Synthesis of biodiesel from Schizochytrium oil using renewable catalyst and study of its quaternary blend phase behaviour

C N Kowthaman¹ and Arul Mozhi Selvan V²

¹,²Department of Mechanical Engineering, National Institute of Technology, Tiruchirappalli – 620015, India.
E-mail: arulmozhi@nitt.edu

Abstract. In this present work, waste animal bone is used for the first time to synthesis nano hydroxyapatite heterogeneous catalyst. The sodium nitrate salt was doped with synthesized nano hydroxyapatite to form sodium modified nano hydroxyapatite for transesterification of biodiesel from schizochytrium algae oil. Locally collected waste bone was washed, cleaned, powdered and calcined at different temperature at 900 °C for 2 h to convert into tri-calcium phosphate and it is characterized. The synthesized heterogeneous catalyst was tested for biodiesel production. The maximum biodiesel yield of 96% was achieved at 9 wt.% catalyst concentration, 1:12 molar ratio and 2 h reaction time. The produced biodiesel was characterized to evaluate the quality for the application in diesel engines and the results exhibited that the properties are in ASTM standard limit. Blending of biodiesel, lower alcohol with diesel have been considered as the common fuel modification for reducing the pollution. In this study, the phase behaviour of the synthesized Schizochytrium biodiesel, diesel and higher alcohol (Octanol) was studied with water in oil emulsions (Quaternary blend). Octanol was used because of its high carbon number and better fuel property. The effects of different hydrophilic lipophilic balance were studied to find an optimum HLB number by varying the Span 80 and Tween 80 ratio (20 to 100%) in the quaternary blend. The optimum fuel blend was found at the HLB number of 12 (Span 20%: Tween 80%) and the quaternary blend at the HLB 12 showed no phase separation for two months.

Keywords: Biodiesel, Emulsion, Octanol, Water, Span 80, Tween 80.

1. Introduction

Biodiesel has gained more attention for many years because of its several advantages such as biodegradable, non-toxic, renewable, similar physical and chemical properties with the diesel and direct application in the diesel engine. Biodiesel does not cause socio-economic and geographical imbalances [1,2]. The production of biodiesel started from first generation feedstock’s such as soybean, coconut, peanut and corn oil. Biodiesel was also mainly produced from various sources like waste cooking oil, vegetable oil, animal fats, rubber seed, jatropha, pongamia and mahua which are termed as a second generation sources. These two generation sources affect the food security, increases the environmental

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and soil pollution. Recently, microalgae are focused by the researchers due to its several advantages such as high lipid content, more biomass production and carbon sequestration. Moreover, microalgae need not require arable land which grows anywhere like brackish, sea and fresh water [3]. The lipids from the microalgae oil can be converted into alkanes, alcohols and methyl esters for the application of internal combustion engines, aircraft gas turbines and spark ignition engine. The problem of using edible or non-edible sources can also be reduced by switching into microalgae biodiesel. In terms of engine emissions, biodiesel emits lower carbon monoxide, hydrocarbons and particulate matter, but the formation of NO\(_x\) is higher than the diesel fuel [4]. This NO\(_x\) formation is due to the availability of excess oxygen and high temperature in the combustion chamber. Excess oxygen in the biodiesel and increased ignition delay during combustion increased the peak temperature and NO\(_x\) emission. This excess emission harms the environment by contributing the acid rain and global warming. In the past five years, the world health organization (WHO) reported air pollution has increased by 8% [5]. Recently, higher alcohols have emerged as an alternative biofuel to reduce the emission in diesel engines either by neat or blended mode because they provide high calorific value and better stability [6]. Imdadul et al., 2016 reported that the increase in pentanol and butanol concentration showed higher brake thermal efficiency, brake power and reduced brake specific consumption [7]. Arkadiusz 2017 reported that the addition of methanol and ethanol of over 30% in diesel disturbs the combustion process and decrease in in-cylinder pressure [8]. However, biodiesel and octanol has a higher viscosity than conventional diesel which result to the poor engine tail pipe emissions. Many attempts have been made in order to reduce the viscosity, one of the best way is to blend with diesel fuel. Various techniques such as preheating, transesterification, dilution, micro emulsion and modifying injection strategy are adopted to resolve the high viscosity. This method not only reduce the cost of feedstock but also enhances the quality of the fuels. Micro emulsification method has been evaluated as a best method to synthesize fuel with standard properties due to low energy consumption [9,10]. Additionally, micro emulsion fuels are thermodynamically stable isotropic nature due to small size of micelle [11]. The micro emulsion between diesel and biodiesel was achieved with the addition of water by using additives such as ethanol, methanol and 1-butanol [12,13]. The emulsion is mainly comprised of two phase emulsion: oil-in-water (O/W) or water-in-oil (W/O), and three phase emulsion: water-oil-water (W/O/W) or oil-water-oil (O/W/O). In water in oil micro emulsion method the small droplets of water are surrounded with oil and micelles were stabilized by surfactant or co-surfactant. Several researchers have investigated the blending of water in diesel emulsion. But the combination of quaternary phases such as diesel-biodiesel-octanol with water emulsion has not been explored. Emulsion fuels can be prepared by blending of fuel (non-polar liquid) and water (Polar liquid) with surfactants that could reduce the surface tension of the two liquids [14]. The surfactant which is affinity to polar is called hydrophilic and the surfactant affinity to non-polar is termed as lipophilic, these both surfactants are incorporated to weaken the surface tension of the immiscible liquids. In general, hydrophilic lipophilic balance (HLB) was used to find an optimal surfactant performance in emulsion fuels. In W/O emulsion the HLB value of 3-8 were required and O/W the emulsion can be prepared with HLB of 9-12. The quantity of the surfactants varies from 0.5 to 2%, further on increasing the percentage, the stability of the emulsion fuels decreases because of the rapid coalescence [15].

In this research, the optimal HLB was found in the quaternary phase of diesel/biodiesel-ethanol-water emulsification and then the dynamic viscosity values are compared with neat diesel fuel. Various literatures have been reported that biodiesel blend of B5 has no difference in engine power and fuel economy than the neat diesel. Up to 20% of fuel blends in diesel was recommended by ASTM D7469. For this study, diesel with biodiesel B20 was considered as oil phase and blended with the ethanol and water. The main objectives of this research work is to formulate quaternary blend using diesel, biodiesel, alcohol and water. Several works on blending the diesel and biodiesel have addressed but the clear concept of chemical and physical characteristics between various blending percentages need to be listed out for the better blend qualities. Furthermore, viscosity of Schyzochytrium biodiesel and different HLB of span and tween are also studied.
2. Materials and methods

2.1. Catalyst preparation, biodiesel production and Emulsion preparation

Cow bones are collected from nearby butcher shop; it was washed twice with distilled water to remove all the fleshy portion. The bones are dried, crushed and powdered using hot air oven, crusher machine and ball mill, respectively. Then the obtained nano powder was dried and the predetermined quantity of nano powder was poured into beaker solution (3 gram of sodium nitrate and 50 ml of distilled water) and stirred vigorously for 2 hr. The solution was filtered and the resultants powder was calcinated at various temperature. In this research work, schizochytrium oil was used for biodiesel. Prior to transesterification, schizochytrium oil was pretreated using 1% of sulphuric acid under optimal molar ratio, reaction time. After pretreatment, the mixture was kept for phase separation and obtained oil was used for transesterification process under 1:12 molar ratio, 9% catalyst concentration and 120 min reaction time and achieved 96% of yield. Then, the obtained biodiesel was characterized and utilized for its stability studies. Chemicals such as Sorbitanmonoolate (Span 80), Polyethylene glycol sorbitanmonoolete (Tween 80) octanol and methanol were of analytical grade and purchased from Sigma Aldrich. Schizochytrium algae oil was procured from Navchetena Kendra, Punjab. Diesel was procured from nearby gas station. All the glasswares were purchased from Borosil and washed using hot water to remove the contaminants and oven dried for an hour before use. Distilled water was utilized for all the experiment.

2.2. Hydrophilic-lipophilic balance and Ternary phase diagrams

To measure the optimum stability of hydrophilic and lipophilic character of Span and Tween, the surfactants are numbered from 0 to 40 to indicate the behavior of hydrophilic and lipophilic balance of the molecule. The numbers are determined from structure of molecule. In this work, Span 80 as lipophilic surfactant was mixed with Tween 80 as a hydrophilic surfactant in varying HLB numbers to obtain the optimum HLB balance of the system. Fig. 4 shows the different stages of preparation of emulsified fuels. The surfactant which is affinity to polar is called hydrophilic and the surfactant affinity to non-polar is termed as lipophilic, both these surfactants are incorporated to weaken the surface tension of the immiscible liquids. In general, hydrophilic lipophilic balance (HLB) was used to find an optimal surfactant performance in emulsion fuels. In W/O emulsion the HLB value of 3-8 were required and O/W, the emulsion can be prepared with HLB of 9-12. The quantity of the surfactants varies from 0.5 to 2%. On further increasing the surfactants percentage, the stability of the emulsion fuels decreases because of the rapid coalescence [16]. Ternary phase diagram is an equilateral triangle graph representing two vertices at the bottom side, oily phase (A) and right side water (B). The third vertices bounded at the top of the triangle represent the co-surfactant (C). All the mixtures were used to investigate the miscibility and phase behavior of the emulsification system at constant temperature. The mixture of the fuels at each point in the ternary phase diagram was demonstrated by weight basis.

3. Results and discussion

3.1. Catalyst characterization and biodiesel production
From the FTIR analysis, both calcined and uncalcined nHAP were compared, the peaks at 559 and 1045 cm$^{-1}$ were evidenced the vibration of PO$_4^{3-}$ group. Uncalcined catalyst shows the carbonated peaks at 1642 cm$^{-1}$. XRD peaks also confirmed the presence of sodium on hydroxyapatite at 2 theta of 35, 40 and 44 are observed. Whereas, the peaks were not observed in the fresh samples. The synthesized catalyst was studied for its thermal behavior using Thermogravimetric analyser. The sample exposed multistage decomposition. The first stage up to 250 $^\circ$C occur due to the de-moisturization and evaporation of volatile compounds. The second stage was due to the decomposition of hydroxide compounds in the catalyst. The third stage is the controlled stage where the catalyst was subjected to high temperature forms sintering effect and subsequently weight loss was observed. The confirmation of the biodiesel can be done easily using thin layer chromatography (Fig. 2A). TLC results reported that the raw SCO exhibited several spots such as monoglycerides, diglycerides and triglycerides at the retention factor of 0, 0.25 and 0.85. However, fatty acid methyl ester showed the spots at retention point of 0.95. Hence, the result confirmed that the composition of mono, di and tri-glycerides of the oil were converted into fatty acid methyl esters. The produced biodiesel was pure and found no glycerin contaminant. The results were similar and in closeness with the work reported from fish oil and robu processing waste oil.

Fig. 1 shows the concentration of SCME with respective to the reaction time during transesterification reaction. At minimum time the concentration of biodiesel was observed low, on increasing the reaction time the concentration of the SCME increases. The maximum concentration of SCME was observed at 120 min further increase on reaction time the yield decreases. The Properties of produced biodiesel are as follows: Kinematic viscosity (mm$^2$/s) at 40 $^\circ$C-3.5, Density-835 kg/m$^3$, Acid value-0.23 mg KOH/g of oil, Flash point 138 $^\circ$C, Fire point 146 $^\circ$C, Cloud and pour point are 3.59 $^\circ$C and -1.28 $^\circ$C respectively, and calorific value of 39.8 MJ/kg.

3.2. Droplet size of emulsion fuels
The mean droplet size of the emulsions was found using the microscope software in optical electron microscope Fig. 2B.
The octanol in the emulsions was observed larger in dispersed manner, each larger circular contains tiny droplet of inner liquids are found as biodiesel. The concentrations of a tiny size particles were found higher in the lower water biodiesel emulsions. The diesel was found in the outermost continues phase in uneven distribution. The mean droplet size of dispersed phase was in the rage of 70-300 µm. Based on the optical microscope study, the dispersed phase in the emulsions was observed in the state of instability and changed with respective to time. After sometime the dispersed phase started merging into neighbor droplets to form larger droplets was due to Ostwald ripening. Hence, the droplet size cannot maintain throughout the experiments due to the flocculation and droplet-droplet coalescence.

3.3. FTIR-Emulsification characteristics of diesel-biodiesel-alcohol
An optical electron microscope was used to determine the dispersed phase of octanol, continuous phase of diesel and inner phase of biodiesel in the diesel-biodiesel-octanol blends. All the samples were observed motionless for the period of 30 days in order to check the emulsion layers. The height of each layers was measured for the stability test. The structural and functional groups of blended fuels were determined using Fourier Transform Infrared Spectroscopy FTIR (Fig. 1B), Shimadzu spectrometer with the wavelength between 400 and 4000 cm\(^{-1}\). The FTIR spectra of the emulsion fuels are shown in Fig. 1B. In functional groups, stretching, bending of chemical bonds were investigated for the prepared quaternary blends were represented below. The peaks at 2954 and 2922 cm\(^{-1}\) denoted the aliphatic compounds, the peaks at 1727 cm\(^{-1}\) showed the presence of C=O, the peak at 1169 cm\(^{-1}\) was denoted by esters and at 723 cm\(^{-1}\) represents deformation of C-H vibration peak.
3.4. Phase behavioral study of HLB and emulsion stability

The effect of hydrophilic and lipophilic balance on various emulsion fuels were investigated by mixing of Tween 80 with span 80, five different HLB ratios of the surfactants were prepared; HLB-6/Span 80/Tween 80 (100:0), HLB-12/Span 80/Tween 80 (60:40), HLB-10/Span 80/Tween 80 (50:50), HLB-8/Span 80/Tween 80 (40:60), HLB-15/Span 80/Tween 80 (0:100). By changing the ratio of Span and Tween 80 with different HLB number were prepared to emulsify with water blend and the preparation of emulsion fuels are shown in Fig. 3A-D. HLB at Lower and higher prepared samples are found high viscous as shown in Fig. 3C., this is due to the inappropriate proportion of Span and Tween 80. The test samples prepared at the HLB of 10 and 12 are seriously viewed for its stability. All prepared test samples are investigated for its stability studies at room temperature (Fig. 3D). Test samples with 5% water content exhibits higher stability than the other samples. This is due to the tiny particles present in the lower water emulsions form homogeneous mixture, whereas, the large size particles in the other test samples were found phase separation. The optimum replacement of biodiesel and alcohol in terms of stability was witnessed in D75A20W5, D80A15W5, D90A10W5 at HLB 10 are shown in Fig. 4. The samples mentioned in green colour showed good miscibility with less calorific value.

| Fuel blends     | Calorific value (kJ/kg) | Viscosity (cSt@40°C) |
|-----------------|-------------------------|----------------------|
| Diesel          | 44722                   | 1.82                 |
| Biodiesel       | 39888                   | 2.62                 |
| D75A20W5        | 42528                   | 2.38                 |
| D80A15W5        | 42650                   | 2.48                 |
| D85A10W5        | 42770                   | 2.54                 |
| D90A5W5         | 42890                   | 2.58                 |
| D95A5W0         | 43131                   | 2.60                 |

Fig. 4. Ternary phase diagram of test fuels prepared under HLB 12

4. Conclusions

In this study, Na-nHAP was successfully prepared through wet impregnation technique using sodium nitrate solution. Characterization results confirmed the presence of sodium in the catalyst material. The synthesized catalyst was found effective with 96% of biodiesel yield under 1:12 molar ratio, 9% catalyst concentration and 120 min reaction time. Quaternary blends of various levels of water concentrations were investigated. The optimum replacement of biodiesel and alcohol from this research work was found to be D75A20W5, D80A15W5, D90A10W5 at HLB 10. Thus, the increased concentrations of alcohol and water in the emulsions decreases the stability and calorific value. With these optimum quaternary blend, performance, combustion and emission studies can be performed in the direct injection diesel engine. From the stability studies, the droplet of the prepared emulsions was unstable with respective time. After sometime the tiny droplet merge with neighbour droplet to form larger and it was difficult to maintain after certain period of time.
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