A REVIEW PAPER ON BIODIESEL PRODUCTION VIA NON CATALYTIC SUPERCRITICAL ALCOHOL

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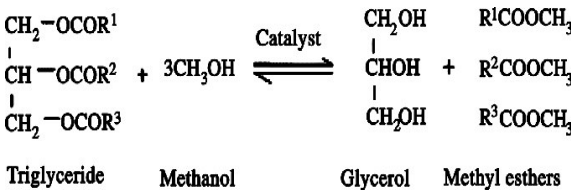
***Abstract*- This paper reviews the production of Biodiesel using supercritical alcohol. Biodiesel is an attractive alternative fuel because it is environmentally friendly and can be synthesized from edible and non-edible oils. Biodiesel is made from renewable biological sources such as vegetable oils and animal fats by non-catalytic supercritical alcohol transesterification methods. A non-catalytic Biodiesel production route with supercritical methanol has been developed that allows a simple process and high yield within short reaction time because of simultaneous transesterification of triglycerides and methyl esterification of fatty acids.**

***Keywords*:** transesterification; biodiesel; Supercritical methanol

I. INTRODUCTION

The decrease of world petroleum reserves and the atmospheric pollution caused by petroleum based-fuels has necessitated the need for an alternative source of energy. Biodiesel, an alternative fuel, presents a suitable renewable substitute for petroleum base-fuel [2]. Biodiesel, an alternative fuel, made from renewable biological sources such as vegetable oils and animal fats. It is biodegradable and nontoxic, has low emission profiles and so is environmentally beneficial [1]. Biodiesel has been defined as the mono-alkyl esters of long-chain fatty acids derived from renewable feedstock, such as vegetable oils and is synthesized from the triglycerides in vegetable oils by transesterification with alcohol.



General equation for transesterification of triglycerides

In this technique, the oil reacts with an alcohol in a number of consecutive, reversible steps to form esters and glycerol. Though a molar ratio of alcohol to oil required is only 3 by stoichiometry, excess alcohol is often used. Several parameters such as molar ratio of oil to alcohol, reaction temperature, time and water content of the reactants influence the reaction. The transesterification can be conducted either in the presence or absence of a catalyst. The usual catalysts used are alkalis (NaOH, KOH), acids (sulfuric acid, HCl) or enzymes (lipases) [5].

Alkali catalyzed process is very sensitive to the purity of reactants, the presence of minor amount of free fatty acid (FFA) and moisture in the reaction mixture produces soap. Acid catalyzed process does not produce soap, however it requires a long time for the reaction to complete. In the acid catalyzed method, a reaction system with 20% of fatty acids resulted in a reduction of the conversion to about a half, while in the alkaline-catalyzed method only 35% methyl esters were obtained [4].

A two-step transesterification process in which acid catalyzed transesterification is followed by alkali catalyzed reaction has been developed to improve the yield of biodiesel production from oil with high FFA content. Although the reaction time could be reduced, no recovery of catalyst and high cost of reaction equipment were still the main disadvantages of this process [2].

In the homogeneous transesterification with liquid catalysts, recovery of the catalyst was not possible. Heterogeneous catalyst can therefore be used, nevertheless, there still appear to be some problems with this technique and finding a suitable catalyst that is active, selective, and stable under the specified process conditions is the major challenge. Alternatively, transesterification using enzyme catalyst such as lipase can also convert oils and fats into methyl esters. Although the method is more environmentally friendly, the high cost of enzymes and requirement of high reaction makes the process unattractive for industrial scale [2].

Saka and Dadan (2001) and Demirbas (2002) have reported a novel method of synthesis of biodiesel

fuels from vegetable oil via non catalytic transesterification in supercritical fluid like methanol, to overcome the problems of conventional methods. At supercritical condition (300^{o} C, 20 MPa) complete conversion of fatty acids to methyl esters within 8 min. was observed.

II. CONTINUOUS TRANSESTERIFICATION REACTOR SYSTEM

Fig 1 shows the continuous transesterification reactor system for Biodiesel production. The oil and methanol were pumped in two different lines by high-pressure high-performance liquid chromatographic pumps (Jasco, model PU-1580) up to 19 MPa (total flow rate of 1.5-9.0mL/min) depending on space time and molar ratio of methanol-to oil [3].

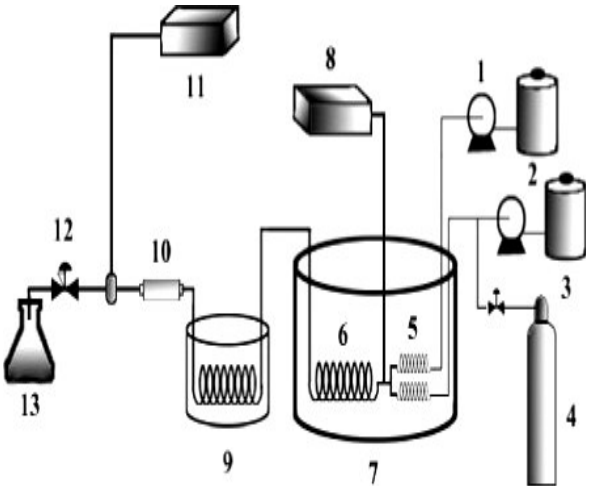


Fig1. Schematic diagram of the continuous transesterification reactor system [3]

1. High-pressure pumps, 2. Methanol reservoir,
3. Vegetable oil reservoir 4. Nitrogen cylinder,
5. Preheater 6. Reactor 7.Salt bath 8.Temperature monitoring system 9.Cooling bath 10.Inline filter, 11.Pressure monitoring system, 12.back pressure regulator, and 13.Sample collector

Preheated while flowing in the preheat lines (SS316 tubing of 1/8-in. OD, 0.035-in. thickness, and 2-m length). After being preheated, the two lines were mixed at the reactor inlet using a SS316 mixing tee, and the temperature of the fluid was monitored directly using a thermocouple located within this mixing tee. The reactor was constructed from a 5.5-m length of 3/8-in. OD, 0.035- in. thickness SS316 tubing. The preheat lines and the reactor were immersed in an electrically heated salt bath. The fluid product exiting from the reactor was promptly cooled by an external water cooling bath and depressurized using a back-pressure regulator. After pressure and temperature were constant, approximately 10 mL of liquid product was collected, and then methanol was Evaporated by a rotary evaporator. The liquid product was checked for % methyl esters by gas chromatography to ensure that the system reached steady state. The final product was collected and left to settle for several hours, preferably overnight, to ensure complete separation. Two liquid phases were obtained: ester and crude glycerin. The top ester layer was separated by separatory funnel and put in rotary evaporator remove any excess methanol. The % methyl ester in liquid product was then analyzed by gas chromatography [3].

III. MECHANISM OF ACTION

Saka and Kusdiana (2004) proposed the reaction mechanism of transesterification of vegetable oil in the supercritical methanol and ethanol. The basic idea of supercritical fluid treatment is in the effect of the relationship between pressure and temperature upon the thermo physical properties of the solvent (methanol), such as dielectric constant, viscosity, specific gravity, and polarity. For example, ionic product, which is an important parameter for chemical reactions, can be improved by increasing the pressure. Therefore, in the supercritical methanol treatment of vegetable oil, in addition to acting as a reactant, methanol is expected to be an acid catalyst.

Table1. Physicochemical properties of methanol in ordinary and supercritical condition [4]

Properties	Ordinary condition (25 °C, atmospheric pressure)	Supercritical condition (250 °C, 20 MPa)
Specific gravity, kg/l	0.7915	0.2720
Ionic product, log *Kw*	−0.77	Not available
Dielectric constant	32.6	7.2
Viscosity, Pa s	5.4×10^{-4}	0.58×10^{-4}
Hydrogen bonding, number	1.93	<0.7
Solubility parameter, $(MPa)^{1/2}$	7.1	4.1

In addition, its dielectric constant dramatically changes to a number closer to that of vegetable oil

allowing a homogenous mixture in supercritical condition Table 1 presents a comparison of some physicochemical properties of methanol in an ordinary condition and supercritical state. In a catalyst free transesterification with supercritical methanol it is assumed that an alcohol molecule directly attacks the carbonyl atom of the triglyceride because of the high pressure. In the supercritical state, depending on pressure and temperature, hydrogen bonding would be significantly decreased, which would allow methanol to be a free monomer. As shown in Table 1, the hydrogen bonding is weakened to 0.7 in the supercritical state from 1.9 in an ordinary condition. The transesterification is completed via a methoxide transfer, whereby the fatty acid methyl ester and Diglyceride are formed. In a similar way, Diglyceride is transesterified to form methyl ester and Monoglyceride which is converted further to methyl ester and glycerol [4].

IV. EFFECT OF REACTION PARAMETERS ON TRANSESTERIFICATION IN SUPERCRITICAL ALCOHOLS

The molar ratio of methanol and ethanol to oil is one of the most important variables influencing the conversion into methyl and ethyl esters. The effect of molar ratio is shown here at 300 ^{o}C & 40 min. Fig. 2 shows the effect of the molar ratio on the conversion into methyl and ethyl esters for Jatropha oil in supercritical methanol and ethanol. The conversion increases from 30 to 40% at a molar ratio of 10 to 80–85% at a molar ratio of 50. This indicates that the higher molar ratio of methanol/ethanol results in better transesterification, perhaps due to the increased contact area between methanol or ethanol and triglycerides [6].

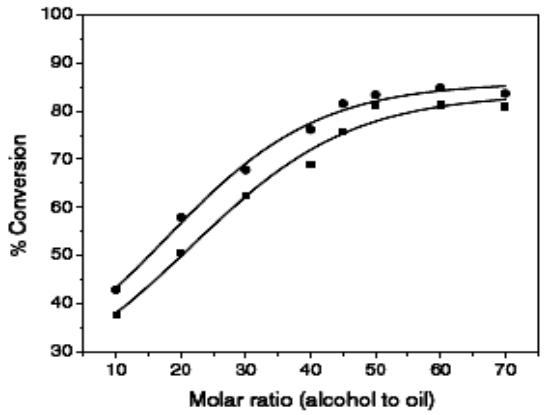


Fig. 2 Effect of molar ratio for synthesis of alkyl esters with Jatropha oil, treated at 300 oC and 40 min in supercritical methanol/ethanol [6].
Legands: (■) Methyl esters, (●) Ethyl esters.

The effect of temperature is shown here with an optimum molar ratio of 50:1 for jatropha oil at 200 to 400 ^{0}C and 200 bar. At 200 ^{0}C, the relatively low conversion to alkyl esters is evident due to the subcritical state of alcohols. A maximum conversion of 70% is obtained between 200 and 250 ^{0}C. However, at 300 ^{0}C, a conversion of 70% was observed in 10 min and 85% at 40 min. The conversion into ethyl esters is higher than that of methyl esters. Figs. 3 and 4 depict the plot of conversion with time for the formation of methyl and ethyl esters, respectively. However, decomposition reactions take place at temperature above 400 ^{0}C due to the thermal degradation of alkyl esters. The higher conversions observed in the supercritical state can be attributed to the formation of a single phase between alcohol and oil. Under supercritical conditions, the solubility parameter of alcohol reduces and is close to the solubility parameter of oil [6].

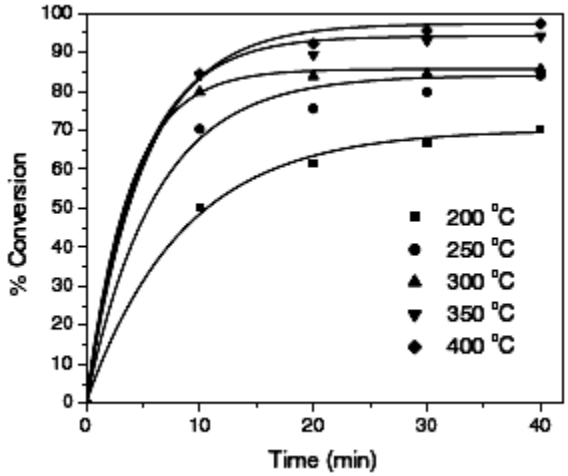


Fig 3 Synthesis of methyl esters of Jatropha oil at various temperatures in supercritical methanol [6]

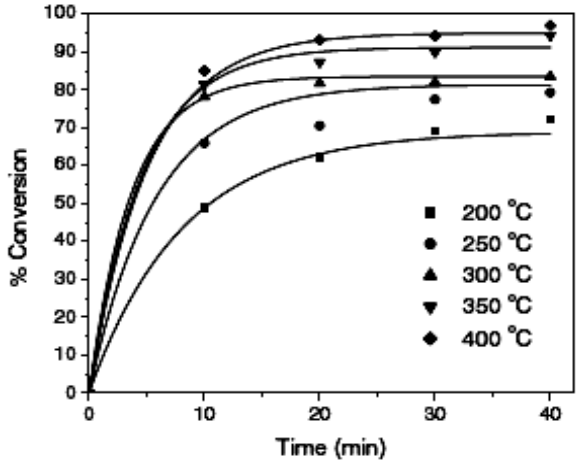


Fig 4 Synthesis of ethyl esters of Jatropha oil at various temperatures in supercritical ethanol [6]

V. SUMMARY

Biodiesel has become attractive alternative to replace petroleum fuel because of its environmental benefits. Most biodiesel industries use the alkali-catalyzed process but the process is limited by its sensitivity to both water and free fatty acids. The absence of pre-treatment step, soap removal, and catalyst removal can significantly reduce the capital cost of a biodiesel plant for the synthesis in supercritical alcohol but the Expected high operating cost due to high temperature and pressure can be a drawback. However, since significant conversions are obtained at a very short time, it may compensate the cost.

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