Adsorption of FFA, Soap and Glycerine in Biodiesel Using Magnesium Silicate

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The effect of SiO_2/MgO molar ratios of magnesium silicate on adsorption of free fatty acid (FFA), soap and glycerine in biodiesel was studied. The magnesium silicate adsorbent was prepared by the precipitation of magnesium sulfate and sodium metasilicate. The molar ratios of SiO_2/MgO in synthetic magnesium silicate,i.e.,0.31:1, 0.76:1 and 2.04:1 were obtained by varying concentrations of $Na_2SiO_3:MgSO_4$. The element analysis, crystal structures and surface area and pore size of the adsorbents were characterized by X-ray fluorescence method (XRF), X-ray diffraction method (XRD) and Brunauer-Emmett-Teller technique (BET), respectively. FTIR technique was used to confirm the chemical characteristics of the adsorbents. The adsorption efficiency of synthesized magnesium silicate in biodiesel containing different amount of SiO_2 / MgO molar ratios was studied by varying dosage amount of adsorbents (1, 2 and 3 g) for 150 g of biodiesel at 60°C for 5 hours. The results showed that the magnesium silicate at 2.04:1 SiO_2/MgO molar ratio and 3 g of adsorbent showed the highest efficiency in adsorption of FFA, soap and glycerine at 77.39%, 77.11% and 82.92%, respectively. While the adsorption capacity was 52.57 mg/g of FFA adsorption, 1.37 mg/g of soap adsorption and 155.06 mg/g of glycerine adsorption. The 2.04:1 molar ratio of SiO_2/MgO in magnesium silicate had the biggest pore size, 105 A°, that was proportional to the contaminates adsorbed. Noticeably, the structure size of concerned contaminates were large, so the pore size of adsorbents could play a significant role on adsorptivity of adsorbate.

1. Introduction

Nowadays, the demand of energy and environmental concerns about air pollution from gas cars are steadily increasing. Biodiesel is an alternative and renewable fuel (Ceclan et al, 2012). It presents outstanding characteristics as non-toxicity, absence of sulphur, high energy content and biodegradability. Transesterification is a chemical reaction relating triglycerides and alcohol using homogeneous or heterogeneous substances as catalyst to yield alkyl esters (biodiesel) and glycerol as by-product. The methyl ester has contaminants frequently that have effects on the quality of biodiesel. Glycerol is a potential cause of biodiesel instability. During transesterification, reaction conditions could result in the formation of oxidizes byproducts that cause discoloration, especially when glycerol is exposed to either high temperature or alkaline pH. Glycerol can oxidize or thermally degrade to form diols or acids that can contribute to biodiesel instability. (Sangita and Pradeep, 2010).The water content in biodiesel causes corrosion of the automobile system (such as fuel tubes and injector) or might react with glycerides to form soap and glycerine as by-products (Predojevic, 2008). In addition, soap and free fatty acids cause the deterioration of engine components. Therefore, the amount of water and free fatty acids affect the quality of biodiesel. Conventionally wet washing is the most employed technique to remove contaminants such as soap, catalyst, glycerine and residual alcohol from biodiesel. However, the major disadvantages in the use of water to purify biodiesel are emulsion formation (preventing the separation of the esters), formation of free fatty acids and soap, wastewater formation; which all increase in cost and production time (Ignat and Kiss, 2012). Adsorption technique was introduced to substitute wet washing to remove biodiesel contaminants. The use of adsorbents turns the process more rapid and there is not a formation of aqueous residues. The adsorbent such as magnesium

silicate has the potential of selectively adsorbing hydrophilic materials such as glycerine, mono- and diglycerides. Magnesium silicate surface consists of partially hydrophobic and partially hydrophilic sites. The hydrophobic part includes siloxane ($\equiv$Si$-$O$-$Si$\equiv$) groups and the hydrophilic portion contains isolated hydroxy groups ($-$Mg$-$OH), individual silanol groups ($\equiv$Si$-$OH) and hydrogen bonds formed due to close vicinity of hydroxy groups linked to neighboring silicon atoms. In this paper, the adsorption of free fatty acid, soap, and total glycerine in biodiesel was studied by using magnesium silicate as an adsorbent

2. Experimental

2.1 Synthesis of magnesium silicate
Three different concentration ratios of sodium silicate and magnesium sulphate (VI) were chosen for magnesium silicate synthesis. The concentration (Molar) ratios of Na_2SiO_4: $MgSO_4$ were 0.5:0.5, 0.5:1.5 and 3.0: 0.5. The sodium silicate was dropped into the magnesium sulphate (VI) solution with stirring speed of 200 rpm at room temperature. Centrifugation at 2000 rpm was used to separate the precipitate and the liquid phase was removed by filtration. The precipitate was dried at 100°C for 24 h, then mashed and sieved.

2.2 Characterization of magnesium silicate
Chemical characterization of representative sample was undertaken by X-ray fluorescence spectrophotometer (XRFs) for major element detection. Analysis by X-ray diffractometer (XRD) revealed major crystalline phases in magnesium silicate samples. Structural characterization of the sample was investigated by Fourier transform infrared spectrometer (FT-IR). In order to determine magnesium silicate adsorptive potentials, their BET specific surface area and pore diameter were estimated using multipoint BET surface area, and meso pore volumes was determined by using BJH equation.

2.3 Adsorption capacity of synthetic magnesium silicate
1, 2 or 3 grams of adsorbent was added into 150 g of biodiesel (palm oil) to study the contaminates adsorption. The shaker machine (ZHWY-100B, ZHICHENG) was set at 60°C, 200 rpm and 2 h. After shaking, the adsorbent was removed and purified biodiesel was analysed for the contaminations. In order to determine the effectiveness of purification, the soap, free fatty acid, and total glycerine contents were measured before and after processing. The amount of remaining free fatty acid was determined by acid value titration according to AOCS Official Methods Cd 3a-63. Soap level was determined using AOCS Method Cc 17-79. The amount of total glycerine was determined according to EN14105. Adsorption efficiency was defined as percentage of fraction between adsorbed and initial contaminate.

3. Results and discussion

3.1 Adsorption synthesis and characterization
The synthesized magnesium silicate was a fine white powder. The chemical composition of the synthesized magnesium silicates was analysed by X-ray fluorescence (XRF). Table 1 exhibited the chemical compositions of magnesium silicate which were synthesized by varying Na_2SiO_4: $MgSO_4$ concentration ratios. The molar ratio of SiO_2: MgO in synthetic magnesium silicate was 0.36:1, 0.76:1 and 2.04:1 according to the Na_2SiO_4: $MgSO_4$ concentration ratio of 0.5:1.5, 0.5:0.5 and 3.0:0.5, respectively. Na_2SiO_4: $MgSO_4$ concentration ratio of 3.0:0.5 exhibited highest molar ratio of SiO_2: MgO, while the concentration ratio of 0.5:1.5 showed lowest molar ratio of SiO_2: MgO. Thus, the molar ratio of synthetic magnesium silicate was in agreement with the used concentration ratio.

Table 1: Chemical compositions of magnesium silicate by various Na_2SiO_4: $MgSO_4$ concentration ratios

Concentration(Molar) ratios Na_2SiO_4: $MgSO_4$	SiO_2 (wt%)	MgO (wt%)	Other (wt%)	Molar ratio of SiO_2: MgO
0.5:1.5	26.34	72.31	1.35	0.36:1
0.5:0.5	43.18	56.81	0.01	0.76:1
3.0:0.5	52.88	25.85	21.27	2.04:1

The average surface area, pore volume and pore size of magnesium silicate were characterized by BET method. The result is showed in the Table 2. The magnesium silicate has surface area between 15 58 m²/g and average pore size is between 50-105 A° which could described that synthesized magnesium silicate was mesoporous. Higher SiO_2: MgO molar ratio provided larger pore size. From the results, the 2.04:1 molar ratio of SiO_2: MgO has the biggest pore size diameter, 105 A°.

Table 2: Chemical compositions of magnesium silicate by various Na$_2$SiO$_4$: MgSO$_4$ concentration ratios

Molar ratio of SiO$_2$: MgO	Surface area (m^2/g)	Pore volume (cm^3/g)	Pore size diameter (A$^\circ$)
0.36:1	15.1	0.0192	50.9
0.76:1	67.2	0.1098	65.3
2.04:1	57.8	0.1516	105.0

Crystalline structure of magnesium silicate was characterized by X-ray diffraction technique. XRD patterns of magnesium silicate were demonstrated in Figure 1. The structure of the synthesized magnesium silicate was amorphous as there were no sharp peaks appearing at any 2θ. The XRD patterns of the samples were in an agreement with commercial magnesium silicate (Clowutimon et al., 2011).
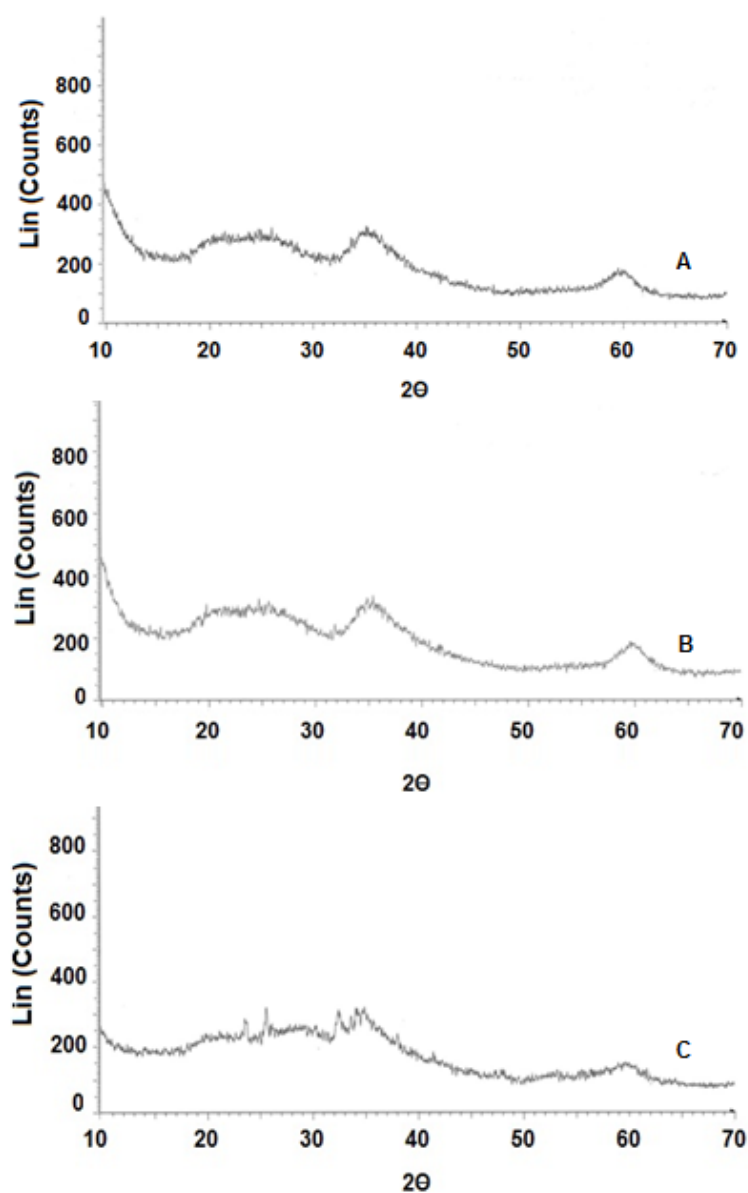

Figure 1: The XRD pattern of magnesium silicate with molar ratio of SiO$_2$: MgO at (A) 0.36:1, (B) 0.76:1, (C) 2.04:1

The FT-IR spectra of magnesium silicate with different molar ratio of SiO_2:MgO are shown in Figure 2. Normally, the strong band between 1,100 - 900 cm^{-1} represented the characteristics of siloxane (Si-O-Si) groups (Battisha et al., 2007) and the band around 600 cm^{-1} due to Si-O-Si bending vibration (Mostafa et al., 2009).The synthesized adsorbent showed strongest absorption band at 1,025, 987 and 968 cm^{-1} according to Si-O-Si asymmetric stretching. At the right hand side of this band, there is a small shoulder, assigned to the Si-O stretching (Silva et al., 2011). The broad band between 3,800-3050 cm^{-1} assigned to the O-H stretching (Karbowiak et al., 2010) did not appeared in the adsorbent. The bending vibration band of molecular H_2O appears at 1,632 cm^{-1} (Mostafa et al., 2009). The band at 1,400 cm^{-1} was related to the presence of Si-O-Na and Mg-O-Na (Narasimharao et al., 2014). The band at 400 - 450 cm^{-1} is attributed to Mg-O stretching vibration (Brew and Glasser, 2005). It was found that all magnesium silicate have a similar chemical nature. Nevertheless, only for magnesium silicate at 2.04:1 SiO_2/MgO molar ratio was a peak detected at 1432 cm^{-1} that represent Si-O-Na and Mg-O-Na bonding.

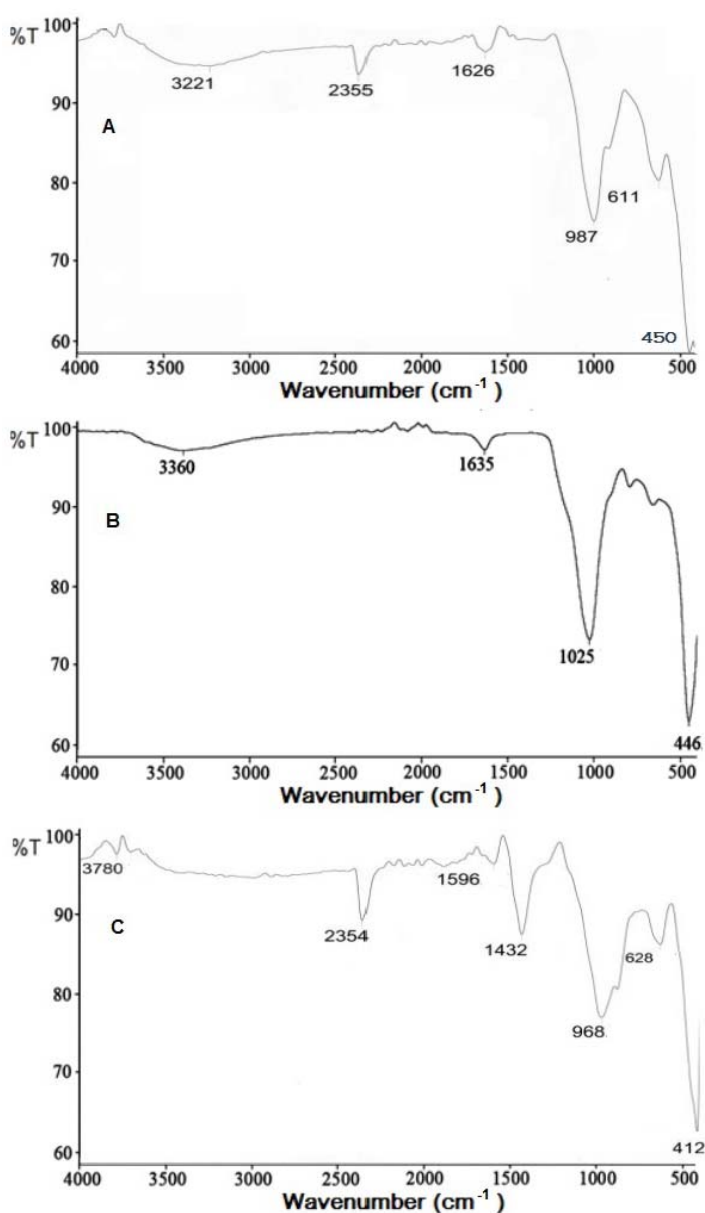Figure 2: FT-IR spectra of magnesium silicate with the molar ratio of SiO_2: MgO at (A) 0.36:1, (B) 0.76:1, (C) 2.04:1

3.2 Adsorbent Efficiency

Adsorption of free fatty acid, soap and total glycerine in biodiesel by synthesized magnesium silicate, which different molar ratio of SiO2/MgO were investigated and shown in Figure 3.
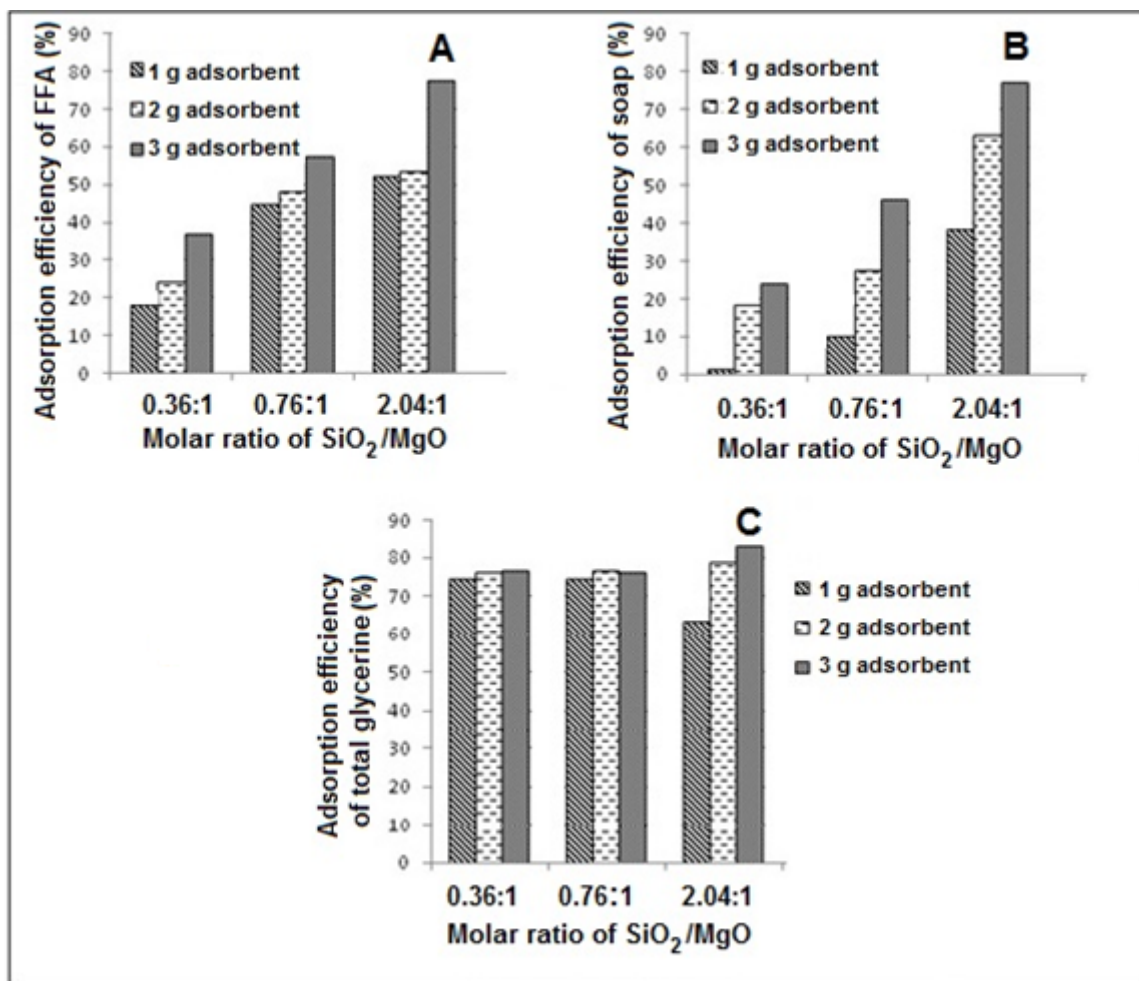

Figure 3: Comparison of adsorption efficiency of contaminates from different molecular ratios of SiO2/MgO; (A) free fatty acid, (B) soap, and (C) total glycerine

From the results, dosage amount of adsorbent had direct variation with efficiency of contaminates adsorption and trends of free fatty acid, soap and total glycerine adsorption. Magnesium silicate at 2.04:1 SiO2/MgO molar ratio and 3 g of adsorbent showed the highest efficiency in adsorption of FFA, soap and glycerine at 77.39 %, 77.11 % and 82.92 %. In addition the adsorption capacity was 52.57 mg/g of FFA adsorption, 1.37 mg/g of soap adsorption and 155.06 mg/g of glycerine adsorption. Magnesol, a commercial adsorbent for biodiesel purification, was reported to adsorb FFA 90 mg/g of adsorbent and soap 0.75 mg/g of adsorbent (Jintanavasan and Assawasaengrat, 2012). On the other hand the trends of magnesium silicate, 0.36:1 molecular ratio of SiO2/MgO, present low adsorbed efficiency of free fatty acid and soap (Figure 3A, 3B). This is because 2.04:1 molecular ratios of SiO2/MgO of magnesium silicate had high silica content than other concentration ratios of magnesium silicate which related to XRF result. It means that silica content in magnesium silicate effect on efficiency of free fatty acid and soap adsorption. However, the adsorption of glycerine was not affected by different molar ratios of SiO2/MgO as shown in Figure 3C. Physically, BET results presented the largest pore size, 105 A°, at 2.04:1 SiO2/MgO molecular ratio of magnesium silicate which influenced the adsorption efficiency. Free fatty acid and soap have larger molecular size than glycerine (Oleic acid and glycerine molecular size were estimated to be 28 A° (Eva et al., 2008) and 3.6 A° (Chen, 2013), respectively. Therefore, larger pore size can enhance diffusion of large molecules into the adsorbents.

4. Conclusions

The magnesium silicate adsorbent was prepared by the precipitation of magnesium sulphate and sodium metasilicate. The molar ratios of SiO_2/MgO in synthetic magnesium silicate (0.31:1, 0.76:1 and 2.04:1) were obtained by varying concentrations of $Na_2SiO_3:MgSO_4$. The adsorption efficiency of synthesized magnesium silicate in biodiesel containing different amount of SiO_2/MgO molar ratios was studied by varying dosage amount of adsorbents (1, 2 and 3 g) for 150 g of biodiesel at 60°C for 5 h. The magnesium silicate at 2.04:1 SiO_2/MgO molar ratio and 3 g of adsorbent showed the highest efficiency in adsorption of FFA, soap and glycerine at 77.39 %, 77.11 % and 82.92 %. The adsorption capacity was 52.57 mg/g of FFA adsorption, 1.37 mg/g of soap adsorption and 155.06 mg/g of glycerine adsorption. The adsorption efficiency of free fatty acid and soap was increased when silica content in magnesium silicate increased. However, the adsorption of glycerine was not affected by different molar ratios of SiO_2/MgO. BET results presented the largest pore size at 2.04:1 SiO_2/MgO molecular ratio of magnesium silicate which influenced the adsorption efficiency. Free fatty acid and soap have larger molecular size than glycerine. Therefore, larger pore size can enhance diffusion of large molecules into the adsorbents.

Acknowledgements

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