Modern Developments in Biodiesel Production Technology

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ABSTRACT

Biodiesel can be produced by various conventional methods, such as: alkali catalysis, acid catalysis, lipase catalysis etc. Considering various limitations of these methods, there is a strong quest to develop an efficient, time-saving, economically functional and environmental friendly biodiesel production processes at industrial scale having superiority over the classical procedure. Keeping this aspect into consideration, some of the recently developed biodiesel production technologies are power ultrasound, hydrodynamic cavitation and supercritical methanol processes. Power ultrasound is a useful tool to strengthen mass transfer of liquid liquid heterogeneous system. In this process cavities are created by the irradiation of power ultrasonic with sufficient energy in the immiscible liquids. Among recently developed techniques, another cavitation technique, which is popularly known as hydrodynamic cavitation is a potential method for biodiesel production at industrial scale due to its easy scale-up property. This is a rapid technique for preparing alkyl esters from triglycerides at pilot plant scale operation. Supercritical methanol is a simple and fast process and produces high yield because of simultaneous transesterification of triglycerides and methyl esterification of fatty acids at critical state. All these methods have future potential for biodiesel production at industrial scale. The present paper deals with the details of development of biodiesel production test rigs developed at Internal Combustion Laboratory of Mechanical Engineering Department, Delhi Technological University.

Keywords: *- Biodiesel Production, Power ultrasound, Hydrodynamic Cavitation, Transesterification.*

1. INTRODUCTION

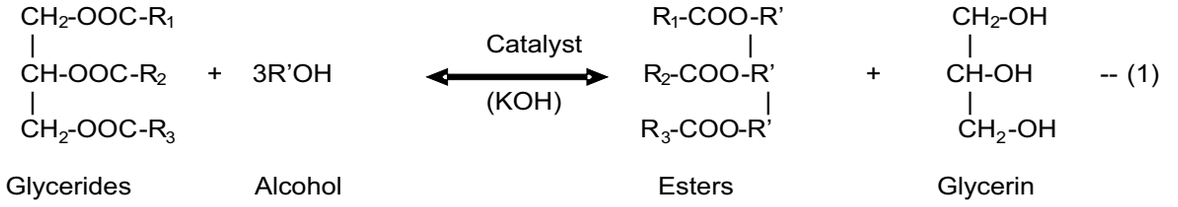
1.1 Background

The world is presently facing the problems of fossil fuel depletion in very near future and severe environmental degradation. Indiscriminate extraction and lavish consumption of fossil fuels resulted in reduction of underground carbon resources. The search for alternative fuels, which promise a harmonious correlation with sustainable development, energy conservation, efficiency and environmental preservation, has become highly pronounced in the present context. In the last decade, several researchers have examined that vegetable oils may be proved as one such alternative fuel and their potential. Vegetable oils have their own advantages because of their easy availability, being renewable and eco-friendly to the environment, and they are free of sulphur content in them. This makes vegetable fuel studies become current issue among the various popular investigations. Bio-diesel has many advantages over petroleum diesel fuel; produce less smoke and particulates, have high cetane number, produce lower carbon monoxide and hydrocarbon emissions, renewable, biodegradable and non-toxic. In developed countries, the focus has been mainly on edible oils like soybean, rapeseed, sunflower etc., whereas few attempts have made for producing biodiesel from non-edible sources like waste cooking oil, greases, tallow and lard. In India, with abundance of forest resources, there are a number of other non-edible tree borne oilseeds with an estimated annual production of more than 20 million tones, which have large potential

for making biodiesel to supplement other conventional sources. Among these, Karanja (Pongamia glabra) and Jatropha (Jatropha curcas) have been successfully proved for their potential as biodiesel [1-3]. Biofuels applicable as alternative fuels for internal combustion engines is discussed by Agrawal[4] with a focus on performance and emission of biodiesel in CI engines, combustion analysis, wear performance, and economic feasibility.

1.2 Transesterification Process

Transesterification is not a new process as scientists Duffy and Patric conducted it as early as 1853. Transesterification involves the reaction between an alcohol and a vegetable oil that are mixture of triglyceride (esters of glycerin with long chain fatty acids). A 3:1 molar ratio of alcohol to triglyceride in the presence of catalyst (KOH) is necessary for stoichiometric completion of the reaction (given below).



1.3 Classification of Biodiesel Production Technologies

Several biodiesel production methods have been developed[5-13], among which transesterification using alkali catalyst gives high level of conversion of triglycerides to their corresponding methyl ester in short reaction time. The process of transesterification is affected by the reaction condition, molar ratio of alcohol to oil, type of alcohol, type and amount of catalysts, reaction time and temperature, purity of reactants, free fatty acids and water content of oils or fats. Process optimization for biodiesel production has been studied by Tashtoush et al.[14] and Ghadge and Raheman [15]. The other studies for biodiesel production using various vegitable oils are discussed in [16-20].

Biodiesel can be produced by various methods such as: Alkali catalysis, Acid catalysis, Lipase catalysis, Hydrodynamic cavitation, Ultrasound energy, Supercritical Methanol etc. Due to the fact that the transesterification is an equilibrium reaction, an excess of alcohol is used to displace the reaction towards esters formation. Non-edible oil and alcohols are immiscible, so that their reaction takes place at the interface and it is a very slow process. The reaction is catalyzed by alkali, acid or enzyme. Enzymes-catalyzed procedures, using lipase as catalyst, do not produce side reactions, but the lipases are very expensive for industrial scale production and a three step process is required to achieve a 95% conversion. Acid catalyzed process is useful when a high amount of free fatty acids are present in the vegetable oil, but the reaction time is very long (48-96 hr), even at the boiling point of the alcohol, a high molar ratio of alcohol is needed (20:1 wt/wt to the oil). In the base-catalyzed procedure, some soap is formed and it acts as phase transfer catalyst, thus helping the mixing of the reactants. Base-catalyzed process is strongly affected by the mixing of the reactants and/or by efficient heating that produces tiny droplets, thus increasing the reaction area. Therefore, considering all these limitations, there is a strong quest to develop an efficient, time-saving and economically functional, environmental friendly biodiesel production process at industrial scale having superiority over the classical procedure.

2. Cavitation technology

The generation, subsequent growth and collapse

of cavities resulting in very high energy densities of the order of 1 to 1018 kW/m3. Cavitation can occur at millions of locations in a reactor simultaneously and generate conditions of very high temperatures and pressures locally, with the overall environment being that of ambient conditions. The chemical reactions requiring stringent conditions can be effectively carried out using cavitation at ambient conditions. Moreover, free radicals are generated in the process due to the dissociation of vapours trapped in the cavitating bubbles, which results in either intensification of the chemical reactions or in the propagation of certain unexpected reactions. Cavitation also results in the generation of local turbulence and liquid micro- circulation (acoustic streaming) in the reactor, enhancing the rates of transport processes. The two principle types of cavitations[21] and their application for transesterification process are described below.

2.1 Ultrasound Energy

Power ultrasonic is a useful tool for strengthening mass transfer of liquid- liquid heterogeneous system. In this process cavities are created by the irradiation of power ultrasonic with sufficient energy in the immiscible liquids. As a result micro fine bubbles are formed. The asymmetric collapse of the cavitation bubbles disrupt the phase boundary and impinging of the liquids create micro jets, leading to intensive emulsification of the system. The transesterification of vegetable oil with short-chain alcohols in the presence of base-catalyst, by means of low frequency ultrasound (28 and 40 kHz) in order to obtain biodiesel fuel was studied by Stavarache et al. [22-23]. By using ultrasounds the reaction time was observed much shorter (10-40 min) than as compared to mechanical stirring. The quantity of required catalyst was 2 or 3 times lower. A typical schematic representation of ultrasonic bath is shown in Fig. 1.Other significant studies for biodiesel production using ultrasound irradiation are discussed in Hanh et al. [24-26].

An alkali-catalyzed biodiesel production method with power ultrasonic (19.7 kHz) has been developed by Ji et al.[27] that allows a short reaction time and high yield because of emulsification and cavitation of the liquid-liquid immiscible system. Continuous ultrasound give a short reaction equilibrium time of 10-20 min and almost 100% yield under 6:1 substrate molar ratio. According to range of factors, substrate molar ratio was the prime factor, while temperature and pulse frequency of ultrasonic were secondary. The order of the effect on FAMEs yield of the factors was substrate molar ratio>temperature>pulse frequency>ultrasonic power. In this study, the optimal reaction conditions was at 6:1 substrate molar ratio, 45 0C, continuous ultrasonic and 150 W ultrasonic power. The schematic diagram of ultrasonic horn setup is shown in Fig. 2.

One kg dry seeds of Jatropha and Thumba produces approximately 330 and 280 gms of nonedible vegetable oil respectively. Experiments have been performed with one of the main objectives of present study to prepare biodiesel from three non-edible oils (Thumba, Jatropha and Waste Cooking Oil) by ultrasonic cavitation technique and to compare the same with conventional magnetic stirring method in terms of biodiesel production time and yield (%). Tables 1 and 2 represent the data for biodiesel production time and yield (%) using mechanical stirring and ultrasound caviation respectively for parameters such as ratio of non-edible oil to alcohol and ratio of catalyst to oil. For mechanical stirring method(For a sample size of 100 gm), time duration and yield (%) varies as 34 to 42 minutes and 79 to 90% respectively whereas for ultrasound time duration and yield (%) values are 9 to 20 minutes and 81 to 95% respectively. From the experimental results it is very clear that there is a significant reduction in time for biodiesel production and an increase in yield (%) in ultrasound technique as compared to mechanical stirring method. It can be seen from Table 2 that ultrasound cavitation can be successfully applied to transesterification reactions with more than 90% yield of the product for molar ratio 4.5:1 and minimum catalyst percentage of 0.5%. The role of catalyst

Table 1: Reaction time and yield (%) data for biodiesel production using conventional mechanical stirring method for Jatropha, Thumba and WCO.

% of catalyst	Molar ratio (alcohol/oil) 6:1						Molar ratio (alcohol/oil) 4.5:1					
	Jatropha		Thumba		Waste cooking oil		Jatropha		Thumba		Waste cooking oil	
	Time (min)	Yield (%)	Time (min)	Yield (%)	Time (min)	Yield (%)	Time (min)	Yield (%)	Time (min)	Yield (%)	Time (min)	Yield (%)
0.5%	42	86.4	38	87	38	87.1	45	88.2	42	88.7	42	89.8
0.75 %	40	80	34	84.2	36	85.8	38	84.4	39	86.3	37	87.2
1%	34	78.8	30	79.8	30	84.8	36	81.2	36	84.1	35	85.3

Table 2: Reaction time and yield (%) data for biodiesel production using ultrasound energy method for Jatropha, Thumba and WCO.

% of catalyst	Molar ratio (alcohol/oil) 6:1						Molar ratio (alcohol/oil) 4.5:1					
	Jatropha		Thumba		Waste cooking oil		Jatropha		Thumba		Waste cooking oil	
	Time (min)	Yield (%)	Time (min)	Yield (%)	Time (min)	Yield (%)	Time (min)	Yield (%)	Time (min)	Yield (%)	Time (min)	Yield (%)
0.5%	16	89.8	20	92.8	16	91.6	18	90	21	95.2	18	94.2
0.75 %	15	86.1	14	90.7	15	88.7	18	87.3	18	93.4	16	91.3
1%	12	81.2	9	90	10	84	15	83.9	15	87.7	15	87.5

Table 3: Transesterification of different vegetable oils [21]

Vegetable oil	Product	Time (in min)		Yield (%)	
		Acoustic	HC	Acoustic	HC
Soyabean oil	Soyabean oil ester	15	15	97	98
Castor oil	Castor oil ester	10	10	99	99
Peanut oil	Peanut oil ester	10	10	99	90

is very important in conventional mechanical stirring process where mixing strongly depends on surface area of catalyst. In case of ultrasound technique, localized cavitations conditions enhance the transport processes and therefore the role of surface area of catalyst is relatively reduced.

Therefore, the ultrasound energy technique appears to be a rapid and effective technique compared to the conventional approach, for preparing alkyl esters from triglycerides at laboratory scale of operation. It can be seen that using ultrasonic method reaction time is almost half as compared to the conventional method which is beneficial for industrial purpose.

2.2 Hydrodynamic cavitation

Hydrodynamic cavitation is another technology developed recently [21,27-28] which allows the generation of cavity collapse conditions similar to acoustic cavitation, thereby enabling different applications requiring different cavitational intensities, which have been successfully carried out using acoustic cavitation phenomenon but at much lower energy inputs. Hydrodynamic cavitation is a potential method for biodiesel production at industrial scale due to its easy scale-up property. The schematic diagram of the test rig developed at DTU is shown in Fig. 3. The setup consists of a closed loop circuit comprising a feed tank, centrifugal pump (2.2 kW), control valve and a coupling. The suction side of the pump is connected to the bottom of the feed tank. Discharge from the pump branches into two lines, which help in the control of inlet pressure and inlet flow rate into the main line housing and the orifice with the help of valves V1 and V2. The main line consists of a coupling to accommodate the orifice plate (single or multiple holes with different configurations). Four orifice plates with the numbers of holes 1, 3, 5 and 7 are used during experimentation. The diameter of each hole was 3 mm. The cavitating conditions are generated just after the orifice plates in the main line and hence the intensity of the cavitating conditions strongly depends on the geometry of the orifice plate. When the liquid passes through the orifice plate (single or multiple holes), the velocities at the orifice increase due to the sudden reduction in the area offered for the flow, resulting in the decrease of the pressure. If the velocities are such that their increase is sufficient to allow the local pressure to go below the medium vapour pressure under operating conditions, cavities are formed. Cavitating conditions are generated just after the orifice plates in the main line and hence the intensity of the cavitating conditions are strongly depend on the geometry of the orifice plate. At the downstream of the orifice, however, due to an increase in the area of cross-section, the velocity decreases giving rise to increasing pressure and pressure fluctuations, which control the different states of cavitation, mainly formation, growth & collapse. The feed tank is provided with a cooling jacket to control the temperature of the circulating liquid. The biodiesel yield of Thumba oil obtained for 1:4.5 molar ratio is shown in Fig. 4, for different orifice plates. It can be observed that for all the orifice plates, around 80% yield is obtained within 30 min. The yield increases with increase in the number of holes and afterwards it provided with a cooling jacket to control the temperature of the circulating liquid. The biodiesel yield of Thumba oil obtained for 1:4.5 molar ratio is shown in Fig. 4, for different orifice plates. It can be observed that for all the orifice plates, around 80% yield is obtained within 30 min. The yield increases with increase in the number of holes and afterwards it remains more or less constant for all type of orifice plates. The above observations were repeated for 1:6 molar ratio and the results obtained were similar to Fig. 4.

The transesterification reaction of vegetable oils using base catalyst and short-chain alcohols was studied by Gogate et al.[21] in the presence of hydrodynamic cavitation and compared with the results of the reaction under acoustic cavitation in terms of energy utilization. The results obtained for a variety of oils as starting materials are shown in Table 3. It can be concluded that

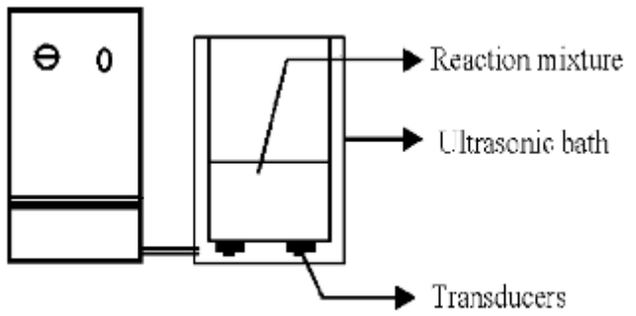


Figure 1: Schematic representation of ultrasound bath [21]

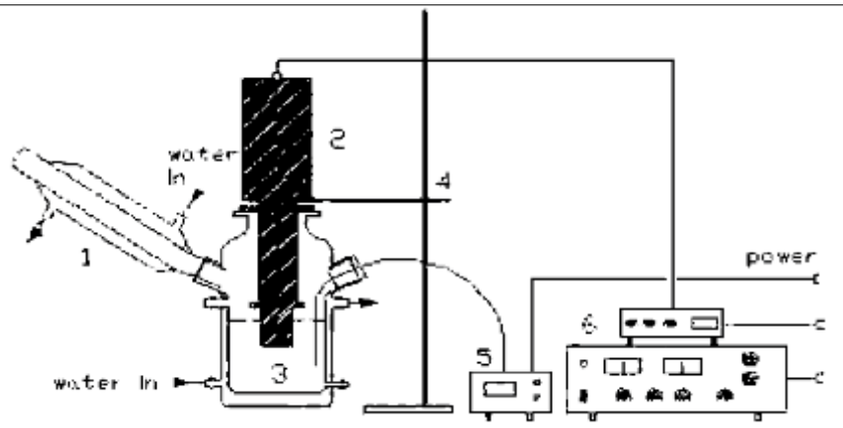


Figure 2: Schematic diagram of ultrasonic horn setup [27] [1-condenser; 2-transducer; 3-ultrasonic reactor;4-stand support;5-thermometer, 6-generator]

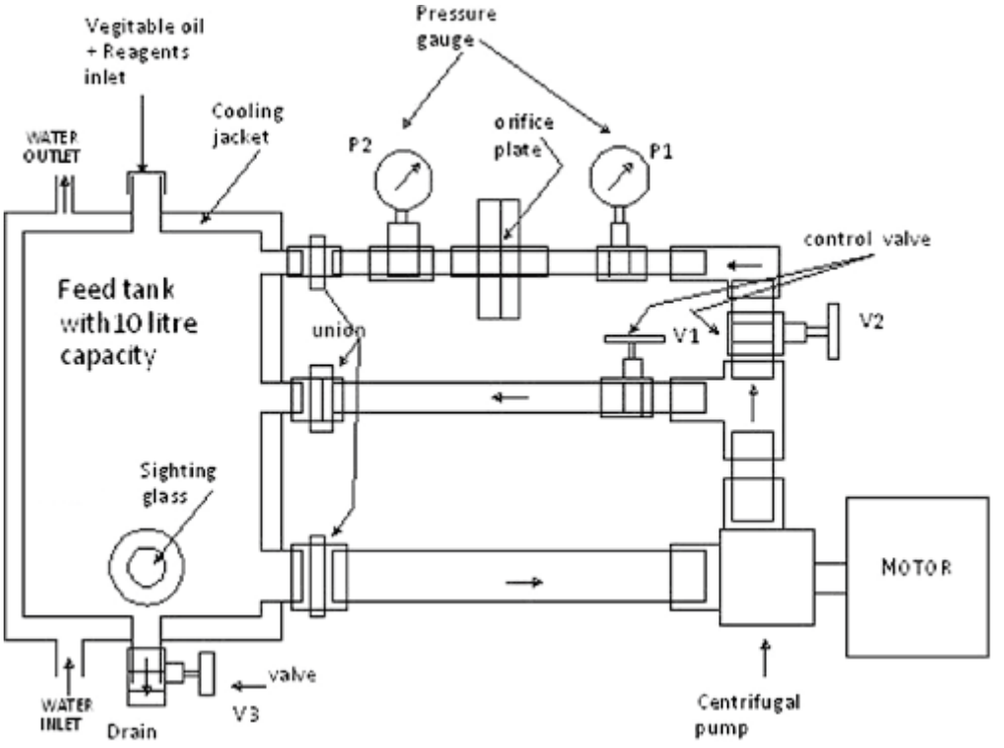


Figure 3: Schematic diagram of hydrodynamic cavitation system setup [28]

cavitation can be successfully applied to transesterification reaction with more than 90% yield of the product according to stoichiometry is as low as 15 min of the reaction time.

As reported by Ji et al. [27] that cavitating conditions identical to acoustic cavitation could be generated in hydrodynamic cavitation (HC), which even had a better effect on mixing immiscible liquids. Furthermore, scale-up of hydrodynamic cavitation to meet industrial-scale operations had better opportunities than the ultrasonic reactor due to its easier generating and less sensitivity to the geometric details of the reactor. The reaction time is shortened in the order of PU, HC and MS [where PU= Power Ultrasound, HC= Hydrodynamic Cavitation, MS= Mechanical Stirring]. Power ultrasonic gives the shortest reaction time and the highest yield. Mechanical stirring offered the slowest reaction rate. PU and the HC methods reduced the reaction equilibrium time to 10-30 min. The energy consumption (Wh/kg) for the transesterification of 1 kg of soybean oil by Ms, PU and HC are 500, 250 and 183 respectively. Thus PU and HC processes require approximately a half of the energy that is consumed by the MS method.

3. **Supercritical methanol transesterification process**

Supercritical methanol [29-32] is believed to solve the problems associated with the two-phase nature of normal methanol/oil mixtures by forming a single phase as a result of the lower value of the dielectric constant of methanol in the supercritical state. As a result the reaction is found to be complete in a very short time. SC methanol allows a simple process and high yield because of simultaneous transesterification of triglycerides and methyl esterification of fatty acids. A typical supercritical methanol transesterification system [29] is shown in Fig 5.

All the observations are performed in a cylindrical autoclave made of 316 stainless steel in which the pressure and temperature are monitored in real time covering up to 100 MPa and 850 K, respectively. In a typical run, the autoclave is charged with a given amount of vegetable oil and liquid methanol with changed molar ratios. After each run, the gas is vented, and the autoclave is poured into a collecting vessel. All the contents are removed from the autoclave by washing with methanol. Compared with the catalytic processes, purification of products is much simpler and more environmental friendly. However, the reaction requires temperatures of 350-400^{0}C and pressures of 45-65 MPa, which are not viable from industrial point of view. Furthermore, such high temperatures and pressures lead to high production costs and energy consumption. Transesterification of soybean oil in supercritical methanol has been carried out by Han et al. [8] in the absence of catalyst. A co-solvent was added to the reaction mixture in order to decrease the operating temperature, pressure and molar ratio of alcohol to vegetable oil. With CO_2 as co-solvent in the reaction system, there was a significant decrease in the severity of the conditions required for supercritical reaction. It was demonstrated that, with an optimal reaction temperature of 280 ^{0}C, methanol to oil ratio of 24 and CO_2 to methanol ratio of 0.1, a 98% yield of methyl esters viable as an industrial process. In the absence of catalyst the purification of the products after transesterification is much simpler and more environmental friendly. The relatively mild reaction conditions and high yield of methyl esters using this environment friendly method make it practical use in Industry. A system for continuous transesterification of vegetable oil using supercritical methanol was developed using a tube reactor was investigated by He et al.[9]. Increasing the proportion of methanol, a reaction pressure and reaction temperature can enhance the production yield effectively. However, side reactions of unsaturated fatty acid methyl esters (FAME) occur when the reaction temperature is over 300 ^{0}C, which lead to a very high loss of material.

4. Conclusions

Low frequency ultrasound and hydrodynamic cavitation methods are energy efficient, time saving and economically functional, offering a lot of advantages over the conventional mechanical stirring method. Supercritical methanol with a co-solvent process require relatively lower reaction temperature and pressures and hence energy, as compared to conventional supercritical methanol method. In addition because of the absence of catalyst, the purification of products after transesterification is much simpler and more environment friendly. The relatively mild reaction conditions and high yield of methyl esters using this method makes it viable for industry. All these methods have future potential for biodiesel production at industrial scale due to their easy scale up property.

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