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A REVIEW ON NEW METHODS USED FOR THE PRODUCTION OF BIODIESEL

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Abstract

Biodiesel is a renewable biofuel produced by transesterification process from vegetable oils or fat. The immiscible nature of the reactants during the transesterification process results in poor mass transfer rate which causes long reaction time and low reaction rate. The transesterification is generally carriedout in a batch reactor which uses conventional electrical heating and mechanical stirring. The conventional method used in the batch reactors need more than one hour of electrical energy for both heating and stirring. Hence, few alternative energy stimulant methods were tried for the production of biodiesel. The biodiesel produced by these methods satisfies the biodiesel standards and characteristics of the biodiesel are similar to the biodiesel produced by the conventional method. This paper discus various energy stimulant methods which offer a fast, easy route to produce biodiesel with advantages of enhancing the reaction rate and improving the separation process as compared to the conventional method. These advanced technologies have the potential to significantly enhance the biodiesel production process with considerable potential in reducing production time and cost.

Keywords : Biodiesel; Production; transesterification; Microwave; Ultrasonic.

1. Introduction

The world oil resources are expected to meet the projected growth in energy demand in near future [1]. Shahriar *et al.* [2] analysis indicates that the fossil fuel reserves depletion times for oil, coal and gas are approximately 35, 107 and 37 years respectively. Also, the fuel crisis due to increase in vehicular population have renewed interest to look for alternative fuels of bio-origin. Biomass is considered as a one of the most sustainable, alternative, renewable energy sources and biodiesel is considered as an immediate substitute for the fossil diesel in diesel engine. Biodiesel is produced from vegetable oil or fat by transesterification process. In transesterification process, the vegetable oil or fat is mixed with the mixture of anhydrous methanol and catalyst. This mixture of the reactants is heated and stirred using suitable devices and the transesterification reaction takes more than one hour for completion. A catalyst is usually used to improve the reaction rate and the biodiesel yield. The variables which affects the biodiesel yield are, reaction temperature, reaction time, type of catalysts, alcohol/vegetable oil molar ratio, purity of the reactants and free fatty acid content [3-4]. The transesterification reaction is represented by the general equation shown in Figure 1.

The major obstacle in the commercialization of biodiesel is its higher cost as compared to diesel. A significant amount (25%) of production cost can be reduced if less expensive vegetable oils are used to produce biodiesel [5]. A. E. Atabani *et al.* [6] suggest that there is a huge potential to produce biodiesel from non-edible oils. Also, the production cost can be further reduced by analyzing production process from the seed to the biodiesel end-product and reducing energy inefficiencies [7-8].

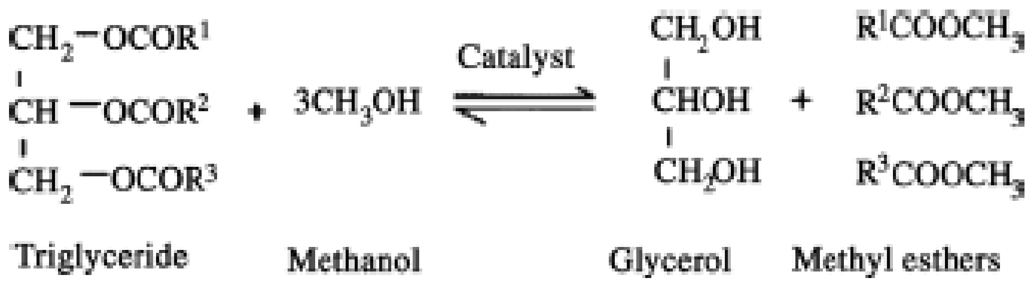

Figure 1 Transesterification of Triglycerides

2. Biodiesel Production by Conventional Method

The conventional biodiesel processes are based on use of high power conventional heating and mechanical stirring. In conventional method, an electrical heater and an electric motor are used for heating and mixing of the reactants respectively. The conventional heating depends upon convection currents and the thermal conductivity of the reaction mixture. The stoichiometry molar ratio of alcohol to oil required for the transesterification is 3:1, but excess molar ratio has been used for better biodiesel yield and to shift the reaction to the product side as this reaction is a reversible one. Generally, the reaction temperature is maintained below the boiling point of the methanol. The biodiesel yield of 80 to 100% can be obtained depending on the feedstock, amount and type of alcohol, catalyst quantity, reaction temperature and reaction time. The conventional biodiesel processes in batch processing is slow and the reaction time is more than one hour and phase separation takes more than 5 hour [3-6].

3. Microwave Technology

Microwave is an electromagnetic wave with frequencies between 0.3 GHz and 300 GHz and is a form of energy that resides fairly low in the electromagnetic spectrum. A domestic microwave oven passes microwave radiation, causing dielectric heating by absorption of energy in the water, fats and sugar contained in the food [9]. During microwave irradiation, the bonds are neither formed nor broken but the energy is rapidly transferred to the sample. From the literature, it is observed that the microwave irradiation can be used as the heat source during transesterification reaction because it accomplishes the transesterification reactions in sec or min. The microwave dielectric properties depend significantly on the temperature, frequency and catalyst [10]. The thermal analysis based on the new method will be helpful for the industrial design of biodiesel production [11].

In microwave assisted biodiesel production unit, the reactants such as vegetable oil, alcohol and catalyst were mixed using suitable stirring device and heated by the microwave heat source. The reactants are subjected to the microwave irradiation for the required reaction time of few min. After that the products of the transesterification were allowed to settle for phase separation. The separation of the biodiesel and glycerin phase takes 30 to 60 min. After that the crude biodiesel is subjected to water wash to remove impurities and dried to remove the moisture content. The reaction time and setting time required for this method is low and hence the production cost also reduces significantly. The fuel properties of the biodiesel produced by this method are similar to the biodiesel produced by conventional method and satisfy the biodiesel standards. Table 1 shows the optimum condition required for biodiesel production from various vegetable oils.

Table 1 Optimum Condition for Biodiesel Production using Microwave Irradiation

Type of oil	Optimum Condition	Reference
Jatropha oil	Methanol/oil molar ratio of 7.5:1, 1.5% KOH, reaction temperature of 65 °C, reaction time of 2 min	12
Pongamia pinnata seed oil	Alcohol/oil molar ratio of 6:1, reaction temperature of 60°C, 0.5% NaOH and 1.0% KOH.	13
Waste cooking oil	Methanol-to-oil molar ratio of 6:1, 0.75wt% CH_3ONa or NaOH, reaction time of 3 min, microwave power of 750W. Biodiesel yield of CH_3ONa is higher than NaOH.	14
Yellow horn oil	Molar ratio of methanol/oil 12:1, temperature of 60°C, reaction time of 10 min, 1% heteropolyacid catalyst ($Cs_{2.5}H_{0.5}PW_{12}O_{40}$)	15
Palm oil	Methanol-to-oil ratio of 18:1, reaction time of 4 min, 900 W microwave power, CaO catalysts derived from eggshells:15%	16
Waste frying palm oil	Ethanol to oil molar ratio of 12:1, 3.0% NaOH, reaction time of 30 sec.	17

Jun Cheng *et al*. [18] used a novel process for the direct conversion of wet microalgae biomass into biodiesel by microwave irradiation. They reported that, the biodiesel production rate and yield from wet microalgae obtained through the one-step process using microwave irradiation were higher than the two-step process using conventional heating. Few researchers observed a significant effect of the reaction time in reducing the catalytic activity which interpreted in terms enzyme deactivation, due to microwave exposure. They concluded that the biocatalyst activity in presence of microwave increased about one order of magnitude [19]. Honglei *et al.* [20] reported that the biodiesel production from waste cooking oil using microwave reached the biodiesel yield of 97.4% under the optimal conditions and with the ion-exchange resin particles catalytic membrane. The real time monitoring and controlling of the process is necessary to adjust the applied power of microwave reactor [21]. Few researchers designed controllers which are based on LabVIEW, to automatically and continuously adjust the applied power and full system real time monitoring [22].

4. Engine Test with Biodiesel

The properties of biodiesel obtained by microwave irradiation are similar to the biodiesel obtained by the conventional method. When waste palm oil biodiesel was used as a substitute in 100 kW diesel generator with B100 and B50 as fuel, the engine thermal efficiency was reduced as compared to the fossil diesel, at all loads. But the engine emissions such as CO, NO_x and HC were reduced, except that at the 75 kW engine load [17].

5. Ultrasonic Technology

The ultrasonication increases the chemical reaction speed of the transesterification and also facilities the change of production method from batch processing to continuous flow processing. The principle of ultrasound action in biodiesel production is primarily based on the emulsification of the immiscible liquid reactants by microturbulence generated by radial motion of cavitation bubbles. It allows a short reaction time and high yield because of emulsification and cavitation of the liquid–liquid immiscible system [23]. The ultrasonic irradiation biodiesel process reduces the reaction time by 30 min or more as compared to the conventional method. The highest biodiesel yield and methyl ester content were observed at an ultrasonic power of more than 450 W [24].

Do Van Manh *et al*. [25] studied the effects of ultrasonic irradiation time (t) on the biodiesel yield (Y) of biodiesel produced from blended oil consisted of 20, 50 and 30% of tung, canola and palm oils, respectively and CH_3OH and KOH. Their results showed that biodiesel yield reaches high value of 87–91% for tung oil as t ≥ 5 min, while of about 92–94% for blended oil as t ≥ 1 min. The researchers suggested that the tung oil should be blended with other oils in order to produce biodiesel satisfying the biodiesel standards. Table 2 shows the optimum condition required for biodiesel production from various oils. The properties of biodiesel obtained by this method are in agreement with the standard biodiesel [26].

Table 2 Biodiesel production using Ultrasonic Technology

Type of oil	Optimum Condition	Reference
Waste cooking oil	Molar ratio of alcohol to oil of 6:1, 1wt.% KOH, temperature of 45°C, ultrasound power of 200 W, irradiation time of 40 min	27
Coconut oil	Molar ratio oil to ethanol of 1:6, 0.75wt.% KOH, 7 min reaction time.	28
Canola oil	Methanol/oil molar ratio of 5:1, 0.7 wt.% KOH, reaction time of 50 min, ultrasonic irradiation of 20 kHz with an input capacity of 1 kW.	29
Coconut oil	Molar ratio oil to ethanol of 1:6, 0.75wt.% KOH of of oil, 7 min reaction time.	30
Jatropha oil	Molar ratio oil to methanol of 1:4, catalyst of 5 wt.% of oil, reaction time 30 min, ultrasonic amplitude 50% (100 W/m^3) and cycle 0.7 s.	31
Crude cottonseed oil	Methanol/oil molar ratio of 6.2:1, 1 wt% NaOH, reaction time of 8 min.	32

Xin Deng *et al.* [33] pretreatment jatropha oil with H_2SO_4 for 1 h in the first step and in the second step biodiesel was obtained with 96.4% yield. They reported that the total production time with ultrasonic method was 1.5 h which is just half of the conventional method (4h). Hamed et al carriedout batch process assisted biodiesel production from palm oil by 20 kHz ultrasonic cavitation with the catalyst such as CaO, SrO and BaO. They reported that the catalytic activity was in the sequence of CaO < SrO < BaO. The biodiesel produced from this method satisfies the biodiesel standards [35].

Ali Sabri *et al.* [36] reported that a biodiesel yield of 91% was achieved in just 40 min from jatropha oil at a moderate ultrasonic amplitude (~60%), high molar ratio (25:1) and low reaction temperature (65°C) using carbon-supported tungstophosphoric acid catalyst. Pedro et al suggested that the biodiesel can be produced with a considerable reduction in energy consumption, by a two-step procedure: first a conventional heating under mechanical stirring, followed by ultrasound irradiation at the same temperature.

6. Combination of Microwave and Ultrasonic Technologies

Vitthal *et al.* [38] used sequential effect of microwave and ultrasound in a two-step synthesis method for high acid value nagchampa oil and its comparison with individual approaches of microwave, ultrasound and conventional approach. They reported that the reaction time for the esterification and transesterification using ultrasound alone was 60 min and 20 min respectively and it reduced to only 15 min and 6 min for the sequential approach. Ming-Chien *et al.* [40]work shows that the optimal procedure involved 1-min ultrasonic mixing and 2-min closed microwave irradiation and the optimal reaction conditions were amount of catalyst used, 1.0 wt%; reaction temperature, 333 K; and methanol/oil molar ratio, 6:1.

Xiulian Yin *et al.* [39]studied four different methods such as mechanical stirring (MS), flat plate ultrasonic irradiation (FPUI), flat plate ultrasonic irradiation with mechanical stirring (UIMS) and probe ultrasonic irradiation (PUI), to select a better one that need less catalyst, energy consumption and time for preparing biodiesel through trans-esterification of sunflower oil. Their results showed that under the same condition, UIMS and PUI used less catalyst, less methanol, shorter time and less energy consumption than MS and FPUI with the same biodiesel conversion.

7. Pyrolysis

Few researchers found that the biodiesel can be produced by pyrolysis of the oleaginous materials, instead of the traditional processing of oil extraction and trans-esterification. Takuya Ito et al. used pyrolysis method to produce biodiesel from waste cooking oil. from their work, they reported that, compared to the biodiesel obtained by transesterification, the biodiesel obtained by pyrolysis showed improvement of about − 5°C in the pseudo-cold filter plugging point. Xiaowei Peng *et al.* [42] pyrolyzed the dry fermented wheat straw mass in a fixed-bed reactor in order to convert the microbial oil to biodiesel. They reported that the conversion rates of hexadecanoic acid methyl ester and 9-octadecenoic acid methyl ester can be increased by pyrolysis with catalyst permutit. It can be speculated that during pyrolysis, the fatty acid methyl esters were produced by transesterification of microbial oil with methanol which was another pyrolysis product of the fermented mass.

8. Conclusion

The biodiesel is produced by transesterification of vegetable oils and the reaction rate depends on the free fatty acid composition of the oil and heating mode of the reaction. In recent years, unconventional heating methods such as microwave irradiation and ultrasonic irradiation were used for the transesterification of vegetable oils. The ultrasonic irradiation had two effects, those were heating and mixing of the reactants. From the literature it is observed that these two methods were efficient, energy saving and economically feasible way to produce biodiesel. Also, the possible combinations of sonochemical reactors with other techniques of intensification such as use of microwave and hydrodynamic cavitation can also be used to produce biodiesel. The biodiesel produced by these unconventional heating methods are similar to biodiesel produced by conventional heating method and satisfies the biodiesel standards. These methods will reduce the operating cost and reduces the cost of the biodiesel.

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