esters). That discussion is divided in two parts (1) trends, prices, and limitations of vegetable oils used today as biodiesel feedstock, and (2) promising plant oils that could be used as biodiesel feedstocks.

Part B of this report – "Biodiesel – Advanced Options" will cover the biomass resources and advanced technologies that will be used to produce the 2nd generation of biodiesel fuels.

2.2 Definition of Biomass

Biomass can be defined as any plant related material that has captured energy of sun by photosynthesis. The renewable organic matter that is available includes agricultural crops and trees, wood and wood wastes and residues, plants such as oil plants, aquatic plants, grasses, residues, fibers, and animal wastes. (U.S. Roadmap 2002). The US DOE EERE divides biomass into three categories:

- woody biomass
- non-woody biomass and
- organic waste

Currently starchy grains and oily seeds are used mainly as feedstocks for biofuels: ethanol from e.g. sugar cane or corn, and biodiesel produced from vegetable oils. However, woody and grassy materials, cellulosic feedstocks[1], make up 70-90% of the total technically available biomass globally.

When considering the cellulosic biomass, the first new biofuel feedstocks might be industrial residues from forestry and agricultural sectors. In the mid-term, cellulosic stalks, leaves, husks, and straw from agriculture or black liquor from wood pulping could be used, as well as animal manures. In the long term, dedicated energy crops, trees, and grasses are expected to be available. (U.S DOE EERE).

It should also be noticed that promising feedstocks should be considered as future options for traditional biofuel processes, such as oil plants that are not utilized today for energy (e.g., algae).

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[1] *Cellulose* represents some 40% to 60% of the carbon content of biomass. Cellulose is a complex sugar polymer, or polysaccharide, made from the glucose (six-carbon sugar). Its crystalline structure makes it resistant to hydrolysis, the reaction that releases simple, fermentable sugars.
Hemicellulose represents some 20% to 40% of carbon in cellulosic biomass. It is a complex polysaccharide made from a variety of five- and six-carbon sugars. It is relatively easy to hydrolyze into simple sugars, but the sugars are difficult to ferment to ethanol.
Lignin is a complex polymer, which provides structural integrity in plants. It makes up 10% to 24% of the carbon in biomass. It remains as residual material after the sugars in the biomass have been converted to ethanol. It contains a lot of energy and can be burned to produce steam and electricity.

2.3 Vegetable Oils – Today's Biodiesel Feedstocks

2.3.1 Vegetable Oils for Food or Fuel?

The growing demand for biodiesel from vegetable oils can eventually put a strain on the balance between fuel uses and food uses. The Promar analysis (Promar 2005) paid considerable attention to this potential concern. Addressing the question from the perspective of the U.S., the analysts found the following:

- Total revenue for U.S. soybean farmers will rise by about $2 billion by 2012/13
- Meal will become the burden on the market instead of vegetable oil.
- High vegetable oil prices will stimulate world production of high-oil seeds and palm oil.
- The pressure on vegetable oil prices from biodiesel demand will raise concerns in the global food industry.

Promar projected the world vegetable oil use for fuel up to 2012/13. This projection is shown below in Figure 2.1 in terms of the global mix of oils as well as the distribution by geographic region. The EU will continue to be the major user of vegetable oils for fuel, but their proportion of the total will shrink from 90% in 2005 to about 60% in 2012. Rapeseed oil use will diminish from 70% in 2005 to less than 40% in 2012. At the same time, soy oil use will rise to about one third of the world use in 2012.

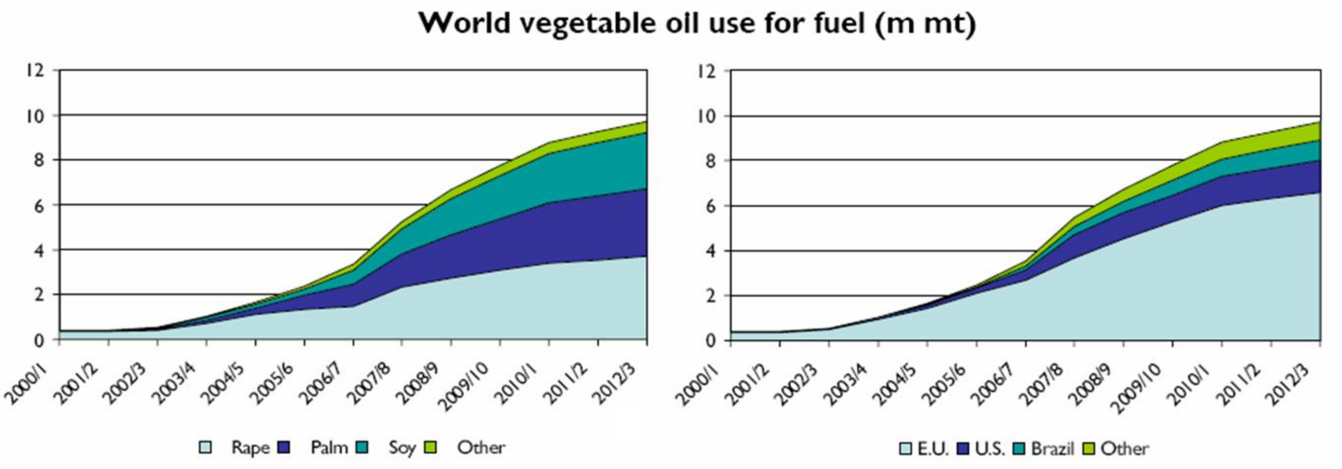

Figure 2.1 - World Vegetable Oil Use for Fuel to 2012/13 (Promar 2005)

Demand for vegetable oil is growing even without the increment brought on by the demand for biodiesel. So, in total, vegetable oil use will rise quite substantially as illustrated in Figure 2.2 below.

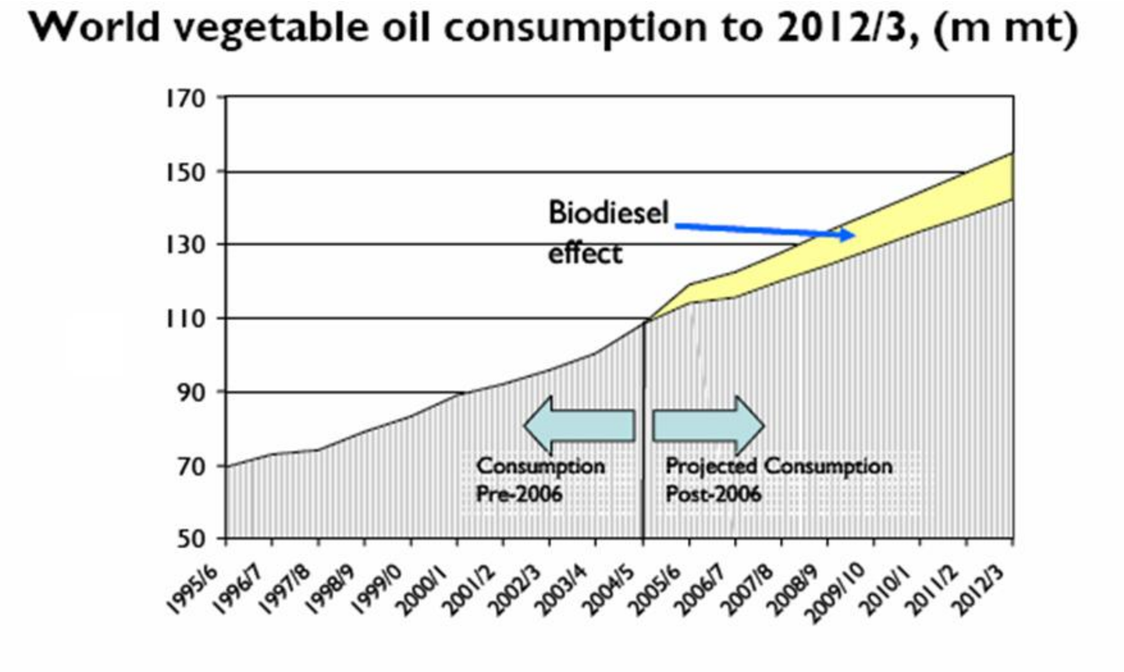

Figure 2.2 - World Vegetable Oil Consumption to 2012/13 (Promar 2005)

Growth of this magnitude in demand for vegetable oil will exceed the growth in world demand for protein meal, thus lessening protein meal's value on the market. Oil for food and oil for fuel have important linkages, and in their study Promar examined the key linkages that result from the incentives to produce, process, and market oilseeds and corn and their products. Their findings are as follows:

- Higher demand for vegetable oil for production of biodiesel and industrial use will encourage more crushing of oilseeds for their oil and increased planting of oil palm
- More oilseed production will increase the availability of protein meals from the oilseed crush
- Vegetable oil prices will be higher and protein prices will be lower (as a result of increased production)
- Since world oil and protein markets are interlinked, the overall impact will be determined by the interaction of global supply and demand

Using a model, the analysts made forecasts for biodiesel scenarios for both the EU and the U.S. In the EU the main driver is the rapid growth in demand for vegetable oil for fuel. The EU is currently a net exporter of soybean and rapeseed oil, but in the future scenario the EU will become a net importer of soy, rape, sun, and palm oils. Figure 2.3 below shows the rising net imports pattern. Negative numbers represent net exports, and those all rise above zero by 2012 in this scenario.

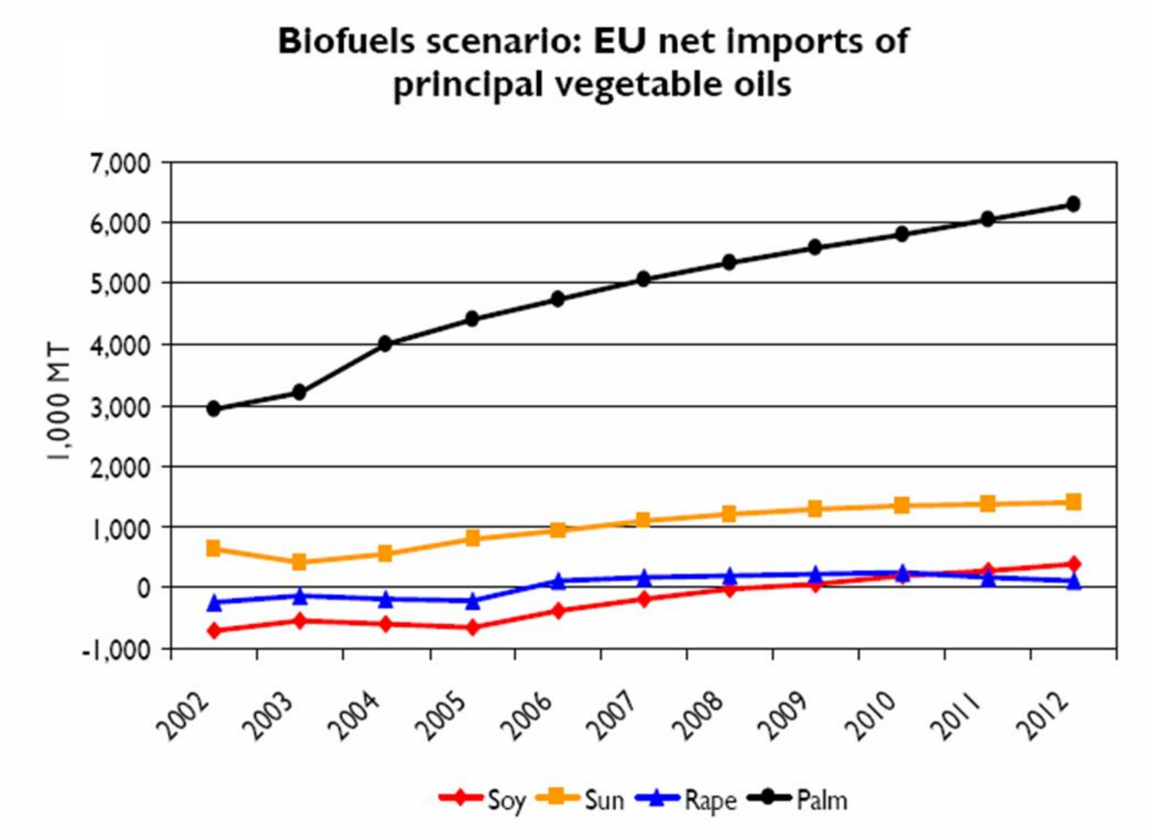

Figure 2.3 - Scenario for EU Net Imports of Principal Vegetable Oils (Promar 2005)

The scenario for the U.S. is represented in Figure 2.4 below. In this case the trade impacts are not as severe because of the greater ability of the U.S. to generate additional vegetable oil supplies through domestic production. For the four oils studied, the biofuels scenario shows the net imports rising to 1 million metric tons as rape and palm oil imports increase and soybean oil exports decrease.

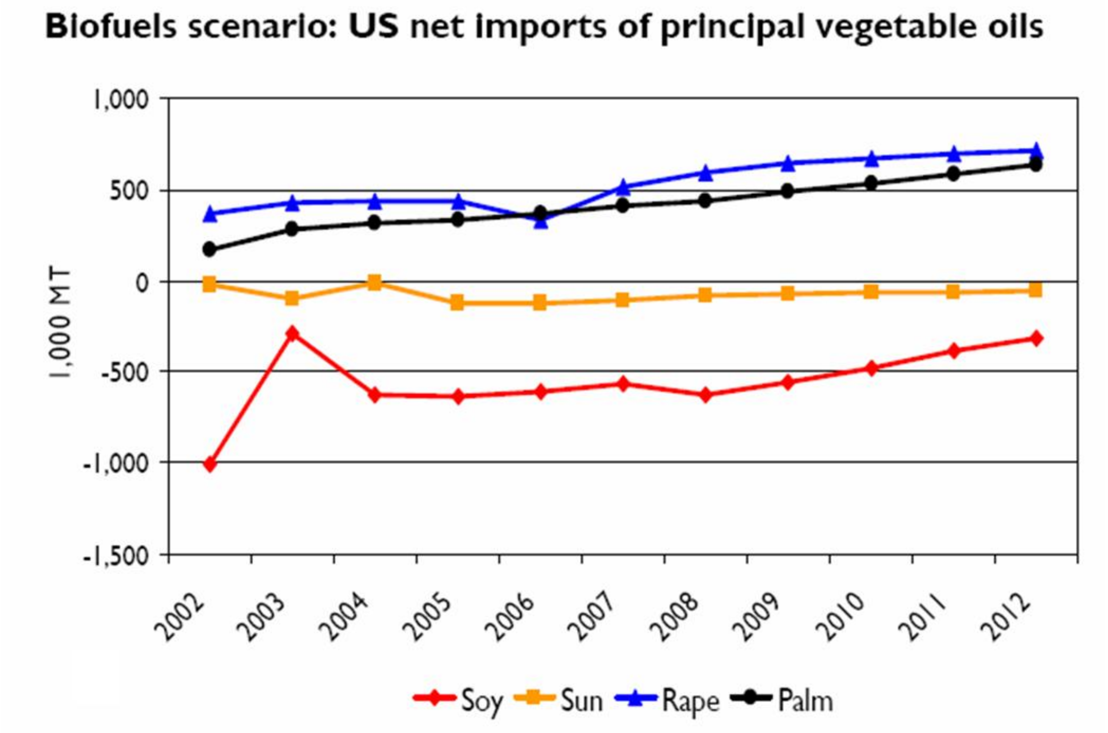

Figure 2.4 - Scenario for US Net Imports of Principal Vegetable Oils (Promar 2005)

In addition to the dilemma with the competition for food or fuel, other competing uses of vegetable oils or biomass in general exist. One such competing use is combustion and co-firing and cannot be ignored when we consider future use of biomass resources[2]. In general, solid biomass is more efficiently used for power and heat than for transportation fuels.

2.4 Promising Oil Plants and Crop Yields of Various Options

There is a strong search for oil plants, which would give high crop yields without demanding requirements on the soil quality. Especially palm oil and jathropa have gained a lot of attention lately as promising oil plants for biodiesel production.

For a reference point related to selection of oilseed for optimum yield, we include here a table of yields of a number of oilseed crops and other sources of vegetable oils to serve as a resource for biodiesel production. We should note that just because a crop has a high yield per unit area of land does not necessarily mean that it is, therefore, a good candidate

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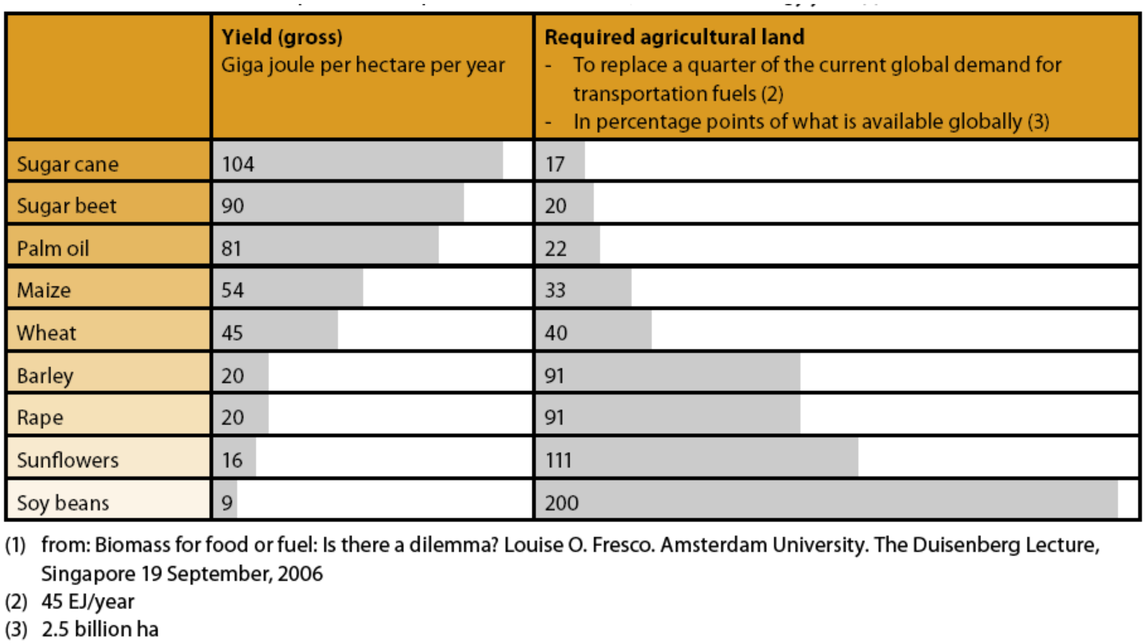
[2] Combustion and co-firing are processes not directly related to biodiesel issues. However, it must be taken into account as a major competitive sector for usage of biomass feedstock. Co-firing of biomass in traditional coal-fired boilers represents one combination of renewable and fossil energy utilization. Biomass combustion and co-firing can be utilized for heat and power generation, and on small and medium scale CHP plants and with coal in traditional coal-fired boilers. Biodiesel production can also be combined with CHP plants.

for biodiesel in all cases. For example, palm oil has a relatively huge yield per hectare, but it also has a very high cold flow point, which would present problems if used as FAME but not as hydrotreated oil.

Crop	kg oil/ha	litres oil/ha	lbs oil/acre	US gal/acre
corn (maize)	145	172	129	18
cashew nut	148	176	132	19
oats	183	217	163	23
cotton	273	325	244	35
hemp	305	363	272	39
soybean	375	446	335	48
linseed (flax)	402	478	359	51
hazelnuts	405	482	362	51
pumpkin seed	449	534	401	57
mustard seed	481	572	430	61
camelina	490	583	438	62
sesame	585	696	522	74
safflower	655	779	585	83
sunflower	800	952	714	102
cocoa (cacao)	863	1,026	771	110
peanuts	890	1,059	795	113
rapeseed (Canola)	1,000	1,190	893	127
olives	1,019	1,212	910	129
castor beans	1,188	1,413	1,061	151
jojoba	1,528	1,818	1,365	194
jatropha	1,590	1,892	1,420	202
macadamia nuts	1,887	2,246	1,685	240
Brazil nuts	2,010	2,392	1,795	255
avocado	2,217	2,638	1,980	282
coconut	2,260	2,689	2,018	287
oil palm	5,000	5,950	4,465	635

Table 2.1 - Yields for Various Vegetable Oil Sources (Wikipedia 2007)

Table 2.2 shows the influence of crop yield on the agricultural land required. For instance, if 25% of global demand for transport fuels would be covered by soy bean based fuels, this would require twice as much arable land that is globally available. With sugar cane, only 17% of arable land would be needed, respectively. Of course, all arable land is not suitable to grow high yield plants.



	Yield (gross) Giga joule per hectare per year	**Required agricultural land** - To replace a quarter of the current global demand for transportation fuels (2) - In percentage points of what is available globally (3)
Sugar cane	104	17
Sugar beet	90	20
Palm oil	81	22
Maize	54	33
Wheat	45	40
Barley	20	91
Rape	20	91
Sunflowers	16	111
Soy beans	9	200

(1) from: Biomass for food or fuel: Is there a dilemma? Louise O. Fresco. Amsterdam University. The Duisenberg Lecture, Singapore 19 September, 2006
(2) 45 EJ/year
(3) 2.5 billion ha

Table 2.2 Indication of land required for the production of biomass (1) (Cramer 2007).

The oil palm is originally from West Africa. It does not have any particular demands on the soil quality. In the tropics at 24-28°C temperature, the fruits can be harvested all year round. The oil palm bears fruit after three years, and gives full yield for 12 to 60-year old plants (can live for up to 120 years). The palm fruit consists of fatty flesh (some 40% of fat), a hard shell, and 2-3 kernels (seeds). Yield from oil palm can be 3.5-6.0 tons of oil per hectare. (Wikipedia 2007).

Palm oil is commonly used as cooking oils, in margarine, bakery, animal feed, and many other food applications. It is also used in some industrial applications such as candles and soaps. About 80% of production is used as food. Palm oil is used increasingly also for power generation and biodiesel production. In Europe, 1.5 Mtons of palm oil was used in power generation in 2005. In total, 4,400 ktons of palm oil was imported in Europe. (Reinhardt 2007 Fediol).

The world production of palm and soy oil has about doubled since 1993, whereas production of rapeseed oil and sunflower oil has stayed more or less at a constant level (Fediol statistics). About 44% of palm oil is produced in Malaysia, and about 41% in Indonesia. These countries are planning to increase palm oil production, which would be in FAO's opinion a threat to rain forests (Reinhardt 2007). Indonesia may have difficulties in increasing palm oil production as planned due to lack of confidence towards sustainability. There are alternative options to clearing natural forests for palm oil plantations. Reinhardt (2007) referred to several studies claiming that 8.6-64.5 million hectares of fallow land growing alang-alang grass is available in Indonesia. Another option is to convert other plantations, such as cocoa and rubber, to palm oil plantations. However, for oil palm and timber industries it is most profitable to clear natural forests.

Jatropha is a new candidate for biofuel feedstock, and as non-food option it does not compete with food. Jatropha curcas, a relative of castor, grows well in marginal and poor soils, and even in the crevices of rocks. It is easy to establish, it grows relatively quickly and produces seeds for 50 years. Jatropha trees endure heat, withstand a light frost, and its water requirement is low. It is suitable for preventing soil erosion and shifting of sand dunes. Estimates of yield from a Jatropha plantation varies a lot, from some 700 to 3000 liters/ha, which is low yield when compared to oil palm, but high when compared to soy oil. Jathropa is toxic, with exception of one variety living in Mexico. (Green Car Congress, Wikipedia, Jathropa World)

China plans to establish 13 million hectares jatropha plantation, producing some 6 million tons of biodiesel yearly, and fuel for a 12 MW power plant, by 2010. Currently, 2 million hectares is devoted to jatropha in China for candles, soap etc. (DieselNet 2007). Jatropha is planted in India with target to replace around 5% of India's 40-million tons/year diesel consumption (www.mozlegal.com). Jatropha plantations exist also in other countries, like the Philippines, Thailand and African countries, Ghana and South-Africa, for instance. Sweden is considering using Jatropha in addition to tall oil in Piteå's black liquor gasification pilot. (Miljöbilens värld 2007).

2.5 Total View on Biomass Potential and Limitations

World energy demand is projected to increase from 467 EJ to 714 EJ by 2030, and transport energy demand from 94 EJ to 143 EJ, respectively. As a reference, resources of fossil fuels are shown in Table 2.32. Today bioenergy covers some 40-55 EJ/a of world energy (IEA Bioenergy 2007). In 2004, biomass & waste[3] represented 10.5% of global annual energy demand (IEA WEO2006). IEA Bioenergy (2007), estimates that 200-400 EJ/a of biomass could be harvested annually for energy during this century. Another report, the IEA "Technology Essentials – Biofuel Production" (IEA 2007), claims that biomass potential will be 100-200 EJ/year by 2050. Both of these estimates indicate that the potential of feasible biomass is relatively high.

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[3] Biomass includes wood, wood waste, and black liquor from pulp mills and to lesser extent wastes like municipal solid waste, landfill gas, sludge waste, tires and agricultural by-products.

Table 2.3 - Resources and consumption of major fossil fuels (BP 2007)

	Resources Billion toe	Resources to Production (R/P)
Coal	564	147
Crude oil	165	41
Natural gas	163	63

The IEA World Energy Outlook 2006 predicts that the usage of biofuels will cover 4-7% of world transport fuel demand in 2030, which means about 6-10 EJ. Another report, the IEA "Technology Essentials – Biofuel Production" (IEA 2007), estimates that biofuels could cover 65 EJ of the transport fuels by 2050 (biodiesel 20 EJ and ethanol 45 EJ). This would represent a significant share of transport fuels.

Biofuel production today uses 14 million hectares (1% of arable land), which could increase to 2.5-3.8% by 2030, and possibly to 4.2%, if enzymatic hydrolysis and gasification of biomass will become feasible. (IEA WEO 2006). Cramer et al. (2007) evaluated how much land would be needed to replace 25% of transportation fuels using different feedstocks. Table 2.4 shows yields in the left-hand side, and in the right-hand side the amount of agricultural land needed to replace 25% of the current demand of transportation fuels in absolute terms (bars) and as share of agricultural land that is globally available today (numbers). When using sugar cane, 17% of globally available agricultural land would be needed to replace 25% of transportation fuels, whereas with rape seed 91% of land would be needed. When using soy beans, agricultural land area should be doubled to cover 25% of transport fuels.

Biomass potential for energy is expected to increase based on higher plant yields per hectare, which is achieved by improved cultivation methods and by the use of dedicated energy crops. Selective breeding and genetic engineering may result in plant strains that produce greater amounts of desirable feedstocks or chemicals or even compounds that the plant does not naturally produce. (U.S. DOE EERE). This is also raising cautions on risk of developing crops, which may become invasive species. (Raghu 2006).

The highest increase and usage of biofuels is expected in the U.S; Europe will take the second place from Brazil.

In the U.S. it is estimated that 512 million dry tons of biomass equivalent to 8.09 quads (~200 Mtoe) of primary energy could initially be available at less than $50/dry ton delivered (Walsh et al. 2000, 2003, Ugarte et al. 2003, U.S. DOE EERE). It is estimated that there is potential to replace some 30% of US gasoline consumption by biofuels by 2030. In the US over 1 billion tons/year lignocellulosic biomass could be available, enabling long-term potential to displace 50-70% of the gasoline demand. (Russo 2007). Nair (2006) reported that projected potential of cellulosic waste would be globally some 80% of transport fuels and in U.S. about 54%.

Dayton (2007) estimated U.S. biofuel production in different scenarios with respect to yield growth and energy crops (Figure 2.5). Biofuels would be primarily produced with a biochemical platform (fermentation is a biochemical process also), and secondly with a thermochemical platform. Volumes of biofuels obtained with traditional technologies would stay at a low level.

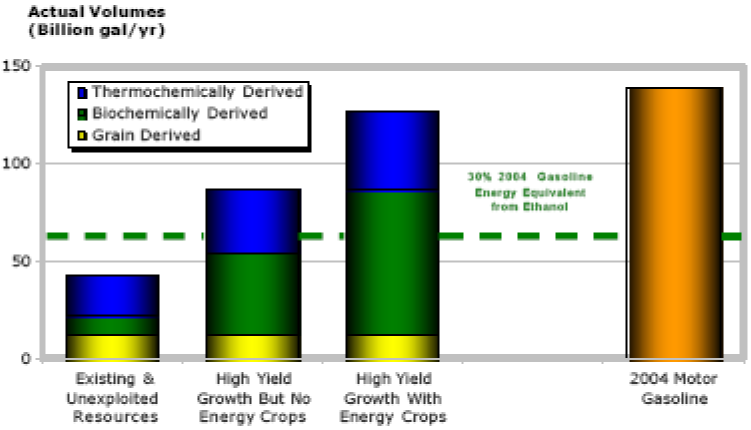


Figure 2.5 - U.S. Biofuel Production Scenarios (Dayton 2007)

The European Environment Agency (EEA) concluded that the technically available biomass potential could represent 15–16 % of the projected energy demand of the EU-25 in 2030. (EEA 2006). However, the biomass potential is strongly dependent on the price development, which is seen in Figure 2.6 (EEA 2007).

In Europe, the potential for bioenergy would come from the waste sector, bioenergy crops, from forestry and some would be released from competing industries by 2030. Examples of the calculation of European biomass potential taking limitations into account are as follows:

- In the EU, 30% of the total straw resources can be brought to large processing plants. Total straw resources are 820 PJ, and cereal straw represents some 90% of agricultural waste.
- In the EU, an additional potential in forest residuals and complimentary fellings is 1008 PJ/year. It is estimated that at price of 4 €/GJ, some 30% of forest residuals could reach biofuel plants. In the BTL plants wood use of 471 PJ could result in 170 PJ of synthetic diesel. 2/3 of forest residuals are expected to be used in pulp mills. (Edwards 2007).
- The organic waste from the European compost network is 56 Mtons in EU-25, and the quantity of manure is much larger (Edwards 2007). One estimate of biogas potential is 770 PJ by 2020, which means around 4% of European transport energy (Jönsson 2004). However, the question is whether to use it for heat and electricity or as transport fuel?

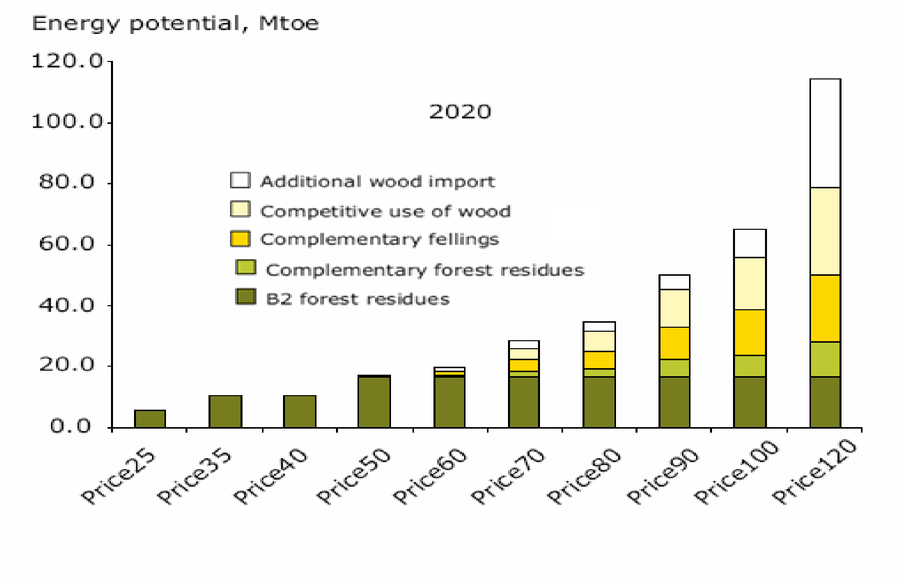


Figure 2.6 - Energy Potential of Forest Biomass at Different Cost Scenarios in EU-25 by 2020 (EEA 2007)

The estimation of the biomass potential depends on many factors, such as collection and removal, transportation, sustainability, and desired characteristics. (U.S. DOE EERE). Environmental impacts and costs also play a major part in the equation. Despite of a substantial biomass potential, there are a number of limitations to be taken into account when the true commercial potential is evaluated, especially as concerns liquid biofuels.

- Costs of collection, storing, and transporting biomass feedstocks
- All potential biomass is not suitable for conversion to liquid biofuels (e.g., municipal waste)
- Large biorefineries cannot use inaccessible biomass
- Competitive usage, e.g. wood for black liquor (a side product of the pulp and paper industry)
- Priority on biomass usage is on heating and electricity, not on biofuels
- Crop yield projections are questionable

One problem with biomass is low energy density. For instance, for salix bundles energy density is 160 kg/m^3, for tree logs 460 kg/m^3 and pellets 650 kg/m^3. Drying (torrefaction) can increase density to 1200 kg/m^3, which is at the same level as for pyrolysis oil (Vliet 2007). In comparison with fossil fuels high biomass volumes are needed for equivalent energy content (Figure 2.7).

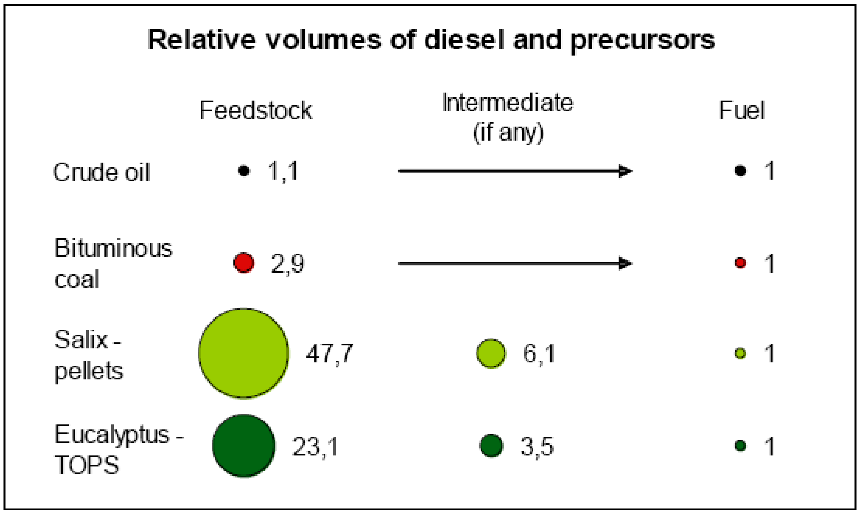


Figure 2.7 - Biomass Volumes Needed to Produce Same Amount of Energy as Fossil Fuels (Vliet 2007)

A. BIODIESEL – FATTY ACID ESTERS

3 What is Biodiesel?

In general terms, the word “biodiesel” refers to a fuel made from biologically derived resources that has properties similar to those of petroleum-based diesel fuels. More specifically though, in common use today, the word refers to a fuel that is a mixture of fatty acid alkyl esters and made from vegetable oils, animal fats, or recycled greases.

History of Biodiesel

The first known use of vegetable oil as a fuel was in a diesel engine, built by the Otto company and demonstrated at the 1900 World’s Fair. Pure peanut oil was used in that demonstration. But, widespread use of vegetable oils as fuels never materialized since petroleum-based fuels came into existence at about the same time, and at least in those early years, mineral oil appeared to be quite abundant. Nevertheless, oil shortages in the 1930s, 40s, and even in the latter part of the 20th century focused attention on the potential for replacement of petroleum diesel fuel with fuels derived from vegetable oils.

Use of Straight Vegetable Oil as a Diesel Fuel

Vegetable oils as such cannot be used as diesel fuel in today’s on-road diesel engines: engine damages are foreseen, warranties will not apply and exhaust gases can be extremely harmful. Engines that have not been manufactured or modified for use of vegetable oils should not use vegetable oils, not even as blends of vegetable oils with diesel fuel.

A number of properties of straight vegetable oils are out of range when considering usage in diesel engine. To start with, viscosity of vegetable oils are typically more than 10-fold when compared to diesel fuel. Also cetane number and distillation range are unsuitable. Straight vegetable oils needs to be processed by transesterification of hydrotreatment to products, which are more suitable to be used in diesel engines or as blends with diesel fuel.

The use of unsaturated triglyceride oils as a fuel may cause significant problems, which make their use inadvisable or impractical. The usage is recommended only in diesel engines specifically developed for straight vegetable oils, such as Elsbett engine. The main problems relates to the higher viscosity of the triglyceride oils and their chemical instability, which leads to incomplete combustion. These properties can also cause poor cold weather performance, gumming of injectors, and coking of valves. Generally, one should expect possible serious damage to engines from the use of vegetable oils in engines that have not been manufactured specifically for vegetable oils as fuels. There have been also indications of extremely high mutagenicity when using plant or animal oils as such in diesel engines.

Properties of vegetable oils

As mentioned, properties of vegetable oils are unsuitable for diesel engine, or to be used as blends with diesel fuel.

Properties of vegetable oils vary between the types of vegetable oils. Freezing point, viscosity, and cetane number can vary greatly depending on the selection of plants from which the oils are derived. For example, oils from tropical plants, such as coconut and palm, have the highest cetane numbers but also the worst cold flow properties.

The viscosity of plant and animal oils varies widely from crystalline solids to light oils at room temperature. High melting points can cause problems in fuel systems such as partial or complete blockage as the triglyceride thickens with falling temperatures. To some extent, the same phenomena can happen with diesel fuel itself, but it is much easier to control in the refining process, which is a common practice in the oil refineries, prior to distributing the fuel to the customer.

Many vegetable oils have drying or semi-drying properties which further restricts their use as fuels. The drying properties result from the double and triple bonds’ in the unsaturated oil molecules being broken by atmospheric oxygen and being converted to peroxides. Cross-linking can then occur, and the oil irreversibly polymerizes into a plastic-like solid. In the high temperatures of internal combustion engines the process is accelerated, and the engine can quickly become gummed-up with the polymerized oil.

The traditional measure of the degree of bonds available for this process is the "Iodine Value" (IV); it is determined by adding iodine to the fat or oil. The amount of iodine adsorbed per 100 mil of oil is then the IV. A higher value of IV is due to a greater number of double bonds, and the oil has a higher potential for polymerizing. The IV can be reduced with hydrogenation of the oil, wherein the hydrogen breaks the double bonds and converts the oil to a more saturated oil. This reduces the tendency for the oil to polymerize, but it also increases the melting point of the oil.

Table 3.1 below illustrates this point by comparing the melting points and IV of various vegetable oils and animal fats. Note that the melting points are higher with lower iodine values, that is for example, linseed oil has a very low melting point and a very high iodine value.

Waste vegetable oils can also be used as feedstocks for biodiesel. In the U.S. alone, more than 11 billion liters of waste vegetable oil is available annually from food producers, fast food restaurants, etc. This volume of waste vegetable oil represents the equivalent of 1% of U.S. oil consumption. However, to use waste vegetable oil as a motor fuel feedstock requires even more precautions.

In order to make the use of vegetable oils and animal fats in engines more practical and less problematic, the vegetable oil must be transesterified to biodiesel – a chemical process. This process will ameliorate some of the undesirable properties of straight vegetable oils and animal fats. But, as we shall see later, the selection of feedstock will still affect the properties of the "finished" fuel – biodiesel.

Table 3.1 - Melting Points and Iodine Values for Various Vegetable Oils And Animal Fats

Oils and their melting points and Iodine Values		
Oil	**Approx. melting point deg C**	**Iodine Value**
Coconut oil	25	10
Palm kernel oil	24	37
Mutton tallow	42	40
Beef tallow	-	50
Palm oil	35	54
Olive oil	-6	81
Castor oil	-18	85
Peanut oil	3	93
Rapeseed oil	-10	98
Cotton seed oil	-1	105
Sunflower oil	-17	125
Soybean oil	-16	130
Tung oil	-2.5	168
Linseed oil	-24	178
Sardine oil	-	185

Journey to Forever (http://journeytoforever.org/biodiesel_yield.html)

How is Biodiesel Made?

Biodiesel is made from oils in a process called transesterification. In this process the triglyceride oils in the vegetable oils, animal fats, or recycled greases are reacted with an alcohol (most commonly, methanol and to a lesser extent, ethanol), forming fatty acid alkyl esters (biodiesel) and glycerin. The process requires heat and the use of a strong base catalyst, e.g., sodium hydroxide or potassium hydroxide.

Feedstocks with less than 4% free fatty acids (vegetable oils and some food-grade animal fats) can be processed in the simple transesterification process as simplified in the illustration below:

Triglycerides + Free Fatty Acids (<4%) + Alcohol - - > Alkyl esters (biodiesel) + Glycerin

Feedstocks with greater than 4% free fatty acids (inedible animal fats and recycled greases) must go through a pretreatment process – and acid esterification – before the transesterification process. Here the feedstock is reacted with an alcohol with a strong *acid* catalyst (sulfuric acid). This process converts the free fatty acids to biodiesel, and the remaining triglycerides are converted to biodiesel in the transesterification process. The pretreatment process is illustrated in the simplified equation below:

Triglycerides + Free Fatty Acids (>4%) + Alcohol - -> Alkyl Esters (biodiesel) + Triglycerides + Glycerin

A typical biodiesel plant combining the pretreatment process and the transesterification process is illustrated in the schematic diagram, Figure 3.1 below:

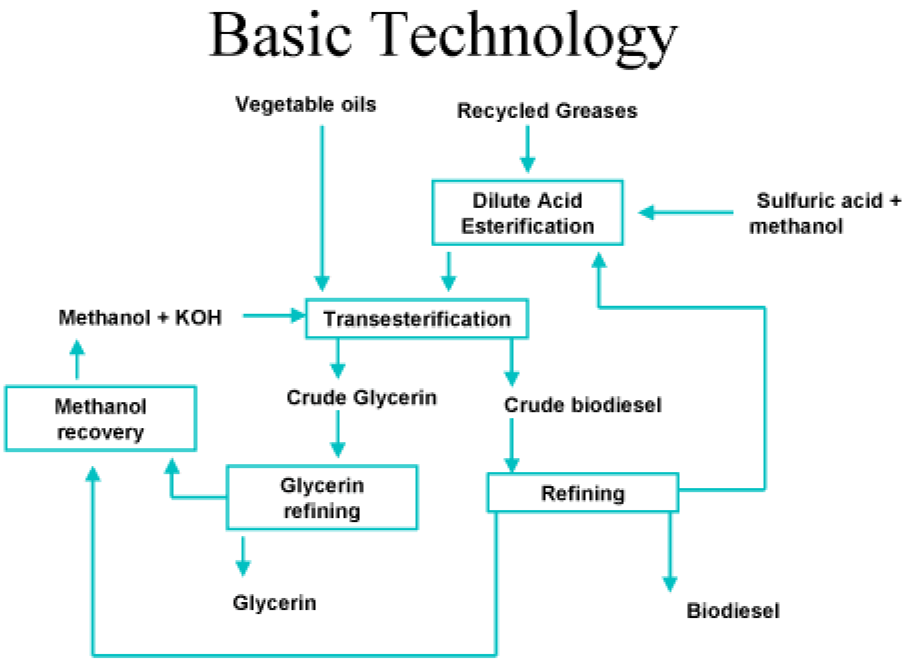


Figure 3.1 - Schematic Diagram of Typical Biodiesel Transesterification Plant (DOE Biomass Program)

Processes within the transesterification plant are described as follows[2]:

- ***Acid Esterification.*** *Oil feedstocks containing more than 4% free fatty acids go through an acid esterification process to increase the yield of biodiesel. These feedstocks are filtered and preprocessed to remove water and contaminants, and then fed to the acid esterification process. The catalyst, sulfuric acid, is dissolved in methanol and then mixed with the pretreated oil. The mixture is heated and stirred, and the free fatty acids are converted to biodiesel. Once the reaction is complete, it is dewatered and then fed to the transesterification process.*
- ***Transesterification.*** *Oil feedstocks containing less than 4% free fatty acids are filtered and preprocessed to remove water and contaminants and then fed directly to the transesterification process along with any products of the acid esterification process. The catalyst, potassium hydroxide, is dissolved in methanol and then mixed with and the pretreated oil. If an acid esterification process is used, then extra base catalyst must be added to neutralize the acid added in that*

step. Once the reaction is complete, the major co-products, biodiesel and glycerin, are separated into two layers.

- ***Methanol recovery.*** *The methanol is typically removed after the biodiesel and glycerin have been separated, to prevent the reaction from reversing itself. The methanol is cleaned and recycled back to the beginning of the process.*
- ***Biodiesel refining.*** *Once separated from the glycerin, the biodiesel goes through a clean-up or purification process to remove excess alcohol, residual catalyst and soaps. This consists of one or more washings with clean water. It is then dried and sent to storage. Sometimes the biodiesel goes through an additional distillation step to produce a colorless, odorless, zero-sulfur biodiesel.*
- ***Glycerin refining.*** *The glycerin by-product contains unreacted catalyst and soaps that are neutralized with an acid. Water and alcohol are removed to produce 50%-80% crude glycerin. The remaining contaminants include unreacted fats and oils. In large biodiesel plants, the glycerin can be further purified, to 99% or higher purity, for sale to the pharmaceutical and cosmetic industries.*

Figure 3.1 above represents the transesterification process when methanol is used as the alcohol in the process, and the product is a fatty acid methyl ester. In fact, the use of methanol is the most common production technique and the least expensive, but not the only one. Ethanol and higher alcohols such as isopropanol and butanol can also be used for the same purpose. So, for example, if ethanol is used instead of methanol, the product will be a fatty acid ethyl ester. The alcohols of higher molecular weight will produce biodiesel fuels with improved cold flow properties at the cost of a less efficient transesterification process.

Any free fatty acids (FFAs) in the base oil are either converted to soap or 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 major byproduct of the transesterification process is glycerin, which has thousands of industrial and chemical uses in household products and foods. As such, the glycerin has market value which helps to offset the cost of production of biodiesel fuels. However, that value will become less and less as production of biodiesel from esterification of vegetable oils goes up and the market for glycerin becomes over-supplied.

3.1 Impacts of Feedstock Properties on the Transesterification Process

Animal fats and vegetable oils are composed of triglycerides, each of which is composed of long-chain fatty acids attached to a glycerin backbone. Biodiesel consists of fatty acid chains that are bonded to a methanol molecule, with the glycerin having been removed during the transesterification process. When the fatty acid chains break off the triglycerides, they are free fatty acids (FFA), which are still desirable as biodiesel feedstocks, but require different production processes. Biodiesel feedstocks are classified depending on their free fatty acid content as follows:

- Refined oils, such as soybean and rapeseed with FFA less than 1.5%
- Yellow greases and animal fats with low FFA content – less than 4%
- Greases and animal fats with high FFA – greater than 20%

Commercial biodiesel production technologies can be grouped according to the categories of feedstocks above as follows:

- Refined oils - Base catalyzed transesterification
- Greases and fats with low FFA content - Base catalyzed transesterification
- Greases and fats with high FFA content - Acid esterification followed by transesterification

There are different considerations with each of these production technologies, so the following is a brief explanation of the differences (Kinast, 2003).

Refined Oils: The base catalyzed transesterification process produces biodiesel with high efficiencies – up to 99.9% after removal of all of the excess methanol, catalyst, and glycerin. The chemical reaction requires 3 molecules of methanol (or other alcohol) representing about 10% by weight of methanol to vegetable oil. The typical input and output streams are shown below:

Input:

Refined oil	1,000 kg
Methanol	107 kg
Potassium Hydroxide	10 kg
Acid	8 kg
Water	17 kg
Electricity	20 kWh

Output:

Biodiesel	1,000 kg
Glycerin	125 kg
Fertilizer	23 kg
Byproduct chemicals	nil

Different catalysts can be used, and anhydrous ethanol, isopropyl, or butyl alcohols can be substituted for methanol, but yields might be lower. Most biodiesel today is produced by this process for several reasons:

- It requires only low temperature and pressure (approximately 60^{o} C and atmospheric pressure)
- The yield is high, and the reaction times are short, plus there are minimal side reactions
- It is a direct conversion to biodiesel with no intermediate compounds
- Materials of construction are common and not exotic

Greases and fats with low FFA content: The process for this category of feedstocks is simply a variation from the basic process described above. A small amount of the base catalyst is added to the feedstock to react with the free fatty acids, forming soap. The soaps are removed, and the transesterification process then is used on the remainder.

Greases and fats with high FFA content: This process involves acid esterification followed by transesterification. The free fatty acids are first reacted with methanol and acid catalysts such as sulfuric acid to form methyl esters. The yield in this process is about 96% where the other 4% is made up of free fatty acids that will react with the base catalyst in the transesterification step to follow. Total yield can approach 99% depending on the amount of free fatty acids in the feedstock and the bi-products that are produced. The largest cost in producing biodiesel is the feedstock as illustrated in Figure 3.2 below. Depending on the size of the facility, the cost of the feedstock can be 65% to 78% of the overall production expense. This represents a strong incentive to use the lowest-cost feedstock.

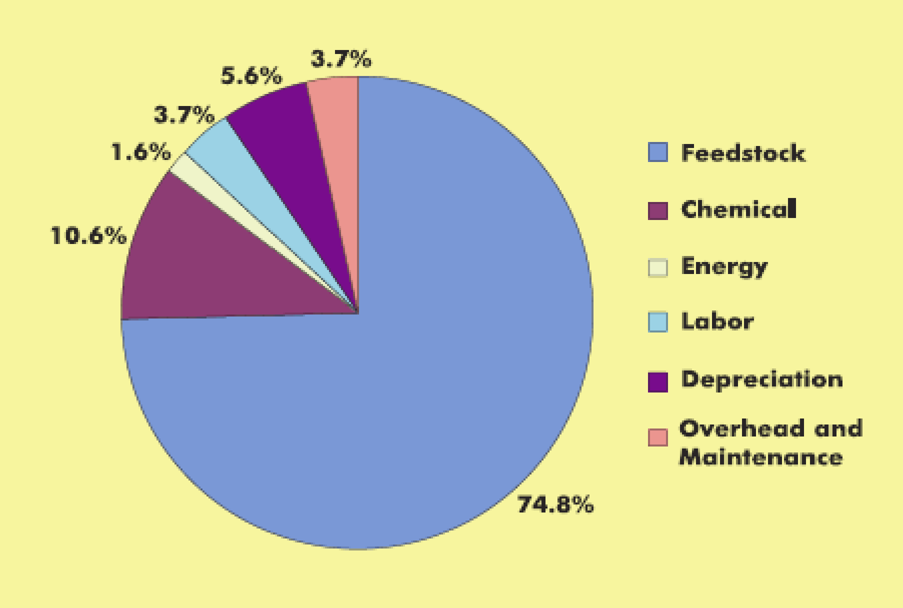


Figure3.2 - Typical cost elements for biodiesel production (Pruszko, 2006)

Feedstocks Other than Vegetable Oils: Beef tallow, pork lard, and waste yellow grease (used vegetable oil) are also candidates for feedstocks for producing biodiesel. Typically, they are lower in cost, but they also require additional processing to produce a satisfactory product. Because waste yellow greases have been used in cooking processes, they contain larger amounts of free fatty acids, ranging from 2% to 20%, that have resulted from the cooking processes. The variations in compositions of these feedstocks are much wider than those of the vegetable oils.

4 Properties of Finished Biodiesel Fuels

In the previous section, we saw how the selection of feedstock can have tremendous effects on the esterification process and that one must take account of the feedstock and adjust the esterification process accordingly. This section deals with the varying properties of the finished biodiesel fuels. Those properties also depend greatly on the choice of feedstock. Affected properties can cause large differences in performance in the areas of emissions (especially NOx), cetane number, cold flow properties, and stability. The "Biodiesel Handling and Use Guidelines" (NREL, 2006) contains an excellent discussion of the differing fuel properties from differing feedstocks, and the reader is encouraged to consult that reference. We have drawn heavily from the reference for the materials in this section.

As described above, biodiesel can be made from a variety of vegetable oils and fats, including:

Animal Fats
Edible tallow
Inedible tallow
Lard
Yellow grease
Poultry fats
Fish oil

Vegetable Oils
Soy
Corn
Canola (Rapeseed)
Sunflower
Cottonseed

Recycled Greases
Used cooking oils
Restaurant frying oils

The oils and fats above are made up of 10 common types of fatty acids. All have between 12 and 22 carbon atoms with the great majority of them being between 16 and 18 carbons. Some of these feedstocks are saturated (fully saturated with hydrogen – no double bonds between carbons), some monounsaturated (one double bond in the fatty acid chain), and some polyunsaturated (multiple double bonds in the fatty acid chain). The different feedstocks listed above are made up of different proportions of saturated, monounsaturated, and polyunsaturated fatty acids. This is illustrated in Figure 4.1 below.

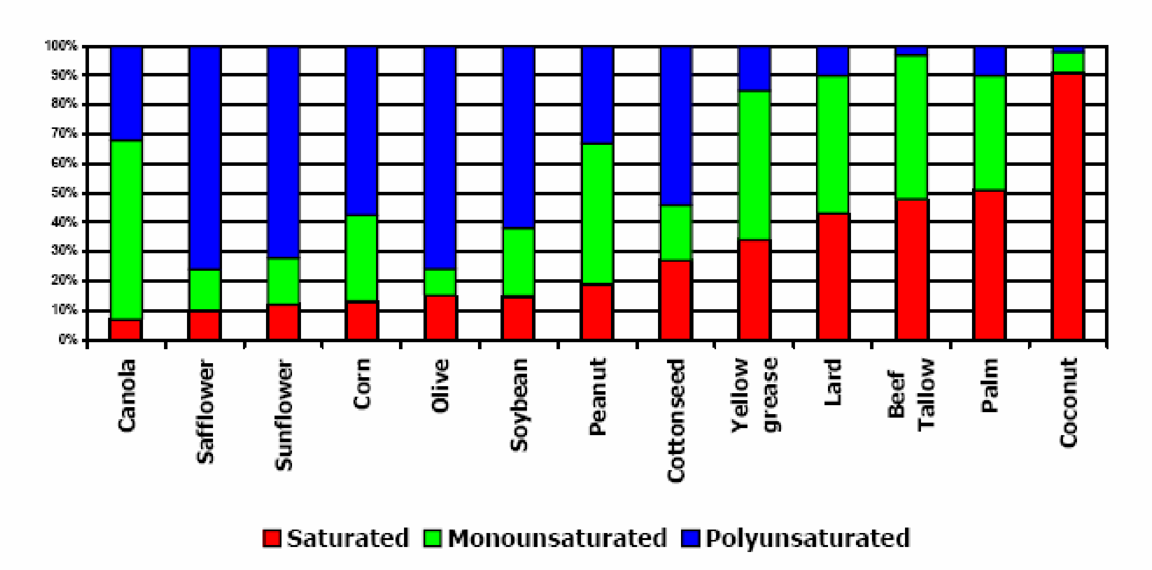
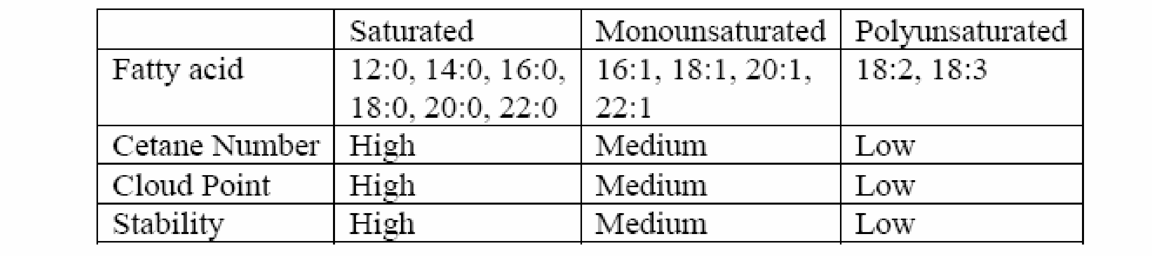


Figure 4.1 - Compositions of types of fatty acids in various biodiesel feedstocks (NREL 2006)

The different levels of saturation of the feedstock can affect the finished biodiesel fuel's properties, and this proves to be a significant factor in selecting the best feedstock for the particular application planned for the finished biodiesel fuel. This fact is illustrated in Table 4.1 below. In the table, general trends in three fuel properties, Cetane number, Cloud point, and Stability, are shown to be related to the degree of saturation of the feedstock. Shown are typical fatty acids of different carbon content and different levels of saturation. The fuels from saturated fatty acids are generally better performing in Cetane number and Stability, and as the number of double bonds increase, performance in those properties generally degrades.

Table 4.1 - Variation of finished biofuel properties with feedstock composition (NREL, 2006)



	Saturated	Monounsaturated	Polyunsaturated
Fatty acid	12:0, 14:0, 16:0, 18:0, 20:0, 22:0	16:1, 18:1, 20:1, 22:1	18:2, 18:3
Cetane Number	High	Medium	Low
Cloud Point	High	Medium	Low
Stability	High	Medium	Low

4.1 General Properties of Biodiesel Related to Feedstock Properties:

The above discussion dealt with how the selection of feedstock has general effects on the product of the esterification process, biofuels. Just as petroleum-based fuels, the finished products, gasoline and diesel fuels, will vary in desirable properties depending on feedstock. In this section, we examine how the choice of feedstock affects the properties of the biodiesel that are most important in determining the usability of the biodiesel fuel.

Fuel properties, physical as well as chemical, affect the performance of both gasoline and diesel engines. However, in the case of the diesel engine there is a stronger link between fuel parameters emission performance than in the case of the gasoline engine. The variations in fuel quality also tend to be stronger in the case of diesel fuels compared with gasoline. However, both engine types are sensitive to e.g. engine cleanliness and deposit build-up, which is closely related to fuel quality.

For the diesel engine, fuel parameters like ignition quality (cetane), density, boiling range and content of aromatic compounds and sulfur affect engine performance and emissions. Properties like viscosity, lubricity, and content of impurities may be decisive for engine durability, and this performance can vary by region depending on the weather of the region.

4.2 Energy Density

The most basic of fuel properties, energy density (energy per unit of volume), is one of the largest determinants of fuel economy, torque, and power delivered by the fuel. Energy content of petroleum diesel fuels can vary up to 15% between suppliers or between seasons of the year because of different refining parameters. Number 2 diesel (U.S.) usually has larger energy density than Number 1 diesel, and blends of the two have energy densities between the two. With biodiesel (B100 if not blended with diesel fuel) the process of making the fuel has less effect on the energy density than the choice of feedstock, when compared to petrol-diesel. This results from the fact that the feedstocks for biodiesel do not vary as much as crude oil does for making diesel fuel. But, biodiesel, as an oxygen-containing fuel (about 12.5% by weight), generally has lower heat content than petrol-diesel, and this results in lower power, torque, and fuel economy for B100. Figure 4.2 below shows a comparison of biodiesel heating values for various feedstocks compared with petrol-diesel.

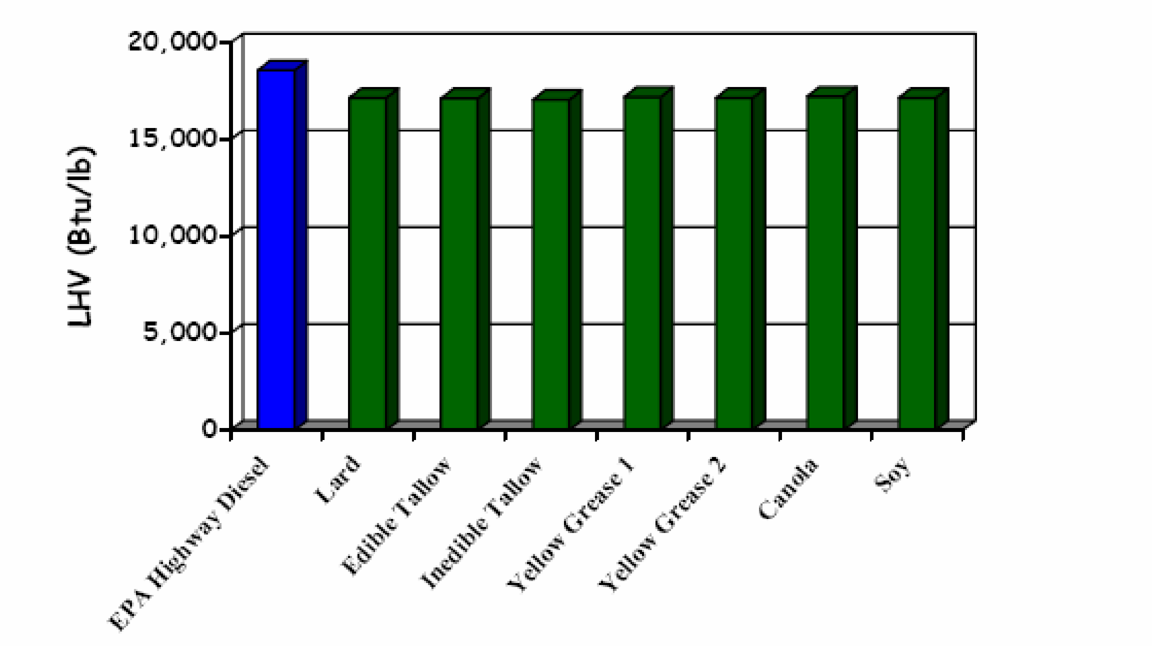


Figure 4.2 - Lower Heating Value for Diesel Fuel and Biodiesel Fuels (B100) (NREL 2006)

4.3 Cold Flow Properties

These properties can have significant impact on whether a fuel, petroleum-derived or bio-derived can be used reliably in certain geographic areas and in the cold seasons of the year. Both petrol-diesel and biodiesel can freeze or gel at cold temperatures and, as a result, clog filters or become too viscous to pump, thus disabling a vehicle. Cold flow properties of fuels are described with three different measures. They are: Cloud point, Cold filter plug point, and Pour point.

It should be noted that the standardized test methods have been developed for petroleum products, and do not necessarily depict the true performance of various biofuels.

Cloud Point: This represents the temperature at which the fuel begins to become visually cloudy; technically, this is the point where small solid crystals of fuel can be observed. The fuel can probably still be used at this point as long as the filters do not plug.

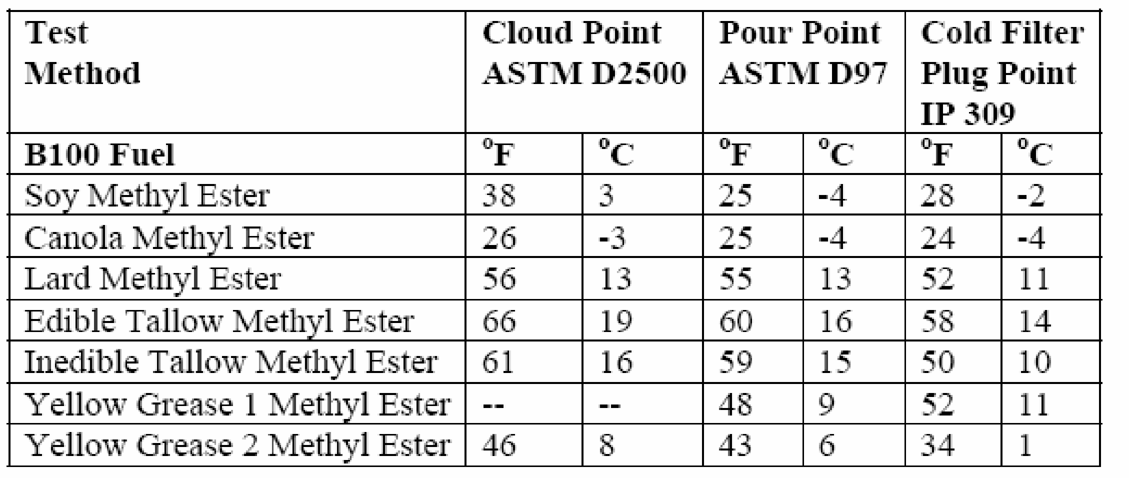
Cold Filter Plug Point: This is a more serious measure of cold flow properties. It is the temperature at which the fuel crystals have amassed in such quantities as to cause a test filter to plug. Most consider this to be a better measure of cold flow properties and of cold flow performance.

Pour Point: This is the temperature at which, basically, the fuel has gelled to the point where it will not flow. Related to vehicle operation, this measure is not as useful as the cold filter plug point because the filters have already plugged by the point when the fuel will not flow at all.

The cloud point for B100 is around -1C to 0 °C for most vegetable-oil-derived biodiesel fuels, but it can go as high as 27 °C for biodiesels from animal fats and frying oils. Table 4.2 shows the cold flow properties for various B100 biodiesel fuels made from different feedstocks. Note that there is not a great difference in temperatures between the cloud point and the pour point, which suggests that when the freezing process begins, it proceeds quickly to the point where the fuel is not usable.

The cold flow properties of biodiesel can be improved with special additives, or by blending it with winter grade diesel fuel.

Table 4.2 - Cold Flow Properties for Various B100 Fuels (NREL 2006)



Test Method	Cloud Point ASTM D2500		Pour Point ASTM D97		Cold Filter Plug Point IP 309	
B100 Fuel	**°F**	**°C**	**°F**	**°C**	**°F**	**°C**
Soy Methyl Ester	38	3	25	-4	28	-2
Canola Methyl Ester	26	-3	25	-4	24	-4
Lard Methyl Ester	56	13	55	13	52	11
Edible Tallow Methyl Ester	66	19	60	16	58	14
Inedible Tallow Methyl Ester	61	16	59	15	50	10
Yellow Grease 1 Methyl Ester	--	--	48	9	52	11
Yellow Grease 2 Methyl Ester	46	8	43	6	34	1

4.4 Cetane Number:

We saw earlier in Table 2 and in general terms that Cetane Number of biodiesel can be affected by the choice of feedstock. Most of the biodiesel in the U.S. has cetane numbers higher than 47, compared to a low of 40 for highway diesel fuel (average for U.S. is 42-44; minimum in Europe is 51). So, biodiesel enjoys an advantage in cetane number over petrol-diesel in the U.S., but not in Europe. Highly saturated biodiesels, including those from animal fats and used vegetable oils can have very high cetane numbers, as high as 70. In a sense this principle also applies to petro diesel: paraffinic diesel yields high cetane but poor cold properties, while aromatics are good for cold flow but not for cetane.

Biofuels made from polyunsaturated feedstocks will generally have cetane numbers at the low end for biodiesel. Figures 4.3 and 4.4 illustrate the varying cetane numbers and their feedstock makeup. Note that in Figure 4.3 the nomenclature is Cxx:y – where xx is the number of carbon atoms in the feedstock and y is the number of double bonds.

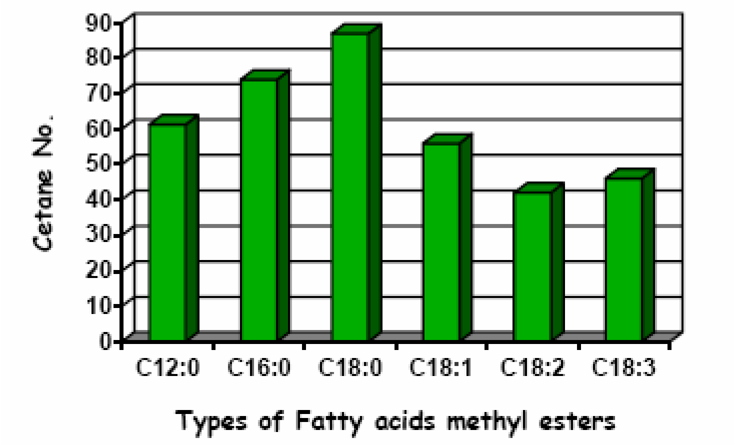


Figure 4.3 - Variation in Cetane Number with Feedstock (NREL, 2006)

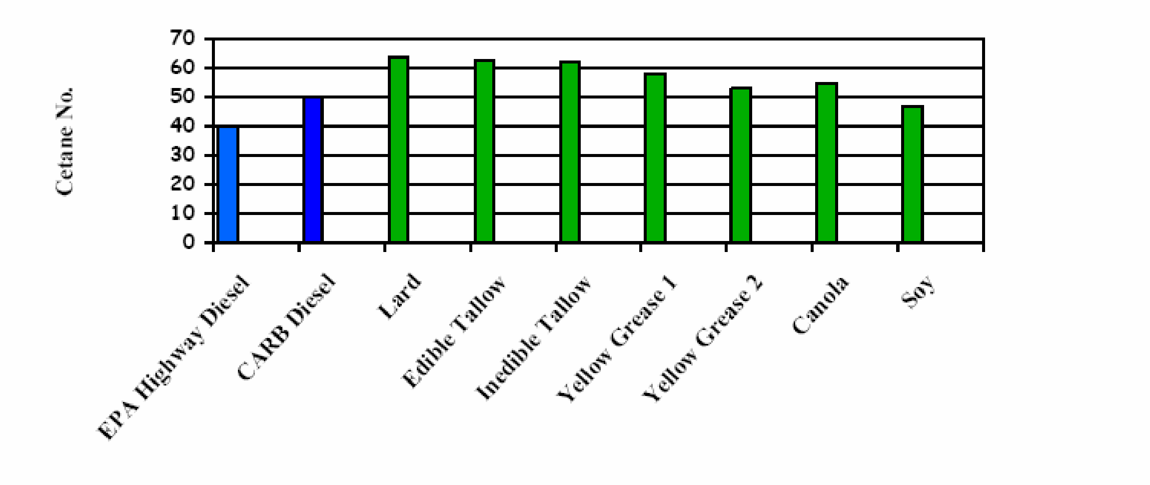


Figure 4.4 - Cetane Numbers of Petrol-Diesel and Biodiesel Fuels from Various Feedstocks (same feedstocks as in Figure 4.2) (NREL, 2006)

4.5 Biodiesel Stability (Oxidative Stability):

Two forms of stability are important for biodiesel fuels; one is stability during long-term storage and the other relates to stability while the fuel is subjected to high temperatures and/or high pressure, as is the case with an engine's fuel injection system. There is not a lot of analysis experience with either case to date, but that experience base is growing as the use of biodiesel grows.

Fuel aging and oxidation over a long term can lead to high acid numbers, high viscosity, and the formation of residues and sediments that eventually could clog filters. The following are factors that can influence the degree of instability of the fuel:

- A fuel with a higher level of unsaturation will oxidize more readily than a fully saturated fuel. For example, a fuel composed primarily of C18:3 is 100 times more unstable than a fuel made of C18:1.
- Heat and sunlight can accelerate the oxidation process.
- B100 should not be stored in systems that contain copper, brass, bronze, lead, and tin. Those metals will accelerate the aging process and will contribute to higher sediments.
- Antioxidants, whether resulting from the feedstock oil and the manufacturing process or by way of additives introduced down the line from biodiesel production, can help to protect the fuel against degradation over time. Many vegetable oils and fats are produced with natural antioxidants and remain in the fuel unless certain processes such as bleaching are used at the end of the production. Those processes will remove the antioxidants.
- Avoiding exposing the biodiesel fuel to oxygen in storage can help to extend shelf life.

4.6 Biodiesel Cleaning Effect:

Methyl esters have been used for many years as cleaners and solvents. It should not be surprising, then, that biodiesel will have a tendency to dissolve sediments and residues that might accumulate over time in storage tanks. The released sediments then can lead to filter plugging. Therefore, when storing B100 it is advisable to clean the storage tank if has been used previously for other fuels. With biodiesel blends of less than 35% biodiesel, the problem is not as great.

As polar compound, biodiesel dissolve also materials of cars and vehicles, such as seals of fuel system or paint coatings, more efficiently than diesel fuel. Many engine and vehicle manufacturers have taken this into account, but for many cars and vehicles problems may occur.

4.7 Biodiesel Lubricity:

Biodiesel, even in small blend quantities, actually improves the lubricity of petroleum diesel fuels. Of course, this effect depends heavily on the lubricity of the petroleum diesel fuel into which the biodiesel is blended. Typically, the diesel fuels in North America have some of the worst lubricity qualities in the world. This derives from several factors. For many years the lubricity of diesel fuel was adequate to maintain performance. In recent years, however, the reductions required in fuel sulfur and aromatic content has also caused reductions in the lubricity properties. Furthermore, the process to remove sulfur and aromatics, namely hydrotreating, also removes other compounds that help to provide good lubricity qualities to the fuel.

Typically, the lubricity of low-sulfur number one diesel fuel will be lower than that of number 2 diesel, and the typical lubricity of number 2 diesel (at least in North America) is appreciably lower than that which the Engine Manufacturers Association, the European EN Standards, and the California Energy Commission have established as acceptable levels for diesel fuel lubricity (Schumacher, 2005).

As little as 1 or 2% of biodiesel blended with number 2 ultra-low-sulfur (less than 15ppm sulfur) can improve the lubricity to acceptable levels. More biodiesel is required to bring the number 1 ultra-low-sulfur diesel fuel up to acceptable levels, as much as 5 to 6%. Lubricity additives can also be used to improve the lubricity of ultra-low-sulfur diesel fuel.

5 Exhaust Emissions of Finished Biodiesel Fuels and Blends

Biodiesel fuel, whether in neat form or in blends, generally have a beneficial effect on engine emissions – an effect that can vary with feedstock, engine technology, and the properties of the diesel fuel into which the biodiesel is blended. A large number of test reports that document the effects of biodiesel on emissions have been generated over the last 15 years or so. The U.S. Environmental Protection Agency (EPA) undertook a thorough survey and analysis of the emissions effects of biodiesel using publicly available data and information (EPA 2002). They used statistical means to develop correlations of the blend levels of biodiesel (blended with conventional diesel fuel) and the levels of emissions of both regulated and unregulated emissions. The overall results of their analyses are presented in Figure 5.1 below where the average emission impacts of soybean-based biodiesel are shown as a function of blend level.

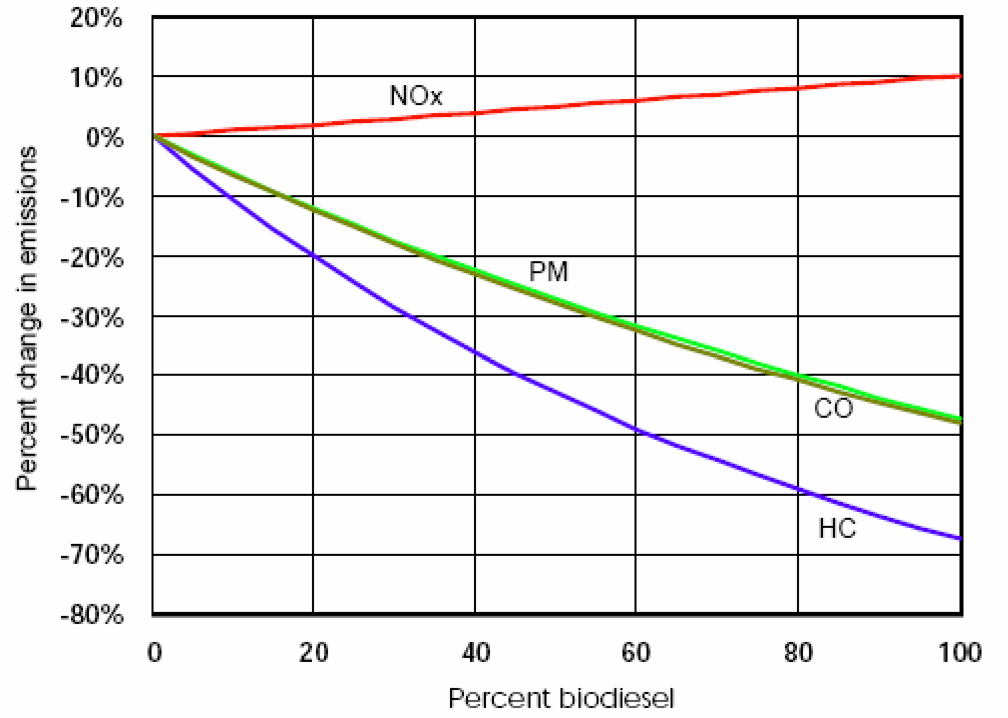
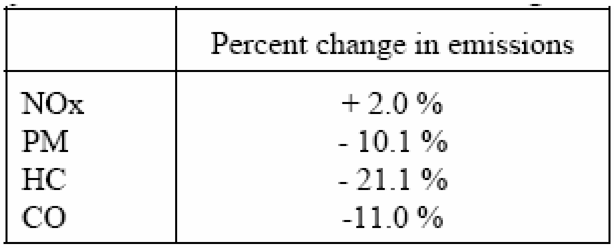


Figure 5.1 - Average Emission Impacts of Biodiesel for Heavy-Duty Highway Vehicles (EPA 2002)

Noteworthy in the figure are the dramatic reductions in HC, CO, and PM along with the modest, but troubling, increase in NOx emissions. These trends are commonly attributed to the oxygen content in biodiesel, giving rise to better oxidation of the HC, CO, and PM as well as, possibly, adding to the rise in NOx.

A common blend of biodiesel is one with 20% biodiesel blended into number 2 petro-diesel. A summary of the results for that common blend level is contained in Table 5.1 below.



	Percent change in emissions
NOx	+ 2.0 %
PM	- 10.1 %
HC	- 21.1 %
CO	-11.0 %

Table 5.1 - Average Emissions Impacts from a 20 vol % Biodiesel (Soybean-Based) Added to Petro-Diesel (EPA 2002)

In addition to the above, it was found that, typically, fuel economy suffers a 1-2% loss with a 20% biodiesel blend, owing to the lower volumetric heating value of the biodiesel. EPA's analysis also revealed that biodiesel emission impacts varied depending on the biodiesel feedstock (soybean, rapeseed, or animal fats) and on the base fuel to which the biodiesel was blended. These issues will be expanded in text that follows later. It should be noted that 98% of the data analyzed in this study was collected on 1997 or earlier model-year engines. In studies subsequent to EPA's there have been differences reported between the older-technology engines and the newer technologies. We will examine those effects later. EPA drew no conclusions related to light duty diesel engines or nonroad vehicles.

5.1 Effect of feedstock on biodiesel emissions

We saw above how the selection of biodiesel feedstock can affect many properties of the final biodiesel fuel product. Not surprisingly then, the selection of feedstock also affects emissions. Figures 5.2 and 5.3 below highlight those differences in NOx and PM emissions, respectively. Notice the large difference, for example, in NOx emissions between the soybean-based biodiesel and the animal-based biodiesel. The difference is also striking with PM emissions.

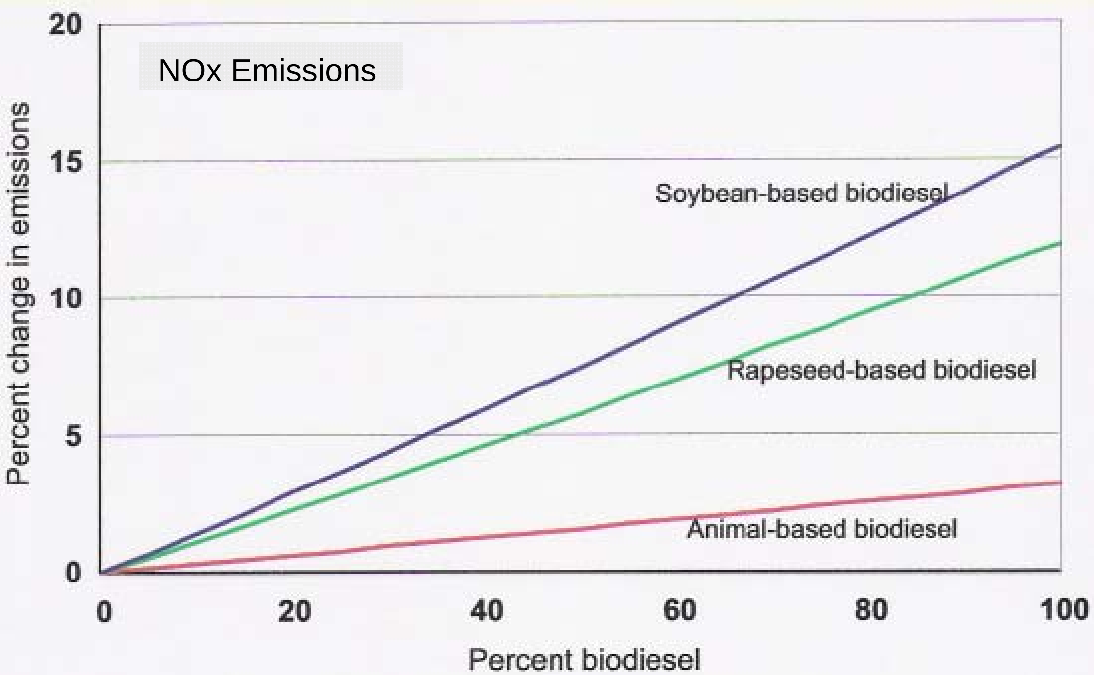


Figure 5.2 - Changes in NOx Emissions with Biodiesel Feedstock Selection (EPA 2005)

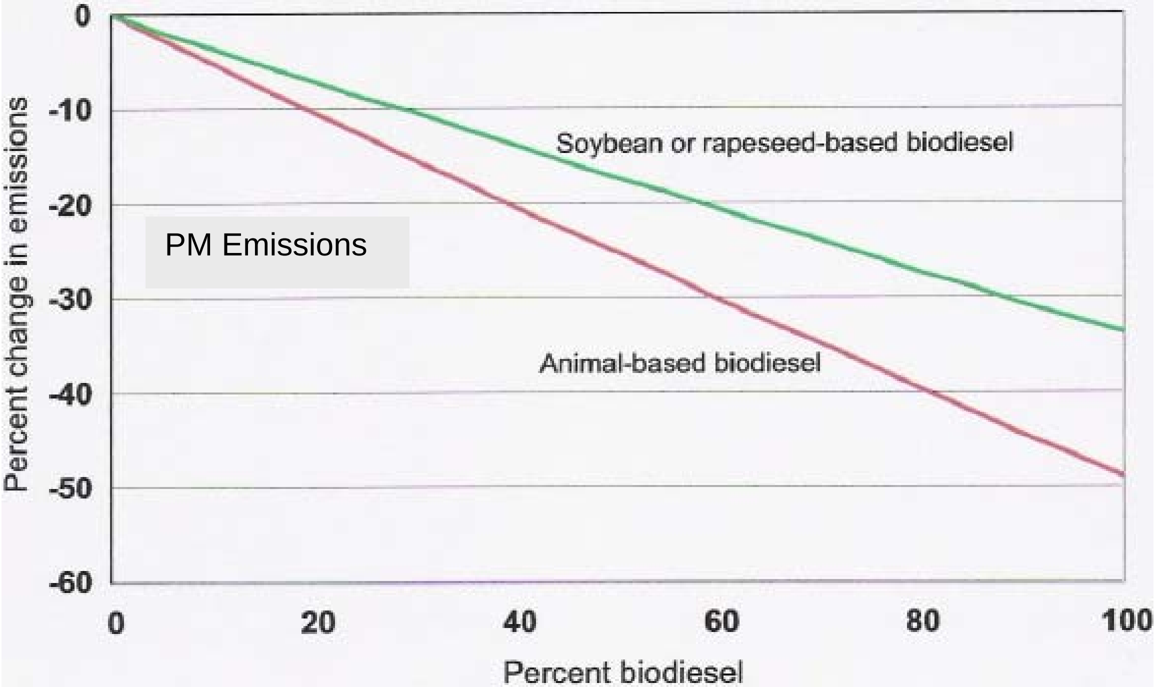


Figure 5.3 - Changes in PM Emissions with Biodiesel Feedstock Selection (EPA 2005)

5.2 The NOx Dilemma

Since biodiesel fuel blends appear to increase NOx emissions, a storm of controversy about the issue has arisen. Some policy-makers are worried about the implications of greater levels of NOx while others argue that the other emissions benefits of biodiesel outweigh the small increases in NOx emissions. Nowhere is this controversy more visible than in the U.S. State of Texas, currently the second largest consumer of biodiesel fuels of all U.S. states. There, the Texas Commission on Environmental Quality (TCEQ) ruled in 2005 that biodiesel usage in the state would be banned beginning in 2006 because of the NOx problem. Texas cities have some of the worst photochemical smog conditions in the U.S., and NOx directly contributes to the formation of photochemical smog. The TCEQ said that blending 20% or more of biodiesel with diesel fuel could "increase the amount of nitrogen oxide emissions above levels permitted by the state." On December 23, 2006 the TCEQ delayed the enforcement date by one more year in order to study the issue for another year. Therefore, another decision point will come in December 2007. Needless to say, the decision at that time will have a serious impact on the future of biodiesel in the U.S., one way or the other.

Considerable R&D on the NOx question already exists, but the body of knowledge is growing at a great pace because of this controversy. Here, we examine some of the important findings thus far.

Several NOx-affecting factors have been examined, including:

- Adjusted injection timing
- Cetane additives
- Variation with biodiesel composition
- Effect of degree of unsaturation of biodiesel fuel

Examinations of the differences in emissions performance of biodiesel fuels in new and older engines have been done as well as comparisons of results between engine versus vehicle emissions tests.

Graboski and McCormick (1998) examined the possible reduction in NOx emissions from biodiesel blends in a study reported in 1998 and summarized again by McCormick (2005) in a presentation in 2005. They found that retarding the injection timing can, indeed, reduce the NOx emissions, but the reduction comes at the expense of higher fuel consumption and greater PM emissions, which at the normal injection timing are greatly reduced. This is illustrated in Figure 5.4 below.

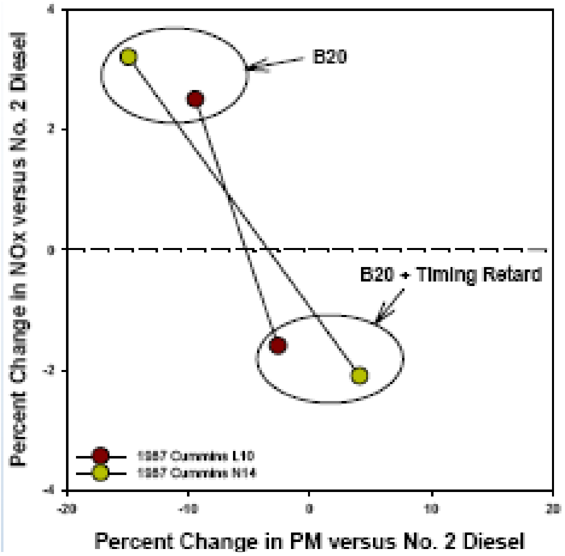


Figure 5.4 - Effect of Retarding Injection on NOx and PM (McCormick 2005)

McCormick et al studied the use of cetane improvers for reducing the increased NOx effect in B20 blends of soy-based and yellow-grease-based biodiesel in certification diesel fuel and with a 1991-vintage diesel engine (McCormick et al 2002). Cetane improver additives were di-tert-butyl-peroxide (DTBP) and 2-ethyl-hexyl-nitrate (EHN). The two biodiesel fuels vary greatly in properties such as degree of saturation, cetane number, iodine number, and fuel density. Figure 5.5 below shows the improvement in NOx emissions with different blending levels of DTBP and EHN in soy-based B20. These results are shown in comparison with the NOx emissions from the certification diesel fuel alone. In the case of the soy biodiesel, the cetane number was increased from 48 to 60 with 1% of DTBP.

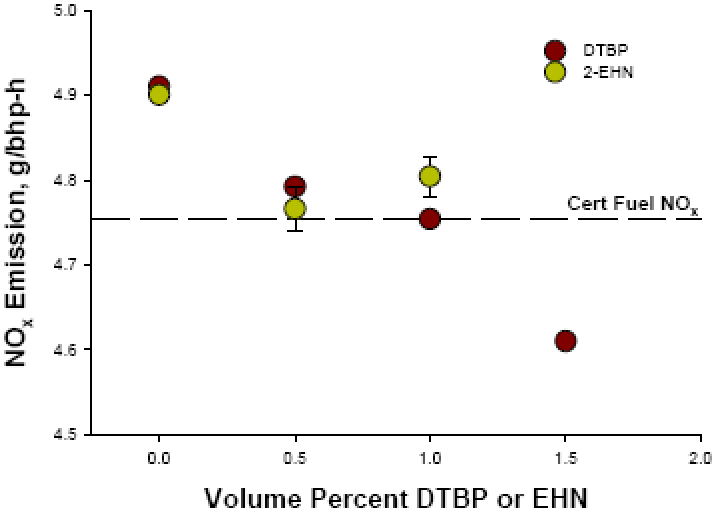


Figure 5.5 - Improvement in NOx Emissions with Addition of Cetane Improver Additive (McCormick 2005)

Similar reductions in NOx emissions were achieved with the cetane additives used in the yellow-grease-based biodiesel even though the improvement in cetane numbers for the fuel was not as great.

The test engine in these tests was of a fairly old technology, and that might have influenced the results. Interestingly, McCormick et al reported in a 2005 SAE paper (McCormick et al 2005) tests of the cetane improver EHN mixed with B20 fuel and tested with heavy-duty engines that met 2004 U.S. emissions standards (newer technology engines). In this case, there was "no measurable effect on NOx emissions" with the cetane additive and the newer engines. These engines had a more highly retarded injection timing (to reduce engine-out NOx) and were less sensitive to the cetane improvement from the additive. Engines were a Cummins ISB and a Detroit Diesel Series 60. EHN was blended in the fuel at 4,000 ppm and 5,000 ppm respectively.

These results are shown in Figures 5.6 and 5.7 below for the two different engines. Note that in the figures BP15 = ultra-low sulfur (<15ppm) diesel fuel.

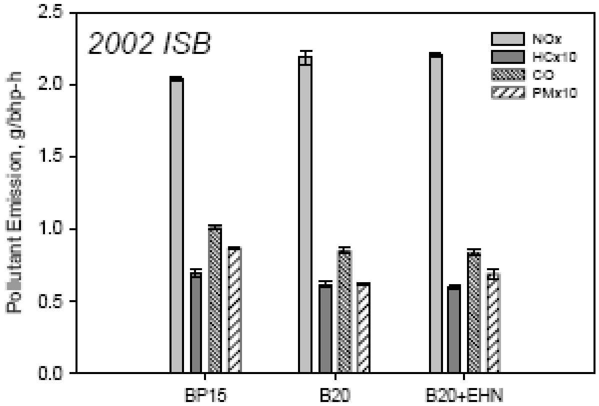


Figure 5.6 - Emissions Results for Soy B20 with 4,000 ppm EHN In the Cummins ISB Engine (McCormick et al, 2005)

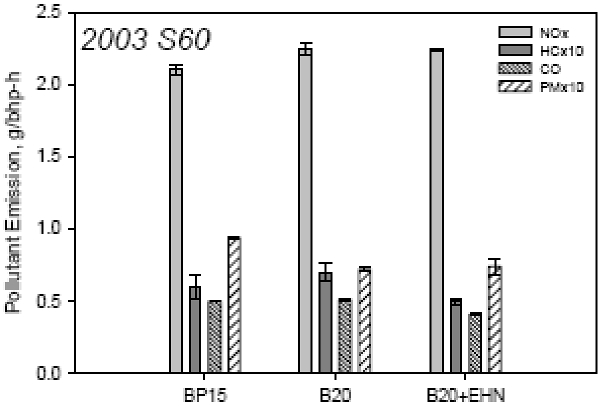


Figure 5.7 - Emissions Results for Soy B20 with 5,000 ppm EHN In the Detroit Diesel Series 60 Engine (McCormick et al 2005)

We saw earlier in Figure 5.2 how the selection of biodiesel feedstock could have some influence on NOx emissions. McCormick elaborated more on that issue in the 2005 presentation to a California Air Resources Board Biodiesel Workgroup (McCormick 2005). Figure 5.8 shows the NOx emissions variation with biodiesel feedstock. Fuels were tested in a 1991 Detroit Diesel Series 60 engine on an engine dynamometer. The tests were with straight B100 biodiesel fuels (not blended with diesel fuel) and compared against low-sulfur diesel fuel (<15 ppm sulfur) The data were reported in Environmental Science and Technology, Volume 35, pages 1742-1747, 2001. NOx results were plotted against the iodine number of the various biodiesel fuels, and it is clear that the NOx emissions correlate well with the iodine number. We saw in Chapter 3 how the iodine number correlates with degree of unsaturation. For example, a highly unsaturated fatty acid, like soybean oil, will produce biodiesel fuel with a high iodine number and higher NOx emissions. Conversely, a highly saturated feedstock, like beef tallow, will produce a biodiesel fuel with a low iodine number and lower NOx emissions. In fact, we have seen many correlations of this type. Highly saturated feedstocks will produce biodiesel fuels with higher cetane numbers, higher cloud point, and lower NOx emissions, when compared to biodiesel fuels made from less saturated feedstocks. (Typically, all types of diesel fuel with higher cetane numbers will reduce NOx emissions when compared to lower-cetane-number fuels.)

In only the last two or three years, the biodiesel NOx effect has become even more confusing. First, tests with newer engines were beginning to show NOx results different from those from older engines. In fact, on average the newer engines were showing an even higher increase in NOx emissions on engine dynamometer tests. This is illustrated dramatically in Figure 5.9, which is taken from McCormick (2005). The differences are most dramatic at the B100 level.

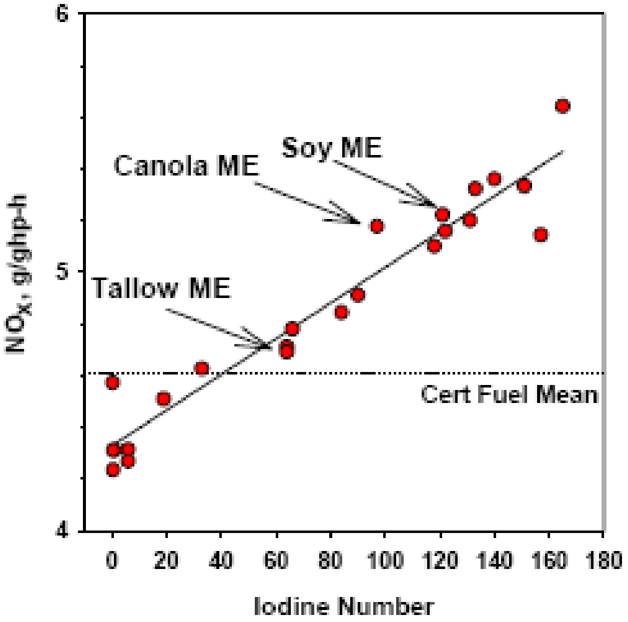


Figure 5.8 - NOx Emissions as a Function of Biodiesel Iodine Number (McCormick 2005)

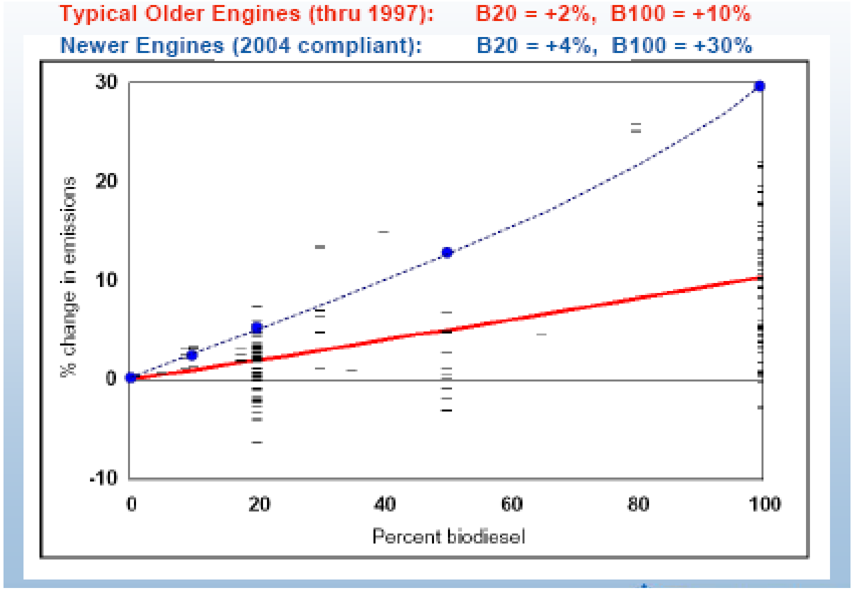


Figure 5.9 - Biodiesel Effects on NOx Emissions - Newer versus Older Engines - Engine Test Data (McCormick 2005)

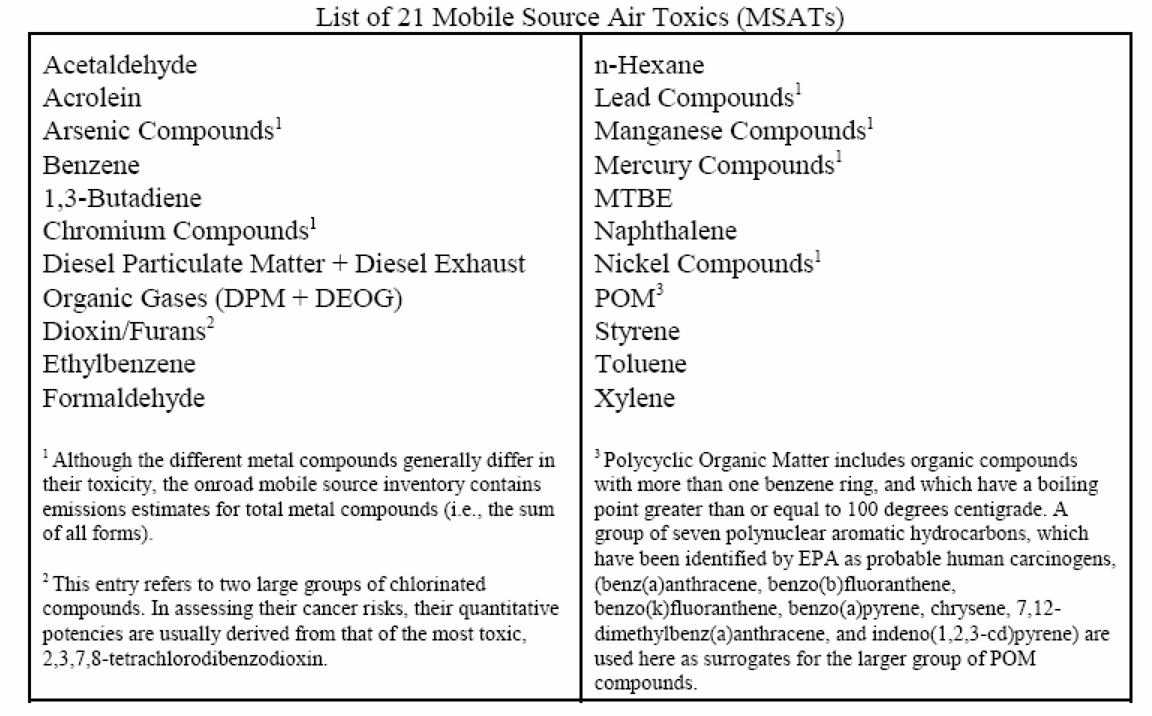
Then, as more researchers were beginning to use vehicle dynamometer tests of biodiesel fuels, even another dimension in the NOx variation phenomenon was added. In this case, vehicle-based tests are often, but not always, showing NOx reductions with biodiesel rather than NOx increases. We must emphasize, however, that there is still great inconsistency between tests, both in engine tests and in vehicle tests. Because of these uncertainties, the US Department of Energy (DOE) commissioned the National Renewable Energy Laboratory (NREL) to "determine if testing entire vehicles on heavy-duty chassis dynamometer provides a better, more realistic measurement of the impact of B20 on regulated pollutant emissions." (McCormick et al, 2006) NREL reviewed recently published engine testing studies (including the extensive review by the US EPA cited in reference 7) and several recently published vehicle testing studies. They also reviewed three vehicle studies using portable emissions measurement systems, all of which showed no substantial NOx increase. NREL also did vehicle testing of three transit buses, two school buses, two US class 8 trucks, and one motor coach. Four of these met the 1998 US emissions requirement of 4 g/bhp-h NOx, and four met the 2004 limit of 2.5 g/bhp-h NOx + HC.

Based on all the studies they reviewed, plus the new data generated in their own tests they concluded that:

- "There does not appear to be a discrepancy between engine and chassis testing studies for the effect of B20 on NOx emissions."
- "Individual engines may show NOx increasing or decreasing, but on average there appears to be no effect, or at most a very small effect on the order of ± 0.5%."
- "The small apparent increase in NOx reported for engine-testing results in EPA's 2002 review occurred because the dataset was not adequately representative of on-highway engines."

5.3 Toxic Emissions

Toxic emissions are unregulated, hazardous air pollutants that are known or suspected to cause cancer or other serious health effects. Generally, they are forms of hydrocarbons, but several metals are also identified as toxic emissions. The U.S. Environmental Protection Agency has identified 21 toxic emissions that might be exhausted by mobile sources; these are referred to as Mobile Source Air Toxics (MSATs). Table 5.2 lists the 21 MSATs as defined by the EPA (EPA 2002).



List of 21 Mobile Source Air Toxics (MSATs)

- Acetaldehyde
- Acrolein
- Arsenic Compounds[1]
- Benzene
- 1,3-Butadiene
- Chromium Compounds[1]
- Diesel Particulate Matter + Diesel Exhaust Organic Gases (DPM + DEOG)
- Dioxin/Furans[2]
- Ethylbenzene
- Formaldehyde

[1] Although the different metal compounds generally differ in their toxicity, the onroad mobile source inventory contains emissions estimates for total metal compounds (i.e., the sum of all forms).

[2] This entry refers to two large groups of chlorinated compounds. In assessing their cancer risks, their quantitative potencies are usually derived from that of the most toxic, 2,3,7,8-tetrachlorodibenzodioxin.

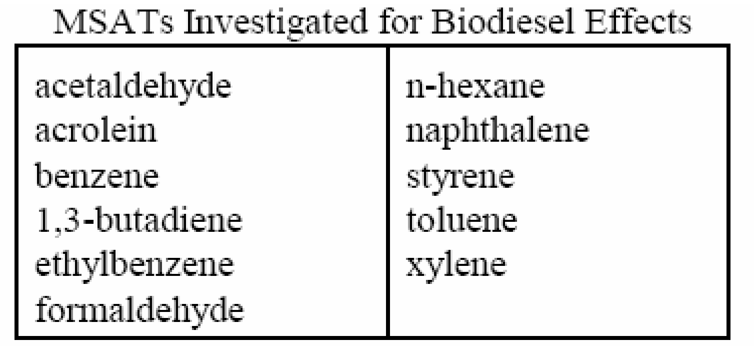
- n-Hexane
- Lead Compounds[1]
- Manganese Compounds[1]
- Mercury Compounds[1]
- MTBE
- Naphthalene
- Nickel Compounds[1]
- POM[3]
- Styrene
- Toluene
- Xylene

[3] Polycyclic Organic Matter includes organic compounds with more than one benzene ring, and which have a boiling point greater than or equal to 100 degrees centigrade. A group of seven polynuclear aromatic hydrocarbons, which have been identified by EPA as probable human carcinogens, (benz(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, chrysene, 7,12-dimethylbenz(a)anthracene, and indeno(1,2,3-cd)pyrene) are used here as surrogates for the larger group of POM compounds.

Table 5.2 – U.S. EPA List of Mobile Source Air Toxics (EPA 2002)

The EPA did a comprehensive, statistical analysis of pre-existing data and reports on the effects of biodiesel fuel on emissions (EPA, 2002). A large number of results from different researchers were included in the analysis. However, the data on toxic emissions were much fewer than for the regulated emissions. Therefore, EPA's conclusions are to be taken as "preliminary."

They found data that existed for only 11 of the 21 MSATs. Those are listed in Table 5.3 below. Aggregate results for toxics and total hydrocarbons are shown plotted against the biodiesel blend level in Figure 5.10 below.



MSATs Investigated for Biodiesel Effects

acetaldehyde
acrolein
benzene
1,3-butadiene
ethylbenzene
formaldehyde
n-hexane
naphthalene
styrene
toluene
xylene

Table 5.3 - MSATs Studied in EPA Report (EPA 2002)

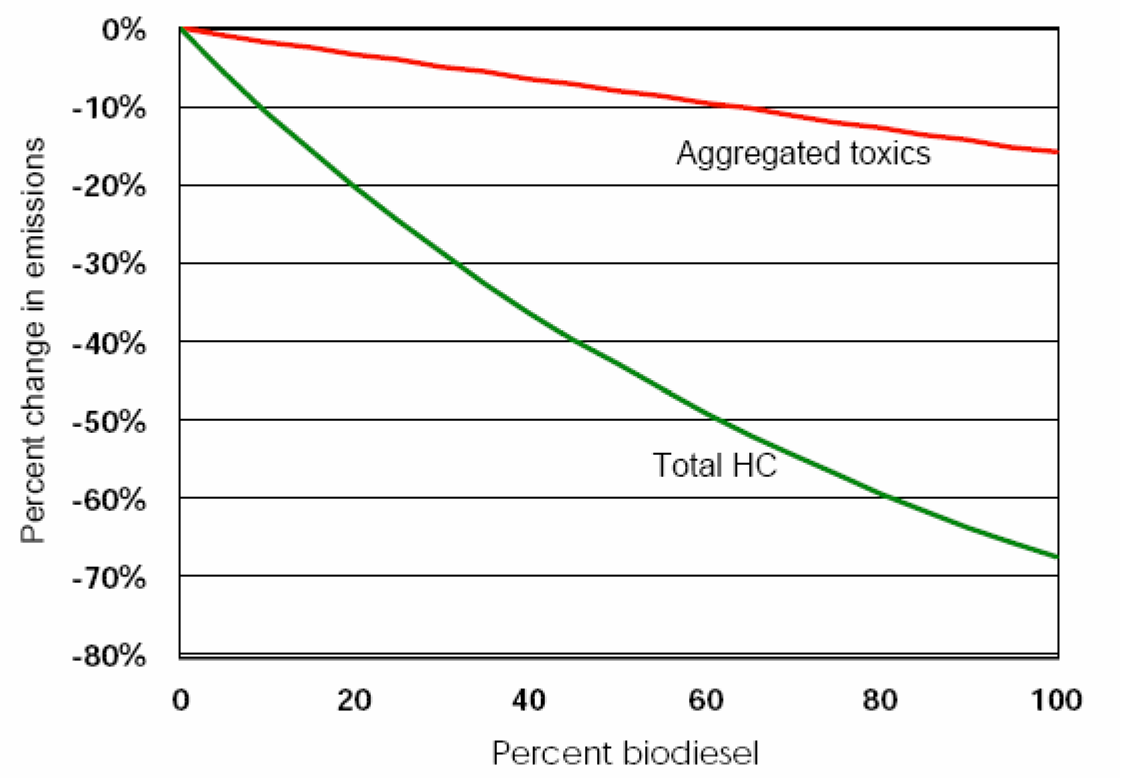
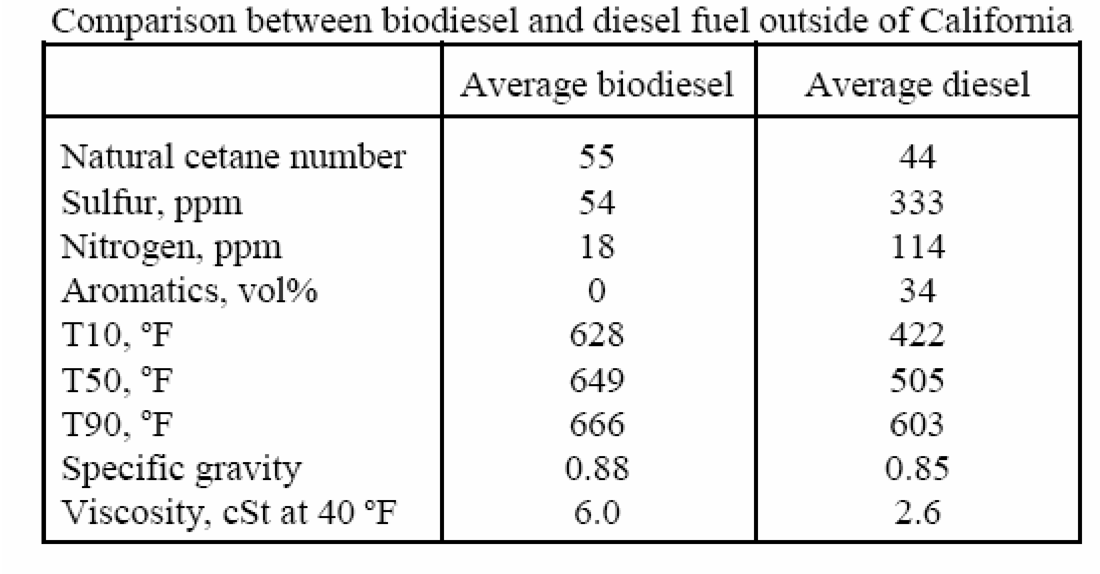


Figure 5.10 - Reductions in Toxic Emissions with Increasing Blend Levels of Biodiesel (EPA 2002)

Clearly, biodiesel blends reduce levels of air toxics. In these data, biodiesel was blended with conventional diesel fuel (Diesel 1 or 2). Examining the properties of the average biodiesel with the average conventional diesel fuel for this analysis will help to understand why biodiesel reduces air toxic emissions. Table 5.4 below shows a comparison of properties.



Comparison between biodiesel and diesel fuel outside of California

	Average biodiesel	Average diesel
Natural cetane number	55	44
Sulfur, ppm	54	333
Nitrogen, ppm	18	114
Aromatics, vol%	0	34
T10, °F	628	422
T50, °F	649	505
T90, °F	666	603
Specific gravity	0.88	0.85
Viscosity, cSt at 40 °F	6.0	2.6

Table 5.4 - Comparison of Properties between Neat Biodiesel and Conventional Diesel Fuel (EPA 2002) Note: "Average Diesel" refers to the U.S. 49-state diesel fuel.

Two important properties to note are the aromatics and sulfur contents. Aromatics are known to contribute to toxic emissions, and sulfur also compounds emission problems. Biodiesel has no aromatics and a sulfur content much less than conventional diesel.

Being that this EPA studied dealt with data that pre-existed prior to the publication date in 2002, ultra-low sulfur diesel (ULSD) fuel did not exist in abundance in the U.S., and data included in the EPA analysis did not represent tests with ULSD. Properties of ULSD, including reduced levels of aromatics and sulfur, are much more favorable for reduced levels of toxic emissions compared with the conventional diesel fuel represented in Table 5.4. Therefore, the benefit gained in toxic emissions with biodiesel blends should be expected to be less than those represented in Figure 5.10.

5.4 Health and Air Quality Effects

We have seen that biodiesel blends can reduce tailpipe emissions of most regulated pollutants, with the possible exception of NOx, which is either slightly increased or in more recent analyses possibly unchanged. We have also seen that biodiesel blends will reduce levels of unregulated, toxic emissions. The question now is whether those emissions benefits will translate into improvements in ambient air quality and in health risks associated with air quality.

To address these questions NREL in the U.S. contracted with the ENVIRON International Corporation to research the issues and produce a series of reports on their findings. They published five reports and a summary report, all in 2003, titled **"Impact of Biodiesel Fuels on Air Quality and Human Health"** –

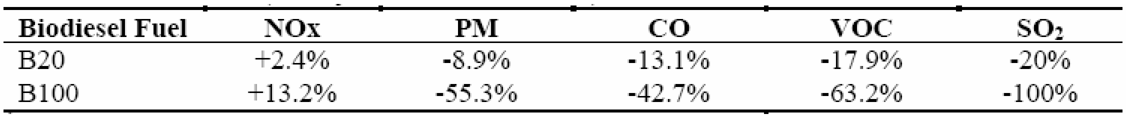
Task 1. Incorporate Biodiesel Data into Vehicle Emissions Databases for Modeling
Task 2 – The Impact of biodiesel Fuels on Ozone Concentrations
Task 3 – The Impact of Biodiesel Fuels on Ambient Carbon Monoxide Levels in the Las Vegas “Nonattainment Area” (i.e., not conforming to ambient air quality standards)
Task 4 – Impacts of Biodiesel Fuel Use on PM
Task 5 – Air Toxics Modeling of the Effects of Biodiesel Fuel Use on Human Health
Summary Report

All of these reports can be found at the NREL web site – www.nrel.gov. Here we are citing results from the Summary Report (Morris et al 2003).

To accomplish the tasks researchers at Environ used emissions inventory and air quality modeling to analyze the impacts of biodiesel use in vehicle heavy-duty fleet in selected geographic areas as follows:

- Ambient ozone concentrations in the Northeast (U.S.) Corridor, Lake Michigan, and the South Coast Air Basin (SoCab - Los Angeles area)
- Carbon monoxide in Las Vegas, Nevada
- Particulate matter in the SoCab
- Air toxics, risk, and human health in the SoCab

Biodiesel test data were averaged for cases of B100 and B20 to develop a profile of tailpipe emissions data for use in the models. Compared to a standard diesel fuel at that time (up to 500 ppm sulfur), the average emissions reductions (or increase) for these cases are shown in Table 5.5 below.



Biodiesel Fuel	NOx	PM	CO	VOC	SO_2
B20	+2.4%	-8.9%	-13.1%	-17.9%	-20%
B100	+13.2%	-55.3%	-42.7%	-63.2%	-100%

Table 5.5 - Average Changes in Emissions for B20 and B100 Compared to Standard Diesel Fuel (Morris et al 2003)

They also found that the PM emissions from B100 and B20 fuels have 20% and 5% less toxicity, respectively, than the standard diesel fuel.

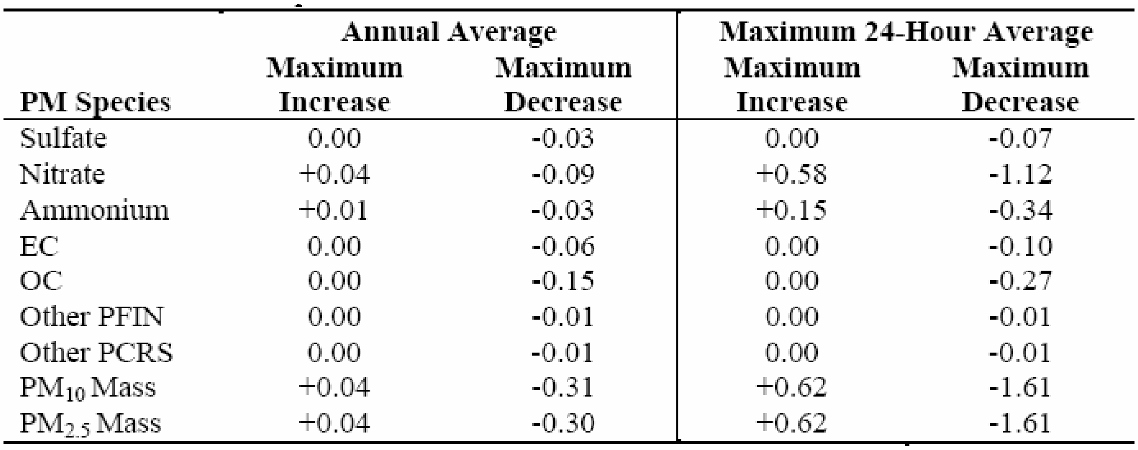
They developed three hypothetical scenarios: a standard diesel base case, a 100% penetration of B20 in the heavy-duty fleet, and a 50% penetration of B20 in the heavy-duty fleet. Then, these scenarios were used in the ambient air quality models.

Results were as follows:

Ozone: The maximum projected increase for ozone resulting from either the 100% or 50% penetration of B20 in both the SoCab (Southern California) and the Eastern U.S corridor was 0.26 parts per billion (ppb). Therefore, the conclusion was that the use of biodiesel is projected to have no measurable adverse impact on the 1-hour or 8-hour ozone attainment in the studied areas.

Carbon Monoxide: The use of biodiesel was projected to reduce CO concentrations in the Las Vegas Valley, but these reductions would be extremely small, from 0.01 to 0.03 ppm, or less than 0.2%.

Particulate Matter: The southern California region was chosen for this scenario analysis because it is in nonattainment for PM_{10} and because ammonium nitrate is a major component of PM in that area. Since NOx is a precursor for ammonium nitrate and since the selection of this geographic area would be a conservative case (overestimating the effects) as related to the rest of the country, then SoCab was selected for the analysis. The effects of biodiesel were assessed for particulate sulfate, nitrate, ammonium, elemental carbon (EC), organic carbon (OC), other fine particulate (PFIN), coarse matter (PCRS), total PM_{10} mass, total $PM_{2.5}$ mass, and exposure to PM_{10} and $PM_{2.5}$.



PM Species	Annual Average Maximum Increase	Annual Average Maximum Decrease	Maximum 24-Hour Average Maximum Increase	Maximum 24-Hour Average Maximum Decrease
Sulfate	0.00	-0.03	0.00	-0.07
Nitrate	+0.04	-0.09	+0.58	-1.12
Ammonium	+0.01	-0.03	+0.15	-0.34
EC	0.00	-0.06	0.00	-0.10
OC	0.00	-0.15	0.00	-0.27
Other PFIN	0.00	-0.01	0.00	-0.01
Other PCRS	0.00	-0.01	0.00	-0.01
PM_{10} Mass	+0.04	-0.31	+0.62	-1.61
$PM_{2.5}$ Mass	+0.04	-0.30	+0.62	-1.61

Table 5.6 - Projected Maximum Increases and Decreases in PM Concentration ($\mu g/m^3$) in the SoCab with 100% Penetration of B20 in the Heavy-Duty Fleet (Morris et al 2003)

The researchers concluded that the maximum increases and decreases in PM_{10} and $PM_{2.5}$ are extremely small. The largest effect was for particulate nitrate which produced both increases and decreases due to the B20 fuel. The decreases occurred in the densely populated portions of the SoCab area, while the increases occurred in the eastern portion of the region, in the desert. The 100% B20 scenario was projected to reduce the exposure to annual and 24-hour exceedances of the PM_{10} standard by 4% and 7% respectively when compared to the case using standard diesel fuel alone.

PM Emissions Mass and Toxicity: It was projected that the use of B20 in the heavy-duty fleet would reduce the per million risk of premature death due to exposure to air toxics in the SoCab area by 2% and 5% respectively for the 50% and 100% B20 penetration scenarios.

6 Life Cycle Emissions and Energy

In order to be viable as an alternative fuel, any biofuel must meet certain criteria as follows:

- It should provide a net energy gain, not use more energy to produce than it provides itself
- It should provide environmental benefits
- It should be economically competitive
- It should be producible in sufficient quantities without impacting the availability or price of the same feedstocks to be used as food

To determine whether any biofuel meets these requirements requires a thorough accounting of the inputs and outputs of all processes utilized in their production and delivery throughout the entire life cycle. Such an accounting is called a "life cycle analysis."

Conducting a life cycle analysis is a very complicated and meticulous process. One must make a large number of assumptions about the numerous processes which will be modeled in the analysis. The selection of a given set of processes to model tends to limit the universality of the results. Therefore, it is imperative that one choose the most representative processes to model in the analysis. Even then, the availability of technical data with which to represent the processes becomes a critical factor in the analysis. Nevertheless, it is reasonable to expect that a very good, thorough and representative analysis will yield results that will at least be of sufficient quality that will allow policy makers to make choices.

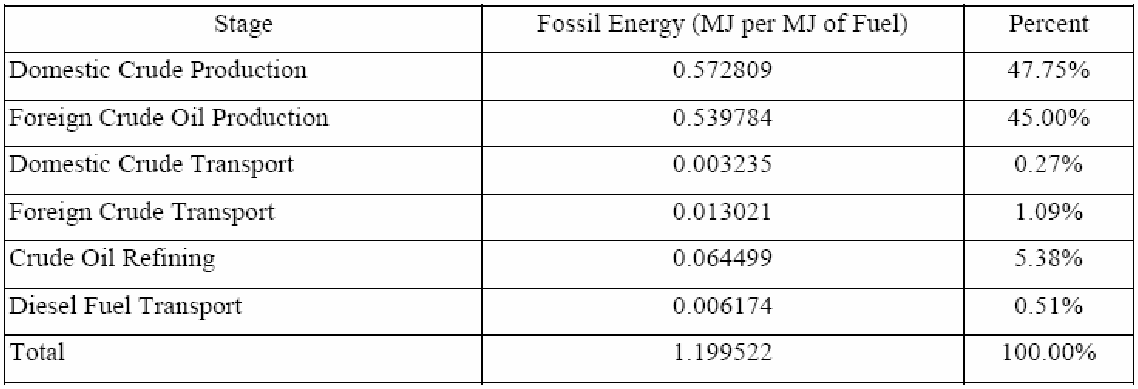
One such study, which is well regarded and widely accepted, was commissioned by the U.S. Department of Agriculture and the U.S. Department of Energy and carried out by NREL and reported in 1998 (Sheehan et al 1998) The basic application for which the analysis was done was for biodiesel made from soybeans and used in a city bus. Certain results, e.g. vehicle emission comparisons, are therefore related to the vehicle application, a city bus.

As an example of the extensive nature of a life cycle analysis, listed below are some of the processes that had to be modeled in the NREL study:

Petroleum Diesel System	**Biodiesel System**
Extract crude oil from the ground	Produce soybeans
Transport crude oil to oil refinery	Transport soybeans to soy crushing facility
Refine crude oil to diesel fuel	Recover soybean oil at the crusher
Transport diesel fuel to point of use	Transport soybean oil to a biodiesel manufacturer
Use the diesel fuel in a diesel bus	Convert soybean oil to biodiesel
	Transport biodiesel fuel to point of use
	Use biodiesel fuel in a diesel bus

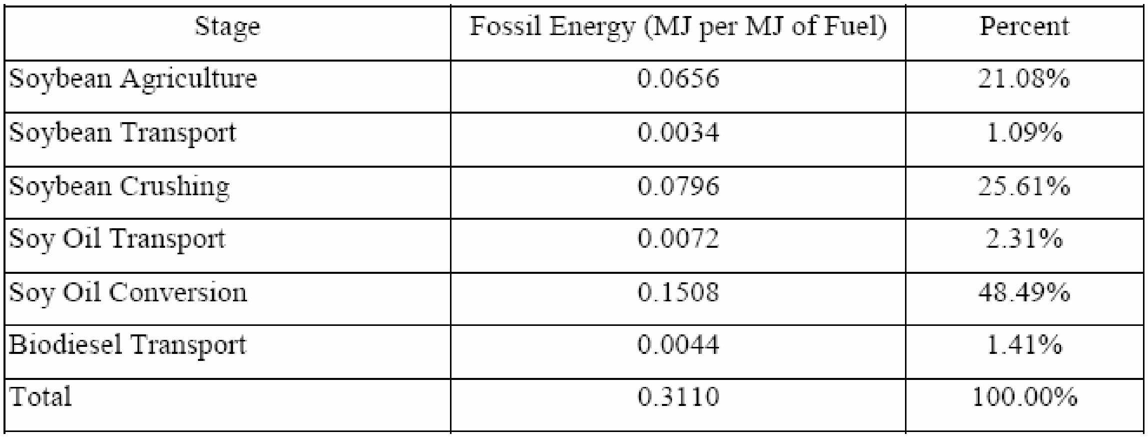
Results of the NREL life cycle analysis were largely encouraging for soybean biodiesel. Following is a summary of the major findings.

Fossil energy requirements for the biodiesel life cycle were much lower than those for the petroleum diesel life cycle. Tables 6.1 and 6.2 show the fossil energy requirements at each state of the life cycle for petroleum diesel and biodiesel respectively.



Stage	Fossil Energy (MJ per MJ of Fuel)	Percent
Domestic Crude Production	0.572809	47.75%
Foreign Crude Oil Production	0.539784	45.00%
Domestic Crude Transport	0.003235	0.27%
Foreign Crude Transport	0.013021	1.09%
Crude Oil Refining	0.064499	5.38%
Diesel Fuel Transport	0.006174	0.51%
Total	1.199522	100.00%

Table 6.1 - Fossil Energy Requirements for Petroleum Diesel – Life Cycle (Sheehan et al 1998)



Stage	Fossil Energy (MJ per MJ of Fuel)	Percent
Soybean Agriculture	0.0656	21.08%
Soybean Transport	0.0034	1.09%
Soybean Crushing	0.0796	25.61%
Soy Oil Transport	0.0072	2.31%
Soy Oil Conversion	0.1508	48.49%
Biodiesel Transport	0.0044	1.41%
Total	0.3110	100.00%

Table 6.2 - Fossil Energy Requirements for Biodiesel - Life Cycle (Sheehan et al 1998)

The results for fossil energy used (MJ per MJ of fuel produced and delivered) show that delivered biodiesel fuel product produces 3.2 energy units for each fossil fuel energy unit used in its production and final delivery. This is contrasted to 0.83 petroleum diesel energy units for each fossil fuel energy unit used in its production and final delivery. Thus, biodiesel is definitely a renewable energy product. The carbon dioxide emissions follow in like fashion. The benefits of biodiesel with regard to carbon dioxide are illustrated in Figure 6.1 below.

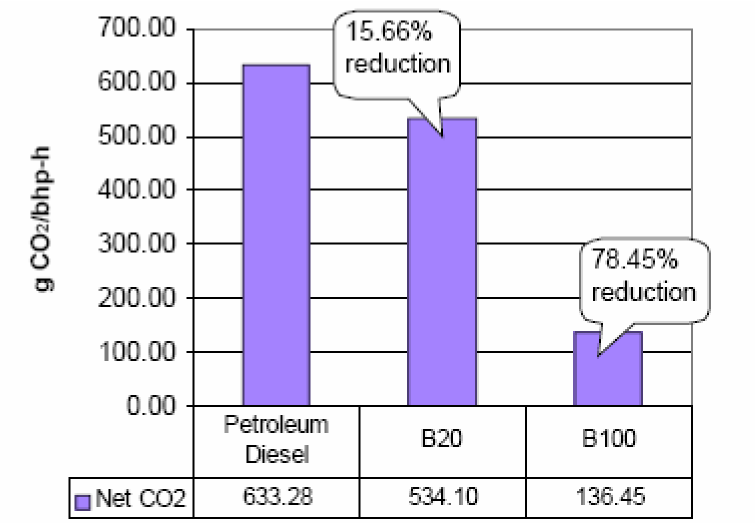


Figure 6.1 - Comparison of Life Cycle CO_2 Emissions for Petroleum Diesel and Biodiesel Blends (Sheehan et al 1998)

The European Institute for Environment and Sustainability (IEA 2007) issued an updated well-to-wheel analysis of future automotive fuels including ethanol and biodiesel. They found generally similar results for the advantages of biodiesel in reducing fossil energy use and CO_2 emissions. Their summary for biodiesel is shown in Figure 6.2 below. Note that they included different options for feedstocks and for end uses of the glycerin. These choices impact both the amount of fossil energy used and the CO_2 emissions. They show results for soy methyl ester (SME), rape ethyl ester (REE), and rape methyl ester (RME), and for uses of the glycerin they included both the animal feed route as well as the chemical feedstock route.

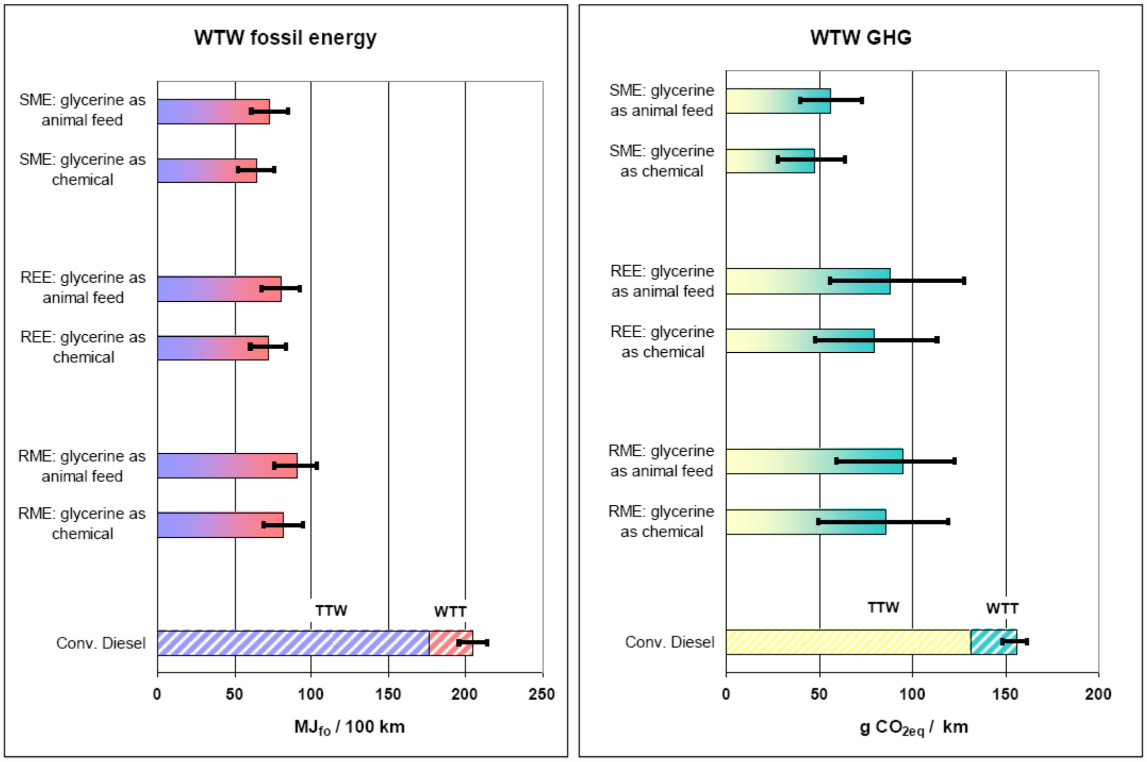
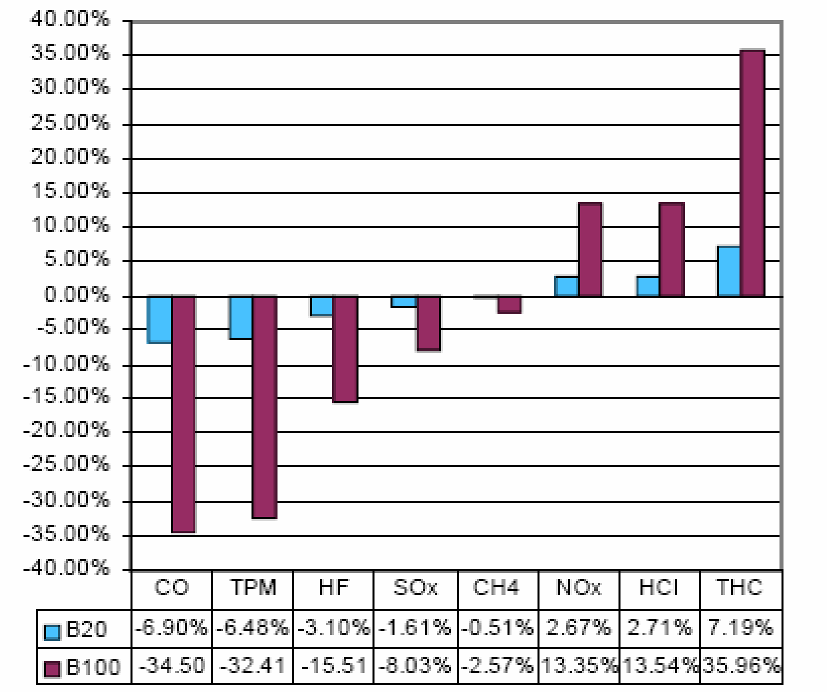


Figure 6.2 - Well-to-Wheel Fossil Energy Requirement and CO_2 Emissions for Different Biodiesel Pathways (IES 2007)

Life cycle air emissions favor biodiesel blends for most air pollutants except for NOx, hydrogen chloride, and total hydrocarbons. The life cycle comparison against petroleum diesel is shown in Figure 6.3. In this comparison, petroleum diesel emissions are the starting point, so the figure shows decreases or increases relative to petroleum diesel values.



	CO	TPM	HF	SOx	CH4	NOx	HCl	THC
🟦 B20	-6.90%	-6.48%	-3.10%	-1.61%	-0.51%	2.67%	2.71%	7.19%
🟪 B100	-34.50	-32.41	-15.51	-8.03%	-2.57%	13.35%	13.54%	35.96%

Figure 6.3 - Life Cycle Air Emissions for Biodiesel Blends Compared to Petroleum Diesel (Sheehan et al 1998)

In figure 6.2 the abbreviations are as follows:

CO	Carbon Monoxide
TPM	Total Particulate Matter
HF	Hydrogen fluoride
SOx	Sulfur oxides
CH4	Methane
NOx	Nitrogen oxides
HCL	Hydrogen chloride
THC	Total hydrocarbons

Also note that while HF and HCL are not typically included in discussions of tailpipe emissions, they are included here because they are present in the emissions from some of the processes in making fuels.

Life cycle emissions of NOx are shown as being greater with biodiesel. Tailpipe emissions in this case greatly influence the NOx life cycle emissions, and these conclusions were reached using emissions data from the early 1990's in heavy duty engines. Recall in Chapter 5 that more recent NOx emissions results are trending to show that the NOx penalty with biodiesel might not be so significant.

Many other similar life cycle analyses over the years have tended to agree with the conclusion that biodiesel yields more energy than is required to make and distribute it. The International Energy Agency in 2004 included a review of several biofuel life cycle studies in their 2004 publication, “Biofuels for Transport” (IEA 2004). The reviewed studies all reported that biodiesel from rapeseed had a positive net energy balance even though the ratios of energy out / energy in varied somewhat between studies.

However, in 2005 a controversy arose when two American researchers published the results of their life cycle analysis (Pimentel and Patzek 2005) in which they concluded that both biodiesel and ethanol **are not**, in fact, sustainable. That is, according to their analysis biodiesel and ethanol both require more fossil energy to make them than they contain themselves. This work was criticized by many as being not realistic. The U.S. National Biodiesel Board, jointly with the U.S. Departments of Energy and Agriculture issued a response (NBB 2005) in a news release. In it they pointed out that the authors:

- Allocated 79% of the energy inputs for growing soybeans to the oil. But, soybean oil is only 20% of the soybeans while 80% is protein
- Did not give biodiesel credit for the co-product, glycerin
- Used energy data for growing soybeans from 15 years before while much more recent data were readily available
- Included the energy used to manufacture construction materials for biodiesel plants and farm equipment. Most researchers do not generally include those amounts.

7 International Biodiesel (FAME) Technical Standards and Specifications

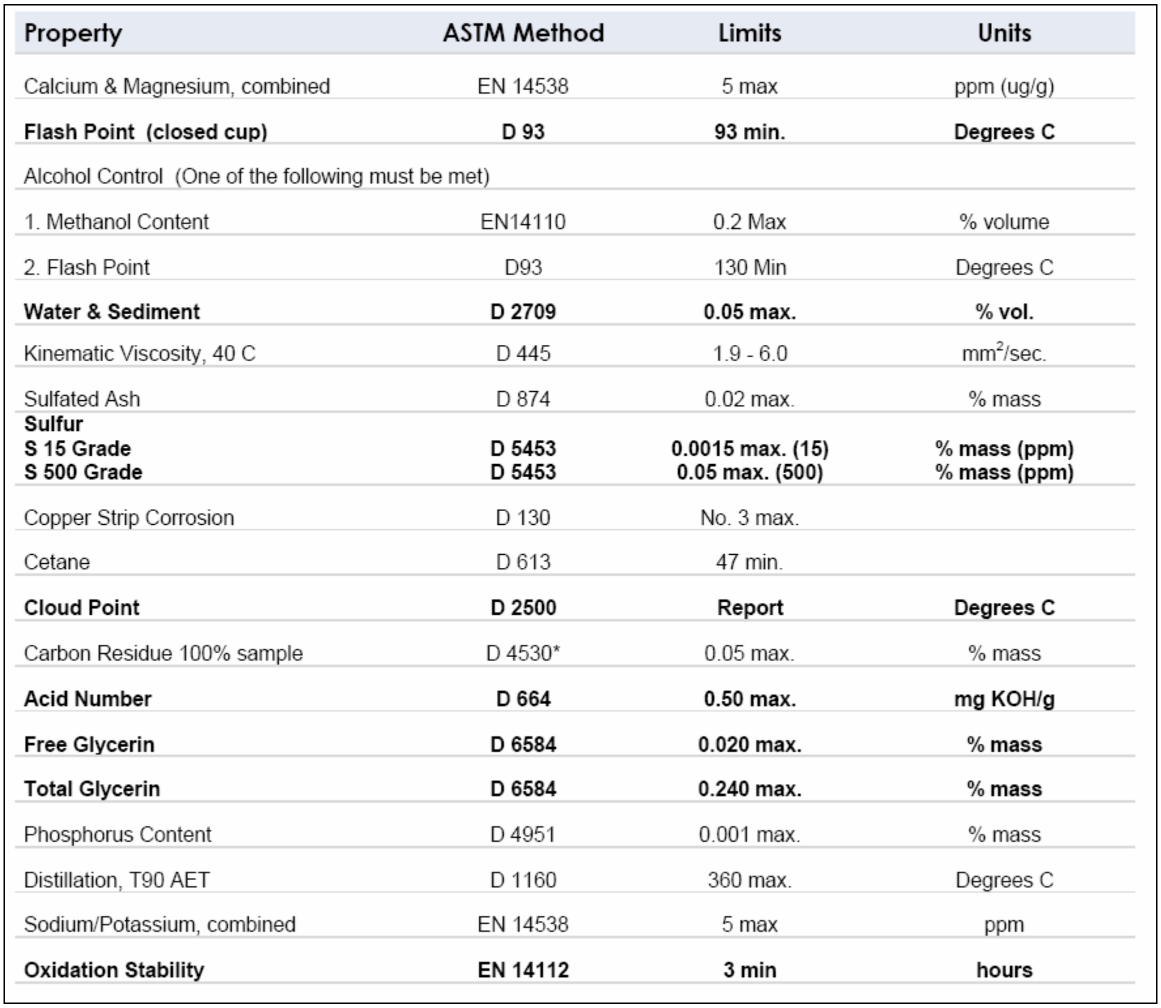
International standards exist for biodiesel fuels in order to assure that certain minimum requirements are met by the fuel. The standards ensure that important factors in the fuel production process are satisfied. These include low sulfur content and absence of glycerin, alcohol, catalyst, and free fatty acids. Basic industrial tests to determine whether the products conform to standards are specified in the standards rules.

The common international standard is the European EN 14214 which is tabulated in Table 7.1 below. There are additional national standards. ASTM D6751 is the most common standard referenced in the U.S. and Canada. It is shown in Table 7.2 below. In Germany, the requirements for biodiesel are fixed in the DIN EN 14214 standard, and in the UK the requirements for biodiesel is fixed in the BS EN 14214 standard, although these last two standards are essentially the same as EN 14214 and are just prefixed with the respective national standards institution codes.

All of these standards apply to 100% biodiesel – B100. For blend levels of 5% or lower biodiesel, the standards for petroleum diesel fuels apply to the blend of fuels, provided that the biodiesel fuel does meet the biodiesel standards for B100. There is great interest in a standard for B20 because that level of biodiesel use is the target for replacement of petroleum diesel in some countries. Standards organizations in various countries have been struggling for some time now with the process of establishing a B20 standard. In the U.S. a major step towards full B20 support is the finalization of a defined B20 ASTM specification. That specification moved closer to reality in early 2007 when new limits in ASTM D6751 were approved for oxidation stability and other parameters for the 2007-2010 diesel engines. Essentially, the B100 standard has been redesigned so that it is “protective” of the B20 and lower blends.

Property	Units	lower limit	upper limit	Test-Method
Ester content	% (m/m)	96,5	-	pr EN 14103d
Density at 15°C	kg/m³	860	900	EN ISO 3675 / EN ISO 12185.
Viscosity at 40°C	mm²/s	3,5	5,0	EN ISO 3104
Flash point	°C	> 101	-	ISO CD 3679e
Sulfur content	mg/kg	-	10	-
Tar remnant (at 10% distillation remnant)	% (m/m)	-	0,3	EN ISO 10370
Cetane number	-	51,0	-	EN ISO 5165
Sulfated ash content	% (m/m)	-	0,02	ISO 3987
Water content	mg/kg	-	500	EN ISO 12937
Total contamination	mg/kg	-	24	EN 12662
Copper band corrosion (3 hours at 50 °C)	rating	Class 1	Class 1	EN ISO 2160
Thermal Stability	-	-	-	-
Oxidation stability, 110°C	hours	6	-	pr EN 14112k
Acid value	mg KOH/g	-	0,5	pr EN 14104
Iodine value	-	-	120	pr EN 14111
Linolenic Acid Methylester	% (m/m)	-	12	pr EN 14103d
Polyunsaturated (>= 4 Double bonds) Methylester	% (m/m)	-	1	-
Methanol content	% (m/m)	-	0,2	pr EN 14110l
Monoglyceride content	% (m/m)	-	0,8	pr EN 14105m
Diglyceride content	% (m/m)	-	0,2	pr EN 14105m
Triglyceride content	% (m/m)	-	0,2	pr EN 14105m
Free Glycerine	% (m/m)	-	0,02	pr EN 14105m / pr EN 14106
Total Glycerine	% (m/m)	-	0,25	pr EN 14105m
Alkali Metals (Na+K)	mg/kg	-	5	pr EN 14108 / pr EN 14109
Phosphorus content	mg/kg	-	10	pr EN14107p

Table 7.1 - European B100 Standard – EN 14214 (Wikipedia Encyclopedia 2007)



Property	ASTM Method	Limits	Units
Calcium & Magnesium, combined	EN 14538	5 max	ppm (ug/g)
Flash Point (closed cup)	**D 93**	**93 min.**	**Degrees C**
Alcohol Control (One of the following must be met)			
1. Methanol Content	EN14110	0.2 Max	% volume
2. Flash Point	D93	130 Min	Degrees C
Water & Sediment	**D 2709**	**0.05 max.**	**% vol.**
Kinematic Viscosity, 40 C	D 445	1.9 - 6.0	mm^2/sec.
Sulfated Ash	D 874	0.02 max.	% mass
Sulfur			
S 15 Grade	**D 5453**	**0.0015 max. (15)**	**% mass (ppm)**
S 500 Grade	**D 5453**	**0.05 max. (500)**	**% mass (ppm)**
Copper Strip Corrosion	D 130	No. 3 max.	
Cetane	D 613	47 min.	
Cloud Point	**D 2500**	**Report**	**Degrees C**
Carbon Residue 100% sample	D 4530*	0.05 max.	% mass
Acid Number	**D 664**	**0.50 max.**	**mg KOH/g**
Free Glycerin	**D 6584**	**0.020 max.**	**% mass**
Total Glycerin	**D 6584**	**0.240 max.**	**% mass**
Phosphorus Content	D 4951	0.001 max.	% mass
Distillation, T90 AET	D 1160	360 max.	Degrees C
Sodium/Potassium, combined	EN 14538	5 max	ppm
Oxidation Stability	**EN 14112**	**3 min**	**hours**

Table 7.2 - U.S. ASTM B100 Standard (NBB 2007)

The European EN590 standard currently limits FAME to 5%. In January 2008, the Commission published a proposal for a new Directive on renewable energy. It would mandate 10% renewable fuels in 2020. It also states that EN590 should be modified to allow higher blending of FAME. The proposal defines two diesel qualities, one with 0-7% FAME and one with 5-10% FAME.

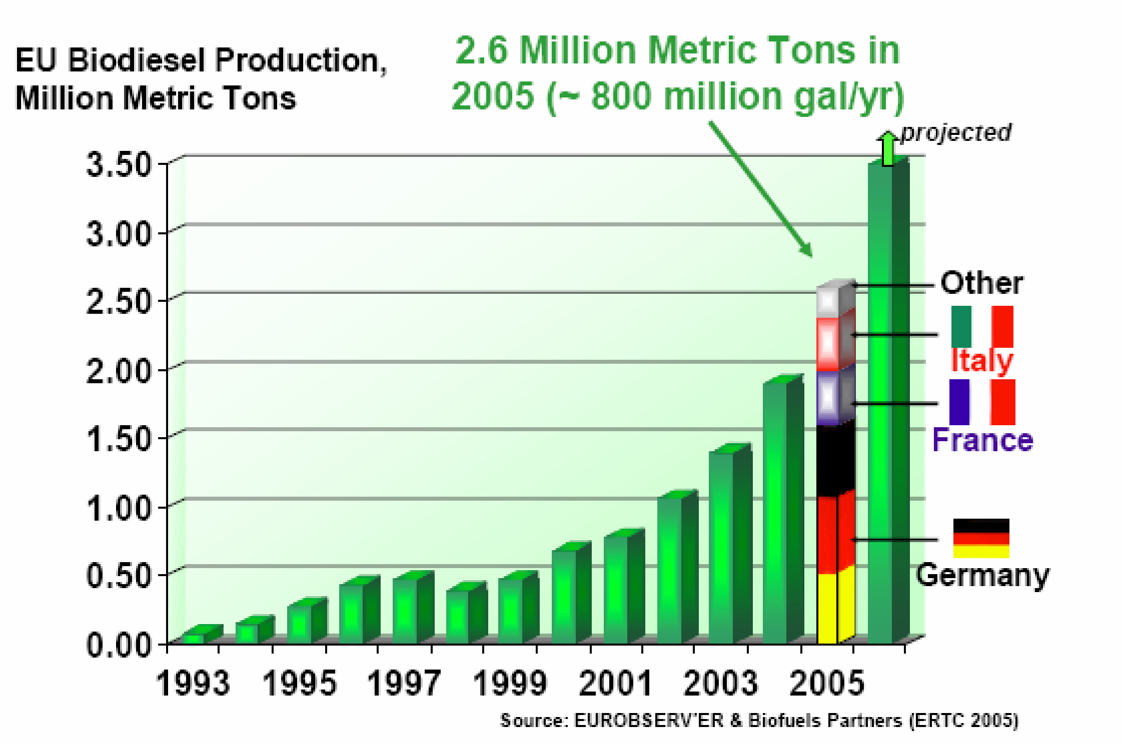
We should note here that there is a big difference in diesel fuel quality in Europe and in the US. The minimum cetane number set by the European diesel fuel standard EN590 is 51, whereas ASTM 975 requires only a minimum of 40. In Europe, diesel is, in practice, the only fuel used in heavy-duty vehicles, and the share of diesel cars in new registrations within the European Union is around 50 %. In the U.S., the use of diesel fuel is basically limited to heavy-duty commercial vehicles with only few diesel-powered light duty vehicles.

For these reasons, the issue of diesel fuel quality and in particular high quality biobased diesel fuels has received more attention in Europe than in the U.S. For example, the German car manufacturers are in strong opposition to allowing more than 5 % FAME-type biodiesel in conventional diesel fuel. The reasons for this are problems with clogging of particulate filters and fuel dilution of the engine oil in engines using post-injection for particulate filter regeneration. The latter phenomenon is caused by the high boiling range of FAME, resulting in fuel condensation on the cylinder walls when fuel is injected late in the working cycle. On the other hand, European vehicle manufacturers are strongly promoting the biomass-to-liquids (BTL) type of pure hydrocarbon bio-components, both to be used as blending components with petro-diesel and as fuel itself.

8 Growth of Production and Use of Biodiesel Fuels

Interest in biodiesel has exploded around the world in the first decade of the 21st century. Europe led the way in the 1990s and still has a large lead in terms of tons of biodiesel produced and used. Since the start of this decade, though, the U.S. and many other countries around the world have "joined the bandwagon" and instituted policies and incentives that will spur the development and use of biodiesel.

Biodiesel production started in the European Union with small-scale facilities producing less than 10,000 metric tons per anum (mtpa). Today, however, the expansion in the market has resulted in plant sizes increasing significantly, first to 100,000 mtpa up to 250,000 mtpa today. (Biodiesel Center 2007) Figure 8.1 below illustrates the growth in production of biodiesel in the EU from 1993 to 2005.



Source: EUROBSERV'ER & Biofuels Partners (ERTC 2005)

Figure 8.1 - Biodiesel Production in the EU (Biofuels Center 2007)

By comparison, the biodiesel market is still in its infancy in the U.S. For example, in 2005 Europe produced about 800 million gallons of biodiesel, much of it from Germany, but production in the U.S. that same year was only about 10% of that number but still growing rapidly. The U.S. production levels since 1999 are illustrated in Figure 8.2 below.

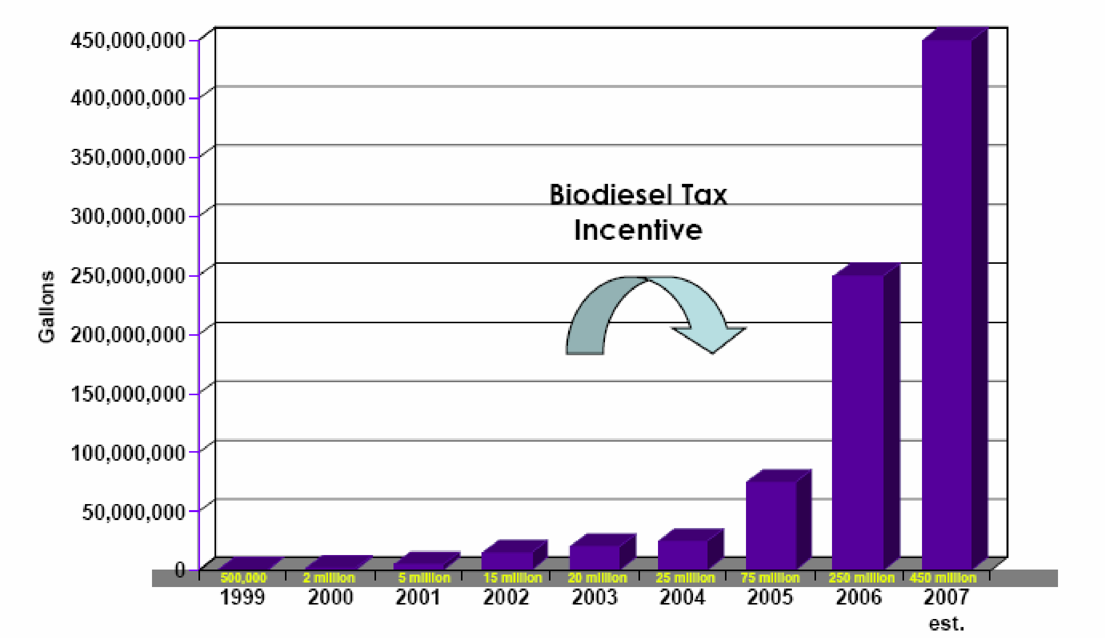


Figure 8.2 - U.S. Production of Biodiesel since 1999 (NBB 2007)

In the U.S. there are approximately 56 biodiesel production facilities operating and another 89 that are in the development stages. A number of these produce rather small quantities of biodiesel each year (less than 1 million gallons). In Europe there are at least 75 facilities operating with additional facilities under construction.

In Europe, the demand of diesel fuel is growing while the consumption of gasoline is leveling. Therefore the discussion of diesel fuel quality and diesel substitution is highly topical in Europe.

8.1 Incentives and Policy Initiatives:

A number of incentives and policies have been adopted around the world to spur the development, production, and use of biodiesel. The highlights of some of those initiatives are summarized in this section.

In the U.S. the Energy Policy Act of 1992 (EPACT 1992) required government fleets to use a certain percentage of alternative-fuel vehicles and established a goal of replacing 10% of motor fuels with non-petroleum alternatives by the year 2000. That number of replacements increased to 30% by the year 2010. Currently 75% of all government vehicles purchased (with the possible exception of military vehicles) are required to have alternative fuel capability.

In 2004 the U.S. Congress passed legislation known as the Biodiesel Tax Credit which provides a tax credit for using biodiesel blends. The credit is 1 cent ($0.01) for each percentage point of vegetable-oil based biodiesel blended with petroleum diesel and on-half cent ($0.005) for each percentage point of biodiesel made from recycled cooking oils. For example, 20% of biodiesel made from soy or other vegetable oils blended with petroleum diesel will enjoy a 20 cent tax credit, while 20% of biodiesel made from used vegetable oils will receive a 10 cent tax credit. This savings is generally passed on to the consumer. The incentive was intended to lower the cost of biodiesel close to the cost of petroleum diesel.

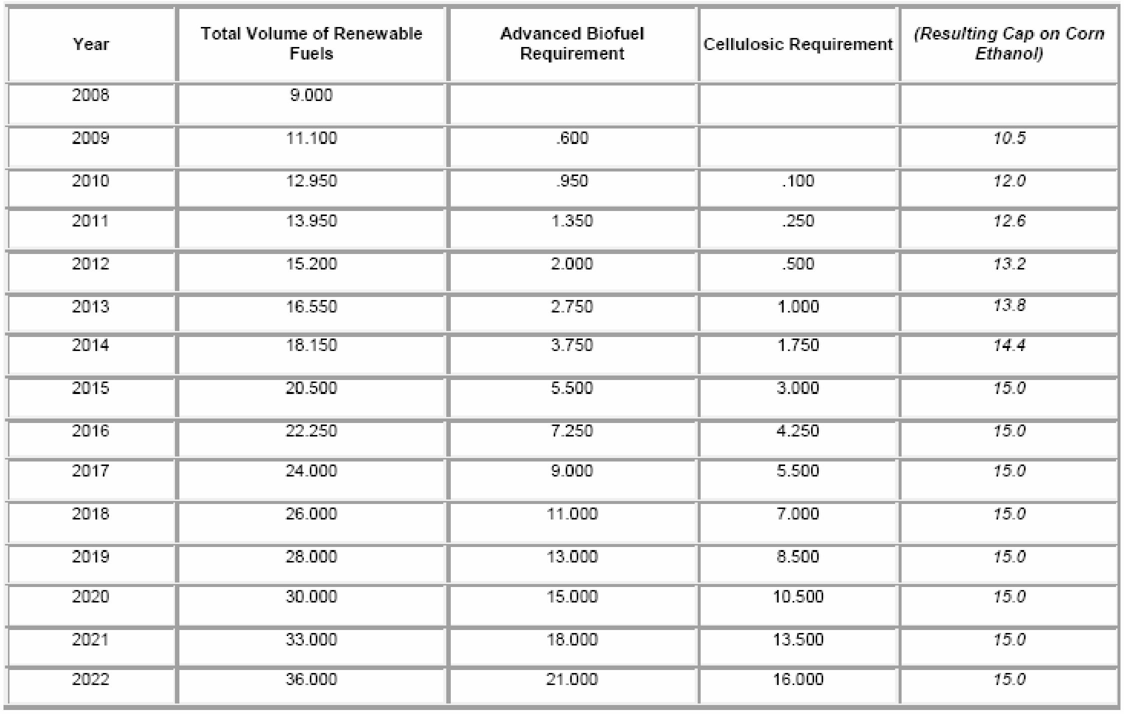
The U.S. Energy Policy Act of 2005 (EPACT 2005) established a renewable fuels standard to be administered by the Environmental Protection Agency (EPA). Effective September 1, 2007 EPA established a national Renewable Fuel Standard Program, or RFS program. The program is designed to encourage the blending of renewable fuels into the U.S. motor vehicle fuel. This rule establishes the annual renewable fuel standards, responsibilities of refiners and other fuel producers, a trading system and other compliance mechanisms. Much of the targets relate to ethanol, but biodiesel has an important role as well. The targets are aimed at conventional biofuel, advanced biofuels, cellulosic biofuels, and biomass-based diesel. These terms are defined as follows:

- ***Conventional biofuel*** is defined as ethanol derived from corn starch. Conventional ethanol facilities that commence construction after the date of enactment must achieve a 20 percent greenhouse gas (GHG) emissions reduction compared to baseline lifecycle GHG emissions. The 20 percent GHG emissions reduction requirement may be adjusted to a lower percentage (but not less than 10 percent) by the U.S. Environmental Protection Agency (EPA) Administrator if it is determined the requirement is not feasible for conventional biofuels.
- ***Advanced biofuel*** is defined as renewable fuels other than ethanol derived from corn starch, that is derived from renewable biomass, and achieves a 50 percent GHG emissions reduction requirement. The definition – and the schedule -- of advanced biofuels include cellulosic biofuels and biomass-based diesel. The 50 percent GHG emissions reduction requirement may be adjusted to a lower percentage (but not less than 40 percent) by the Administrator if it is determined the requirement is not feasible for advanced biofuels. (Cellulosic biofuels that do not meet the 60 percent threshold, but do meet the 50 percent threshold, may qualify as an advanced biofuel.)
- ***Cellulosic biofuel*** is defined as renewable fuel derived from any cellulose, hemicellulose, or lignin, that is derived from renewable biomass, and achieves a 60 percent GHG emission reduction requirement. The 60 percent GHG emissions reduction requirement may be adjusted to a lower percentage (but not less than 50

percent) by the Administrator if it is determined the requirement is not feasible for cellulosic biofuels.

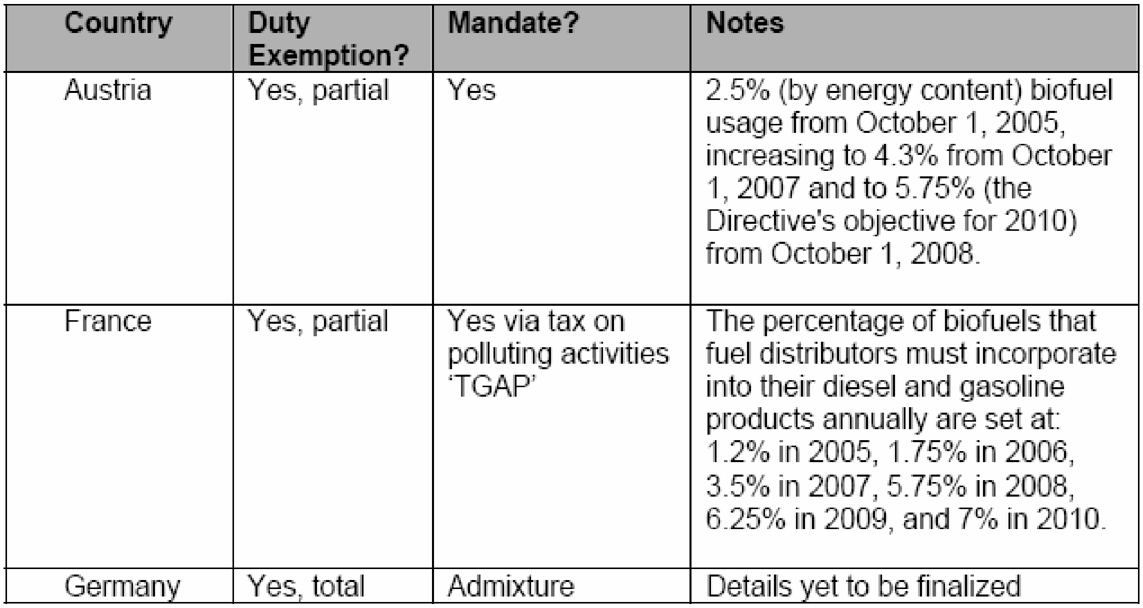
Table 8.1 below shows the required amounts of renewable fuels to be used in the nation's fuel pool each year up to 2022. Targets are for the total displacement of petroleum fuels by renewable fuels. So, it includes biodiesel along with ethanol and other renewables.

Table 8.1 - Renewable Fuel Standards (Billion Gallons per Year) (Renewable Fuels Association 2008)



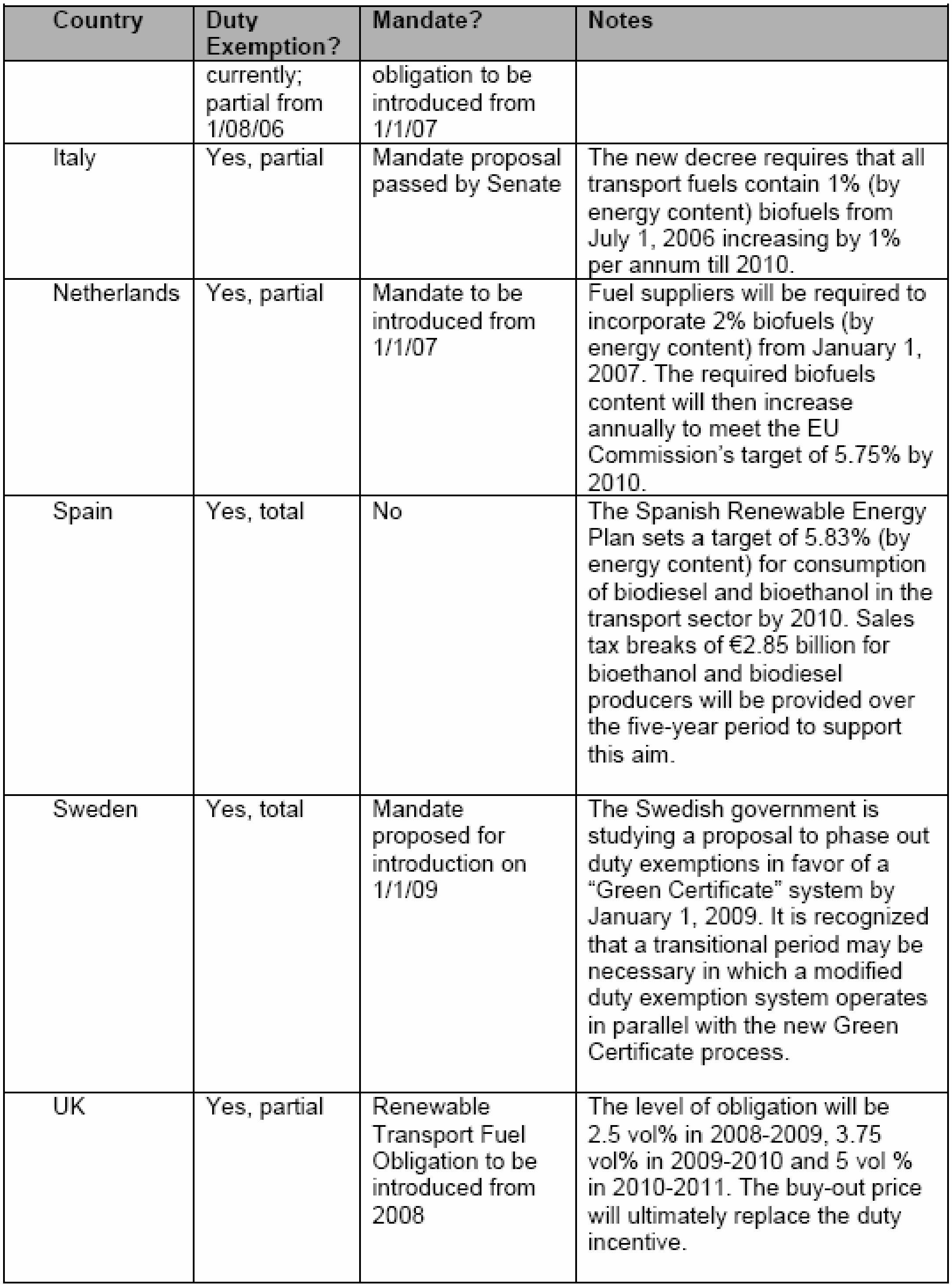
Year	Total Volume of Renewable Fuels	Advanced Biofuel Requirement	Cellulosic Requirement	*(Resulting Cap on Corn Ethanol)*
2008	9.000			
2009	11.100	.600		*10.5*
2010	12.950	.950	.100	*12.0*
2011	13.950	1.350	.250	*12.6*
2012	15.200	2.000	.500	*13.2*
2013	16.550	2.750	1.000	*13.8*
2014	18.150	3.750	1.750	*14.4*
2015	20.500	5.500	3.000	*15.0*
2016	22.250	7.250	4.250	*15.0*
2017	24.000	9.000	5.500	*15.0*
2018	26.000	11.000	7.000	*15.0*
2019	28.000	13.000	8.500	*15.0*
2020	30.000	15.000	10.500	*15.0*
2021	33.000	18.000	13.500	*15.0*
2022	36.000	21.000	16.000	*15.0*

The policy in effect in Europe for biofuels is the EU Directive 2003/30/EC, which promotes the use of biofuels or other renewable fuels for transport. The Directive set a voluntary target of 2% biofuel consumption (by energy content) in 2005 with a provision that the target will rise by 0.75% each year till reaching 5.75% in 2010. The Directive includes both ethanol and biodiesel. Individual member states have also set additional standards and incentives. They are summarized in Tables 8.2 and 8.3 below.



Country	Duty Exemption?	Mandate?	Notes
Austria	Yes, partial	Yes	2.5% (by energy content) biofuel usage from October 1, 2005, increasing to 4.3% from October 1, 2007 and to 5.75% (the Directive's objective for 2010) from October 1, 2008.
France	Yes, partial	Yes via tax on polluting activities 'TGAP'	The percentage of biofuels that fuel distributors must incorporate into their diesel and gasoline products annually are set at: 1.2% in 2005, 1.75% in 2006, 3.5% in 2007, 5.75% in 2008, 6.25% in 2009, and 7% in 2010.
Germany	Yes, total	Admixture	Details yet to be finalized

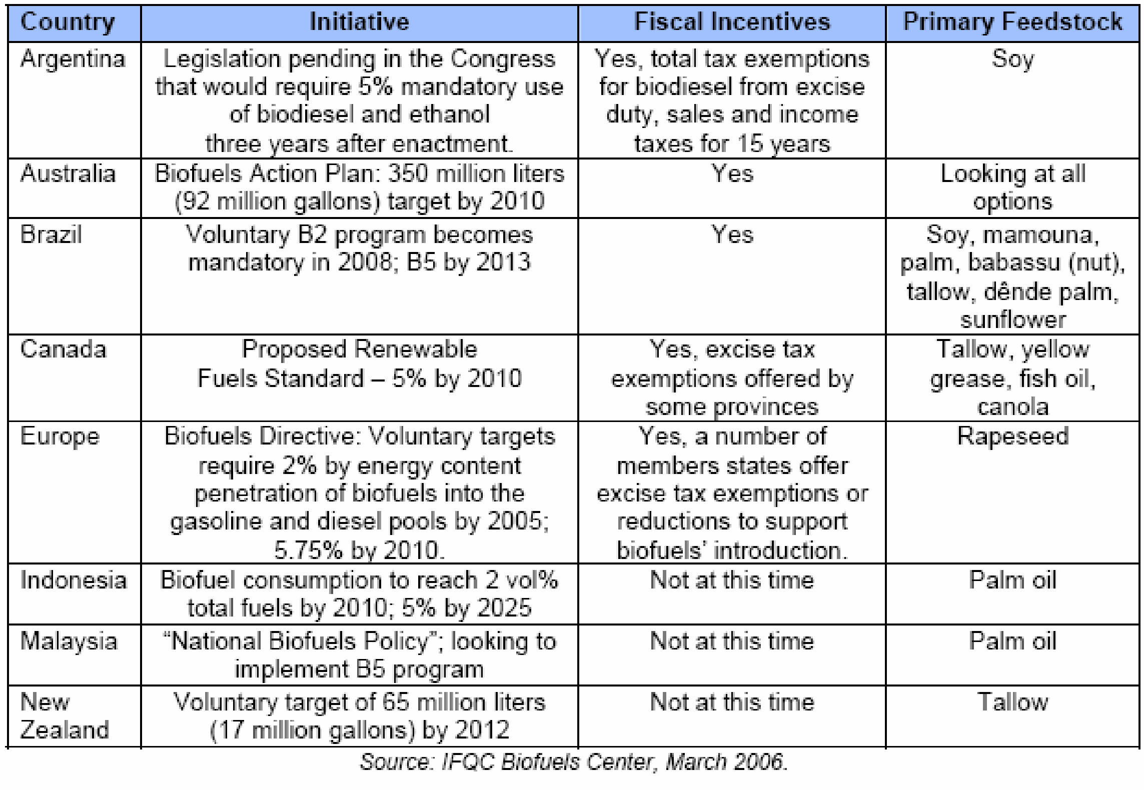
Table 8.2 - Biofuels Developments in the EU Member States (Biofuels Center 2007) (Table continued in Table 8.2 below)



Country	Duty Exemption?	Mandate?	Notes
	currently; partial from 1/08/06	obligation to be introduced from 1/1/07	
Italy	Yes, partial	Mandate proposal passed by Senate	The new decree requires that all transport fuels contain 1% (by energy content) biofuels from July 1, 2006 increasing by 1% per annum till 2010.
Netherlands	Yes, partial	Mandate to be introduced from 1/1/07	Fuel suppliers will be required to incorporate 2% biofuels (by energy content) from January 1, 2007. The required biofuels content will then increase annually to meet the EU Commission's target of 5.75% by 2010.
Spain	Yes, total	No	The Spanish Renewable Energy Plan sets a target of 5.83% (by energy content) for consumption of biodiesel and bioethanol in the transport sector by 2010. Sales tax breaks of €2.85 billion for bioethanol and biodiesel producers will be provided over the five-year period to support this aim.
Sweden	Yes, total	Mandate proposed for introduction on 1/1/09	The Swedish government is studying a proposal to phase out duty exemptions in favor of a "Green Certificate" system by January 1, 2009. It is recognized that a transitional period may be necessary in which a modified duty exemption system operates in parallel with the new Green Certificate process.
UK	Yes, partial	Renewable Transport Fuel Obligation to be introduced from 2008	The level of obligation will be 2.5 vol% in 2008-2009, 3.75 vol% in 2009-2010 and 5 vol % in 2010-2011. The buy-out price will ultimately replace the duty incentive.

Table 8.3 - Biofuels Developments in the EU Member States (Biofuels Center 2007) (Continued from Table 8.1 above)

In addition to the U.S. and the EU there are a number of additional nations around the world who are adopting biodiesel initiatives. These are summarized in Table 8.4 below.



Country	Initiative	Fiscal Incentives	Primary Feedstock
Argentina	Legislation pending in the Congress that would require 5% mandatory use of biodiesel and ethanol three years after enactment.	Yes, total tax exemptions for biodiesel from excise duty, sales and income taxes for 15 years	Soy
Australia	Biofuels Action Plan: 350 million liters (92 million gallons) target by 2010	Yes	Looking at all options
Brazil	Voluntary B2 program becomes mandatory in 2008; B5 by 2013	Yes	Soy, mamouna, palm, babassu (nut), tallow, dênde palm, sunflower
Canada	Proposed Renewable Fuels Standard – 5% by 2010	Yes, excise tax exemptions offered by some provinces	Tallow, yellow grease, fish oil, canola
Europe	Biofuels Directive: Voluntary targets require 2% by energy content penetration of biofuels into the gasoline and diesel pools by 2005; 5.75% by 2010.	Yes, a number of members states offer excise tax exemptions or reductions to support biofuels' introduction.	Rapeseed
Indonesia	Biofuel consumption to reach 2 vol% total fuels by 2010; 5% by 2025	Not at this time	Palm oil
Malaysia	"National Biofuels Policy"; looking to implement B5 program	Not at this time	Palm oil
New Zealand	Voluntary target of 65 million liters (17 million gallons) by 2012	Not at this time	Tallow

Source: IFQC Biofuels Center, March 2006.

Table 8.4 - Biodiesel Initiatives in Other Countries (Biofuels Center 2007)

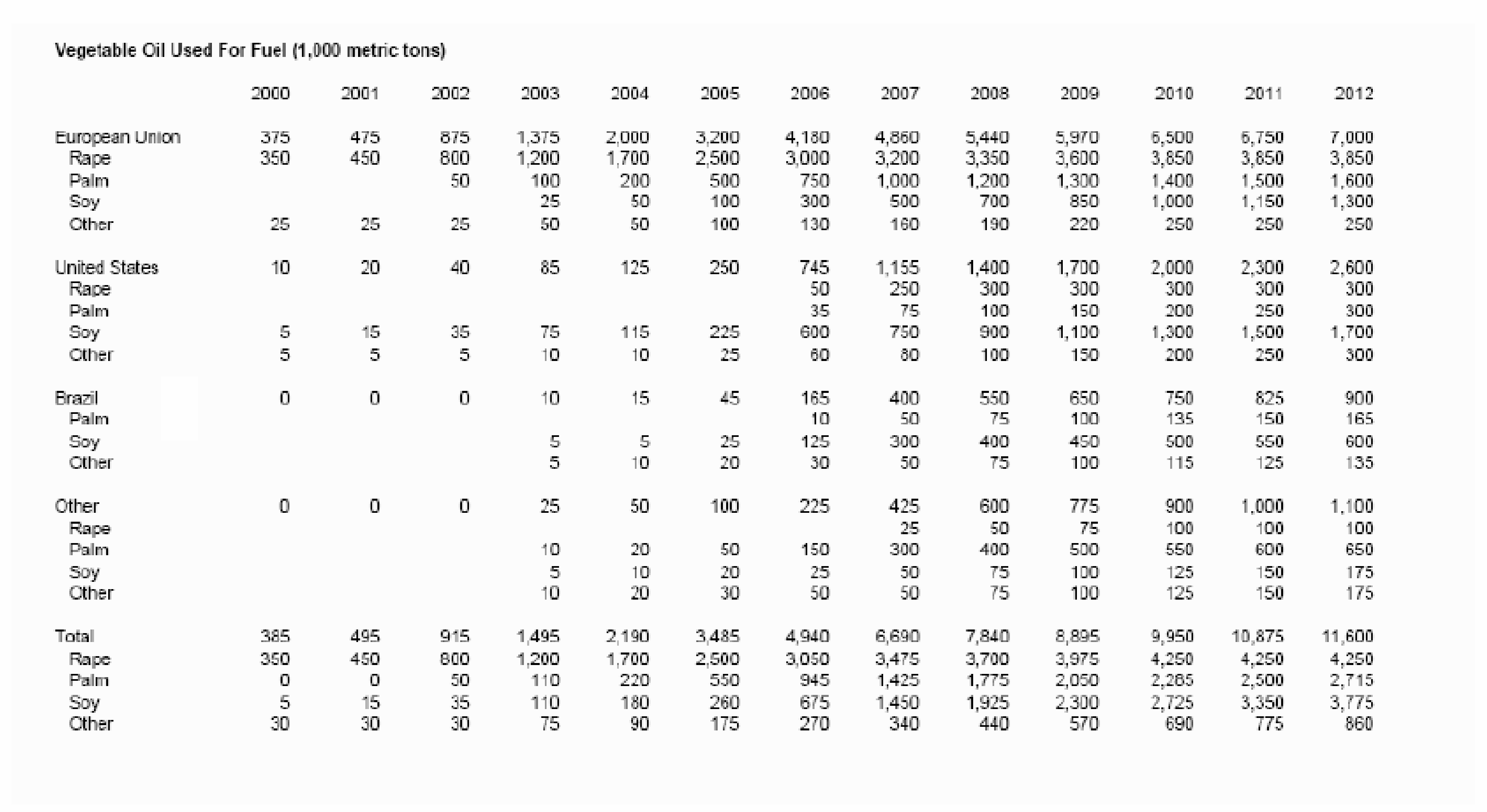
In addition to that detailed in the table, the government of Canada intends to put in place a requirement for an average 2% renewable fuel content in diesel fuel and heating oil, upon successful demonstration of renewable diesel fuel use under the range of Canadian conditions. This would not be in place for 2010, but is intended to come into effect by no later than 2012. This requirement is approximately equivalent to a renewable fuel content requirement for 5% of on-road diesel fuel.

Promar International, a strategic marketing and business consulting firm in the U.S., made an excellent analysis of worldwide vegetable oil markets to determine the effects that a fast-rising biodiesel market would have on the markets for vegetable oils and their derivatives. (Promar 2005) We will discuss their results in greater detail in the next section. Included in their analysis was a projection of the increased use of vegetable oils for fuel to the year 2012. Among their assumptions were the following:

In the U.S. biodiesel will make up no more than 10% of the Renewable Fuels Standard, and soy will be the main feedstock. In Europe, rapeseed will continue to be the main feedstock, but soy and palm oil will be used because Europe will be forced to import more vegetable oils. Brazil will use a mix of soy, castor, and palm oils, while Malaysia and other Asian countries will use palm oil.

Their projections are shown as Table 8.5.

Table 8.5 - Projections of Vegetable Oils Used for Fuel in the EU, US, Brazil, and Other (Promar 2005)



Vegetable Oil Used For Fuel (1,000 metric tons)

	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012
European Union	375	475	875	1,375	2,000	3,200	4,180	4,860	5,440	5,970	6,500	6,750	7,000
Rape	350	450	800	1,200	1,700	2,500	3,000	3,200	3,350	3,600	3,850	3,850	3,850
Palm			50	100	200	500	750	1,000	1,200	1,300	1,400	1,500	1,600
Soy				25	50	100	300	500	700	850	1,000	1,150	1,300
Other	25	25	25	50	50	100	130	160	190	220	250	250	250
United States	10	20	40	85	125	250	745	1,155	1,400	1,700	2,000	2,300	2,600
Rape							50	250	300	300	300	300	300
Palm							35	75	100	150	200	250	300
Soy	5	15	35	75	115	225	600	750	900	1,100	1,300	1,500	1,700
Other	5	5	5	10	10	25	60	80	100	150	200	250	300
Brazil	0	0	0	10	15	45	165	400	550	650	750	825	900
Palm							10	50	75	100	135	150	165
Soy				5	5	25	125	300	400	450	500	550	600
Other				5	10	20	30	50	75	100	115	125	135
Other	0	0	0	25	50	100	225	425	600	775	900	1,000	1,100
Rape								25	50	75	100	100	100
Palm				10	20	50	150	300	400	500	550	600	650
Soy				5	10	20	25	50	75	100	125	150	175
Other				10	20	30	50	50	75	100	125	150	175
Total	385	495	915	1,495	2,190	3,485	4,940	6,690	7,840	8,895	9,950	10,875	11,600
Rape	350	450	800	1,200	1,700	2,500	3,050	3,475	3,700	3,975	4,250	4,250	4,250
Palm	0	0	50	110	220	550	945	1,425	1,775	2,050	2,285	2,500	2,715
Soy	5	15	35	110	180	260	675	1,450	1,925	2,300	2,725	3,350	3,775
Other	30	30	30	75	90	175	270	340	440	570	690	775	860

B. BIODIESEL – ADVANCED OPTIONS

9 Biofuel Refineries – The Path to the Future?

9.1 General

Demand for energy, fuels, and chemicals is growing, while fossil resources are diminishing, and environmental pressures are increasing. Huge efforts are given to develop new technologies and processes to increase the usage of biomass in sustainable ways. One of the basic targets is to move from traditional biofuels to the next generation fuels based on non-edible feedstocks (U.S. DOE EERE, IEA Bioenergy Task 42).

Today biofuels for the transport sector are ethanol and biodiesel, produced from grains and vegetable oils. However, the greatest energy potential of biomass is in lignocellulosic biomass such as residues from forestry, the agricultural sector and energy crops. (U.S. DOE EERE).

Solid biomass cannot be practically used as such for transportation, but it needs to be converted to gaseous or liquid fuels. This can be done with a number of Biomass-to-Liquids (BTL) processes. Somewhere in between of the traditional biodiesel and BTL lays biodiesel obtained by hydrotreatment of oils and fats.

One benefit of the new biomass-to-liquids (BTL) technologies is that the whole plant can be utilized, whereas production of traditional biofuels uses only parts of the plant. In addition, a variety of feedstocks can be used in BTL process, meaning that production potential and efficiency is improved, and less land area under cultivation is needed than in traditional biofuel production.

A variety of biomass feedstocks are suitable for BTL processes. However, there are also limitations based on the characteristics of feedstocks. For instance, the composition of cellulose and sugars are important for fuel production.

9.2 Biorefinery concepts

The concept of biorefinery implies an integrated production of fuels, energy, and chemicals from biomass. This resembles oil refineries producing many fuels and products from crude oil. One definition of a *biorefinery* is a unit delivering *multiproducts-from-biomass*.

A biorefinery can be *stand-alone* or *integrated* in, for example, heat and power plants, pulp and paper mills, and oil refineries. Co-production of many different products and high-value chemicals means that synergetic benefits can be obtained regarding e.g. the energy balance, infrastructure and economy. (U.S. DOE EERE).

NREL defines two biorefinery concepts classified by process technology:

- the "sugar platform" based on biochemical conversion processes (hydrolysis, fermentation) and
- the "syngas platform" based on thermochemical conversion processes such as synthesis gas or pyrolysis oil path. (Figure 9.1).

A fully integrated biorefinery is a complex plant, in which both biochemical and thermochemical conversion processes can be combined.

In the “sugar platform” hemicellulose and cellulose are hydrolysed to sugars, which are further processed to ethanol or other chemicals[4]. Ethanol can be produced from lignocellulosic material also via fermentation of syngas and anaerobic fermentation. Separated lignin can be processed into valuable products or can be burned to provide heat, steam, and electricity.

The thermochemical or “syngas platform” means gasification of biomass to syngas, a mixture of carbon monoxide (CO) and hydrogen (H_2), which can be further processed to fuels and other chemicals, or liquefaction to pyrolysis oil. Synthesis gas, pyrolysis oil, or liquid fuel burns more efficiently than biomass as such. (U.S. DOE EERE). Synthesis gas can also be obtained from coal and natural gas, and these feedstocks are discussed in this report as a reference for biomass conversion technologies.

A well-known technology to decompose biomass with microorganisms in an anaerobic process produces methane that can be used as fuel, in energy production or as a chemical (U.S. DOE EERE). For vehicle applications, the biogas has to be cleaned to a quality corresponding to high quality natural gas. Methane or biomethane is not suitable for conventional diesel engines, and is therefore not a diesel substitute. Methane can be used in spark-ignited engines or in engines with pilot injection.

Figure 9.2 shows the research, development, demonstration, and deployment pathway to integrated biorefineries.

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[4] A variety of technologies can be used for hydrolyzing biomass, e.g., concentrated acid and dilute acid hydrolysis or enzymatic hydrolysis. Biomass goes through a mechanical milling process, and in the dilute-acid hydrolysis the hemicellulose is broken to make cellulose wrapped in a sheath of hemicellulose and lignin more accessible. Cellulose is enzymatically hydrolyzed to release its sugars. Then, fermentation to fuel ethanol or to biocatalytic processing to other products can take place, and the lignin is gasified, converted into desired products, or combusted for heat and power (U.S. DOE EERE).

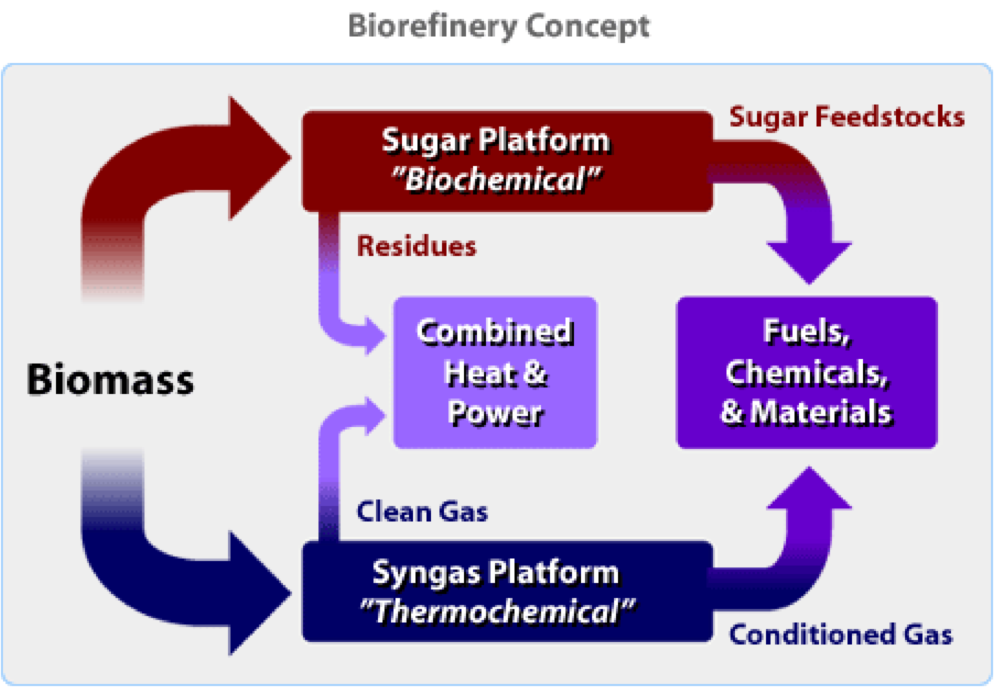

Figure 9.1 - Biorefinery Concepts (NREL).

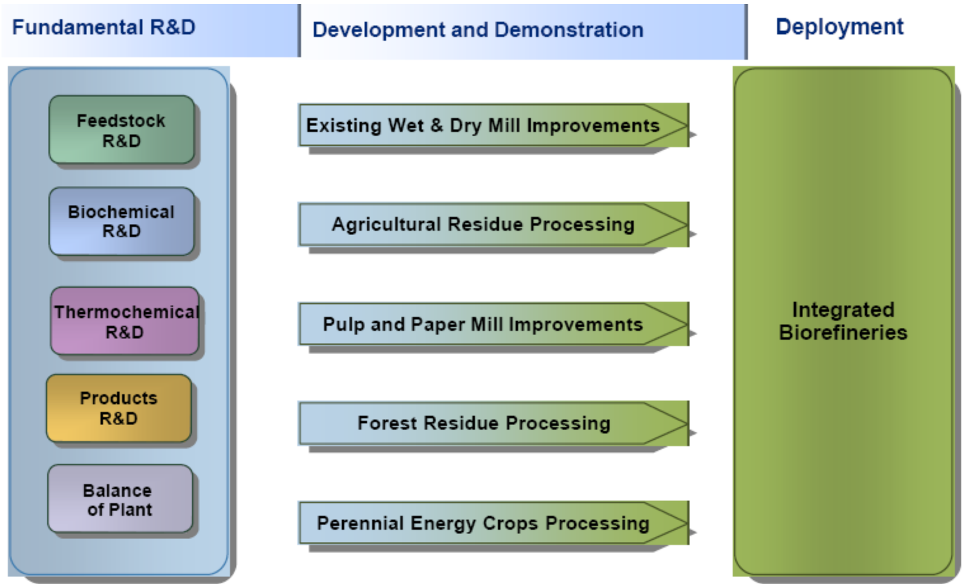

Figure 9.2 - Research and Development Towards Integrated Biorefineries (Russo 2007)

10 Process Technology

A number of different technologies can be used to convert biomass to fuels (Table 10.1, Figure 10.1). Diesel-type biofuel can be processed via gasification followed by liquefaction step, such as the Fischer-Tropsch process. Pyrolysis of plants can produce bio-oil, a kind of bio-crude which can be further processed to biodiesel. Catalytic depolymerization can be used to separate biodiesel from hydrocarbon wastes. Hydrotreatment of oils and fats into paraffins is also one option, and this process is already commercialized.

Biorefineries can also produce fuels other than diesel-type biofuels, such as biogasoline, methane, ethanol, and methanol.

Table 10.1 - From Biomass to Biofuels

Process	**Product**	**End-use**
Natural oils →		
Esterification	Biodiesel (by-product glycerol)	Transport fuels
Hydrotreatment	Biobased diesel	Transport fuels
No processing	Oils	Food, energy
Biomass → syngas →		
Fischer-Tropsch	FT-fuels, ethanol, various other products, chemicals	Transport fuels and chemical industries
Methanol-to-liquids	Gasoline type fuels ("MTG" process)	Transport fuels and chemical industries
Syngas to alcohols, ethers	Methanol, ethanol etc.	Transport fuels and chemical industries
Water-shift	H_2	Fuel cells
No processing	Syngas	Power and heat
Biomass → pyrolysis oil →		
Hydroprocessing	Biobased fuels, other products	Transport fuels and chemical industries
No processing	Pyrolysis oil	Power and heat
Biomass → sugars →		
Biochemical	Ethanol	Transport fuels and chemical industries
Anaerobic digestion	Methane (biogas)	Transport

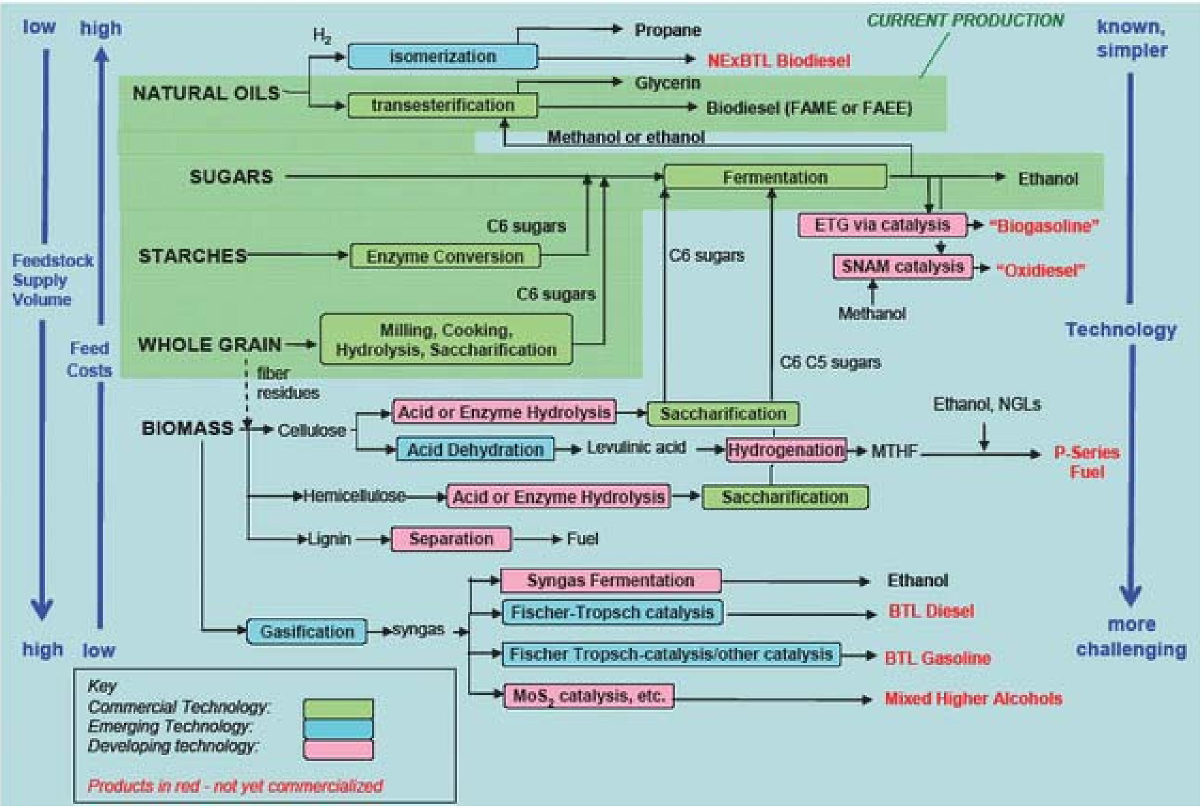

Figure 10.1 - Technologies to Utilize Biomass for Liquid Biofuels (Nexant 2006)

When diesel-type fuels are considered, the thermochemical platform based on gasification and a liquefaction step is seen as the most promising option for large-scale production. Several types of feedstocks can be used for the syngas/liquefaction path. When the feedstock is biomass, the process is called Biomass-to-liquids, BTL. Feedstock can be also a mixture of, for example, coal and biomass, in which case the process is called XTL (Figure 10.2). Well-known technologies for fossil feedstocks, Coal-to-liquids (CTL) and Gas-to-liquids (GTL), are discussed in this report as reference cases.

When biomass is heated with no oxygen, or with only about one-third of the oxygen needed for efficient combustion, it gasifies or pyrolyzes, depending on the conditions. Gasification of carbon containing-material produces syngas, a mixture of carbon monoxide (CO) and hydrogen (H_2). The product from gasification, syngas, can be used in various ways (Figure 10.3). It can be burned in gas turbines, or converted to different type of products, fuels and chemicals; e.g. the Fischer-Tropsch (FT) conversion to liquid fuels. The water-gas shift process can convert synthesis gas to concentrated hydrogen, which can be used in fuel cells. (U.S DOE EERE). Syngas can also used for ethanol production through catalytic process or a fermentation step. Efficient cleaning of the gas is crucial in most applications.

Regarding a complex set of different options available, it is essential to evaluate carefully which chain or route is the most beneficial. For example, Bernoux (2007) points out that liquefaction options other than FT synthesis should also be considered, such as gasoline via a methanol path (MTG) or DME synthesis. Lurgi has a lab-scale "MtSynfuels" scheme that converts syngas first to methanol and then to olefins and distillates, enabling production of diesel or gasoline. This scheme avoids making naphtha, which is a byproduct from FT process.

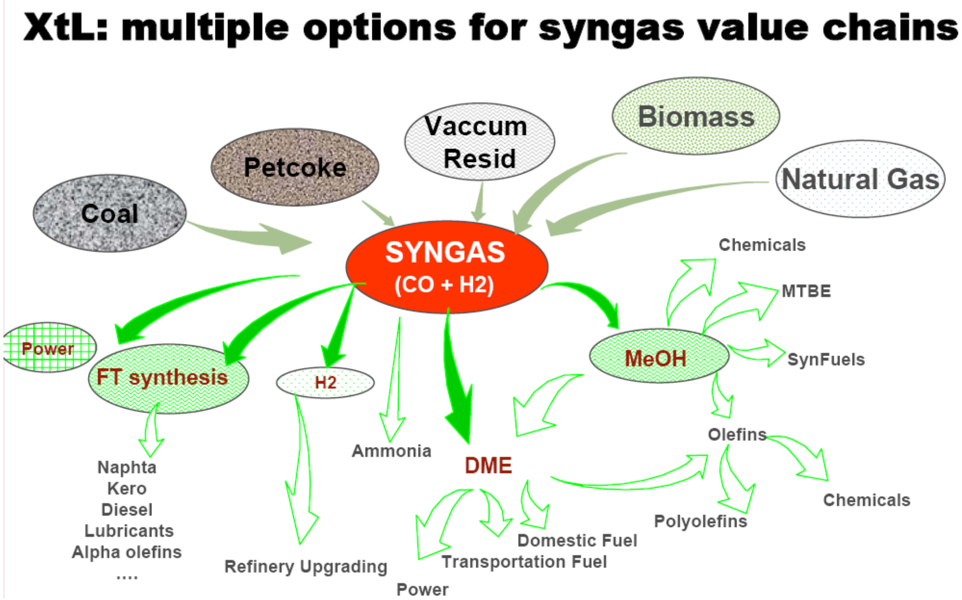

Figure 10.2 - Feedstocks and Products Obtained via Syngas Path (Hervouet et al. 2007)

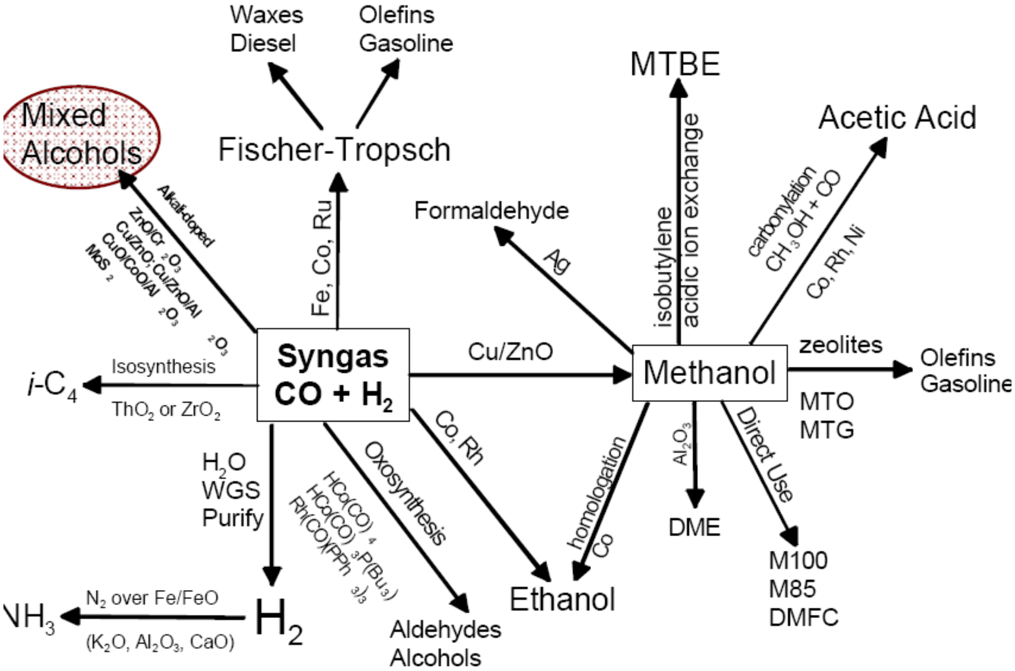

Figure 10.3 - Different Products from Syngas (Dayton 2007)

10.1 Syngas “BTL” Path

10.1.1 Gasification

Gasification is a process that converts carbonaceous materials into gas, using limited amount of oxygen, air, steam or combination of these as reacting agents. The product gas, also called syngas, contains mainly carbon monoxide (CO), hydrogen (H_2), and carbon dioxide (CO_2), but also methane, water, nitrogen, and impurities (char, ash, tars). Thus, it needs to be cleaned up before being used in boilers, engines, turbines or liquefaction processes.

The gasification process was developed in the 1800s to produce town gas for lighting and cooking. Gasification has been used since the 1920s for the production of synthetic fuels (FT fuels) and chemicals. Wood gas or coal gas generators were used during World War II in Europe to help with fuel shortages. Today gasification is used in the production of electricity, chemicals like ammonia and methanol, and liquid fuels. In power generation the Integrated Gasification Combined Cycles (IGCC) offers better efficiency than conventional steam cycles. There are a number of IGCC and gasification co-firing projects running at commercial-scale. Production of methane and hydrogen for fuel cells is also possible in future. Recent development of low-energy gasifiers has enabled dozens of small-scale facilities.

Syngas can be produced from natural gas by reforming or partial oxidation. Coal and solid biomass is gasified to obtain syngas. Biomass is a more challenging feedstock for gasification than coal and natural gas. Gasification of mixtures of biomass and fossil feedstocks can help in this respect (Larson et al. 1999).

Gasification of biomass is, in principle, similar to gasification of coal. Biomass is more reactive than coal, and thus lower temperatures can be used in gasification. Today, gasification of biomass is mainly based on un-pressurized gasification using air as the oxidizing agent. If the product gas (syngas) is to be used for the FT process, probably pressurized gasification and oxygen should be used. (Rehnlund 2007).

Four steps are typical for gasification of solid material (BTG Biomass Technology Group): drying, pyrolysis (volatiles released, and char, tar and methane formed), combustion to form CO_2, reduction (char + CO_2 produce CO + H_2).

Various options are available for the gasification process:

- Pressurized or un-pressurized gasification
- Reactor can be “Fixed bed” (counter-current or co-current), “Fluidized bed” or “Entrained flow”[5]

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[5] The “updraft” fixed bed gasifier: steam, oxygen and/or air flows through a fixed bed of fuel, and the ash is removed. The fuel must have high mechanical strength and must be non-caking. The throughput is rather low, thermal efficiency high and the gas exit temperatures relatively low. Methane is formed, thus product gas must be cleaned before use or recycled to the reactor. (Wikipedia)

- Oxidizing agent can be limited amounts of oxygen or air
- Cleaning step and other parameters can be also selected.

Reforming: In the case of coal the product gas almost solely consists of CO and H_2. When using biomass as feedstock, the product gas contains also methane and other hydrocarbons. Thus reforming, conversion of methane into CO and H_2, is needed when biomass is used.

Cleaning: The Fischer-Tropsch process sets stringent requirements for gas cleanliness. Traditional “wet gas cleaning” can be used for cleaning-up gas from gasification for the FT process. “Dry hot gas cleaning” has benefits, but also requires ultra cleaning steps. Clean-up steps can be combined with tar removal based on cracking (thermal or catalytic) or scrubbing by using oil-based medium and stripping (Rehnlund 2007). The cleaning-up technologies that are in commercial use in large-scale coal based FT processes may not be profitable for small-scale production.

Shifting: The ratio of CO and H_2 varies depending on the feedstock and process parameters. The water shift reaction is needed to optimize the share of hydrogen for Fischer-Tropsch synthesis. (Laan 1999).

The quality of biomass as feedstock varies a lot. Marano (2007) mentions that many properties of feedstock are important in gasification process, for example, H/C ratio, oxygen content, contaminants, moisture and ash content. In the CHOREN BTL plant in Germany, the following requirements are listed for the feedstock according to Bienert (2007): Conformity with the German biomass regulation, water content <35%, impurities <5%, Size <120x50x30 mm and cost-effectiveness.

CHOREN is developing gasification technology for solid feedstocks in the co-operation framework with Shell, Daimler, and VW. CHOREN’s Carbo-V process is shown in Figure 10.4 (CHOREN 2007).

The "downdraft" fixed bed gasifier: similar to the “updraft” type, but the gas flows in co-current configuration with the fuel. The exit temperature of produced gas is high (heat can be transferred to the gasification agent). Tar levels are lower than in the “updraft” type. (Wikipedia)
The fluidized bed gasifier: the fuel is fluidized in oxygen or air and steam, and the ash is removed. Fuel throughput is higher than for the fixed bed, but not as high as for the entrained flow gasifier. The conversion efficiency is rather low, so recycle or subsequent combustion of solids is necessary to increase conversion. Fluidized bed gasifiers are most useful for fuels that form highly corrosive ash (such as biomass) that would damage some other gasifiers. (Kurkela 2005)
The entrained flow gasifier: a pulverized solid, an atomized liquid or fuel slurry is gasified with oxygen or air in co-current flow. Most coals are suitable because of the high operating temperatures and the fine coal particles. Throuhgput is rather high, but thermal efficiency is lower as the gas must be cooled before it can be cleaned. Tar and methane are not present in the product gas; however more oxygen is needed than for the other types of gasifiers. Some fuels, e.g. certain biomasses, can form corrosive slag that damage a ceramic inner wall (not all gasifiers own this). (Wikipedia, Kurkela 2005)

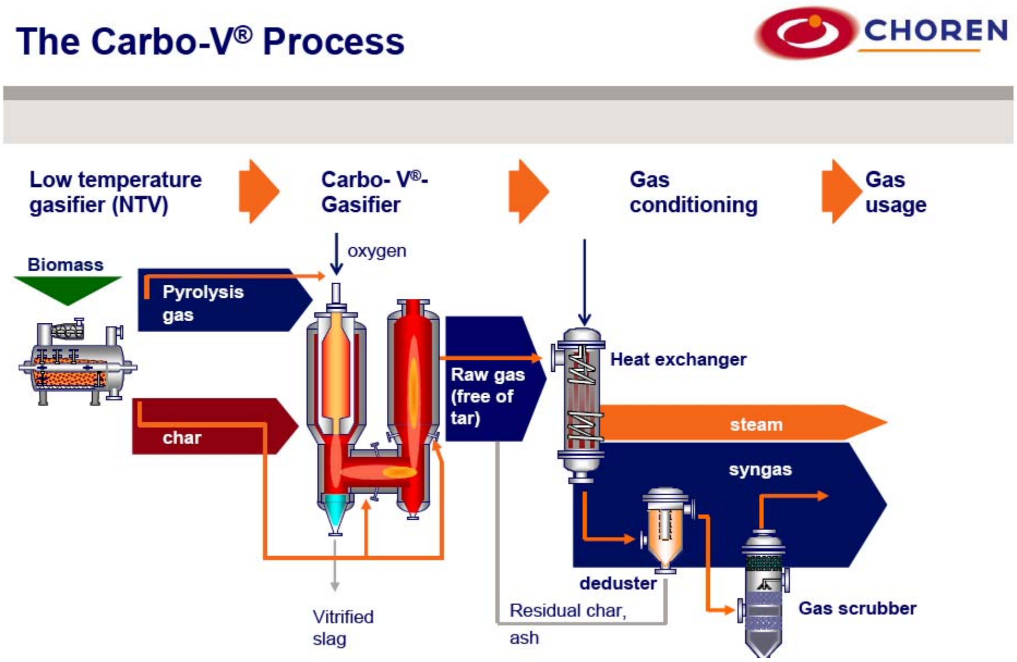


Figure 10.4 - The Carbo-V Process of CHOREN's BTL Technology (www.choren.com)

10.1.2 Fischer-Tropsch Conversion

Syngas, consisting of carbon monoxide and hydrogen, can be liquefied to synthetic fuels. The most common technology for liquefaction is the so called Fischer-Tropsch process, which is commercial technology for coal and natural gas. As described earlier, the process is called CTL when the feedstock is coal, GTL in the case of natural gas, BTL in the case of biomass, and XTL in the case of combined feedstocks.

The Fischer-Tropsch process was originally developed by German coal researchers, Franz Fischer and Hans Tropsch, in 1923 (Laan 1999). It was used in World War II, and later on in South Africa by SASOL to produce liquid fuels from coal (Table 10.2). Shell has developed the Shell Middle Distillate Synthesis (SMDS) process, which aims at maximum middle distillate production. Also e.g. Exxon and Norway's Statoil have been developing FT processes. Later on, interest in the Fischer-Tropsch process focused on utilization of low-value remote natural gas fields. Recently China has shown great interest in coal based synthetic fuels.

Table 10.2 - Fischer-Tropsch Activities Running or Announced on Commercial Scale (Vliet 2007, Schultz 2007, Blades 2008)

1935-1953: CTL plants in Germany and USA	Closed
1955-1983: CTL, South Africa, Sasol	162 500 bpd (6 960 ktons/a) iron catalyst, fixed bed and fluid bed reactor
1992 -> GTL South Africa, PetroSA (Mossgas)	40 000 bpd (1 900 ktons/a) iron catalyst, circulating fluid bed
1993 -> GTL, Malaysia, Shell	14 700 bpd (700 ktons/a) cobalt catalyst, fixed bed reactor
2005-2011: GTL, Qatar, Sasol, Shell and others	240 000 bpd (11 000 ktons/a) cobalt catalyst, Sasol - slurry reactor, Shell - fixed bed reactor
2007 -> GTL, Nigeria, Sasol/Chevron	34 000 bpd (1 600 ktons/a) cobalt catalyst, slurry reactor
2010 -> BTL, announced production at Choren's Sigma plants (Schwedt and the U.S.)	~10 600 bpd (~200 kton/a + ~300 kton/a)

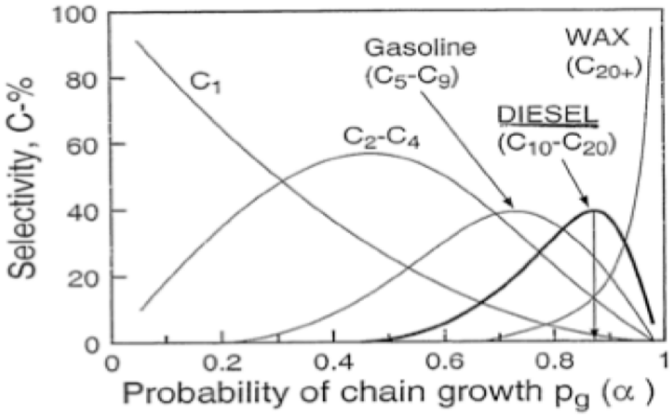
Fischer-Tropsch synthesis is a surface polymerization reaction, which produces a mixture of different hydrocarbons from syngas. The process is catalyzed by iron or cobalt at around e.g. 200-300 °C and at pressures from 10 to 60 bar. (van der Laan 1999). Also, ruthenium is an option as a FT catalyst. The main reactions of the FT process are formation of paraffins and olefins.

1) Formation of paraffins and olefins: $nH_2 + mCO \rightarrow C_xH_y + mH_2O$
2) Water gas shift reaction: $CO + H_2O \leftrightarrow CO_2 + H_2$
3) Alcohols as side reaction, other side reactions

The Fischer-Tropsch process sets strict requirements for cleanliness of syngas, which is critical issue when coal or biomass is used as feedstock. Rehnlund et al. (2007) lists the following requirements for cleanliness of syngas:

Particulates	max. 0 ppb
Tars	max. 0 ppb
$HCN+NH_3$	max. 20 ppb
H_2S+COS	max. 10 ppb
HCL	max. 10 ppb
Alkalis	max. 10 ppb

An important parameter describing the FT reaction is the selectivity, which can be expressed in terms of chain growth probability (α). Figure 10.5 shows the selectivity of different products as a function of α. Maximum once-through Fischer-Tropsch diesel production is about 40% at chain growth probability (α) of around 0.87. With hydrocracking of FT waxes diesel selectivity can be improved to around 60%. (Schulz 2007). The α factor depends on catalyst, H_2/CO ratio of feed, temperature, pressure, and residence time (Rehnlund 2007).



Adapted from M. Dry (1990)

Figure 10.5 - Selectivity of Different Products as a Function of α (Schultz 2007)

Syngas from coal, heavy oil, and biomass has lower H_2/CO ratio than syngas from natural gas. Syngas generated from natural gas contains some 50-70% of hydrogen (H_2/CO ratio of 3:1 by stoichiometry[6]), whereas from coal only some 30-40%, depending on the process details. Biomass tends to produce a H_2:CO ratio lower than 2:1, but this ratio depends on moisture content of biomass. The stoichiometric H_2/CO ratio for FT synthesis is 2, and with some feedstocks it is necessary to increase H_2/CO ratio by using the water shift reaction (van der Laan 1999).

The critical parameters for the Fischer-Tropsch process are temperature, catalyst, and reactor type. (Figures 10.6 and 10.7) Figure 10.6 shows that an iron catalyst can convert syngas along wide-scale of H_2/CO ratio due to its water shift activity, whereas cobalt catalyst can directly convert syngas with a narrow H_2/CO ratio. (van der Laan 1999).

Fused iron is used in high-temperature fluidized bed reactors and precipitated iron or cobalt in low temperature slurry reactors. Iron catalysts predominantly produce olefins, whereas cobalt favors paraffins. Cobalt requires very clean syngas to avoid catalyst poisoning. It is used with natural gas and coal based FT processes. Iron catalysts are less expensive than cobalt catalyst (Rehnlund 2007).

The reactor type can be fixed-bed, fluid-bed, or slurry-bed reactor (Figure 10.8, Schulz 2007). “Liquid-phase” synthesis, in which gas is bubbled through heavy oil in which catalyst particles are suspended, was an important development step to increase conversion to some 80% from that of some 40% of fixed bed reactors (Larson 1999). The slurry reactor is favorable to maximize the yield of high molecular weight products. With high H_2/CO ratios the reactions are comparable in gas-solid and gas-slurry systems. Costs of multi-tubular fixed bed systems are higher than for slurry reactors (van der Laan

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[6] For practical purposes, stoichiometric H_2/CO ratio of syngas from natural gas may be too high.

1999). Rehnlund 2007 mentions that the slurry reactor is less sensitive towards inert gas than the other reactors, and this might be favorable for biomass-based process.

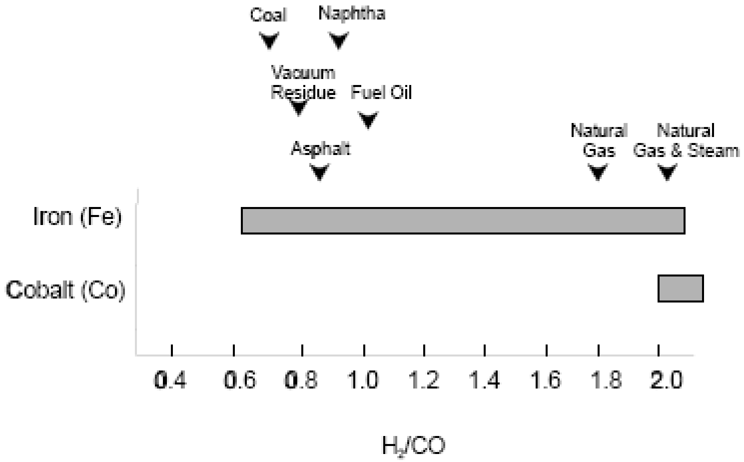


Figure 10.6 - Feedstocks and Catalysts (van der Laan 1999)

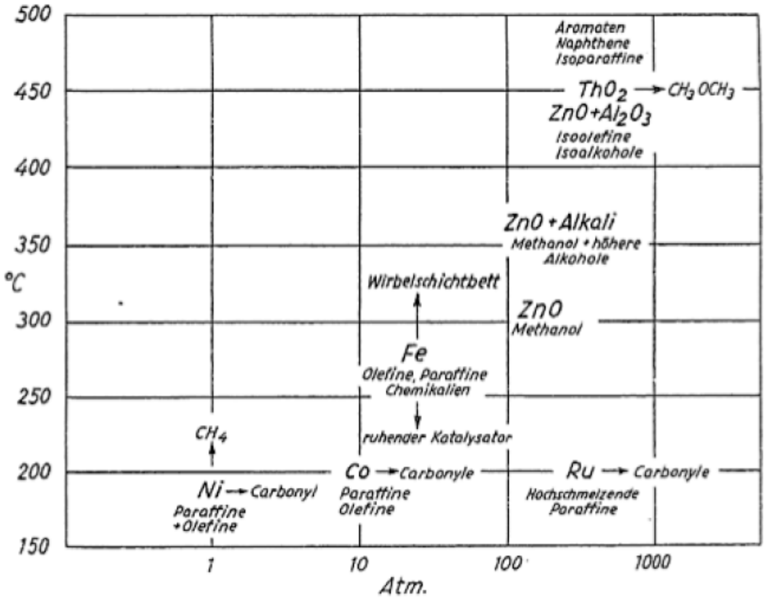


Abb. 1. Optimaler Reaktionsbereich verschiedener Katalysatoren für die Kohlenoxydhydrierung

Figure 10.7 - Catalysts in Relation to Temperature and Pressure (Schulz 2007)

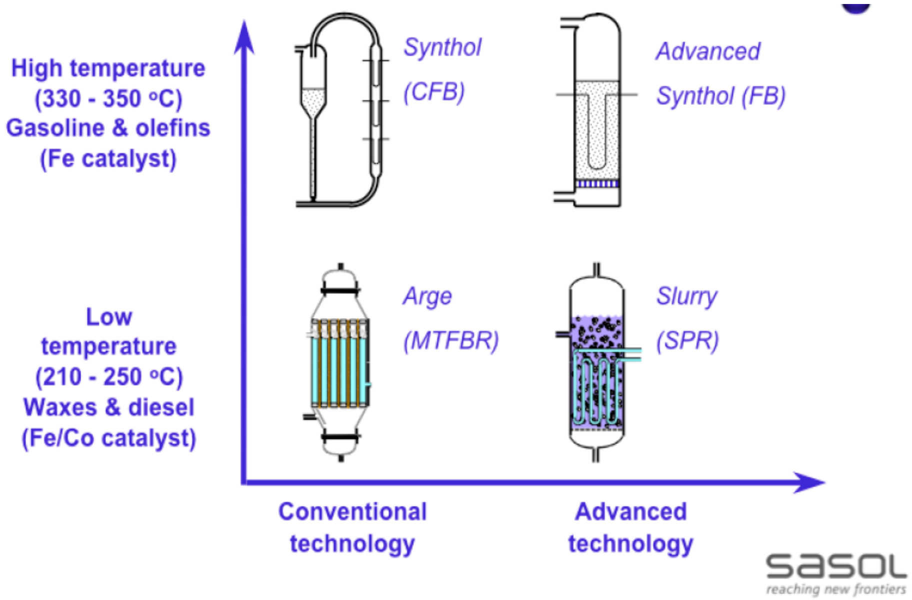


Figure 10.8 - Sasol's Fischer-Tropsch Reactor Portfolio (Schulz 2007)
CFB=Circulating fluidized bed, FB=fluidized bed, MTFBR=Multitubular fixed-bed
SPR=Slurry phase reactor

10.1.3 FT Products and Upgrading

The quality and properties of FT crude varies depending on feedstock, process, and parameters selected. FT crude consists of n-paraffins, α-olefins, and n-alcohols in various ratios. Boiling range of FT crude is from about -42°C to about 570°C. The distillate fractions include gases, gasoline, kerosene, diesel, and wax. (Marano 2007)

Conventional oil refinery processes can be used to upgrade FT liquids, but tailored processes can maximize benefits. Examples of some processes that are used for FT crude refining are hydrocracking, hydrotreating, catalytic reforming, alkylation, oligomerisation, and isomerization (Maranao 2007, Laan 1999).

- FT light-end: C4-C6 paraffins - alkylation; C6 olefins - catalytic polymerization
- FT naphtha/distillates: Isomerization, catalytic reforming, olefin metathesis
- FT wax: hydrocracking, catalytic cracking, olefin metathesis

The FT processes and upgrading can be optimized to produce a maximum amount of gasoline or diesel (Table 9.3, Figure 10.9). FT gasoline has low octane number, but contains no sulfur, benzene, or aromatics. Octane number can be increased by alkylation and isomerization. Higher-octane fossil blending components can also compensate for the low octane number of FT gasoline. Catalytic reforming is not the best option for middle distillates as it produces aromatics, volume losses are high, and n-paraffins are, in the first place, poor feedstock for reforming. (Marano 2007).

Table 10.3 - Adjusting Gasoline/Distillate-ratio (Marano 2007)

Increase Gasoline/Distillate ratio	Decrease Gasoline/Distillate ratio
• Minimize wax – raise FT reactor temperature • Alkylation of Catalytic polymerization to gasoline • Wax catalytic cracking • Wax/Distillate hydrocracking (gasoline mode)	• Maximize wax – lower FT reactor temperature • Catalytic polymerization to kerosene or diesel • Wax hydrocracking • Olefin metathesis

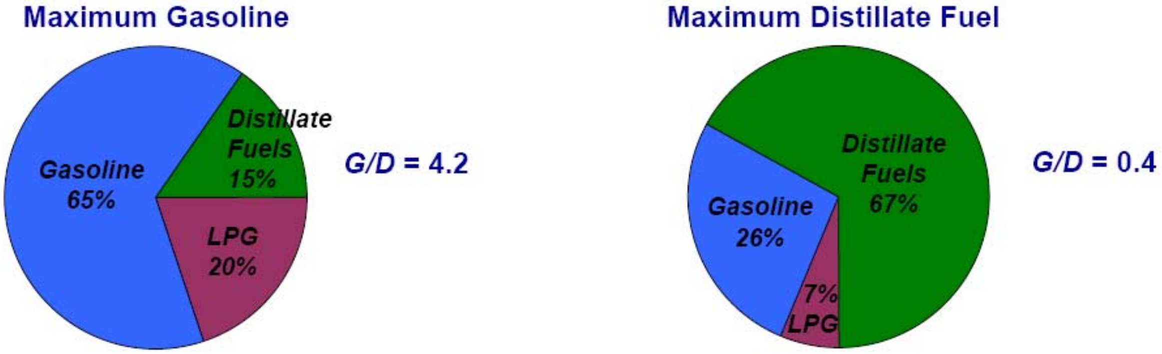


Figure 10.9 - Estimated Product Distributions from Upgrading & Refining FT Crude (Marano 2007)

Location and scale of the FT plant limit the upgrading options. The volumes have to be substantial to make complex on-site upgrading investments economically reasonable. In the near future, the diesel fraction is expected to be of major interest. In long-term, FT naphtha could be upgraded to gasoline and jet fuel. (Marano 2007).

Syntroleum has developed the "Synfining" process to upgrade Fischer-Tropsch waxes to produce renewable FT fuels targeting the diesel, jet, and military fuel markets (Figure 10.10). This can be combined with the "Biofining" process to upgrade vegetables oils and fats to renewable diesel and jet fuel. The costs using this technology are lower than with a traditional biomass-to-liquids pathway. Dynamic Fuels LLC is a joint venture of Tyson Foods and Syntroleum Corporation to utilize this technology. (Green Car Congress 2007)

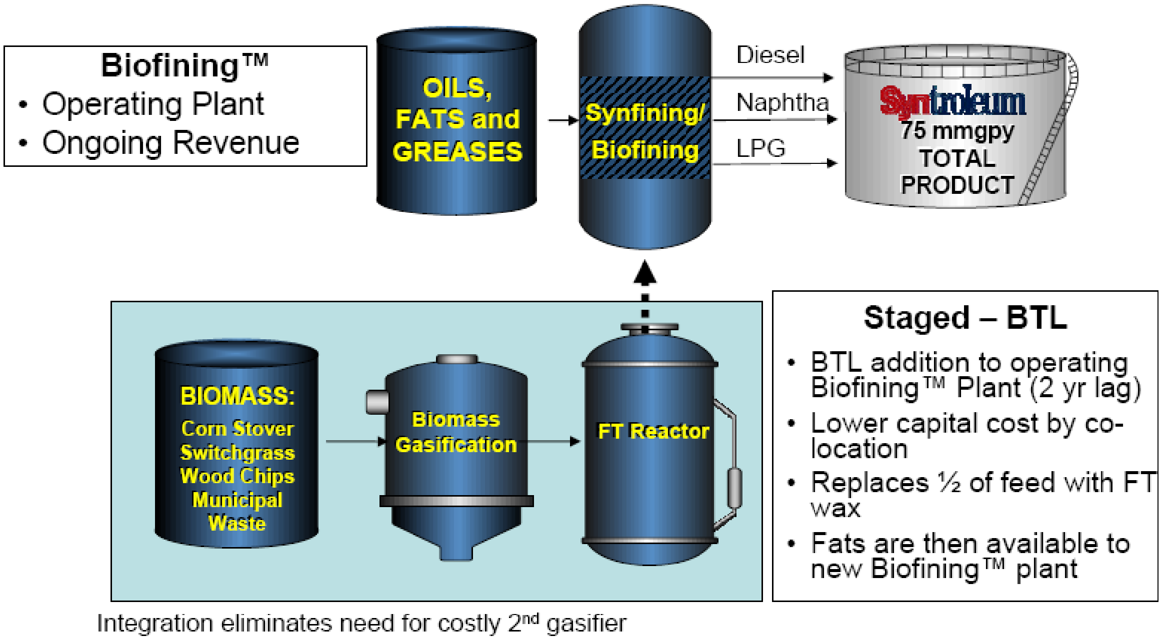


Figure 10.10 - Synfining/Biofining Upgrading Processes by Syntroleum (Syntroleum 2007)

10.2 Pyrolysis Path

Considerable efforts have been directed toward the development of processes for producing liquid fuels from biomass. One of the most viable methods for such conversion is fast pyrolysis. (Scott et al. 1985)

Fast pyrolysis is a thermal decomposition process in which material is thermally (about 500 °C) cracked using a short vapor residence time (typically below 2 seconds) in the inert reaction zone. A typical product distribution for bark-free wood is, on average, 64 wt % organics, 12 wt % pyrolysis water, 12 wt % char, and 12 wt % product gas. The yields and properties of the pyrolysis liquid (pyrolysis oil, bio-oil) depend on the feedstock, process type and conditions, and the product collection train. The reactor systems used include fluid beds, transport reactors, and cyclonic reactors. (Boukis 1997, Bridgwater et al. 1999)

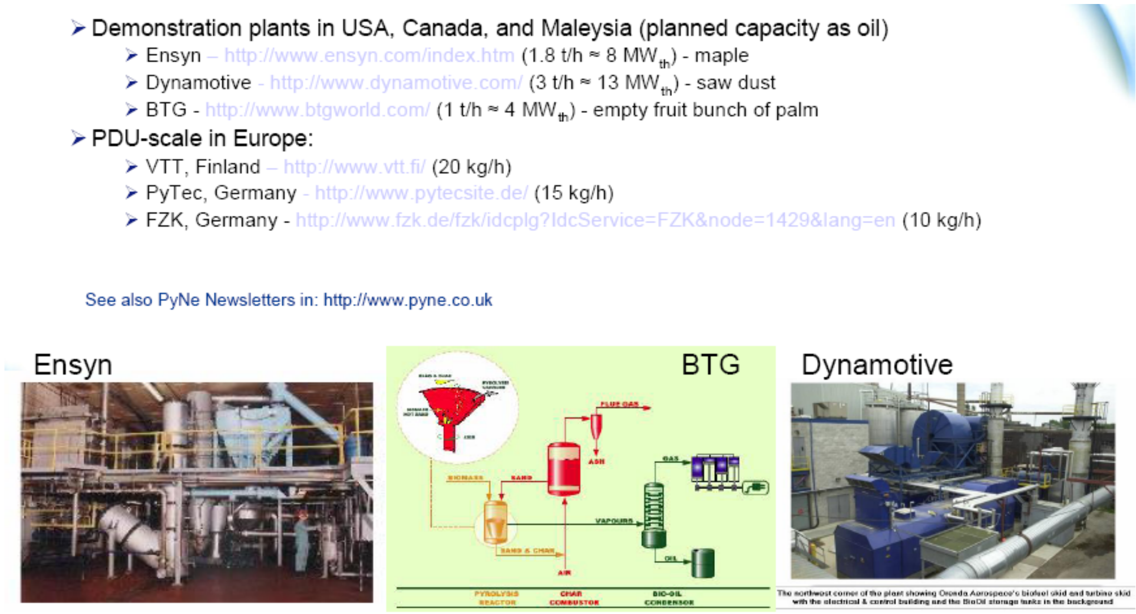
Biomass pyrolysis liquids are totally different than petroleum-based fuels (Table 10.1). Pyrolysis liquids are high in water, density and viscosity and low in heating value. They are acidic, thermally unstable, and immiscible with mineral oils. The unusual properties of pyrolysis liquids must be taken into account in applications. In order to promote the acceptance of a new fuel into markets, fuel characterisation methodology should be very similar to that of the conventional fuels. Standard fuel oil analyses originally developed for mineral oils have been modified for pyrolysis liquids when needed and some new methods have been developed. ASTM standard for fuel oil specifications of pyrolysis liquid are under work in Canada and USA (Elliott 1983, Piskorz et al. 1988, Diebold 2002, Oasmaa 2003).

Table 10.4 - Selected properties of pyrolysis liquids (Oasmaa et al. 2005)

analysis	Dynamotive	Dynamotive	Dynamotive	Forestera	Ensyn	
feedstock	pine/spruce (100% wood)[a]	pine/spruce (53% wood, 47% bark)[a]	bagasse[a]	spruce (100% wood)[b]	oak/maple[b]	LFO No. 2
moisture (wt %)	2.4	3.5	2.1	6−9		
particle size (mm)	<1.2	<1.2	<1.2	3−5		
ash (wt %)	0.42	2.6	2.9			
pyrolysis liquids						
water (wt %)	23.3	23.4	20.8	23.8	22	max. 0.05
solids (wt %)	<0.1	<0.1	<0.1	0.05	0.045	0
ash (wt %)	<0.02	<0.02	<0.02	<0.02	0.01	0
nitrogen (wt %)	<0.1[21]	0.3−0.4[21]	0.7[22]	0.04	0.2	
sulfur (wt %)	<0.01[17]	<0.05[17]	<0.1[22]	<0.01[17]	<0.01	0.5
viscosity (cSt)						
@ 20 °C	73	78	57		650	
@ 40 °C				15	50 at 50 °C	3.4
@ 80 °C	4.3	4.4	4		12	
density @ 15 °C (kg/dm^3)	1.20	1.19	1.20	1.19	1.18	0.876
flash point (°C)				38	55	min. 38
pour point (°C)					−25	min. −6
higher heating value, HHV (MJ/kg)	16.6	16.4	15.4	17.6	17	
lower heating value, LHV (MJ/kg)				16.0	15.7	40
pH	2.3	2.4	2.6	2.4	2.5	
distillability	not distillable	not distillable	not distillable	not distillable	not distillable	distillable
water insolubles (wt %)	25	25	24	21	50	100

In a recent study fast pyrolysis was evaluated to a promising alternative in replacing fossil fuels in European Pulp & Paper Industry. The European P & P industry has a potential to build up to 50 pyrolyzers integrated to fluidised bed boilers. In the short-term, pyrolysis oil market is in fuel oil and natural gas replacement in lime kilns and boilers, while long-term RTD is focused on transportation fuels. The major challenge is to develop and demonstrate technical and economical feasibility of the concept and availability of woody biomass at competitive price. (Sipilä et al. 2007)

The fuel oil production is under demonstration. Several demonstration and pilot plants on fuel oil production are running in Canada, USA, Europe, and Maleysia (Figure 10.11). Dynamotive has announced to build the first fully commercial industrial biofuel plant in the U.S. (Dynamotive 2007, Oasmaa et al. 2007)



- Demonstration plants in USA, Canada, and Maleysia (planned capacity as oil)
  - Ensyn – http://www.ensyn.com/index.htm (1.8 t/h ≈ 8 MW_{th}) - maple
  - Dynamotive - http://www.dynamotive.com/ (3 t/h ≈ 13 MW_{th}) - saw dust
  - BTG - http://www.btgworld.com/ (1 t/h ≈ 4 MW_{th}) - empty fruit bunch of palm
- PDU-scale in Europe:
  - VTT, Finland – http://www.vtt.fi/ (20 kg/h)
  - PyTec, Germany - http://www.pytecsite.de/ (15 kg/h)
  - FZK, Germany - http://www.fzk.de/fzk/idcplg?IdcService=FZK&node=1429&lang=en (10 kg/h)

See also PyNe Newsletters in: http://www.pyne.co.uk

The northwest corner of the plant showing Orenda Aerospace's biofuel skid and turbine skid with the electrical & control building and the BioOil storage tanks in the background

Figure 10.11 - Pyrolysis liquid production -Plants in operation 2007. (Oasmaa et al. 2007)

10.1.2 Pyrolysis Paths to Biodiesel

Presently three pyrolysis paths are under study for biodiesel production (Figure 10.12):

- Direct conversion of biomass by catalytic hydrocracking into liquid transport fuel
- Production of pyrolysis liquid and the deoxygenation of the liquid or its fractions into oil refinery feed and i.e. into biodiesel
- Use of pyrolysis liquid as a pre-treatment step in biomass syngas production and biodiesel conversion

The U.S. Department of Energy (DOE) announced in April 2008 the issuance of a funding Opportunity Announcement (FOA) for up to $7 million in federal funding over two years (FY 2008 – 2009) in advanced research and development in converting non-food based biomass to advance clean and affordable biofuels. Combined with private minimum cost share of 20 percent, up to $8.75 million would be invested in this research effort. (http://www.energy.gov/) ConocoPhillips is one of the companies investing in biorenewable fuels. An eight-year, $22.5 million research program including fast pyrolysis, is under way at Iowa State University in the U.S.

The direct hydroprocessing of biomass into biodiesel has been studied intensively over two decades. Elliott (PNNL, USA), Piskorz (RTI, Canada), Gagnon (Universite Laval, Canada), Maggi and Churin (Universite Catholique de Louvain, Belgium), Gevert (Chalmers, Sweden), and Meier (vTI, Germany) among others have done extensive research on catalytic hydrotreating of pyrolysis liquids. (Elliott 2007)

UOP (USA) is exploring the possibility to use pyrolysis oil or its fractions as a feedstock for refinery based hydroprocessing (Marker et al. 2005) to fuels. UOP, NREL, PNNL, Dynamotive and Ensyn Group have a pyrolysis oil upgrading project (2004-2009), which aims at refining bio-oils in petroleum refineries. (http://www.energy.gov/)

In Europe, the EU-BIOCOUP (2006-2011) project aims at upgrading pyrolysis liquid or its fractions for refinery based hydroprocessing to fuels and chemicals (Figure 10.13).

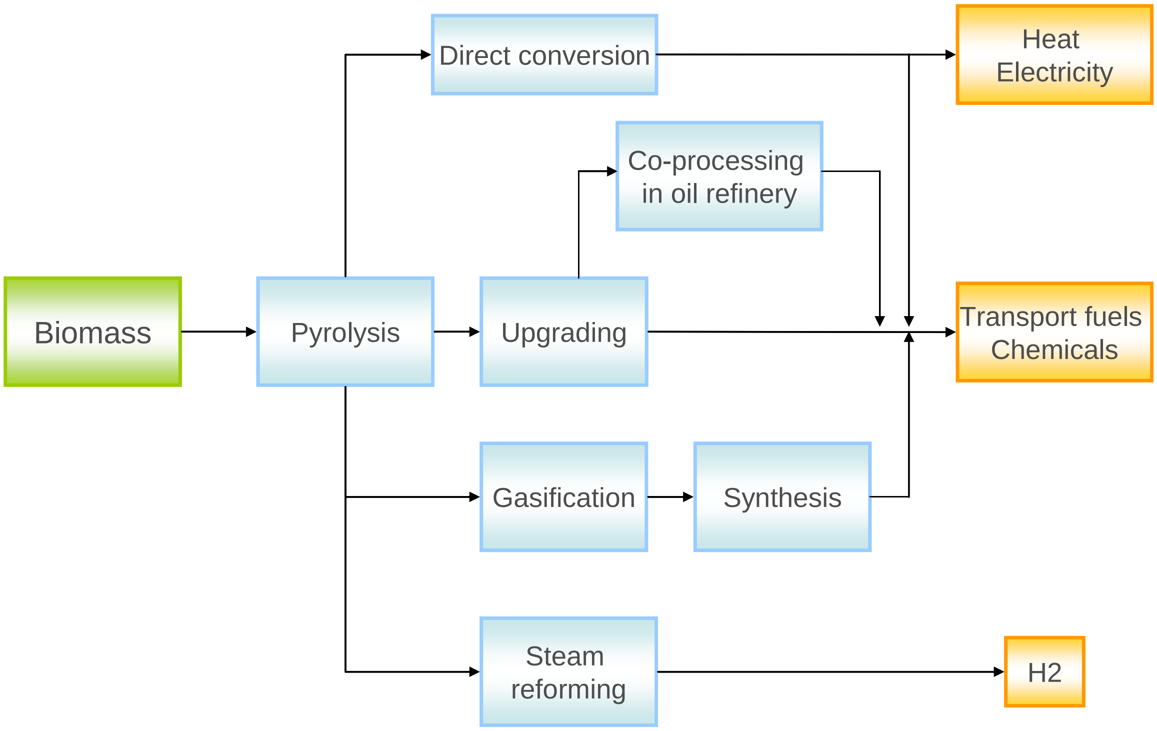


Figure 10.12 - Schematic illustration of utilization pathways using pyrolysis (compiled according to Bridgwater 2007b, Marker et al. 2005 and Solantausta 2006).

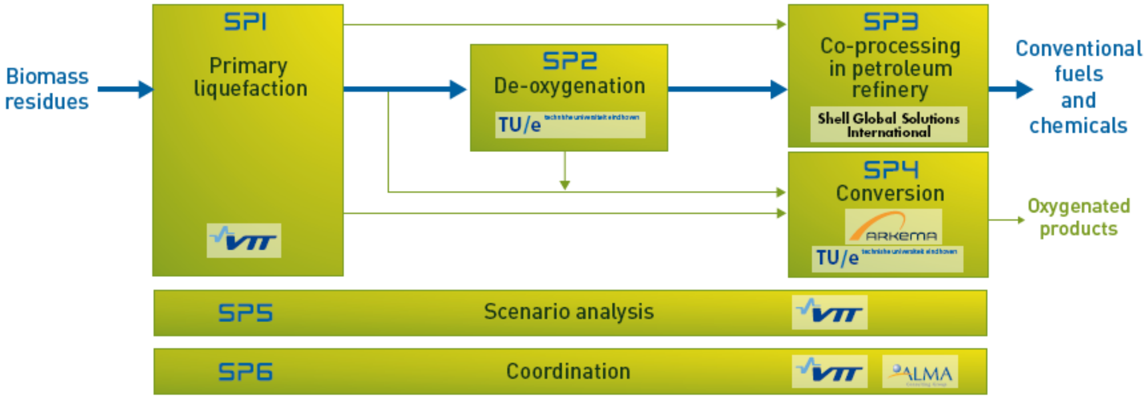


Figure 10.13 - Pyrolysis as a feed to oil refinery (EU-BIOCOUP)

Pyrolysis can also be used as a pre-treatment step in biodiesel production (Figure 10.14). There are advantages when comparing the use of pyrolysis liquid to use of solid fuel. One clear benefit is logistic. Small-scale fast pyrolysis plants may be located adjacent, like in forest areas or integrated with a pulp mill. Energy density of pyrolysis liquid is higher than that of solid biomass and when properly designed the transportation and storage of pyrolysis liquid is easier than that of solid fuel. In combustion, the emissions from pyrolysis liquid are much lower than those from use of solid biomass, especially the particulates. (Oasmaa et al. 2005) Another advantage of liquid feed compared to solid one is its easier feeding.

FZK (Germany) and Lurgi (Germany) are developing the Bioliq-process (Figure 10.14) where pyrolysis liquid is produced from straw in small decentralized plants, transported into a refinery where it is used as feedstock in synthesis gas production followed by conversion into biodiesel.

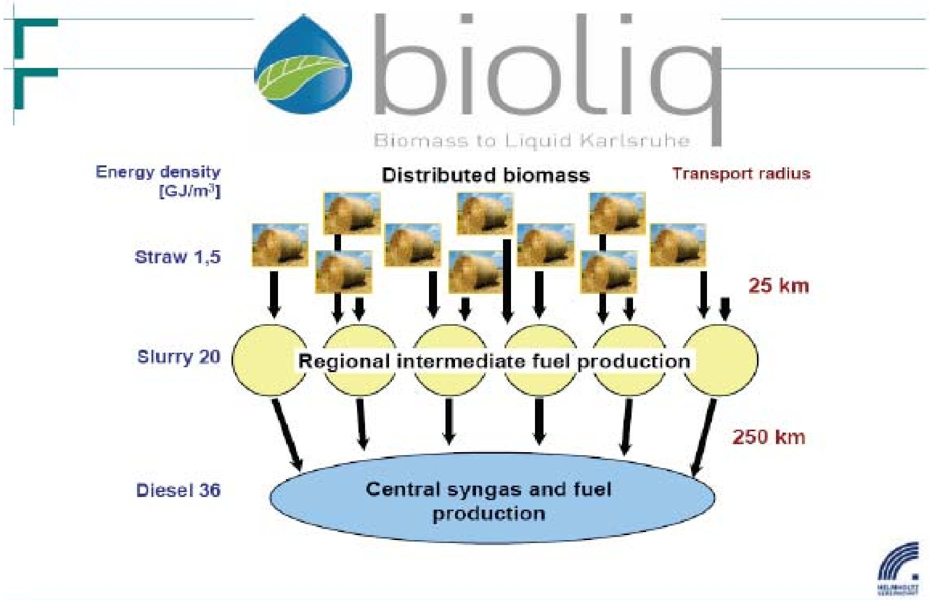


Figure 10.14 - FZK Bioliq Concept (Dinjus 2006)

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10.3 Hydrotreatment of oils and fats

Hydrotreatment of oils and fats is one route to utilize biobased material (Figure 10.11). It is an alternative option to utilize vegetable oils as biodiesel feedstock instead of esterification of those oils to FAME. Hydrotreatment can produce high-quality biobased diesel resembling F-T diesel from a variety of feedstocks. Several types of vegetable oils can be used, even non-food crops, as well as animal fats. In future, even algae and bacteria could be used.

Hydrogenation is standard technology in oil refineries for fuel upgrading and sulfur removal. The hydrotreatment of triglycerides, such as vegetable oils and animal fats, produces non-oxygenated hydrocarbon biodiesel with similar chemistry and properties as present synthetic GTL and future BTL fuels (Figures 10.15 - 10.17). This process is typically integrated in a refinery, and thus benefits from the refinery's infrastructure including energy, blending facilities, logistics and laboratories (Rantanen et al. 2005). In the future, large-scale stand-alone plants could be a reality in addition to refinery integrated units.

Neste Oil in Finland has developed a process, NExBTL, combining hydrotreatment and isomeration to produce renewable diesel fuel from vegetable oils and animal fats (Figure 10.18). (Mikkonen 2007). Hydrotreatment is applied also in Brazil by Petrobras using the H-Bio process, which treats mixtures of vegetable oil and petroleum (co-hydrogenation) producing a blend of fossil and hydrogenated diesel. (AMFI Newsletter 3/2006). There are a number of other activities on hydrotreated biodiesel. Status of these processes and plants are dealt with in Chapter 11.

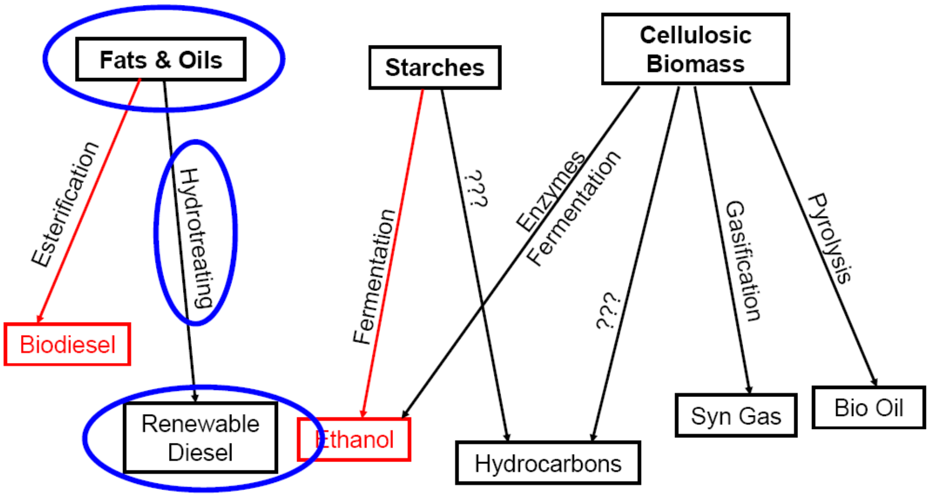


Figure 10.15 - Different Paths to Utilize Biobased Material (Kaufmann 2007)

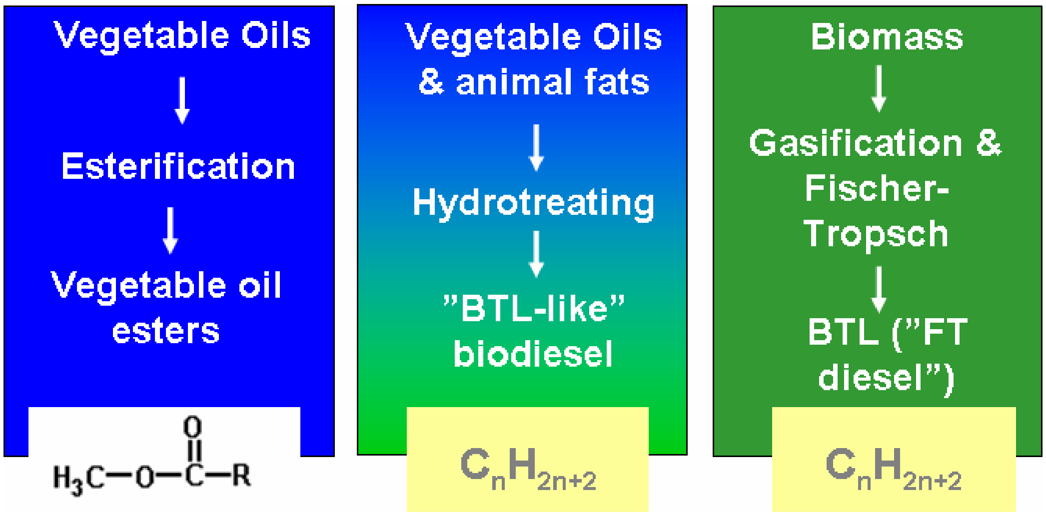


Figure 10.16 - Similar Feedstock as For Esterification Can Be Used to Obtain Similar Product as From Gasification/FT process (Rantanen 2005)

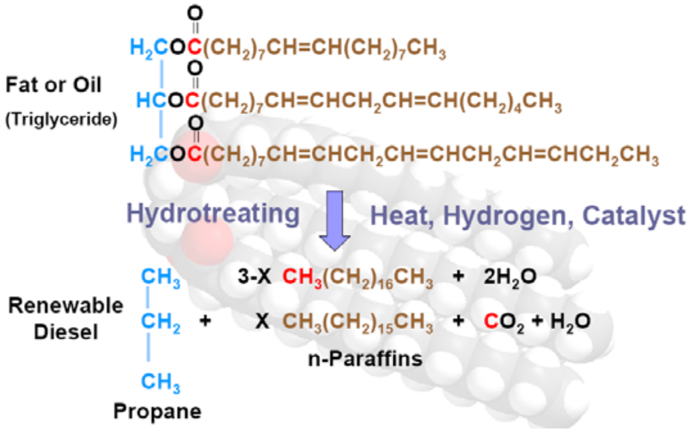
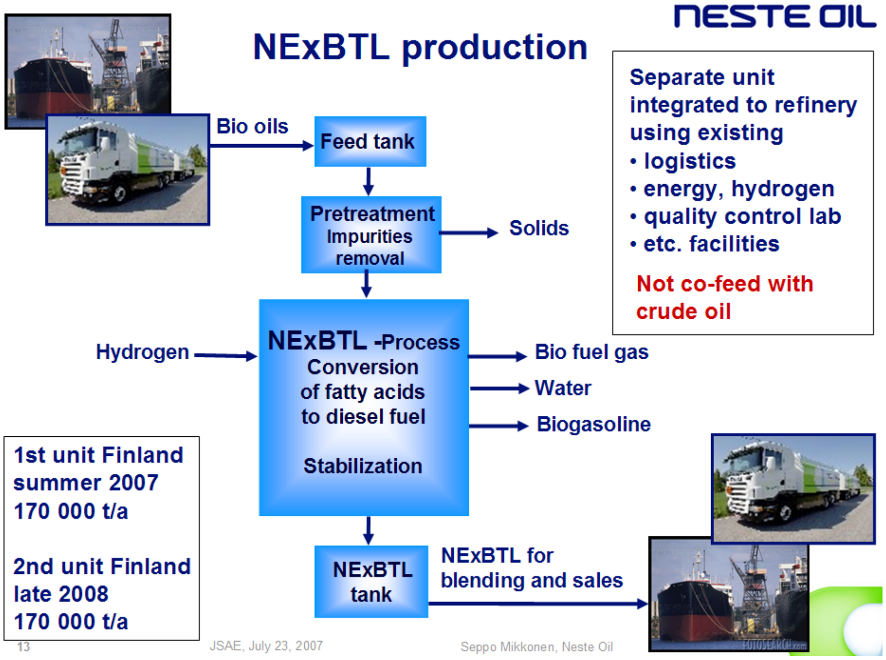


Figure 10.17 - Hydrotreatment of Triglycerides Produce Paraffins, Propane, Carbon Dioxide and Water (Kaufmann 2006)



NESTE OIL

NExBTL production

Separate unit integrated to refinery using existing
- logistics
- energy, hydrogen
- quality control lab
- etc. facilities

Not co-feed with crude oil

Bio oils → Feed tank → Pretreatment Impurities removal → Solids

Hydrogen → NExBTL -Process Conversion of fatty acids to diesel fuel Stabilization → Bio fuel gas, Water, Biogasoline

NExBTL tank → NExBTL for blending and sales

1st unit Finland
summer 2007
170 000 t/a

2nd unit Finland
late 2008
170 000 t/a

13 JSAE, July 23, 2007 Seppo Mikkonen, Neste Oil

Figure 10.18 - Neste Oil's NExBTL Process (Mikkonen 2007)

10.4 Properties of Finished BTL-type Biodiesel

10.4.1 Fuel properties

BTL and hydrotreated biobased diesel (HO) are hydrocarbon fuels in the same way as conventional diesel fuel. However, conventional diesel fuel contains a mix of different kinds of hydrocarbons, aromatic compounds, napthenic compounds as well as paraffins, whereas BTL and hydrotreated biodiesel are paraffinic fuels. Paraffinic diesel has very high cetane number, excellent ignition properties, no sulfur, nitrogen nor aromatics. BTL and HO contain no oxygen. Storage stability of this fuel is good and water solubility is low. From a safety point of view paraffinic fuel is equivalent to conventional diesel fuel. Table 10.5 lists properties of paraffinic NExBTL fuel obtained by hydrotreatment of oils and fats in comparison with other fuels. The table contains data for syngas based GTL, and the data for GTL also is representative for BTL.

BTL and HO are fully miscible with conventional diesel fuel. The current European EN590 specification for diesel fuel can be met with blends containing up to 30% BTL or hydrotreated biofuel, whereas maximum concentration for FAME is 5% (10% in the near future). BTL or hydrotreated biofuel could be used as a high-concentration blending component, or even as such in existing vehicles. Practically no investments are required in the fuel distribution infrastructure or existing vehicle fleet.

Table 10.5 - A Comparison of Diesel Fuel Properties. (Rantanen et al. 2005)

FUEL PROPERTIES *)	NExBTL	GTL diesel	FAME (RME)	Diesel EN590/2005
Density @15°C, kg/m^3	775...785	770....785	≈ 885	≈ 835
Viscosity @40°C, mm^2/s	2.9...3.5	3.2...4.5	≈ 4.5	≈ 3.5
Cetane number	84...99 **)	73...81	≈ 51	≈ 53
Distillation, 10 vol%, °C	260...270	≈ 260	≈ 340	≈ 200
Distillation, 90 vol%, °C	295...300	325...330	≈ 355	≈ 350
Cloud point, °C	- 5...- 30	0...- 25	≈ - 5	≈ - 5
Lower heating value, MJ/kg	≈ 44	≈ 44	≈ 38	≈ 43
Lower heating value, MJ/liter	≈ 34	≈ 34	≈ 34	≈ 36
Polyaromatics, wt%	0	0	0	≈ 4
Oxygen, wt%	0	0	≈ 11	0
Sulfur, mg/kg	≈ 0	< 10	< 10	< 10

10.4.2 Exhaust Emissions and Engine Performance

Excellent fuel properties of BTL and HO fuels, almost no sulfur, high cetane number, and low aromatic content, result in significant emission reductions and good engine performance when compared with conventional diesels. This is illustrated in a simplified manner in Figure 10.19, which shows a comparison of conventional and paraffinic diesel burning in an open beaker.

Figure 10.19 - Burning of Conventional Diesel (left) and Paraffinic Diesel (right) Source: ASFE (Alliance for Synthetic Fuels in Europe)

Paraffinic diesel typically reduces NO_x and PM emissions when compared to conventional diesel fuel. Both of these components are important with regard to urban air quality. In an engine were specifically tuned for paraffinic fuel, this could either be done for reduced emissions or for improved fuel efficiency at a given emission level. Conventional FAME biodiesel has been demonstrated to effectively reduce particulate emissions, but this comes at the expense of increased NO_x emissions.

BTL and HO resemble GTL and thus emission results with GTL can be used to demonstrate the emission effects with these new types of biofuels. Figure 10.20 shows that GTL blends reduce emissions of a light-duty diesel vehicle even at a concentration of only 20%.

A study in Germany compares ordinary diesel fuel (DK), GTL, and rapeseed methyl ester (RME) and blends. The fuels were tested in a 205 kW Euro 3 certified Mercedes-Benz bus engine (Figure 10.21). With RME NO_x emissions are increased, but particle emissions reduced. The blended fuel containing ordinary diesel, GTL, and RME (PDK) performed well for particles and the GTL fuel with 5% RME well for NO_x.

In Sweden, emission tests made on GTL on a Euro 2 engine with a retrofitted $DeNO_x$ system showed 8% less NO_x, 30% less PM, and up to 90% less toxic emissions than Swedish Environmental Class 1 fuel, which has been the world's cleanest diesel fuel to date. (Framtidsbränslen, http://www.framtidsbranslen.se/)

The Alliance for Synthetic Fuels in Europe (ASFE) has summarized the influence of synthetic FT diesel on exhaust emissions (Figure 10.22). The emission reductions with engines optimized for FT diesel are substantial. NO_x and PM emissions can be close to half of emissions with conventional diesel fuel.

Emission data for hydrotreated biofuel, Neste Oil's NExBTL, is also available. Emission studies with NExBTL fuel show significant emission reductions. Two studies with heavy-duty engines showed significant reductions in NO_x and PM emissions with neat NExBTL when compared with conventional diesel fuel. NO_x emissions decreased 10-20% and PM emissions 20-30% with pure NExBTL.

NExBTL has also been tested in passenger cars. Rantanen et al. (2005) compared emissions from NExBTL blends with emissions from Swedish Environmental Class 1 and sulfur free EN590 diesel. NExBTL also reduces gaseous toxic emissions such as aldehydes, 1,3-butadiene, benzene, and in addition, particulate phase PAHs and mutagenicity. (Rantanen 2005)

Fuel consumption is one of the interesting aspects when fuel options are discussed. BTL and HO diesel have higher hydrogen-to-carbon ratio, and higher mass-based heat content than conventional diesel. Thus the mass based fuel consumption is lower for BTL and HO diesel than for conventional diesel. However, volumetric fuel consumption is higher for BTL and HO diesel than for conventional diesel due to the low density of BTL-type fuels. In addition, maximum power output is somewhat reduced due to low density.

Tailpipe CO_2 emissions are slightly lower with paraffinic fuels than with conventional fuels thanks to higher hydrogen-to-carbon ratio. However, the major benefit in greenhouse gases originates from bio-feedstock.

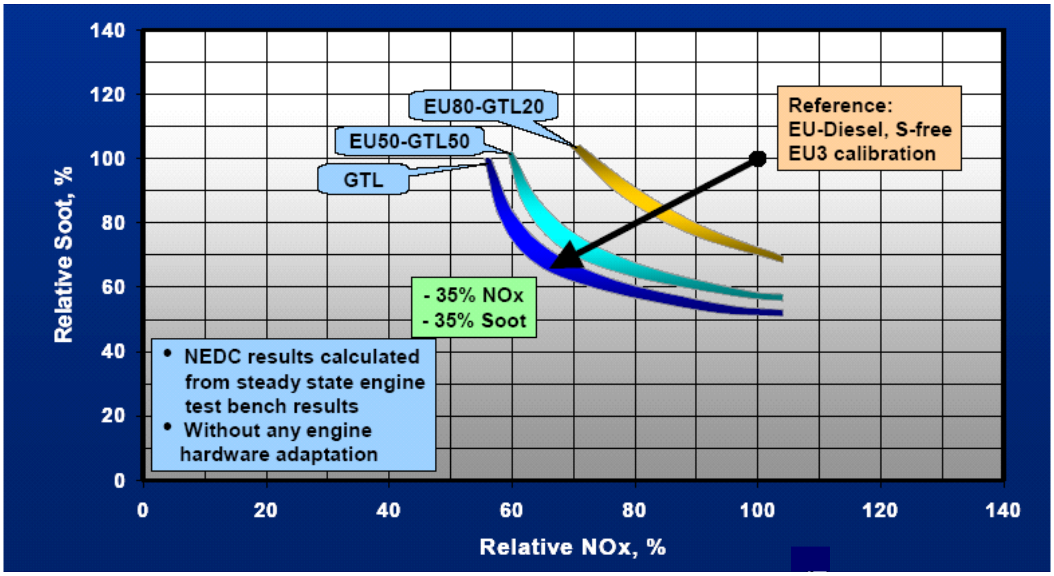


Figure 10.20 - The Effect of GTL Diesel on Passenger Car NO_x and PM Emissions (Maly 2004)

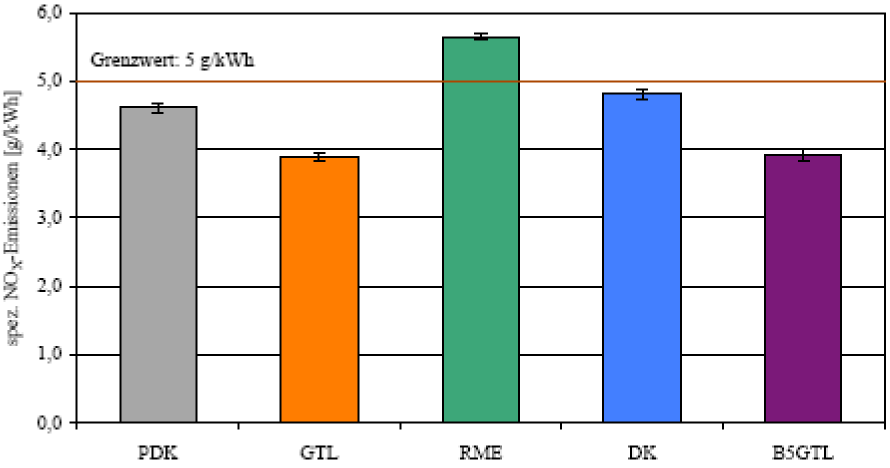


Figure 10.21 - NO_x Emissions With Various fuels. (Munack et al. 2005) PDK= diesel+ GTL+ RME; DK= diesel fuel, GTL=Gas-to-Liquids, RME=rapeseed methyl ester (RME), B5GTL=blend

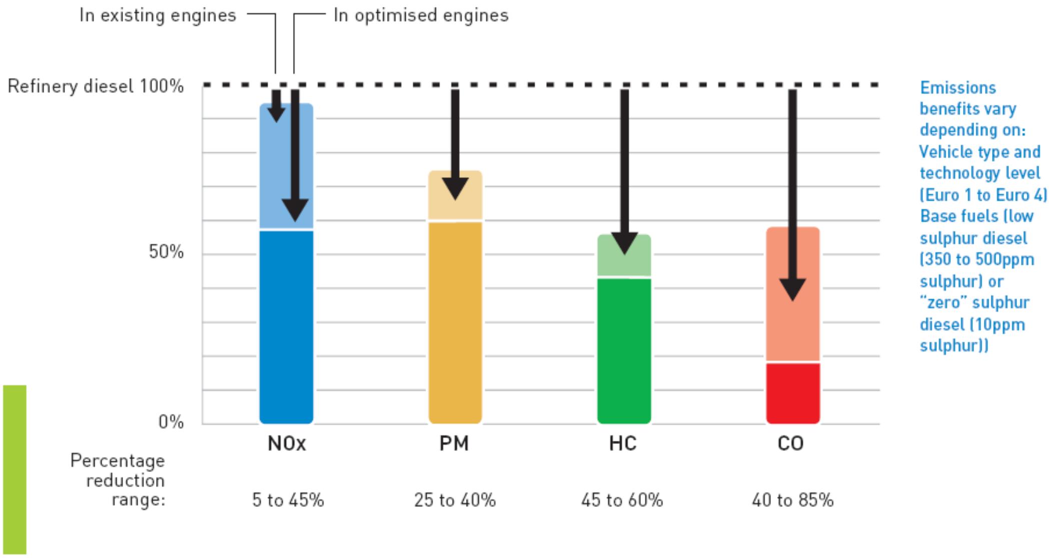


Figure 10.22 - A Summary of Emission Reduction Potential with FT Diesel in Conventional and Optimized Engines. (ASFE)

10.4.3 Life-Cycle Emissions

Evaluation life-cycle analysis is challenging even for existing traditional fuels, and it is even more difficult for future options. There are many steps that need to be taken into account in the evaluations from well (or fields) to wheels (Figure 10.23) (Vliet et al. 2007). In addition, alternative options for land/biomass utilization should be considered.

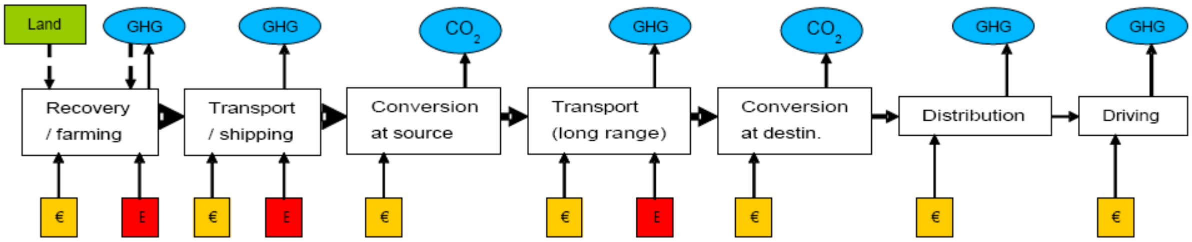


Figure 10.23 - WTW Model Used in the Evaluation of Vliet et al (2007)

Figure 10.24 shows evaluation by EUCAR, CONCAWE and JRC of costs to avoid CO_2 emissions with replacement of fossil fuels with biofuels (Edwards 2007). Far the best cost/benefit ratio is obtained for liquid fuels produced from wood in the case where production is integrated in the paper mills. However, global potential of integrated production of fuels in the paper mills is low, even though this can be significant option for some regions.

Liquid fuels from wood in stand-alone plants can be in some cases as good option as production of ethanol from straw, compressed biogas or conventional biofuels, but generally costs for this option are high.

There are a number of other studies on lifecycle emissions from different transport fuels. ICCT compiled lifecycle emission factors from major lifecycle models and studies from U.S. GREET, European WTWs, Canadia GHGenius and Brazil Macedo. This analysis included US corn ethanol, European rapeseed biodiesel, and sugarbeet ethanol, Canadian wheat ethanol, and Brazilian sugarcane ethanol with or without transport emissions. Figure 10.25 shows, despite of variation, substantial benefits in lifecycle greenhouse gas emission for biofuels when compared to gasoline and diesel. (Kodjak 2007).

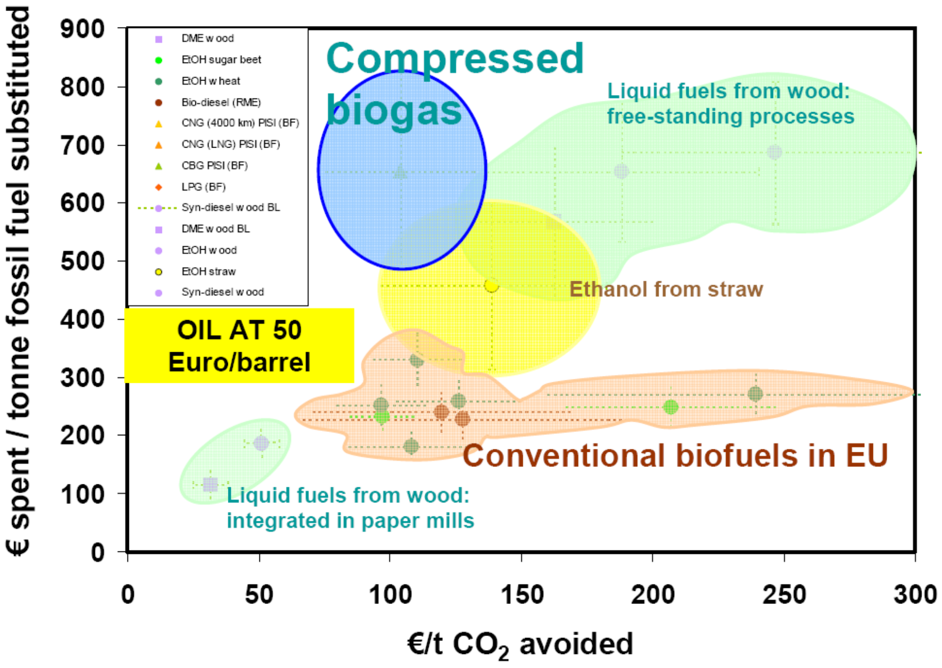
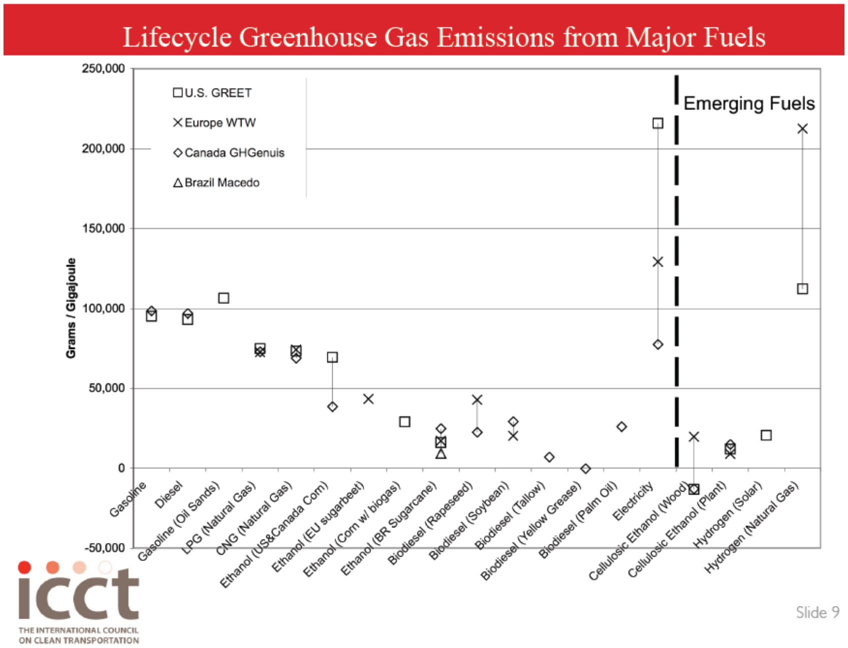


Figure 10.24 - Costs of Replacing Fossil Fuels With Biofuels Versus CO2 Emissions Avoided (Edwards 2007)


Lifecycle Greenhouse Gas Emissions from Major Fuels

Slide 9

Figure 10.25 - Life-cycle Greenhouse Gas Emissions from Major Fuels. (ICCT)

Neste Oil has announced that WTW greenhouse gas emissions of NExBTL, hydrotreated biobased diesel fuel, are 0.7 – 2.4 kg CO_2eqv per kg fuel depending on feedstock, which is much lower emission than 3.8 kg CO_2eqv per kg for fossil diesel (Linnaila 2005). The lowest CO_2 emission is obtained when animal fat is used as a feedstock.

Evaluation of life-cycle greenhouse gas emissions for NExBTL produced from rapeseed oil and palm oil in comparison with fossil diesel and rapeseed based FAME biodiesel is shown in Figure 10.26. This Figure is based on IFEU's calculations for rapeseed and palm oil as feedstocks. For palm oil, the study took into account clearing of forest, loss of carbon sink, harvesting, refining (methane emission included), transportation, hydrotreatment to biodiesel and end-use. Forest fires[7] and degradation of peat were not taken into account.

The assessment of energy and greenhouse gases by IFEU (Reinhardt 2006) showed significant benefits in greenhouse gas emissions and energy balance for replacing fossil fuel with NExBTL produced from rapeseed oil or palm oil. The study pointed out that the results depend on the feedstock, not on the NExBTL process itself. Thus evaluation needs to be carried out for each feedstock separately.

The results for the two feedstocks studied are collected in Table 10.6 (Reinhardt 2006). The results regarding NExBTL from palm oil depend on the alternative options on land usage. The greenhouse gas savings were higher if alternative land use option was a food oil plantation when compared to untouched forest or coconut plantation.

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[7] Greenhouse gases originating from forest fires in Southeast Asia are equivalent to some 10% of the GHG emissions originating from fossil fuels, globally. Natural forests are often converted to plantations using forest fires. Natural forests in tropic do not burn without external help. (Humalisto 2006).

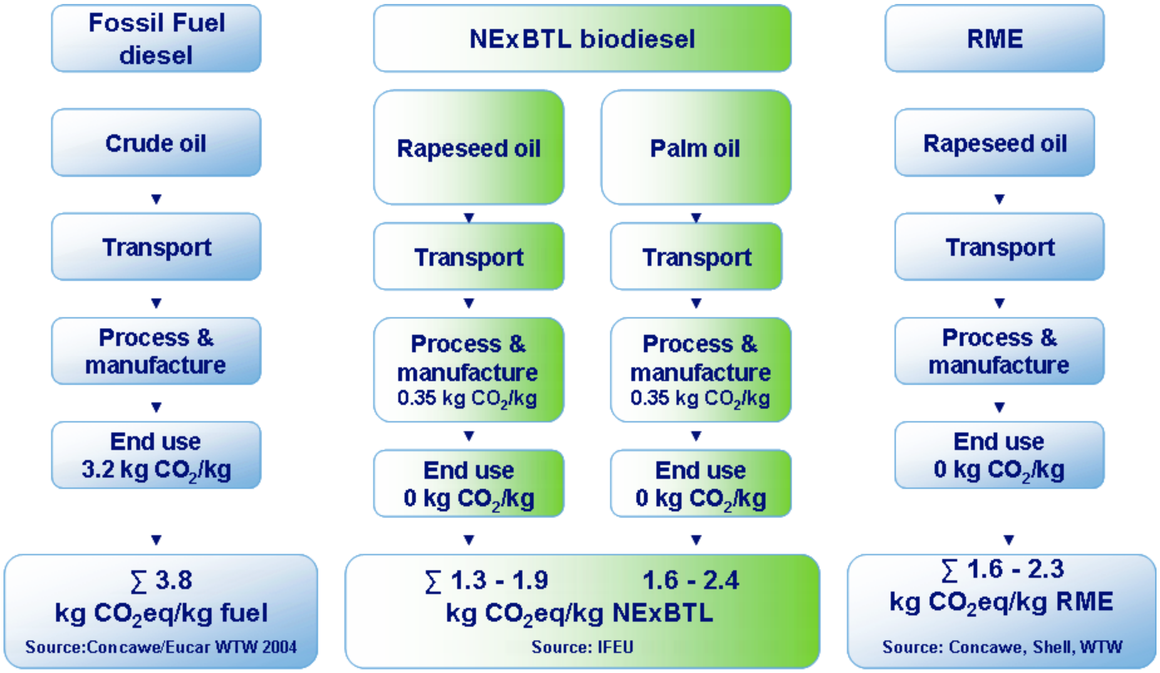

Figure 10.26 - Life-cycle greenhouse gas emissions for NExBTL produced from rapeseed oil and palm oil in comparison with fossil diesel and rapeseed based FAME biodiesel (Juva 2007).

Table 10.6 - Energy and greenhouse gas savings when fossil diesel is replaced by NExBTL (Reinhardt 2006).

	Savings per tons of NExBTL	
Feedstock	**Primary energy (GJ)**	**t CO2eqv**
Rapeseed oil	30-33	1.2 - 2.5
Palm oil, alternative use as untouched natural forest	44	1.4
Palm oil, alternative use as food oil plantation	33	2.2
Palm oil, alternative use as coconut plantation	16	1

A study on life-cycle analysis of different BTL options is reported by Vliet et al. (2007). The critical issues for biomass utilization are transportation, conversion processes, and alternative options such as co-gasification with coal. As concerns transportation of feedstock, Vliet et al. assumed that coal is transported as such, gas is shipped as FT, biomass is shipped as intermediate or as FT. There are huge uncertainties in WTW evaluations of BTL and XTL technologies. The evaluation concluded that for the time being BTL is expensive, but could be a clean option on WTW basis (Figure 10.27). Vliet et al. (2007) evaluated also the effect of Carbon Capture and Storage (CCS) on life-cycle

CO2 emissions (Table 10.7). BTL production combined with CCS proved to be very clean option.

Table 10.7 - Vliet et al (2007) Reported the Following CO2 Emissions (WTW)

	Without CCS gCO2/km	With CCS gCO2/km
Diesel	164	
GTL	179-226	90-102
CTL	343-359	205-207
BTL	43-50	-162

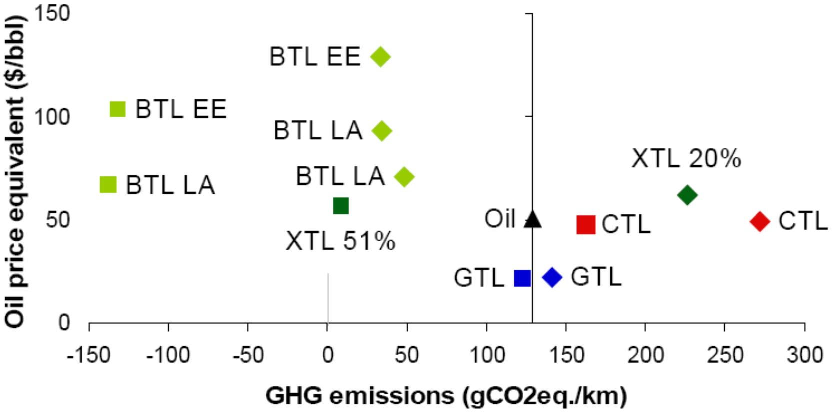

Figure 10.27 - Costs versus GHG emissions (Vliet et al. 2007).

One important aspect in life-cycle analysis concerns alternative options to use biomass. Figure 10.28 shows that the benefit of using wood for electricity is substantially higher than usage of wood to produce road fuels, when efficiency of land use in CO_2 avoidance is the main criteria. In addition, benefit of using wood for electricity is huge when compared to benefit of using conventional biofuels to avoid CO_2 emissions.

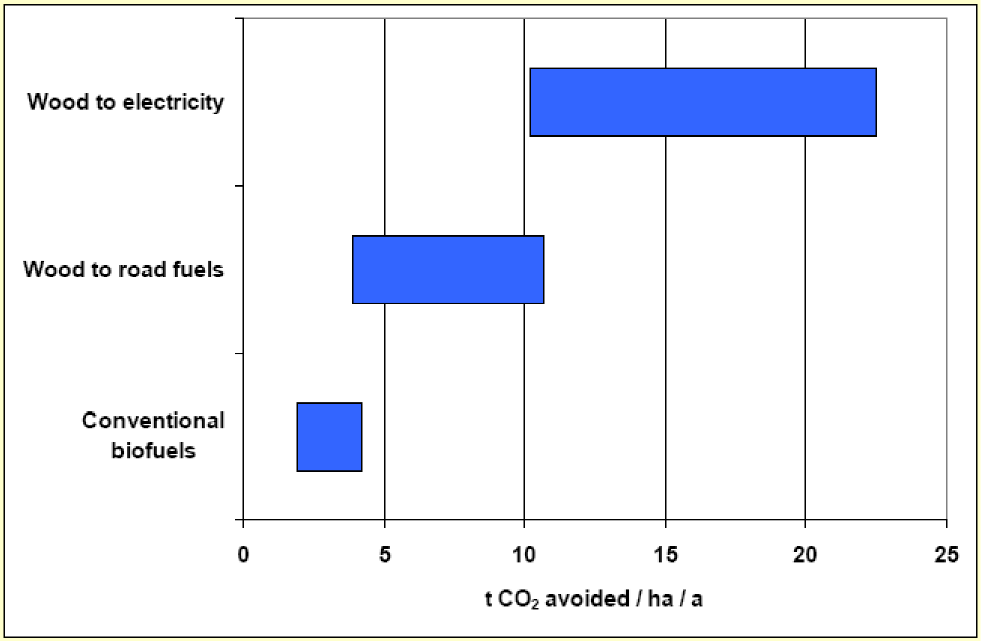

Figure 10.28 - Comparison of CO_2 benefits with different biomass utilization options. Larivé, J-F. (2007)

10.4.4 Sustainability discussion

Sustainability issues will become ever more important when large-scale utilization of biomass will start, even though sustainability discussion is not a new topic. Discussion of sustainability will concern all new biomass options, forests, peat, water, and all plants. In addition, this will concern also new fossil resources such as new fields discovered in untouched arctic areas.

As concerns advanced biofuels for diesel engines, sustainability discussion started in 2007 concerning palm oil, which is the primary feedstock for the first biofuel in large scale production. This discussion is given as an example of the issues considered.

Over the past few years, palm oil has been increasingly used for food industry, but also for energy. In 2007, Greenpeace and environmental organizations brought problems linked to palm oil on the table. The food prices have not played the major role for palm oil. The main problem has been disappearance of tropical rain forests in Asia for oil palm plantations. This leads to loss of diversity, conflicts with the original population, and questionable benefits in greenhouse gas emissions. The problems with palm oil are culminated in Asia, because oil palm and timber industries gain economical benefits when clearing natural rain forests for oil palm plantations due to high wood price. There would be a plenty of fallow land that could be used for oil palm plantations instead of rain forests (Reinhardt 2007). The situation with palm oil plantations e.g. in Africa are not similar.

One questionable issue in sustainability evaluations concerns the depreciation period of 100 years, which is used in calculations. For instance, with depreciation period of 25 years no GHG benefit would be gained for using palm oil as biofuel feedstock (Figure 10.29). In addition, calculations are criticized for not taking into account that clearance of moor woodland and degradation of peat releases huge amounts of CO_2. Carbon storage capacity of natural forest is also higher than that of an oil palm plantation (in Asia ~138 tons of C/ha, oil plantations 30-50 tons C/ha). These issues combined with short life-time of palm oil plantations practically leads to unreasonable carbon balances. (Reinhart et al. 2007).

Ecological issues related to oil palm plantations concern e.g. residues of the oil palm, which are burned to generate energy resulting in substantial emissions. Effluent is practically led into rivers, even though it could go through anaerobic treatment producing methane for power generation. Social problems like poor working conditions on the plantations and competition of energy and food sector are other important topics. (Reinhart et al. 2007).

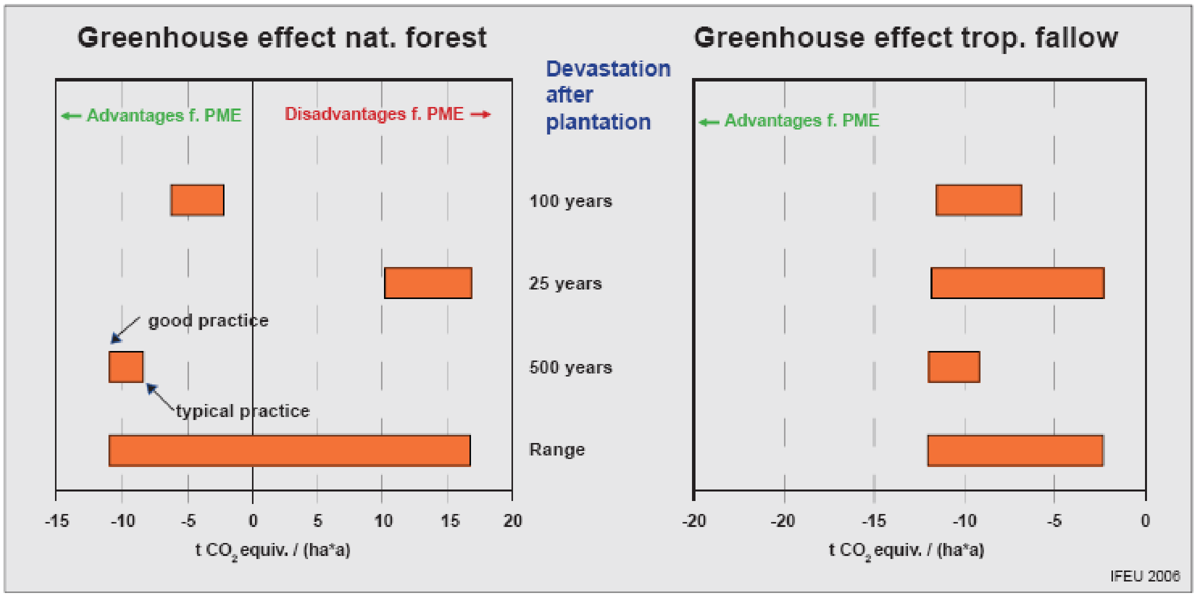

Figure 10.29 - Greenhouse Gas Effect Depends on the Depreciation Period of Plantation. (Reinhardt et al. 2007)

The Roundtable on Sustainable Palm Oil (RSPO), in which the WWF and organizations around the entire supply chain for palm oil are represented, are aiming to define criteria for the sustainable production and use of palm oil, and to promote best practices and solutions. (www.rspo.org). The RSPO guideline set a number of requirements for the new oil palm plantations, such as:

- Environmental impact assessment
- Social impact assessment

- Clearance of valuable natural forests is prohibited

The RSPO guideline does not include greenhouse gas requirements, but prevention of methane emissions is mentioned as a general goal (RSPO website). One problem with voluntary guidelines is that they are limited to a certain group. For example China and India do not belong to RSPO. China is already investing on palm oil businesses in Indonesia. It will be also challenging to control sustainability after trading, e.g. Malesian oil refineries in Borneo may use feedstock from Indonesian Kalimantan (Humalisto 2006).

Also in Europe, efforts are made to avoid usage of non-sustainable biomass feedstocks by developing sustainability criteria and certification systems.

11 Development and Status - Biorefineries

11.1 BTL-type Biorefineries

The investments in the research of BTL processes are huge today, but no industrial scale plants are running, yet. However, there are a number of projects going on.

The first BTL biorefinery using biomass gasification and liquefaction step is being built in Freiberg, Germany by CHOREN in co-operation with Shell, Daimler Chrysler, and VW. CHOREN is planning to start the world's first commercial BTL-plant (Beta-Plant) at its Freiberg site with production of 15,000 tons/year BTL in autumn 2008. The next step will be an industrial-scale BTL plant. Sigma plant with production of around 200,000 tons/year would operate in Schwedt as of 2012, and sigma plant with production of around 300,000 in the U.S. as of 2013 (Blades 2008). CHOREN's 200,000 tons/year plant requires 1 million tons/year biomass. (CHOREN 2007, Bienert 2007).

In Finland, the oil company, Neste Oil, and pulp and paper company, Stora Enso,will build up a demonstration plant at Stora Enso's Varkaus Mill with start-up in 2008, and a full-scale plant producing around 120 million liters of diesel is expected in 2012-2014. The focus will be on developing new gas clean-up technology to produce clean synthesis gas from wood, and on Fischer-Tropsch process to produce crude biodiesel. (Stora Enso 2007, Neste Oil 2007).

The Finnish forestry company UPM and the international technology group Andritz with its associated company Carbona intend to co-operate to develop technology for biomass gasification and syngas purification for BTL production. The testing will start using Carbona's gasification technology at the Gas Technology Institute's pilot plant in Chicago, U.S. (UPM 2007)

Finnish Vapo, a supplier of local and renewable fuels, bioelectricity and bioheat, is developing a process to manufacture biofuel from peat. Vapo is considering a facility, which would produce "biocrude" from such biofeedstocks as peat and wood. The "biocrude" would be then sold to an oil refinery, where it would be converted into diesel fuel for vehicular use. (Vapo 2007). GHG impact of peat-based F-T-diesel depends on many factors, and is worse than for fossil diesel in many cases. The GHG impact of the peat F-T-diesel can be lowered, if the peat land is utilized for afforestation or cultivation of reed canary grass after peat production. CCS can decrease the GHG impact of peat F-T-diesel to the same level as with fossil diesel, or even below. (Kirkinen et al. 2007).

MPM Technologies Inc. and Losonoco Inc. are developing biofuel and chemical manufacturing facilities based on the Skygas waste gasification process. MPM has done development work on the Skygas plasma arc gasification process. Losonoco builds, owns, and operates manufacturing facilities for ethanol and biodiesel and focuses on commercializing technologies that use waste streams as feedstock for the biofuels. (Green Car Congress 2007).

Chevron Corporation and Weyerhauser Company will jointly assess the feasibility of commercializing the production of biofuels from cellulose-based sources. Feedstock options include a wide range of materials from Weyerhauser's existing forest and mill system and cellulosic crops planted on Weyerhauser's managed forest plantations. (Green Car Congress 2007)

The above-mentioned projects utilize gasification and Fischer-Tropsch synthesis. However, there are also options other than Fischer-Tropsch for liquefaction of syngas. Lurgi has a lab-scale "MtSynfuels" scheme that converts syngas first to methanol, then via olefins to distillates (COD), enabling production of diesel or gasoline. This scheme avoids making naphtha, a coincidental byproduct of Fischer-Tropsch XtL schemes.

Co-refining of Biomass and Fossil Feedstocks (XTL)

Hervouet (2007) presented Total's view on the integrated biorefinery using mixture of fossil and biobased feedstocks converted to liquid fuels, "XTL". A few refinery integrated XTL units exist for production of chemicals, but so far no transport fuels are produced with this scheme. The XTL option may be interesting to refineries as prices of oil and natural gas increase.

XTL for synfuel production integrated in a refinery provides feedstock flexibility, many synergies for industry infrastructure, logistics, product quality control, and specifications. Biomass as feedstock would reduce local emissions (Hervouet 2007). Co-refining of biomass and fossil feedstocks can be realized in two ways:

- Gasification and liquefication step (XTL)
- Pyrolysis and refining of biocrude

There are number of open questions on possible co-gasification - feedstock compatibility, gasifier issues, syngas treatment, and overall integration and operation performance (Hervouet 2007).

Black-liquor gasification

Integration of transport fuel processing with black liquor mills is one option to meet technical, environmental, and safety requirements at large scale production of biofuels. The pulp and paper industry is energy intensive. Energy self-sufficiency is generally some 57% when black liquor is burned in boilers. Gasification of black liquor could improve the energy efficiency, reduce toxic emissions, and also eliminate the danger of recovery boiler explosions. The gas could be used in boilers, in synfuel production or in future, in gas turbines, or in fuel cells. (US DOE EERE).

Rehnlund (2007) reported that in 2003 there were 57 old recovery boilers world-wide that could be replaced with gasification technology, the majority being in U.S., Canada, and Japan. In some regions the potential for black-liquor gasification is high, e.g., in Finland and Sweden liquids from black liquor gasification could contribute substantially in energy demand in the transport sector. However, globally black liquor gasification could represent only a fraction of energy supply. (Rehnlund 2007)

Black liquor gasification plants already exist. However, commercial systems with integration for fuel synthesis or hydrogen separation technologies are not available. (U.S. DOE EERE).

In Sweden, a black liquor gasification pilot with ChemRec technology is running in Piteå (ChemRec). This technology is suitable for large-scale gasification (>500 MW).

In Sweden, the so called "BLGMF2" project evaluated the possibility to produce FT fuels from black liquor gasification in comparison with methanol and DME as products. The total energy efficiency for FT diesel and naphtha was 65%, whereas for methanol 66% and for DME 67% (Table 10.8) (Rehnlund et al. 2007)

Table 10.8 - Evaluation of Alternative Products from Black Liquor Gasification (Rehnlund 2007)

	Methanol	DME	FT-diesel
Fuel production (tons/a)	410 600	286 000	109 700 (+56 200 naphtha)
Energy efficiency (LHV), black liquor to fuel	56%	56%	33% diesel + 17% naphtha = 50%
Energy efficiency (LHV), biomass to fuel	66%	67%	43% diesel + 22% naphtha = 65%

11.2 Hydrotreatment / Oil Refineries

Hydrotreatment of different biobased feedstocks at oil refineries seems to be the fastest growing area to produce non-traditional biofuels. There are a number of projects going on, and several processes are already running in commercial scale. Development has been very fast, refineries have adopted this technology almost "overnight".

Hydrotreatment has been used for decades at oil refineries to upgrade heavier fractions to middle distillates. Hydrotreatment of biobased feedstock to high quality diesel-fractions has also been studied earlier. In the beginning of 90's Arbokem reported of a bio-cetane enhancer for diesel fuel using co-products of the wood pulp industry, tall oil (pine oil), as feedstock. The basic idea at that time was to convert vegetable oils, fats, and tree oils into cetane enhancer (cetane 55-90) for diesel fuels. The Arbokem's catalytic bio-oil hydrotreating technology typically produces a mix of 5-15% light distillate (naphtha), 40-60% middle distillate (cetane), 5-15% heavy distillate, and 5-10% burner gas. A medium-severity refinery hydroprocess has been reported to yield a high cetane product in the diesel boiling range with benefits of low production costs, compatibility with infrastructure, engines and fuel standards, and feedstock flexibility. (Arbokem information).

<u>NExBTL – Neste Oil</u>: The first commercial refinery scale hydrotreatment process for bio-oils and fats was developed by Neste Oil in Finland. The process, called NExBTL, converts triglycerides such as vegetable oils and animal fats to high-quality synthetic biodiesel (HO) resembling synthetic GTL-type diesel fuel. This fuel can be used as a blending component for diesel or even by itself. This refinery-based process benefits from a refinery's infrastructure including energy, blending facilities, logistics, and laboratories. The first NExBTL plant started production of 170,000 tons of neat biocomponent per year in the summer of 2007, and the second plant with equivalent capacity in 2008. With the new biodiesel plant Neste Oil will have the first major "biorefinery" in Europe. In November 2007, Neste Oil announced of building a NExBTL plant with capacity of 800 000 t/a in Singapore by 2010. (Neste Oil).

<u>UOP LLC and Eni S.p.A</u> will build a production facility in Liverno, Italy using catalytic hydroprocessing of vegetable oils, UOP/Eni Ecofining^{TM} technology. The production of around 300 000 tons/year will start in 2009. Eni is planning to install several Ecofining units at its refineries in Europe. (UOP Press release 2007). UOP has also announced that it will work on development of technology to convert vegetable and algal oils to military jet fuels. (UOP Press release 2007)[8]

<u>H-Bio – Brazil</u>: In Brazil, Petrobras has developed the H-Bio process, which hydrogenates mixtures of vegetable oil (soy oil) and petroleum (co-hydrogenation). The output is a mixture of diesel and hydrogenated vegetable oil, not a neat biodiesel component as in the case of NExBTL. Petrobras announced the start of production of the H-Bio in December 2006, but this plan is postponed due to high soy prices. In the beginning, Petrobras plans to use 256,000 m3 of vegetable oil per year. According to Petrobras, the investments needed in the existing refineries to produce the new fuel are small; US $38 million in the three chosen plants. Later on, the company plans to introduce production in two more refineries. Then the quantity of vegetable oil used will

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[8] UOP also develops technology to co-process vegetable oils in Fluid Catalytic Crackers (FCC) to produce gasoline and olefins. (www.uop.com)

be 425,000 m3 per year, which will represent a reduction of 25% in imported diesel (The Brazil-Arab News Agency 2006). There are also other activities on hydrogenated biodiesel, e.g. the UK (AMFI Newsletters).

Galp Energia, an oil and gas company in Portugal, and Petrobras in Brazil have a 50-50 joint venture to produce renewable diesel via hydrogenation of vegetable oils with production of 600,000 tons/year. Half of this would be for domestic use in Portugal and half would be exported. Portugal will require the use of 10% biofuels domestically beginning in 2010. (Green Car Congress 2007)

ConocoPhillips has developed processing technology to converts animal fats into renewable diesel. This process was tested at the company's Whitegate refinery in Cork, Ireland, in 2006. ConocoPhillips will partner with meat producer Tyson Foods Inc. who provide animal fat in North America to refinery based hydrotreatment to produce about 500,000 tons/year (175 million gallons) of renewable diesel. Production would start in late 2007 and expand in 2009 (ConocoPhillips 2007).

Dynamic Fuels LLC, a renewable fuels venture of Tyson Foods and Syntroleum, will produce renewable diesel, jet, and military fuel markets using Syntroleum's Biofining™ process. Animal fats, greases, and vegetable oils supplied by Tyson will be used as feedstocks. The first facility will produce about 225,000 tons/a (75 million gallons) of synthetic fuel in the south central United States, with production in 2010. The project will cost $150 million. The Biofining™ process can upgrade also Fischer-Tropsch wax. (Syntroleum 2007)

BP Australia (2006) announced of a Memorandum of Understanding to provide about 100,000 tons/year of tallow based renewable diesel by 2008.

Nippon Oil and Toyota in Japan are also exploring hydrotreatment of vegetable oils. (Takei 2007)

Hydrotreatment of oils and fats is currently integrated into existing oil refineries. However, if the scale were sufficient to improve technical and economical feasibility, they could be designed as stand-alone plants.

11.3 Pyrolysis Oil

There are a number of extensive projects developing pyrolysis technology for liquid fuels. There are also several pyrolysis oil production plants in operation, however, these do not produce biodiesel.

Ensyn's RTP™ process produces bio-oil from biomass with high yields, typically 75% by weight. Ensyn's bio-fuel has been used commercially for industrial heat since the early 1990's. Ensyn's commercial RTP™ plants presently produce liquid fuel and charcoal that are combusted on-site for process and space heat. Large quantities of bio-fuel have been produced and exported for use in extensive bio-fuel test programs worldwide. (Ensyn website).

Dynamotive announced its plans to invest US $24 million to build the first fully commercial industrial biofuel plant in the U.S. The modular, second-generation biomass-to-biofuel plant is designed to use Dynamotive's proprietary "fast pyrolysis" process to convert 200 tons per day of wood by-products and residues from nearby sawmills into 34,000 gallons per day of BioOil®. (Dynamotive 2007).

BTG Biomass Technology Group in the Netherlands is running a pilot plant of 1 MWth for pyrolysis of biomass and residues. The 250 kg/h pilot plant has processed in total 50 tonnes of oil for a number of clients. BTG is involved in the engineering of a 50 ton/day fast pyrolysis plant for clean wood residues. (BTG World website)

There are also demonstration plants in USA, Canada, and Maleysia.

ConocoPhillips is one of the companies investing in biorenewable fuels. An eight-year, $22.5 million research program including fast pyrolysis, is under way at Iowa State University in the U.S. Plus, UOP has been exploring the possibilities to use pyrolysis oil as a feedstock for refinery based hydroprocessing to fuels (Figure 11.1).

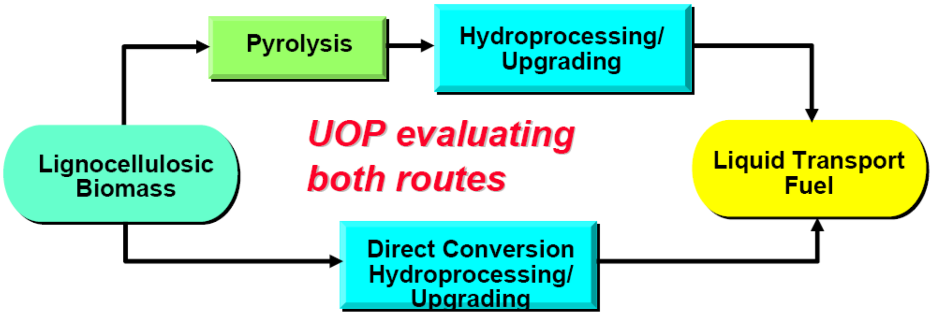


Figure 11.1 - UOP Considers Pathways Using Pyrolysis

11.4 Small-Scale Biorefineries

Development of feasible small-scale BTL technology would help with logistics and increase utilization of biomass feedstock. The U.S. Roadmap for Biomass Technologies (2002) puts emphasis on development of rural-based biorefineries. Products could be power and heat for use on-farm, on-site, and in small industrial systems. Modular biomass systems could also be integrated with fuel cells, microturbines, other distributed systems and transport fuels. The high cost of transporting biomass to larger facilities could be avoided and this would help rural communities and farmers. (US DOE EERE)

Development of small-scale units is challenging, even for GTL. Bernoux (2007) presented small-scale GTL unit. Conversion efficiency may be high, but hydrocracking required for waxes reduces total energy efficiency to about 50%. Bernoux called for innovative modular processes and consideration of other liquefaction options such as methanol to gasoline (MTG) or DME.

11.5 Cost Evaluation and Energy Efficiency

11.5.1 Feedstock and capital costs

A number of factors, such as feedstock, process, land, labor, by-products, subsidies, and role of competitive industries, influence the costs of biodiesel. (Table 11.1). In this Chapter, different factors are discussed and prospects for prices available in literature are reviewed.

Table 11.1 - Factors Affecting Cost Evaluation.

Feedstock	Process	Others
Feedstock price?	Biorefinery option?	Land costs?
Transportation of feedstock?	By-products?	Labor costs?
		Competitive industries?
		Subsidies?

Typical biomass fuel costs are in the range of 0 to 5 \$/GJ (PRP website). However, feedstock prices are not steady and new demand may lead quickly to a substantial increase in prices.

Selections of plant location, size and transport options (what is transported) are critical factors for economical feasibility of production. Most biomass feedstocks are of relatively low energy density, thus transport costs may represent high share of costs. Pre-treatment of feedstock can lower the transport costs per energy unit, but even then it may be cost effective to put biomass plants close to the feedstock. Refining of BTL products to transport fuels can take place on-site, or for example, FT crude can be transported to another refining and blending site, such as oil refinery.

Zwart (2007) evaluated large-scale BTL production in the Netherlands with two 8 GW_{th} plants and 16 GW imported biomass. The transport options considered were: FT products, wood chips or pellets, wood oil/char slurry, or torrefied wood pellets. The study concluded that it is better to handle pre-treatment before overseas transportation, if pre-treatment is obligatory for gasification. Transportation as wood pellets can be acceptable, but transportation as pyrolysis or torrefaction products is better, and transportation as FT crude was the best option.

There is not much data available on economy evaluations for BTL plants. In Germany, CHOREN has reported that the investment on the industrial-scale (~200 kton/a) BTL plant at Schwedt would be €500 million (US$660 million) (CHOREN 2007). As a reference, it is mentioned that Neste Oil plans to invest approximately €550 million in building a NExBTL plant in Singapore with a design capacity of 800,000 t/a (Neste Oil 2007).

In Sundsvall, Sweden a project is under way to develop economically feasible technology for small-scale biomass gasification to decrease the costs of biomass transportation. A feasibility study of the Sundsvall Demonstration Plant showed investment costs around €88 - €106 million for a 100 MW plant producing 700 bpd (~30 kton/a) BTL diesel. A corresponding GTL demonstration plant would be around €15 million. The outcome was that the BTL pilot plant will not be built in Sundvall, yet, but instead a GTL pilot (5MW) plant. (Sundsvall)

Gasification and cleaning steps represent some 65% of investment costs of a BTL plant (Sundsvall). Also for a GTL plant the capital costs break-down is largest for synthesis gas preparation (66%), and lower for FT synthesis (22%) and upgrading (12%) (van der Laan 1999). For a GTL plant with power co-production (~400 ktons/a FT liquids and 84 MW power) about 50% of the capital costs accumulated from synthesis gas preparation, 17% for FT synthesis, 9% for product upgrading and 25% for the combined cycle plant (Choi et al. 1997). According to Dayton (2007) gas cleanup and conditioning has the largest economic impact on GTL economy.

Figure 11.2 shows an economic evaluation of FT fuel production at a stand-alone plant and at a plant integrated with pulp and paper (200 MW). In addition to costs shown in Figure, FT-crude refining to diesel fuel will cost about 4 EUR/MWh (Kurkela 2006).

Figure 11.3 shows estimate of capital costs for different combinations of gasification, pyrolysis and FT units.

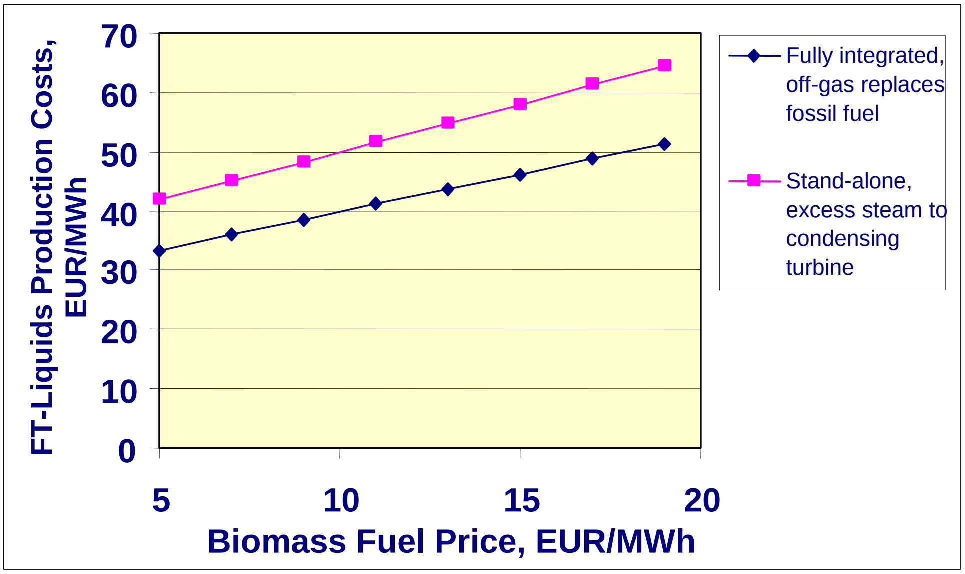
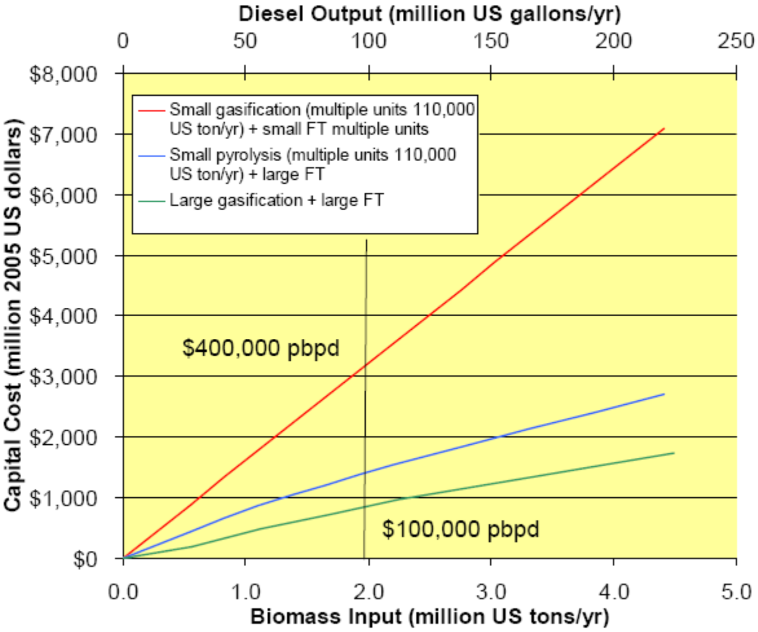


Figure 11.2 - Costs of FT Fuel Production at Stand-Alone Plant and at a Plant Integrated With Pulp and Paper (200 MW)
(In addition, refining to diesel fuel about 4 EUR/MWh) (Kurkela 2006)



Adapted from: Bridgwater, ACS Meeting, Washington, D.C., 2005

Figure 11.3 - Capital costs for different combinations of gasification, pyrolysis and FT units (Bridgwater 2005).

Larson et al. (1999) evaluated the energy balance of two BTL plant options compared to GTL and CTL. The efficiency for GTL and CTL was higher than for conversion of biomass due to the low cold-gas efficiency of biomass gasification and need for reforming of product gas before FT synthesis. In the "full recycle" option biomass conversion efficiency is 49%, whereas in the "once-through" only 44%.

11.5.2 Price of Biodiesel

The lowest production costs could be achieved by integration with existing industry for example, with oil refineries, pulp and paper plants, heat and power production. Most biorefineries target a biofuel price of about US$1/gallon (below US$8/GJ) (IEA Bioenergy ExCo 59). IEA estimates that the cost of BTL diesel from ligno-cellulose is currently more than $0.9 per liter of diesel equivalent, with a potential reduction to $0.7 - $0.8 per liter of diesel equivalent (Table 11.2 and 11.3, Figure 11.4). (IEA Technology Essentials 2007)

Table 11.2 - Estimates for different biofuels given in IEA Technology Essentials in January 2007.

Biodiesel from animal fat	$0.4-0.5/liters of diesel equivalent ($11-14/GJ)
Biodiesel from vegetable oil	$0.6-0.8/liters of diesel equivalent ($17-23/GJ)
BTL from lingo-cellulose	$0.9/ liters of diesel equivalent ($26/GJ) at $3.6/GJ feedstock (potential reduction to $0.7-0.8/lde)
Ethanol from lingo-cellulose	$1.0/liters of gasoline equivalent ($49/GJ) at $3.6/GJ feedstock (potential reduction 50%)
Ethanol from maize, sugar-beet	0.6-0.8/liters of gasoline equivalent ($29/GJ) potential reduction to $0.4-0.6/lge from sugar cane in Brazil $0.3/lge ($14.6/GJ)

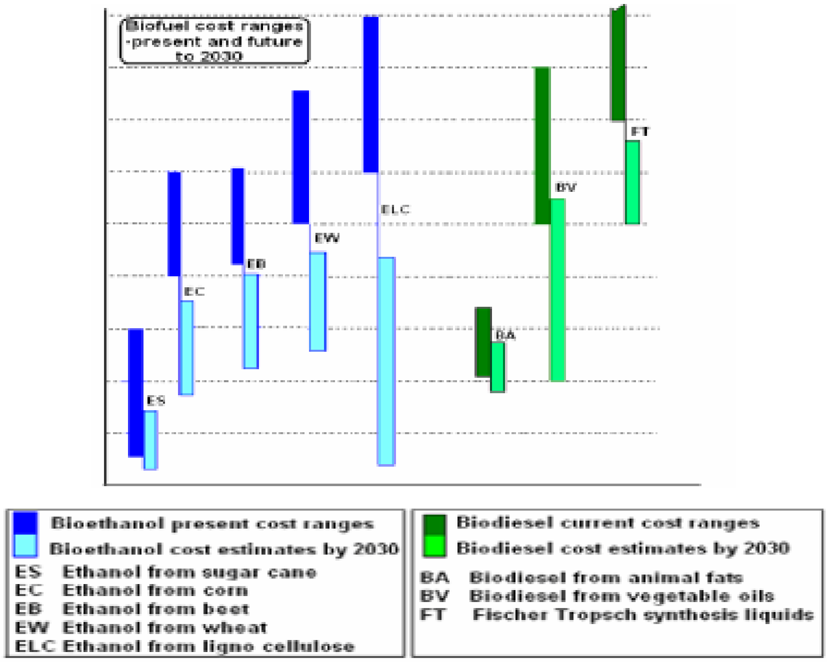
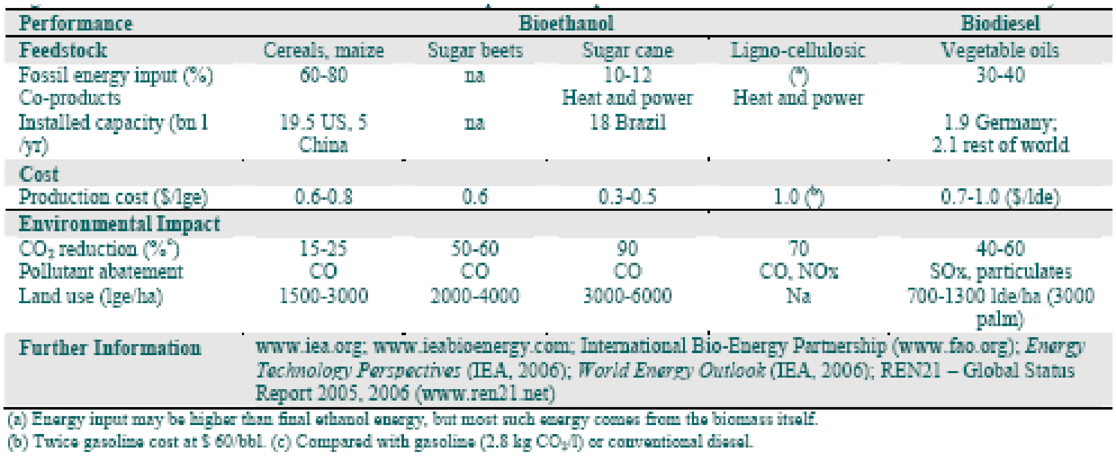


Figure 11.4 - Current and Projected Costs of Biofuels Compared with Gasoline and Diesel prices (IEA Technology Essentials 2007) ©OECD/IEA 2007

Table 11.3 - Energy Input, Costs, and Emissions for Bioethanol and Biodiesel Production (IEA Technology Essentials 2007) ©OECD/IEA 2007



Performance	Bioethanol				Biodiesel
Feedstock	Cereals, maize	Sugar beets	Sugar cane	Ligno-cellulosic	Vegetable oils
Fossil energy input (%)	60-80	na	10-12	(a)	30-40
Co-products			Heat and power	Heat and power	
Installed capacity (bn l /yr)	19.5 US, 5 China	na	18 Brazil		1.9 Germany; 2.1 rest of world
Cost					
Production cost ($/lge)	0.6-0.8	0.6	0.3-0.5	1.0 (b)	0.7-1.0 ($/lde)
Environmental Impact					
CO_2 reduction (%[c])	15-25	50-60	90	70	40-60
Pollutant abatement	CO	CO	CO	CO, NOx	SOx, particulates
Land use (lge/ha)	1500-3000	2000-4000	3000-6000	Na	700-1300 lde/ha (3000 palm)
Further Information	www.iea.org; www.ieabioenergy.com; International Bio-Energy Partnership (www.fao.org); *Energy Technology Perspectives* (IEA, 2006); *World Energy Outlook* (IEA, 2006); REN21 – Global Status Report 2005, 2006 (www.ren21.net)				

(a) Energy input may be higher than final ethanol energy, but most such energy comes from the biomass itself.
(b) Twice gasoline cost at $ 60/bbl. (c) Compared with gasoline (2.8 kg CO_2/l) or conventional diesel.

Vliet et al (2007) has conducted a well-to-wheel (WTW) analysis of many options for BTL and XTL processes. With estimated efficiency of a FT plant is 50% - 55% (feed to fuel, LHV); investment of 500-650 €/MWth input led to conclusion that investment cost for GTL was the lowest and for BTL the highest (Table 11.4). In the pathway comparison by Vliet et al. it was seen that all options studied, GTL, CTL, BTL and XTL, were inefficient as regards to overall energy use when compared to oil based fuel. Well-to-tank (WTT) energy ratio was 0.14 MJ/MJ for oil based fuel, 0.70-0.73 for GTL, 0.84-0.91 for CTL, 0.83-1.19 for BTL and 0.89-0.93 for XTL.

Table 11.4 - Vliet et al (2007) used the following costs (WTT) in the evaluation.

	€/l	$/bbl$_{eq}$
Diesel	0.31-0.36	51
GTL	0.14-0.24	21-36
CTL	0.32-0.35	47-52
BTL	0.44-0.85	67-129

Hydrotreatment of oils and fats can be an economically profitable concept depending on feedstock price. Although the capital investment is slightly higher than in conventional biodiesel production, the premium quality and market value of the product will compensate the investment. The competitiveness is based on the superior quality of the end product, which is also widely preferred among vehicle manufacturers.
One of the critical success factors for the production plant is the right kind of infrastructure which will support the efficiency of the production plant. The first production plants will be refinery based set-ups utilizing the refinery’s infrastructure for

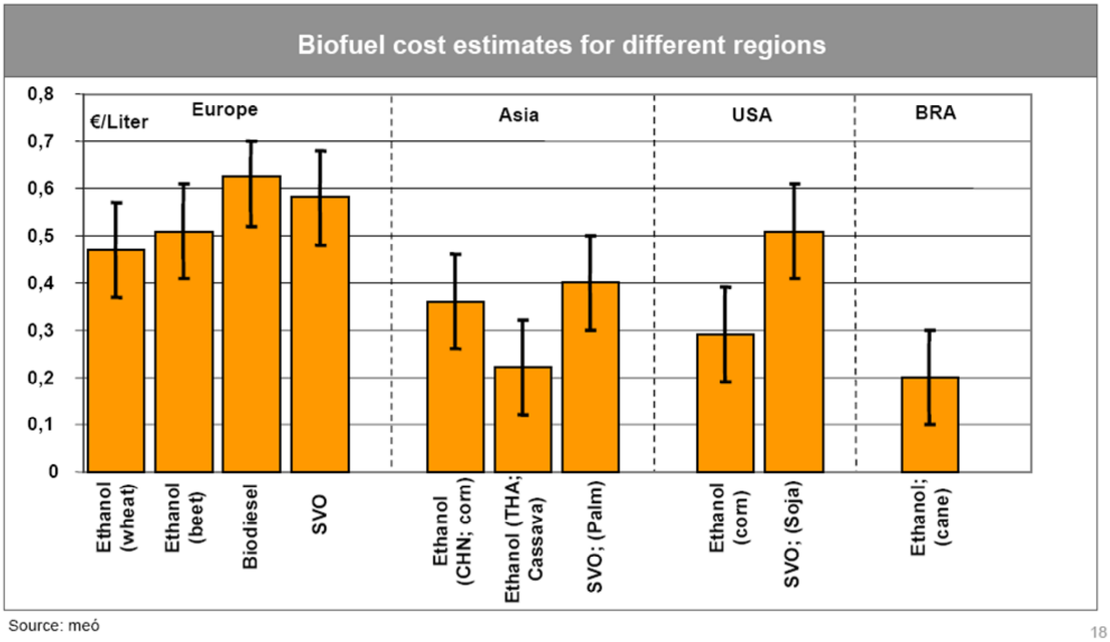
energy, blending facilities, logistics, waste water treatment, and laboratories. In the future, large scale production plants will not necessarily be linked to the refinery infrastructure.

One estimation of the production costs for hydrotreated renewable diesel from soybean oil showed costs of 5.01 $/gallon, when production costs for FAME were 4.36 $/gallon. If tallow was used as feedstock, the costs would be 3.41 $/gallon for renewable diesel and 3.20 $/gallon for FAME. (PIRA 2008).

There is limited information on the economy of pyrolysis oil production units. Costs of bio-oil production depend i.a. on feedstock (pre-treatment) costs, plant scale, type of technology etc. According to some studies pyrolysis oils can be produced for between 75 and 300 € per ton oil (4 to 18 €/GJ), assuming feedstock costs between 0 and 100 €/t (0 to 1.9 €/GJ) (Bridgwater A.V., 1999). BTG has reported for 2 t/hr unit a bio-oil production cost of less than 85 €/t (approx. € 5/GJ) assuming feedstock costs of 25 €/t (BTG 2000).

Regional variation

The costs for diesel-type biofuels vary significantly between different regions. Figure 11.5 shows cost estimates for biofuels from Europe, Asia, USA and Brazil. In 2007, the refinery cost for conventional fuels (gasoline, diesel) was some 0.40-0.50 €/l. Straight vegetable oil produced in Asia (palm oil) was the cheapest, rapeseed oil produced in Europe the most expensive and soy oil produced in the U.S. in between that of Asia and Europe.



Source: meó

Figure 11.5 - Biofuel cost estimates (Schmitz 2007)

12 Comparison of Options to Produce Biobased Diesel Fuels

Today biofuels for the transport sector are produced from oils, sugars, and starch. However, the highest potential is in lignocellulosic biomass, which can be utilized for transport biofuels by using BTL technologies.

The primary biodiesel option has traditionally been to biodiesel (FAME). Today, hydrotreatment of oils and fats, the HO process, provides a commercial alternative to FAME. HO is an efficient process , which benefit from industrial-scale logistics and infrastructure. In addition, a variety of oils and fats, even non-food crops, can be hydrotreated, whereas the feedstock basis for FAME is very limited. Methanol is not needed for the hydrotreatment process, and no such by-products as glycerol are produced as is the case from the FAME process. One of the major benefits of parafinic BTL and HO fuels over FAME is the high-quality of the end-product.

The next generation, BTL-type paraffinic biodiesel fuels have the following advantages when compared with FAME-type biodiesel:

- Can be based on non-food crops
- Can be used at high concentrations without investments: fully miscible with conventional diesel fuel and fully compatible with existing refueling infrastructure and existing vehicles
- Excellent performance in engines/after-treatment devices
    - sulfur-free, low aromatic, no oxygen
    - higher cetane, lower boiling range
    - no risk for engine oil dilution
    - lower risk for carry-over of impurities (e.g. phosphor from fertilizers causing particulate filter clogging)
    - better heating value (mass based)
- Low exhaust emissions
    - significant reductions in regulated and unregulated exhaust emissions
    - reduction in NO_x emissions instead of increase with FAME
- Handling and storage without problems
    - no limitation on storage life
    - less affinity to water
    - lower risk for microbiological growth
    - no attacks on elastomers
    - almost odorless, colorless liquids
- Enables development of future engines/after-treatment devices
    - enables the development of engines with improved engine efficiency
    - the bio-alternative preferred by the automotive industry
    - FT technology makes it possible to tailor fuels for future advanced combustion systems

Advantages for FAME when compared to BTL-type paraffinic fuels in the end-use:

- FAME has -better lubricity, and can even serve as a lubricity additive. On the contrary, paraffinic fuels need additives for protection against injection equipment wear.
- The production process of FAME is simple, inexpensive and suitable for distributed production.

To summarize, regarding end-use properties, BTL and hydrotreated oils show superior quality compared with conventional diesel fuel or FAME. This is typical for paraffinic diesel fuels regardless of the feedstock.

FAME is addressed with serious technical drawbacks in the end-use. Thus manufacturers of on-road diesel engines want to limit usage of FAME to maximum 5% in diesel blends. One option might be combination of FAME/BTL/diesel to maximize bio-content of fuel pool.

In spite of the advantages listed above for next generation paraffinic BTL-type fuels, Nexant (2006) reports that conventional biodiesel (FAME), being a biodegradable, low-toxicity product, will likely stay on the market far into the future. However, it can substitute for only a small fraction of diesel.

Integrated thermochemical platforms will probably take the lead in producing both gasoline and diesel range biofuels, in conjunction with power generation and chemicals. Ethanol may be dehydrated to hydrocarbon gasoline fractions that are more compatible with the existing fuel distribution and vehicle infrastructure. (Nexant 2006)

Nexant sees that the potential for an early conflict between the fuel and the food industries is underestimated. The role of byproducts as animal feed, on the other hand, is underrated or even missed. The study outlines need for development of, for example, in-field pyrolysis of biomass to help with logistics.

13 Barriers and Gaps in Knowledge

Barriers for biodiesel are related to costs, competition with food and other industries, arable land, regional markets, transport costs, poor agricultural practices in developing countries, water and fertilizer use, conservation of biodiversity, logistics, and distribution networks.

In this discussion we should make a distinction between first and second generation biodiesel fuels, because the challenges are quite different between the two.

First Generation Biodiesel Fuels – The Fatty Acid Esters

These fuels are generally made from vegetable oils through a transesterification process, and the worldwide capacity to produce greater amounts of vegetable oils for fuels is enormous. However, at some point (and perhaps the world is already at that point) their use as fuels will compete for the same resources that are used as food feedstocks. This will lead to huge price increases in both food and fuel, much as we are now seeing in the first half of 2008 that is resulting from the rise in oil prices and the strain on the markets from the rising use of corn for ethanol. Therefore, the authors of this report believe that the ultimate level of production and use of FAME for biodiesel fuel will be limited to the point where there is balance in the market between fuel and food use of the same feedstocks. Exactly where that level is, we do not know. Nevertheless, this will be the ultimate barrier for use of FAME as fuel. Until that time, though, there are still a number of technical barriers that inhibit the growth in use of FAME as biodiesel fuel (all have been discussed in detail in this report), and these are summarized here:

- **Cold Flow Properties** – Depending on feedstock, some biodiesel fuels can have poor cold weather performance when blended with diesel fuel in portions greater than 5-10%. Of course, it is desired to use greater blend levels of biodiesel, but doing so is limited by the cold flow properties in the extreme northern climates.
- **Oxidative Stability** (shelf life) – Biodiesel fuel from vegetable oils tends to degrade when stored for long periods. Therefore, if this characteristic cannot be overcome with additives or processing, then good practice will require that the fuel not be allowed to be stored for long lengths of time.
- **NOx Emissions** - for biodiesel fuel blends have been reported to be higher than those of petro-diesel fuel, although there is some disagreement within the literature. If true, though, the concern with NOx emissions might limit the use of biodiesel to some extent.
- **Lack of Technical Standards** – While standards have been generally accepted worldwide for low level blends of biodiesel with petro-diesel fuel (5% or less), the acceptance of higher level blends (20% or more) has been elusive. The engine manufacturers have generally opposed the higher level blends because of the potential for damage to the engines from plugging fuel filters or degraded fuel from storage, etc. Because of the potential for higher NOx emissions some governments (e.g. the state of Texas) have temporarily banned the use of biodiesel blends.

Second Generation Biodiesel Fuels – Fuels from Biorefineries

Second generation biodiesel fuels are just now coming into being and the range of options for manufacture of biodiesel fuel from biomass is large. Many of the options would center on a gasification process for the initial stage of biomass conversions, and there are a number of challenges with the gasification of biomass materials:

- Overall, biomass is a more challenging feedstock for gasification than coal and natural gas. Gasification of mixtures of biomass and fossil feedstocks can help in this respect (XTL).
- Requirements on feedstocks – feedstock will need to be uniform. The feed preparation should be reliable and proper storage and handling is required.
- Syngas cleanup and conditioning are a focus area for development of gasification of biomass.
- New sensors and analytical instrumentation for process control is needed.
- The major issues regarding costs are feedstock costs, process costs, land costs, labor costs, by-products, subsidies, and the role of competitive industries. Evaluation of costs for different biorefinery options is complicated task. Especially today there are many uncertainties regarding future feedstock prices and transportation costs.

Barriers on the end-use side for FAME are issues related to compatibility with existing refueling infrastructure and existing vehicles. These issues are not barriers for the fuels that will be produced by biorefineries since those fuels will have the same qualities or better than those produced today from petroleum.

Ultimately, integrated thermochemical platforms will probably take the lead in producing both gasoline and diesel range biofuels, serving as the first solution combining large-scale production and high-quality products. However, the potential for an early conflict between the fuel and the food industries might be underestimated at this time, as well as the question of sustainability.

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