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Effects of Raw Materials and Production Practices on Biodiesel Quality and Performance

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1. Introduction

The demand for transportation fuels is increasing around the world, especially the demand for petroleum-based fuels. To cope with rising demand and dwindling petroleum reserves, alternative motor fuels such as biodiesel are at the forefront of commercialization. Biodiesel is an environmental renewable clean burning fuel. Biodiesel is a replacement for diesel in compression-ignition engines. Biodiesel is composed of mono-alkyl esters of long chain fatty acids. These esters are produced when virgin vegetable oils, i.e., soy, canola, palm and rapeseed oil, animal fats from tallow, poultry offal and fish oils or used cooking oils and trap grease from restaurants are reacted with an alcohol. The major chemical components of vegetable oils, fats and greases are triacylglycerols. The chemical reaction of converting triacylglycerols into methyl esters is termed transesterification. A stochiometric excess of alcohol and a catalyst is required for the effective transesterification of triacylglycerols into alkyl esters. The transesterification reaction is depicted in Figure 1. The alcohol used for producing biodesel is usually methanol. Methanol is the least expensive alcohol and therefore the alcohol of choice. The catalyst can be an acid or a base depending on the amount of free fatty acids present. The catalyst bases most commonly used are NaOH or KOH. The acid catalyst is usually H_2SO_4. In order to be commercially available in the United States and Canada, biodiesel must meet the specifications in ASTM D6751, Standard Specification for Biodiesel Fuel (B100) Blend Stock for Distillate Fuels. In Europe they follow the requirements and test methods for fatty acid methyl esters (FAME). The requirements are specified in EN 14214. The requirements for these two standards are given in Table 1. These specifications are designed to meet the requirements necessary for the proper performance of compression-ignited engines. Feedstock, feedstock quality and production practices can influence the quality of the biodiesel and therefore, the performance and commercial approval of the final product.

Feedstock

As previously stated, the feedstock sources can be virgin vegetable oils, animal fats and greases. The virgin vegetable oils that are commonly used are soybean, canola, rapeseed, sunflower and palm. Soybean vegetable oil, fats and yellow grease are mainly used in the United States [1]. Canola is used in Canada. Rapeseed and sunflower oil are the primary feedstock in Europe [2]. Palm oil, which is mainly produced in the tropics, is the main feedstock used there [3, 4]. The feed stock source can influence the cetane number, oxidation stability, cold soak filterability (deposition), and cold flow properties.

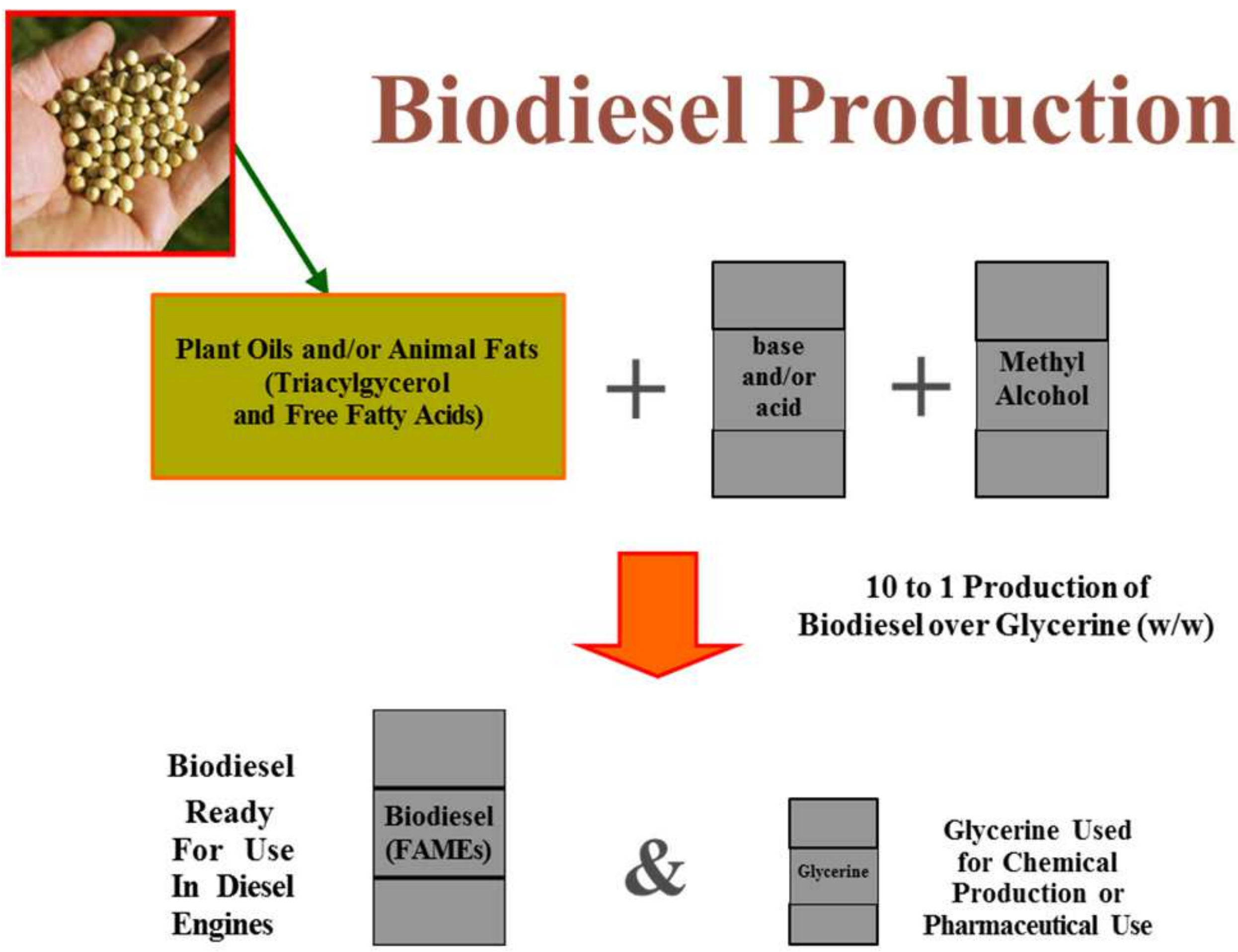


Fig. 1. The transesterification reaction for the production of Biodiesel from triacylglycerol.

Cetane Number

The performance of diesel engines depends on the compression ratio, injection timing, fuel/air mixture and ignition delay. The cetane number is a measurement based on the ignition delay of compression-ignition engines (the lower the ignition delay, the higher cetane number). ASTM D613 and EN ISO 5165 are the standard procedures for determining cetane number. The lower the ignition delay, the better the compression-ignition engines performs. The low ignition delay increases power, engine efficiency and the engine's ability to start at lower temperatures. The composition of the biodiesel influences the cetane number. The minimum acceptable cetane number necessary for acceptable performance in modern compression-ignition engines is 40 [5].

	ASTM D6751-10			EN 14214:2008	
Properties	Test Method	Grade S15	Grade S500	Test Method	
FAME				EN 14103	96.5 % (m/m)min.
Ca & Mg (total)	EN 14538	5 ppm (µg/g) max.	5 ppm (µg/g) max.	EN 14538	5 ppm (µg/g) max.
Density, 15˚C				EN ISO 3675/EN ISO 12185	860-900 kg/m^3
Flash Point (close cup)	ASTM D93	93˚C min.	93˚C min.	EN ISO 2719/EN ISO 3679	>101˚C
Alcohol Control					
One of the following must be met: **1. Methanol Content** **2. Flash Point**	EN 14110 ASTM D93	0.2 % mass max. 130˚C min.	0.2 % mass max. 130˚C min.		
Methanol				EN 141101	0.2% mass max.
Water and Sediment	ASTM D2709	0.050 % volume max.	0.050 % volume max.	EN ISO 12937	500 mg/kg max.water
Total contamination				EN 12662	24 mg/kg max.
Kinematic viscosity, 40˚C	ASTM D445	1.9-6.0 mm^2/s	1.9-6.0 mm^2/s	EN ISO 3104	3.5-5.0
Sulfated Ash	ASTM D874	0.020 % mass max.	0.020 % mass max.	ISO 3987	0.02 %(m/m) max.
Sulfur	ASTM D5453	0.0015 % mass max.	0.05 % mass max.	EN ISO 20846/EN ISO 20884	10 mg/kg max.
Copper strip corrosion	ASTM D130	No. 3 max.	No. 3 max.	EN ISO 2160	Class 1 rating
Cetane Number	ASTM D613	47 min.	47 min.	EN ISO 5165	51.0 min.
Cloud point	ASTM D2500	Report	Report		
Carbon Residue	ASTM D4530	0.050 % mass max.	0.050 % mass max.	EN ISO 10370	0.3 % (m/m) max. at 10% dist. remmant
Acid Number	ASTM D664	0.50 mg KOH/g Max.	0.50 mg KOH/g max.	EN 14104	0.50 mg KOH/g max.
Cold soak filterability	ASTM D 6751 Annex A1	360 seconds max.	360 seconds max.		
Free glycerin	ASTM D6584	0.020 % mass max.	0.020 % mass max.	EN 14105/EN 14106	0.02 %(m/m) max.
Total glycerin	ASTM D6584	0.240 % mass max.	0.240 % mass max.	EN 14105	0.25 % (m/m) max.
Phosphorous Content	ASTM D4951	0.001 % mass max.	0.001 % mass max.	EN 14107	4 mg/kg max.
Distillation temperature A.E. temp., 90% recovery	ASTM D1160	360˚C max.	360˚C max.		
Na & K (total)	EN 14538	5 ppm (µg/g) max.	5 ppm (µg/g) max.	EN 14108/EN 14109/EN 14538	5 mg/kg max
Oxidation stability	EN 15751	3 hrs. min.	3hrs. min.	prEN 15751/EN 14112	6hrs. min.
Iodine Value				EN 14111	120 max.
Linolenic Acid Methylester				EN 14103	12 % max
Polyunsatureted Methyl Esters >=4double bonds				EN 14103	1 % (m/m) max.
Mono, Di and Tri glyceride content				N14105E	0.8/0.2/0.2 %(m/m) max.

Table 1. Biodiesel Standard Specifications for North America (ASTM D6751) and Europe (EN14214).

The chemical composition of the triacylglycerols from different feedstocks varies in chemical composition. Therefore, the methyl esters produced from different feedstocks varies according to the source. The cetane numbers of the methyl esters from different feedstocks are given in Table 2.

Feedstock	Cetane Number (Average of Lit. Values)
Soybean	48.8
Rapeseed	52.2
Sunflower	53.4
Beef Tallow	56.2
Palm	62.3
Yellow Grease	62.6

Table 2. Comparison of average cetane numbers from published data [6].

Oxidation Stability

All fuels, including biodiesel, have stability problems. Biodiesel is susceptible to oxidative degradation of the fuel quality. The oxidation degradation of the fuel is determined by the amount and position of the olefinic unsaturation in the fatty acid methyl ester molecular chains. All of the biodiesel feedstocks have polyunsaturated chains that are methylene-interrupted in their triacylglycerols molecules. The oxidation proceeds at different rates depending on the number and position of the olefinic unsaturation [7]. The fatty acids chemical composition of triacylglycerols used as feed stocks is given in Table 2. EN 15751 specifies a procedure to measure the propensity of biodiesel to oxidation.

Oxidation stars by attacking the methylene carbons between the olefinic carbons. Hydrogen is removed and a hydroperoxide and conjugated dienes are formed. The hydroperoxide decomposes and interacts to form aldehydes, alcohols, carboxylic acids and high molecular weight polymers [9]. Aldehydes detected in the oxidation process include hexenals [10], heptenals, propanal [11,12] and 2,4-heptadienal [12]. Short chain aliphatic acids and alcohols have also been detected [13, 14]. Increase acidity due to formation of organic acids increases corrosion. Polymerization products from oxidation will increase viscosity of the fuel and therefore it will influence the performance.

Cold Soak Filterability

In cold weather, the most common problem associated with biodiesel or biodiesel blends is the plugging of the fuel filter. In 2008, a cold soak filtration test was added to the ASTM specifications, to address this problem. Cold soak filterability is a measurement of how well biodiesel flows when chilled and poured through a filter. Previous studies showed that the formation of precipitates during cold weather conditions depends on the feedstock, blend concentration and storage time [15, 16]. Most of the precipitate formed at lower temperatures will be re-dissolved when they are warmed to room temperature [17]; however, minor precipitate components remain as precipitates after warming to room temperature.

Insoluble precipitates from soybean biodiesel can be attributed to sterols present in the soybean oil feedstock. Soybean oil contains approximately 0.36% sterols. Sterols are composed of a group of steroid alcohols present in plants. The culprit sterol was found to be sterol glucoside(SG) [15]. Soybean oil may contain up to 0.23 % SG [16].

The insoluble precipitates from palm biodiesel are due to both sterol glucoside and monoacylglycerols; while, the precipitates from poultry fat biodiesel are due only to monoacylglycerols [15].

Feedstock	Unsat./Sat. ratio	Saturated					Mono unsaturated	Poly unsaturated	
		C10:0	C12:0	C14:0	C16:0	C18:0	C18:1	C18:2	C18:3
Beef Tallow	0.9			3	24	19	43	3	1
Canola Oil	15.7				4	2	62	22	10
Lard	1.2			2	26	14	44	10	
Palm	1.0			1	45	4	40	10	
Soybean	5.7				11	4	24	54	7
Sunflower	7.3				7	5	19	68	1

Table 3. Composition of tracylglycerols used as feedstock in biodiesel production. Percent by weight of total fatty acids [8].

Cold flow properties

All diesel fuels, as well as biodiesel are subject to performance problems when they are subjected to cold temperatures. As a fuel is cooled, high molecular weight components present in the fuel begin to precipitate and this causes the fuel to start to solidify or gel.
The cold flow properties of the biodiesel are dependent on the fatty acids composition of the triacylglycerol feedstock. The transesterification does not change the chemical compositions of the fatty acids; it just makes methyl esters of these acids. Therefore, biodiesel made from triacylglycerol feedstock composed of high concentration of high molecular weight fatty acids will have poor cold flow properties. Tallow and palm biodiesel are the worst offenders. They start to have cold flow problems between 18 to 10°C. Canola, rapeseed, sunflower and soybean biodiesels start having problems around 0°C [18].

Feedstock Quality

Pure triacylglycerols feedstock is easy to convert to biodiesel. However, impurities that may be present in the feedstock can impact quality and cost of the final product. Common impurities present with the triacylglycerol feedstock are water, solids, free fatty acids and sulfur [19].

Water

In the production of biodiesel, it is important to keep water below 1%. The presence of water in the feedstock will produce soaps during the transestercation process and affect the completeness of the reaction. The soap and water can form a water in oil emulsion which will affect the final biodiesel fuel quality; since, it will create deposits, viscosity and engine performance problems.
These water emulsions can be broken by heating. Therefore, the oil can be heated and the water allowed settling to the bottom of the container. Water removal is performed by pumping the water out from the bottom of the container from under the oil.

Solids

Insoluble particles can be present with the feedstock. This is a particular problem with yellow and trap grease. These particles can create fuel filter plugging and engine deposits. Therefore, it is recommended to filter the feedstock before transesterification.

Free fatty acids

Base catalyzed transesterefication of high free acid feedstock will react with the catalyst and produce soaps. Feedstock with more than 2% free fatty acid needs to be caustic striped before being used in base catalyzed transesterification. Feedstocks with characteristic high amounts of free fatty acids are tallow and yellow grease. These feedstocks usually contain over 15% free fatty acids.

On the other hand, acid catalyzed transesterification produces water as a byproduct of the reaction. Water needs to be removed in order to drive the reaction to completion. This reaction also requires higher temperatures and a higher ratio of alcohol to free fatty acids, usually around 20:1 to 40:1.

A combination of acid catalyzed esterification followed by a base catalyzed reaction offers a good alternative for biodiesel production from high free fatty acid feedstocks. In this case, the acid catalyst of choice is phosphoric acid, H_3PO_4. After esterication, the H_3PO_4 is reacted with excess KOH. Finally, at the end of the process, the remaining KOH is reacted H_3PO_4. The K_3PO_4 is dried and sold as fertilizer.

Sulfur

The EPA regulates the amount of sulfur in fuels. For on road fuels, the EPA mandates 15 ppm sulfur maximum. In Europe, the sulfur level in biodiesel has to be lower than 10 ppm.

Biodiesel made from pure feedstocks has virtually no sulfur. However, sulfur levels in waste grease can reach to 200 – 400 ppm. During production, the final sulfur concentration can be reduced by approximately 40 to 50%. Vacuum distillation can also reduce sulfur by 50%. Treatment with activated carbon can reduce sulfur in biodiesel to acceptable low levels.

Production Practices

Quality of the final product is also dependent on production practices. Good practices will insure completeness of the reaction, good separation of the glycerol from the reaction product, stripping of the alcohol, splitting of soaps and water and catalyst removal.

Reaction completeness

The trasesterication of triacylglycerols into biodiesel occurs by first producing a diacylglycerol, which in turn is converted to a monoacylglycerol and finally a glycerol molecule. Each of the reaction steps produces a molecule of fatty acid methyl ester. If left with the final product, they can produce cold flow problems and engine deposits and the biodiesel may not pass ASTM or EN specifications. However, there are absorbents in the marketplace that through filtration can selectively remove acylglycerols and glycerol.

Glycerol

Glycerol is an undesirable product in biodiesel production. It is insoluble in biodiesel and could be easily removed by settling to the bottom of the tank or by centrifugation. Excess methanol and high concentration of soaps will inhibit the separation. Glycerol in the biodiesel will create viscosity, engine combustion and filter plugging problems. Water washing or absorbents can reduce the concentration of glycerol in biodiesel to acceptable levels.

Alcohol

Biodiesel may contain up to 4% after glycerol separation. Excess methanol in the fuel will provide a dangerous explosive mixture in compression-ignited engines. The methanol present in the fuel influences the flash point. The change in flash point of fatty acid methyl ester biodiesel versus methanol and ethanol concentrations is given in Figure 2. Water washing or vacuum stripping will reduce alcohol to acceptable levels and meet ASTM and EN specifications.

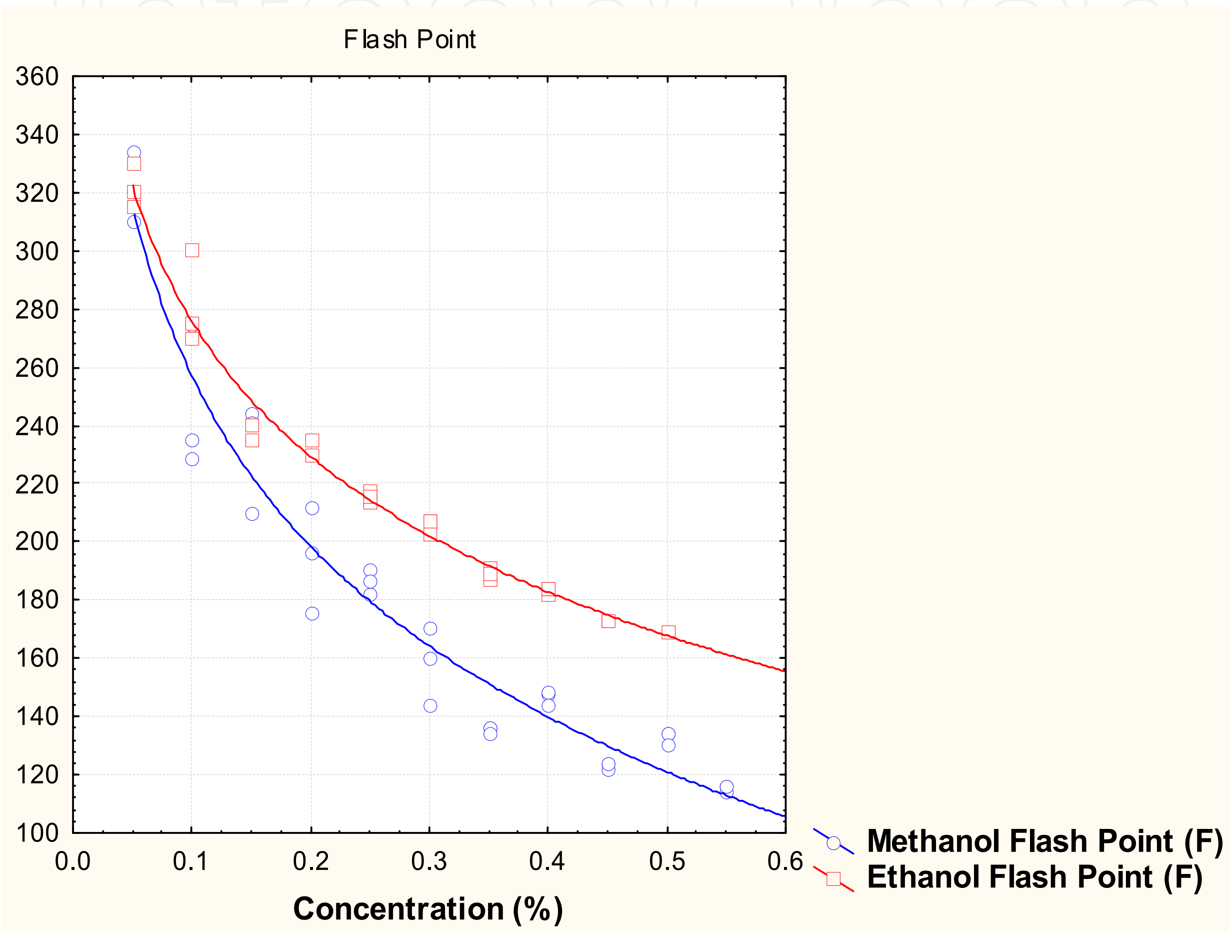


Fig. 2. Flash point of methanol and ethanol versus concentration in biodiesel.

Soaps

Soaps have been previously discussed. They can form microemulsions and influence the performance of the fuel. Soaps can be removed by water washing of the final product.

Water and catalyst removal

Water can be present as microemulsion or dissolved in the fuel. Biodiesel can contain up to 0.15% dissolved water. Water can contribute to corrosion, microbiological grows, sedimentation, etc.

Water can be removed by allowing it to settle to the bottom of the tank, boiling it off or by using solid absorbers.

Residual catalysts can form engine deposits and abrasion and wear of the fuel engine parts. Catalyst is usually removed with the glycerol and with the final water wash of the fuel.

BQ-9000 (Quality Assurance Program)

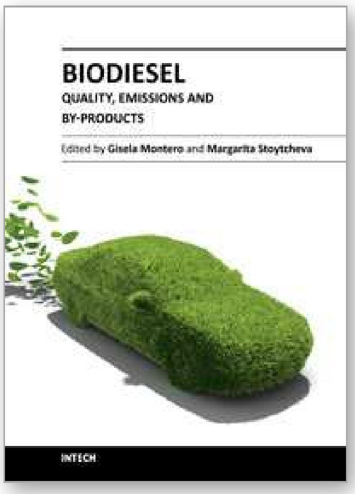
Finally, we could not leave this subject without mentioning BQ-9000.
The National Biodiesel Accreditation Program is a cooperative and voluntary program for the accreditation of producers and marketers of biodiesel fuel called BQ-9000. The program is a unique combination of the ASTM standard for biodiesel, ASTM D 6751, and a quality systems program that includes storage, sampling, blending, shipping, distribution and fuel management practices. BQ-9000 is open to any biodiesel manufacturer, marketer or distributor of biodiesel blends in the U.S. and Canada.

2. Conclusion

Biodiesel is a renewable fuel manufactured from feedstocks such as virgin and used vegetable oils, animal fats and recycled restaurant greases. It serves as a substitute for conventional diesel.
Feedstocks, feedstock quality and production practices can influence the quality of the final product. However, by taking appropriate steps in the production of biodiesel, a high quality fuel can be produced.

3. References

[1] Jewett, B., Inform 14: 528-530 (2003).
[2] Harold, S., Lipid Technol. 10: 67-70 (1997).
[3] Masjuki, H.H., Sapuan, S. M., J. Am. Oil Chem. Soc. 72: 609-612 (1995).
[4] Sii, H. S., Masjuki, H., Zaki, A. M., J. Am. Oil Chem. Soc. 72: 905-909 (1995).
[5] Clerc, J. C., “Cetane Number Requirements of Light Duty Diesel Engines at Low Temperatures,” Report No. 861525, Society of Automotive Engineers, Warrendale, PA 1986.
[6] Gopinath, A., Puhan, S., Nagarajan, G., Proc. IMechE Vol. 223 Part D: J. Automobile Engineering, 211(4), 565-583 (2009).
[7] Frankel, E. N. , Lipid Oxidation, The Oily Press, Dundee, Scotland, 1998.
[8] http://www.scientificpsychic.com/fitness/fattyacids1.html
[9] Waynick, J. A., SwRI Project No. 08-10721. Task 1Results. August 2005.
[10] Andersson, K., Lingnert, H., J. Am. Oil Chem. Soc. 75(8), 1041-1046 (1998).
[11] Neff, W.E, Mounts, T. L., Rinsch, W. M., Konishi, H., J. Am. Oil Chem. Soc. 70(2), 163-168 (1993).
[12] Neff, W.E, El-Agaimy, M. A., Mounts, T. L., J. Am. Oil Chem. Soc. 71(10), 1111-1116 (1994).
[13] Loury, M., Lipids, 7, 671-675 (1972).
[14] DeMan, J. M, Tie, F., deMan, L., J. Am. Oil Chem. Soc. 64(7), 993-996 (1987).
[15] Tang, H. Y., Salley, S. O., Ng, K. Y. S., Fuel 87: 3006-3017 (2008).
[16] Tang, H. Y., De Guzman R. C., Salley, S. O., Ng, K. Y. S., J Am Oil Chemo c 85: 1173-1182 (2008).
[17] http://biodieselmagazine.com/article.jsp?article_id=196
[18] Dunn, R. O. in The Biodiesel Handbook, edited by G. Knothe, J.Van Gerpen and J. Krahl, AOCS Press, Champaign, Illinois 1962.
[19] Van Gerpen, J., Pruszko, R., Clements, D., Shanks, B., Knothe, G., Building a Successful Biodiesel Business, January 2005.



Biodiesel- Quality, Emissions and By-Products

Edited by Dr. Gisela Montero

ISBN 978-953-307-784-0

Hard cover, 380 pages

Publisher InTech

Published online 16, November, 2011

Published in print edition November, 2011

This book entitled "Biodiesel: Quality, Emissions and By-products" covers topics related to biodiesel quality, performance of combustion engines that use biodiesel and the emissions they generate. New routes to determinate biodiesel properties are proposed and the process how the raw material source, impurities and production practices can affect the quality of the biodiesel is analyzed. In relation to the utilization of biofuel, the performance of combustion engines fuelled by biodiesel and biodiesels blends are evaluated. The applications of glycerol, a byproduct of the biodiesel production process as a feedstock for biotechnological processes, and a key compound of the biorefinery of the future is also emphasized.