Appendix VI

Studies Related To Production of Biodiesel

The appendix reviews the different techniques utilised for production of biodiesels by various investigators around the globe. The most preferred technique is transesterification as it yields the biodiesel whose properties are very close to diesel. Transesterification can be carried out in various ways by maintaining different equilibrium conditions. A new technique called peroxidation process in being highlighted in this review. The appendix also consists of a study wherein tools of biotechnology are employed in order to change the chemical structure of oils.

Ramadhas et al [21] developed a two-step esterification method to produce biodiesel from crude rubber seed oil. The esterification process consists of the following two stages, viz. (i) Acid-esterification: The acid-catalyzed pre-treatment process reduced the high FFA content of the crude oil to about 2% FFA, (ii) Alkaline-esterification: The products of first step were transesterified using alkaline catalyst. Sulphuric acid is used as catalyst. Alcohol to vegetable oil molar ratio is one of the important factors that affects the conversion efficiency of the process. For the stoichiometric transesterification, 3 mol of alcohol are required for each mole of the oil. However, in practice, the molar ratio should be higher than this theoretical ratio in order to drive the reaction towards early completion.

Usta et al. [26] investigated the effects of the methyl ester produced from a hazelnut soapstock/waste sunflower oil mixture using methanol, sulphuric acid and sodium hydroxide in a two stage process on the performance and emissions of a Ford XLD 418T four stroke, four cylinder, turbocharged indirect injection (IDI) Diesel engine at both full and partial loads. The CR of the engine was 21.5:1. During the production of biodiesel, Hazelnut soapstock and waste sunflower oil were mixed in approximately equal volume proportions. It was found that when a base catalysed transesterification process was directly applied to the mixture, the high free fatty acid content in the soap stock causes fairly high soap formation, which diminished the ester yield. Therefore, it was necessary to reduce the free fatty acid content of the mixture using an acid catalysed pre-treatment at 35 ^{0}C to esterify the free acids before transesterifying the triglycerides with an alkaline catalyst to complete the reaction at 55 ^{0}C.

Reyes and Sepulveda [29] Biodiesel production was carried out in a 20 litre non pressurized reactor, with control of stirring speed and temperature. Waste non-refined salmon oil with high free fatty acid content from food industry was used as oil source to make biodiesel. Two types of biodiesel fuels were produced. One of the fuels, called crude biodiesel was produced by sulphuric acid esterification at 60^0C for 65 minutes followed by a caustic soda transesterification at 55^0C for 60 minutes and then a gravitational separation of glycerine. In both reactions, a molar ratio of 6:1 methanol to triglycerides was used. The final biodiesel was carefully washed to eliminate residues of Glycerine and acid-base compound formed in the process. After a final washing and heating of the crude biodiesel at 70^0C for 30 minutes, the resulting viscosity and melting point of the fuel were 4.96 Cs and -11.0 ^{0}C respectively. This fuel held red colour impurities which were due to the artificial colorants added to the pellets. They were fed to the salmons and therefore were transferred to the fish oil. The final percentage conversion of glycerides to methyl ester obtained in crude biodiesel was 90%. On the other hand, the refined biodiesel fuel was produced from distillation of the crude biodiesel, which permits to achieve elimination of colour residues coming from salmon feeding and unconverted glycerides. Viscosity and melting point of refined biodiesel were 3.46Cs and -10.5 ^{0}C respectively.

Lin and Lin [30] produced biodiesel using peroxidation process. In this study, soybean oil (used as raw oil) and methanol in a molar proportion of 1:6 were reacted to produce biodiesel. Then, 1wt% of NaOH was added as a catalyst in the transesterification reaction. Hydrogen peroxide agent, which has a strong chemical activity, was used to react with sample of biodiesel in the peroxidation process. The oxygen content was significantly increased from 9.09 to 9.94 wt%, and the saturated carbon bonds increased significantly by 1.6 wt%, from 16.6 to 18.2 wt%, for the biodiesel produced with the additional peroxidation process.

Sahoo et al. [36] produced high acid value Polanga (Calophyllum Inophyllum L.) oil based mono esters by triple stage transesterification process and blended with high speed diesel on a small-size water-cooled direct injection diesel engine. The density and viscosity of the polanga oil methyl ester formed after triple stage transesterification were

found to be close to those of petroleum Diesel oil. The three stages used for transesterification were.

(i) Zero catalyzed transesterification: In the first stage, the organic matters and other impurities present in the unrefined filtered polanga oil using reagent were removed.

(ii) Acid catalyzed transesterification: The intermediate stage, the acid value of the oil about 4 mg KOH/gm corresponding to a FFA level of 2% was reduced.

(iii) Alkaline catalyzed transesterification: The product of the intermediate stage (pure triglycerides) was transesterified to mono-esters of fatty acids (biodiesel) using alkali catalyst.

The formation of methyl ester by three stage transesterification stochiometrically required six moles of alcohol for every mole of triglyceride. However, transesterification is an equilibrium reaction in which an excess of the alcohol is required to drive the reaction close to completion. The optimum ratio was found to be 6:1 molar ratio of methanol to oil (triglyceride) which is sufficient to give 85% yield of ester.

Meng et al. [61] studied the production of biodiesel from Waste cooking oil (WCO) through experimental investigation of reaction conditions such as methanol/oil molar ratio, alkaline catalyst amount, reaction time and reaction temperature. With the methanol/oil molar ratio increasing, WCO conversion efficiency was found to be correspondingly increasing. The maximum conversion efficiency (88.9%) was achieved at 7:1 methanol/oil molar ratio. With further increase in molar ratio, the conversion efficiency more or less remained the same. The WCO conversion efficiency also was found to be increasing proportionally with increasing amount of NaOH. The maximum WCO conversion efficiency (85.0%) was observed at 1.0 wt % NaOH. Addition of excess amount of catalyst, gave rise to the formation of an emulsion, which increased the viscosity and led to the formation of gels. The WCO conversion efficiency rapidly increased with the reaction time ranging between 30 minutes and 60 minutes, thereafter, the conversion efficiency kept rising very slowly and then practically constant above 86% at 90 minutes. The maximum WCO conversion efficiency was obtained at 50 °C temperature. Based on the results of preliminary experiments, a four-factor (A. methanol/oil molar ratio, B. NaOH amount, C. Reaction temperature and D. Reaction time) and three-level (for A 3:1, 6:1, 9:1; for B 0.7 wt.%, 1.0 wt.%, 1.3 wt.%; for C 35 °C, 50 °C, 60 °C and for D 30 minutes, 60 minutes, 90 minutes) orthogonal test was designed to determine optimum conditions for the transesterification process of WCO.

The optimum experimental conditions, which were obtained from the orthogonal test, were methanol/oil molar ratio 9:1, with 1.0 wt. % sodium hydroxide, temperature of 50 °C and time of 90 minutes. Verified experiments showed methanol/oil molar ratio 6:1 was more suitable in the process, and under that condition WCO conversion efficiency increased to 89.8% and the physical and chemical properties of biodiesel sample satisfied the requirement of relevant international standards.

Kinney and Clemente [106] implemented the tools of biotechnology to modify the fatty acid profile of soybean for performance enhancement. The content of linoleic and linolenic acids was reduced in order to reduce oxidative reactivity of the oil. It was also found that addition of ricinoleic acid increase the lubricity of soyabeen oil. Finally, it was concluded that designing soybean oil with 10–20% ricinoleic acid coupled with 70–80% oleic acid would enhance the performance of biodiesel fuel. They quoted also an economic analysis conducted by the Minnesota Department of Agriculture which revealed that if soybean oil-derived biodiesel was used at either 2% or 5% blend with petroleum diesel, this in turn would generate a significant economic stimulus, including job creation in rural areas.

Lertsathapornsuk et al. [107] modified a household microwave (800W) into a biodiesel reactor (Refer Figure VI.1) for continuous transethylation of waste frying palm oil. The waste palm oil biodiesel was then tested in a 100 kW diesel generator as a neat fuel (B100) and 50% blend with diesel No. 2 fuel (B50). It was reported that transmethylation under microwave radiation was very rapid. The biodiesel obtained was found to be having cetane number higher than Diesel oil. HC emissions increased with the increase in load of the engine in all types of fuels. The reason was reported to be a consequence of the increase in fuel consumption at higher loads. It was also reported that as the biodiesel contained about 11% oxygen and its cetane index is much higher than diesel more complete combustion took place which resulted in reduction of CO emissions.

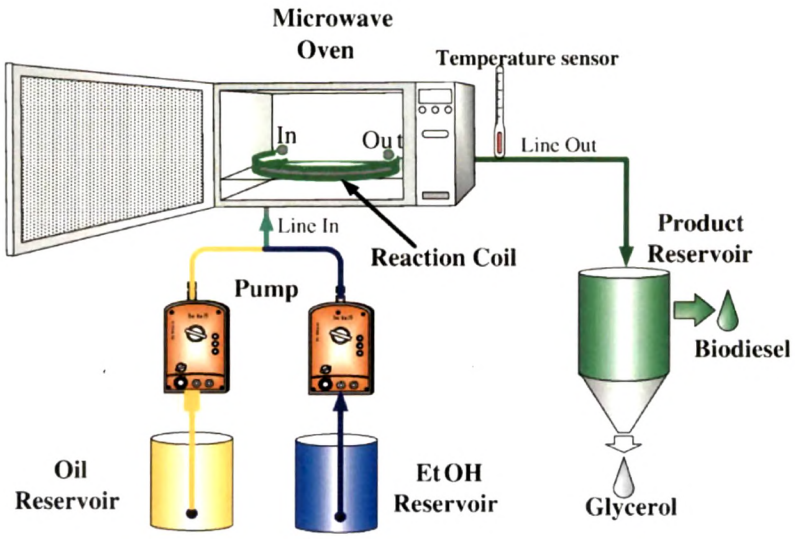

Figure VI.1 Schematic of Continuous Microwave Reactor [107]

Ali Keskin et al. [108] studied the usability of cotton oil soapstock biodiesel–diesel fuel blends as an alternative fuel for diesel engines. The biodiesel was produced using the following process as given in Figure VI.2

It was found that high calorific value and cetane number, low sulphur and low aromatic content, and similar characteristics are advantageous of cotton oil soap stock biodiesel–diesel fuel blends. The investigators by studies reported that the properties of blend fuels, such as oxygen content, higher cetane number and low levels of sulphur content improved combustion process.

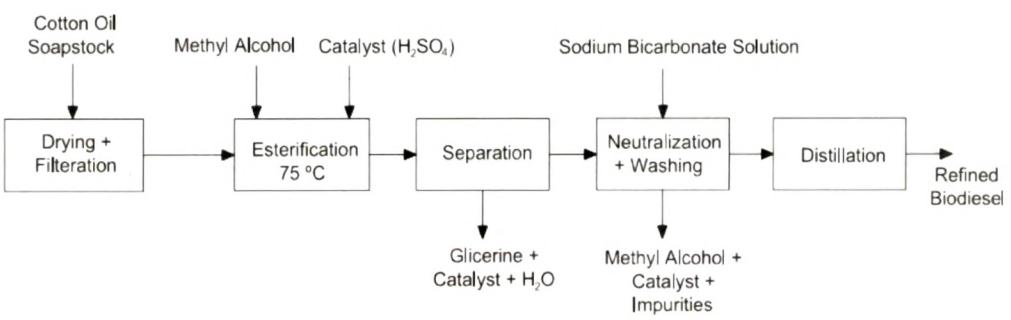

Figure VI.2 Flow Diagram of Cotton Oil Soap stock Biodiesel Production Process [108]

S. Murugan et al. [109] studied the use of tyre pyrolysis oil (TPO) in diesel engines. In order to produce oil, pyrolysis of rubber pieces obtained from an automobile tyre was carried out. After determining its properties, it was found that the viscosity of TPO was higher than diesel by about 1.5 times and the flash point and the fire point of TPO were closer to those of diesel. It was reported that the TPO-diesel fuel blend had longer ignition delay, higher NO_x and higher HC emissions. The ignition delay was longer due to the higher viscosity of TPO–diesel fuel blends that results in poor atomization. Fuels with longer ignition delays exhibit higher maximum rates of heat release, resulting in higher cylinder temperatures. Thus, NO_x is produced in the local high temperature region. Higher HC emissions are probably due to higher viscosity, density, poor volatility, and rich fuel mixtures at higher loads.

Ayhan Demirbas [110] conducted an experiment to demonstrate the production of bio-diesel from linseed oil fuels in non catalytic super critical method using fuels such as methanol and ethanol. Methanol was commonly used due to its lower cost. Methyl esters are renewable and are new clean engine fuel alternatives to petro diesel. It was stated that the most important variables affecting the yield of methyl esters during the transesterification reaction are the reaction temperature and the molar ratio of alcohol to vegetable oil. The yield conversion rate rises from 50% to 95% for first 10 minutes. The reaction temperature was in the range of 503K to 523K. The viscosity of linseed oil ethyl esters was slightly higher than that methyl ester. As seen in Figure II.3, the most volatile fuel was diesel fuel. The volatility of linseed oil methyl ester was higher than that of ethyl ester at all temperatures. The volatility of linseed oil was lower than those of corresponding methyl and ethyl esters at all temperatures.

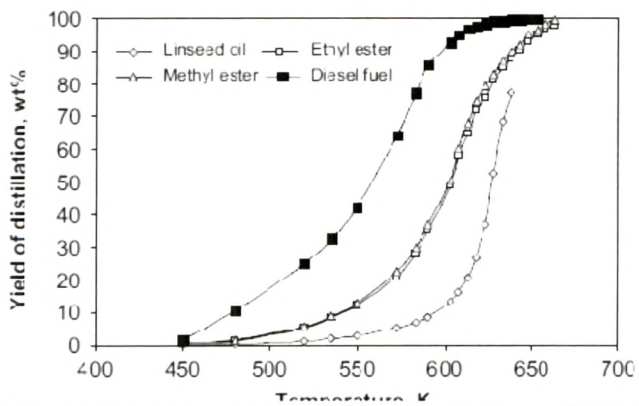

Figure VI.3 Distillation Curves of Diesel Fuel, Linseed Oil, and Methyl and Ethyl Esters of Linseed Oil [110]

TableVI.1 Summary of Studies Carried out on Production of Biodiesels

Sr. No	Investigators	Year	Fuel	Remarks
1	Ramadhas et al.	2005	Biodiesel from rubber seed oil	Developed a two-step esterification method to produce biodiesel from crude rubber seed oil.
2	Usta et al.	2005	Biodiesel from a hazelnut soap stock	It was found that when a base catalysed transesterification process was directly applied to the mixture, the high free fatty acid content in the soap stock causes fairly high soap formation, which diminished the ester yield.
3	Kinney and Clemente	2005	Biodiesel from soybean oil	Implemented the tools of biotechnology to modify the fatty acid profile of soybean for performance enhancement.
4	Reyes and Sepulveda	2006	Biodiesel from refined salmon oil	Biodiesel production was carried out in a 20 litre non pressurized reactor, with control of stirring speed and temperature.
5	Lin and Lin	2006	Biodiesel from soybean oil	Biodiesel is produced using peroxidation process. A hydrogen peroxide agent, which has a strong chemical activity, was used to react with sample of biodiesel in the peroxidation process
6	Sahoo et al.	2007	Biodiesel from polanga seed oil	Biodiesel was produced by triple stage transesterification process. The density and viscosity of the polanga oil methyl ester formed after triple stage transesterification were found to be close to those of petroleum Diesel oil.
7	Meng et al.	2008	Biodiesel from Waste cooking oil	Verified experiments showed methanol/oil molar ratio 6:1 was more suitable in the process, and under that condition WCO conversion efficiency led to 89.8% and the physical and chemical properties of biodiesel sample satisfied the requirement of relevant international standards.
8	Sinha and Agarwal	2008	Biodiesel from rice bran oil	Carried out the transesterification process for production of biodiesel. Its characteristic properties were found suitable to be used as fuel in diesel engines as they were comparable to that of diesel. However, the density, flash point temperature was slightly higher.
9	Lertsathapornsuk et al.	2008	Biodiesel from waste frying palm oil	Modified a household microwave into a biodiesel reactor for continuous transethylation of waste frying palm oil.
10	Keskin et al.	2008	Biodiesel from cottonseed oil	Before the transesterification, cotton oil soap stock was filtered and dried for removing water and impurities at 100 ^{0}C. After transestrification Crude biodiesel was distillated for obtaining pure methyl ester by means of batch distillation apparatus.
11	Murugan et al.	2008	Biodiesel from Tyre pyrolysis oil	Pyrolysis of rubber pieces obtained from an automobile tyre was carried out.
12	Krishnakumar et al.	2008	Biodiesel from rice bran oil and Jatropha oil	Catalytic transesterification method was used for converting oils into methyl esters. Transesterification reaction was carried out in a batch reactor.
13	Demirbas	2009	Biodiesel from linseed oil	Biodiesel was produced using Non catalytic super critical

				method using fuels such as methanol and ethanol.

The studies carried out on production of biodiesel from the year 2005 to year 2009 are listed in Table VI.1. From the table it can be observed that transesterification is the best and optimum method for production of biodiesel. However various investigators have developed different methods of transesterification, most of the methods yields almost same results. The various transesterification methods developed are two-step transestrification, base catalysed transesterification, triple stage transesterification, transethylation etc. The properties of biodiesel produced by all the transesterification processes are comparable to that of conventional Diesel oil and hence this throws some light on a point that biodiesel can be successfully used in existing diesel engines.