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Advancements in Biodiesel Production Methods

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Abstract—*Biodiesel has drawn more and more attention in recent years because it is renewable and has less detrimental effects on environment as compared with conventional diesel derived from petroleum .It consists of mono alkyl esters that are usually produced by transesterification of plant or animal oil with alcohol in the presence of catalyst. Catalysts mainly belong to the categories of homogeneous or heterogeneous. Several processes for biodiesel fuel production have been developed, among which the transesterification using alkali catalysis gives high yields of conversion. The main problem of transesterification reaction is that the reactants are not readily miscible. This leads a longer reaction time and so higher fixed capital investments and product costs .Few other drawbacks of this traditional catalyzed batch methods include glycerin removal, and a need for removal of catalyst, in addition to soaps or other unwanted byproducts. In an effort to bypass these issues, some new processes were developed to produce biodiesel, like supercritical method, ultrasonic method, co-solvent method and microwave method etc. Hence the purpose of this review is to highlight the previous studies conducted as well as the future direction of these technologies.*

Keywords*: Biodiesel, Monoalkylesters, Transesterification, Supercritical method, Ultrasonic method, Co-solvent method, Microwave method etc.*

1. INTRODUCTION

The depleting reserves of fossil fuel, increasing demands for diesels and uncertainty in their availability, increasing emissions of combustion-generated pollutants, and their augmented costs will make biomass sources more attractive [1]. Biodiesel refers to a diesel-equivalent, processed fuel derived from biological sources [2].

Biodiesel is mainly produced by transesterification of oils and fats with a monohydric alcohol in the presence of homogeneous basic catalysts, like sodium and potassium hydroxide, carbonates and alcoxides [3]. However, the use of acid catalysts requires the neutralization and separation of the final reaction mixture, leading to environmental problems related to the use of high amounts of solvent and energy [4]. Therefore, this reaction system can result in soap production, especially when oils and fats with free fatty acids and moisture contents higher than 0.5 wt% and 2% (v/v), respectively, are used as reactants [5]. Other problem associated with transesterification reaction is that the reactants are not readily miscible. This leads a longer reaction time and so higher fixed capital investments and product costs[6] .Few other drawbacks of this traditional catalyzed batch methods include glycerin removal, and a need for removal of catalyst, in addition to soaps or other unwanted byproducts[7]. In an effort to bypass these issues, some new processes were developed to produce biodiesel, like supercritical method, ultrasonic method, co-solvent method and microwave method etc. Hence the purpose of this review is to highlight the previous studies conducted as well as the future direction of these technologies.

2. MICROWAVE METHOD

Microwave technology relies on the use of electromagnetic waves to generate heat by the oscillation of molecules upon microwave absorption. The electromagnetic spectrum for microwaves is in between infrared radiation and radiofrequencies of 30 GHz to 300 MHz, respectively, corresponding to wavelengths of 1cm to 1m [8]. In microwave-assisted heating, unlike the conventional methods, the heat is generated within the material, thus rapid heating occurs. As a result of this rapid heating, many microwave-assisted organic reactions are accelerated, incomparable with those obtained using the conventional methods[9]. Thus, higher yields and selectivity of target compounds can be obtained at shorter reaction times. In addition, many reactions not possible using the conventional heating methods, had been reported to occur under microwave heating[10]. Microwave heating method allows for rapid increase of solvent temperature and quick cooling as well, whereas in conventional heating rate of heating and cooling are very slow.

Microwave-assisted transesterification is energy-efficient and is a quick process to produce biodiesel[11]. Methanol, with its high microwave absorption capacity and high polarity, is the solvent which is used in biodiesel transesterification reactions[12]. In feedstock containing water, microwave assisted supercritical reactions can turn the water as organic solvent ,this is because water molecules possess a dipole moment. A dipole is sensitive to external electrical fields and will attempt to align itself with the field by rotation to generate local superheating[13]. It is estimated that energy consumed per liter of biodiesel produced via microwave heating is

significantly less than that required for conventional heating. This is due to the more efficient heating via stimulation of the dipoles of polar molecules within the compound; which encourages rapid molecular rotation and heat generated from molecular friction[14].

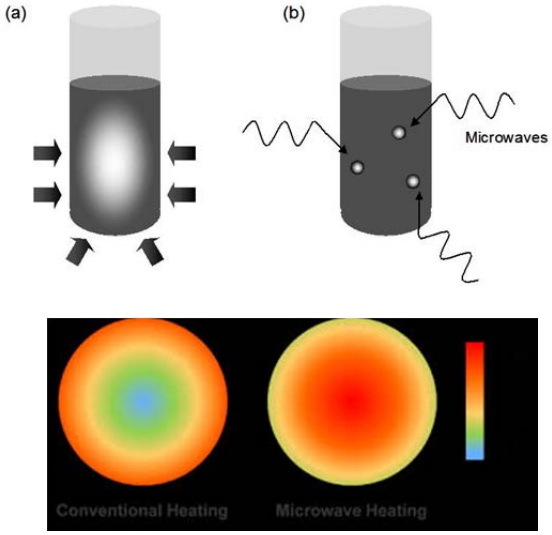

Fig. 1: Conventional heating (a),and microwave heating(b)

3. ULTRASONIC METHOD

Ultrasonic mixing induced effective emulsification and mass transfer. Thus the rate of ester formation under ultrasonic condition is higher than that under stirring conditions [15-17]. Researchers have indicated the use of ultrasonic mixing is efficient, time-saving and economically functional, offering several advantages over the classical procedure [18,19]. The collapse of the cavitations bubbles cleavages the phase boundary and leads to emulsification by ultrasonic jets that impinge one liquid against another. Droplets of denser oil move upwards while the alcohol moves downwards, thus fostering the mixing and increasing the contact area between alcohol and oil. The ultrasonic properties of an emulsion vary significantly and increase the contact area for fats and alcohol [20]. Therefore, ultrasonic-assisted transesterification might be an efficient way to reduce reaction time [16,18-20].

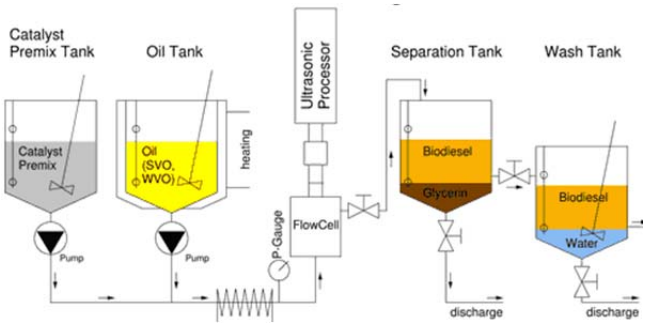

Fig. 2: Ultrasonic method of biodiesel production

4. CO -SOLVENT METHOD

Conventional method had been found effective in producing the desired quality & yield of Biodiesel but the rate of reaction is very slow often is extended beyond 1 hr[21]. The main problem for the inferior rate of transesterification reaction is that the reaction mixture is not homogeneous because the oils and alcohols are not completely miscible with each other because of their chemical structures [22]. Oil disperses in the methanol medium, so the probability and the rate of collision of the glyceride and the methoxide(mixture of methanol and alkaline catalyst , KOH or NaOH) molecules becomes less. This decreases the rate of collisions of molecules and so the rate of reaction causes longer reaction times, increased operating expenses and labor cost [23].

To overcome this difficulty of mixing of the reactants, a single phase reaction is proposed [24]. The proposed model involves a Co solvent introduced in the reaction mixture which makes both the oil and alcohol miscible and reduced the mass transfer resistance. There are various solvents that can be used with the boiling point up to 100^0C [22-24]. Various co-solvents like propane, hexane, heptanes, tetrahydrofuran(THF), carbon dioxide (CO2), mixture of THF and hexane, dimethyl ether, diethyl ether, tert-butyl methyl ether are used to increase the yield of biodiesel due to enhancement of the miscibility of the phase by enhancing the rate of reaction[21-25].

5. SUPERCRITICAL METHOD

To minimize the drawbacks of conventional transesterification technique, a catalyst-free technique for the transesterification of vegetable oils using an alcohol under supercritical conditions has been proposed, keeping the benefits of fuel quality and taking into account environmental concerns[26-28]. According to the current literature, catalyst-free alcoholysis reactions at high temperature and pressure conditions provide improved phase solubility and decreased mass-transfer limitations. The reaction rate increases significantly in the supercritical state and thus the reaction is complete in shorter periods with consequent simpler separation and purification steps[26]. In supercritical conditions, the alcohol is not only a reactant but also an acid catalyst [29]. Besides, it has been shown that the supercritical method is more tolerant to the presence of water and free fatty acids than the conventional alkali-catalyzed technique. Hence the technique is much more flexible to various types of vegetable oils, which increases the interest in research involving the application of this methodology[30].

6. CONCLUSIONS

Biodiesel can be produced by conventional transesterification method by vegetable oil and animal fat. The reaction rate of biodiesel production depends upon the temperature of reaction, heating method, oil composition ,mixing of reactants

etc. In conventional transesterification reaction the heating method used are inefficient and costlier. The mechanical mixer used for mixing are also not very effective. To overcome these problems some new and advanced techniques like microwave,supercritical,ultrasonic and co solvent methods are used. In microwave method the reaction time and setting time required is low and hence the production cost also reduces significantly, due to the heating characteristics inherent to microwaves. In ultrasonic method the mixing and heating is more effective as compare to conventional method. Co solvent method make the system more homogeneous and hence enhanced rate of reaction. Supercritical method carried out reaction without catalyst and reduces the cost of by-product separation. The biodiesel produced by all 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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