ISSN 2278-3091
Volume 8, No.1.6, 2019
International Journal of Advanced Trends in Computer Science and Engineering
Available Online at http://www.warse.org/IJATCSE/static/pdf/file/ijatcse0781.62019.pdf
https://doi.org/10.30534/ijatcse/2019/0781.62019

Transesterification for biodiesel-a review

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ABSTRACT

Synthesis of fuel from various low cost feed stocks solves the problem of solid waste management while synthesizing the biofuel. In transesterification, the oil is converted to biodiesel. Transesterification can be categorized into three categories namely base catalyzed, acid catalyzed and acid-base catalyzed. Also lipase made transesterification is one another category of such reactions. Transesterification consists of number of reversible reactions. Microwave assisted and ultrasonic transesterification are two advanced categories of transesterification reactions. The economy of transesterification process depends largely on the use of feed stock. Also use of appropriate catalyst has a major role to play. The performance of the reaction process with use of various acid, base and organic catalysts is one promising field of investigation. Transesterification of the palm oil and seed oil is widely investigated research area. Various aspects of this process such as catalyst use, affecting parameters, starting materials, reaction steps, kinetics and modeling are are being studied in order to make the process more acceptable and practical on industrial scale.

Key words: Feed stock, catalyst, enzymes, kinetics, conversion, yield, modeling.

1. INTRODUCTION

Rapid industrialization and growth has become important aspect of civilization and development. This has resulted in ever increasing demand of energy. Conventionally wood coal, petrol, diesel and kerosene, liquefied petroleum gas (LPG, Compressed natural gas (CNG) etc. are used as fuel for various industrial and domestic needs. Depleting fossil fuel sources have made it necessary for us to look beyond these conventional sources. Various studies are reported by investigators on heat transfer enhancement by various techniques, optimization of resources, pinch analysis, heat recovery (1-5). Use of non-conventional natural resources like tidal energy, solar energy is considered as the future of energy revolution (6-10). Other possibilities such as fuel cells, use of solid waste are being explored for energy (11-15). Synthesis of fuel from various low cost feed stocks solves the problem of solid waste management while synthesizing the biofuel (16-17). This aspect makes the biofuel very sought after alternative for fuel.

Energy efficient practices in various energy intensive industries coupled with non-conventional energy can help in solving the problem of energy crises (18-20). The bio-diesel is derived from vegetable or plant oil and consist of long chain alkyl esters. In transesterification, the oil is converted to biodiesel. Methyl, ethyl or butyl alcohol can be used along with sodium hydroxide catalyst for this synthesis. Various investigators have investigated transesterification for studying affecting parameters, catalysts, conversion and yield with various starting materials. This review paper sheds light on some significant investigations on transesterification with emphasis on biodiesel synthesis.

2. VARIOUS ASPECTS OF TRANSESTERIFICATION

Transesterification is replacement of the 'R' group of an ester with 'R' group of an alcohol. In transesterification of vegetable or animal oils, methanol, ethanol or other alcohol type is used to react with glycerides in presence of catalyst like sodium hydroxide to form fatty acid alkyl ester. The properties of fatty acid alkyl esters are very close to fossil fuel derived diesel (21).Transesterification reactions can be catalyzed by acid or base catalysts (22). Incoming functional group from the catalyst attacks the carbonyl carbon of the ester. This results in transesterified product and glycerol. Transesterification can be catalytic and non-catalytic (22). The transesterification occurs at different temperatures depending on the raw material (23). Higher temperature favors reaction, but beyond certain temperature denaturation starts. Use of guanidine as catalyst has got attention due to its ability to easily heterogenize on organic polymers (24).

Kinetic modeling for transformation processes is important tool for analysis and optimization of the process (25). Efforts are being done to use enzymes like lipase for the biodiesel production (26). Fatty acid methyl esters can be obtained at ambient conditions ambient with less waste compared to the chemical-based methods by using Lipase enzyme (26). Many investigations are reported on various aspects of transesterification reactions. This is one of the most convenient way to produce esters (27). Use of micro-mixer reactor for fast transesterification from microalgae has been found to be very effective by investigators (28). Use of waste frying oil for biodiesel production with sodium methoxide catalyst was reported with excellent yield (29).

3. INVESTIGATIONS ON TRANSESTERIFICATION

Biodiesel has many advantages such as low toxicity, lower emission, rapid degradation and high flash point (30). Transesterification can be categorized into three categories namely base catalyzed, acid catalyzed and acid-base catalyzed (31). Also lipase made transesterification is one another category of such reactions. Transesterification consists of number of reversible reactions. Microwave assisted and ultrasonic transesterification are two advanced categories of transesterification reactions. The reaction between triglycerides (oil /fats) and methanol forms two immiscible phases. The reaction taking place in interfacial area of two phases can be assisted by the sonication. Ultrasonic waves help is mixing and increases the conversion (31). Instantaneous heating of the oil can be obtained by using microwave. The microwave assisted transesterification produces the biodiesel with low performance. Factors such as catalyst separation, unreacted methanol, recovery of glycerol and inorganic salts imposes limitations on chemical synthesis of biodiesel, though it is cost effective and efficient method (31).

Use of enzyme catalyzed reaction is one of the promising alternative to chemical production of biodiesel. Lipase and hydrolytic enzymes can be employed for the biodiesel (31). Castor oil is one of the feed stocks for biodiesel. It can be used with reagents like ethanol and catalysts potassium hydroxide (32). Microwave assisted transesterification yields reaction times (32). In The low temperature conditions the microwave influence is not hampered as in case of conventional methods.

Research on biodiesel production is focused on use of various low cost raw materials for the biodiesel production. Use of efficient contact equipment can increase the conversion and reduce the processing cost. Conventional reactors used for biodiesel production reactions are limited in efficient use of alcohol. Excess alcohol calls for processing for separation and recovery of alcohol, which increases the cost of production. Reaction distillation is a method to carry out reaction and separation in the same equipment. It serves two purposes, one is reduces space requirements and also gives more conversion, as the volatile products can be removed continuously shifting the reaction towards right side. An investigation with palm oil and methanol as reagents has endorsed the application of reactive distillation for biodiesel production (33). The reaction time was shortened. Purity of ester was slightly less in this experiments, which can be improved with optimization of parameters (33). Use of different raw materials has attracted many investigators. Linoleic and oleic sunflower oils were used for biodiesel by Predojevic et al. (34). Calcium oxide was used as solid base catalyst. Linoleic acid is one of the important fatty acid for human beings. Typically sunflower oil contains seventy percent polyunsaturated Linoleic acid (35).The esters obtained from Linoleic acid were higher in terms of yield. In general the reaction conditions have very little effect on the properties of methyl esters (35). Similar research was reported by Tan et al. with modified calcium oxide (36). The calcium oxide was modified by using chemical agents. The conversion reached close to ninety percent by use of activated catalyst.

The economy of transesterification process depends largely on the use of feed stock. Also use of appropriate catalyst has a major role to play. The performance of the reaction process with use of various acid, base and organic catalysts is one promising fields of investigation. According to Ejikeme et al., use of strong basic site catalyst such as zeolite can be very promising option (37). Sodium methoxide and sodium hydroxide, both offer good catalytic properties in the process (38).The methoxide needs less oil to methanol ratio (38). Use of butanol for transesterification has also been explored (39). Mild reaction conditions and high yield of butyl esters makes this fuel practically feasible for synthesis and application on industrial scale. Use of jatropha seeds for biodiesel production is widely explored research topic. The simultaneous extraction and transesterification of the jatropha oil can reduce the cost and increase the economy of transesterification process (40). The process has drawback of solid waste management. Use of the solid cake obtained after the process for the binder less particleboard can add value to the process (40).

Various catalyst are being explored for maximum yield of the product by using various raw materials such as jatropha seeds (41). Metal triflate salts have been explored for the reaction by Daniel et al. (41). They used triflates of scandium, bismuth, aluminum, lanthanum, copper, and zinc for the catalysis. The one of aluminum gave highest conversion. In case of in situ transesterification, factors such as moisture content of seeds, agitation intensity, molar ratio of alcohol to oil, catalyst concentration, particle size, alcohol type catalyst type and reaction temperature affect the conversion (42). In this reactive extraction process, the seeds are grinded and reacted directly alcohol and catalyst. This reduces production and capital cost considerably.

Many of the school and college projects are focused on biodiesel production from waste and low cost raw materials (43). On laboratory scale these projects are massive success. On industrial scale, this has many disadvantages such as raw material with consistent quality and quantity and competitive use of such raw materials. Two step transesterification can be used to achieve the conversion above 95 percent (44). Increase in residence time for the second transesterification step can help in improving the conversion. Supercritical methanol has been used for the transesterification for kinetic study by Liu with various feed stocks (45). Also they synthesized biodiesel from microalgae oil. They observed that free glycerides reduces with temperature and residence time. They used three step kinetic model for the transesterification reaction.

Cooking oil is one of the source of biodiesel production. Used cooking oil should not be reused repeatedly as it contains higher fatty acids (46). This used cooking oil can be used for the biodiesel production. This can solve the disposal problem of used oil. Reacting the oil with methanol is preferred due to efficiency. Also ethanol and isopropyl alcohols can be used for the purpose. Alkali-catalyzed transesterification of edible vegetable oils is major method used for biodiesel (47). A typical two step catalyzed process for biodiesel from Jatropha curcas crude oil includes first step of esterification of free fatty acid in the presence of sulphuric acid (47). Also reaction with methanol reduces free fatty acid to less than 0.2 percent (47). The second step is the reaction between the first step product and methanol with potassium metaoxide as a catalyst takes place. Transesterification of non-edible oil can yield very good lubricating properties (48). These biolubricants find application in the drilling applications. Drilling mud with biolubricant exhibits relatively high viscosity high lubricating film strength and high corrosion inhibition (48). Transesterification reactions for different vegetable oils with sodium hydroxide as a catalyst and ethanol as reagent is one of the most commonly investigated research area (49). When ethanol is produced from corn, and meat and bone meal, dry grains are obtained, which can be used as raw material as a raw material in transesterification for the production of fatty acid methyl esters (50). The cost of the biodiesel and availability of distribution network is problem in adoption of biodiesel as fuel (51). Efforts are on to overcome this issue. However it cannot be denied that biodiesel has given some kind of energy security for the countries depending on fossil fuel and facing environmental problems. Literature shows that large variety of catalysts have been tried for the biodiesel production by various investigators (52). Heterogeneous catalysts are more enviro-friendly than the homogeneous. Simulation studies are also reported for optimization of the parameters (53).

4. CONCLUSION

Biodiesel is attracting attention of the world and research community due to energy needs and increased awareness about environment (54). Transesterification of the palm oil and seed oil is widely investigated research area. Various aspects of this process such as catalyst use, affecting parameters, starting materials, reaction steps, kinetics and modeling are being studied in order to make the process more acceptable and practical on industrial scale. Reduction of the production and hence market cost is major challenge for the biodiesel production by using transesterification of various low cost starting materials. Waste cooking oils and diesel blends are also tested for a single cylinder diesel engine (55). There is wide scope for research for optimization of the process.

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