

BIODIESEL POTENTIAL IN ICELAND

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A 30 credit units Master's thesis

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ABSTRACT

The importance of increasing the global share of biofuels in transportation goes without saying. Iceland, where the consumption of fossil fuels is considerable, has a viable potential for introducing biodiesel in its otherwise exceptional renewable overall energy portfolio.

In this study, a full picture of the possibilities of biodiesel production in Iceland was provided. After the theoretical introduction of all major aspects of a biodiesel economy, an assessment of its applicability in Iceland was performed.

A survey of potential feedstocks was performed. It was concluded that in a short term perspective, a small scale production (300-2,000 tons/yr) can be carried out using domestically available waste raw material, and full scale production (15,000-80,000 tons/yr) will depend on imported feedstock.

After laboratory research, including waste vegetable oil (WVO), the main domestic feedstock currently available, the recommendation for the production process of a small production plant was made. It includes acid esterification of free fatty acids (FFA) followed by alkali transesterification and methanol recovery from the reacted mixture. At this stage, distillation of crude FAME was suggested, however further research is necessary.

The full scale production could substitute 8%-44% of the fossil diesel fuel needs for transportation and machinery. The estimated production costs in a full scale biodiesel plant, 0.63-0.76 EUR/L, are within the European average.

PREFACE

The research for this thesis was performed at Mannvit Engineering's facilities and with the company's strong support.

So far, Iceland has had little experience with biodiesel. Mannvit, the largest engineering company in Iceland, has been investigating the biodiesel potential in Iceland for a couple of years and in my opinion, this company will be a strong force behind technological breakthroughs and the merits for biodiesel economy in this country. Given my special interest in the subject, I feel privileged to have been able to learn from these pioneers. My task was merely to gather and report updated information on the development of the involved projects.

My most special thanks go to Asgeir Ivarsson, my thesis advisor and mentor, who has been tactfully guiding and motivating me along the way; thank You for Your hard work, incredible patience and enthusiasm. Never before had I learned so much from one person.

I would like to acknowledge the crew at Mannvit Akureyri. Thank You for a warm welcome and always reaching out for me. Working in this wonderful environment was a real pleasure.

I am endlessly thankful to the RES Academic Administration, who are people with big hearts and open minds: Sigrun Loa Kristjansdottir, Bjorn Gunnarsson, Arnbjorn Olafsson and Gudjon Steindorsson, for making it all happen.

Thanks go to Johann Orlygsson, my academic coordinator, for keeping his finger on the pulse of the project, yet being ever so relaxed, and to my examiner Sigthor Petursson, for a thorough job reviewing my thesis and apt remarks.

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I. INTRODUCTION

The importance of increasing the share of biofuels in the energy portfolio of every country goes without saying. Iceland, a world leader in utilizing renewable energy, still meets a considerable part of its energy demand by burning fossil fuels.

Iceland will have to take part in the increasing world trend of implementing biofuels in the transportation sector, especially in the light of possible prompt accession to the European Union. In the EU, according to the Biofuel Directive, a 10% share of biofuels in transportation is required by the year 2020, and the US Renewable Fuel Standard for 2009 requires a 10.21% share. Brazil has already implemented a mandatory biodiesel participation in the diesel market at 3%, increasing to 5% in 2013.

Diesel fueled vehicles already constitute about 50% of the European transportation fleet. The related demand caused a fuel shortage last year and the diesel fuel price exceeded that of gasoline. In Iceland, only 16% of passenger cars have diesel engines, but the tendency for diesel passenger vehicles is upward. Some of the increasing consumption of fossil diesel could be met by domestically produced sustainable biodiesel.

Iceland has so far had little experience with biodiesel. However, this can be seen as an advantage, considering how the rest of the world struggles with the prematurely shaped biodiesel markets. The consequence of the hitherto lack of consistent strategy and solid policy in biofuels implementation is that governments today are forced, first and foremost, to protect the interests of the involved stakeholders, even at the price of overlooking the initial objective, which was the reduction of GHG emissions.

Iceland can only learn from these experiences when creating its green energy policy. Newest scientific evidence should be taken under consideration, and a thorough analysis of the present conditions and natural assets of the island should be carried out.

Biodiesel has become a broad term, with the advancement of the technology. Today, it can refer to biofuel produced from oils and fats, either fatty acid methyl ester (FAME) or hydrogen derived renewable diesel (HDRD). Additionally, pure or used vegetable oil itself can be used as fuel, however due to its high viscosity it is only viable in certain engine applications. Renewable biodiesel, produced from gasified biomass by Fischer-Tropsch synthesis, is another branch of the technology which uses different kinds of feedstock. Only FAME and HDRD will be covered in this study.

II. OBJECTIVES

The purpose of this study is to provide a full picture of the possibilities of biodiesel production in Iceland. This is done by introducing the general idea of a biodiesel economy and subsequently assessing its applicability in Iceland.

The theoretical investigation covers state of the art of biodiesel technology, as well as the issues concerning used feedstocks, the properties and emissions of presented fuels, and finally political, social and sustainability issues in a biodiesel economy.

The case study is approached on a few levels. A baseline survey describes the current situation of biodiesel in Iceland and potential available feedstocks. Subsequently, the results of the performed laboratory work and recommended production process are presented. Finally, the main assumptions of the economical viability of the various plant capacity options for biodiesel production are introduced.

III. THEORETICAL APPROACH

Biodiesel, as well as the whole biodiesel economy, has many advantages. In a global energy context, it decreases the reliance on petroleum fuel imports. If employed in a sustainable way, it can boost up local labor markets and general regional development, especially in the third world. After a false start and years of uncontrolled, very often harmful exploitation, the biodiesel economy seems to be getting on the right track. The newly adopted European Climate and Energy Package, as well as initiatives like Roundtable on Sustainable Biofuels and the Roundtable on Sustainable Palm Oil are aimed to compensate for the hitherto lack of internationally agreed-upon criteria for sustainable biofuels production.

Biodiesel is a renewable fuel. The carbon dioxide produced by its combustion takes part in the present carbon cycle, whereas burning fossil diesel releases the carbon trapped in mineral deposits millions of years ago. Therefore, because the CO₂ is recycled by photosynthesis, the impact of biodiesel combustion on the greenhouse effect is minimized.

Biodiesel is biodegradable and non toxic. Compared to fossil diesel, biodiesel has a more favorable combustion emission profile with lower emissions of carbon monoxide, particulate matter and unburned hydrocarbons. However, in case of FAME, challenges remain in the issues of oxidative stability and NO_x emissions. On the other hand, HDRD bears more resemblance to fossil diesel in this respect.

The relatively high flash point of FAME makes it less volatile and safer to transport and handle than fossil diesel. Its elevated lubricity reduces engine wear, thus contributing to its extended lifetime. The higher cetane number of both biodiesel fuels implies shorter ignition delay, and thus better engine performance and fewer emissions. FAME can be used in traditional diesel engines with little or no modifications, depending on the original feedstock, blend grade with fossil diesel, and the engine speed. HDRD has no limitations in this respect.

Nevertheless, many aspects of biodiesel production still have to be researched and improved, in terms of feedstock acquisition, overall energy balance and sociopolitical implications. However, there is no doubt that biodiesel is a good and indispensable alternative to a fossil based fuel economy.

The following chapters will cover the main aspects of biodiesel production, in order to provide an understandable overview and a theoretical background for the case study. An effort has been made to maintain an objective approach and provide a full picture of a biodiesel economy, with all its advantages and disadvantages.

1 BIODIESEL FEEDSTOCK

Biodiesel can be produced using a variety of feedstocks. They can be generally divided into:

- Pure plant oil (PPO);
- Waste vegetable oil WVO and waste animal fat (WAF);
- Algae oil.

Pure plant oil remains the main raw material used. Figure 1 presents the proportions in the world's major oils and fats production. As far as vegetable oils are concerned, soybean, palm, and rapeseed are the main sources of edible oils, but at the same time, they are the most popular biodiesel feedstocks. The world production of vegetable oil in 2004/5 was 387.7 million tons (1). However, its past sharp price rises in 2007-2008 accompanied by the soaring prices of crude oil (see Figure 2) and the food vs. fuel debate have caused an increasing interest in alternative feedstocks. There is intensive research being carried out to develop the effective production of non edible crops, which would not compete with food production.

Recycled feedstocks, like WVO and WAF are also gaining more and more interest. It is a limited resource, but its utilization has a double advantage: it is cheap and using it eliminates the need for troublesome waste disposal. This material became a serious liability after 2002, when the EU prohibited the use of waste WVO and WAF as animal feed.

Nevertheless, the most promising feedstock in overall terms seems to be algae. Although it is only considered for the third generation of biofuels and many technological and economical issues have yet to be overcome, its commercial application might be nearer than expected.

The description of different feedstocks covered in this chapter includes information about the degree of their applicability to biodiesel production. See the chapter titled Physical and chemical properties of biodiesel, for necessary explanations.

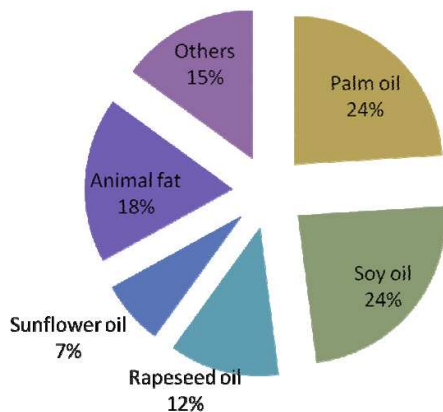


Figure 1 World oils and fats production 2005 (2)

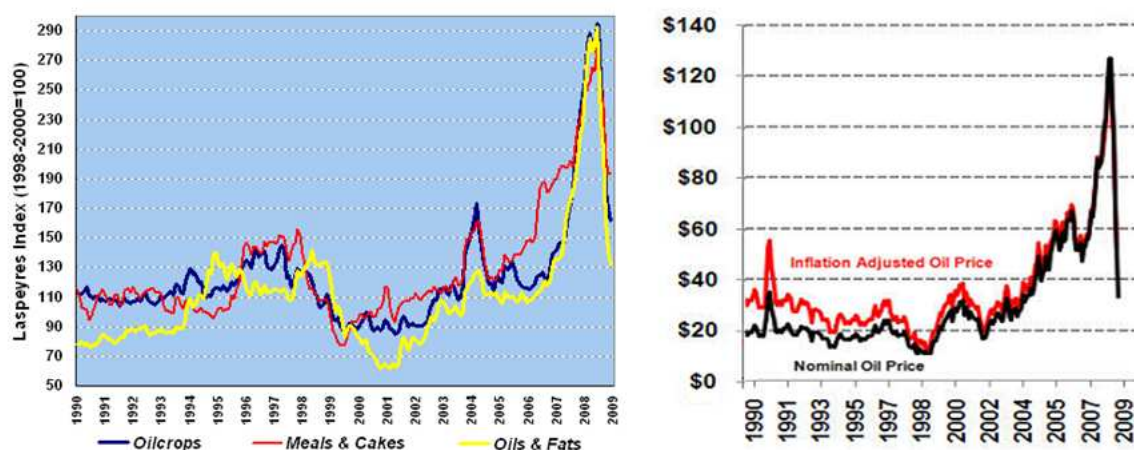


Figure 2 Comparison of the prices development of oils and fats, and crude oil (3) (4)

1.1.1 Pure plant oil

The main plant oils that have so far been used for biodiesel production are: soybean oil, rapeseed oil, palm oil, sunflower oil and jatropha oil.

Nevertheless, there are many more potential feedstocks worldwide. The following is a complete list of plant oils that are being considered as potential raw material for biodiesel production (in alphabetical order): artichoke oil, canola oil, castor oil, Chinese tallow tree oil, coconut oil, corn oil, cottonseed oil, flaxseed oil, hemp oil, jatropha oil, jojoba oil, karanj oil, kukui nut oil, milk bush oil, pencil bush oil, mustard oil, neem oil, olive oil, palm oil, peanut oil, radish oil, rapeseed oil, rice bran oil, safflower oil, sesame oil, soybean oil, sunflower oil and tung oil (5).

Generally, these sources can be divided into edible and non edible. The main focus is currently on developing nonedible feedstocks, and those that would not compete for land and water with edible crops. There is ongoing research, including genetic modifications, into improving crop and oil yields.

Edible oils:

Soybean, next to palm, is the most harvested oil plant worldwide, accounting for 39% of total world oilseed production (6). However, since its oil content accounts only for 17.5% of dry soybeans by weight, the total oil yield is not in such a predominant position, representing only roughly a quarter of world oils and fats production (see Figure 1) (6). A comparison of major oil yields (Figure 3) shows that soybean is least beneficial in these terms. Slightly higher yields have also been reported (0.42 tons/ha/yr), but clearly soybean is not a very efficient crop for the production of biodiesel (7).

The fatty acid composition is also little favorable for biodiesel production, since it is fairly unsaturated oil: 40-57% of its composition constitutes linoleic acid (18:2), and 20-35% is oleic acid (18:1) (8). However, its common use for food products in the United States, and extensive lobbying has led to soybean oil becoming the primary feedstock for biodiesel in that country (5).

In the 2005/06 campaign, the U.S. produced 8.8 million tons of soybean oil, from the total world production of 33.5 million tons/yr. It was followed by Brazil (5.7 million tons), China (5.5 million tons) and Argentina (5.4 million tons) (6).

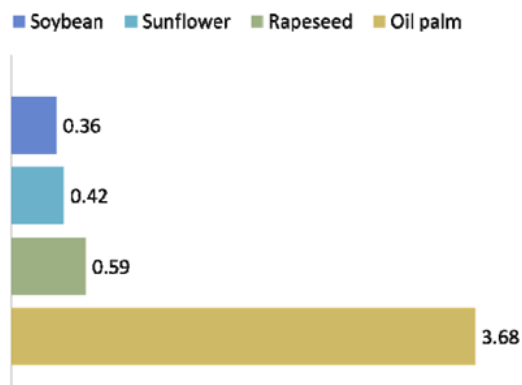


Figure 3 Major oil yields (tons/ha/yr) (2)

Palm oil is a promising feedstock for biodiesel production because of its low cost and high productivity per unit of planted area (9). Figure 3 indicates a 3.68 tons/ha/yr yield; however usually higher numbers are reported; e.g. 5.60 tons/ha/yr yield (7). Such high yield is, amongst others, a function of elevated oil content.

The palm fruit is a source of both palm oil (extracted from palm fruit; 40% oil content) and palm kernel oil (extracted from the fruit seeds; 50% oil content) (6). Both are highly saturated; palm oil at about 50% (mainly with palmitic acid (16:0)), palm kernel oil at about 80% (mainly with lauric acid (12:0)) (8). Because of high saturation, these oils have high melting points (30-40°C for palm oil and 24-26°C for palm kernel oil) (8). This is an obstacle for the utilization of neat palm oil biodiesel in most of the Europe; it can only be used in blends. On the other hand, also owing to the low grade of unsaturation, such biodiesel has a uniquely high ignition quality (9).

The main producers are Malaysia (14.9 million tons in 2005/2006) and Indonesia (13.9 million tons). The total world production is 33.6 million tons/yr (6). The growing interest in palm oil as biodiesel feedstock is a controversial issue since it coincides with recent high palm oil production and the resulting increase in cultivation area. This issue will be discussed in more detail in the chapter: Economy, policy and sustainability.

Rapeseed, originally grown for animal feed and vegetable oil for human consumption, is the most used feedstock for biodiesel production in the European Union (5). It is also one of the four (next to soy, corn and cotton) most common genetically modified crops grown around the world (10). Canola is a variety cultivated mainly in Canada and the United States.

The oil content of rapeseed is around 40 %, with a high content of monounsaturated fatty acids (50-65% oleic) (6) (8). This composition is more favorable than that of soybean oil, since monounsaturated oils have higher oxidative stability, although a low level of saturation is not particularly beneficial. Also, relatively high oil yields compared to soybean and sunflower make rapeseed a popular feedstock (see Figure 3). Depending on the variety, the oil yield can be almost twice as high, reaching 1.1 tons/ha/yr; however this estimation probably includes two harvests per year (7).

The main producer of rapeseed oil is the EU (5.6 million tons in 2005/2006, in equilibrium with consumption), followed by China (4.6 million tons), India (1.8 million tons) and Canada (1.3 million tons). The total world production is 16 million tons/yr (6).

Coconut oil appears to be a good candidate for biodiesel feedstock. It is highly saturated (90%), much more than even palm oil (8). Its composition resembles that of palm kernel oil, with lauric acid (12:0) being the main constituent (37-52%) (8). Although the short chains of lauric acid contribute to lowering the melting point temperature, coconut oil solidifies at only 24-26°C (8). Therefore using its neat form implies the same climate limitations as using palm oil. On the other hand, it guarantees a high ignition quality of the produced fuel.

The oil yields are approximately half of those of the palm, but still far higher than those of traditional crop feedstocks. With a high oil content of 63-70%, the oil yield of coconut can be as high as 2.53 tons/ha/yr (7).

The main producers are Philippines (1.3 million tons in 2005/2006), Indonesia (0.8 million tons) and India (0.4 million tons). The total world production is 3.2 million tons/yr. The EU imports 0.8 million tons of coconut oil, mostly for the food industry (6).

Sunflower oil is being tested in quite a few places worldwide for its biodiesel capability (5). Nevertheless, in spite of high oil content (30-45%), it seems that it cannot compete with rapeseed, due to lower yields (see Figure 3) and a high concentration of unsaturated fatty acids (20-40% oleic and 45-68% linoleic) (6) (8). However, if harvested two times a year, sunflower can yield up to 0.88 tons/ha/yr (7).

Russia is the biggest sunflower oil producer (2 million tons in 2005/2006), followed by the EU (1.7 million tons, in equilibrium with consumption), Argentina (1.5 million tons) and Ukraine (1.3 million tons). The total world production is 9.7 million tons/yr (6).

Corn, so far used rather for bioethanol production, is under intensive research in the United States as the feedstock for biodiesel production. Until a few years ago, corn was not favored in these terms because of the low effectiveness of the extraction process and variable quality of received oil. However, newer extraction processes seem to have overcome these problems (10). Nevertheless, although maize germs contain as much as 45% oil, their removal from the seed is complicated, energy intensive and requires expensive equipment (11).

Incorporating a corn oil extraction system onsite at bioethanol production facilities is a new approach that will increase the overall effectiveness and profitability of maize use. The alcohol product of the plant can be recirculated and used as solvent for oil extraction from corn (11). Therefore, an additional oil product will increase bioethanol producer's revenues; so far the only extra profit was from selling inexpensive distiller's grain for fodder.

Maize oil has linoleic acid content of about 57% and has a composition similar to sunflower oil, but is more heat stable (6).

The United States is the main corn oil producer (1.1 million tons in 2005/2006, out of the total world production of 2.1 million tons) (6).

Hemp is an industrial kind of Cannabis. Traditionally used in Asia for fiber production, it is a multipurpose plant, yielding nutritious seeds, and recently it has also been considered for fuel production. While the bush is a potential feedstock for bioethanol, the seeds contain 33% oil that has been tested as biodiesel feedstock (12). The oil is fairly saturated, with 52% linoleic and 23% linolenic (18:3) acid, but the produced biodiesel has a unique green color, which is an effective marketing hint (13) (12). Hemp has been cultivated in Canada for a few years, but due to the high price the seed is instead sold to the food

industry. A legal battle has been going on in the US to distinguish hemp from marijuana and thus allow growing it, as it could be very profitable.

The oil yields are not very high, due to low seed yield per area. The Canadian farmers report seed yields between 800-1350 tons/ha/yr and oil yields of 0.25-0.45 tons/ha/yr. This is a range comparable to soybean yields. Nevertheless, the hemp has significant agricultural advantages. It grows rapidly with little or no need for pesticides, it can grow on rocky soil, and it is a good rotational crop (12).

Non edible oils:

Jatropha is a plant native to India and Southeast Asia, where it has been used as fuel source for many years. It has recently started to gain popularity as biodiesel feedstock due to its versatile useful qualities. Firstly, it is a non edible plant, which eliminates the food vs. fuel discussion. Secondly, it requires no fertilization, no irrigation and it can grow in severe arid conditions, where many other biodiesel candidates could never thrive. Moreover, *Jatropha* is also planted for watershed protection in dry areas and for other environmental restoration functions. It is a perennial bush and it yields seeds for decades. Another useful feature of *Jatropha* is its oil yield, which is significantly higher than the yields of many other biodiesel feedstocks, up to 1.76 tons/ha/yr (7).

Jatropha is a very important energy source for developing countries and it may become one of the most important feedstock sources for biodiesel production in the coming years in many parts of the world (10).

Castor oil has a few characteristics that could make it a suitable candidate for biodiesel. It has a very low cloud point (-12°C to -18°C) and relatively high oil content (50-55% in the seed, although approximately 90% is a monounsaturated ricinoleic acid (18:1)) (10) (8). However, the main obstacle is its exceptionally high density (0.96 kg/l compared to an average 0.92 kg/l, the highest of all vegetable oils) (10). It is still being researched as to whether the final viscosity for castor oil biodiesel is within acceptable limits for use in diesel engines. The oil yields are also not very impressive, only 0.46 tons/ha/yr (7). On the other side, it has very limited use in the food industry, these being mainly in food additives. It is rather used in pharmaceuticals (as laxative) and other industries (14).

The total world production of castor oil was 0.5 million tons in 2005/2006, out of which India produced 0.3 and China 0.1 million tons. The EU imported 0.1 million tons (6).

Cottonseed oil is extracted from the seeds of the cotton plant after the cotton lint has been removed. It contains gossypol, a naturally occurring toxin that protects the cotton plant from insects. The antioxidant properties of this pigment may also potentially translate into a high oxidative stability of the biodiesel and increase its shelf life (15).

The main component of cottonseed oil is linoleic acid, which constitutes 42-52% of the oil's content (8). The seeds contain only 20% oil and the oil yield is no more than 0.31 ton/ha/yr (15) (7). Nevertheless, considering that the oil is only a side product of cotton cultivation, it is worthy of further research.

The total world production of cottonseed oil is 5 million tons/yr, with China in the leading position, producing 1.5 million tons (6).

Linseed (flax) oil is also under research for biodiesel production. It has an unusual composition, not very favorable for biodiesel (35-65% linolenic acid); however its very

high yield (1.33 tons/ha/yr) and the fact that it is non edible (it is mainly used for production of paints and coatings), make it an interesting feedstock (8) (7).

Linseed oil is mainly produced in the EU (0.2 million tons in 2005/2006), in China and in the United States (0.1 million tons each). The total world production is 0.6 million tons/yr.

1.1.2 Waste vegetable oil and waste animal fat

To reduce biodiesel production costs and make it competitive with fossil diesel, low cost feedstocks, such as WVO and WAF can be used as raw materials (16). In addition, the application of these feedstocks solves the issue of their troublesome disposal. However, the relatively higher amounts of free fatty acids and water in WVO and WAF constitute a challenge for biodiesel production and require additional processing.

Waste vegetable oil:

Significant quantities of waste vegetable oil from cooking are available throughout the world, especially in the developed countries. The average annual per capita WVO generation in the United States was reported to be 9 pounds (over 4 kg); therefore in total the U.S. produce around 9 million tons of WVO per year (17). In the EU countries, the total WVO production is approximately 0.7-1.0 million tons/yr (17). Even though some of this waste cooking oil is used for soap production, a major part of it is discharged into the environment. China, on the other hand, is generating more than 4.5 million tons of WVO annually, roughly half of which could be collected through the establishment of an integrated collection and recycling system. Those 2 million tons of feedstock would guarantee the smooth operation of all current biodiesel production lines (18).

Waste vegetable oil is a low cost feedstock in comparison with fresh vegetable oil. Practically, its price is only comprised by the collection and transportation, since the suppliers release it free of charge, avoiding disposal fees at the same time.

The key to the successful utilization of WVO is establishing a reliable and continuous supply. The main providers are food manufactures, food processing plants, restaurants and fast foods. However, a well organized collection from the domestic sector can also be effective, especially in southern Europe, due to traditional high vegetable oil consumption (19).

Waste animal fat:

Animal fat usually comes from the rendering industry. While some fraction of rendered fat is suitable for human consumption (food, cosmetics, etc.), the inedible part, after adequate refining, is a potential feedstock for biodiesel production. These fats include tallow, lard and poultry fat and are categorized into yellow fat (FFA content below 15%) and brown fat (higher FFA contents) (20). Between 1993 and 1998, the average supply of yellow grease in the U.S. was 1.2 million tons/yr. It was estimated, that roughly 1/3 of this amount could be used for biodiesel production (21).

The byproducts of the fish industry are also under research; however their application in the food industry seems more probable, given the high nutritional value.

The use of trap grease, a kind of waste collected in grease traps of restaurants before it goes down the sewer, is also considered (22). Its utilization is particularly challenging because of the highest FFA contents; from 40 to 100%. In the U.S. about 13 pounds

(almost 6 kg) of trap grease per capita is produced annually (22). Another source of animal fat are unrendered fat cutoffs from slaughter houses. This raw material is more valuable for biodiesel production because of lower FFA contents (no thermal processing); however, it is usually primarily used for human consumption.

Animal fat based biodiesel has particular properties. It is better if it is used in blends, because of its higher cloud point. On the other hand, biodiesel made from waste animal fat has a higher cetane number than that of fossil diesel, which indicates better ignition qualities and thus cleaner and more efficient burning (23).

1.1.3 Algae

Recently, algae are in the main focus of researchers. Eventually they are to replace the traditional feedstocks and thus create a new, third generation of biofuels. Biodiesel production is one of the possible applications of algae, which is currently being examined.

Algae have become appealing because of the potential for significantly higher average photosynthetic efficiency than that of typical land crops. Better access to water, CO₂, and nutrients translate into more intensive growth, and thus higher yields (16).

Several studies provided various results on potential algal oil yields. The application of a combination of photobioreactors and open ponds in a small commercial scale production plant in Hawaii yielded on average 10 tons/ha/yr of oil (with only 25% oil content), which is double the yield of palm, the most efficient feedstock so far (16). However, experiments on microalgae cultivation in photobioreactors in New Zealand, reported oil yields as high as 50 to 120 tons/ha/yr, depending on the oil content (30% and 80% respectively) (24).

Nevertheless, there are significant challenges that have to be overcome in order to make algae an economically viable biodiesel feedstock. Most species tend to store energy in the form of carbohydrates, rather than oil, and therefore a careful selection of strains must be performed. However, the production of oil slows down the reproduction rate of high oil algae, and therefore makes it more vulnerable to the competitive low oil strains. The result is that an open system is readily taken over by lower oil strains, which decreases the overall oil yields. The attempts to grow high oil extremophiles, which are able to survive in highly saline or alkaline conditions, have given poor results. While they were able to survive in an extreme condition, they did not thrive well and the yields were low. On the other hand, using enclosed photo bioreactors increases the capital and operational costs tremendously. Moreover, higher oil concentrations are achieved only when the algae are stressed, particularly due to nutrient restrictions. However, those restrictions also limit growth, thus careful modeling is an awaiting challenge (16).

2 TECHNOLOGY

The production of biodiesel involves several processes. This chapter will cover major technological steps; however it is important to keep in mind that a choice of particular methods highly depends on available feedstocks, climate, economic determinants, etc.

Biodiesel is always obtained from fatty acid glycerides, regardless of further technological processes. Alkali based transesterification, which yields fatty acid methyl esters, is a traditional and well known process used for biodiesel production. However, recently emerging technological improvements involve new catalysts (e.g. polymers and enzymes) or an employment of different reaction conditions in which catalysts are not used at all.

Another method attracting much interest in recent years is the hydrogenation derived renewable diesel (HDRD) technology. This process differs from conventional biodiesel (FAME) production in that it consumes hydrogen and yields hydrocarbons (alkanes and alkenes). The catalysts used are based on nickel, molybdenum and palladium.

Both processes generate specific byproducts – or, more accurately, coproducts – which have certain value and constitute an important economic variable of the plant operation. Therefore, an adequate treatment and management of these coproducts is essential.

The choice of the production process is dictated mainly by the used feedstock. Whereas pure plant oil is a typical raw material that is fairly easy to convert to biodiesel, recycled feedstocks, like waste vegetable oil and waste animal fat are much more troublesome. The elevated content of free fatty acids (FFA) resulting from previous thermal processing is the main obstacle and it requires more complicated technological solutions.

2.1 Fatty acids

In order to understand the process of biodiesel production, it is important to have knowledge about the basic characteristics of fatty acids and their esters.

All oils and fats are a mixture of triglycerides, an organic compound consisting of a glycerin backbone and three long chains of fatty acids (R_n).

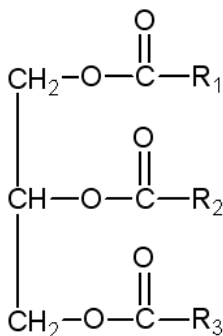


Figure 4 Chemical structure of triglyceride

The composition of triglycerides, i.e. proportions of certain fatty acid chains, depends on the type of oil or fat, its origin (how it has been processed) and storage.

Fatty acids (also known as long chain carboxylic acids) can be saturated or unsaturated. An unsaturated chain can contain up to six double bonds, therefore it is called mono- or polyunsaturated. According to the chemical nomenclature, each fatty acid is designated by two digits separated by a colon. The first one is the number of carbon atoms in a chain (including the so called carboxylic carbon, double bonded to the oxygen atom) and the other one shows how many double bonds there are in a fatty acid chain.

Five types of chains are most common in vegetable oil and animal fats:

Palmitic:	$R = -(CH_2)_{14}CH_3$	(16:0)
Stearic:	$R = -(CH_2)_{16}CH_3$	(18:0)
Oleic:	$R = -(CH_2)_7CH=CH(CH_2)_7CH_3$	(18:1)
Linoleic:	$R = -(CH_2)_7CH=CH-CH_2-CH=CH(CH_2)_4CH_3$	(18:2)
Linolenic:	$R = -(CH_2)_7CH=CH-CH_2-CH=CH-CH_2-CH=CH-CH_2CH_3$	(18:3)

Figure 5 Most common fatty acid chains

Unlike our dietary recommendations, it is generally preferable that the feedstock for biodiesel production contain mostly saturated chains. For both fatty acids and their esters, the more unsaturated they are, the more prone they are to react with oxygen from air and form degradation products with time. On the other hand, biodiesel made from saturated oils or fats (usually recycled feedstocks) has a higher cloud point, which can constitute a serious problem in colder climates, as the fuel gets too dense for the proper functioning of the engine. This can be modified by blending feedstocks with different proportions of saturated and unsaturated fatty acid chains.

The composition of various oils and fats are compared in Table 1. Fatty acids can be defined by two numbers separated by a colon. The first one is the number of carbon atoms in the fatty acid chain and the second one is the number of double bonds in this chain.

Table 1 Composition of various oils and fats (8) (25)

Oil or fat	6:0	8:0	10:0	12:0	14:0	16:0	16:1	18:0	18:1	18:2	18:3	20:0	22:1
Soybean						7-10	tr-1	3-6	20-35	40-57	5-14	0-2	
Oil palm (fruit)					0.5-5	32-47		2-8	40-52	5-11			
Oil palm (kernel)	1.6	3-10	3-14	37-52	7-17	2-9	tr-0.6	1-3	11-23	1-3		tr-0.6	
Hi oleic rapeseed					0.7-1.1	1-5	trace	0.5-2	50-65	15-30	6-13	0-1	
Hi erucic rapeseed					0-1.5	1-4	trace	0.5-2		11-29	6-13	0-1	40-55
												20:1=5-12	
Coconut	0.2-0.8	6-9	6-10	44-51	13-18	8-10	tr-0.4	1-3	5.5-7.5	tr-2.5			
Sunflower						4-8	trace	2-5	20-40	45-68	trace		
Corn					1-2	8-12		2-5	19-49	34-62	trace		
Castor						1-2		1-2	tr-8.5 (oleic)	3-6			
									86-92 (ricinoleic)				
Cottonseed					0.5-2	20-27	0-2	1-3	22-35	42-52	tr-2	0.2-1	
Linseed oil						4-7		2-5	12-34	14-20	35-65		
Lard				trace	2-6	26-32	2-5	12-16	41-51	3-14	tr-1		
Beef tallow				0-1	12-14	20-33	2-4	14-29	35-50	2-5	tr-1.5	0.4-1.5	
Yellow grease					2.43	23.24	3.79	12.96	44.32	6.97	0.67		

2.2 Production of fatty acid glycerides

Pure plant oil (PPO) is the predominant raw material for biodiesel production worldwide. Nevertheless, recycled feedstocks, like WVO and WAF are gaining more and more attention. Different kinds of feedstocks were described in the previous chapter. The processes involved in their extraction and refining will be discussed here.

Prior to extraction, the biomass undergoes several pretreatment steps, which depend on the kind of raw material used. They usually include cleaning, dehulling, crushing and conditioning. Hulls are removed because their oil content is very low (less than 1%) (20). They also have an abrasive effect, therefore dehulling reduces wear on the screw press. It can also increase the yield of oil because the hulls tend to absorb it. Crushing is performed in order to facilitate the extraction. The term conditioning refers to heating the seeds so as to soften them for the same purpose: the extraction of oil.

Plant oil used for biodiesel can be purchased as crude, degummed or fully refined (suitable for edible purposes, i.e. refined, bleached, deodorized (RBD)). On the one hand using RBD feedstocks simplifies the production process. However, full refining removes the natural antioxidants from oil, which later on have to be artificially reintroduced to biodiesel in order to eliminate storage problems.

Animal fat usually comes from the rendering industry. Some fraction of rendered fat is suitable for human consumption or production of cosmetics after it has been refined, bleached and deodorized. The inedible part, i.e. yellow fat (FFA content below 15%) and brown fat (higher FFA contents) can be used as feedstock for biodiesel production, after adequate refining.

General steps in the production of FA glycerides are shown in Figure 6.

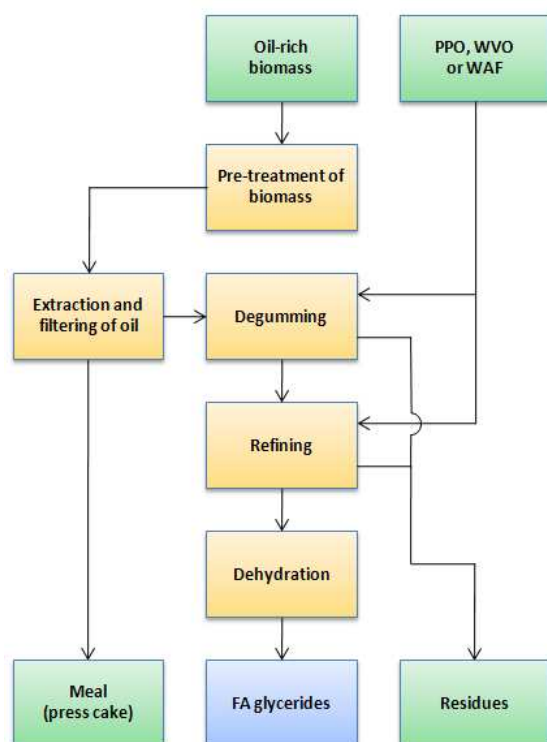


Figure 6 Production of FA glycerides (26)

2.2.1 Extraction

There are three well-known methods used to extract the oil from biomass:

- Mechanical extraction;
- Solvent extraction with hexane;
- Supercritical fluid extraction.

Mechanical extraction:

The raw material is generally preheated to destroy enzymes, so that the meal can be further used as animal feed. This can be done by cooking or using an extruder, which applies a high enough pressure to increase the temperature to 150-160°C. Subsequently, the biomass is fed to the screw press. If the feedstock has not been extruded, then prepressing should be employed to facilitate the oil release. The yields vary from typically about 80% (cold pressing) to at least 90% (high pressure pressing) of oil from the raw material (27).

Solvent extraction with hexane:

Biomass that is to be processed by solvent extraction is usually flaked to increase the exposure of the oil to the solvent. The most common equipment currently utilized is the percolation extractor. The solvent drips down on and through the feedstock and dissolves the oil in a manner similar to coffee making in a percolator. Subsequently, the oil-hexane mixture, also called miscella, is filtered. The solvent is removed from the miscella by vaporization and steam stripping. The resulting minimum yield of oil extraction is 99.5% (28) (29).

It is often assumed that mechanically extracted oil has poorer quality than oil extracted with solvent. A recent comprehensive study comparing the qualities of the two products showed that the former had unique qualities compared to the latter. For example, the mechanically extracted oils were easily degummed by mere natural settling, and they had lower free fatty acid contents, which translated into lower refining loss (30).

Supercritical fluid extraction:

In supercritical fluid extraction, CO₂ is liquefied under pressure and heated to a temperature above the critical one. This liquefied fluid then acts as a solvent in extracting the oil. The yields are thus similar to those from solvent extraction with hexane. This method also gives more valuable meal, however it is considerably more expensive. Therefore, it is still in the R&D stage.

2.2.2 Degumming

After extraction, crude plant oil contains some naturally occurring impurities. The oil-insoluble substances like meal fines, free water, waxes or other long-chain hydrocarbons are usually removed by filtration. The degumming process eliminates phospholipids and heavy metals. Gums have to be removed because they affect the oil stability and can be strong emulsifiers, which complicates the biodiesel production process (31) (20). Most importantly however, because of the toxic phosphorus compounds that may form in the fuel combustion process.

There are two well known methods of degumming. Water degumming involves hydrating the phospholipids at 70°C for 30-60 minutes, which then become insoluble in oil and can be separated by settling, filtering or centrifuging. The byproduct of water degumming has value as a feedstock for lecithin production (20).

Nevertheless, not all phospholipids are hydrated by contact with water alone. Wet degumming can therefore be followed by an acid process. It is completed by the addition of citric or phosphoric acid to the oil, which is preheated to 60-85 °C. The residence time is no longer than 1-2 minutes. Citric acid is preferred if the byproduct is to be used as feedstock for lecithin production (20).

Degumming is a crucial preliminary step before physical refining. If chemical refining is employed, the gums are removed in the process as well.

2.2.3 Refining

Refining is the next step in crude oil processing and it involves the removal of FFA. The process can be completed either by steam stripping of the free fatty acids (physical refining) or by chemical neutralization (caustic refining). Combined physical and chemical treatment can also be applied. Physical refining is a distillation process carried out at 220 to 250°C, with 5% direct steam (31). In chemical refining, an alkali solution, usually sodium hydroxide, is added. This reacts with the FFA to produce soaps that are subsequently separated by water washing. The alkali solution also neutralizes any acid remaining from the degumming stage. Since it will also react with the triglycerides, the reaction parameters must be optimized to minimize the yield loss.

2.2.4 Further processing

As has already been mentioned, the oil, after dehydration, can be used as biodiesel feedstock at this stage of processing. However, further treatment can be applied, in order to attain RBD oil. Bleaching and deodorization are the subsequent steps.

The primary purpose of bleaching is removing pigments from the oil. Additionally, remaining soaps, trace metals, phospholipids and sulfur compounds are eliminated. The process involves mixing bleaching clays with the oil for 10-30 minutes. The temperatures applied are between 90 and 120°C and the reaction is carried out under slight vacuum (20). The amount of bleaching clay can be reduced with an addition of silica (31).

Deodorization removes trace components that give oil an unpleasant taste and color. The process is essentially a distillation process that occurs at high temperatures (200-260°C) and low pressure (2.5-9.2 mbar) (20).

Although the use of RBD feedstock simplifies the biodiesel production process, the energy balance as well as the economy has to be taken under consideration when choosing a raw material.

Final dehydration, usually performed by vacuum, is a crucial step in the preparation of fatty acid glycerides for biodiesel production. The presence of water can significantly complicate the process, leading to the creation of undesirable products and losses of yield. The concomitant chemistry reactions will be discussed in the following section.

2.3 Fatty acid methyl ester (FAME)

Until recently, the term ‘biodiesel’ generally referred to fatty acid alkyl esters, mainly methyl esters (FAME). It is a product of the transesterification reaction of fatty acid glycerides, received from vegetable oil or animal fat. The use of recycled feedstocks, like WVO & WAF, imply a series of technical complications (i.e. an elevated content of free fatty acids), which will be discussed further. The purpose of the transesterification is to lower the viscosity of the raw material.

Figure 7 shows all the technological steps of FAME production from crude oil. This outline does not include the pretreatment of the feedstocks with high FFA content.

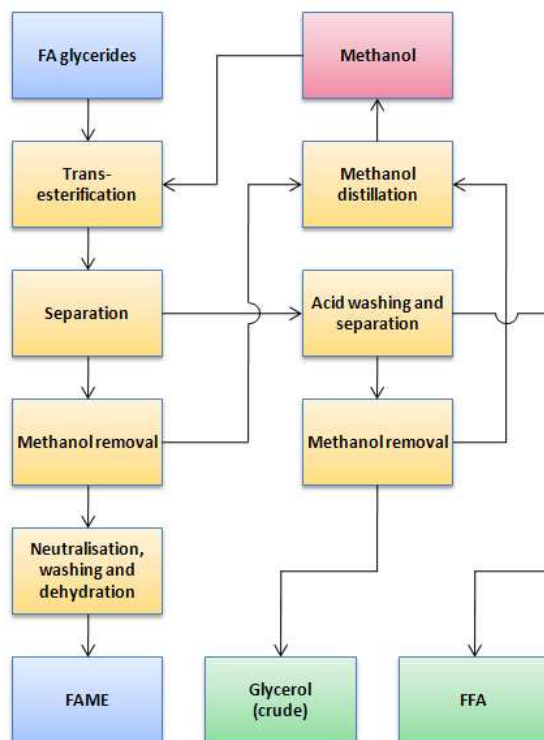


Figure 7 Production of FAME (26)

2.3.1 Transesterification

The term ‘transesterification’ refers to a chemical reaction of exchanging an alkoxy group (-OR) of an ester with that of an alcohol, in the presence of a catalyst. A new ester and a new alcohol are formed. In the case of biodiesel, the components referred to are usually triglyceride (TG-ester of glycerin) and methanol on the left side of the reaction; the products are a mixture of fatty esters and glycerol (glycerin). The operating temperature is usually about 65°C and typical reaction times range from 20 minutes to more than 1 hour.

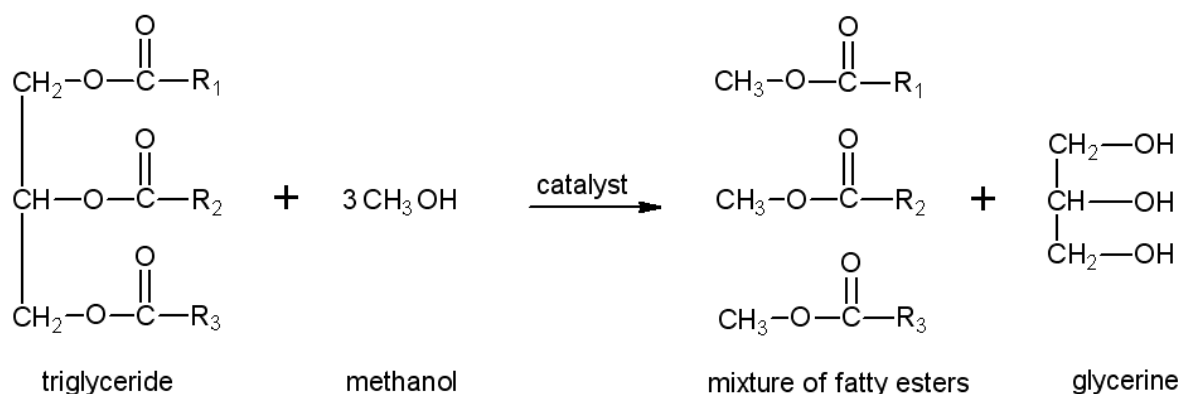


Figure 8 Transesterification reaction

Theoretically, only 3 moles of alcohol take part in the reaction. In reality, however, a 60% to 100% excess (XS) of alcohol is added, to ensure that the reaction goes to completion.

In order to initiate and accelerate the reaction a catalyst must be added. It is usually an alkaline catalyst, such as sodium hydroxide (NaOH) or potassium hydroxide (KOH), in the amount of about 1% of the weight of the feedstock; it mostly ends up in the glycerin phase.

After the reaction the alkaline catalyst must be neutralized with a strong acid, usually sulfuric acid (H₂SO₄), hydrochloric acid (HCl) or phosphoric acid (H₃PO₄).

The approximate proportions of reactants and products are as follows:



2.3.2 Parallel reactions

Normally the oils and fats contain certain amounts of water and FFA that have been formed by hydrolysis of the triglyceride (see Figure 10). When a feedstock containing free fatty acids is used to produce biodiesel it will consume a part of the alkaline catalyst by soap formation.

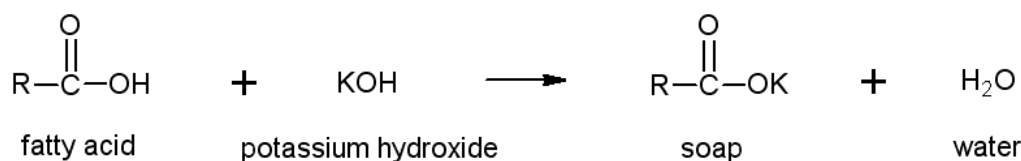


Figure 9 Formation of soap

Soap is an undesirable product because it takes up the feedstock intended for the original product, which is biodiesel. More importantly, however, it neutralizes the catalyst, preventing it from accelerating the reaction.

Another problematic product of this reaction is water. There is usually some water present in the feedstock which is mostly removed in the pretreatment step. However, even trace amounts of water lead to the formation of unwanted compounds. It can hydrolyze the

triglycerides into diglycerides and form fatty acid (Figure 10). This in turn is followed by the reaction mechanism presented in Figure 9, generating more and more undesirable products.

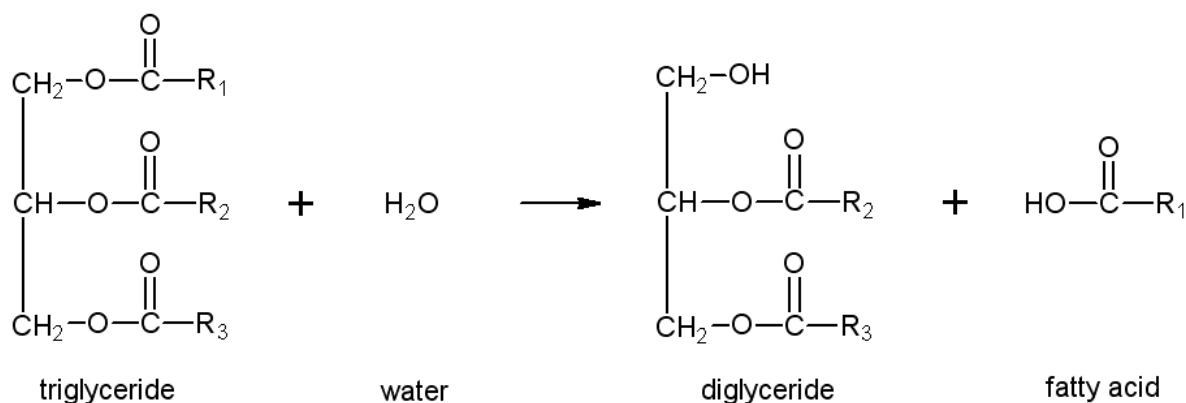


Figure 10 Hydrolysis of a triglyceride to form FFA

Chemical water is also formed in the reaction of free fatty acids with alcohol:



Figure 11 Formation of methyl ester

Nevertheless, this process is not a competing reaction, since it transforms unwanted FFA into the main product, biodiesel.

When an alkali catalyst is mixed with alcohol prior to the transesterification reaction, additional chemical water is produced:

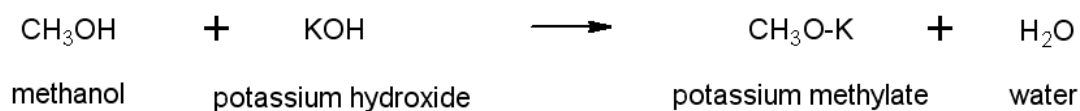


Figure 12 Formation of potassium methylete

2.3.3 Chemicals

Apart from the feedstock (fat or oil), several chemicals are used to make biodiesel. These are:

- Alcohol;
- Catalyst;
- Neutralizer.

Alcohol:

The most commonly used primary alcohol is methanol, although other alcohols, such as ethanol, isopropanol and butyl, can be used (25).

The main issues considered when choosing an alcohol include its cost, the amount needed for the reaction, the ease of recovering and recycling the alcohol, fuel tax credits and the sustainability of its production.

From an environmental point of view, ethanol is a preferred alcohol in the transesterification process compared to methanol because it is derived from agricultural products and is renewable and biologically less objectionable in the environment (32). However, in practice, methanol is used because of its low cost and its physical and chemical advantages. Methanol is considerably easier to recover than the ethanol. Ethanol forms more of an azeotrope with water so it is expensive to purify the ethanol during recovery. If the water is not removed it will interfere with the reactions. Therefore, even though methanol is more toxic, it is the preferred alcohol for producing biodiesel (25).

In a base catalyzed process a typical operating mole ratio is 6:1 (alcohol to oil or fat), on a molar basis, rather than the 3:1 ratio required by the reaction (25). Due to different viscosities of the reactants, the extra alcohol, apart from using a catalyst, intensive mixing and elevated temperatures, is needed to increase the reaction yield and ensure that the final product meets the requirements of quality standards for biodiesel. The effect of alcohol to oil ratio was found to be the most important variable affecting the yield, while temperature had a significant effect on the initial reaction rate (16).

Catalyst:

The most commonly used catalysts are alkali compounds, KOH or NaOH, in the amount of about 1% of the weight of the feedstock. They are well known and economic; however their application should depend on the feedstock used for biodiesel production. Since base catalysts will form soap with free fatty acids (see Figure 9), only the raw material with small content of FFA (<1%) should be used (25). Another drawback of alkali catalysts is their hygroscopic character; they absorb water from the air during storage. Moreover, they form chemical water when dissolved in the alcohol (see Figure 12). As it was previously discussed, the presence of water is very undesirable in the transesterification, since it favors the formation of FFA (see Figure 10).

In order to avoid chemical water formation, alkaline metal alkoxides (as CH_3ONa or CH_3OK) are applied. They are the most active catalysts, and give very high yields (>98%) in short reaction times. Also, smaller amounts of methoxide are required for the reaction; only 0.25% of the weight of the feedstock, compared to 1% if KOH or NaOH are used.

However, they require an absence of water, which makes them inappropriate for typical industrial processes (32).

The transesterification process catalyzed by sulfuric acid is generally slow and requires a high alcohol to TG mole ratio (20:1 and more) (25). Therefore, although this catalyst gives very high yields in alkyl esters, it is generally used in a pre-transesterification step of highly acidic feedstocks. Acid esterification will be discussed in the next section.

Utilization of enzymes for catalyzing a synthesis of FAME is currently under research. Particularly lipase, a digestive enzyme processing dietary lipids, has been investigated. The application of these catalysts seems attractive because of the low energy consumption of the process (lipase is active at 30°C) and more environmentally inert effluents, compared to traditional chemical methods (33). However, the reaction conditions, including the pH, type of microorganism that generates the enzyme, solvents, etc. need further optimization. The cost is another limiting factor for the large scale production of biodiesel. Nevertheless, according to the recent findings, lipase is also a more interesting option for esterification (33). The method will be discussed in the next section.

Recently, the production of biodiesel using heterogeneous catalysts has been investigated. The sulfonated metal catalysts ($\text{SO}_4^{2-}/\text{SnO}_2$ and $\text{SO}_4^{2-}/\text{ZrO}_2$) gave the highest FAME yields in the reaction carried out at 200°C, 50 bar, 3 wt% catalyst, and a 6:1 molar ratio of methanol to oil. The zirconium gave an 86.3% yield for coconut oil and 90.3% yield for palm oil. The study shows that it was deactivated quickly but could easily be regenerated (34).

Neutralizer:

Neutralizers are only required in alkali or acid catalyst systems. They are used to remove the catalyst from transesterification products, both biodiesel and glycerin (in which the most catalyst concentrates). If a base had been used, then an acid would act as a neutralizer and vice versa. The choice of a neutralizer should be based on the cost of a chemical, but also on the value of an end product. As an example, while hydrochloric acid (HCl) is a cheaper option of neutralizing a base catalyst, if phosphoric acid (H_3PO_4) is used, the resulting salt (K_3PO_4) can be sold as a chemical fertilizer.

In the case of biodiesel, the neutralization can be carried out together with the washing. The post transesterification processing will be discussed in more detail in a later section.

2.3.4 Handling of high fatty acid feedstocks

It has already been discussed that a high level of FFA in the feedstock for biodiesel production is an obstacle for the transesterification reaction. The alkali catalyst will react with the free fatty acids to form soap (see Figure 9). The formation of soap will use up the feedstock intended for the original product, and consume the alkali catalyst required for the transesterification before it even begins. Therefore, when FFA levels are above 1%, some measures have to be taken before converting the feedstock to FAME.

When FFA levels are only slightly above 1% it is possible to simply add extra base catalyst and devote it to neutralizing the FFAs by forming soap. It will be washed off after the transesterification reaction. This approach to neutralizing the free fatty acids can be applied at FFA levels as high as 5%, given that the feedstock is anhydrous. If traces of water are present 2-3% FFA may be the limit (25). For feedstocks with higher amounts of FFA, the addition of extra catalyst will cause emulsification and prevent the separation of the

glycerin from the ester. Moreover, too much of the feedstock will be turned into waste product. For highly acidic raw material other techniques must be applied.

The most common pre-transesterification process applied to feedstocks with high FFA content is a direct acid esterification. In this reaction the free fatty acids react with methanol to form FAME (see Figure 11). A catalyst, usually H_2SO_4 , must be added in the amount of 5 wt% of the FFA content. The excess of methanol must also be much higher than during transesterification. Molar ratios of alcohol to FFA range from 20:1 to as high as 40:1 (25). Temperature is usually raised to 50-60°C. This process requires constant water removal; otherwise the reaction will be quenched prematurely. An elevated excess of methanol is also dictated by the formation of chemical water; alcohol is used to dilute the mixture. The residence time is about 1 hour. The resulting mixture of esters and TG is usually subsequently used in a conventional base catalyzed transesterification.

In a study of biodiesel synthesis from trap grease with 50% FFA content, it was shown that in order to achieve the highest ester content of crude biodiesel (89.67%), the optimal reaction conditions included a 35:1 methanol-to-oil molar ratio, 11.27 wt% catalyst concentration (based on trap grease) and a reaction time of 4.59 hours, while the reaction temperature was set at 95°C (22). However, the conversion process involved only esterification (without subsequent transesterification), therefore it is a rather costly and time consuming biodiesel production option.

Esterification can be also catalyzed by enzymes. These methods require expensive enzymes but seem to be less affected by water (33). On the other hand, the reaction yields as well as the reaction times are still unfavorable. A study of production of alkyl ester from fractionated lard gave only 74% yield of conversion. Furthermore, because lipase activity was hindered by excess amounts (more than 1 mol) of methanol, each mole of methanol had to be added sequentially every 8 hours in a three step reaction (33).

Another recent invention in esterification is polymer catalysts. They have several advantages over mineral acid catalysts: higher thermal stability, higher conversion (thus smaller yield losses), lower reaction times and smaller methanol to FFA ratio. Safety, handling and corrosion issues are also more favorable. These catalysts are particularly suitable for low cost feedstocks with high FFA content (brown grease, trap grease) and soap recovery from alkali transesterification. However, the systems are energy costly because of high temperatures and pressures applied.

Caustic stripping is a method for removing the FFA from the raw material. NaOH is added to the feedstock and the resulting soaps are stripped out using a centrifuge. They can be disposed off or esterified and reintroduced to the transesterification process.

FFA can be also removed from feedstock using potassium carbonate (K_2CO_3). This is a method used for feedstocks with very high FFA content, like WAF. The fat is mixed with water and heated. Subsequently, K_2CO_3 is added, and CO_2 is formed together with soaps. The CO_2 bubbles rise to the surface of the fat, and the soaps adsorb on the surface of the bubbles, forming foam, that can be easily separated from the fat. The soaps are then esterified and reintroduced to the transesterification process. This method is much more expensive than the regular caustic stripping, but the soap separation is easier (35).

Another method of dealing with highly acidic feedstocks is to hydrolyze them into pure FFA and glycerin (see Figure 10). The free fatty acids are then esterified into methyl esters. The yields can exceed 99% and the feedstock is inexpensive. However, it is an additional step in the overall biodiesel production process and the equipment needs to be acid resistant, thus more expensive.

A different technique is glycerolysis. It involves adding glycerol to the feedstock and heating it to high temperature (200°C), usually with a catalyst such as zinc chloride. The glycerol reacts with the FFA to form mono- and diglycerides. The product is a low FFA feed that is subsequently processed in transesterification.

2.3.5 Post reaction processing

After transesterification, the resulting ester/glycerin phase has to be separated and further processed. Excess alcohol can be recovered from the transesterification mixture or from each phase after separation. Biodiesel has to be refined to meet quality requirements. Glycerin, depending on the production plant size and the economy, can be sold crude or refined onsite. Wastewater treatment is also a very important issue; however it will not be discussed here.

Separation:

The separation process is based on the density difference between the phases. Methanol mainly stays in the glycerin phase; however its presence in the mixture affects the solubility of FAME in the glycerin and vice versa. On the one hand it is claimed that the alcohol acts as a dispersant for both phases, inhibiting the separation. This would suggest methanol recovery before the separation of the ester/glycerin mixture. However, it is also argued to the contrary, that alcohol aids in phase separation, which is the reason why the mixture is regularly separated before methanol recovery.

The rate of separation also depends on the intensity of the mixing during transesterification. Therefore, while it should be intensive at the beginning to enhance the incorporation of sparingly soluble alcohol into the oil phase, it should be slower towards the end in order to reduce the time required for the coalescence of fine glycerol droplets.

The pH also affects the phase separation. This is one of the reasons to minimize the use of an alkali catalyst. In some systems, the transesterification mixture is neutralized before the separation.

As it was mentioned before, the presence of soaps inhibits the separation because of their tendency to emulsify. However, the same problem occurs with unreacted mono-, di- and triglycerides. If the reaction was not completed, a third layer will form between the ester and glycerin. As with soaps, these unreacted glycerides will complicate the washing process. Depending on the quantities, this can cause a significant yield loss or, in the worst case, the ester phase will not meet the biodiesel quality requirements.

There are three categories of equipment used to separate the ester and glycerin phase. Decanter systems rely solely on the density difference to achieve the separation. The residence time needed for separation and the flow rate of the mixture determines the size of the unit. Usually, decantation is used for relatively small throughputs and batch systems. The temperature in the decanter affects the alcohol solubility in both mixture phases, as well as their viscosity. Too high a temperature might cause the residual methanol to flash. Too low a temperature increases the viscosity of both phases and thus slows down the coalescence rate in the system.

The continuous processes usually apply centrifuge systems. The centrifuge creates an artificial, high gravity field by spinning at very high speeds. The separation here is much faster and more effective than in decantation. Nevertheless, the initial cost of such a system is higher, and maintenance more demanding.

Hydrocyclones are relatively new devices in biodiesel production that are still at the experimental stage. A hydrocyclone uses an inverted conical shape and the incompressibility of the liquids to accelerate the liquid entering the cyclone. The separation effect is similar to a centrifuge; the heavier material (biodiesel) is forced towards the wall and downward, and the lighter one (glycerin) is forced to the center and upward. Since the presence of volatiles appears to disrupt the cyclone, excess methanol should be removed from the mixture before separation.

Ester washing and neutralizing:

This step is used to neutralize residual catalyst and to remove the soaps as well as residual glycerin and methanol. Water is used as a medium for neutralizing acid, and therefore these two processes can be combined into one step. Traces of methanol can either be removed from biodiesel before washing or from wastewater effluent after washing.

The use of warm water (50-60°C) as well as gentle agitation prevents the precipitation of saturated FAME and retards the formation of emulsions, resulting in a rapid and complete phase separation.

The use of resin purification media is a complex solution for ester treatment. Any impurities, soaps, residual methanol and glycerin, as well as trace water are removed in one step. No further filtering is required. The polymer is regenerated with methanol, which is later recycled and reintroduced into the transesterification unit. Spent resin has to be replaced periodically. These systems are usually applied in a continuous production.

Ester drying:

Since the equilibrium solubility of water in esters is higher than required by the quality specifications, the removal of excess water is necessary. Drying is usually performed by vacuum. The system is operated at low pressure, which allows the water to evaporate at a much lower temperature. Because of the low water content in biodiesel, it is also possible to use passive systems like molecular sieves or silica gels. However, these systems must be periodically regenerated.

Other ester treatments:

Several processes of biodiesel treatment are dependent on the feedstock used. For instance, WVO and WAF can leave an objectionable color in the resulting biodiesel. Therefore some producers apply activated carbon bed or other bleaching technologies in order to remove excessive color. However, it is more of a marketing measure than a technological requirement.

Since sulfur content requirements for biodiesel are quite stringent, the use of vacuum distillation for the removal of sulfur compounds can be necessary. The added benefit of this process is the removal of other minor contaminants, which is especially effective in the case of biodiesel produced from highly degraded feedstocks like WVO or WAF.

Filtering of the final biodiesel product is essential to ensure that no contaminants, which could damage the engine, are carried with the fuel. The biodiesel leaving the plant must not contain any particles bigger than 5µm (20).

Additivization of the fuel is a measure to improve certain physical and chemical properties like lubricity, oxidative stability, corrosion resistance, etc. Nevertheless, the additive technology for biodiesel is less advanced than that for fossil diesel fuels. The properties of biodiesel as well as the quality requirements will be discussed in further sections.

Methanol recovery:

The consumption of methanol for biodiesel production is high, since excess alcohol is used to facilitate the transesterification reaction. The recovery of methanol is essential both for economic and environmental reasons. It saves the input costs for the process and eliminates the emissions of methanol to the surroundings.

Methanol is fully miscible with water and with glycerin. It has little solubility in oils, although it has somewhat more in their esters. Therefore, in a fully reacted transesterification mixture, the concentration of unreacted alcohol is higher in the glycerin phase, approximately 60% (36).

The physical properties of alcohol are decisive in designing a recovery system. Methanol has a relatively low boiling point (64.7°C), which means that it is highly volatile and therefore can be effectively removed from ester, glycerin and effluent water. On the other hand, a low boiling point along with a low flash point (8°C) also means that methanol is highly flammable, therefore adequate safety measures have to be undertaken.

Methanol can be recovered using distillation, either at atmospheric pressure or in vacuum. Usually a flash evaporation with recondensation is applied. Recovered methanol from ester, glycerin and effluent water streams is recycled and reused in transesterification.

Glycerin refining:

The separated glycerol contains residual alcohol, traces of catalyst and water, insolubles, unreacted TG and some esters. Depending on the used feedstock, other impurities might be present. Generally, WVO and WAF will contain different amounts of proteins, ketones and aldehydes, sulfur compounds, etc, which end up in the glycerin phase.

The glycerin produced in the transesterification is of crude grade and thus of low value. There are different approaches to its utilization. Small producers usually limit the glycerin treatment to dehydration and either sell it to the refiners or burn it onsite for steam production. On the other hand, a refined glycerin can constitute an important economic variable for the production plant. Therefore, most big production plants refine glycerol, at least to a technical grade (26).

Conventional methods include a three step treatment. Chemical refining neutralizes the remaining alkali catalyst, yielding salts. These are mostly removed during physical refining, together with other solids and moisture. This step involves filtration or centrifugation, and water removal by evaporation. The control of pH is important at this stage, since low pH leads to dehydration of glycerin, and high pH causes its polymerization. All physical processing is typically conducted at 65-90°C, when glycerin is less viscous, but still stable (20). Subsequently, the glycerin is purified by distillation or by ion exchange. However these traditional methods are quite costly. In order to keep up with an increasing glycerin production as a biodiesel byproduct, certain complex processes are being designed especially for this business. An application of gas chromatography in glycerin purification, in addition to the heat and water consumption well combined with

the rest of the biodiesel production process improves the economy significantly and yields a 99.5% pure, pharmaceutical grade glycerin (37).

2.3.6 Production process options

Several methods of biodiesel production can be applied, depending on the plant capacity, production technology, and used feedstock. The basic division distinguishes batch and plug flow reaction (continuous). Batch production is the simplest and easiest option to control, and is normally used for small scale installations and for recycled feedstocks. A PFR system incorporates a series of continuous stirred reactor tanks (CSRT). This option usually has shorter residence times and it is applied in most big production plants. The installation technology is a vast subject on its own; therefore it will not be discussed here in further detail.

2.4 Hydrogenation derived renewable diesel (HDRD)

Biodiesel production by hydrogenation of fatty acid glycerides is a new technology, although the method itself has been known for many years. Hydrogenation is also called catalytic cracking and is a process used in petroleum refining, for transforming hydrocarbons with higher molecular weight into lighter hydrocarbon products. Therefore, the industrial application of HDRD is especially convenient for oil companies, since they already have proper facilities. Moreover, since such biodiesel consists of alkyl chains having very similar properties to commercial fossil diesel, an existing distribution infrastructure can be used.

A simplified route of HDRD production is presented in Figure 13. The production of hydrogen is a separate and broad technological issue and although of a great importance, it will not be discussed here.

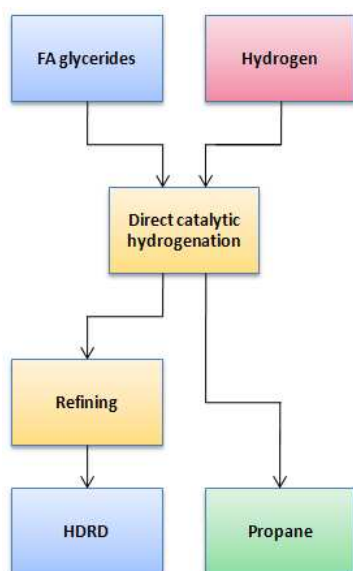


Figure 13 Production of HDRD (26)

The basic concept of hydrogenation for biodiesel production involves the cracking of the triglycerides into corresponding alkyl chains. The other main product is propane from the glycerin moiety, which can constitute an important economic variable for the plant. Depending on the reaction pathway, a number of side products are generated in different proportions: water, carbon monoxide, methane and carbon dioxide (38) (39).

The process is continuous, usually involves heterogeneous solid bed catalyst system, and reaction conditions with elevated temperature and pressure (39) (see section: The role of catalyst).

In general, the reaction of hydrogen cracking can take four directions, depending on the used catalyst, temperature and pressure (40) (39):

- Dehydration;
- Decarboxylation;
- Dehydration & decarboxylation;
- Decarboxylation side reaction yielding CO.

The prevailing reaction pathway also highly depends on the feedstock. Since the composition of oils varies drastically between types, a particular set of reaction conditions and catalyst type will give different products according to the starting oil. Nevertheless, the same problem occurs in the production of FAME.

Alkane chains originating from the dehydration reaction have the same carbon number as the original fatty acid chain, i.e. even carbon number, typically 16 or 18. The main reaction byproducts of this route are water and propane. On the other hand, decarboxylation yields hydrocarbons with an odd carbon number; they have one carbon atom less in the molecule than the original fatty acid chain (38).

The schemes of all four types of reactions, including theoretical hydrogen consumption are presented in Figure 14:

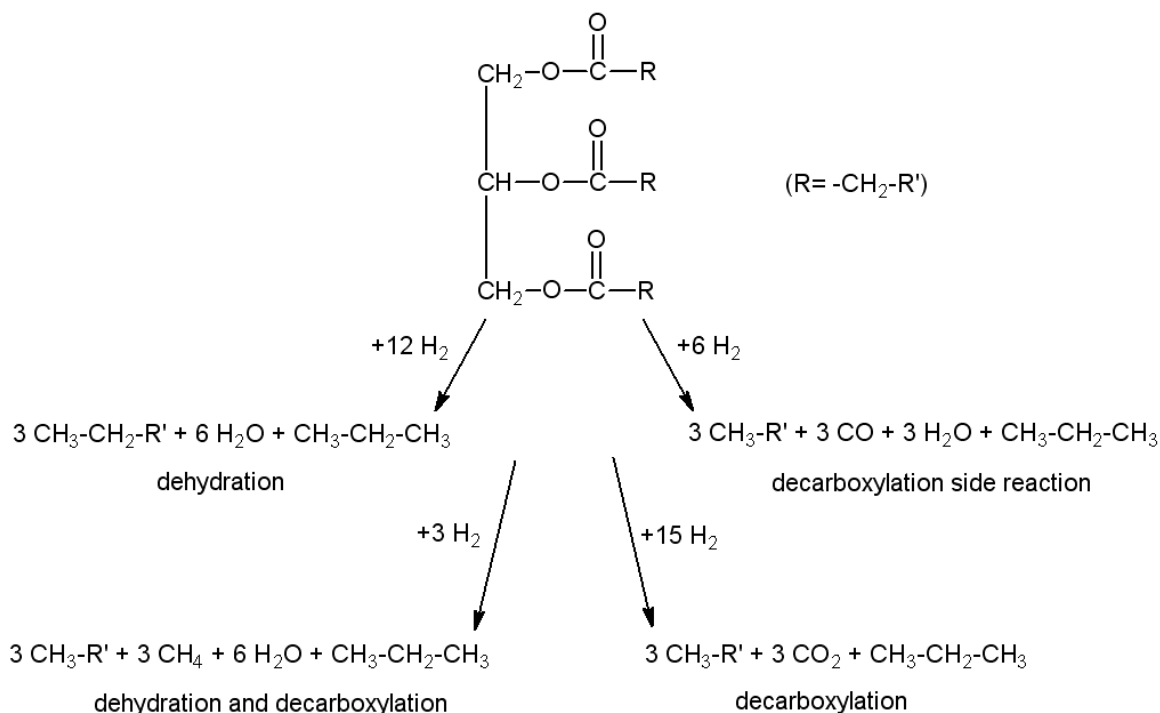


Figure 14 Reactions of hydrogenation

Each of these pathways consumes specific number of hydrogen moles for cracking the TG molecule. However, additional atoms are normally used for the saturation of unsaturated alkyl chains and their disruption or isomerization due to elevated temperatures (38). It is also important to keep in mind, that usually a biodiesel production process involves all the above reactions, in certain proportions. A spontaneous reaction is decarboxylation, due to favorable thermodynamics, and the role of a catalyst is to moderate the process, shifting it towards a more beneficial pathway (dehydration or dehydration with decarboxylation), and away from the undesired side reaction. Decarboxylation, although it requires less hydrogen, is only the third choice because of a poor mass balance, due to CO₂ production. Thus a biodiesel yield from this reaction is smaller (26).

2.4.1 The role of catalyst

While the major role of a catalyst and its selectivity in the production of HDRD fuel is indisputable, there is still very little scientific literature available on the subject. Also the companies that have already applied this technology in commercial trials are normally reluctant to share the knowhow.

The experiments performed using commercial hydrotreating and hydrogenation catalysts (nickel and molybdenum on silica support: Ni-Mo/Al₂O₃ and Ni/Al₂O₃), under elevated pressure and temperature (250 and 450 °C, and 7 to 70 bar) demonstrated the linkage between the reaction rate and hydrogen diffusion. The hydrogenation was limited because of low hydrogen solubility in vegetable oils, i.e. by hydrogen transfer (38).

Another study investigated the use of pillared clay as a catalyst. This material has a porous structure with acidic properties, comparable to that of zeolites. Zeolites are microporous aluminosilicate minerals of high activity and selectivity, which have been used since the 1960s. However, the use of pillared clays has received considerable attention because of their ability to achieve large pore sizes. Therefore they can play an important role in the conversion of vegetable oils into HDRD. A major problem associated with the use of pillared clays as catalysts has been their lack of thermal and hydrothermal stability above a certain temperature. Therefore current research focuses on the introduction of various pillaring species (cations) that would improve these parameters (41).

Catalytic deoxygenation of lauric acid in a solvent was studied in a continuous fixed bed reactor over Pd/C. The selectivity to the desired products was very high under all conditions, being above 95%. However, the catalyst stability was low. The initial concentration of lauric acid was decisive for the catalyst deactivation; the higher was the initial concentration of fatty acid, the more extensive was the catalyst deactivation. The reasons for the catalyst deactivation were poisoning by the product gases, CO and CO₂, and cooking (42).

Nippon Oil Corporation, a Japanese petroleum company, explored reaction temperatures ranging from 80°C to 360°C, with reaction pressures of 6MPa and 10MPa, and used a common hydrodesulfurization catalyst (39).

Neste Oil, a Finnish refining corporation, has very recently patented their decarboxylation process. They use mainly Pd on carbon and sulfided NiMo on alumina support. Hydrogen may be used optionally. The reaction is carried out at a temperature of 100-400°C, preferably 250-350°C. The pressure ranges from atmospheric pressure to 20 MPa and preferably from 0.1 to 5 MPa of inert gas/hydrogen mixture (43).

2.4.2 Estimated yields

Neste Oil has applied a decarboxylation process. Their feedstock is comprised mainly of rapeseed oil, soybean oil and palm oil. Having this information, an approximate maximum yield can be calculated. According to the reaction presented in Figure 13, 1 kg of FA glycerides reacts with at least 20 g of hydrogen, yielding up to 775 g of NExBTL and around 48 g of propane (26).

Petrobras, a Brazilian oil company, does not report on the method used for the production of their H-BIO diesel. However, there is information provided about the amounts of products from process (44). Knowing that 100 liters of soybean oil gives 96 liters of diesel and 2.2 m³ of propane, it can be recalculated that 1 kg of FA yields 880 g of H-BIO and 43 g of propane. The received yield suggests that the production process employs a dehydration reaction.

3 STATE OF THE ART

The technology employed in biodiesel production has been explained in the previous chapter. This section will introduce the ongoing projects which apply the state of the art processes and technologies in everyday life. Both the fatty acid methyl ester and hydrogen derived renewable diesel technological solutions will be covered.

3.1 FAME

The following processes are recently invented modifications of this known biodiesel production technology, in terms of reaction conditions, used catalysts and alternative, recycled feedstocks.

The *Mcgyan*® process, called so after the names of the inventors, is a novel continuous fixed bed reactor process that employs a metal oxide based catalyst. Porous zirconium, titanium and alumina micro particulate heterogeneous catalysts have been shown capable of continuous rapid esterification and transesterification reactions. Simultaneous conversion of FFA and TG into FAME biodiesel is carried out under high pressure (ca. 17 MPa) and elevated temperature (300-450°C), with residence times as low as 5.4 seconds. Methanol or ethanol can be used, however using longer chain alcohols such as propanol and butanol is also researched. These offer some distinct advantages, like very low cloud point values (-25°C for tall oil butyl ester). The reaction is not affected by the presence of water, and the catalyst does not get poisoned over time. The process only yields trace amounts of glycerin, probably due to its conversion to methanol, or other alcohols, in the presence of the catalyst; thus the high temperature and pressure of the reaction. There is no soap generation and the biodiesel product does not need to be washed, therefore the amount of waste and wastewater is significantly reduced. The ability of using cheap feedstocks such as WAF and WVO mixed with crude vegetable oil is another advantage. The process has been commercialized by a new company, Ever Cat Fuels Corporation, whose plant construction in Isanti (Minnesota) is nearing completion. The designed production capacity is 3 million gallons/yr (around 10,000 tons/yr) with a possible expansion to 30 million gallons/yr (around 100,000 tons/yr) (45) (46) (47).

SunPine is a forest industry based biorefinery located in Sweden. It is one of the participants in the Solander Science Park, a network of Swedish companies that are collaborating to advance the pulp mill biofuels concept. The company has developed a technology to produce biodiesel via esterification from crude tall oil (40-50% FFA), a byproduct of the Kraft pine pulping process, combined with crude vegetable oil like *jatropha* or castor. The conversion product is crude FAME, which can be distilled to meet the quality standards for biodiesel, or hydrogenated to HDRD. SunPine is constructing a production plant in Pitea, Sweden, with a capacity of up to 100,000 m³ of crude tall diesel (around 87,000 tons/yr) (48) (49).

Chemical engineering researchers at the University of Arkansas have investigated *supercritical methanol* as a method of converting chicken fat and tall oil into fatty acid methyl esters. The use of a catalyst in the traditional transesterification process implies relatively time consuming and complicated separation of the product and the catalyst, which results in high production costs and energy consumption (50). A large excess of methanol, heated and pressurized to a critical point, dissolves and reacts with feedstock substrates in a one step process which does not require a catalyst. The best performance for

chicken fat was showed at 325°C with a methanol to oil ratio of 40 (89% yield). The maximum yield for tall oil fatty acid was achieved at 325°C with a methanol to oil ratio of 10 (94%) (51). Since no alkali catalyst is used, there is no soap formation, thus no loss of yield. Although this method actually prefers feedstocks with high FFA content, some studies using crude vegetable oils have also been done. Production of FAME biodiesel from soybean oil using supercritical methanol and CO₂ as cosolvent gave 98% yield. Optimal reaction conditions were the following: temperature of 280°C, methanol to oil ratio of 8 and CO₂ to methanol ratio of 0.1, pressure of 14.3 MPa and reaction time of 10 minutes (50).

BIOX Corporation operates a 53,000 tons/yr biodiesel production plant in Hamilton, Canada (52). Their patented process converts both TG and FFA in a two step, single phase continuous process at atmospheric pressures and near ambient temperatures in less than 90 minutes. The BIOX process uses a cosolvent, tetrahydrofuran, to solubilize the methanol. Cosolvent options are designed to overcome slow reaction times caused by the extremely low solubility of the alcohol in the triglyceride phase. The process allows achieving feedstock conversion yields above 99%, even when using higher FFA feedstocks (up to 10% FFA content) such as animal fats or crude palm oil. They claim to recapture 99.9% of the cosolvent and excess methanol used in the process, which is then recycled and reused (53).

3.2 HDRD

A number of manufacturers around the world are developing HDRD refining processes and testing them in commercial trials. Understandably, the knowhow is still strictly confidential. Following are brief descriptions of some of the projects.

Neste Oil is producing HDRD from vegetable oils and animal fats in a process they called NExBTL. The company's first NExBTL facility was commissioned in Finland at Neste Oil's Porvoo refinery in summer 2007. A second facility is due to arrive there in 2009. They both have a capacity of 170,000 tons/yr. In addition Neste Oil is building 800,000 tons/yr plants in Singapore and Rotterdam. The Singapore facility is due to be completed by the end of 2010 and the Rotterdam facility in 2011 (54). NExBTL fuel is used in buses of Helsinki City Transport. Previously buses have been filled up with a blend of NExBTL and fossil diesel, but since 2008 neat NExBTL diesel is being used. The hundred percent NExBTL was introduced in close cooperation with Scania (55).

ConocoPhillips, a North American corporation, is the fifth largest refiner worldwide. The company is partnering with *Tyson Foods* (the world's largest meat processor, also North American) to produce HDRD using animal fat. Their plant in Arkansas, opened in late 2007 with the capacity of 1.5 million gallons/yr (around 5,000 tons/yr), increased the production in February 2008 up to 7.6 million gallons/yr (around 25,000 tons/yr) and is expected to ramp up to as much as 175 million gallons/yr (around 600,000 tons/yr) in its full production, in 2009 (56) (57). The production technology applies a thermal depolymerization process to coprocess animal fat with hydrocarbon feedstocks; however, the percentage of the recycled raw material in the overall feedstock stream is not stated. The process was developed at the company's Whitegate refinery in Cork, Ireland, in 2006 (58).

Dynamic Fuels is a joint venture between Tyson Foods and Syntroleum Corporation (North American producer of synthetic fuels). The process developed by Syntroleum is called Bio-Synfining™ and is able to use a wide variety of renewable feedstocks such as

vegetable oils, fats, and greases, to produce synthetic diesel and jet fuel. The companies are planning to build a plant with a capacity of 75 million gallons/yr (around 250,000 tons/yr) to begin production in 2010. Additional plants are already in the planning stages (59) (60).

UOP is a North American company delivering technology for petroleum refining, gas processing and petrochemical production. With the support of the U.S. Department of Energy it has developed a process called Ecofining, for vegetable oil feedstocks. UOP is partnering with *Eni* (Italy's biggest oil company) in designing the first unit of a plant, which is expected to come online in 2009. The facility will be located in Livorno, Italy. Eni also plans to install several additional Ecofining units at other refineries throughout Europe (61).

Petrobras introduced a process called H-BIO in 2006. It was developed to employ a renewable oil source in a diesel fuel production scheme, while taking advantage of existing refining plants. A blend of triglycerides and mineral oil (a byproduct of petroleum refining) is hydrogenated in existing hydrotreating units and then mixed with fossil diesel. This technology improves the parameters of the diesel pool in the refinery, mainly by increasing the cetane number and reducing the sulfur content and density (44). The corporation has adapted 4 of its 12 refineries to produce H-Bio and was to start commercial production by the end of 2007. However, the plans have been suspended due to the high international soy and other vegetable oil prices at a time (62).

Nippon Oil Corporation, a Japanese petroleum company, in cooperation with *Toyota Motor Corporation* and *Hino Motors* started a joint project with the *Tokyo Metropolitan Government* aimed at commercializing Nippon's bio hydrofined diesel (BHD). Since 2005, Nippon and Toyota have worked jointly on the development of the BHD technology, and this project will allow verification of its environmental performance. Tokyo city buses will be used for demonstration. At the same time, an examination of a supply system in Japan for BHD will be carried out (63).

4 PHYSICAL AND CHEMICAL PROPERTIES OF BIODIESEL

Biodiesel differs from fossil diesel in terms of chemical composition; therefore its physical and chemical properties are also distinct. It is important to keep in mind that today the term biodiesel refers both to FAME and HDRD. The chemistry of these two biofuels is different, which also translates into specific properties. These properties depend on the original feedstock too, and if unfavorable, can be minimized by blending biodiesel with fossil diesel. As in the case of fossil diesel, the quality issues of biodiesel and its blends are defined in specification standards.

4.1 Blending

Biodiesel can be used as B100 (neat) or in a blend with fossil diesel. Blends only refer to FAME and are designated as 'B' followed by a number, e.g. B20 is 20% biodiesel and 80% fossil diesel. Blending of HDRD has no legal restrictions due to its chemical resemblance to fossil diesel.

Even in very low concentrations, FAME improves fuel lubricity and raises the cetane number. Blending of biodiesel with fossil diesel in small proportions (B2, B5) is already a part of renewable energy policy in some countries.

In Europe a biodiesel share of up to 5% in fossil diesel does not have to be labeled, according to norm EN590. In some countries, like France, B5 is already an obligatory blend.

Blending can be necessary in some cases. Saturated FAME, like palm or coconut oil methyl esters cannot be used neat in colder climates because of their very high cloud points. Therefore, their mixing with fossil diesel is a condition of their utilization in Europe.

The acceptance of the use of biodiesel by car producers is generally an upward trend. EPA confirms that most manufacturers accept biodiesel blends of up to B5 (64). NBB goes further and reports that most major engine companies have stated formally that the use of blends up to B20 will not void their parts and workmanship warranties, provided that the fuel meets quality specifications (65).

4.2 Specification standards

Engine manufacturers and biodiesel plants in different parts of the world use slightly different standards for biodiesel. The diversity among existing specifications is the result of a number of factors. The first is that some of the standards have been formulated primarily around their locally available feedstock. Another factor is that some specifications are based on biodiesel's use as blendstock and others on the use of neat biodiesel. Further, some biodiesel standards are applicable to both FAME and FAEE, while others only relate to one of the two (66). Table 2 compares european and north american standards.

EN590 is a European standard that describes the properties of fossil diesel fuel and up to its 5% biodiesel blends. **DIN 51606** is a German standard for biodiesel, considered to be

the highest standard currently in existence. **EN14214** is the standard for biodiesel approved in 2003 by the European Committee for Standardization (CEN). It is broadly based on DIN 51606. Brazil was using biodiesel standards similar to those of Europe and the US until March 2008, when new specifications, more adequate to the local reality, were introduced (67) (68). In the US, the industry organization that defines the consensus on fuels is the American Society for Testing and Materials (ASTM). **ASTM D6751** was the first standard designed to control B100. At the end of 2008 new specifications came into force, and ASTM D6751 got updated. The new norms include (69):

- ASTM D975-08a, specification for diesel fuel oils. Used for on and off road diesel applications; revised to include requirements for up to 5% biodiesel;
- ASTM D396-08b, specification for fuel oils. Used for home heating and boiler applications; revised to include requirements for up to 5% biodiesel;
- ASTM D7467-08, specification for diesel fuel oil and biodiesel blends (B6 to B20). A completely new specification that covers finished fuel blends for on and off road diesel engine use.

Table 2 Specification standards for diesel & biodiesel fuels (65)

Biodiesel Standards		EUROPE	GERMANY	USA	PETROLEUM DIESEL
		EN 14214:2003	DIN V 51606	ASTM D 6751-07b	EN 590:1999
Density 15°C	g/cm ³	0.86-0.90	0.875-0.90		0.82-0.845
Viscosity 40°C	mm ² /s	3.5-5.0	3.5-5.0	1.9-6.0	2.0-4.5
Distillation	%, °C			90%, 360°C	85%, 350°C-95%, 360°C
Flashpoint (Fp)	°C	120 min	110 min	93 min	55 min
CFPP	°C	*country specific	sum.0,spr./aut.-10,win.-20		* country specific
Cloud point	°C			* report	
Sulphur	mg/kg	10 max	10 max	15 max	350 max
CCR 100%	% mass		0.05 max	0.05 max	
Carbon residue (10% dist.residue)	% mass	0.3 max	0.3 max		0.3 max
Sulphated ash	% mass	0.02 max	0.03 max	0.02 max	
Oxid ash	% mass				0.1 max
Water	mg/kg	500 max	300 max	500 max	200 max
Total contamination	mg/kg	24 max	20 max		24 max
Cu corrosion max	3h/50°C	1	1	3	1
Oxidation stability	hrs;110°C	6 hours min		3 hours min	N/A (25 g/m ³)
Cetane number		51 min	49 min	47 min	51 min
Acid value	mg KOH/g	0.5 max	0.5 max	0.5 max	
Methanol	% mass	0.20 max	0.3 max	0.2 max or Fp <130°C	
Ester content	% mass	96.5 min			
Monoglyceride	% mass	0.8 max	0.8 max		
Diglyceride	% mass	0.2 max	0.4 max		
Triglyceride	% mass	0.2 max	0.4 max		
Free glycerol	% mass	0.02 max	0.02 max	0.02 max	
Total glycerol	% mass	0.25 max	0.25 max	0.24 max	
Iodine value		120 max	115 max		
Linolenic acid ME	% mass	12 max			
C(x:4) & greater unsaturated esters	% mass	1 max			
Phosphorus	mg/kg	10 max	10 max	10 max	
Alkalinity	mg/kg		5 max		
Gp I metals (Na,K)	mg/kg	5 max		5 max	
GpII metals (Ca,Mg)	mg/kg	5 max		5 max	
PAHs	% mass				11 max
Lubricity / wear	µm at 60°C				460 max

The worldwide diversity of biodiesel testing standards is hindering the international trade of this fuel, and an effort is underway to make biofuels standards internationally compatible. A Biofuels Standards Roadmap was developed in April 2007 that delineated the steps needed to be undertaken by the United States, Brazil and the EU to achieve greater compatibility among existing biofuels standards (66).

4.3 Biodiesel properties

Although biodiesel standards are somewhat different around the world, they all refer to a similar set of properties. The critical biodiesel properties are summed up below (in alphabetical order).

Acid Value is a direct measure of the free fatty acids in B100. The FFA can lead to corrosion and may be a symptom of water in the fuel. Although initially low, the acid value may increase with time as the fuel degrades due to contact with air or water.

Cetane number is analogous to the octane rating in a spark ignition engine; it is a measure of how easily the fuel will ignite in the engine. It is measured to guarantee good engine performance. Higher cetane numbers indicate a short ignition delay, and thus help to ensure good cold start properties and minimize the emissions. For biodiesel the cetane number is seldom an issue because all of the common fatty acid esters have high cetane numbers, by far exceeding the values for fossil diesel. The cetane number can be predicted $\pm 10\%$ using the esters composition.

Cloud point, a temperature at which dissolved solids precipitate, giving the fuel a cloudy appearance, is a critical factor in cold weather performance. Biodiesel, due to the chemical composition of some feedstocks, usually has a higher cloud point than that of fossil diesel, which is a disadvantage. The cloud point, however, is another parameter that can be predicted $\pm 5\%$ with knowledge of the esters composition. Since the saturated methyl esters are the first to precipitate, the amounts of these esters are the determining factors. Producers can modify the cloud point by using additives and by blending feedstocks that are relatively high in saturated fatty acids with feedstocks that have lower saturated fatty acid content.

The *flash point* is the lowest temperature at which a flammable liquid can form an ignitable mixture in air. A minimum flash point for diesel fuel is required for fire safety, therefore the higher the number the better. This requirement is much stricter for biodiesel than for fossil diesel, to ensure that the manufacturer has removed excess methanol used in transesterification. Therefore, flash point is in part a measure of residual alcohol in the B100. Excess methanol in the fuel may also affect engine seals and elastomers and corrode metal components.

Iodine number is a measure of fuel's unsaturation. The higher the iodine number, the more unsaturated fatty acid bonds are present in FAME. The oxidative stability of biodiesel can be estimated using the iodine number.

Kinematic viscosity is a basic design specification for the fuel injectors used in diesel engines. A minimum viscosity is required because of the potential for power loss. If viscosity is too high, the fuel injectors do not perform properly and the poor fuel combustion can lead to deposit formation. The viscosity of biodiesel can be predicted $\pm 15\%$ using the esters composition.

Phosphorus content is limited to avoid the damage of catalytic converters and the formation of toxic compounds during the combustion process. Phosphorus comes from the incomplete refining of vegetable oil, and from bone and proteins encountered in the fat rendering process.

Total glycerin is the sum of free and bonded glycerin. Free glycerin comes from incomplete separation and washing of biodiesel. Bonded glycerin is the glycerin backbone of the unreacted mono-, di-, and triglyceride molecules, thus it is an indicator of an incomplete esterification reaction. Fuels that exceed the limit are highly likely to plug filters and cause other problems.

Total sulfur is an indicator of biodiesel contamination with protein material and/or carryover catalyst or neutralization material from the production process. This is especially valid for producers using rendered or waste feedstocks, since the use of these chemicals is substantial. Other than that, biodiesel feedstocks typically have very little sulfur. The sulfur content is measured to reduce sulfate and sulfuric acid pollutant emissions and to protect exhaust catalyst systems when they are deployed on diesel engines in the future.

Water and sediment is a measure of cleanness of the fuel; it refers to the presence of free water droplets and sediment particles. For B100 it is particularly important because water can react with the esters, making free fatty acids, and can support microbial growth in storage tanks as well as corrosion. Sediments may plug fuel filters and contribute to other engine damage. Sediment levels in biodiesel may increase over time as the fuel degrades during extended storage.

4.4 Fossil diesel vs. FAME

Some of the properties of fatty acid methyl esters, depending on the feedstock, differ significantly from those of fossil diesel. These properties include energy content, cetane number, cold flow, oxidative stability and lubricity.

Energy content:

Compared with diesel fuel, neat FAME has about 10% lower energy content (42.8 MJ/kg vs. 37.5 MJ/kg). Potential losses in power and fuel economy coming from this difference have to be compensated by the fuel price. However, since the energy content of biodiesel/fossil diesel blends is proportional to the amount of biodiesel in the mix, blending is an effective remedy. It has been reported, that B20 users experience only a 1% loss in fuel economy on average and rarely report changes in power (70).

Cetane number:

FAME, in general, has a higher cetane number than fossil fuel, due to the presence of oxygen in the molecule. The cetane number of FAME is a function of the iodine number and the fatty acid chain length. The length of the fatty acid chain determines the percentage of oxygen per mole of fuel. The more saturated and shorter the fatty acid chains, the higher the cetane number of the fuel. Therefore FAME produced from highly saturated feedstocks (WAF, WVO, palm or coconut oil) has especially high cetane numbers.

Figure 15 shows the cetane numbers of various biodiesel samples in comparison with those of fossil diesel. The palm oil methyl ester, which is not included in this chart, has a cetane number as high as 68 (9).

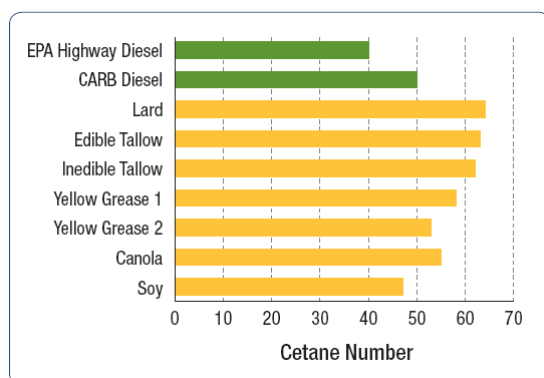


Figure 15 Cetane number of two fossil diesel and several biodiesel fuels (64)

Cold flow properties:

So far, only cloud point (CP) has been discussed. Nevertheless, recently the cold filter plugging point (CFPP) is often used instead of cloud point as the criterion to predict the low temperature performance of diesel. The CP is the temperature at which dissolved solids precipitate, giving the fuel a cloudy appearance. The CFPP is the lowest temperature at which fuel will still flow through a specific filter, thus this indicator is around 3°C below CP.

The cold flow properties are extremely important. Unlike gasoline, fossil diesel and biodiesel can gel or even freeze as the temperature drops. As the fuel begins to gel, it can clog filters and eventually become too thick to pump. The cold flow properties of FAME biodiesel are less advantageous compared to those of fossil diesel (CFPP of -18°C). This is especially valid for FAME with low iodine numbers, like palm or coconut oil methyl esters, or animal fat methyl esters. Saturated molecules solidify at higher temperatures. For example, the CFPP of soy methyl ester is -2°C, whereas the CFPP of palm oil methyl ester is 12°C (9). The saturation of different biodiesel feedstocks is compared in Figure 16.

To reduce the impact of high CFPP, highly saturated methyl esters are mainly used in blends with diesel fuel. These problems can also be controlled by the use of cold flow improver additives. Additionally, fuel line heaters and fuel tank heaters are used on some European vehicles to keep the fuel liquid at cold temperatures.

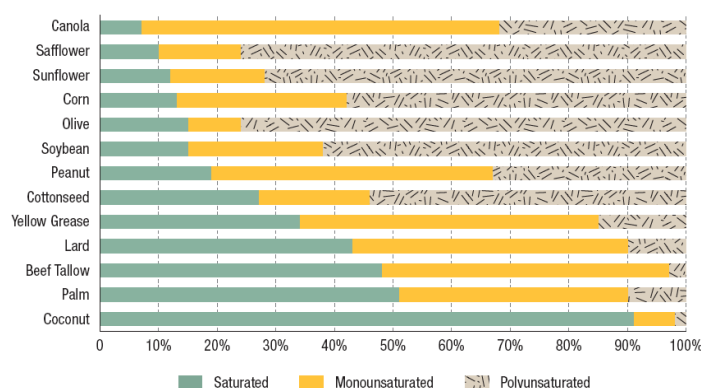


Figure 16 Composition of various biodiesel feedstocks in order of increasing saturated fatty acid content (70)

Oxidative stability:

This parameter is important in terms of fuel storage. Oxidation is an indication of biodiesel degradation and it can lead to high acid numbers, causing corrosion, too high viscosity and the formation of gums and sediments that clog filters. This problem hardly concerns the conventional fossil diesel.

Oxidative stability is another parameter that also has to do with the iodine number. The higher the level of unsaturation, the more likely the biodiesel will oxidize. The points of unsaturation will react with oxygen. Saturated fatty acids are usually stable. Therefore saturated FAME has better oxidative stability. Check Figure 16 for the most stable biodiesel.

In order to prevent biodiesel degradation, heat and sunlight must be avoided and certain metals, such as copper, brass, bronze, lead, tin, and zinc should not be used for storage, or used together with metal chelating additives. Contact with atmospheric air should be minimized as well. Antioxidants, whether natural or incorporated as additives, can significantly increase the oxidative stability of FAME. Naturally occurring antioxidants are very often removed from biodiesel feedstock as it undergoes bleaching or deodorizing.

Lubricity:

FAME is a good lubricant (about 66% better than fossil diesel) (32). Blending biodiesel with fossil diesel, even in small amounts, can increase the lubricity of the mix significantly and thus reduce long term engine wear. The exact blending level required to achieve adequate lubricity depends on the properties of the fossil diesel. Preliminary evidence suggests that 2% biodiesel almost always imparts adequate lubricity (70).

4.5 FAME vs. HDRD

HDRD have different chemistry than FAME. Traditional biodiesel is composed of methyl esters of long chain fatty acids carrying oxygen in their ester group, whereas HDRD is a hydrocarbon with no oxygen.

HDRD has several significant advantages over FAME. It is not hygroscopic, thus it does not attract water like FAME. Therefore it is less likely to cause corrosion or plug fuel filters. It has a very high cetane number (~90). Cold properties of HDRD can be adjusted in the production from -5 to -30°C to meet the needs of various climatic conditions. Moreover, using HDRD blends does not affect the fuel consumption, as opposed to using FAME blends (71).

However, the lubricity of HDRD has to be improved with additives. Doses similar to those for sulfur free fossil diesel fuels are used (71).

5 EMISSIONS

The emission profiles of biodiesel, both FAME and HDRD, have been proven more favorable than that of fossil diesel. Nevertheless, currently experts point out the importance of the increased upstream emissions, apart from tailpipe emission savings. Until a few years ago, the upstream emissions were considered a small print and were simply neglected. The total life cycle GHG emissions are greatly subjected to the sustainability of biodiesel feedstock acquisition. This mainly concerns crop cultivation in the third world. Clearing rainforest or peat swamps for arable land increases the overall carbon dioxide equivalent (CO₂ eq.) emissions tremendously.

5.1 Upstream emissions

The upstream processes of biodiesel production include the use of machinery in connection with soil preparation, sowing, fertilizing and harvesting. The manufacture of fertilizers itself is still mainly based on fossil fuels. However, it seems like most potential upstream GHG emissions come from the extension of arable land connected with deforestation. As for fossil diesel, the upstream emissions come from its refining.

An Australian study from 2007 performed by CSIR (Commonwealth Scientific and Industrial Research Organization) gave an interesting insight into the matter and some shocking numbers (72):

‘Growing and harvesting canola lead to upstream GHG emissions that are approximately 3.5 times higher than upstream emissions from refining the diesel. Tallow has upstream GHG emissions that are approximately 50% higher than the upstream emissions of diesel, whereas those of used cooking oil are slightly lower. Upstream GHG emissions of palm oil depend on whether the plantation was established before 1990, in which case the emissions associated with land clearing and with soil disturbance are not counted as greenhouse gas emissions under present methods of carbon accounting. In this case upstream greenhouse gas emissions are approximately 25% higher than the upstream emissions associated with diesel refining. If, however, rain forest or peat swamp forest is cleared for palm oil growing, then the upstream emissions range from 50 to 136 times higher.’

These numbers incorporated in the total life cycle emissions are of course to a large extent balanced by the tailpipe emissions savings of biodiesel, normally resulting in overall emissions savings. However, the unsustainable palm oil biodiesel stands out as a serious pollution source:

‘Overall this results in savings in total life cycle GHG emissions when the feedstock is canola (422 g CO₂ eq./km saving; 49%), tallow (646 g CO₂ eq./km saving; 76%), used cooking oil (746 g CO₂ eq./km saving; 87%) or palm oil from existing plantations (680 g CO₂ eq./km saving; 80%) when compared to fossil diesel, which emits 855 g CO₂ eq./km. GHG emissions from palm oil that is sourced from cleared rain- or peat swamp forest are 8 to 21 times respectively greater than those from diesel. Therefore, the highest savings in total life cycle GHG emissions are obtained by replacing fossil diesel with biodiesel from used cooking oil.’

The incredibly high emissions from the unsustainable palm oil biodiesel are inflicted by the release of enormous carbon accumulated in the cleared rain or peat swamp forests.

The obtained results are gathered in Figure 17.

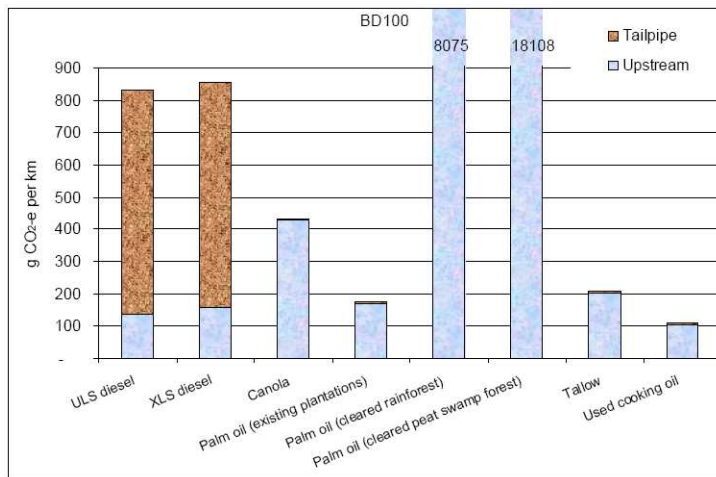


Figure 17 Full life cycle GHG emissions from 100% biodiesel (66)

5.2 Tailpipe emissions

The tailpipe emission profiles are different for FAME and HDRD, due to their dissimilar chemical composition. Nevertheless, they generally both burn cleaner than fossil diesel, and do not emit toxic compounds, because they contain no aromatics and little to no sulfur.

The presence of oxygen atoms in the FAME molecule (10-11% w/w) promotes more complete combustion (73). Therefore less unburned hydrocarbons (HC), polycyclic aromatic hydrocarbons (PAH), particular matter ((PM), mainly soot), and carbon monoxide (CO) are produced. All these combustion products are proven to have an adverse effect on human health. The studies have shown that the combustion of neat biodiesel provides a 90% reduction in total unburned HC, a 75-90% reduction in PAH, and 75-83% reduction in PM exhaust emissions (53). These benefits are also predictable over a wide range of biodiesel blends. Figure 18 shows how the emission profile of a blend depends on the percentage of FAME.

Testing has shown that PM, HC, and CO reductions are independent of the biodiesel feedstock (70).

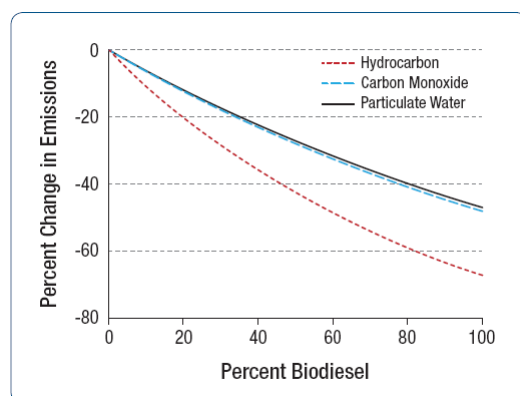


Figure 18 Average emission impacts of biodiesel fuels in internal combustion engines (64)

On the other hand, a great deal of uncertainty remains concerning NO_x emissions, since the mechanism of their formation is still not well understood fundamentally.

It is evident, that NO_x emissions of biodiesel depend on the fuel characteristics, i.e. cetane and iodine numbers, oxidation rate, thermal stability, volatility, flammability, etc. (74). However it seems like they also depend on the engine family. A study performed by NREL showed that in newer engines (2004 compliant), the iodine value has a much smaller effect on NO_x emissions than in the old type of engines (thru 1997). It was also observed that the new engines emitted more NO_x. Moreover, apparently the NO_x emissions vary also depending on the testing procedures. The engine tests generally showed an increase in NO_x emissions, while the experiments performed on vehicles reported NO_x reductions (75) (53).

In general, higher cetane number translates into lower NO_x emissions. The higher the cetane number, the shorter the ignition delay. In brief, this means lower pressure and temperature in the cylinder at the engine start up. Thus, in theory, NO_x production is reduced, since it is strongly dependent on the flame temperature.

On the other hand, the NO_x emissions also depend on the iodine value, i.e. the saturation of the fuel. Therefore, burning FAME will produce more NO_x than burning HDRD or fossil diesel, although highly saturated fatty acids, like those of palm, coconut, or WAF will have lower NO_x emissions (9) (76).

The studies, which showed an increase in NO_x emissions from burning FAME, report that neat soy methyl ester increases these emissions by approximately 10-12% when compared with fossil diesel. However, a more widely used blend, B20, causes an increase in NO_x emissions of only 2-4%, and B5 causes no change (76) (75) (70).

The HDRD biodiesel also shows reductions in PM, HC, and CO emissions. It contains saturated hydrocarbon chains and has a much higher cetane number, so theoretically its NO_x emissions should also be lower. However, the studies performed by Neste Oil showed that while significant reductions were reported in heavy duty engine tests, the light duty vehicles tests detected no significant differences while using HDRD (71).

The NO_x emissions are of high concern in the cities, since NO_x is a photo oxidant and thus an ozone precursor. High concentrations of near-ground ozone are detrimental to human health, animals and plants. However, with respect to biodiesel it does not seem to be much of an issue. Firstly, because neat biodiesel is still hardly used, secondly because it is gasoline engines that emit major amounts of NO_x. Thus it seems like the effect of increased NO_x emissions from biodiesel would be negligible, especially in Europe, where already almost 50% of the car fleet runs on fossil diesel, so the NO_x levels are low (77). Nevertheless, the research into biodiesel and NO_x emissions is ongoing. At this time, researchers note that there are still insufficient data to draw any definite conclusions.

6 ECONOMY, POLICY AND SUSTAINABILITY

A biodiesel economy is still a relative novelty in the world energy portfolio. The initial rash commercial and political actions and the lack of clear and reliable information have created a great deal of skepticism, backed up by popular myths. Although it seems like today the social awareness has somewhat increased and political actions are gaining integrity, there is still a long way to go. Many crucial issues have to be addressed in order to achieve an authentic and favorable biodiesel, or so far as it is concerned, biofuel economy. Marginalizing the importance of sustainable production, accounting for total life cycle GHG emissions, or a strongly positive energy balance creates the threat of missing the main goal of introducing biofuels, which is to fight climate change.

6.1 Energy balance

A common myth among environmental skeptics is that biodiesel (or all biofuels for that matter) has an overall worse energy balance than fossil diesel (or all fossil fuels). The energy balance is the amount of energy consumed over the life cycle to produce a fuel (the energy from photosynthesis used for biomass growth is excluded) versus the amount of energy stored in the fuel's chemical bounds. An overall and reliable methodology is crucial for correct calculations. Many controversies arose over the Pimentel and Patzek study, published in 2005, which claimed that biodiesel has an overall negative energy balance. An immediate opposition from many scientific circles backed up by the educated response from the US National Biodiesel Board, pointing out the inaccurate and incoherent methodology used in the study, seemed to have cleared up the issue, however the damage had been done (78).

The energy balance of biodiesel depends on the feedstock used, the efficiency of the production process and the use of renewable energies in the overall process. Nevertheless, biodiesel has a positive energy balance in any case (79). It means that for every unit of fossil energy consumed in its life cycle, biodiesel yields more than one unit of fuel product energy. By contrast, petroleum diesel's life cycle yields only 0.83 units of fuel product energy per unit of fossil (80). Table 3 compares the energy balance indices for biodiesel from different origins.

Table 3 Energy balance of different biodiesel fuels (81)

Biodiesel product	Energy balance
Palm oil (imported from Asia to Europe)	9 : 1
WVO	5-6 : 1
Soybean oil (USA)	3.2 : 1
Rapeseed oil (Germany)	2.5 : 1

6.2 International trade and production costs

The overall production cost of biofuels is higher than that of fossil fuels, therefore tax exemptions and other incentives are needed to make it competitive. Developing countries usually produce biofuels at lower prices and are keen on exporting, but the international trade is restricted by several factors. Firstly, since there are no internationally recognized criteria governing the promotion of biofuels, countries set up their own schemes, creating a non uniform market that hinders the trade. Moreover, incentives are often aimed towards the promotion of domestic agricultural feedstocks and interests, rather than the promotion of biofuels. Additionally, import standards vary from country to country and it is not even known whether biofuels should be considered as an agricultural or industrial good. For example, according to the World Customs Organization's Harmonized Coding System (HS) biodiesel, unlike bioethanol, is considered to be an industrial product, therefore its producers cannot benefit from the tariff protection, which the agricultural goods producers are entitled for (82).

The lack of internationally recognized criteria resulted in another paradox a few years ago. The US producers of so called B99.9 were accused of price dumping practices in Europe. The high biodiesel blend containing as little as 0.1% of fossil diesel was produced in the US shipping docks, by adding minute amounts of fossil diesel to biodiesel cheaply imported from countries like Indonesia or Malaysia. This qualified the producers for biofuel subsidies according to the US law. Subsequently, the B99 was exported to Europe and resold as pure biodiesel, therefore once more eligible for subsidies, within the European blending subsidy schemes. This shady business undercut the EU prices by as much as 30%, and put many European biodiesel producers out of business. The European Biodiesel Board (EBB) filed a complaint to the European Commission (EC) in April 2008, and in June the investigation was launched. The deadline for the EC to take any provisional measure is in March 2009 (83).

The production cost of biodiesel depends on the price of the raw material, the plant capacity and technology, and the management of the byproducts. The yield of biodiesel and the price of byproducts, i.e. the meal and glycerin, can be decisive for the feasibility of production. Additionally, all costs usually fluctuate with the price of crude oil.

According to an Energy Research Centre of the Netherlands (ECN) study, the estimated production cost of biodiesel in the EU was about 0.50 EUR/L in 2006 (84). Oleoline (a B2B platform specializing in oleochemicals) reports, that the production cost of biodiesel from rapeseed oil was about 0.60 EUR/L in Germany in March 2007 (85). According to the Energy Information Administration (EIA), in the U.S., biodiesel was produced from soybean oil for 0.36-0.48 EUR/L and from yellow grease for 0.18-0.22 EUR/L in 2007 (86). On the other hand, a comparative study of global biodiesel production costs performed in 2006 reports number ranges of 0.41-0.56 EUR/L for Eastern and Central Europe, 0.57-0.70 EUR/L for Germany and France, and as high as 1.01-2.00 EUR/L for Spain and Italy. The estimation for the U.S. was at 0.56 EUR/L (87).

No one can predict with certainty the price of fuel at the pump. Many factors affect the sales price including production costs, crude oil's price, taxes, inventory levels, and supply and demand. Geopolitical factors, weather, transportation, and economic events also can affect the sales price (64).

6.3 International trade and sustainability

The growth of a successful biodiesel economy is hindered by the lack of internationally agreed upon criteria for sustainable production and the muddle of different government measures aimed mainly at sheltering domestic markets.

These matters will have to be clarified and developed, considering that the demand for biodiesel will grow in order to meet the new EU and US biofuel commitments. In the EU, according to the Biofuel Directive, a 10% share of biofuels in transportation is required by the year 2020, and the US Renewable Fuel Standard for 2009 requires a 10.21% share (see [Appendix A](#)) (88).

An increasing importation of biodiesel or biodiesel feedstocks from developing countries is inevitable (82). Therefore a close look at the sustainability of their production is necessary, as naturally, the farmers across the world will tend to expand their cropland as much as possible. There is a need for international cooperation and separating the relevant policy from the producers' interests. During the last few years several international measures have been taken.

In November 2005 the Roundtable on Sustainable Palm Oil, an international stakeholder on sustainable palm oil adopted The RSPO Principles and Criteria for Sustainable Palm Oil Production (89). In order to get certified, full traceability from the plantation through the end product is required.

In August 2008 the Roundtable on Sustainable Biofuels, an international stakeholder initiative on sustainable biofuels, presented the 'Version Zero Sustainability Standards'. The proposed standards include the respect of international treaties on labor conditions and human rights, the need for 'significant' lifecycle greenhouse gas emissions reductions compared to fossil fuels, the respect of local communities and land rights, the need to guarantee food security, as well as the minimization of soil degradation, water depletion, air pollution and biodiversity loss (82).

In December 2008 the European Parliament endorsed the energy and climate change package, including the 'Directive on the promotion of the use of energy from renewable sources'. Originally, it was to include very strict sustainability criteria, however in the final negotiations they got very much watered down (see [Appendix A](#)).

6.4 Biodiesel production and sustainability

Recently, the production of palm oil is increasing in tropical countries like Malaysia and Indonesia, Thailand, Nigeria and Colombia (9). This rapid growth is controversial, because an unsustainable expansion of the cultivation land can lead to biodiversity loss, deforestation, forced evictions and population displacement, food shortages and price increases, and water scarcity (90).

It is commonly believed that this recent increase of palm oil production is linked solely to the higher biodiesel demand. However, the 2005 EC Biofuels Progress Report states that, while the global palm oil production increased by 10 million tons in the years 2001-2005, only 30,000 tons of palm oil was used for biodiesel production in 2005 (91). Although obviously it is an intended understatement, since this number only includes the biodiesel produced in the EU, it is clear that an increasing biodiesel production is not the main driving force of the development of the palm oil market. The European consumption of palm oil rose above all due to the EU ban for using WAF and WVO for fodder production

in 2002. Other major non food markets, like those of cleaning agents and cosmetics, have been growing globally in the preceding years as well.

Another controversial issue is the fuel vs. food debate. Indeed, today most of the biodiesel feedstock comprises of edible vegetable oils. In 2007-2008 the prices of vegetable oil were skyrocketing and it was believed by many that this was caused by an increased demand for biodiesel. However, it is enough to take a look at how the vegetable oil price fluctuations were accompanied by those of crude oil, to realize that there was much more to it than the production of biodiesel. Additionally, the low harvest in the preceding years has decreased the world food reserves, and China and India were undergoing an economical boom. Inevitably, following the known market rule, an increased demand coupled with an unchanged supply, caused the prices to rise.

There is no doubt that a rapid and uncontrolled growth in biodiesel production in recent years must have had its share in the mentioned environmental impairments. However, a somewhat hysterical attack on biodiesel was clearly exaggerated. The vast number of involved stakeholders defending their businesses has been misleading the public opinion for years, which created a great deal of confusion. Therefore, there is no reliable data on how the biodiesel economy has affected the environment so far, because not even the reports issued by the EU are completely objective.

IV. CASE STUDY

The purpose of this study is to provide a full picture of the possibilities of biodiesel production in Iceland. This is investigated on a few levels. Firstly, the operation of a small biodiesel plant in Akureyri running on WVO and WAF is examined. Subsequently a projection for a full size production plant is made, followed by a short description of a biorefinery this full size plant will be a part of.

Potential feedstocks available in Iceland have been introduced, with their possible sources and generated amounts. The main focus was on WVO and WAF, a basic feedstock for the small scale production plant.

Laboratory work has been conducted in order to gather information about the mass balance and the yield of FAME. It involved research of the most adequate production process for the given feedstock (WVO) and given production scale (300 tons/yr).

The main assumptions of the economical viability of the small and full scale production plant were presented.

1 BACKGROUND INFORMATION

Even though Iceland is a world leader in utilizing renewable energy, a considerable share of its energy demand is still met by burning fossil fuels. Iceland has no proven crude oil reserves and all fossil fuels are imported. Transportation and fishing are their main consumers, with a diesel fuels demand of 400,000 tons in 2007 (92). Figure 19 presents their consumption by major sectors.

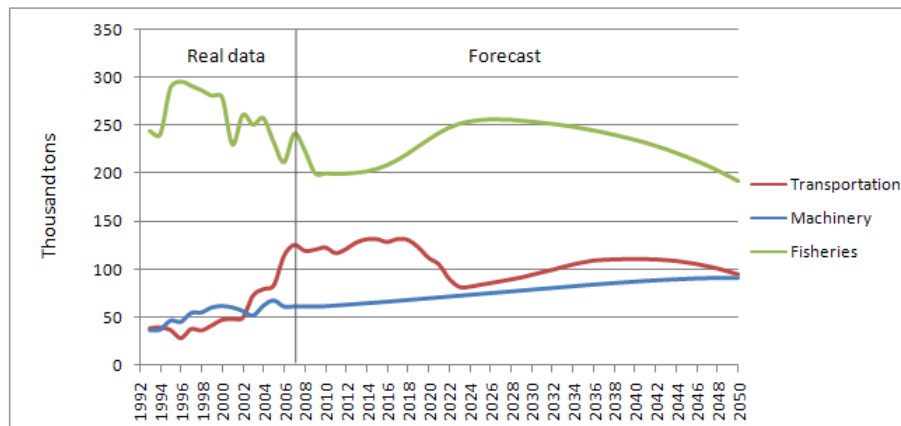


Figure 19 Fossil diesel fuels consumption in Iceland

This scenario was prepared by the National Energy Authority (Orkustofnun) in fall 2008, when the price of crude oil was at around 100 USD/bbl. It was a period of skyrocketing crude oil prices, which were nevertheless expected to decline. The predictions on the long term crude oil price were based on Energy Information Administration (EIA) estimations, which at that time forecasted 70 USD/bbl in 2020, 90 USD/bbl in 2040 and 100 USD/bbl in 2050. The report assumed that in 2020 the fuel efficient applications of existing technologies will be implemented, and that in 2030 alternative technologies (hydrogen driven and electric cars) will kick in. However, should this report have been prepared today, the curves might be somewhat different, due to the current economical crisis (92) (93).

Biofuels in Iceland have been used since the year 2000, when the first biomethane pumping station opened. In 2008 a total number of 111 vehicles (passenger cars, trucks and buses) in Reykjavik and surrounding communities were running on biomethane from the landfill site in Alfsnes (94). Additionally, some amounts of bioethanol and biodiesel are being imported. The most popular blends are B5 and E85 respectively. Biodiesel blend is sold commercially; however, the bioethanol is only used by a small fleet of 2 flexifuel cars (95). Considering that the total number of cars in Iceland was 246,000 in 2008, the share of biofuels in the overall fossil fuel consumption is still minute (92).

Some share of the fossil diesel demand could be replaced by biodiesel. It has been estimated, that using biodiesel for the fishing fleet is not economically viable, because the prices of heavy fuel oil (HFO) and marine gas oil (MGO) are too low for the biodiesel to compete. However, a partial substitution of fossil diesel in the transportation and machinery sectors might be feasible, depending on the taxation applied to biofuels in the

nearest future. This will be even more viable when the world economy recovers from the present crisis, and the crude oil prices bounce back.

Akureyri, together with its surroundings, is the second largest human settlement in Iceland. The estimated fossil fuel consumption in Akureyri, for transportation only, was 16,000 tons in 2007, of which 44% was made up of diesel (7,000 tons). However, the main consumer is the extensive fishing fleet in this region. The construction sector, although somewhat slowed down these days due to the crisis, and the agricultural sector, also use a considerable amount of diesel to run heavy machinery (92).

A couple of years ago Mannvit Engineering came up with the idea of developing and building a biorefinery that would produce various biofuels, for both the local market and possibly also for export.

There are several factors that make Akureyri a potentially feasible location for developing such a project in Iceland. The organic waste generation per capita is quite high due to the well developed food industry and extensive agriculture. This fact allows easy access to different feedstocks. Furthermore, the town has a convenient location in Eyjafjörður and a number of available unused sites, left over by former industries, which could be used for building different parts of the biorefinery.

The overall concept and timeline of this long term project are presented in the table below.

Table 4 Timeline of the biorefinery project development

Biorefinery - stages	Operation starts	Jobs on annual basis (total)
1. Biodiesel - small scale production (WVO, WAF, etc.)	2009	2
2. Biodiesel - increased production (other sources)	2011	10
3. Biomethane production	2012	20
4. Bioethanol production	2015	30

In June 2008 Mannvit received a ministerial grant for research & development for the realization of the preliminary research, which includes the installation of a pilot unit for biodiesel production using WVO and WAF.

The pilot plant was installed in early 2009 and it will be monitored for a year. The information gathered during its operation will be used to set up the parameters for a small scale production. The small plant, with a capacity of 300 tons/yr, is scheduled to start operating in the summer of 2009. It will be run by Orkey, a joint stock company, whose shares are partly owned by Mannvit. Should this undertaking be successful, Orkey will investigate the possibilities of using other sustainable feedstocks for biodiesel production in a full scale plant. Eventually other types of biofuels will be considered, such as biomethane and bioethanol. It has been estimated that a biorefinery at its full operation capacity will give jobs to 30 people by the year 2015. Additionally, some job positions will be created indirectly, e.g. in servicing the plants, and it will be a potential research field for higher education institutions in Akureyri and Iceland.

2 SITUATION OF BIODIESEL IN ICELAND

Biodiesel is not currently being produced in Iceland. However, a small amount is imported by N1. The company imports neat biodiesel, which is blended in Iceland, labeled B5 and sold. Sometimes it is blended in higher proportions according to specific customer request. Often, transportation companies buy B10 for their trucks (96). N1 is planning on increasing their biodiesel imports. There are neither maximum biodiesel blend restrictions nor biodiesel quality standards in Iceland. Therefore, the blends are only required to meet the standards for fossil diesel (96).

In addition, some WVO is collected at restaurants by a private initiative. Organized collectives use it for their old Land Rover trucks, modified in such a manner that a second tank has been added for filtered WVO. In Akureyri, approximately 10 tons of WVO were collected this way in 2008 (77).

2.1 Previous attempts

So far, there has been only one attempt at commercial biodiesel production in Iceland. In 2000, a rendering plant was built in Selfoss, in the South of Iceland. It was producing meat meal, for animal fodder for export, and WAF that was to be used as biodiesel feedstock. The FAME was produced by UNDRI, a manufacturer of cleaning agents. The company produces detergents using esters from tallow and soybean oil, and therefore has a unit to produce alcohol esters from fat (97). Nevertheless, the project never exceeded the pilot scale, because in 2002 the EU prohibited the use of waste WVO and WAF in animal feed, and the demand for meat meal ceased. Only 1 ton of FAME was produced and it was used in trucks as B20 (35).

2.2 Taxation and policy

All fuels in Iceland are submitted to the same taxation system. In general, biofuels do not benefit from any preferential tax regulation; however, exemptions are made for specific projects. Thus, there is no excise tax on biodiesel and E85 imported by Brimborg in cooperation with Olis, and temporally on biomethane produced in Reykjavik.

Iceland has not yet a formal energy policy, let alone a green energy policy (98). Unlike the EU, it is not bound by the Biofuel Directive and made no official commitment of increasing the share of biofuels in transportation. The lack of incentives and solid policy is hindering the potential demand for biofuels in Iceland. However, some efforts have been made.

In 2006 an interministerial working group prepared a proposal for a bill favoring automotive vehicles with exceptionally efficient fuel consumption or run by alternative fuels. In short, the report included two recommendations; an increase of general fossil fuel excise tax coupled with a decrease of vehicle excise tax for environmentally friendly automobiles. The proposal was well received by the government, however it was never voted on in parliament in its original shape. Nevertheless, in December 2008 the government increased the excise tax on fuel, although that was mostly seen as a response to the financial crisis (93).

3 POTENTIAL BIODIESEL FEEDSTOCKS

Today, recycled feedstocks are the major potential source for biodiesel production in Iceland. The domestic crop production does not look promising due to the rough climate. Thus, the importation of plant oil and oilseeds has also been considered. Nevertheless, the geothermal character of the island providing abundant heat and easy-to-harvest CO₂ creates the greatest prospective, which is algae cultivation.

So far, two studies have been carried out, in Iceland, in order to estimate the amount of available waste material. The first one, published in 2006, was a part of the report on the Selfoss rendering plant project operation (see chapter: Situation of biodiesel in Iceland) (35). It contained data gathered in 2004. A more recent estimation was performed by Mannvit in 2007 (99). The collected data is compared in Table 5.

Table 5 Estimated amounts of available recycled feedstocks in Iceland (99) (35)

Feedstock	Reykjavik 2004 [tons/yr] ^a	Iceland 2004 [tons/yr] ^a	Iceland 2007 [tons/yr] ^b
WVO	65	approx. 130	500-1,000
WAF	approx. 1,000	2,000-3,000	1,000
Waste fish oil ^c	-	-	2,000-2,500
Waste fish oil ^d	60	-	-
Trap grease ^e	approx. 220	-	-

a See reference

b See reference

c From fish meal plants

d From Lysi

e From sewage

3.1 Waste vegetable oil

In Iceland, WVO could be collected from restaurants and food processing plants. Domestic collection, however, is not feasible at the moment.

Table 5 compares two estimations on the availability of WVO in Iceland; however the methodologies, and thus the results, differ substantially. The WVO generation assessment of 130 tons/yr seems to be underestimated (35). It is based on data obtained from a waste management company (Efnamottakan), which collects WVO from some locations. However, it is a well known fact that a considerable part of generated WVO is disposed of into the sewage system (77). The estimation performed by Mannvit is probably more accurate (99). It was originally approximated by the amount of vegetable oil imported to Iceland, out of which 30-50% can be recovered as WVO (77). Subsequently, the numbers were confirmed based on personal communication with all restaurants in Akureyri and food production plants in Akureyri and Husavik. In Eyjafjörður, 75-80 tons of WVO could be collected annually. This number was scaled up, giving a final estimation for Iceland, 500-1,000 tons of WVO/yr (99). These calculations seem reasonable, when compared to the data for the annual WVO generation, e.g. in the U.S. (4 kg) (17). Recalculating this estimation according to the population of Iceland (slightly over 313,000 people), the annual production per capita would result at 1.6-3.2 kg of WVO.

The preliminary examination of the WVO collected in Akureyri showed that it has a lower content of FFA, compared to the literature data. This is probably due to the fact that it is used less and changed often compared to multiple reheating, a typical practice in the food business in other parts of the world (see chapter: Laboratory work).

3.2 Waste animal fat

The WAF obtained from meat processing in Iceland is only available as fat cutoffs, unlike in most countries where a considerable amount of WAF also comes from rendering plants. Currently there are no rendering plants operating in Iceland.

Normally, fat cutoffs are used for human consumption, but there is not enough market demand for this material in Iceland, and exportation is also limited. Minor amounts of WAF are used in traditional Icelandic cuisine and fur (mink) farming; some lamb fat cutoffs are exported for food consumption (77).

Depending on the estimation, 1,000 to 3,000 tons of WAF is generated annually in Iceland (99) (35). Compare that to the data provided in Table 5. In Akureyri, the amount of produced WAF is 70 tons/yr (77). Nevertheless, based on the numbers for meat production in Iceland, more WAF could be obtained if there was a rendering plant in operation.

Some amounts of trap grease are also generated. However, the number of approximately 220 tons/yr was estimated based on the grease found in sewage (35). Therefore, firstly some additional amounts might be trapped in restaurants and disposed with the rest of the organic waste, and secondly this material would be impossible to recover unless it was effectively collected in the grease traps.

3.3 Fish waste

Fishing is a substantial business in Iceland, and the fish processing technology is very well developed and generates little waste.

The main fish caught in Iceland are cod and capelin. Depending on the total allowable catch (TAC) allocated by the Ministry of Fisheries, in some years more herring is caught (100). Only capelin and herring are oily fish.

Fish in Iceland are used mainly for food production. The remaining waste is not useful for biodiesel production, since it contains mainly bones and has little oil content. In the years of high TAC for the oily fish, the fish meal plants are in operation. Fish meal is a product obtained by the rendering of whole fish and fish trimmings. Another product of rendering is fish oil. This waste fish oil is a potential feedstock for biodiesel production; however, it has a high FFA content. The estimated number of 2,000-2,500 tons/yr provided in Table 5, is an average amount of waste fish oil that would be available during the operation of the fish meal plants (99). Therefore, this cannot be considered a regular source.

Another estimate considers the amount of waste fish oil coming from Lysi. Being the major fish oil processing company in Iceland, Lysi would probably be the largest regular source of waste fish oil for biodiesel production (77). The generated amount of this potential feedstock in Lysi is 60 tons/yr (35).

3.4 Imported feedstock

As it has been mentioned before, the bulk of potential feedstock for biodiesel production in Iceland is made up of different kinds of organic waste material. This fact imposes serious capacity restrictions in the planned full scale production plant. Thus importing of the feedstock is considered; either as oilseeds to be pressed in Iceland, taking advantage of the low energy prices, or as PPO.

3.4.1 Navigation through the North Pole

The North Pole ice cap is melting faster than the researchers had been expecting. In the summer of 2007 a shipping shortcut to Asia from Western Europe and eastern North America known as the Northwest Passage was nearly ice free for several weeks. Until now this route was only available for icebreakers. Moreover, some researchers estimate that already around the year 2030 the entire North Pole will be free from sea ice during the Arctic summer (101). Although environmentally disastrous, these are options for intercontinental trade which many are looking forward to. The specific, remote, northern location of Iceland will make the North Pole shortcut even more advantageous there than for the rest of Europe. For example, the distance to the Philippines through the North Pole is about 30% shorter, than through the Suez Canal (102). Thus, importing copra or coconut oil or other feedstocks from the Philippines might be a viable option.

3.4.2 Churchill Gateway Development project

The Port of Churchill is a Canadian arctic seaport located in Hudson Bay. It is extensively used for grain exports to Europe and North Africa. Unfortunately, due to climate conditions, the shipping season runs only from mid July to the beginning of November. Therefore, the Churchill Gateway Development Corporation (CGDC), a public and private partnership, is looking into new opportunities for the region. One of the ideas is the cultivation of canola for export to Iceland.

Canadian crops are normally traded at the Winnipeg Commodity Exchange (WCE) in Manitoba. However, the high cost of railway transport to Winnipeg would mean less profit for the producers. Selling the crops to Iceland would involve only maritime transport, which although more time consuming, is considerably less expensive. The major drawback of such an undertaking would be the high capital cost of grain storage facilities. In 2005 a feasibility study was performed to analyze if it was economical to transport grain from Saskatchewan and Manitoba through the Churchill port, store it in Iceland and distribute it from there. While the transport itself was proved to be viable, the high capital cost of the storage facilities that would have to be built in Iceland were an obstacle at that time (103).

In 2007 Mannvit performed a feasibility study for a project which would involve importing canola seeds to Iceland, the subsequent extraction of oil, and then using it for biodiesel production. For a plant capacity of 200,000 tons of seeds/yr (thus 84.5 thousand tons of biodiesel/yr), at the price of crude oil at 110-115 USD/bbl, the price of canola seeds at 420 USD/ton, and the price of meal at 14.5 USD/ton, the project was at the verge of feasibility (99). However, it was assumed that the feedstock will be bought at the already existing grain storage facilities, and the capital cost of their construction was not included in the calculations. Therefore, the final viability of this project depends on whether or not the Canadian plans of building such facilities will be realized. Moreover, since it is yet uncertain if the biodiesel produced in Iceland will be subjected to the excise tax in the near future, it is also difficult to make reliable viability estimations.

3.5 Domestic crop production

Arable land in Iceland is about 15.6% (16,000 km²) of the country's total land area. Currently only 8% of arable land is in use, while another 11% is forested. However, there is potential for increasing the efficiency of the land that is already in use as well as breaking in new land for energy crop use (104).

So far a few experiments have been made in growing potential biofuel feedstock crops in Iceland. The research was performed by the Agricultural University of Iceland (AUI) (105).

In the summer of 2008 five varieties of hemp were tested at Mothruvellir experimental station. The aim was to measure the potential dry matter (DM) yield of the hemp under Icelandic conditions and to record growth stages and maturity. The biomass was mainly to be used for bioethanol production and fiber. However hemp could also potentially yield seeds, which could in turn be used as feedstock for biodiesel production. Planted in the beginning of May and harvested in the end of September, the hemp unfortunately gave no seeds. This was probably due to the specific conditions of the Icelandic late summer. The days are still very long, which stimulates flowering, but the temperature is too low for effective seed formation. Nevertheless, the achieved average dry DM yield of 7.75 tons/ha is a decent biomass result. It is possible that AUI will continue the research next year.

The AUI has also made limited experiments with winter rape (*Brassica napus var. oleifera*) and stubble turnip (*Brassica rapa var. oleifera*) for oilseed production. These experiments were done in a somewhat protected environment at Korpa experimental station in Reykjavik. Rape and stubble turnip yielded up to 2.5-3.0 t/ha DM of seeds. Spring varieties of rape have also been tested but they do not produce mature seeds in Iceland. Subsequently, a bigger project, funded by the Icelandic Maritime Administration, started in 2008. In late July, winter rape (Falstaff variety) and stubble turnip (Largo variety) were planted in 9 locations all around Iceland. The aim is to evaluate the seed yield potential on these very variable 'free range' locations. Nevertheless, it is already clear that cultivation of winter rape for seed production in Iceland is quite risky. These crops are not very winter hardy and they might later perish completely because of winter damages. Also, because of windy conditions in Iceland, lodging (crop falling over) and seed shedding before harvesting might become a problem.

3.6 Algae

The unique geothermal energy resources in Iceland could be used for algae cultivation. A biotech company, Prokatin, prepared a project called GEOGAS, which incorporated bacteria biomass production and algae cultivation on the site of an existing geothermal power plant, Nesjavellir. The idea is to capture the geothermal gases emitted during energy harvesting and use them as substrates for the metabolism of these organisms. The mentioned gases include hydrogen sulfide (H₂S), hydrogen (H₂) and carbon dioxide (CO₂). The bacteria use H₂S and H₂ to produce energy. The CO₂, together with additionally supplied nitrogen, phosphate and other nutrients, is converted into high protein biomass. The byproduct of the process is sulfuric acid (H₂SO₄). However, bacteria are only capable of processing 25% of the CO₂ emitted by the plant. Therefore the second process, algae cultivation, involves utilization of the remaining 75% of emitted CO₂. Algae only require the CO₂ and additionally supplied nutrients to grow. The oil content of this algae variety would be 50%. It is still more of an idea than a definite project, however, according to

Mannvit's calculations, the annual production of algae in Nesjavellir power plant could be as high as 9,200 tons of DM (77). Table 6 contains the amounts of crude and refined algae oil and the amounts of FAME that could be potentially produced from it.

Table 6 Estimated products yields from Nesjavellir power plant

Product	Mechanical pressing	Solvent extraction
	[tons/yr]	[tons/yr]
Raw oil	4,250	4,650
Refined oil	4,150	4,600
FAME	4,150	4,600

Prokatin has been performing experiments in Nesjavellir since June 2007. The pilot project of the first process (bacteria biomass production), utilizing about 10% of the exhaust from the power station, is scheduled to start operating in the summer of 2009. The laboratory unit was designed in cooperation with Mannvit, and the company will also be involved in designing the pilot plant. It has not yet been decided when the second process, algae cultivation, will be implemented. First, the performance of the first process needs to be proven, and further laboratory work needs to be done before scaling up an algae system (77).

On the basis of CO₂ measurements in all the geothermal power plants in Iceland, it is possible to estimate the potential of algae production. Theoretically, 100,000 tons of algae DM (with 50% oil content) could be obtained from currently operating power plants. According to the forecast of the Icelandic Environmental Agency, the CO₂ emissions from geothermal power plants will increase in the upcoming years. Therefore, the potential theoretical production of algae could be as high as 112,000 tons in 2020 and 117,000 tons in 2030. Assuming, that only 50% of emitted CO₂ could be captured and used for algae cultivation, today's production of FAME could yield up to 25,000 tons/yr (77).

The biodiesel produced from algae cultivated onsite in geothermal plants will not be 'renewable' in the common sense of this word. The total life cycle net GHG account will not be neutral, since the CO₂ for its production will not be captured from the air. On the other hand, the emissions from the plant will not pollute directly, but will be given a second life cycle as biodiesel before discharging into the atmosphere. Thus, the burning of the equivalent amount of fossil diesel, and the connected carbon release, will be avoided.

4 LABORATORY WORK

Laboratory work was conducted in order to determine the most adequate FAME production process for the given feedstock (WVO) and given production scale (300 tons/yr).

The production of FAME is a well established technology, however using highly acidic feedstocks, like WVO and WAF, poses a particular challenge for the known processes. The conversion of FFA requires an additional pre-transesterification step, the esterification, and the yields vary according to the reaction temperature and time, FFA content, methanol excess and used catalyst.

Several issues were investigated. Firstly, the methanol management of the process was explored, in effort to minimize the production costs. The effect of different ratios of methanol excess on the esterification process was observed. Secondly, phase distribution of methanol in the transesterification mixture was determined. This information served to propose an adequate methanol recovery system. Furthermore, the effects of water content in the feedstock and a choice of catalyst on the esterification process were estimated. An approximate mass balance of the production process and resulting biodiesel yield were calculated. Finally, the basic characteristics of the produced biodiesel were examined and a recommendation was made as for further research and a suggested production process.

All data presented in this section, describing proportions, ratios and percentage concentration, are expressed by mass (w/w), unless stated otherwise.

4.1 Procedure

WVO from two restaurant sources was examined. Four samples were taken from source A (A1, A2, A3, A4), and one from source B. The pretreatment of the samples included filtering, dehydrating (except for sample A2) and FFA content measurement. All samples were esterified. Transesterification and subsequent treatment of FAME and glycerin were performed on sample A1.

4.1.1 Pretreatment of the WVO stock

All samples were filtered through a coffee filter. The content of the impurities had been previously measured by Mannvit personnel; it was estimated at 1-2% depending on the source.

Subsequently, water stripping was performed at 60 mbar, using a vacuum pump, for approximately 30 minutes. The boiling point of water at this pressure is around 35°C. No evaporation was observed below this point, and the process was stopped immediately after the water had evaporated; therefore other substances potentially present in the sample were not stripped.

The average water content of the samples from both sources was estimated to be 0.1%, based on the weight difference before and after the stripping.

Sample A2 was not dehydrated, in order to examine the influence of the initial water content on the esterification process.

After the samples had been filtered and dried, the concentration of FFA was estimated. It was calculated based on acid value (AV), using the following formula:

$$\%FFA \approx \frac{1}{2} AV$$

The acid value was determined by a titration of the prepared samples with 0.1 M KOH solution. The samples were prepared by being mixed with a stock solution of ethanol and turpentine (1:1 by volume), and with a few drops of phenolphthalein indicator. The following formula was used to calculate the acid value:

$$AV = (A - B) * 0.1 * \frac{56.1}{W}, \text{ where:}$$

A = the number of ml of KOH to neutralize the sample beaker

B = the number of ml of KOH to neutralize the blank beaker

W = weight of the sample in grams

The average FFA content of the samples from source A was 3.74% and from source B, 0.60%. These numbers are quite low, compared to the literature data. Depending on the country and the type of source (restaurant, fast food, food processing plant), the FFA content can range from 2-7% in the U.S. and EU, or even 9-11% in Asia (25) (33) (106) (107). The low acidity of examined samples is attributed to the lower degradation of oil, which is normally caused by multiple reheating, a typical practice in the food business in other parts of the world.

The water content is also relatively low, for the same reason. Typical values are in the range of 0.2-0.4% (33) (106).

The examined characteristics of the WVO from both sources are gathered in Table 7.

Table 7 Characteristics of the examined samples

Source	%Impurities	%Water	%FFA
A	1-2	0.1	3.74
B	1-2	0.1	0.60

4.1.2 Esterification

Since the FFA content was higher than 0.5%, the FFA were esterified prior to the transesterification. Acid esterification using concentrated H_2SO_4 as a catalyst was performed, except for sample A4, where Amberlyst 70, a polymer catalyst product of Rohm and Haas was used. The acid was added in the amount of 0.05g/g of FFA. The required amount of polymer catalyst was calculated by mass, based on the number of acid sites with respect to H_2SO_4 , and it was 0.2g/g of FFA.

For samples A1, A2, B the amount of added methanol was 2g/g of FFA (2:1 MeOH to FFA). For samples A3 and A4 the initial 2:1 MeOH to FFA ratio was increased to 10:1 and 25:1 in (in 2 hour periods). Methanol was first mixed with the catalyst and then added to the preheated sample. The reaction temperature was 60°C. The esterification was performed for 24 hours, agitating. The FFA measurements were taken at the beginning and

after 2, 4, 8 and 24 hours. Water was not removed during the reaction. Figure 20 compares the esterification rate for a dehydrated and a not dehydrated sample (A1 and A2 respectively).

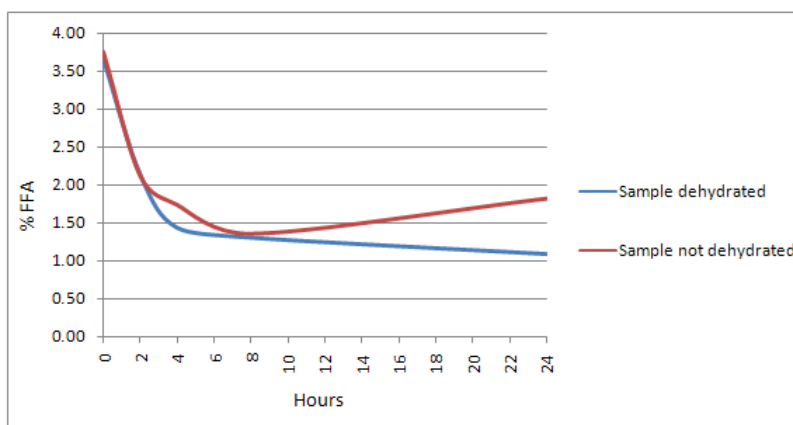


Figure 20 Esterification rates of different samples

In both samples the reaction rate slowed down significantly after the initial period, which is longer for sample A1 (approximately 4 and 2 hours respectively). This fact is attributed to the generally low excess of methanol used. Methanol has two functions in the esterification reaction; it is a substrate, but it also acts as a solvent for any water present in the sample or created during the reaction (see Figure 21). Water hinders the esterification, because the catalyst (H_2SO_4), due to better solubility, tends to migrate into it, and out of the methanol, so the reaction is prematurely quenched (25).

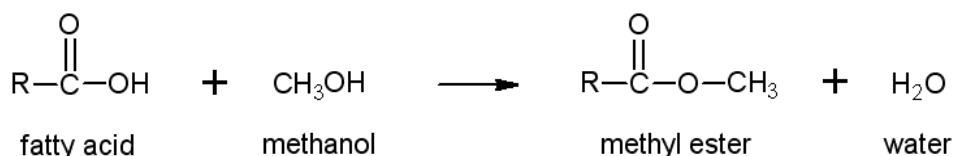


Figure 21 Formation of methyl ester

It was also observed that the FFA content in sample A2 started to increase slowly after 8 hours of reaction. This is attributed to the increased total water content, a sum of chemical water created during the formation of methyl esters, and the additional amount of water initially present in the sample. The subsequent hydrolysis of triglycerides caused an effect opposite to that which was intended, the production of additional FFA.

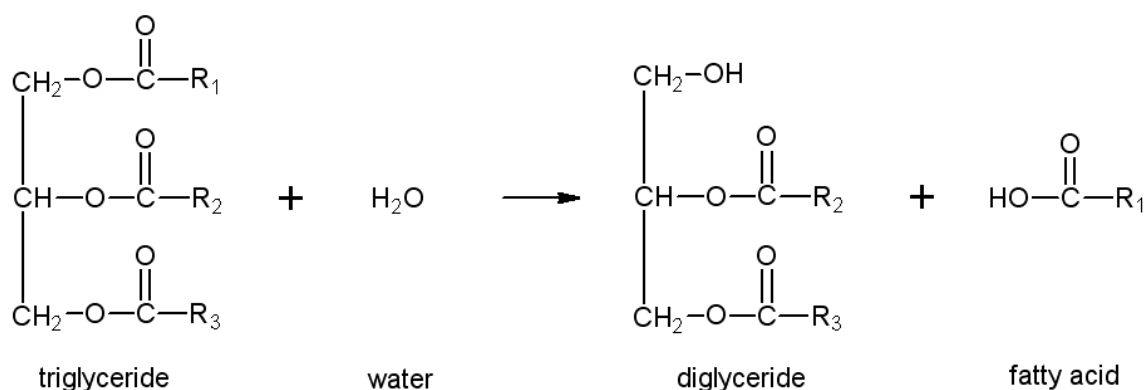


Figure 22 Hydrolysis of a triglyceride to form FFA

Table 8 compares the change in the FFA content per hour for both samples.

Table 8 Esterification rates per hour for samples A1 and A2

Reaction time	A1 %FFA	A2 %FFA	Δ (%FFA)/hour	
			A1	A2
0	3.65	3.65	-	-
2	2.13	2.11	-0.76	-0.82
4	1.44	1.73	-0.35	-0.19
8	1.31	1.35	-0.03	-0.10
24	1.09	1.81	-0.01	+0.03

Sample A1 was transesterified after 24 hours, since the rate of esterification was already too slow to continue. Sample A2 was discharged.

Esterification was also performed on sample B, with the same amount of H_2SO_4 (0.05g/g of FFA) and the same methanol excess (2g/g of FFA). However, the reaction showed practically no effect after 2 hours (FFA content dropped from 0.60 to 0.59%), and the sample was sent to transesterification.

Samples A3 and A4 were first esterified with 2:1 MeOH to FFA ratio for two hours. Subsequently, additional methanol was added to both samples in order to achieve a 10:1 MeOH to FFA ratio. The reaction was continued for 2 hours and then the same procedure was performed with a 25:1 MeOH to FFA ratio. Two catalysts were compared, H_2SO_4 and the polymer catalyst (samples A3 and A4 respectively). Increasing the MeOH to FFA ratio proved to be an effective measure to increase the reaction rate, however the two catalysts responded differently. In case of H_2SO_4 , the reaction with the 10:1 MeOH to FFA ratio was not more effective than the analogous 2 hour reaction with an unchanged MeOH to FFA ratio performed on sample A1 (0.35 vs. 0.33% FFA/hour drop). However, applying the 25:1 MeOH to FFA ratio seems to have improved the reaction rate significantly. Although, since sample A3 was only esterified for 2 hours in the third cycle, and sample A1 for 4 hours, this hourly FFA content drop could have been less favorable if sample A3 had been reacted for 4 hours as well. On the other hand, for the polymer catalyst, a significantly improved performance was already observed with a 10:1 MeOH to FFA ratio.

The hourly FFA content drop was doubled compared to the first 2 hour reaction with 2:1 MeOH to FFA ratio (0.41 vs. 0.17% FFA/hour). Increasing the MeOH to FFA ratio to 25:1 (upper limit suggested by the producer), caused less effect and would not be justified.

As for the overall performance of both catalysts, H₂SO₄ was more effective. However, the polymer catalyst caused an excellent phase separation. Therefore, combining these two catalysts for esterification should be considered, if only for the better final FAME yield.

Further experiments with H₂SO₄ catalyst and 20-25:1 MeOH to FFA ratios are suggested in order to determine the most favorable amount of methanol excess, which will cause a desirable FFA content drop after 2 hours of esterification (<0.5%).

The results of the esterification of samples A3 and A4 are summarized in Table 9.

Table 9 Esterification rates per hour for samples A3 and A4

Reaction time	MeOH:FFA	A3 %FFA	A4 %FFA	Δ (%FFA)/hour	
				A3	A4
0	-	3.82	3.82	-	-
2	2:1	1.61	3.48	-1.10	-0.17
4	10:1	0.96	2.66	-0.33	-0.41
6	25:1	0.76	1.65	-0.10	-0.50

4.1.3 Transesterification

Transesterification was performed on samples A1 and B. Based on the mass calculations of the esterified mixtures, KOH was added in the amount $0.015 \times [\text{grams of triglycerides in the mixture}] \text{ g} + 0.002 \times [\text{grams of FFA in the mixture}] \text{ g} + 0.572 \times [\text{grams of added H}_2\text{SO}_4 \text{ in the mixture}] \text{ g}$. Methanol was added in the amount of $0.217 \times [\text{grams of triglycerides in the mixture}] \text{ g}$; for a 100% excess methanol. The alcohol was first mixed with KOH and then added to the preheated sample. The transesterification was performed for 2 hours, agitating. The reaction temperature was 60°C.

Subsequently, the samples were left overnight in a separation funnel. The glycerin phase, being heavier, accumulated at the bottom, and FAME remained on top.

4.1.4 Biodiesel treatment

FAME produced from sample A1 was washed with a 1% solution of H₂SO₄ in order to neutralize the remaining KOH catalyst and remove residual glycerol, methanol and impurities. A 1:1 mixture of FAME and acidic water was agitated for about 30 seconds and left to settle for approximately 2 hours. The procedure was repeated 3 times, due to the unexpectedly pale color of the two first wash mixtures. This was attributed to an elevated amount of soaps. Their formation was caused by a relatively high (1.09%) content of FFA in the transesterified sample.

Afterwards, water stripping was performed at 60 mbar, using a vacuum pump, for approximately 30 minutes, until the evaporation has stopped. The boiling point of water at this pressure is around 35°C.

Subsequently, a 10 g representative sample of dehydrated FAME was distilled at 40 mbar, for approximately 50 minutes. The FAME fraction was collected at 220°C, which is a

boiling point of FAME at this pressure. A fraction of distilled FAME constituted 92% of the distilled sample. The remaining 8% of heavy, dark residue presumably consisted mainly of unreacted mono-, di-, and triglycerides and FFA, but also trace amounts of glycerin, and potentially other unidentified compounds present in the WVO, originating from processed food.

4.1.5 Glycerin treatment

Glycerin produced from sample A1 was distilled in order to determine its composition and estimate how much methanol could be recovered from this phase in the biodiesel production process. The distillation was performed at atmospheric pressure for 50 minutes. The boiling point of methanol and water at this pressure is around 62 and 100°C respectively. The concentration of methanol in the glycerin phase was 21%.

4.2 Biodiesel yield and characteristics

According to the norm EN 14214 the minimum ester content of FAME must be 96.5%. The distillation result of the examined sample revealed that it was only 92%; however the distilled product would have most probably met the specification requirement. The low ester content of the biodiesel product is attributed to the initial elevated FFA content of the sample, which caused a lower yield of transesterification.

The FFA content of the crude FAME was 0.33%, which is above the EN 14214 limits ($1/2 \cdot AV = 0.25\%$). This parameter is also attributed to the initial elevated FFA content of the sample. Nevertheless, the FFA content of the distilled FAME was zero, because FFA have a higher boiling point than FAME. The characteristics of the biodiesel products are summarized in Table 10.

Table 10 Characteristics of the biodiesel products

Biodiesel	%Ester content	%FFA
Crude FAME	92	0.31
Distilled FAME	≤100	0.00
EN 14214	96.5	0.25

Based on the results from glycerin distillation it was calculated that approximately 40% of unreacted methanol stayed in the biodiesel phase, which is similar to the literature data (42%) (36).

The estimated yields of WVO conversion are summarized in Table 11. The yield of 75% is not particularly favorable in terms of mass balance of biodiesel production. Nevertheless, one has to keep in mind that the feedstock is acquired at the sole cost of transportation. Moreover, the results are submitted to a considerable error given the small scale of the experiment. The weight of the original sample, approximately 80g, means that a direct scaling up will not reflect the real production process. The percentage of the mixtures, remaining on the surfaces of the equipment at different stages of the production process, created considerable losses at such a small scale. What is also very relevant, the relatively high FFA content of the transesterified mixture generated further losses at each production stage. The excessive production of soaps created feedstock loss on its own, but also

required a 3 step washing of the biodiesel phase, every time causing further yield losses. Finally, only one full production experiment was performed, and it is expected that acquired experience will result in an improved overall performance. Thus, further experiments need to be done on the laboratory scale before starting the pilot production. Moreover, only the results from the pilot plant operation (50L) can be considered suitable for scaling up.

Table 11 Estimated yields of WVO conversion

Biodiesel	%Yield
Crude FAME	75
Distilled FAME	69

It is difficult to compare the yield of this process with the literature, because mainly biodiesel from PPO has been investigated so far, which involves only alkali transesterification. The reported yields range from 90% to 98% (53) (108). On the other hand, the studies of recycled feedstocks, involve raw material with much higher FFA contents, like trap grease or yellow grease, and other technological processes, usually involving only a one step reaction. A prolonged acid transesterification yielded biodiesel product from 90% for trap grease to 93% for mutton fat and 99% for chicken fat (22) (109). An alkali transesterification gave 78% and 88% yields for mutton and chicken tallow, respectively (109). Two studies using WVO involved a pretreatment step of FFA removal by adsorption on silica gel. In an analysis comparing the performance of WVO with and without pretreatment (0.23% and 10.6% FFA respectively), a 24 hour alkali transesterification was carried out, giving 96% and 25% conversion rates (33). On the other hand, an alkali transesterification of a WVO with original FFA content of 9.3%, subsequently reduced to 6.2% by the same pretreatment method, gave an 80% yield; however the reaction time was not given (107).

In current practice, a two step process involving acid esterification followed by alkali transesterification is used in most commercial application, however companies are reluctant to reveal the obtained yields (106).

4.3 Proposed production process

Based on the performed laboratory research and a technology review, the production process for a small scale biodiesel plant was recommended. Considering that the feedstocks will be acquired from diverse sources, a batch process was suggested. Such a process is easier to control in case the parameters of the received raw material should vary. A batch process is also justified economically, given the production scale. A block diagram of the process is showed in Figure 23 Proposed process of FAME production.

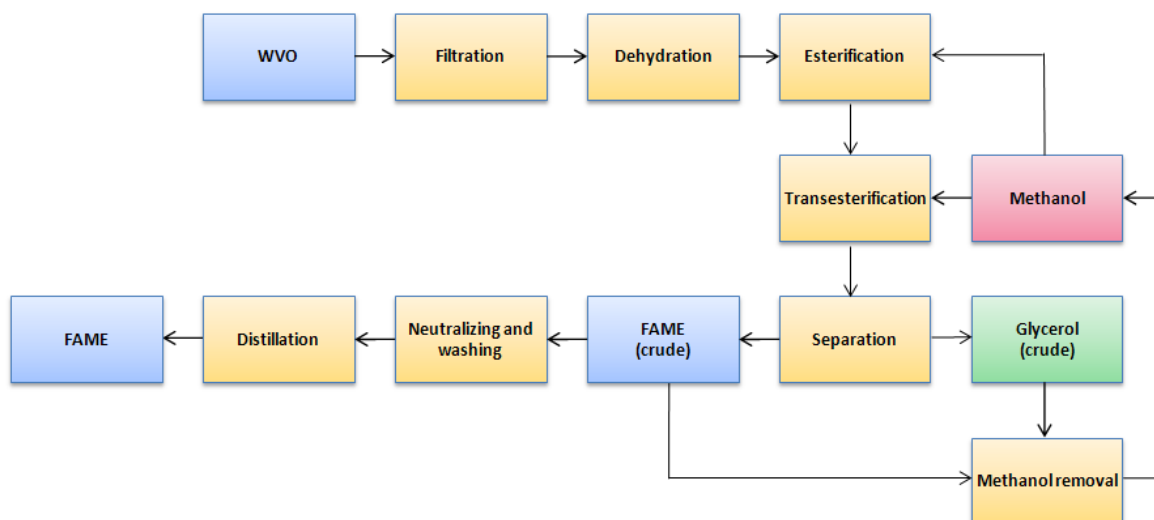


Figure 23 Proposed process of FAME production

Nevertheless, further research is necessary because this recommendation was made based on only one complete production process experiment. It is crucial that the necessity of the distillation of the biodiesel product is revised. Distillation of the crude FAME was suggested, at this point, in order to keep to the EN 14214 quality requirements.

Distillation of the biodiesel product is not performed when PPO is used. However, in case of recycled feedstocks, it is a much more common practice. Stocks del Valles, a Spanish production plant converting WAF and WVO feedstocks with the FFA range of 5-30% uses a distillation unit; however their product is a transparent biodiesel, by far exceeding the quality requirements (see Appendix B). In the study of biodiesel production from trap grease with 50% FFA content a distillation step was also included (22). Analyzing the yield results of the previously discussed study of chicken and mutton tallow, one can conclude that the product would have to be distilled in most cases as well (109). On the other hand, processes designed for WVO conversion via acid transesterification do not include distillation (108).

The feedstock that will be used in Akureyri has a much lower FFA content compared to the presented processes. Therefore it is probable, that the final distillation process will not be necessary. The addition of this production step would increase several cost constituents. The capital cost of the installation would be higher, although less than one could imagine. The crude biodiesel product undergoes methanol and water stripping anyway, and the same unit could be used after some modifications. The cost of electricity would be doubled, although this would only increase its share in the total production cost from 2 to 4%. Maintenance costs of such a unit are also expected to be somewhat higher, because of the more complicated installation. Thus, it would be advantageous to avoid its implementation if possible.

Furthermore, additional experiments with H_2SO_4 catalyst and 20-25:1 MeOH to FFA ratios are suggested in order to determine the most favorable amount of methanol excess, in a desirable reaction time, preferably 2 hours. It was observed, that prolonged esterification yields poor results as far as FFA conversion is concerned.

Another useful conclusion is that methanol should be recovered from FAME, as well as from the glycerin phase. More alcohol remains in the FAME phase than was initially suspected. This should be done before the neutralizing and washing step, otherwise alcohol will remain in the washing water. Methanol recovery from the effluent water would be much more complicated.

5 SMALL SCALE BIODIESEL PLANT IN AKUREYRI

The small scale biodiesel plant, using WVO and WAF feedstocks, is scheduled to start its operation in the summer of 2009, in Akureyri. The plant will use the feedstocks available locally and its initial production will be 300 tons/yr. However, considering that there is more waste raw material generated in Eyjafjörður and it is possible to transport waste raw material to Akureyri from communities outside of Eyjafjörður, there is a possibility of increasing the production after the operation has started. The plant capacity can be increased up to 800 tons/yr at no additional capital cost, only by extending the daily operation time. It has been estimated that there is an adequate potential feedstock supply for such production capacity. Should the project be successful, a further enlargement could be considered, using WVO and WAF from the whole country. A production increase of up to 2,000 tons/yr is feasible with a moderate refurbishment of the plant. Such capacity is considered to be the maximum production that can rely on the regular feedstock supply in Iceland at the moment (see Table 5). Further development into a full size production plant is considered with regard to imported feedstocks or future domestic algae cultivation.

The project, although commercial, is a low risk and low profit initiative, mainly intended to enhance the regional development. The key principle is a sustainable employment of used equipment left over from former local industry, and using recycled feedstocks, mainly those available locally, in order to eliminate the need for transportation. The investment will also create new jobs in the region.

The plant will be operated by Orkey. The company has already made preliminary sales agreements. The buyer is a transport shipping company who made a voluntary commitment to using a share of biodiesel in its fleet fuel needs. The remaining product will be sold locally.

Table 12 summarizes the main aspects of the feasibility study performed by Mannvit, with respect to two main capacity alternatives. All prices were calculated assuming the price of crude oil at 45 USD/bbl, the ISK/EUR exchange rate at 125, 10% discount rate, and based on the current price of raw material (relatively high compared to the average price from the last 10 years).

Table 12 Feasibility study of a small scale biodiesel plant

Capacity (tons/yr)	Capital cost (mEUR)	Operation & maintenance (mEUR/yr)	Expected income (mEUR/yr)	Payback time (yr)	Production cost (EUR/L)
300	0.24	0.16	0.14-0.25	≥3.2	0.70
2,000	0.82	0.68	0.91-1.65	0.9-4.6	0.43

The expected income was calculated for two options. The lower numbers are based on the assumption that the same tax policy will apply for biofuels as for fossil fuels. The higher numbers are based on the assumption, that no excise tax for biofuels will be implemented. The small capacity project will only be feasible if given a preferential tax treatment, whereas the bigger one will be profitable both with or without tax exemptions. The production cost decreases significantly as the plant capacity increases and it is visibly lower than the average European estimation for biodiesel, due to the utilization of the recycled feedstock (see section: International trade and production costs).

6 BIOREFINERY

In the years 2012-2015 the production of biodiesel is to be followed by biomethane and bioethanol production. The final goal is to incorporate the production processes of all these biofuels in a biorefinery.

A biorefinery is a facility that integrates biomass conversion processes and equipment to produce fuels, power, and chemicals from biomass. The biorefinery concept is analogous to today's petroleum refineries, which produce multiple fuels and products from petroleum. By producing multiple products, a biorefinery can take advantage of the differences in biomass components and intermediates and maximize the value derived from the biomass feedstock (110). This approach has the potential advantage of localizing CO₂ emissions, making physical sequestration easier. In a modern biorefinery the sequestered CO₂ should be recycled for the sustainable generation of replacement biomass (111).

The biorefinery project in Akureyri will be a somewhat simplified version of this scheme, modified according to the local needs. The power generation from biomass would be a redundant process, given the favorable Icelandic energy portfolio and a high cost of investment. Due to the relatively low capacity, the final byproducts of the biorefinery will not be extensively processed, but rather sold as animal feed and organic fertilizers.

Nevertheless, combining the production of the three biofuels (biodiesel, biomethane and bioethanol) in one project will be more efficient and profitable than running separated production plants. The byproducts of some processes will constitute the feedstocks for others, the overall energy consumption will be lower, and a fair share of transportation costs will be eliminated.

The timeline of the biorefinery project was presented in Table 4. Figure 24 outlines the incorporated processes together with the potential feedstocks sources and the involved stakeholders.

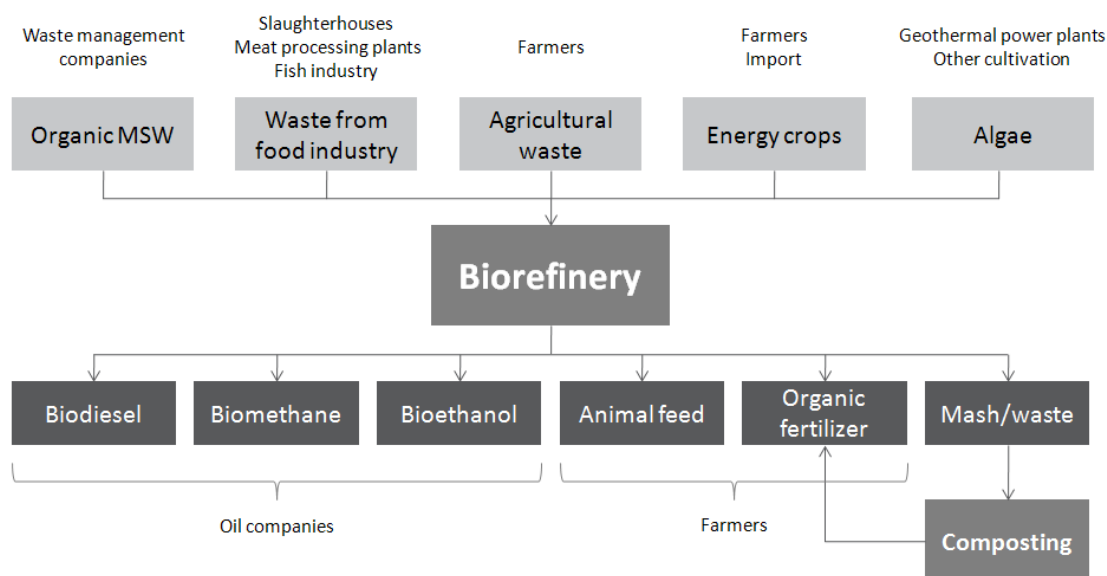


Figure 24 Production outline of the biorefinery in full operation

6.1 Biodiesel production

A full scale biodiesel production plant is the first stage of the biorefinery project, scheduled to start its operation in 2011. As previously mentioned, the increased production will be connected with an import of the feedstock, and further into the future, domestically cultivated algae. The main focus is on the Canadian canola seeds, which could be pressed in Iceland, taking advantage of the low electricity cost. Feasibility studies for three capacity assumptions were made: 15,000; 30,000; 80,000 tons/yr.

The possible location of the plant was a former fish meal plant in Krossanes (which is within Akureyri), but now Dysnes, 23 km from Akureyri, is considered as a possible location, as the site in Krossanes is no longer available. The majority of the left over equipment from fish meal plants can be used for processing oil seeds, refining vegetable oil, and production of FAME to lower the capital costs. Such reusing will substantially decrease the capital cost of the plant.

Table 13 summarizes the main aspects of the feasibility study performed by Mannvit, with respect to the three main capacity alternatives. All prices were calculated assuming the price of crude oil at 45 USD/bbl, the ISK/EUR exchange rate at 125, 10% discount rate, and based on the average price of the raw material and byproducts from the last 10 years. The estimation of the capital cost was made for new equipment, although considering the dynamics of the Icelandic industry market, purchasing used equipment, at least partially, is a plausible option.

Table 13 Feasibility study of a full scale biodiesel plant

Capacity (tons/yr)	Capital cost (mEUR)	Operation & maintenance (mEUR/yr)	Expected income (mEUR/yr)	Payback time (yr)
15,000	7.5-8.3	13.1	9.4-14.9	≥5.5
30,000	12.4-13.8	25.6	18.8-29.9	≥3.5
80,000	25.6-28.9	67.3	50.2-79.7	≥2.4

The expected income was calculated for two options. The lower numbers are based on the assumption that the same tax policy will apply for biofuels as for fossil fuels. The higher numbers are based on the assumption that no excise tax for biofuels will be implemented.

The projects are only feasible if given preferential tax treatment. It can be observed, that the profitability increases with the size of the production plant. The highest capacity will be most beneficial and with lowest payback time, however a construction of storage facilities for only 20% of the used feedstock was included in the calculations. Therefore, this project will only be viable, in case of the full implementation of the Churchill Gateway Development project (see section: Imported feedstock).

The production costs of biodiesel, reduced by the income from selling the byproducts and depending on the plant capacity, are compared in Table 14. The obtained calculations comply with the general rule of thumb; the bigger the capacity, the lower the unit production price.

Table 14 Biodiesel production cost in Iceland

Capacity (tons/yr)	Production cost (EUR/L)
15,000	0.69-0.76
30,000	0.66-0.73
80,000	0.63-0.70

A comparative study of global biodiesel production costs performed in 2006 places Iceland in the lowest range of 0.23-0.40 EUR/L (87). Nevertheless, the estimation seems incoherent. The survey was based on existing lipid exports, and the main Icelandic lipid export commodity is fish oil, the prices of which are considerably higher than those of vegetable oils. On the other hand, compared to the production costs of biodiesel in Europe, the obtained numbers are within the range, or only slightly higher, depending on the estimation (see section: International trade and production costs).

The biodiesel produced in a full scale plant can potentially constitute an acknowledgeable share of fuel consumption in Iceland. Table 15 shows at what percentage particular production capacities will meet the diesel fuel needs for transportation and machinery, according to the energy demand scenario for 2011. In case of the biggest planned capacity, the significant amount of produced biodiesel will probably imply a consumption shift, and meet some of the fishing fleet fuel needs.

Table 15 Potential of biodiesel in Iceland

Capacity (tons/yr)	Share of the diesel fuel needs in transportation and machinery
15,000	8%
30,000	17%
80,000	44%

6.2 Biomethane production

In the spring of 2009 Mannvit will perform a feasibility study of biomethane production in Akureyri. The composition of landfill gas will be measured at the city landfill site, run by Flokkun Eyjafjördur, the communal owned waste management company of Eyjafjördur. Additionally, the information about the amounts and the composition of the waste that had been landfilled will serve to estimate the potential emissions of landfill gas for next decades. Mannvit will use these data to calculate the viability of collecting the landfill gas and upgrading it to biomethane fuel, which could be used on vehicles or by the industry.

Should the feasibility study be favorable, a production plant will be constructed by the year 2012 or even sooner.

This is a joint project of Mannvit and Flokkun Eyjafjördur, partially financed by the National Energy Fund (77).

6.3 Bioethanol production

In the first quarter of 2009, the second phase of BioEthanol project will begin. It is a three year continuation of the first phase that has been carried out by UNAK, Matis Prokaria (a biotech company from Reykjavik) and Mannvit for the last two years. The second phase involves further research and the preparation of a bioethanol pilot plant with a capacity of 200-300 tons/yr. The objective is to construct the pilot plant in the year 2012.

UNAK and Matis Prokaria have been performing experiments to supply adequate bacteria strains. The goal is to develop a production process for second generation bioethanol; the feedstock under research is mainly cellulosic biomass such as grass and waste paper.

Mannvit will design the technical part of the project, including fermentation and distillation systems, and develop pretreatment methods with UNAK for cellulosic biomass. The company will also prepare a feasibility study for the construction and operation of the pilot plant.

Should the results of the Bioethanol project be promising, the construction of a full scale production plant is foreseen for the year 2015.

The project will be partially financed by the ministerial Technology Development Fund, administered by the Icelandic Centre for Research (RANNIS) (112).

V. CONCLUSIONS

It has been demonstrated that small scale sustainable biodiesel production using recycled feedstocks is feasible in Iceland. However, local production will only be viable with a preferential tax treatment. Nevertheless, one must keep in mind that using WVO and WAF as biodiesel feedstocks will have the additional advantage of being a means of disposal for this troublesome waste.

The larger scale production will depend, in the near future, mainly on imported feedstock. The potential of domestically cultivated algae is considerable; however, the economical feasibility of using this feedstock will be questionable, given that the technology is still in the R&D stage. Should the domestic oilseed cultivation be successful it could also contribute to the variation of the feedstock; however, considering the hitherto results, it cannot be relied on at this time.

Low electricity cost will be a great asset should the production of HDRD be considered in the long term. Electrolysis is a simple and renewable way of hydrogen acquisition; however it is too expensive almost everywhere outside of Iceland. Moreover, the geothermal character of the island, providing abundant heat and easy-to-harvest CO₂, is a major advantage for future algae cultivation, the most promising feedstock for biodiesel production.

Considering that Iceland has no general energy policy, it is difficult to make projections for the future. The prospect taxation of biodiesel and other alternative fuels, as well as fossil fuels and corresponding vehicles, will be decisive for the success of a biodiesel economy. Whether or not Iceland joins the EU will also be an issue in this respect.

Iceland has the potential for a sustainable biodiesel economy. However, it has to be implemented with regard to the natural conditions of the country, and considering its overall energy portfolio. Therefore, its share in overall diesel fuels demand might not be substantial, at least in the near future. Biodiesel should not be employed at all costs, but only as long as it is environmentally justified, and thus sustainable. The consideration of the newest scientific evidence and an analysis of other countries' experiences are crucial. However, an advanced technology and the general high level of development of the country are promising factors in creating a successful biodiesel economy in Iceland.

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VII. APPENDICES

A. EU policy development on biofuels use in transportation

7 Nov. 2001: European Commission (EC) starts to consider the use of more biofuels for transport, with its ‘Communication on alternative fuels for road transportation and on a set of measures to promote the use of biofuels’.

8 May 2003: EU adopted the ‘Directive on the promotion of the use of biofuels or other renewable fuels for transport’, the so called Biofuels Directive (the first of its kind), requiring member states to set indicative targets for reaching minimum proportions of biofuels in transport fuels of 2% in 2005 and 5.75% in 2010.

10 Jan. 2007: The EC Biofuels Progress Report shows that, in 2005, biofuels reached only 1% of the market and that the EU will miss its 5.75% target for 2010 by a long way. Only two countries, Sweden and Germany, reached the target of 2% by 2005.

8-9 Mar. 2007: EU leaders commit to a binding target ensuring that 10% of transport fuel in each member state is provided by biofuels by 2020.

23 Jan. 2008: EC finally presents its review of the 2003 Biofuels Directive (originally planned for the end of 2006). The Commission presents a proposal for a ‘Directive on the promotion of the use of energy from renewable sources’. The directive confirms the 10% target for 2020 and proposes ‘sustainability criteria’ to prevent mass investment in cheaper but environmentally harmful biofuels. Nevertheless, the discussion on anticipated rising food prices and biodiversity loss begins.

11 Sep. 2008: Parliament's Industry and Energy Committee approved a report drafted by Luxembourg Green MEP Claude Turmes. The report calls for strict social sustainability criteria, including respect for the land rights of local communities or the fair remuneration of all workers, as well as an obligation for biofuels to offer at least 45% carbon emission savings compared to fossil fuels; a figure that would rise to 60% in 2015. The text also specifies that at least 20% of the 2015 target and 40% of the 2020 goal must be met from ‘non food- and feed competing’ second generation biofuels or from cars running on green electricity and hydrogen. European as well as overseas biofuel producers strongly protest, as the interests of both are threatened.

3 Dec. 2008: The final negotiations between the European Parliament, member state representatives and the EC on the ‘sustainability criteria’. The EC and the member state representatives oppose immediate addressing of indirect land use change (ILUC). The EC claims that there is not enough scientific evidence available regarding the impact of ILUC on biofuel emissions. In the end the EU has agreed on the conditions for a massive increase in biofuel sales in Europe but the fundamental issue of indirect land use change (ILUC) was postponed with no legally binding guarantee of it being accounted for in the future. Therefore the EU has failed to guarantee that any greenhouse gas savings will be achieved as a result.

11-12 Dec. 2008: EU summit agreed upon the final version of the energy and climate change package, including the ‘Directive on the promotion of the use of energy from renewable sources’.

17 Dec. 2008: Parliament endorsed the energy and climate change package.

B. Production process of Stocks del Valles

Stocks del Valles, S.A. is a Catalan company that owns a biodiesel plant near Barcelona, with the capacity of 31,000 tons/yr. The feedstock is composed exclusively of WVO and WAF. It is a pioneer plant, the first one of this type in Spain and second in the world. Its construction was inspired by the fact that in the year 2000 the use of waste animal fat and waste vegetable oil as animal feed was prohibited in Spain.

The plant can process feedstocks with FFA content from about 5% up to 20-30%.

It has been in operation since 2002, with a production of 6,000 tons/yr. In 2006 there was a major technology upgrade and additionally the production capacity was significantly increased to its present level. A year later they started the production of transparent biodiesel, which exceeds the requirements of the norm EN 14214 for several parameters. There is a special emphasis on low sulphur content (2mg/kg vs. max. 10mg/kg required by EN 14214), low water content (50mg/kg vs. max. 500mg/kg required by EN 14214), low total contamination (1mg/kg vs. max. 24mg/kg required by EN 14214) and ester content (99.8% vs. min. 96.5% required by EN 14214).

The norm EN 14214 does not specify CFPP (it is defined by each country); therefore legally the quality of the fuel does not depend on this parameter. It only concerns blends, and in Spain it is 0°C for summer and -10°C for winter. The neat biodiesel, B100, does not have any restrictions regarding CFPP.

Today, the biodiesel blends used in Spain are usually between B10 and B30. There are also certain bus companies that run on B100. In order to comply with the EU biofuel directive, the mandatory blends will be as follows: min. 3.4% in 2009 and 5.75% in 2010.

The plant does not receive any subsidies (neither the whole region of Catalonia), however they have a 'zero tax' guaranteed until 2012 (the tax for fuels is 270 EUR/m³). The price of the fuel product depends on the market price of fossil diesel. It is sold at the cost of diesel minus a certain percentage because the biofuel has a lower energy density. The biodiesel price at the moment is around 650 EUR/m³.

The production, due to uncertainty of the feedstock content, is carried out in a batch system (although a continuous system is less expensive). Due to traceability regulations, there are several tanks destined for feedstock storage.

After filtration and dehydration of the feedstock by centrifuge, the first step of the production process is esterification. The company does not reveal the information about the catalyst used. This process takes 9-10 hours and only one tank is used for it. For transesterification (after FFA content goes down to 2%), KOH is used. There are 3 tanks designed for this process, since this part takes more time, approximately 15 hours. Then the whole mixture is decanted.

Solvent recovery is carried out separately from both phases: biodiesel and glycerin, through centrifugation.

Subsequently, the biodiesel is distilled in vacuum at 220°C. At the bottom of a distillation column a low quality part of biodiesel (3-4%) is collected, which is sold as heating oil; it is dark, dense and it contains unreacted compounds, impurities, trace amounts of glycerin and water and methanol, and its quantity depends on feedstock quality.

Before the upgrade of the installation, the biodiesel treatment only included stripping; therefore the final product had a light yellowish color, whereas at present it is completely transparent.

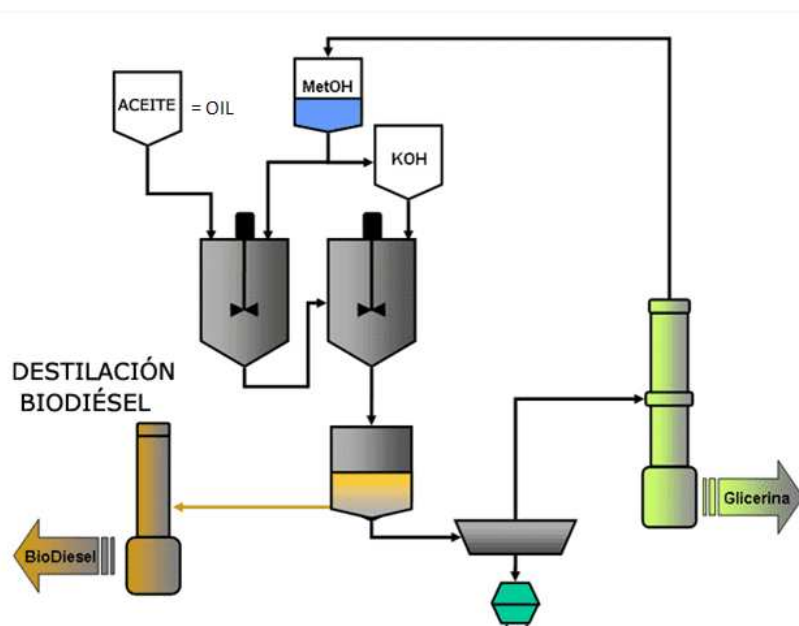


Figure 25 Production process in Stocks del Valles (113)

Glycerin (with 50% water content) is sold to a refinery, since it is not profitable to build a separate unit for this purpose in a plant this size.

As it has already been mentioned, both WVO and WAF feedstocks are used. The oil is obtained at the cost of transport only; there is a company contracted that collects it from restaurants. Animal fat, on the other hand, is purchased (about 50% of the total feedstock used). The plant is adjusted to run on a wide range of FFA content, therefore the selection of feedstocks is flexible and depends on the market prices. In the occasions of particularly favorable purchase costs, bulk amounts are acquired and stored in paid facilities. The storage space at the plant is only for 1,000 tons of feedstock and 1,000 tons of biodiesel.