KINETIC STUDY OF BIODIESEL USING EGG SHELL FOR BASE TRANSESTERIFICATION REACTION

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Abstract

The accumulative oil demands have produced a renewed interest in alternative fuels of biological origin. Alternative fuels, such as biodiesel has been focused unanimously because of current energy crisis. In this study, kinetics of heterogeneous transesterification of waste cooking oil (WCO) with prepared CaO-800 from the calcination of egg shell was discovered. Firstly, the egg shells were calcined at temperature of 800°C and 900°C. Then the catalysts were characterized using Thermal Gravimetry Analysis (TGA), Fourier Transformed Infrared (FTIR), Nitrogen Adsorption Analysis, Field Emission Scanning Electron Microscope (FESEM), and X-ray Powder Diffraction (XRD). The soluble basicity and the basic strength of the prepared catalysts were determined using back titration. The results showed that calcined egg shell at 800 °C was the most suitable catalyst to use in the biodiesel producton as it had high basicity and high surface area compared to calcined egg shell at 900 °C. The product biodiesel prepared was then analyzed using Gas Chromatography- Flame Ionization Detector (GC-FID). The kinetic studies for the reaction was carried out at reaction time of 30, 60, 90, 120, 150 and 180 mins at temperature 45°C, 55°C, 65°C, 75°C and 85°C temperature respectively. The results showed that the reaction follows the zero order reaction, has the rate constant of 0.13 s^{-1} and the activation energy is 23.2 kJ/mol.

Keywords:calcined egg shell, transesterification of waste cooking oil, biodiesel, kinetic study

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INTRODUCTION

Biodiesel, long-chain fatty acid alkyl ester is one of the interesting alternative fuels which can be produced from renewable sources and provides complete combustion with less gaseous pollutant emission [1] The heterogeneous catalysts of alkaline earth metal oxides heteropolyacids and zeolites have been investigated for biodiesel production as they could be operated in continuous processes, could give high quality of products; they are reusable, environmentally and are more effective than acid catalysts and enzymes. Among these, alkaline earth metal oxides, and in particular CaO, have been shown to possess good performance of commercial significance for a wide spectrum of environmentally important reactions.

The biodiesel that were produced can be a renewable alternative to petroleum diesel and by using egg shell as catalyst we can reduce the production costs of biodiesel. Reuse of eggshell as catalyst for biodiesel production was investigated in the viewpoint of the recycle of eggshell waste, minimization of contaminants, reducing the production costs of biodiesel and making the process to produce biodiesel fully ecologically friendly.

Reaction kinetics is essential for reactor and process analysis, design, simulation and control. The previous research of the kinetic study for the transesterification of oil has been carried out for the alkali catalyzed reaction so this study will be carried out for based catalysed reaction.

EXPERIMENTAL

Materials

The chemical reagents used in this research were waste cooking oil, methanol, calcium oxide (CaO). The apparatus used are two-necked round bottom flask, measuring cylinder, hot plate stirrer, mortar and pastel, magnetic stirrer, thermometer, beaker, and retort stand.

Preparationof Egg Shell as Catalyst

The catalyst was prepared by the calcination of egg shell in electric furnace from temperature 800 °C to 900 °C. Firstly, the chicken egg shells were collected from cafeteria and washed with distilled water while the inner content of the egg shell were cleaned. The egg shells were washed again with distilled water, and dried using oven. The egg shells were crushed by using mortar and pastel until become powder and were calcined in an electric furnace from 800°C to 900 °C in 4 h.

Characterizations of Catalyst

The characterization of calcined egg shell has been carried out by using Thermogravimetric Analyzer (TGA), Fourier Transform Infrared (FTIR), X-Ray Diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM), Energy Dispersive X-Ray Spectroscopy (EDX), and N2 Adsorption)

Base Heterogeneous Transesterification and Characterization of Biodesel

A two-necked round bottom flask with a thermometer, a reflux condenser and magnetic stirrer were set up. A mixture containing of 0.1g prepared catalyst and 18.55g of purify methanol were heated 30 minutes with the temperature fixed at 65±5 °C and 20g of waste cooking oil was added into the round bottom flask. The biodiesel was distilled with temperature fixed at 65±5 °C to remove remaining impurities after cooled at room temperature. Then the mixture was centrifuged at 3000rpm for 10 minutes. The middle layer was extracted as biodiesel and was analyzed by using GC. The graphs of rate of reactions of biodiesel were plotted and the order of reaction was determined.

Characterization of biodiesel

The biodiesel that produced were characterized using Gas Chromatography - Flame Ionization Detector (GC-FID).The transesterification reaction for biodiesel production was recorded using a Hewlett Packed Gas Chromatography model 6890. The mobile phase used was helium gas and column DB-Wax with specification 0.25 μm thickness, 30 mm length and 0.20 mm internal diameter was used as stationary phase with Flame Ionization Detector (FID). Temperature conditions which applied in this research were oven temperature was set at initial value 40ºC and hold for 3 min, increase to 195ºC with the rate 25ºC/min , subsequently the temperature rise up to 205ºC with the rate 3ºC/min and finally the temperature goes to 230ºC with rate 8ºC/min. For each temperature points, 5 min holding times was selected in order to complete the separation for each temperature settings. 10 mg heptanes in hexane was prepared, and 1mL of this solution was added into 50 mg of sample. Then, 1 mL of this mixture was injected into GC.

The Kinetic Study

The kinetic study has been investigated to determine the order of reaction of the biodiesel by varied the temperature and time. The temperature and time were varied during the reflux process. The temperatures selected were at 45°C, 55°C, 65°C, 75 °C and 85°C while the time taken were 30 min, 60 min, 90 min, 120 min and 150 min.The graphs of rate of reactions of biodiesel were plotted using the percentage of conversion from the GC-FID results and the order of reaction was determined.

RESULTS AND DISCUSSION

In this study, biodiesel has successfully synthesized using the prepared calcined egg shell as catalyst and the order of reaction will be identified

Characterization of Catalyst

The characterization of calcined egg shell has been carried out by using Thermogravimetric Analyzer (TGA), Fourier Transform Infrared (FTIR), X-Ray Diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM), Energy Dispersive X-Ray Spectroscopy (EDX), and N2 Adsorption

Thermal Gravimetry Analysis (TGA)

Figure 3.1 and 3.2 show the thermogram of egg shell and the Percentage of weight lost with different temperature regions. A few minor increasing of percentage of weight loss at temperature range of 0 to 250 °C was due to the removal of adsorbed water at the surface of egg shell sample. The major weight loss occurred at temperature range of 500 to 750°C with value of 10.2% was due to the removal of organic from the egg shell sample. Other related report indicated that the suitable temperature for the transformation of egg shell was in the range of 800 to 1000 °C .Therefore, in this study, it is expected that the complete transformation of egg shell occurs at temperature above 750 °C.

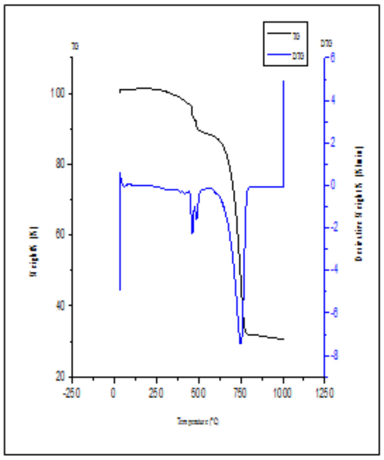

Figure 31: Thermogram of Egg Shell

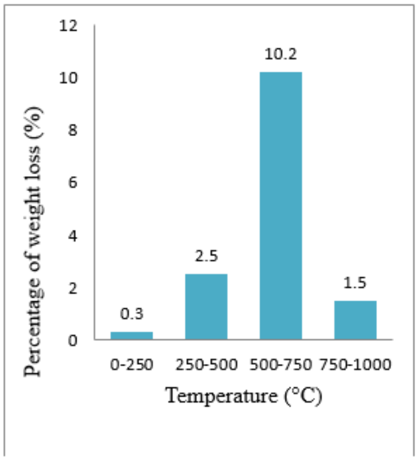

Figure 3.2: Percentage of weight lost with different temperature regions

Fourier Transform Infrared (FTIR)

Figure 3.3 and Table 1 show FTIR spectra of prepared a) CaO-800 and b) CaO-900 and summarization of peak assignment for (a) Ca-800 and (b) CaO-900. The egg shell starts to lose carbonate and produce CaO and carbon dioxide gas during calcination. The intensities of the peaks decrease related to CO_3^{2-} molecules (613 cm^{-1}, 950 cm^{-1} and 1500 cm^{-1}) was observed expect for CaO-800. This phenomenon occurred due to the reduction of the reduced mass of related functional group of CO_3^{2-} molecules. For CaO-800, the intense peaks appear at the wavelength of 950 cm^{-1} and 1500 cm^{-1} (C–O vibration) indicates that the majority compound present in the sample is $CaCO_3$ which may due to incomplete removal of CO_3^{2-} molecules. For CaO-900, the weak peaks for vibration modes of mono and bidentate carbonate shows that the sample contains impurities $CaCO_3$ with the reason of incomplete transformation. On the other hand, CaO-900 may contain higher purity of CaO due to less intense peaks for C–O vibration than CaO-800.

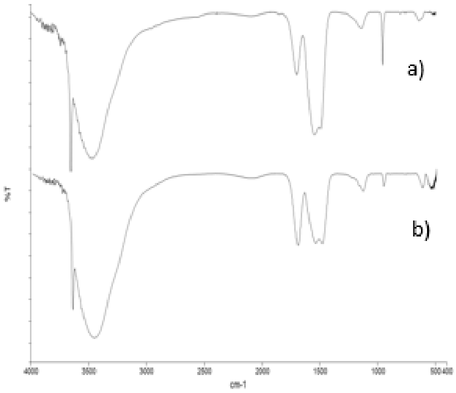

Figure 3.3: FTIR spectra of prepared a)CaO-800 and b) CaO-900

Wavelength (cm^{-1})	Peak Assignment
3640	O-H stretching vibration
3500	O-H stretching vibration
1650	O-H bending vibration
950 and 1500	C-O vibration modes
613	Lattice vibration $CaCO_3$
550	Ca-O symmetric vibration

Table1: Summarization of peak assignment for (a) Ca-800 and (b) CaO-900

X-Ray Diffraction (XRD) Analysis

Figure 3.4 shows that for CaO-900, diffraction reflections characteristics of calcite calcium carbonate, $CaCO_3$ was observed at 2θ= 32.25˚ while the peaks appear at 37.41˚, 53.91˚, 67.43˚ which displays diffraction reflections characteristics of portlandite calcium hydroxide, $Ca(OH)_2$. The prepared catalyst calcined at 800 °C, contains $CaCO_3$ as major component and $Ca(OH)_2$ as minor component since the intensities of the peak of $CaCO_3$ at 32.21˚ is higher than the intensities of the peak of $Ca(OH)_2$ at 28.62˚. In contrast, the major component of prepared catalyst calcined at 800 °C, CaO-800 was $Ca(OH)_2$ while the minor component was $CaCO_3$.

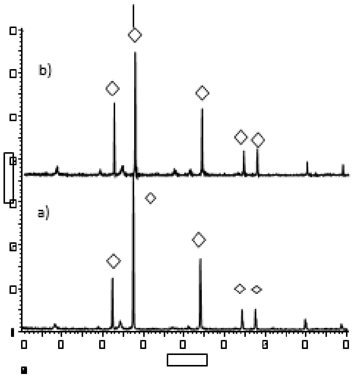

Figure 3.4: XRD Spectra of prepared a)CaO-800 and b)CaO-900

Nitrogen Gas Adsorption

As shown in Figure 3.5, an increase in specific BET surface area after calcination of egg shell (formation of CaO 800 and CaO-900) were observed where the BET surface area of CaO-800 was found to be 15.67 m2/g while the BET surface area of CaO-900 was found to be 14.96 m2/g. This phenomenon may cause the appearance of defect sites on the surface of CaO-900 due to the decomposition of egg shell to CaO at the temperature of 900 °C. This surface defects lead to an increase in catalytic activity of the reaction as the surface area of catalyst had been increased.

As CaO-800 with highest basicity and higher BET surface area had the most probably to exhibit higher catalytic activity for transesterification of waste cooking oil oil to produce biodiesel compared with CaO-900. This assumption is supported by basicity study and FESEM micrograph of the catalyst.

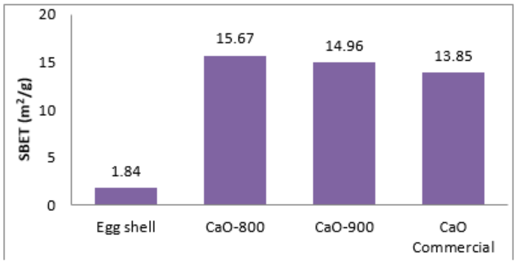

Figure 3.5: The specific SBET surface area of egg shell, CaO-800, CaO-900 and CaO commercial

Field Emission Scanning Electron Microscopy (FESEM)

Figure 3.7 and 3.8 demonstrate the surface morphology of CaO-800 and CaO-900 with magnification of 2.5 kX. From this study, CaO-800 comprises irregular shape of particles with various sizes due to the agglomeration of particles with each other. The surface of CaO-900 was not smooth. In addition, some wave-like surface and cracks on the surface which were not found over commercial CaO could possibly improve the surface area of CaO-900

Energy Dispersive X-Ray Spectroscopy (EDX)

From Figure 3.9, the prepared CaO-800 consists of major element which is calcium 72.67 % and oxygen which are 24.98 % respectively and some impurity elements were found such as Mg and C maybe because carbon element had not completely removed from the sample by emission of carbon dioxide gas during calcination process while in figure 3.10 the prepared CaO-900 consists of major element which is calcium 54.74 % and oxygen which are 40.52 % respectively The percentage of major element, calcium in CaO-900 is less compared to percentage of calcium in CaO-800 that was 72.67 %. That was the reason why CaO-800 was chosen as the catalyst in the transesterification of waste cooking oil.

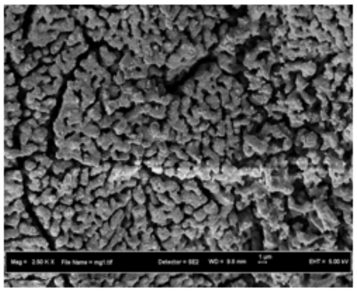

Figure 3.7: FESEM micrograph of CaO-800 with magnification of 2.5 kX

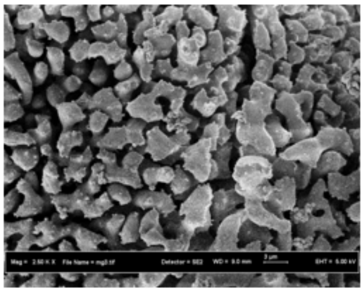

Figure 3.8: FESEM micrograph of CaO-900 with magnification of 2.5 kX

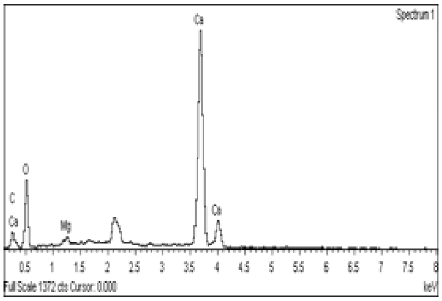

Figure 3.9: EDX Spectrum of CaO-800

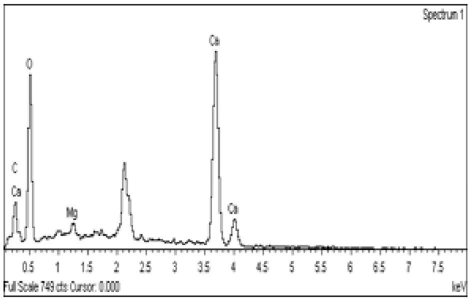

Figure 3.10: EDX Spectrum of CaO-900

Characterization of Biodiesel

The biodiesel, which is fatty acid methyl esters (FAMEs), was analyzed by GC-FID in order to investigate the percentage conversion. Figure 3.11 shows an increase trend in percentage conversion of biodiesel as the reaction time increased. For 30, 60, 90, 120 and 150 minutes of reaction time, the percentage conversion of biodiesel were 67%, 75%, 78%, 82% and 83% respectively. It can be observed that as the reaction time increased, the percentage conversion or biodiesel yield also increased. It showed that the reaction time affect the yield of FAME while Figure 3.12 shows the increasing of percentage conversion of biodiesel when the temperature were increased. For temperature 45°C, 55°C, 65°C, 75 °C and 85°C, the percentage conversion were 36%, 47%, 81%, 83% and 85% correspondingly. When the reaction was carried out at 65°C, which is above the boiling point of methanol, the solvent vaporized and remained in the vapor phase in the reactor causing a reduction in the methanol in the reaction media.

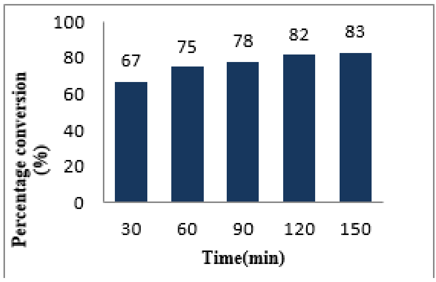

Figure 3.11: Percentage conversion of palm oil to biodiesel vs reaction time

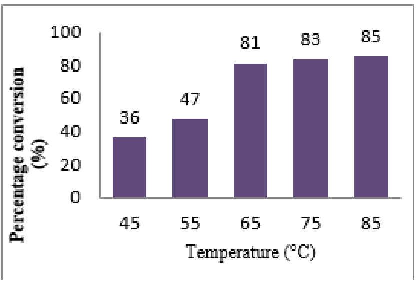

Figure 3.12: Percentage conversion of palm oil to biodiesel vs reaction temperature

The Rate of Reaction

Figure 3.13 shows the three graph of rate of reaction of (a) zero order (b) first order and (c) second order. R^2 obtained were 0.9163, 0.8946 and 0.7206 respectively. The R^2 of zero order was chosen as it was the highest R^2 and the rate constant was 0.13. The zero order signpost that rate of reaction apparently independent of the reactant concentration. The graph of ln K vs 1/T in Figure 3.14 below was plotted to determine the value of activation energy, Ea.

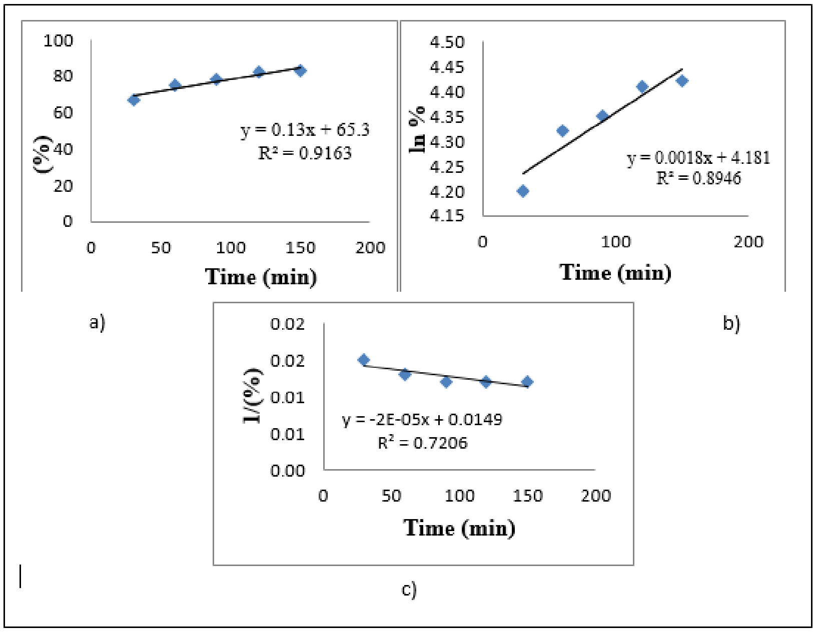

Figure 3.13: The rate of reaction of (a) Zero order (b) First order and (c) Second order

In Figure 3.14: Arrhenius plot for the calculated rate constants at thetemperature of 45°C, 55°C, 65°C, 75 °C and 85°C are presented. The slope define activation energy as a function of the reaction progress. The activation energy obtained was 23.2 kJ/mol. The activation energy which fall below the range of activation energy (26-82 kJ/mol) for heterogeneous transesterification reaction indicates that the reaction is not kinetic controlled

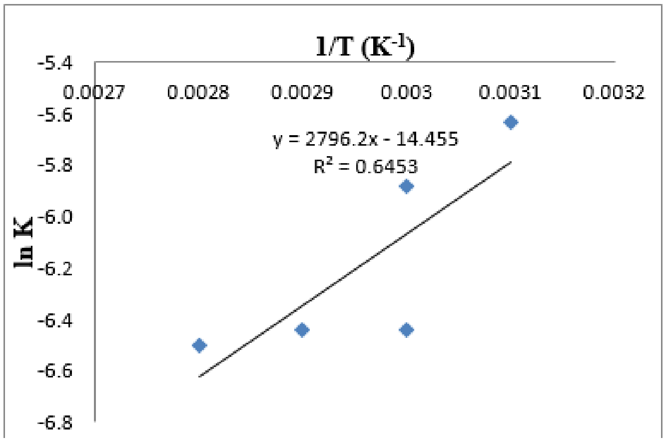

Figure 3.14 : Arrhenius law graph of zero order

CONCLUSION

In this study, calcium oxide that has been successfully prepared from the calcination process of egg shell at 800°C used to synthesize biodiesel. The kinetic reaction of transesterification reaction has been studied and the order of reaction has identified. The kinetic data used to optimize the process of biodiesel synthesis. From the high reaction rate obtained, the process proceeds via zero order and the activation energy obtained was 23.2 kJ/mol.

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