



TRANSESTERIFICATION OF WASTE FRYING OIL (WFO) OVER DOLOMITE AS CATALYST

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ABSTRACT

Human dependency to fossil fuels are currently facing a depletion threat as the number of oil reserves are clenching and this matter can be solved by interchanging the usage of diesel to biodiesel. The production of biodiesel can be achieved by the transesterification process. In this study, transesterification of waste frying oil (WFO) which catalyzed by dolomite have been investigated. The characteristic of the catalyst were tested using XRD (X-Ray Diffractometer) and SEM (Scanning Electron Microscope) to confirm the mineral presents and the morphology of raw dolomite and calcined dolomite respectively. Transesterification process was perform to see the influence of alcohol: oil molar ratio, weight percentage of catalyst, reaction time and reaction temperature towards product yield. From the characterization, calcination of dolomites results in the formation of the MgO-CaO form, which is the active catalytic component and led to the changing of its morphological properties. The transesterification of WFO with methanol can be actively catalyzed over dolomite catalysts with amount of 1.5wt.% at reaction temperature of 60°C, methanol/oil molar ratio, 6:1 and reaction time of 120min. With this reaction conditions, it can produce highest FAME up to 96.7 wt.%.

Keywords: biodiesel, dolomite, transesterification, heterogeneous catalyst, waste frying oil.

INTRODUCTION

Depletion of oil reserves all around the world inducing to the wavering of the stock exchange and affecting proportionally the world economy (Wu *et al.*, 2013). Deployment of biomass in the finding of alternative fuel is a relevant yet economical ideas. Resulting by the increased attention of the limited run of petroleum supply and much greener emission of combustible fuel the focus has been given to biodiesel (Dias *et al.*, 2008). Biodiesel is categorized into an ecological and environmental-friendly fuel due to its reliable qualitative composition (Tomasevic and Siler-Marinkovic., 2003). The biodiesel is renewable and can be produced through transesterification by using either vegetable oil or animal fats with methanol and the addition of either homogenous or heterogenous catalyst (Ilgen, 2012). Acquiring biodiesel in a conventional way is by performing transesterification of triglycerides in vegetable oils and animal fats with the bearing of short mono-alkyl alcohols either methanol or ethanol and assisted by homogenous base or acid catalysts. Unfortunately, the usage of homogenous catalysis system in transesterification reaction have many retreats. Homogenous catalyst causing complicated procedure in purifying the biodiesel at the end of the reaction. Dolomite is found most abundant in Malaysia and there are part of it found in a vast amount in the state of Perlis, Malaysia. The exuberant quantity available in the state makes it cheaper in costs. There are so many excavation sites that extracting the mineral intended for variety form of industries usage.

In this study, transesterification of waste frying oil (WFO) with dolomite as catalyst were studied. The effect of reaction condition such as alcohol:oil molar ratio, weight percentage of catalyst, reaction time and reaction temperature towards product yield were investigated.

METHODOLOGY

Sample preparation and Dolomite characterization

WFO were collected from a regular food restaurant in Perlis, Malaysia. The WFO are stored at room temperature at all time before the pretreatment process. The dolomite stone were collected from Northern Dolomite Sdn. Bhd. in Chuping, Perlis. The dolomite stone were calcined in a furnace at 800°C for 2 hours purposely to increase the poring sizes and surface area of the catalyst. In order to inspect the formation of pores, the catalyst was observed with SEM (JSM-6490LV, Jeol) Scanning Electron Microscope (SEM) and Shimadzu XRD-6000 X-Ray Diffractometer (XRD) instrument to determine the crystalline structure of the mineral.

Transesterification process

The reaction was carried out in a 500 mL three-neck round bottom flask equips with a condenser and a thermometer. The preparation of a magnetic stirring and a water bath on a hot plate are for the purpose of stirring the mixture and controlling the reaction temperature



respectively. Transesterification was conducted by initially filling the flask with 50 g of WFO and heated up to 25°C. For this experiment, the temperature was varied at 25-80°C for the study of reaction temperature affecting the yield of biodiesel.

The amount of dolomite catalyst in this experiment was set between 0.5- 2% wt and let suspended in a required volume of methanol. The molar ratio of methanol to oil is 1:1-8:1 for the study of variation in molar ratio affecting the yield of product. For the factor of reaction time, this experiment required the variation of time range at 60- 180 min.

Purification of biodiesel

The Fatty acid methyl esters (FAME) was poured into a filter funnel in order to separate the solid catalyst. After filtration steps, the FAME was again poured into a separating funnel and left settling for exactly 1 hour. The description notified that once the settling has been done the formation of lower layer inside the funnel is known as the glycerol phase whereas the upper layer is known as the FAME phase.

The FAME was washed with 50% (V/V) of hot distilled water and followed by 50% (V/V) of 0.5% hydrochloric acid (HCl) for the purpose of neutralizing the remaining catalyst besides decomposing the probable formation of soaps during the transesterification reaction before it was washed again with 50% (V/V) of hot distilled water to eliminate impurities. The drying of the FAME was executed by placing the product in an oven at 50°C (Farooq *et al.*, 2013).

Yield of biodiesel

The components of the biodiesel sample was analyzed by using GC-2010 Shimadzu gas chromatography (GC) which is equipped with Flame Ionization Detector (FID) and SGE 30 m x 0.32 mm ID BPX70 x 0.25 μ m of capillary column. The GC was programmed to analyzed the sample at the 1.5 μ L injection volume by auto injector, 245°C of injection and detector temperature while the column was programmed ramping at 4°C/min from 120°C to 245°C, respectively. In addition, the GC was also equipped with nitrogen as the carrier gas and programmed at 20 mL/minute whereas hexane was used as the solvent.

RESULTS AND DISCUSSIONS

Dolomite characterization

The dolomite stone were calcined in a furnace at 800°C for 2 hours which the process increased the poring sizes and surface area of the catalyst (Leung and Guo, 2006). The XRD patterns for natural dolomites shows that all peaks correspond to $\text{CaMg}(\text{CO}_3)_2$ as reported (Ngamcharussrivichai *et al.*, 2007). The XRD pattern for calcined dolomites, however, changes drastically compared to that of natural dolomites. After the calcination, the phases that appearing at 2 θ were in between 30-80°. The changes in the peaks illuminate the fact that calcination of dolomites results in the formation of the MgO-CaO form, which is the active catalytic component as shown in Figure-1.

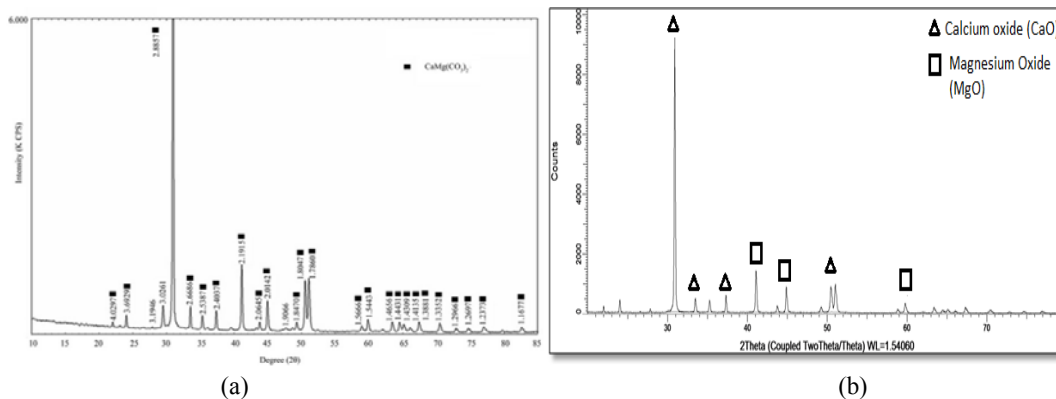


Figure-1. (a) The XRD patterns for natural dolomites (Ngamcharussrivichai *et al.*, 2007). (b) The XRD patterns for calcined dolomites.

Under the observations of SEM, the physical structures of raw and calcined dolomite are compared at several magnifications power respectively. According to Figure-2, at 500x magnification power showing that the raw dolomite is composed of sharp-like and uniform crystalline structure whereby the calcined dolomite is

showing a blunt-like and scattered crystalline structure compared to the raw dolomite.

Besides that, at 5000x magnification power showed that it is clearly seen in Figure-3 that the structure of raw dolomite is in discrete form and having sharp edges whereby the calcined dolomite is having a significant changes to its topography surfaces due to the thermal



decomposition process respectively. Thus, the structure of calcined dolomite is less compacted than the structure of initial dolomite due to heat suppression during the calcination process. Furthermore, the accusations are well approved as the SEM magnification power is increased to 2×10^4 which in Figure-4 showing that the morphological of raw dolomite surfaces are having an apparent cleavages together with a discriminatory orientation respectively. On the other hand, the treated dolomite is showing slots and pores caused due to the thermal decomposition which prominently affected by the decarbonation of the dolomite itself.

The complete thermal decomposition of $\text{CaMg}(\text{CO}_3)_2$ is releasing a substantial amount of CO_2 which led to the formation of the porous structure. Thus, in difference the structure of calcined dolomite is impeccably destroyed and leaving small fragmentations with more reactive surface area compared to the raw dolomite respectively (Ngamcharussrivichai *et al*, 2007). Therefore, the calcination process is considered as a respective method for thermally modification of the dolomite which led to the changing of its morphological properties.

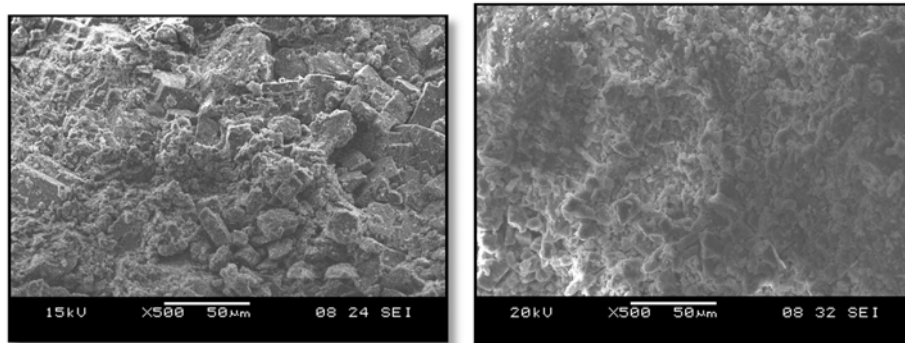


Figure-2. SEM images at 500x magnification power of raw (left) and calcined dolomite (right).

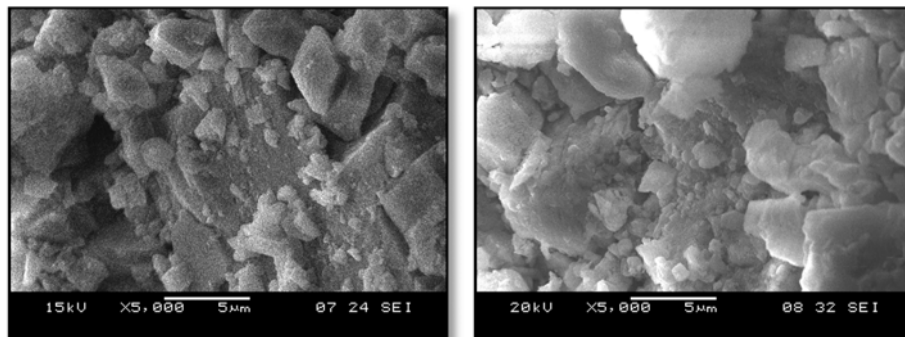


Figure-3. SEM images at 5000x magnification power of raw (left) and calcined dolomite (right).

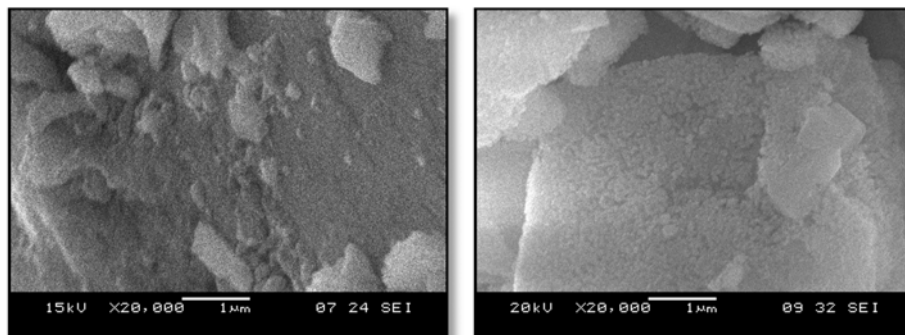


Figure-4. SEM images at 2×10^4 magnification power of raw (left) and calcined dolomite (right).



Effect of temperature

Figure-5 shows the effect of reaction temperature on the FAME yield. As shown in the figure, the transesterification reaction is strongly influenced by the reaction temperature. The FAME yield increased with increase in the reaction temperature from 20° C to 60 °C but decreased when the temperature raised to 80°C.

This is due to higher temperature which exceeded the optimal temperature for the reaction it would caused in the reduction of the FAME yield as higher temperature accelerates the saponification reaction of the triglycerides (Mohammed *et al.*, 2013). The highest FAME yield of 94.3% was obtained nearly at reflux temperature of methanol. Therefore, it is recommended that the reaction temperature for the transesterification process should be slightly lower than the boiling point of the methanol ranging from 50°C to 60°C, respectively.

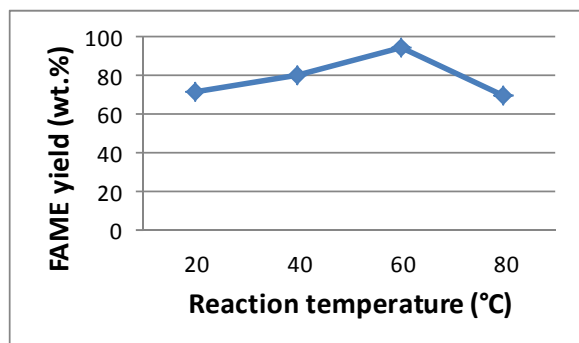


Figure-5. Effect of temperature on the FAME yield.

Reaction conditions: methanol/oil molar ratio, 6:1; catalyst weight (2 wt.%) and reaction time, 120min

Effect of amount of catalyst

The effect of the amount of catalyst of dolomite on the FAME yield was investigated at a 6:1 molar ratio of methanol/WFO at 60°C for 120 min. The catalyst amount referenced to the starting oil weight was varied in the range of 0.5–2.0 wt.%. As shown in Figure 6, FAME yield increased from 82.2% to 96.7% with an increase in catalyst amount from 0.1% to 1.5%. The FAME yield did not increase significantly further after the amount of catalyst exceeded 1.5 wt.%.

It means that an excess amount of catalyst cannot further promote the reaction to form more products because the reaction has already reached equilibrium. (Ngamcharussrivichai *et al.*, 2007) studied the calcined dolomite and modified dolomite to catalyze the transesterification of palm kernel oil to biodiesel and they found that the maximum methyl ester contents were obtained at catalyst amounts of 6 wt.% and 10 wt.%, respectively.

Effect of molar ratio of methanol/WFO

Figure-7 shows the effect of methanol/oil molar ratios on the FAME yield. As shown in this figure, FAME yield increased from 52.3% to 90.5% with an increase in molar ratio of methanol to WFO from the stoichiometric ratio of 2/1 to 6/1. The highest FAME yield of 90.5% was obtained in the reaction carried out at a 6:1 methanol/WFO molar ratio.

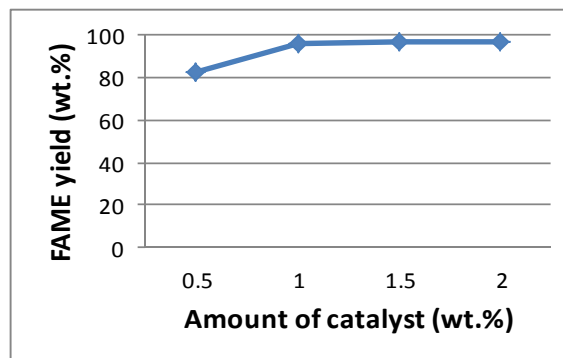


Figure-6. Effect of amount of catalyst on the FAME yield.

Reaction conditions: methanol/oil molar ratio, 6:1; temperature 60°C and reaction time, 120min.

Preferably, if the methanol does not presence in excess it would caused in an incomplete conversion of the FAME whereby if the methanol is exceeding the optimal value for the reaction it would be wasted as the yield of the biodiesel does not reaching its highest value and costly to alcohol recovery steps, respectively.

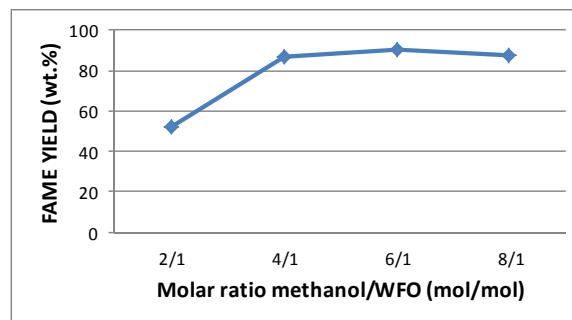


Figure-7. Effect of amount of Molar ratio methanol/WFO

on the FAME yield. Reaction conditions: temperature 60°C; amount of catalyst 1.5wt.% and reaction time, 120min.

Effect of reaction time

The reaction time was an important reaction parameter, which is closely related with energy cost of the biodiesel production process. As shown in Figure-8, FAME yield was increased significantly as the reaction



time increased. The highest FAME yield of 96.5% was obtained at 180 min of reaction time. Similar results were obtained by (Ngamcharussrivichai *et al.*, 2007). They

reported that the suitable reaction time required for obtaining the highest amount of methyl ester was 3h.

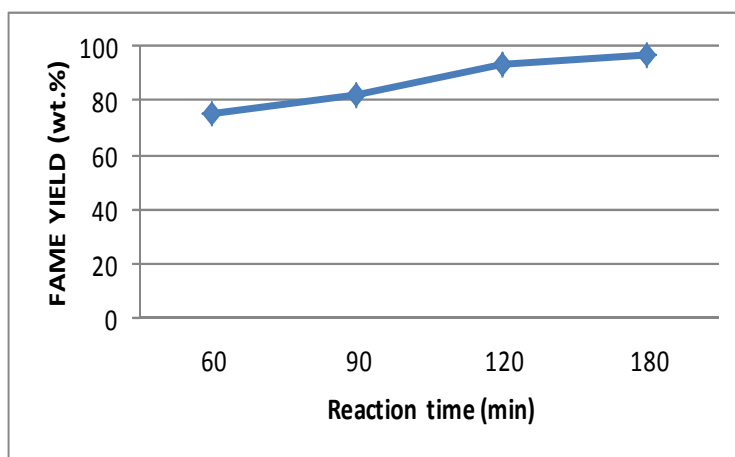


Figure-8. Effect of reaction time on the FAME yield. Reaction conditions: temperature 60°C; amount of catalyst 1.5wt.% and molar ratio 6/1.

Characterization of FAME by using gas

Chromatography

Table-1 shows the chromatogram data of the maximum yield of biodiesel analyzed by GC. Significantly, the composition of the methyl oleate, methyl linoleate, methyl linolenate and methyl arachidate are at

37.4%, 3.5%, 38.7% and 20.4% respectively. Literally, these values are comparable with the other studies (Ciubota-Rosie *et al.*, 2013), thus proving that in this set of experiment the maximum yield is containing a significant high amount of FAME.

Table-1. Data by the chromatogram of the maximum FAME yield.

Peak no.	Methyl ester	Ret. time (min)	Fatty acid composition (%)
1	Methyl oleate	7.276	37.4
2	Methyl linoleate	8.555	3.5
3	Methyl linolenate	10.638	38.7
4	Methyl arachidate	11.456	20.4

CONCLUSIONS

The studies on the transesterification of WFO over dolomite as the catalyst have been done successively. The confirmation of the dolomite elements is checked under XRD scanning whereas the modified morphology of the stone is analyzed by using SEM respectively. The XRD pattern for calcined dolomites, changes drastically compared to that of natural dolomites. The changes in the peaks illuminate the fact that calcination of dolomites results in the formation of the MgO-CaO form, which is the active catalytic component. Under the observations of SEM, the physical structures of raw and calcined dolomite are compared at several magnifications power respectively

The calcination process is considered as a respective method for thermally modification of the dolomite which led to the changing of its morphological properties. The transesterification of WFO with methanol can be actively catalyzed over dolomite catalysts with amount of 1.5wt.% at reaction temperature of 60°C, methanol/oil molar ratio, 6:1 and reaction time of 120min. With this reaction conditions, it can produce highest FAME up to 96.7 wt.%. There was no improvement of FAME yield with the amount of catalyst higher than 1.5 wt.%. For the GC analysis, the FAME yield do contained the significant presence of the methyl oleate, methyl linoleate, methyl linolenate and methyl arachidate respectively.



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