International Journal of Advanced Research Methodology in Engineering & Technology, ISSN 2456-6446
Volume 2, Issue 2, March 2018

A REVIEW ON SUSTAINABLE BIODIESEL PRODUCTION USING DIFFERENT MATERIALS

R. Arjun[a], P. Dinesh[a], K. Karthick[a], S. Melvin Richard[a], S. Balakrishnan[a] & S. Priyarega[b]
[a]Department of Mechanical Engineering
[b]Department of Chemistry
Saranathan College of Engineering
Trichy, Tamilnadu.

Abstract— ***The world is confronted with the twin crises of fossil fuel depletion and environmental degradation. The indiscriminate extraction and consumption of fossil fuels have led to a reduction in petroleum reserves. Petroleum based fuels are obtained from limited reserves. These finite reserves are highly concentrated in certain region of the world. Therefore, those countries not having these resources are facing a foreign exchange crisis, mainly due to the import of crude petroleum oil. Hence it is necessary to look for alternative fuels, which can be produced from materials available within the country.***

Keywords—Biodiesel, homogeneous & heterogeneous catalysts, trans-esterification, esterification, FAME

I. Introduction

The depleting reserves of fossil fuel, increasing demands for diesels and uncertainty in their availability is considered to be the important trigger for many initiatives to search for the alternative source of energy, which can supplement or replace fossil fuels. Rudolf Diesel tested peanut oil as fuel for his engine for the first time on August 10, 1893. In the 1930s and 1940s vegetable oils were used as diesel fuels from time to time, usually only in emergency. The first International conference on plant and vegetable oils as fuels was held in Fargo, North Dakota in August 1982. The primary concern discussed were the cost of fuel, the effect of vegetable oil fuels on engine performance and durability and fuel preparation specification and additives. Oil production, oil seed processing and extraction also were considered in this meeting. Vegetable oils hold promise as alternative fuels for diesel engines. But their high viscosities, low volatilities and poor cold flow properties have led to the investigation of various derivatives. Fatty acid methyl esters, known as Biodiesel, derived from triglycerides by trans-esterification with methanol have received the most attention.

II. LITERATURE SURVEY

The trans-esterification of canola oil with methanol using $AlCl_3$ or $ZnCl_2$ as catalyst was monitored by ^{1}H-NMR. The use of $AlCl_3$ to catalyze the esterification of stearic acid to methyl stearate resulted in 90% conversion. The catalyst therefore is suitable for simultaneous esterification of free fatty acid and trans-esterification of triglycerides. Using $AlCl_3$, the competing saponification reaction of free fatty acid could be eliminated giving higher FAME yield and purity even with the use of starting vegetable oil with high levels of free fatty acids [1].

Oxides of magnesium and calcium (MgO and CaO) have been tried as solid base catalyst owing to their easy availability, low cost, and non-corrosive nature. When both homogeneous and heterogeneous catalysts were tried for biodiesel development by trans-esterification of sunflower oil, NaOH (a homogeneous catalyst) performed much better than MgO (a heterogeneous catalyst) in terms of conversion. The reason attributed is the low surface area of the catalyst. More recently MgO has shown to possess catalytic activity for synthesis of biodiesel [2].

A pioneering work on catalytic activity of MgO has been reported by Di Serio et al. [3] where 92% yield has been achieved using 12:1 methanol to oil molar ratio, 5.0 wt% of the catalyst in 1h.

Dossin et al. [4] reported that MgO was found to work efficiently in batch reactor at ambient temperature during the trans-esterification reaction with production of 500 tonne of biodiesel. As heating is not required during batch process, the overall cost of production of biodiesel is reduced.

Among alkaline-earth metal oxides, SrO has also attracted attention as a heterogeneous catalyst owing to its high basicity and insolubility in methanol, vegetable oil and methyl esters [5]. A yield of 95% has been attained at a comparatively moderate temperature of approximately 65°C within 30 min. The catalyst has been reported to have a longer lifetime and could be reused for 10 runs.

Among the alkaline earth metal oxides CaO is most widely used as catalyst for trans-esterification and report says as high as 98% FAME yield is possible during the first cycle of reaction [6]. CaO has tendency to represent high basic strength and less environmental impacts due to its low solubility in methanol and can be synthesized from cheap sources like limestone and calcium hydroxide.

Martino Di Serio [7] demonstrates that it is possible to obtain molecular species of zinc (II) capable of catalyzing the trans-esterification of soybean oil in mild conditions. Their activity can be modulated by a fine selection of the anions and/or of the substituents on the ancillary bidentate ligand. The compounds are also active in the esterification of fatty acids. Future work will involve the heterogeneization of the catalysts on solid matrices, by employing the -OH group present on the ligand scaffold, and the study of the activity of corresponding complexes containing other Lewis acids.

He also described two efficient strategies for immobilizing catalysts based on Zn (II). Both the homogeneous catalysts supported on silica and the dendrimeric species have proven the capability of promoting the trans-esterification of neutral and acid soybean oil [8].

The properties of various plants and animals feedstocks for biodiesel production were described by Aninidita Karmakar [9]. Rape is a cruciferous crop which is harvested for oil production. Rapeseed (canola) oil is the most significant raw material for biodiesel producing industry in EU and Canada. There is great concern for the use of rapeseed oil for biodiesel production because rapeseed is presently grown with a high level of nitrogen containing fertilizer and the manufacture of these generates N_2O, a potent greenhouse gas with 296 times the global warming potential of CO_2. It has been estimated that 3–5% of N_2 provided as fertilizer for rapeseed is converted to N_2O (Lewis, 2007) [10].

Soybean oil is used as a major source of edible oil throughout the world. Soybeans can be produced without or nearly zero nitrogen. This makes soybeans advantageous for the production of biodiesel as nitrogen fertilizer is one of the most energy costly inputs in crop production. Pimental and Patzek (2005) studied the energy estimation for producing soybean biodiesel. They reported that 5546 kg of soybeans were required for producing 1000 kg of oil and biodiesel production using soybean required 27% more fossil energy than the biodiesel fuel produced [11].

Sunflower with high oil content is one of the more prominent oilseed crops for biodiesel production. At one point, it was considered to be the second primary source of edible oil next to soybean. Sunflower can grow in a variety of climatic conditions but it is considered to be an inefficient user of nutrients. Average yield is approximately reported to be lower than soybean yields, and necessary inputs are greater (Pimental and Patzek, 2005) [12].

Palm oil is derived from both the flesh and the seed of the palm fruit. Crude palm oil is semisolid at room temperature. Palm kernel oil is rich in lauric and myristic fatty acid with an excellent oxidative stability and sharp melting. Palm oil has been proved to be an efficient biodiesel source. It has been stated that palm oil can have high levels of fatty acids, which require extra methanol trans-esterification before it can be used as biodiesel, thus increasing the cost of production somewhat (Crabbe et al., 2001) [13].

Rudolf Diesel, the inventor of compression ignition engines, used peanut oil in 1900. The physicochemical characteristics of peanut oil biodiesel (POB) closely resemble to those of diesel fuel. But the production of biodiesel from peanut oil is not economically viable as peanut oil is more valuable than soy oil in the world market. Studies are going on at the University of Georgia to develop non-edible peanut varieties which are high in oil, but will not compete with peanuts grown for food or cooking oil purposes (Roberson, 2006) [14].

Recently Jatropha is being considered as one of the most promising potential oil source to produce biodiesel in Asia, Europe and Africa. Jatropha can grow under a wide variety of climatic conditions like severe heat, low rainfall, high rainfall and frost. Jatropha oil content varies depending on the types of species, climatic conditions and mainly on the altitude where it is grown. Various parts of the plant have medicinal values. In developing countries like India it has been identified as the major source of biodiesel.

Most of the physical and chemical properties of the directly extracted oil are almost similar to those of diesel, though ‘‘conardson carbon” residue is higher in case of it and due to high viscosity preheating is necessary to start a diesel engine (Shrinivasa, 2001) [15].

The neem tree is native to India and Burma and almost the whole tree is usable for various purposes such as medicines, pesticides and organic fertilizer. The oil contains sulfurous compounds which gives it a pungent odor and a less-clean burn than other vegetable oils.

The kinetics for both acid and base catalyzed trans-esterification reaction are reported by many authors. The experiments were performed with Jatropha curcas oil at different temperatures using different concentrations of H_2SO_4 and NaOH in acid and base catalyzed reactions with respect to FAME yield [16]. Due to high FFA contents of Jatropha Curcas oil (21.5%), a two-step process was selected for converting oil into methyl ester.

The results of variation of ME yield with temperature (20, 30, 40, 50, 60, 70 and 80°C) using different concentration of H2SO4 as acid and NaOH as base catalyst (0.5%, 1%, 1.5%, 2% and 3%, w/w) for esterification and trans-esterification using optimum amount of methanol i.e. 30% of the oil (v/v) show that during esterification, the maximum yield of ME (21.2%) was obtained at 65°C at 1% (w/w) H_2SO_4 concentration, while during trans-esterification, 90.1% yield of ME was obtained at 50°C using 1% NaOH (w/w).

A technique to produce biodiesel from Crude Jatropha Curcas seed Oil (CJCO) having high free fatty acids (15%FFA) has been developed [17]. The high FFA level of JCJO was reduced to less than 1% by a two-step pretreatment process. The first step was carried out with 0.60 w/w methanol-to-oil ratio in the presence of 1% (w/w) H_2SO_4 as an acid catalyst in 1 h reaction at 50°C. After the reaction, the mixture was allowed to settle for 2 h and the methanol–water mixture separated at the top layer was removed. The second step was trans-esterified using 0.24% (w/w) methanol to oil and 1.4% (w/w) NaOH to oil as alkaline catalyst to produce biodiesel at 65°C. The final yield for methyl esters of fatty acids was achieved as 90% in 2 h.

Trans-esterification does not alter the fatty acid composition of the feedstocks and this composition plays an important role in some critical parameters of the biodiesel, as cetane number and cold flow properties [18].

High cetane numbers help ensure good cold start properties and minimize the formation of white smoke. It is well known that biodiesel cetane number depends on the feedstock used for its production. The longer the fatty acid carbon chains and the more saturated the molecules, the higher the cetane number [19].

According to Knothe et al. (2003) [20], high cetane numbers were observed for esters of saturated fatty acids such as palmitic (C16:0) and stearic (C18:0) acids. Palm biodiesel, rich in these compounds, gave the highest cetane number. Olive, almond and rapeseed biodiesels presented a cetane number near to palm biodiesel. Finally, peanut, high oleic sunflower and corn biodiesels, those which were richer in unsaturated ester of linoleic acid (C18:2), presents a cetane number in the medium range [21].

Oxidation stability is one of the major issues affecting the use of biodiesel because of its content of polyunsaturated methyl esters (Knothe, 2006). A minimum Rancimat induction period of six hours is defined for biodiesel samples within UNE-EN 14214. This limit corresponds to the period of time passing before fatty acid methyl esters, aged at 110°C under a constant air stream. It is well known that it is very difficult to meet this limit for biodiesel fuels derived from many common raw materials, unless antioxidants are added to the biodiesel. All the biodiesels obtained did not achieve the minimum limit of six hours for oxidation stability. One feasible solution for increasing resistance of biodiesels against auto oxidation is to treat them with oxidation inhibitors (antioxidants) [22].

The parameters, which define the quality of biodiesel, can be divided into two groups. One group contains general parameters, which are also used for mineral oil based fuel, and the other group especially describes the chemical composition and purity of fatty acid alkyl esters [23].

Among the general parameters for biodiesel, the viscosity controls the characteristics of the injection from the diesel injector. The viscosity of fatty acid methyl esters can go very high levels and hence it is important to control it within an acceptable level to avoid negative impacts on fuel injector system performance. Therefore, the viscosity specifications proposed are nearly same as that of the diesel fuel. Flash point of a fuel is the temperature at which it will ignite when exposed to a flame or spark. The flash point of biodiesel is higher than the petrol & diesel, which is safe for transport purpose.

Cold filter plugging point (CFPP) of a fuel reflects its cold weather performance. At low operating temperature fuel may thicken and might not flow properly affecting the performance of fuel lines, fuel pumps and injectors. CFPP defines the fuels limit of filterability, having a better correlation than cloud point for biodiesel as well as petro diesel. Normally either pour point or CFFP are specified. Pour point is the lowest temperature at which the oil specimen can still be moved. French and Italian biodiesel specifications specify pour point where as others specify CFPP.

Cetane number is indicative of its ignition characteristics. The cetane number measures how easily ignition occurs and the smoothness of combustion. Higher the cetane number better it is in its ignition properties. Cetane number affects a number of engine performance parameters like combustion, stability, drivability, white smoke, noise and emissions of CO and HC. Biodiesel has higher cetane number than conventional diesel fuel, which results in higher combustion efficiency.

Neutralization number is specified to ensure proper ageing properties of the fuel and/or a good manufacturing process. It reflects the presence of free fatty acids or acids used in manufacture of biodiesel and also the degradation of biodiesel due to thermal effects. Carbon residue of the fuel is indicative of carbon depositing tendencies of the fuel. Conradsons Carbon Residue for biodiesel is more important than that in diesel fuel because it shows a high correlation with presence of free fatty acids, glycerides, soaps, polymers, higher unsaturated fatty acids and inorganic impurities. The presence of high level of alcohol in biodiesel causes accelerated deterioration of natural rubber seals and gaskets. Therefore control of alcohol content is required. The presence of mono-, di-, and tri-glycerides causes engine problems like fuel filter plugging affecting the fuel properties and are specified in most of the biodiesel standards [24].

Engelman et al. [25] reported that 10–50% soybean oil fuel blends with diesel minimize the carbon deposition in combustion chamber. Quick [26] used over 30 different vegetable oils to operate compression engines and reported that the use of raw vegetable oil fuels can lead to premature engine failure.

The atomization and injection characteristics of vegetative oils were significantly different from that of diesel fuel due to the higher viscosity of the vegetative oils [27]. Engine performance tests showed that power output slightly decreased when using vegetable oil fuel blends. Nag et al. [28] showed that performance tests using fuel blend as great as 50–50 seed oil from the Indian Ambulate plant and diesel fuel exhibited no loss of power. Knock free performance with no observable carbon deposits on the functional parts of the combustion chamber were observed.

References

[1] Nestor U. Soriano Jr., Richard Venditti, Dimitris S. Argyropoulos, Biodiesel synthesis via homogeneous Lewis acid-catalyzed transesterification, Fuel 88 (2009) 560–565.

[2] Yogesh C. Sharma a, Bhaskar Singh a, John Korstad b, Latest developments on application of heterogenous basic catalysts for an efficient and eco friendly synthesis of biodiesel: A review, Fuel 90 (2011) 1309–1324.

[3] Di Serio M, Ledda M, Cozzolino M, Minutillo G, Tesser R, Santacesaria E., Transesterification of soybean oil to biodiesel by using heterogeneous basic catalysts. Ind Eng Chem Res 2006;45:3009–14. In Di Serio D, Tesser R, Pengmei L, Santacesaria E. Heterogeneous catalysts for biodiesel production. Energy Fuels 2008;22:207–17.

[4] Dossin TF, Reyniers MF, Berger RJ, Marin GB. Simulation of heterogeneously MgO-catalyzed transesterification for fine-chemical and biodiesel industrial production. Appl Catal B: Environ 2006;67:136–48.

[5] Liu X, He H, Wang Y, Zhu S. Transesterification of soybean oil to biodiesel using SrO as a solid base catalyst. Catal Commun 2007;8:1107–11.

[6] Kawashima A, Matsubara K, Honda K. Acceleration of catalytic activity of calcium oxide for biodiesel production. Bioresour Technol 2009;100:696–700.

[7] Martino Di Serio a,b,∗, Giuseppina Carotenutoa, Maria Elena Cucciolitoa,b, Matteo Legaa,b, Francesco Ruffoa,b, Riccardo Tessera,b, Marco Trifuoggia, Shiff base complexes of zinc(II) as catalysts for biodiesel production, Journal of Molecular Catalysis A: Chemical 353– 354 (2012) 106–110.

[8] Vincenzo Benessere a, Maria E. Cucciolito a,b, Giovanni Dal Poggetto a,b, Martino Di Serio a,b, Manuel López Granados c, Francesco Ruffo a, Aldo Vitagliano a,b, Rosa Vitiello a,b, Strategies for immobilizing homogeneous zinc catalysts in biodiesel production, Catalysis Communications 56 (2014) 81–85.

[9] Aninidita Karmakar a,*, Subrata Karmakar b, Souti Mukherjee a, Properties of various plants and animals feedstocks for biodiesel production, Bioresource Technology 101 (2010) 7201–7210.

[10] Lewis, M., 2007. Biofuel mandates cause global warming, scientists say. Available from: <http://www.openmarket.org>.

[11] Pimental, D., Patzek, W.T., 2005. Ethanol production using corn, switchgrass and wood: biodiesel production using soybean and sunflower. Natural Resources Research 14 (1), 65–76.

[12] Pimental, D., Patzek, W.T., 2005. Ethanol production using corn, switchgrass and wood: biodiesel production using soybean and sunflower. Natural Resources Research 14 (1), 65–76.

[13] Crabbe, E., Nolasco-Hipolito, C., Kobayashi, G., Sonomoto, K., Ishikazi, A., 2001. Biodiesel production from crude palm oil and evaluation of butanol extraction and fuel properties. Process Biochemistry 37 (1), 65–71.

[14] Roberson, R., 2006. Peanut Biodiesel Promising But Costly Alternative Fuel. Farm Press Publications, RenewableEnergyWorld.com, Peterborough, USA.

[15] Shrinivasa, A., 2001. A viable substitute for diesel in rural India. A report of the discussion meeting on 'The Potential of Honge Oil as diesel substitute in rural areas' on 9th Feb 2001 at, IISc Bangalore. Current Science 80 (12), 1483–1484.

[16] Siddharth Jain , M.P. Sharma, Biodiesel production from Jatropha curcas oil, Renewable and Sustainable Energy Reviews 14 (2010) 3140–3147.

[17] Hanny Johanes Berchmans a, Shizuko Hirata b, Biodiesel production from crude Jatropha curcas L. seed oil with a high content of free fatty acids, Bioresource Technology 99 (2008) 1716–1721.

[18] María Jesús Ramos , Carmen María Fernández, Abraham Casas, Lourdes Rodríguez, Ángel Pérez, Influence of fatty acid composition of raw materials on biodiesel properties, Bioresource Technology 100 (2009) 261–268.

[19] Bajpai, D., Tyagi, V.K., 2006. Biodiesel: source, production, composition, properties and its benefits. J. Oleo Sci. 55, 487–502.

[20] Knothe, G., 2005. Dependence of biodiesel fuel properties on the structure of fatty acid alkyl esters. Fuel Process. Technol. 86, 1059–1070.

[21] Van Gerpen, J.H., 1996. Cetane number testing of biodiesel. Liquid fuels and industrial products from renewable resources. In: Proceedings of the Third Liquid Fuel Conference, 15–17 September, Nashville, Tennessee.

[22] Rodríguez, L., Pérez, A., Romero, R., Manjavacas, G., Ramos, M.J., Casas, A., 2006.Effect of antioxidants on the oxidation stability of biodiesel from sunflower oil. In: 6th International Congress of Chemistry, ANQUE.

[23] Mittelbach M. Diesel fuel derived from vegetable oils, VI: Specifications and quality control of biodiesel. Bioresour Technol 1996;27(5):435–7.

[24] L.C. Meher, D. Vidya Sagar, S.N. Naik, Technical aspects of biodiesel production by transesterification—a review, Renewable and Sustainable Energy Reviews 10 (2006) 248–268.

[25] Engelman HW, Guenther DA, Silvis TW. Vegetable oil as a diesel fuel. Diesel and gas engine power division of ASME paper number 78-DGP-19. New York, NY: ASME.

[26] Quick GR. Development in use of vegetable oils as a fuel for diesel engine. ASAE paper number 801525. St. Joseph, MI: ASAE.

[27] Ryan III TW, Dodge LG, Callahan TJ. The effect of vegetable oil properties of injection and combustion in two different diesel engine. J Am. Oil Chem Soc 1984;61(10):1610–9.

[28] Nag AS, Bhattacharya KBDe. New utilization of vegetable oils. J Am. Oil Chem Soc 1995;72(12):1591–3.