Production of Biodiesel using Calcined Brine Sludge Waste from Chor-Alkali Industry as a Heterogeneous Catalyst

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Abstract – Biodiesel is an environmentally friendly fuel, produced by a transesterification process using homogeneous catalyst which causes water pollution and cannot be recycled. The present study utilizes industrial brine sludge waste (IBSW) as a heterogeneous catalyst in the transesterification of waste cooking oil (WCO) into biodiesel. One variable at a time design was applied to optimize the transesterification process. The process variables were varied as follows: methanol to oil weight ratio (10–50 %), reaction time (0.5–2.5 h), reaction temperature (30–90 °C) and catalyst to oil weight ratio (0.84–4.2 %). The IBSW before and after calcination and the transesterification process was characterized using X-ray fluorescence (XRF), Fourier-transform infrared spectroscopy and scanning electron microscope (SEM). Biodiesel was produced at maximum yield of 95.51 wt% at reaction time, temperature methanol to oil weight ratio, and catalyst to oil weight ratio of 1 hour, 60 °C, 30 wt%, and 2.52 wt% respectively. The FTIR and SEM results confirms that before and after the transesterification process the modification of IBSW took place. Using the ideal process conditions, biodiesel was produced and vital fuel properties such as viscosity, density, pour point and flash point were measured and were found to be within the specification as per American Society for Testing and Material (ASTM) standards for biodiesel. The reusability of the IBSW catalyst was tested by recycling and it can be established that the catalyst can be utilized up to four times without affecting its catalytic activity.

Keywords – Biodiesel; heterogeneous; industrial brine sludge waste; transesterification; waste cooking oil

1. INTRODUCTION

Chlor-alkali process industries produce hydrogen, chlorine and sodium hydroxides via an electrolytic process. These raw materials are used for producing detergents, soaps, pesticides, pharmaceuticals, titanium dioxide, herbicides and plastics such as polyvinyl chloride (PVC), polyurethanes and epoxy resins [1]. Separators such as a membrane or diaphragm are used to separate the products produced at the anode and cathode [2]. The brine solution produced is treated in a reactor with soda ash to precipitate magnesium hydroxide and calcium carbonate as shown in Eq. (1) and Eq. (2).

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An ionic exchange membrane cell can be poisoned by the presence of trace metals such as magnesium, calcium and manganese in the brine feedstock which affects the chlor-alkali process. Mega tones of brine sludge are produced and contains undesirable non-toxic salts in the form calcium, magnesium and sulphates which end up in landfills [3]. There is a need to develop new forms of renewable fuel, which is biodegradable and nontoxic, biodiesel is one of them [4]–[7]. This is a new renewable form of energy and can be classified as an environmental competitor of fossil fuels. Biodiesel emits less greenhouse gases, has a high cetane number, high combustion efficiency, lower aromatic and sulphur content in contrast to petroleum diesel [8]–[12].

The catalysts used in biodiesel production are classified as either heterogeneous or homogeneous which can be either basic or acidic. Homogenous catalyst which have been used include potassium hydroxide, sodium hydroxide which are classified as basic and sulphuric acid which is acidic [13]. Heterogeneous solid catalyst from egg shells, activated lime, diatomite perlite, zinc, biogenic waste, calcium hydroxide and magnesium zirconate have been used [14]–[22]. One of the most important advantages of heterogeneous catalyst is it can be reused, easy to recover and also it can be easily separated and purified. The main disadvantage of homogenous catalyst is that it cannot be recovered after the transesterification reaction which causes water pollution [23].

Brine sludge waste from chlor-alkali is regarded as a cheap heterogeneous catalyst, it can be used as a catalyst since it contains large amounts of calcium oxide and magnesium oxide which act as basic active site for a transesterification reaction.

This study investigates the feasibility of using industrial brine sludge waste as a heterogeneous catalyst. Moreover, huge quantities of the cooking oil go to waste and may pollute the water and land resources. The influence of process variables such as methanol to oil weight ratio, temperature reaction time, and catalyst to oil weight ratio on the yield of biodiesel from the transesterification reaction process using WCO were investigated. The process was optimized using one variable at a time experimental design. At ideal established process conditions, biodiesel was produced and analysis was done to establish if they are within the ASTM standard of biodiesel.

2. MATERIALS AND METHODS

2.1. Material

The brine sludge waste was obtained from a local petrochemical industry. The chemical composition as determined by XRF as follows: CaO: 89.05 wt%, MgO: 4.65 wt%, Na₂O: 1.12 wt%, K₂O: 0.82 wt%, TiO₂: 0.98 wt%, Al₂O₃: 0.62 wt%, Fe₂O₃: 0.68 wt%, MnO: 0.77 wt%, P₂O₅: 0.06 wt%, Cr₂O₃: 0.04 wt%, SO₃: 1.6 wt%, SiO₂: 0.84 wt%, Loss of ignition: 0.82 wt%. WCO was supplied by the university cafeteria. Methanol, phenolphthalein solution and isopropyl alcohol were supplied by Sigma Aldrich

2.2. Catalyst Preparation and Biodiesel Production

IBSW was washed in distilled water to extract fines and impurities before being dried in a 60 °C oven for 24 hours. An agate mortar was used to crush the solid IBSW and thereafter screened to obtain an average particle size range of 45 µm. At a period 4 hours at 900 °C, the IBSW was calcined using a laboratory muffle furnace.

In order to eliminate solid particles and water from WCO prior to the transesterification process filtration was done and the oil was heated at temperatures above 150 °C for 2 hours respectively.

Since the percent free fatty acid methyl ester content was found to be slightly below 2 %, the one-step alkali transesterification method was used.

The process variables for transesterification reaction for this study were varied as follows: methanol to oil mass ratio (10–50 %), reaction time (0.5–2.5 h), reaction temperature (30–90 °C) and catalyst to oil mass ratio (0.84–4.2 %) using a one factor at a time experimental design.

A known mass of waste cooking oil was weighed placed in a flat bottom conical flask fitted with a condenser, catalyst and methanol were weighed as well, and the mixture was left to react. A constant stirring speed of 200 rpm was used. After the transesterification reaction, the catalyst was filtered out and washed with distilled water. The mixture of biodiesel and glycerol was placed in a separating funnel for separation to take place, thereafter the biodiesel phase was separated.

2.3. Determination of Fatty Acid Methyl Esters

After the transesterification reaction process, the fatty acid methyl esters were analysed using Gas Chromatography equipped with an auto sampler and flame ionization detector. A column made of poly-siloxane of dimensions (30 x 0.3 mm x 0.53 µ) was used. The GC oven temperature was kept at 80 °C and increased at 15 °C /min to 360 °C. Helium was used as a carrier gas and 0.5 µl were injected into the GC and hexane was used as solvent. A calibration method was used to determine FAME using a given determined concentration fatty acid methyl esters (FAME). The biodiesel yield was determined using Eq. (3). An average biodiesel yield was calculated using triplicates of transesterification reactions done.

$$\text{Biodiesel yield (wt\%)} = \frac{\text{Amount of FAME (g)}}{\text{Amount of oil used (g)}} \cdot 100\% \quad (3)$$

2.4. Catalyst Characterization

FTIR analysis was to identify the functional groups present in the sample. The analysis determined using a Perkin Elmer spectrum (400FT-IR/FT-NIR) machine equipped with a universal attenuated total reflectance (ATR) accessory. There was no sample preparation required for the instrument. The samples were scanned at a range of 4000 to 650 cm⁻¹.

The morphology of modified IBSW and IBSW after the transesterification process was studied using a scanning electron microscope. A Phillips XL 30S SEM was used for analysis. This was done by scattering the samples on an adhesive carbon plate and spray coating the sample with a thin layer of gold.

2.5. Fuel Properties Determination of Biodiesel Produced

Biodiesel was obtained at ideal process conditions and it fuels properties were measured and compared to the ASTM biodiesel standard. The ASTM 1298, ASTM D445, ASTM D93 and ASTM D445 were to measure density, viscosity, flash point and pour point respectively.

3. RESULTS AND DISCUSSION

3.1. FTIR and SEM Analysis

Fig. 1. depicts the FTIR spectra of the un-calcined and calcined samples of industrial brine sludge waste and samples after first and fourth transesterification reaction at optimum conditions. The characteristic peaks depicted at 3600 , 1760 , 1430 , 121 and 712 cm^{-1} indicates the presence of calcite (CaO) [10]. This is in excellent agreement with the results obtained from the XRF. The main chemical component in brine sludge waste is calcium in the form of calcilite which is confirmed by the peaks. Low intensity peaks associated between $100\text{--}800\text{ cm}^{-1}$ could be due to the presence Na_2O K_2O and MgO . There is a slight decrease in the intensity of peaks, this shows that calcined IBSW can be reused beyond the fourth transesterification run.

Fig. 1. FTIR results: (a) raw IBSW; (b) Calcined IBSW; (c) Run 1; (d) Run.

The SEM results are depicted in Fig. 2. Fig. 2(a) shows that before transesterification the morphological structure of the IBSW is non-deformed and more regular. After transesterification the morphology was more deformed, rough and irregular as compared to the calcined IBSW as shown in Fig. 2(b). Fig. 2(c) shows an insignificant change on the morphological structure after the first transesterification reaction run. After the catalyst IBSW was used up to four times a gellish morphology was observed as shown in Fig. 2(c). This indicated that the oil and glycerol was deposited on the surface of the IBSW catalyst.

Fig. 2. SEM results for calcined IBSW (a), after 1 run (b) and after 4 runs (c).

3.2. Reaction Mechanism of Industrial Brine Sludge Waste as a Heterogeneous Catalyst

The XRF result chemical composition of IBSW shows that presence of high percentage composition of CaO provides active sites for transesterification reaction to occur. The process of transesterification is as follows: the reaction begins with the active basic sites (CaO) forming a methoxide anion when a proton is removed from methanol. The carbonyl carbon in the triglyceride molecules is attacked by the methoxide anion, consequentially leads to the formation of an alkoxycarbonyl intermediate. At the last step the alkoxycarbonyl intermediate separates to form a fatty acid methyl ester and an anion of diglyceride [24]. Fig. 3 shows the mechanism of transesterification when IBSW is used as a heterogeneous catalyst.

3.3. The Influence of Process Parameters on the Transesterification of WCO into Biodiesel Using IBSW as a Heterogeneous Catalyst

To determine the influence of temperature on the transesterification of WCO using IBSW, the temperature was varied from 30–90 °C, this is shown in Fig. 4(a). This was done by keeping the methanol to oil weight ratio, reaction time, and catalyst to oil weight ratio at constant values 30 wt%, 1.5 hr and 1.84 wt% respectively. A biodiesel yield of a maximum value 95.4 wt% was attained at a temperature of 63 °C. The biodiesel yield at 30 °C was low because the reaction between methanol and triglyceride was incomplete due to insufficient activation energy at low temperature. At temperature above 60 °C, the biodiesel yield decreased, this could be due to reduced molecular interaction between methanol and triglyceride at high temperatures caused by an increase in viscosity of the oil which causes the reaction rate to increase favouring the saponification reaction. Comparable outcomes were reported by [4], [25].

Fig. 3. Transesterification reaction mechanism of triglyceride using industrial brine sludge waste.

Fig. 4(b) depicts the influence of methanol to oil weight ratio on the conversion of WCO into biodiesel using IBSW as a heterogeneous catalyst, the methanol to oil ratio were varied from 10–50 wt%. The temperature, reaction time and catalyst to oil weight ratio were kept constant at 60 °C, 1.5 hr and 1.84 wt%, respectively. A 95.3 wt% maximum yield of biodiesel was attained at methanol to oil weight ratio of 30 wt%. At values above 30 wt%, there was a substantial reduction in the conversion of WCO into biodiesel, this is due to poor separation as more glycerides reacts, which causes an increase in the solubility and alters the separation and leads to the reverse transformation of FAME and glycerol back to triglycerides [4].

The influence of reaction time on the conversion of WCO into biodiesel using IBSW as a heterogeneous catalyst is depicted in Fig. 4(c), the reaction time were varied from 1–2.5 hr. The temperature, methanol to oil mass ratio and catalyst to oil weight ratio were retained at reaction conditions of 60 °C, 30 wt% and 1.84 wt%, respectively. The maximum biodiesel yield of value 95.6 wt%, was achieved at a time of 1 hr. At low residence time, there is less conversion of oil into biodiesel due to insufficient time for mass transfer diffusion of alcohol into the oil. At above the optimum time of 1 hour, there is a slight reduction on the conversion of WCO into biodiesel, this is due to a reversible reaction that causes the creation of soap [25].

The influence of catalyst to oil weight ratio on the conversion of WCO into biodiesel was determined by changing the catalyst to oil mass ratio from 0.84–4.2 wt% and is shown in Fig. 4(d). The reaction conditions of 60 °C, 30 wt% and 1.5 hr were held constant for

temperature, methanol to oil weight ratio, reaction time, respectively. The highest biodiesel yield was acquired at a catalyst to oil weight ratio of 2.52 wt%, with a biodiesel yield of 95.8 wt%. The conversion of oil into biodiesel is low when the catalyst to oil mass ratio is low, due to a lack of enough active sites on the catalyst for transesterification reaction to occur. There would be soap formation due to an increase in glycerine viscosity and a high catalyst to oil mass ratio and consequently a reduction in the yield of biodiesel [4].

Fig. 4. Effect of (a) temperature; (b) methanol to oil ratio; (c) reaction time; (d) catalyst on the transesterification of WCO using IBSW.

3.4. Biodiesel from WCO Fuel Properties and IBSW Catalyst Reusability

Biodiesel derived WCO was produced at the specified ideal experimental conditions specified in this study, its fuel properties were measured and compared with biodiesel ASTM

standard shown in Table 1. The viscosity of biodiesel was 4.34 mm²/s, which is within specified values depicted in Table 1. The density of 887 kg/m³ is within specification range (860–900 kg/m³) as shown in Table 1. Flash point is the lowest temperature at which the vapours of a substance burns in air when exposed to fire. WCO biodiesel flash point of value 181 °C is within the requirement in ASTM standard. A liquid's pour point is the temperature at which it loses its flow features. As illustrated in Table 1, a pour point of value 3 °C is within ASTM D6751-02 of biodiesel.

TABLE 1. FUEL PROPERTIES OF WCO BIODIESEL COMPARED TO THE ASTM STANDARD

Parameter	Biodiesel from WCO	ASTM D6751-02
Viscosity 40 °C, mm ² /s	4.34	1.9–6.00
Density at 25 °C, kg/m ³	887	860–900
Flash point, °C	181	>130
Pour point, °C	3	–15–10

As shown in Fig. 5, the heterogeneous catalyst obtained from IBSW can be used up to four times without noticeable changes in the biodiesel yield. The biodiesel was produced at optimum ideal conditions in the study and the results shows the advantage of heterogeneous catalyst over homogenous catalyst as it can prevent water pollution and can be recycled.

Fig. 5. Effect of catalyst reusability on the biodiesel yield.

4. CONCLUSION

Results showed that chloro-alkali industrial brine sludge waste can be applied as a heterogeneous catalyst to trans-esterify waste cooking oil into biodiesel. The highest yield of biodiesel yield of value 95.51 wt% was obtained at the following reaction conditions: methanol to oil ratio (30 wt%), reaction time (1 hr), reaction temperature (60 °C) and catalyst to oil mass ratio (2.52 wt%). The IBSW as a heterogeneous catalyst can be used up to four times without noticeable changes in the biodiesel yield. The FTIR and SEM results confirms that before and after the transesterification process the modification of IBSW took place. When biodiesel is produced at optimum conditions, its fuel properties are within the specification in the ASTM standard of biodiesel.

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