

Biodistillate Transportation Fuels 1. Production and Properties

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ABSTRACT

Biodistillate transportation fuels include biodiesel (produced via transesterification of animal fats and vegetable oils) and renewable diesel (produced via catalytic hydroprocessing of the same feedstocks). Production and use of biodistillates are increasing dramatically, both in the U.S. and globally. This paper describes the policy drivers prompting growth of biodistillate fuels in the U.S., Europe, and selected other countries. Trends in fuel production volumes and feedstocks supplies are presented for these fuels. Current feedstocks are dominated by soybean oil in the U.S. and rapeseed oil in Europe. However, there is much interest in developing alternative, non-edible feedstocks such as jatropha and microalgae.

Currently, biodiesel is the dominant biodistillate in use, though interest in renewable diesel is increasing. This paper describes different conversion processes used to manufacture these fuels, and discusses the pros and cons of each. Chemical and physical properties of biodistillates are presented, along with a discussion of the relevant fuel specifications established by ASTM and other organizations. Measures to assure satisfactory fuel quality are explained. Finally, in-use handling and performance of biodistillates are discussed, focusing on issues such as fuel stability and low-temperature operability where special precautions may be necessary to ensure satisfactory quality.

INTRODUCTION AND BACKGROUND

In recent years, production and use of biofuels have increased dramatically, both in the U.S. and around the world. This growth is driven by somewhat different factors from one country to the next, but the strongest factors generally include the following:

- National energy security
- Diversity of energy sources
- Concerns over greenhouse gases (GHGs) and global climate change
- Desire for sustainable energy sources
- Rural economic development
- Improved balance of trade

Over the past 10-20 years, most interest and activity regarding biofuels was focused on ethanol, and its use in light-duty gasoline vehicles (LDGV). While ethanol remains a topic of considerable activity and debate, recent years have seen rapid growth in other biofuels meant for blending with diesel fuel and used in vehicles with compression ignition (CI) engines.

Numerous aspects of biofuels are of interest and importance – including feedstocks, production technologies, fuel properties and standards, performance and handling, vehicle emissions, and life-cycle impacts. Due to the evolving nature and rapid growth of information in these areas, the Coordinating Research Council (CRC) sponsored a study to assess the state-of-knowledge regarding plant-derived biofuels as blending materials for ultra-low sulfur diesel (ULSD) fuel in transportation applications.

This paper documents efforts taken in conducting the CRC study, and presents the findings with respect to policy drivers, feedstocks, fuel production technologies, fuel properties and specifications, and in-use handling and performance. Companion papers describe efforts and results with respect to vehicle emissions⁽¹⁾ and life-cycle impacts of biodistillate fuels.⁽²⁾ The complete CRC report provides additional details on all these topics.⁽³⁾

LIMITS OF STUDY

Although our primary interest relates to plant- and animal- derived biofuels used in ULSD, both neat biofuels (e.g. B100) and biofuel blends in non-ULSD fuels are also considered. There is also considerable interest in converting lignocellulosic feedstocks into biofuels. For production of mid-distillates, thermal processes involving gasification and pyrolysis are being developed.^(4,5) However, as these areas of development are evolving rapidly – and largely involve proprietary information – this paper does not emphasize the production of mid-distillate biofuels from lignocellulosic feedstocks. Other topics excluded from this study include the following:

- Ethanol (and other alcohols) intended for use in spark ignition engines
- Mid-distillate fuels used in non-transportation applications (turbines, boilers, other stationary sources)
- Theoretical or fundamental studies of combustion chemistry, kinetics, and modeling
- Analytical methodologies for detecting and characterizing biodistillates
- Toxicity and health impacts of emissions
- Agriculture, agronomy, and food science studies
- Social, political, or economic studies

DEFINITIONS

It is important to define fuel-related terminology that is commonly used within the fuels and automotive industries, and is incorporated into this paper and its companion papers. A detailed list of common abbreviations and acronyms is provided near the end of this paper, and a glossary of fuel terms is provided in Appendix I.

Certain biofuel terminology requires additional explanation. While not universally accepted, we use the term “biodistillate” to designate all common middle distillate fuels (diesel, kerosene, jet fuel, and heating oil) that are produced from biological feedstocks – including animal fats, vegetable oils, and lignocellulose. Thus, “biodiesel” and “renewable diesel” are both subsets of biodistillates.

Biodiesel is defined by ASTM as “a fuel comprised of mono-alkyl esters of long-chain fatty acids derived from vegetable oils or animal fats, designated B100.”⁽⁶⁾

Congress has adopted a similar definition for “Biomass-based diesel,” with the additional requirement that the fuel have life-cycle greenhouse gas (GHG) emissions that are at least 50% less than baseline life-cycle GHG emissions.⁽⁷⁾ Unless otherwise indicated, the term “biodiesel” refers to neat material – i.e. B100. Lower concentrations, such as B20, are properly referred to as “biodiesel blends,” not biodiesel itself.

Terminology regarding “1st Generation” and “2nd Generation” biofuels also requires clarification. Although these terms are in common usage, they have no legal or regulatory meaning. Generally, the term “1st Generation” refers to biofuels produced from commonly available, edible feedstocks using well-established conversion technologies. Most biofuels in use today are classified as 1st Generation. This includes ethanol produced via fermentation of sugars (from corn, sugar cane, sorghum, etc.) and biodiesel produced via transesterification of triglycerides (from vegetable oils and animal fats).

The term “2nd Generation” can refer to biofuels produced from either advanced, non-food feedstocks, or produced via advanced processing technology (or both). Examples of advanced feedstocks include lignocellulose and non-edible triglycerides (such as jatropha and algae). Examples of advanced processing technology include catalytic hydroprocessing of triglycerides and thermal conversion (gasification and pyrolysis) of lignocellulose.

In this paper, which is focused on biodistillate fuels, the term “1st Generation” is used to refer to biodiesel produced via transesterification of edible triglycerides (including waste cooking fats and oils). The term “2nd Generation” is used to refer to Renewable Diesel, Green Diesel, and biodiesel produced via transesterification of non-edible triglycerides. To avoid confusion about variable meanings, the term “3rd Generation” (or other similar terms) is not used in this paper.

INFORMATION SOURCES

Much of the effort in this study consisted of a thorough review of the technical literature regarding feedstocks, production technologies, properties, characterization, testing, performance, and environmental impacts of biodistillate fuels. An excellent starting point for information on all these topics is *The Biodiesel Handbook*,⁽⁸⁾ published in 2005. This handbook consists of numerous chapters on these individual topics, written by experts in each area.

With the field of biodistillates being fairly young, our literature search focused on recent years (2000 to the present) though selected older items of interest were also reviewed. The principal sources used to locate the relevant literature are the following five:

1. Web of Science: Used to search peer-reviewed publications in over 6000 scientific journals/periodicals.

2. SAE literature search engine: Used to search literature published by the Society of Automotive Engineers, International (SAE).
3. ASME literature search engine: Used to search literature published by the American Society of Mechanical Engineers (ASME).
4. DOE citation database: Used to search DOE reports and other DOE-sponsored work reported in conference presentations and technical reports.
5. Trade literature, patents, and other sources: Web sites of trade organizations, fuel producers and marketers, governmental agencies, and other relevant entities were searched to obtain additional information of interest. Also, a few patents of particular interest were reviewed.

Based primarily upon review of abstracts, a reasonably comprehensive bibliography of literature that is relevant for this study was constructed. In the process, specific biodiesel/renewable diesel topics discussed in each literature report were identified. Topic categories were selected to correspond to the organizational structure of the final report, including the following 6 areas:

1. Feedstocks
2. Fuel production technology
3. Fuel properties and specifications
4. Vehicle emissions
5. Fuel handling and performance
6. Life-cycle analysis

The final bibliography, consisting of approximately 1000 citations, was constructed as an Excel Worksheet. This complete bibliography is available in the CRC report.⁽³⁾ Of greater use to most readers is the much smaller bibliography subset containing about 50 citations judged to be most critical for gaining a thorough understanding of the biodistillate technical topics of greatest interest to the automobile and fuels industries. This abbreviated bibliography is included here as Appendix II.

The subject areas related to biodistillate fuels are currently very active, with about 20-30 new items of interest appearing in the literature each month. Because of this rapid expansion of information, the literature search was updated several times throughout the course of this study. The reader should be aware that numerous additional, relevant publications have appeared since the end of 2008.

As shown in Fig. 1, most literature of interest is very recent. Over 75% of relevant journal papers -- and 75% of SAE papers -- have appeared within the past 3 years. In this figure, the category called "Papers" consists mainly of SAE and ASME papers. The category called "Reports" consists mainly of governmental reports (especially from DOE) and company publications. The largest category, called "Journals," consists of peer-reviewed papers appearing in dozens of different science and engineering periodicals.

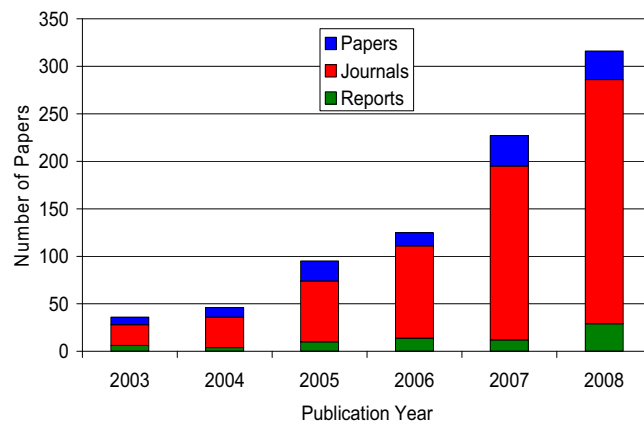


Figure 1. Biodistillate Fuel Publications by Year

POLICY DRIVERS FOR BODISTILLATE FUELS

U.S. FEDERAL

In the U.S., the current dominant policy driver for biodistillate fuels is the recently enacted Energy Independence and Security Act of 2007 (EISA).⁽⁷⁾ (Prior to EISA, the main driver for biodistillates was the \$1/gallon blenders' tax credit.) Through EISA, for the first time, Congress has established specific, volumetric requirements for biomass-based biodiesel of 500 million gallons/year (mg/y) by 2009, ramping up to 1 billion gallons/year (bg/y) by 2012. With current on-road diesel fuel usage in the U.S. at approximately 40 bg/y; the maximum EISA biodiesel requirement represents about 2.5% of this total.

EISA also established a total RFS requirement of 36 bg/y, to be met by 2022, with 21 bg/y of this coming from "advanced biofuels," meaning fuels derived from renewable biomass (excluding ethanol derived from corn) that achieve at least a 50% reduction in GHG emissions, on a life-cycle basis. Biodiesel and renewable diesel may both qualify as "advanced biofuels," though this determination has not yet been finalized. Figure 2 shows the U.S. renewable fuels production requirements stipulated in EISA, as well as the earlier requirements under the 2005 Energy Act. Also shown in this figure are historical production volumes of ethanol and biodiesel from 1999 to 2007.

U.S. STATES

Several U.S. States have also established policies to promote greater use of biodiesel. One of the most aggressive states is Minnesota, which established a statewide B2 requirement in 2005.⁽⁹⁾ More recently, Minnesota has adopted a measure that will require increasing from B2 to B20 by 2015.⁽¹⁰⁾ The State of Washington has also adopted a Renewable Fuels Standard that requires 2% biodiesel state-wide, beginning in 2009.⁽¹¹⁾

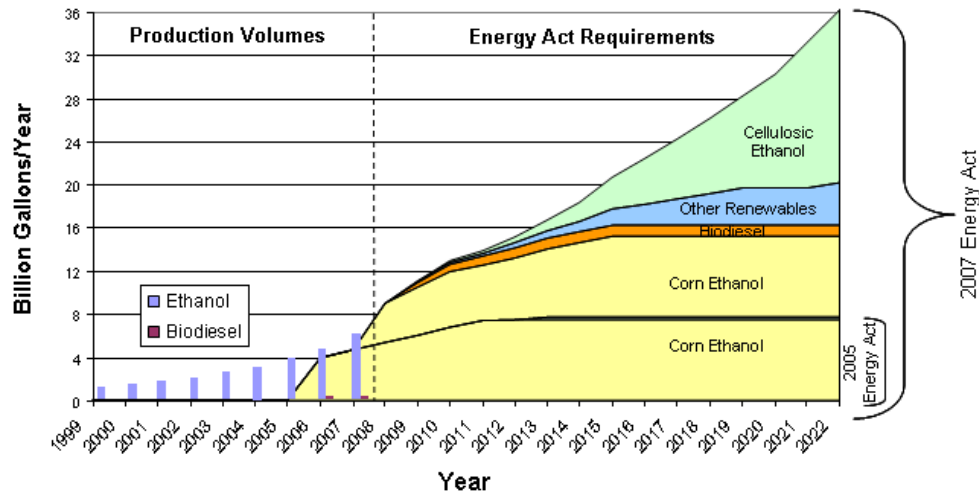


Figure 2. U.S. renewable fuels production and Energy Act requirements (Taken from Reference No. 4)

California is actively promoting increased use of biofuels. As early as 2000 legislation was passed requiring investigation of ways to reduce the State's petroleum dependence.⁽¹²⁾ In response to this, the California Energy Commission (CEC) and the California Air Resources Board (CARB) prepared a joint agency report that recommended increasing alternative fuel usage to constitute 20% of total on-road transportation fuels by 2020, and 30% by 2030.⁽¹³⁾ Subsequently, California Bill AB-1007 required CEC and CARB to "develop and adopt a State Alternative Fuels Plan (AFP) to increase the use of alternative fuels" in California.⁽¹⁴⁾ Biodiesel and renewable diesel are two of the specific biofuels included in this AFP, though there are no specific volumetric requirements for them.

Currently, CARB is conducting an experimental program with biodiesel and renewable diesel to ensure compliance with the AB-1007 requirement of no harm.⁽¹⁵⁾ This program includes detailed engine laboratory work to investigate the emissions impacts of using blends of biodiesel and renewable diesel in petroleum diesel. NOx emissions are of particular interest. This CARB study will also investigate several strategies for mitigating the NOx increase that is anticipated from use of biodiesel.

California is also developing a Low Carbon Fuels Standard (LCFS)⁽¹⁶⁾ and has recently passed legislation (AB-32) to address global warming concerns.⁽¹⁷⁾ AB-32 goals require statewide reduction of GHGs to achieve the 2000 level by 2010, the 1990 level by 2020, and 80% below the 1990 level by 2050. These reductions will be based upon "life-cycle values" by a mechanism that is just now being defined.⁽¹⁸⁾ Meeting California's LCFS and GHG reduction goals will require various aggressive measures, including extensive use of biofuels.

Very recently, Massachusetts adopted legislation, the Clean Energy Biofuels Act, that mandates inclusion of biodiesel in all diesel fuel and heating oil.⁽¹⁹⁾ The biodiesel fraction begins at 2% in 2010, and then increases by an additional 1% absolute per year until

reaching 5% in 2013. In addition, this legislation requires Massachusetts to develop a LCFS (similar to California's) that would reduce GHG emissions from the transport sector by 10%.

In Illinois, state tax policy has prompted use of a unique biodiesel blend, B11. According to the 35 ILCS 105 Use Tax Act, biodiesel blends above B10 are granted preferential tax treatment.⁽²⁰⁾ To take advantage of this situation, B11 has become quite common in Illinois.

EUROPE

Biodiesel has been produced and used in Europe to a much larger extent than elsewhere – particularly in Germany, France, and Italy.^(21,22) While each country has its own policies and incentives, broad European Union (EU) policies have also been established. In 2003, EU Directive 2003-30-EC established targets for biofuels content of transportation fuels.⁽²³⁾ This directive requires biofuels to constitute 2% of transport fuels by 2005, and grow by 0.75% absolute per year until reaching 5.75% in 2010. These targets apply to all transportation fuels, not just diesel fuel, though 75-80% of the requirement is being met by use of biodiesel. Approximately 20% of the EU biofuels requirement is currently being met with bioethanol, and the small remainder is being met with straight vegetable oil (SVO).⁽²⁴⁾

The EU has also defined a "benchmark" of achieving 20% biofuels by 2020, though there is no legally binding requirement for this. At present, this 20% benchmark seems very difficult to attain. A reduced target of 10% biodiesel by 2020 has been proposed and is now being discussed within the EU.

OTHER COUNTRIES

Many other countries are beginning to develop policies to promote greater use of biodiesel.⁽²⁵⁾ Those of particular note are Brazil, China, and India.⁽²⁶⁾ In 2004, Brazil enacted a National Biodiesel Production Program

(PNPB) which established a mandate for all petroleum diesel fuel to contain biodiesel by 2008.⁽²⁷⁾ Later legislation in 2005 (Federal Law 11.097 and Decree 5448) defined the requirement of 2% biodiesel by 2008 (estimated to be 222 mg/y) and 5% biodiesel by 2013 (estimated to be 634 mg/y).

China recently established a Renewable Energy Law which calls for biodiesel consumption of 2 million tons/year (mt/y; approx. 600 mg/y) by 2020.* An interim goal of 0.2 mt/y (approx. 60 mg/y) by 2010 is also in place. The current goals are much less aggressive (by an order of magnitude) compared to targets China had set previously (3 bg/y by 2010; 5 bg/y by 2020). A major reason for this less aggressive stance is China's concern about food security, and the potential competition between food and fuel uses of vegetable oil feedstocks.

In India, the Central Government developed a "National Mission on Biodiesel" in 2003. Subsequently, a detailed project report was developed to lay out a national plan for promoting increased production and use of biodiesel. This plan emphasizes greatly increased cultivation of *jatropha curcas*, and use of its seed oil as a biodiesel feedstock. The government also established a target of 5% biodiesel by 2007 (estimated to be 0.78 bg/y), with a longer term goal of 20% by 2020 (estimated to be 6.71 bg/y).

The nominal sum of these policy-driven biodistillate volumetric requirements is approximately 23 bg/y, as shown in Fig. 3. However, many of these requirements were based upon very optimistic assumptions of feedstock availability and economics. Now having more realistic figures, several countries forecast lower biodistillate production volumes. This leads to expectations that the actual biodistillate volumes in 2020 will likely be only about 6.5 bg/y, which represents a 2.5 fold increase from today's production level. Achieving this projected 2020 level of 6.5 bg/y will require an annual growth rate of about 8%.

BIODIESEL VOLUMES AND FEEDSTOCKS

Recent growth of biodiesel production and use around the world has been dramatic, though exact figures are somewhat difficult to obtain and confirm. In this section, we summarize information gleaned from global market surveys (especially Biodiesel 2020⁽²⁶⁾), industry web sites (especially NBB⁽²⁸⁾ and EBB⁽²⁹⁾), and other published sources to present a picture of current and future fuel volumes and feedstocks.

* In most countries outside the U.S., biodiesel production and usage requirements are expressed as million metric tonnes per year (mmt/y). In this paper, we have converted all mmt/y values to U.S. volumetric values of mg/y. Assuming a specific gravity of 0.88 for biodiesel, 1 metric tonne equals 300 U.S. gallons.

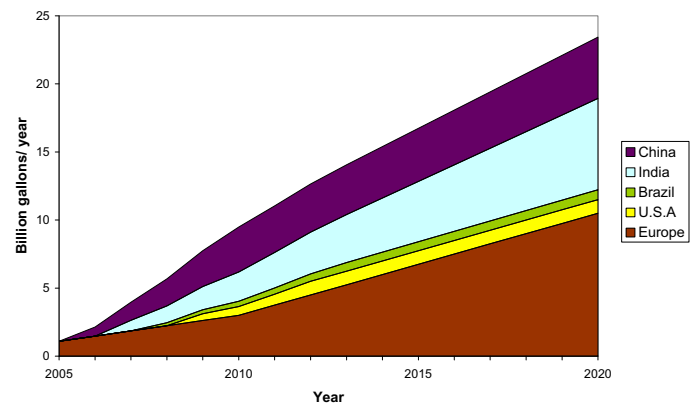


Figure 3. Policy-Driven Biodiesel Requirements

CURRENT/CONVENTIONAL FEEDSTOCKS

While alternative feedstocks are now receiving increased attention, the only biodistillate feedstocks used commercially to-date have been triglycerides from animal fats and seed oils. Figure 4 gives an overall summary of biodiesel production around the world. Clearly, Europe has been – and continues to be – the dominant region for biodiesel.

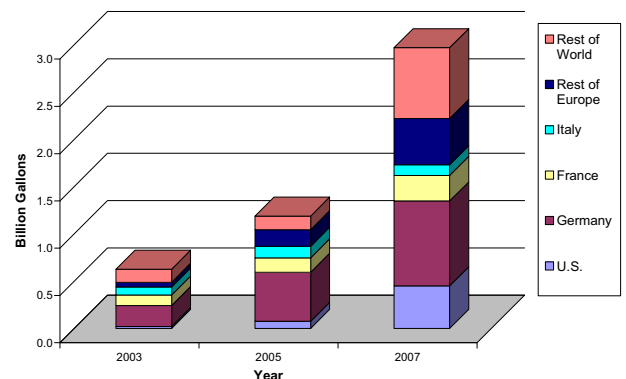


Figure 4. Global Growth in Biodiesel Production

In Europe, the main biodiesel feedstock is rapeseed oil, while soybean oil dominates in the U.S. However, increasing diversity in feedstocks is occurring globally, as the demand for conventional feedstocks is beginning to exceed supply, and producers seek alternative, less expensive feedstocks. In addition, many other oil-bearing plants are now being investigated, with several offering the possibility of greater yields than rapeseed or soybean. This is shown below in Table 1. Of course, actual yields vary significantly depending upon soil type, water availability, fertilizer use, climatic conditions, and other factors.

Europe

According to the European Biodiesel Board (EBB), in 2008 there were 185 fully operational biodiesel plants in the EU, with another 58 under construction. Europe has dominated the global biodiesel industry to-date, with approximately 80% of global production. Currently, the

overall share of biodiesel in the European diesel pool is between 2 and 3%, though the EU goal is to reach a level of 5.75% by 2010. The top three European producers of biodiesel are Germany, France, and Italy, though nearly every EU country has some production, as shown in Fig. 5.^(26,22)

Table 1. Potential Biodistillate Output

Feedstock	Potential Yield, gallons/acre	Source of Info (Reference Nos.)
Corn	18	(30,31,32)
Soybean	40-55	(26,30,31,33,32)
Canola (Rapeseed)	110-145	(26,30,31,32)
Sunflower	102	(31)
Safflower	83	(30)
Cotton	35	(31)
Mustard	60-140	(26)
Jatropha	175-200	(26,31,32)
Coconut	290	(32)
Palm Oil	600-650	(26,30,31,32)
Algae	>5000	(26,30,32)

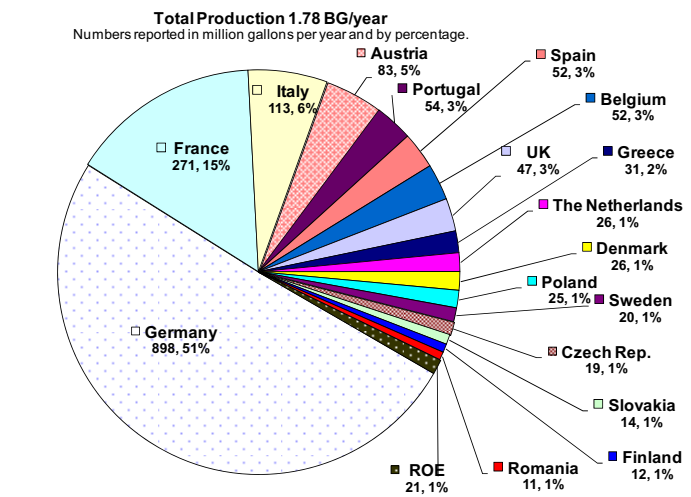


Figure 5. European Biodiesel Production by Country - 2007

While European biodiesel production has been growing, production capacity has grown even faster. This is illustrated in Fig. 6, which shows that in 2007, capacity was twice as large as production. This underutilization of capacity became even more severe in 2008, as difficulties with feedstock supply and cost occurred, and biodiesel tax incentives were reduced.

Despite agricultural incentives and use of set-aside lands for rapeseed cultivation, the amount grown is insufficient to satisfy the goal of 5.75% biofuel by 2010.⁽³⁴⁾ To help meet this policy-driven mandate, Europe has imported significant volumes of biodiesel in recent years – both from the U.S. (soybean-based) and

from Southeast Asia (palm-based). However, due to concerns about sustainability, biodiversity, and GHG emissions, the EU’s Environmental Committee amended their fuel quality directive in late 2007 to ensure that biofuels must meet strict environmental goals.⁽²⁴⁾ In effect, this will restrict the importation of palm oil from Southeast Asia.

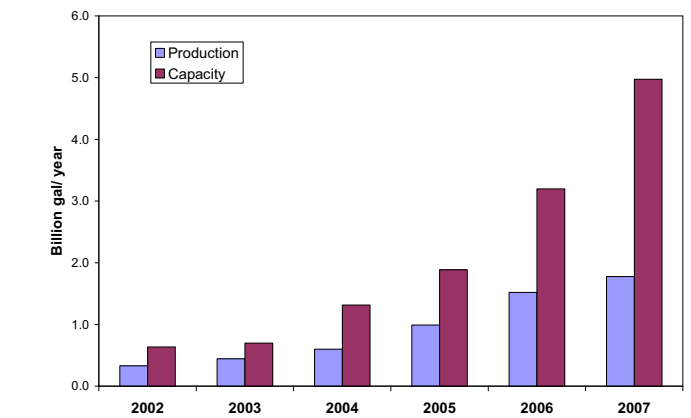


Figure 6. European Biodiesel Capacity and Production

Europe’s reliance upon rapeseed as feedstock has now become very restrictive, as the supply is far less than demand, leading to very high feedstock costs. (80% of total biodiesel cost is attributed to feedstock.) Other, lower-cost feedstocks (such as yellow grease and tallow) are beginning to be used, but their availability is also very limited. For continued growth of the European biodiesel industry, significant new feedstocks are required, such as algal oils and biomass-to-liquids (BTL) products.

U.S.

Current U.S. diesel fuel consumption is approximately 60 bg/y, with 40 bg/y of this being used for on-road transportation applications. U.S. biodiesel production in 2007 was approximately 450 mg/y, or about 1.1% of the on-road diesel volume. However, much smaller volumes of biodiesel were actually consumed in the U.S., as at least ½ of U.S. produced biodiesel was exported to Europe.⁽²⁶⁾ With phase-in of the U.S. EISA requirement of 1 bg/y biodiesel (by 2012), it is likely that a larger share of U.S. produced fuel will remain in this country.

Recent growth in the U.S. biodiesel industry has been very rapid. Figure 7 shows both biodiesel production and total plant capacity over the past several years. This illustrates that while production has grown significantly, capacity growth has been even more dramatic. Consequently, capacity utilization is declining. Utilization was 42% of capacity in 2006, but was estimated to be below 25% in 2008.⁽²⁶⁾ Similar to the European situation, this underutilization is a serious problem for the U.S. industry, caused by limited availability and high costs of feedstocks.

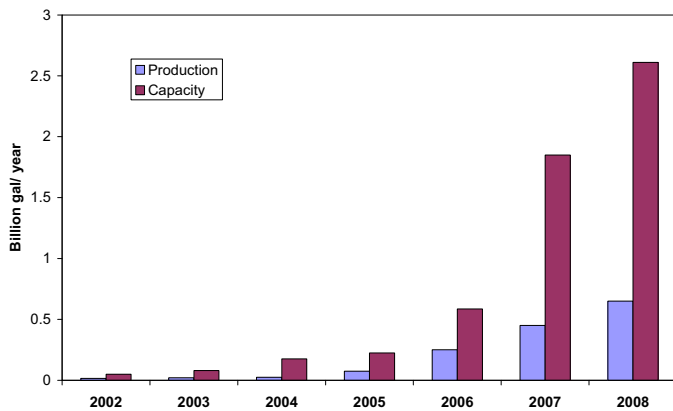
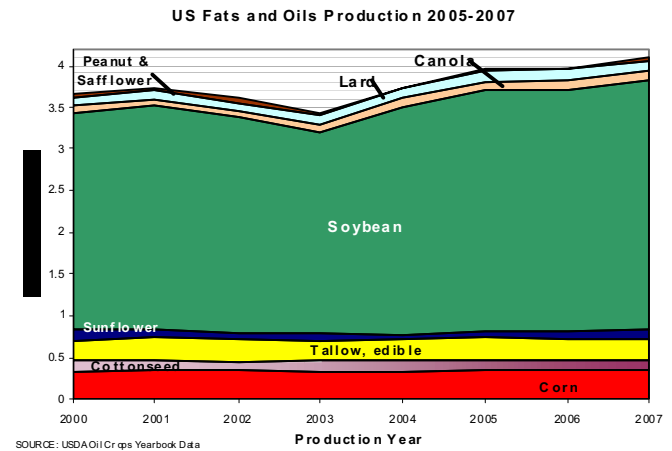


Figure 7. U.S. Biodiesel Capacity and Production

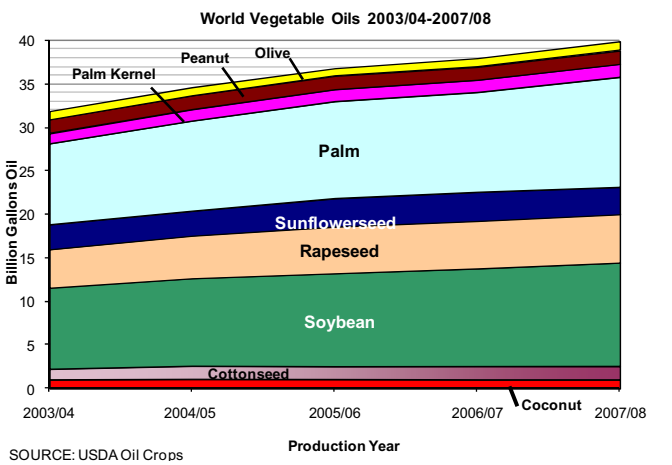
In the U.S., approximately 70 million acres of farmland are used for soybean cultivation. The fraction of the soybean crop used for biodiesel production is small, but increasing. Accurate determinations are difficult to make, since only a relatively small fraction of the soybean is used for fuel production, while most is used for animal feed and other purposes. However, it is estimated that the fraction of total soybean crop devoted to biodiesel was 6% in 2005-2006, 8% in 2006-2007, and could reach 20% in 2008.⁽²⁶⁾ A recent DOE study has concluded that a 3 bg/y U.S. biodiesel industry would require 30 million acres of cropland to be used for seed oil production.⁽³⁵⁾ Achieving this level will also require substantial increases in seed oil yield per acre. Numerous R&D efforts are underway to genetically modify soybeans (and other crops) to enhance yields and improve fuel properties.^(36,37) In addition, improved agricultural practices (fertilizer inputs, low tillage, and other) are leading towards higher yields.

To help put these figures into perspective, trends in total vegetable oil production over the past several years are shown in Figure 8. (Fig. 8a shows U.S. production; Fig. 8b shows world-wide production.) These data were obtained from the Economic Research Service of USDA.⁽³⁸⁾ Current soybean oil production in the U.S. has increased considerably over the past few years, and currently stands at approximately 3 bg/y, with about 0.5 bg/y of this being used for biodiesel production. This amount would need to double to 1 bg/y to satisfy the EISA biomass-based diesel requirement by 2012. Alternatively, greater use of other feedstocks, such as canola, could be employed to satisfy these requirements.

As shown in Fig. 8b, equally rapid growth in vegetable oil production has occurred outside the U.S. Over the past 5 years, total world-wide vegetable oil production has increased at a rate of approximately 7% per annum. The largest global contributor is palm oil, followed by soybean, rapeseed, and sunflower seed.



SOURCE: USDA Oil Crops Yearbook Data



SOURCE: USDA Oil Crops

Figures 8a,b. Vegetable oil production trends: (a) U.S., (b) Worldwide

Growth in total biodiesel capacity in the U.S. is being driven by introduction of several very large production plants. For example, Imperium Renewable Corp. has opened a 100 mg/y plant in Grays Harbor, Washington; Green Hunter Energy has opened a 100 mg/y plant in Houston. Also, ConocoPhillips and Tyson Foods have announced plans to build the largest U.S. biodiesel plant, at 175 mg/y capacity. (Note: due to changes in tax policy, this Renewable Diesel project has been put on hold.) While the average U.S. plant size is still quite small at 12 mg/y, the trend is towards much larger plants. Figure 9 shows the extent of this growth trend in just one year, between 2006 and 2007. Fewer than 20 plants are responsible for 90% of the total biodiesel produced in the U.S.

In addition to biodiesel plant size increasing, the locations are migrating away from the traditional farm belt regions towards international port locations (Houston, Puget Sound, Boston, etc.) The same trend is occurring globally, with very large biodiesel plants existing (or being built) near Rotterdam, Singapore, and other major port locations. These new locations provide access to a much wider range of potential feedstocks. Thus, the historically close connection between biodiesel and local agriculture is starting to weaken.

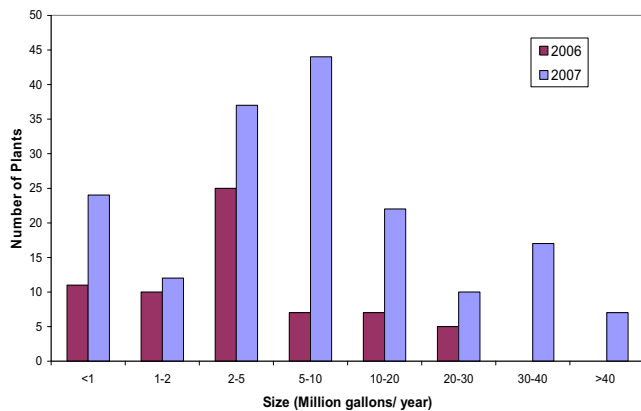


Figure 9. Growth in U.S. Biodiesel Plant Size

Other Countries

Numerous other countries are beginning to develop biofuels in general, and biodiesel in particular.⁽³⁹⁾ In most of these locations, the biodiesel industry is still very small and poorly documented. Three countries that have advanced quite far, and have definite plans for increased development, are Brazil, China, and India. These three are also highlighted in the Biodiesel 2020 Market Survey report,⁽²⁶⁾ and in the more detailed CRC report.⁽³⁾

ALGAL FEEDSTOCKS

Many varieties of microalgae are known to produce large quantities of lipids, containing triglyceride oils, which are potential feedstocks for biodistillate fuels. Of all photosynthetic organisms, microalgae are the most productive users of CO₂, and can fix larger amounts of CO₂ per land area than other plants (see Table 1).⁽⁴⁰⁾ Some of the most commonly cited factors for favoring algae as a biofuel feedstock include the following:

- Rapid growth
- High oil content
- Tolerance for poor quality water
- Use of relatively little land space
- Use of non-productive land
- Mitigation of fossil CO₂ emissions
- Use of wastewater treatment effluents for nutrients
- Production of valuable co-products

Various investigations have been conducted to determine suitable algal strains for maximum growth and oil production under specific conditions. The most comprehensive investigation of algae as a potential fuel feedstock was undertaken by the National Renewable Energy Lab (NREL), who maintained an active Aquatic Species Program (ASP) from 1978 to 1996. The ASP final closeout report was issued in 1998, and remains an excellent source of information about growth conditions and productivities of various algal strains.⁽⁴¹⁾

Due to numerous technical and economic factors, the ASP was discontinued. Now, however, DOE and NREL have expressed renewed interest in promoting algae as

a commercial energy source. In 2008 DOE sponsored an "Algal Fuels Roadmapping" meeting, and plans to issue a roadmap document in mid-2009.⁽⁴²⁾ Reasons cited for this renewed interest include the following:

- High costs of petroleum and other energy sources
- Increased emphasis on energy security
- Concern about CO₂ and climate change
- Advances in biotechnology and photobioreactor designs
- Petroleum refiners' interest in processing lipids

Major barriers to commercial scale implementation of algal systems include numerous technical challenges (maintaining healthy algal growth, avoiding invasive native algae, temperature control, effective light dispersion, reliable harvesting methods, effective extraction of oils, etc.) as well as economics.^(43,44,45) The standard operations currently in use for microalgae biomass production (mainly for producing high-value food supplements) involve open "raceway ponds," with sparging of CO₂-containing gases into the ponds. There is also considerable interest in closed, photobioreactor designs, which help maintain purity of the desired algal strains and offer better control of operating conditions (nutrient levels, irradiation, flow rates, etc.), but with higher capital and operating costs.⁽³²⁾ The economics of algal fuel systems may be improved by combining them with waste water treatment operations that can provide much of the nutrients needed for algal growth.

In addition to lipids, many algal strains produce large amounts of carbohydrates and proteins. The proteins are useful as food/feed supplements, while the carbohydrates are potential feedstocks for fuels via biochemical and thermochemical processing approaches.

Interest in developing algae-to-biofuels systems and technologies is extremely high. Despite this interest, there currently are no functioning, commercial-scale operations producing biodistillate fuels from algae. However, this situation may change soon, as substantial investments by major technology developers and fuel producers are now being made. As one example, the Defense Advanced Research Projects Agency (DARPA) is currently supporting development and demonstration projects to produce military jet fuel (JP-8) from algae.⁽⁴⁶⁾

OTHER TRIGLYCERIDE FEEDSTOCKS

It has been reported that over 350 oil-bearing crops exist in the world.⁽³³⁾ The literature is replete with reports of biodiesel produced from diverse feedstocks. Many of these reports describe use of seed oils from rather obscure, local plants. Table 2 provides a listing of many (but certainly not all) such reports. One feedstock receiving great interest and investigation is *Jatropha*. Very aggressive plans for commercialization of *Jatropha* are being pursued by India and China, in addition to a few other countries. Further information about oil bearing feedstocks is provided in the CRC report.⁽⁹⁾

Table 2. Vegetable Oils used for Biodiesel Production

NORTH AMERICA		SOUTH/CENTRAL AMERICA		ASIA	
Reported Feedstock	Edible	Reported Feedstock	Edible	Reported Feedstock	Edible
Algae	No*	Algae	No*	Ailanthus	No
Beech	No	Andiroba	Yes	Algae	No*
Camelina	Yes	Babassu	Yes	Camelina	Yes
Corn Oil	Yes	Castor Oil	No	Castor Oil	No
Cottonseed Oil	Yes	Coconut Oil	Yes	Cottonseed Oil	Yes
Jatropha	No	Cottonseed Oil	Yes	Hazelnut	Yes
Lesquerella	No	Cumaru		Jatropha	No
Linseed	Yes	Jatropha	No	Karanja	No
Rape Seed	Yes	Lesquerella	No	Linseed	Yes
Safflower	Yes	Linseed	Yes	Mahua	Yes
Soapnut Oil	No	Palm Oil	Yes	Neem	
Soybean	Yes	Peanut	Yes	Olive	Yes
Spruce	No	Rubber Seed Oil	No	Palm Oil	Yes
Sunflower Oil	Yes	Safflower	Yes	Polanga	No
Walnut	Yes	Soapnut Oil	No	Pongamia	No
		Tucum oil	Yes	Poppy Seed	Yes
				Rice Bran	Yes
				Safflower	Yes
				Sesame	Yes
				Soapnut Oil	No
				Spring Mustard	Yes
				Spruce	No
				Vann	Yes
				Walnut	Yes

EUROPE		AFRICA	
Reported Feedstock	Edible	Reported Feedstock	Edible
Algae	No*	Algae	No*
Beech	No	Castor Oil	No
Camelina	Yes	Cottonseed Oil	Yes
Cottonseed Oil	Yes	Crambe	No
Hazelnut	Yes	Cynara	
Jatropha	No	Jatropha	No
Linseed	Yes	Linseed	Yes
Poppy Seed	Yes	Olive	Yes
Rape Seed	Yes	Palm Oil	Yes
Safflower	Yes	Polanga	No
Soapnut Oil	No	Safflower	Yes
Spring Mustard	Yes	Sesame	Yes
Spruce	No	Soapnut Oil	No
Walnut	Yes		

* some algae, or portions of algae, are edible

LIGNOCELLULOSIC FEEDSTOCKS

If plant-derived biofuels are to play a significant role in satisfying transportation fuel demands in the U.S. and elsewhere, it is necessary to consider feedstocks that are more diverse and abundant than triglycerides – such as lignocellulosic biomass. The term “lignocellulose” is used when referring to a combination of the three primary polymers that make up plant cell walls: cellulose, hemicellulose, and lignin. Depending upon plant species and cell type, the dry weight of a cell wall typically contains about 35-50% cellulose, 20-35% hemicellulose, and 10-25% lignin.⁽⁴⁷⁾

Recently, the USDA and DOE collaborated on a study to assess the biomass resource base within the U.S., both currently and in the future.⁽⁴⁸⁾ A particular objective was to determine whether the land resources of the U.S. are capable of producing a supply of biomass sufficient to

displace 30% or more of the country's present petroleum consumption. Achieving this goal was estimated to require a continuous supply of 1 billion dry tons per year (bdt/y) of biomass feedstock.

This so-called “Billion Ton Study” considered several modeling scenarios which included numerous sets of assumptions. In the case of forest biomass resources, the study concluded that today's level of 142 mdt/y could be increased to 368 mdt/y, mainly by: (1) greater use of urban waste residues, (2) use of forest thinnings removed by fire prevention treatments, and (3) greater use of logging residues. Even greater potential biomass amounts are available from agricultural resources. In this area, the Billion Ton Study developed various scenarios having different assumptions regarding crop yields, land use changes, harvesting efficiency, tillage practices, and introduction of perennial crops for biomass. Under optimistic assumptions, it was determined that

approximately 1-bdt/y of lignocellulosic feedstocks could be sustainably produced, without increasing total agricultural acreage in the U.S.

Numerous other assessments of lignocellulosic feedstock availability, logistics, economics, and growth potential have been conducted in recent years. On a national level, these efforts have been driven mainly by DOE and USDA. Relevant documents to consult include the Biomass Multi-Year Program Plan,⁽⁴⁹⁾ the Roadmap for Agricultural Biomass Feedstock Supply,⁽⁵⁰⁾ the Genomics: GTL Roadmap,⁽⁵¹⁾ and the Roadmap for Bioenergy and Biobased Products in the U.S.⁽⁵²⁾

BIODISTILLATE PRODUCTION TECHNOLOGIES

There is a long record of using straight vegetable oil (SVO) as fuel for compression ignition engines, going back to Rudolph Diesel (1853-1913) himself. The literature contains many references to the early use of SVO as a "diesel fuel," and cites numerous advantages of such usage.^(53,54,55,56) Among these advantages are the following:

- SVO is a high energy, easily transported liquid fuel (about 90% the heat content of petroleum diesel)
- Vegetable oils are ubiquitous around the world, making local fuel supply possible
- Some vegetable oils crops can be grown on marginal lands, promoting rural economic development
- Refining SVO involves relatively simple (and inexpensive) processes
- SVO has low sulfur and aromatic levels
- SVO is renewable and biodegradable

On the other hand, SVO has some major disadvantages, which make it unacceptable as a diesel fuel in nearly all situations. Vegetable oils are composed of 90-98% triacylglycerides, commonly referred to as triglycerides, along with small amounts of mono- and di-glycerides, free fatty acids, phospholipids, and other trace constituents.⁽⁵⁵⁾ The molecular weight (MW) range for most triglycerides is 700-950, considerably higher than typical petroleum diesel which has a MW range of 200-350. This results in triglycerides having much higher viscosities than petroleum diesel. Typical viscosities of vegetable oils are 35-60 cSt at 40°C, compared to about 2-3 cSt for petroleum diesel.

The high viscosity of SVO is a major cause of poor fuel atomization that can lead to operational problems of poor combustion, injector coking, deposit formation, and others.^(57,58) Several approaches have been taken to overcome the problem of SVO's high viscosity, and allow vegetable oil-based materials to be used in diesel engines. In general, these approaches can be classified into four groups:

1. Dilution with conventional diesel fuel
2. Microemulsification

3. Transesterification
4. Thermal conversion

Of these four approaches, the first two do not change the chemical structure of the triglyceride molecules, while the second two do. Simple dilution of vegetable oils with petroleum diesel has been widely used, but with mixed success.^(56,59,60) Lower blend levels of SVO (<20%) are generally more acceptable than high blend levels, but long term concerns still remain due to high viscosity, free fatty acid content, storage stability, lube oil thickening, and other problems.^(57,61)

Microemulsions of SVO with alcohols have also been used to reduce viscosity.^(59,60) Often, a surfactant is necessary to maintain stability of the microemulsion. Many different formulations of SVOs, alcohols, and surfactants have been investigated – with somewhat mixed results. Due to difficulties in preparing these microemulsions, maintaining their stability in real-world applications, and gaining consumer acceptance, the use of such fuels has not been widespread.

By far the most common method for overcoming the viscosity problem of SVO is transesterification, though recently there has been growing interest in hydroprocessing and other thermal methods of treating SVO. The remainder of this section deals with these processes.

TRANSESTERIFICATION

Transesterification is the chemical process by which triglycerides are reacted with alcohols to produce fatty acid alkyl esters and glycerol. These fatty acid esters [usually fatty acid methyl esters (FAME)] are commonly known as biodiesel. In the past few years, several excellent reviews on the topic of biodiesel manufacturing have appeared in the literature.^(62,63,64,56) Given below is a discussion of some important aspects of biodiesel production.

Biodiesel Production Chemistry

The basic chemical reactions involved in the production of biodiesel are shown below in Fig. 10. One mole of a triglyceride is reacted with three moles of alcohol (usually methanol) in the presence of an alkaline catalyst to produce three moles of biodiesel and one mole of glycerol. For simplicity, the chemical structures in Fig. 10 only show fully saturated molecules. In reality, triglycerides in fats and oils have varying degrees of unsaturation (carbon-carbon double bonds) which is retained in the biodiesel product. Also, the carbon chain length in triglycerides typically varies from C12 to C20.

For reasons of cost and ease of reaction, the most common alcohol used in the transesterification process is methanol, leading to production of FAME. However, there are also numerous reports of using ethanol in place of methanol, leading to formation of HFAEs.^(65,66,67)

Use of ethanol offers the possibility of total renewable feedstocks, whereas methanol is generally produced from fossil sources (natural gas). Additionally

some locations, such as Brazil, have an abundance of locally-produced, low-cost ethanol.

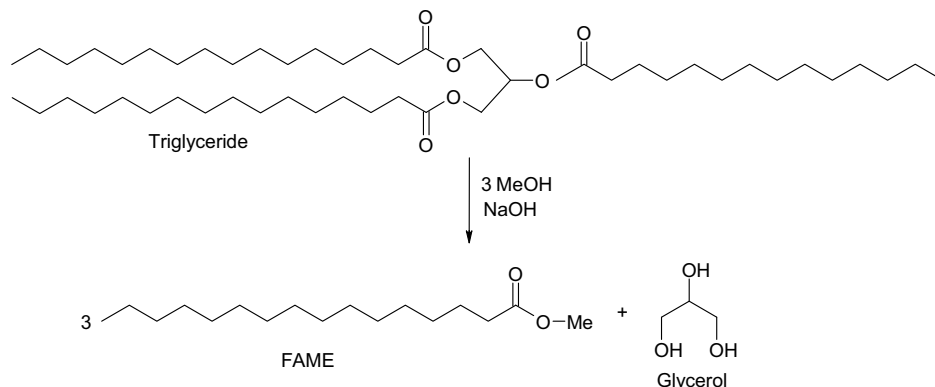


Figure 10. Transesterification Chemistry of Biodiesel Formation (For simplicity, only saturated fatty acids are shown)

Commercial Biodiesel Reaction Conditions

A simplified process flow diagram for producing biodiesel from vegetable oils is shown below in Fig. 11. This depicts a common, small operation utilizing a batch process. Most large biodiesel plants use continuous

processes, which generally include multiple reactors in series, with settling vessels located between the reactors. Several thorough descriptions of common biodiesel production technology are available in the literature.^(64,68)

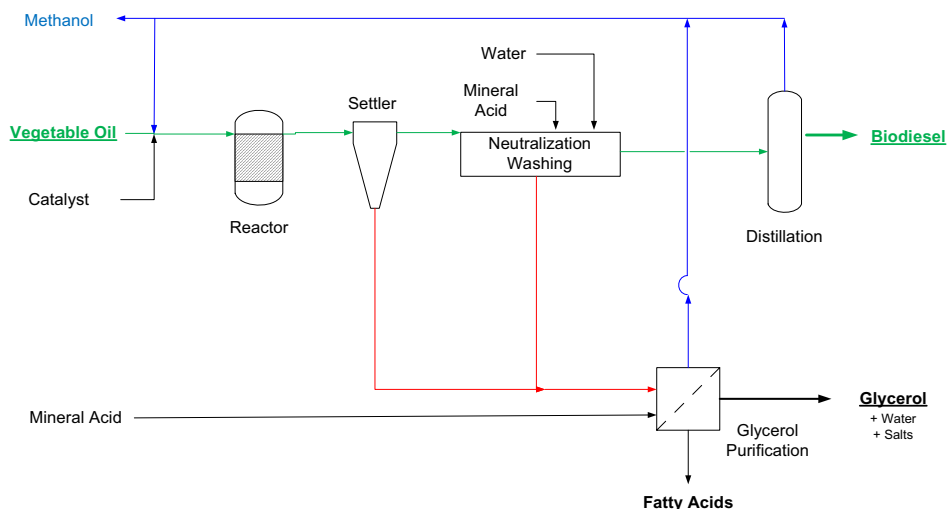


Figure 11. Process Flow Diagram for Typical, Batch-Mode Biodiesel Production

Considerable work has been conducted to determine optimum reaction conditions for producing biodiesel. To some degree, different conditions are required for each triglyceride feedstock. For a given feedstock, numerous factors have been found to have significant impacts on process efficiency and purity of final product.^(56,64,69) Several of the most important factors are discussed below in more detail:

Ratio of Alcohol to Triglyceride

According to the stoichiometry shown in Fig. 10, the theoretical molar ratio of alcohol to triglyceride is 3/1. However, in most commercial operations, a much higher ratio is used – typically around 6/1. The main reason for

using excess alcohol is to drive the transesterification reaction to completion. As shown in Fig. 12, transesterification of triglycerides proceeds through a stepwise process involving intermediate production of a diglyceride and a monoglyceride, before the final glycerol product is released. At each of these three steps, a molecule of FAME is produced. To ensure acceptable biodiesel product quality, it is critical for these reactions to proceed to completion, so that concentrations of the intermediate diglycerides and monoglycerides in the finished fuel are kept very low. Other reasons for using excess alcohol are to provide some solvency for the reactants and to assist in separation of glycerol from the product FAME. However, use of an excessive amount of alcohol is also a concern, as it

considerable energy is required to distill the unreacted alcohol from the final FAME product.

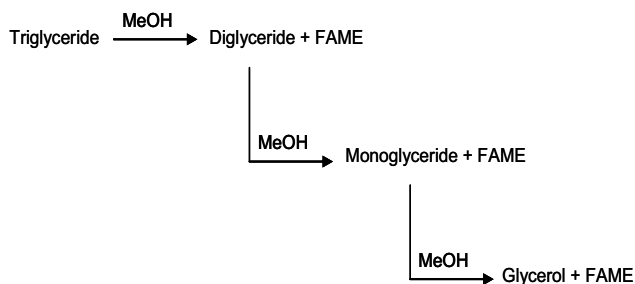


Figure 12. Step-Wise Process of Biodiesel Formation Type of Alcohol

Although nearly any alcohol could be used in the transesterification process, in most cases, methanol is the alcohol of choice. This is not only an economic decision; several technical factors are also involved. First, the transesterification reaction rate is significantly faster with methanol than with higher alcohols.^(70,71,72) Also, higher alcohols are better solvents for glycerol and other impurities, making it more difficult to separate these materials from the desired biodiesel product. Finally, higher alcohols (including ethanol) are more difficult (and more expensive) to dry. As discussed below, the presence of water is very problematic in biodiesel production processes.

Purity of Triglyceride Feedstock

The amount and type of impurities present in triglyceride feedstocks are critical factors dictating optimum conditions for transesterification. Perhaps most important is the free fatty acid (FFA) content of the starting feedstock. As shown in the reactions of Fig. 13, FFA will react with alkali catalyst to produce salts. This is very detrimental. Not only does salt formation “waste” the energy-rich FFA by eliminating its contribution to the final fuel, it also causes foaming and separation problems. To overcome this, it is recommended that feedstocks containing over 1% FFA first undergo a preliminary acid-catalyzed esterification process.⁽⁶²⁾ This pretreatment produces FAME and water, while the triglyceride remains largely unreacted. Following neutralization and drying, the conventional alkali-catalyzed transesterification reaction is then conducted to complete formation of the biodiesel. This 2-step approach appears to be used quite widely.^(73,74,75) While this 2-step process for biodiesel production adds complexity and equipment, it can be financially advantageous since it allows for use of less expensive triglyceride feedstocks, such as waste cooking oils and soapstocks.^(62,73,76,77,78,79)

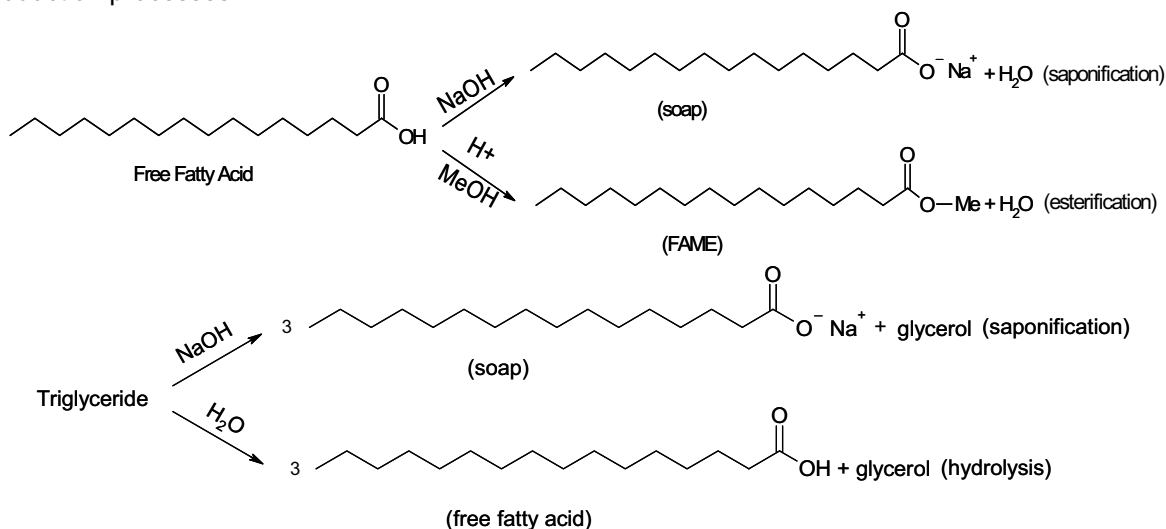


Figure 13. Other Important Reactions in Biodiesel Production Processes (For simplicity, only saturated fatty acid structures are shown)

Amount and Type of Catalyst

There has been much research to investigate use of different catalysts for biodiesel production, but commercially, only two general types are used in significant amounts: (1) hydroxides (NaOH and KOH) and (2) methoxides (NaOMe and KOMe). For reasons of cost and availability, NaOH is often the catalyst of choice.^(62,71) However, sodium methoxide (NaOMe, also

called sodium methylate), is becoming increasingly common, despite higher cost, due to its ease of storage and handling, and the improvements in process efficiency that result.^(69,80) In particular, use of sodium methoxide avoids the problems associated with water formation that occur when hydroxide catalysts are used with alcohols (e.g. NaOH + MeOH → NaOMe + H₂O). The presence of water promotes hydrolysis of triglycerides, producing FFA with the attendant problems

of soap formation (see Fig. 13 above). An additional problem with KOH (and to a lesser extent with NaOH) is that when purchased as a “pure” solid, it still contains appreciable amounts of water.

Reaction Time and Temperature

Reaction time and temperature are generally optimized for each situation. For commercial, alkali-catalyzed, batch-mode transesterification with methanol, typical reaction temperatures are in the range of 50-60°C (slightly below the boiling point of methanol), with a reaction time of about 1-hour.^(68,63,64) With use of ethanol, slightly higher reaction temperatures are used.

Despite many years of experimentation, and the existence of a rich literature database, considerable efforts continue today in defining optimum process conditions for producing biodiesel via transesterification of triglycerides. Evidence of this is the appearance of several very recent publications which describe optimization of reaction conditions for transesterification of rapeseed oil,⁽⁸¹⁾ safflower oil,⁽⁸²⁾ linseed oil,⁽⁸³⁾ and rice bran oil.⁽⁸⁴⁾

Modifications to Typical Transesterification Conditions

The sections above presented typical commercial biodiesel processes and discussed the most important factors affecting biodiesel production. However, several other process issues are under active investigation. The most important of these include: (1) use of co-solvents, (2) use of heterogeneous catalysts, (3) application of supercritical reaction conditions, and (4) use of ultrasonic and microwave irradiation. These issues are more fully discussed in the CRC report.⁽³⁾

Glycerol Considerations

Production of glycerol by-product during the transesterification of triglycerides can lead to numerous problems. While high purity glycerol has many commercial outlets,⁽⁸⁵⁾ the increasing production of biodiesel has led to a surplus of low quality glycerol, which requires extensive treatment to increase its value.⁽⁸⁶⁾ In rough terms, 1 lb. of glycerol is produced for every 10 lbs of biodiesel. The purity of glycerol at a typical, small biodiesel production plant is only 80-85%, even after water washing and further clean-up.^(62,70) Purification involving distillation is generally performed off-site at a glycerol refinery. In contrast, large biodiesel production plants typically refine glycerol on-site.

The presence of glycerol as an impurity in biodiesel can create fuel quality problems and off-spec product. Water washing is typically employed to remove glycerol from biodiesel, but several washes – with intermediate separation steps – are required.⁽⁸⁷⁾ Clearly, any process that avoids glycerol formation offers an advantage in this area.

Developing alternative, higher-value uses of glycerol has been identified by NREL as an important R&D area,⁽⁸⁸⁾ as this would improve the overall economics of biodiesel production. Currently, low-grade glycerol is used as a boiler fuel, where it can be cost competitive with natural gas.⁽⁸⁹⁾ With modest upgrading, glycerol can be used as an animal feed. Numerous approaches are also being investigated to use glycerol as a feedstock for the production of higher-value chemicals, including 1,3-propanediol,^(90,91) epichlorohydrin,⁽⁹²⁾ propylene glycol,^(93,94) and numerous other 3-carbon molecules.⁽⁸⁹⁾ One recent report describes use of glycerol as feedstock for a steam reforming process to produce hydrogen.⁽⁹⁵⁾

CATALYTIC HYDROPROCESSING

In recent years, several academic and industrial organizations have investigated the conversion of triglyceride feedstocks into biodistillate products via catalytic hydroprocessing. One of the first commercial processes was reported in 2005, by Neste Oil Corporation.^(96,97) The product, called NExBTL, is a paraffinic hydrocarbon material (no aromatics, sulfur, oxygen, or nitrogen) suitable for blending into conventional diesel fuel. At about the same time, UOP in conjunction with Eni, reported a similar process called Ecofining™.^(98,99)

The Neste Oil process involves a separate fuel processing unit that is integrated within a petroleum refinery.^(97,100) A variety of vegetable oils and animal fats can be used as feedstocks. The preferred hydroprocessing operating conditions are proprietary. Besides the hydroprocessing unit itself, the entire Neste Oil renewable diesel process includes pre-treatment of the feedstocks and clean-up of the final product. The hydrotreated vegetable oil (HVO) product is called “NExBTL” because it is regarded as a Next Generation biomass-to-liquids (BTL) fuel. Neste Oil indicates that the product composition is similar to that produced from other gas-to-liquid (GTL) or BTL processes.

UOP has investigated the production of renewable diesel by hydroprocessing vegetable oils, both in a stand-alone unit and by co-processing with petroleum feedstocks in a conventional diesel hydrotreater.⁽⁹⁸⁾ While acceptable quality renewable diesel can be produced by either approach, stand-alone operation is preferred.⁽¹⁰¹⁾ Several reasons for this preference are as follows:

- High total acid numbers (TAN) of some triglyceride feedstocks requires metallurgical upgrades to typical ULSD hydrotreaters.
- Pre-processing equipment is often necessary to remove contaminants from feedstocks before feeding triglycerides into mid-distillate hydrotreaters.
- Typical operation of ULSD hydrotreaters favors hydrodeoxygenation reactions (loss of water) of triglycerides, producing water that can adversely affect catalyst performance.

- Stand-alone units allow for optimized selection of catalyst type and operating conditions, which can produce a renewable diesel with improved low temperature operability.

In contrast to the Neste Oil and UOP/Eni Ecofining™ processes, a process recently developed by ConocoPhillips involves co-feeding triglycerides with petroleum feedstocks for hydroprocessing in a conventional diesel hydrotreater unit used for desulfurization.⁽¹⁰²⁾ While detailed processing conditions are proprietary, typical hydrodesulfurization (HDS) conditions are said to be used. Other companies reported to be developing commercial hydroprocessing of triglyceride feedstocks include Petrobras, BP, and Syntroleum.⁽¹⁰³⁾

In all of these hydroprocessing cases several reactions occur, including hydrogenation of the olefinic groups within the triglyceride, decarbonylation (loss of CO), decarboxylation (loss of CO₂) and hydrodeoxygenation (loss of H₂O).^(104,105) These reactions are depicted below in Fig. 14. In these hydroprocessing reactions, most of the glycerol component in the original triglyceride is converted to propane, while most of the carboxyl carbons are converted to CO or CO₂. The ratio of these products varies with the type of catalyst and operating conditions being used. Light hydrocarbon gases (methane, ethane, and propane) and naphtha are produced in some cases. Since triglyceride compositions are dominated by even-numbered fatty acid components, removal of the carboxyl group results in biodistillates consisting mainly of odd-numbered paraffins. This fact could provide a useful way to determine the renewable diesel content in a blend of petroleum diesel fuel.

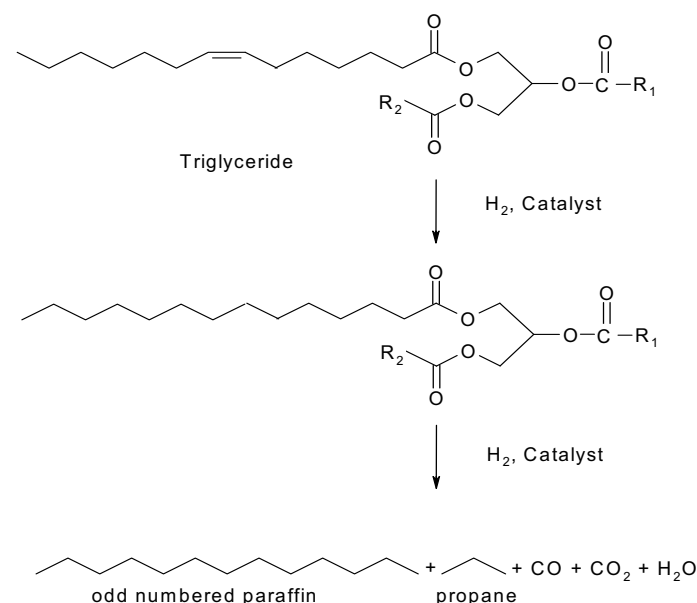


Figure 14. Hydroprocessing of Triglycerides

Various terminology is used to define the biodistillates produced via hydroprocessing. Besides "NExBTL," other common terms are Renewable Diesel, Green Diesel, and hydrotreated vegetable oil (HVO). (In this paper, we refer to all these materials as "renewable diesel.") These products all share several important advantages over conventional biodiesel – including higher mass energy content, improved oxidative stability, complete absence of sulfur and nitrogen, and blending behavior that is totally compatible with petroleum diesel blendstocks. Additionally, the properties of renewable diesel do not vary with feedstock composition as significantly as do the properties of biodiesel.

Lack of glycerol production is a significant benefit of all renewable diesel production processes. In addition, no alcohol is required for this process. Furthermore, production of renewable diesel within a petroleum refinery allows for better integration with other refinery operations, and provides access to product testing laboratories. Finally, hydroprocessed biodistillates may exhibit emissions advantages over conventional biodiesel, though the evidence for this is rather limited.

One disadvantage of hydroprocessed biodistillates is their relatively poor lubricity characteristics. In this regard, they are similar to ULSD, or to paraffinic blendstocks produced by Fischer-Tropsch (FT) or other GTL processes. All these materials generally require additive treatment, or mixing with higher lubricity blendstocks, to achieve satisfactory performance. Other disadvantages of renewable diesel production include the need for additional hydrogen within the refinery, and the high capital cost of hydroprocessing equipment.

PYROLYSIS

In this review, the term "pyrolysis" is used quite broadly to include a variety of processing technologies by which organic feedstocks are treated with heat to break them down to smaller molecules. In the broadest sense, this definition could also include gasification and Fischer-Tropsch (FT) processes by which organic feedstocks (fossil or biomass) are converted to liquid fuels via intermediate production of synthesis gas (syngas). The topic area of gas-to-liquids (GTL) is vast, and well beyond the scope of this review on biodistillates. However, several types of pyrolysis applications that are of direct relevance to the topic of biodistillates are described in the CRC report.⁽³⁾ These include: (1) pyrolysis of triglycerides, (2) gasification and pyrolysis of lignocellulose, and (3) other thermal processes.

MATURITY OF BIODISTILLATE PRODUCTION TECHNOLOGIES

All technologies for producing biodistillate fuels are not equally mature. For example, transesterification of vegetable oils to produce FAME is well established, and has been in commercial application for many years. In contrast, gasification and pyrolysis of lignocellulose

Status of Technologies for Biodistillate Production

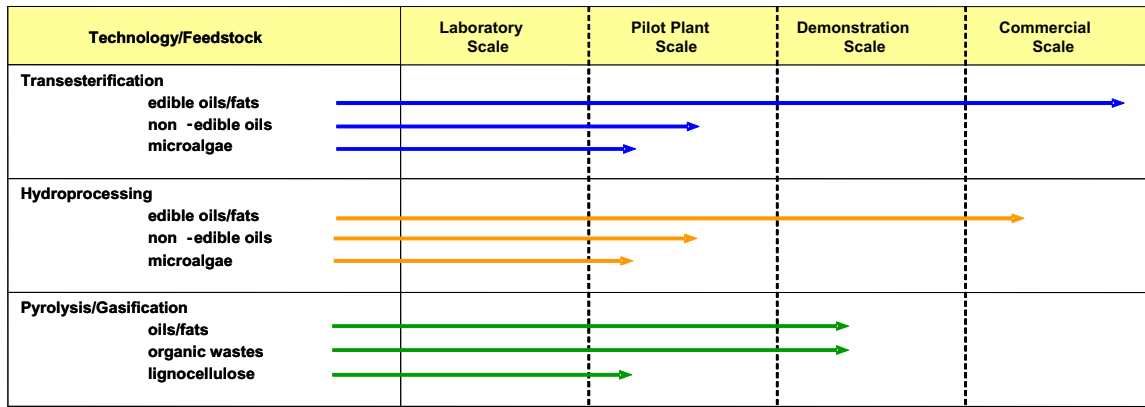


Figure 15. Status of Technologies for Biodistillate Production

feedstocks are far from commercialization. Figure 15 presents the authors' assessment of the technology status for biodistillate production. The progression from laboratory, to pilot plant, to demonstration, to commercialization requires differing lengths of time for each situation. However, in a general case, 2-5 years would be required for each step.

FUEL PROPERTIES AND SPECIFICATIONS

Biodiesel fuel consists of mono-alkyl esters of long-chain fatty acids derived from vegetable oils or animal fats. Since these oils and fats are quite varied in their composition, biodiesel fuels prepared from them also have variable composition. In contrast, the compositions of renewable diesel fuels are less closely tied to their feedstocks, since the hydroprocessing conditions used produce completely saturated paraffins.

Consisting of oxygenated species, biodiesel differs from petroleum diesel in many respects. Some of the most important areas of difference are illustrated below in Table 3, which compares typical properties of biodiesel and petroleum-derived No. 2 ULSD. Also shown here are typical properties of renewable diesel. These values were derived by compositing information from several literature sources.^(99,97,98,96,106,107,108) The properties of individual fuels can vary from those shown here.

Because of its considerable oxygen content, biodiesel has lower carbon and hydrogen contents compared to diesel fuel, resulting in about a 10% lower mass energy content. However, due to biodiesel's higher fuel density, its volumetric energy content is only about 5-6% lower than petroleum diesel. Typically, biodiesel has somewhat higher molecular weight than petroleum diesel, which is reflected in slightly higher distillation temperatures (as measured by T_{90}). Being largely straight chain esters, most biodiesel fuels have excellent cetane numbers – typically higher than No. 2 diesel fuel. The viscosity of most biodiesel fuels is significantly higher than petroleum diesel, often by a factor of 2.

Renewable diesel consists mainly of paraffinic hydrocarbons having 15 or 17 carbon atoms. While some renewable diesel fuels contain primarily straight-chain, normal paraffins, others contain appreciable amounts of branched paraffins. As a consequence of their paraffinic structure, renewable diesel fuels have very high cetane numbers and excellent combustion properties. On a mass basis, the energy content of renewable diesel is very high, slightly exceeding that of typical No. 2 diesel fuel. However, due to its relatively low density, the volumetric energy content of renewable diesel is significantly below that of No. 2 diesel, but is similar to a typical biodiesel.

Table 3. Typical Properties of Petroleum Diesel and Biodistillate Fuels

Property	No. 2 Petroleum ULSD	Biodiesel (FAME)	Renewable Diesel
Carbon, wt%	86.8	76.2	84.9
Hydrogen, wt%	13.2	12.6	15.1
Oxygen, wt%	0.0	11.2	0.0
Specific Gravity	0.85	0.88	0.78
Cetane No.	40-45	45-55	70-90
T_{90} , °C	300-330	330-360	290-300
Viscosity, mm ² /sec. @ 40°C	2-3	4-5	3-4
Energy Content (LHV)			
Mass basis, MJ/kg	43	39	44
Mass basis, BTU/lb.	18,500	16,600	18,900
Vol. basis, 1000 BTU/gal	130	121	122