

Thermal Treatment of Natural Carbonate Catalyst for Biodiesel Production from Yemeni Jatropha Oil

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Abstract:- In this paper, heterogeneous catalysts based on natural dolomite mineral in the transesterification of Jatropha oil into biodiesel. Investigating the applicability of natural basic carbonate minerals as potential catalysts in biodiesel production from Yemeni Jatropha oil. The effect of thermal treatment of these minerals had been addressed and correlating the catalytic behavior with the surface properties of these systems was attempted. XRD measurements show that the dolomite mineral is highly crystalline with small amounts of calcite. Increasing the temperature of thermal treatment up to 500°C has no significant effect on the X-ray diffraction patterns, but upon further increase of the temperature to 600°C the dolomite phase was found to decompose due to the decarbonisation of $MgCO_3$. Temperatures as high as 800°C were found to be necessary to start the thermal decomposition of calcium carbonate, but appreciable amounts of calcite remain even after several hours of thermal treatment at 800°C. The transesterification of Jatropha oil was conducted at 60°C with a methanol-to-oil molar ratio of 6:1. Dolomite samples thermally treated up to a temperature of 700°C showed only low activities in the transesterification of Jatropha oil (conversion~20%). Raising the temperature of thermal treatment to 800°C increased the activity significantly to 95%-conversion, apparently due to the formation of strongly basic CaO. It was found that heating the mineral for at least 30 minutes at 800°C is necessary to produce a highly active system. The optimum catalyst-to-oil mass ratio was determined to be 1:50.

Keywords:- Dolomite, Transesterification, Biodiesel, Thermal Treatment, Heterogeneous, Catalysts.

I. INTRODUCTION

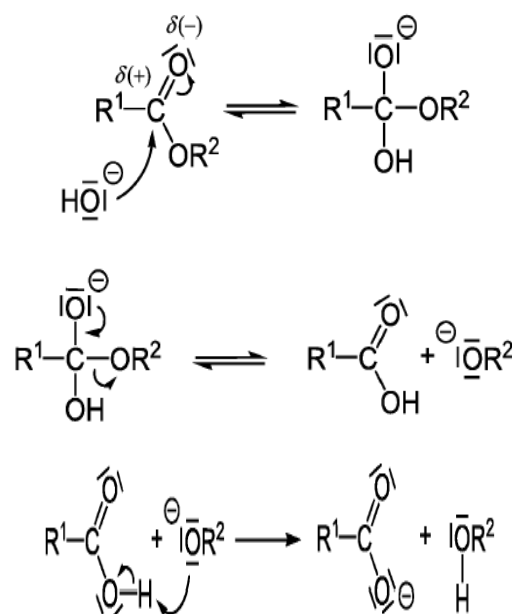
Nowadays, world energy crisis has received considerable attention due to the increased demand for energy and due to the limitation of fossil fuels supplement. Alternative renewable fuels are considered as a feasible route to resolve this serious problem. One of the promising approaches is the use of biodiesel characterizes by several advantages, such as being non-toxic, bio-degradable, and suitable for agricultural countries. Biodiesel is defined as the methyl or ethyl ester produced from vegetable or animal oil/fat with diesel quality. Most probably it is produced through transesterification of triglycerides of vegetable oils

with alcohol. The transesterification is usually carried out using methanol because of its low cost [1, 2].

In general, biodiesel feedstock can be divided into four main categories as below:

- Edible vegetable oil: rapeseed, soybean, peanut, sunflower, palm and coconut oil.
- Non-edible vegetable oil: jatropha, karanja, sea mango, algae and halophytes.
- Waste or recycled oil.
- Animal fats: tallow, yellow grease, chicken fat and by-products from fish oil.

There are four primary ways to produce biodiesel; these include the direct use and blending of raw oils with ordinary fuel [3–7], micro-emulsions [8], thermal cracking [9–14] and transesterification [15]. The most commonly used method is transesterification. Transesterification is regarded as the best method among other approaches due to its low cost and simplicity [16]. Biodiesel is the main product of this process. Transesterification consists of a number of consecutive, reversible reactions. In these reactions, Scheme 1, the triglycerides are converted step wise to diglycerides, monoglyceride and finally glycerol.



Scheme1: Mechanism of Base Hydrolysis

Glycerol is an important by-product and can be burned for heat or be used as feedstock in the cosmetic industry [3]. In this reaction, methanol and ethanol are the two main light alcohols used for transesterification process due to their relatively low cost. However, propanol, isopropanol, tert-butanol, branched alcohols and octanol and butanol can also be employed but the cost is much higher [3].

More than 95% of biodiesel production feedstock comes from edible oils since they are mainly produced in many regions and the properties of biodiesel produced from these oils are much suitable to be used as diesel fuel substitute [14]. However, it may cause some problems such as the competition with the edible oil market, which increases both the cost of edible oils and biodiesel [17]

After oil extraction or pressing, the biodiesel production takes place in two steps: (1) the acid catalyzed pre-esterification with the purpose of removing free fatty acids (FFA) from the stock and (2) the alkali catalyzed transesterification with the purpose of producing fatty acids methyl (FAME) or ethyl (FAEE) esters. Acid-catalyzed transesterification has not gained much attention as the alkali-catalyzed transesterification due to the slow reaction rate and the high methanol to oil molar ratio required [18].

Heterogeneous catalysis refers to the form of catalysis where the phase of the catalyst differs from that of the reactants. Phase here refers not only to solid, liquid and gas, but also immiscible liquids, e.g. oil and water. The heterogeneous catalytic transesterification is included under Green Technology due to the following attributes: (1) the catalyst can be recycled (reused), (2) there is no or very less amount of waste water produced during the process and (3) separation of biodiesel from glycerol is much easier [19]. These catalysts are thus particularly useful for those oils with high free fatty acids [20]. However, when a solid catalyst is used, the reaction proceeds at a slower rate [21, 22].

II. AIMS OF THIS STUDY

This study aims at investigating the applicability of natural basic carbonate minerals as potential catalysts in biodiesel production from Yemeni *Jatropha* oil. The effect of thermal treatment of these minerals will thereby be addressed and correlating the catalytic behavior with the surface properties of these systems will be attempted.

III. EXPERIMENTAL

➤ *Jatropha* Oil: Extraction and Analysis

Jatropha fruits were obtained from Wadi Jannat in Ibb Governorate (Yemen). The fruits were peeled off to obtain the seeds which were found to constitute ~ 60 % of the fruit mass.

➤ Extraction

Jatropha seeds were finely ground by means of a standard kitchen grinder. n-hexane or cyclohexane was then added with the ratio of 1 L hexane/1 Kg seeds. The obtained

slurry was mixed at 2500 rpm for 1 hr at room temperature. The liquid phase was then separated by means of suction filtration and hexane was consequently removed from the liquid phase by evaporation under reduced pressure in a rotor evaporator (Büchi Rota evaporator R110). The remaining *Jatropha* oil was found to constitute about 25% w/w of the seeds.

➤ Analysis

The *Jatropha* oil was characterized with respect to its free fatty acid content (acid value), fatty acid composition, and insoluble impurities in hexane, acidity as oleic acid, value Peroxide number, Iodine number, saponification value, and unsaponifiable matter.

➤ Dolomite

Dolomite is a carbonate mineral composed of a calcium-magnesium carbonate [$\text{CaMg}(\text{CO}_3)_2$]. The Mg:Ca ratio is basically in the range 1:1. Natural dolomite rock samples were generously provided by the agency of Geology and Mineral exploration at Aden Gov. The mineral was analyzed with respect to its Mg and Ca content by means of Atomic Absorption Spectroscopy (Nova 300, Analytik Jena) at the Department of Geology, The Ca:Mg ratio was found to be 0.41:1.00.

The dolomite rock was crushed and finely ground. Then it was subjected to different thermal treatments. These include two hours of heating under oxygen (Arab Company) or atmospheric air at 100°C, 200°C, 300°C, 400°C, 500°C, 600°C, 700°C and 800°C. Thermal treatment at 800°C was also conducted under atmospheric air for different periods (12 h, 8 h, 6 h, 4h, 2 h, 1 h, 1/2 h, 15 min and 5 min). The apparatus consists of an electrically heated tubular furnace connected to gas supply. Thermal treatments at higher temperatures (600°C and 800°C) were conducted in oven under atmospheric air. The prepared catalysts were designated D-T-xh where "x" represents the period of thermal treatment in hours and "T" stands for the temperature in °C at which thermal treatment has been carried out.

All catalytic systems were analyzed with respect to their structure by means of the X-ray diffraction (XRD) using Phillips-PW 1729 device with a Fe- K_{α} -tube ($\lambda=1.937 \text{ \AA}$) FTIR spectroscopy (Bruker Tensor 27 FTIR provided with an ATR probe for in-situ measurements). The heterogeneously base-catalyzed trans-esterification, the reaction was carried out at 60°C as described above whereby the KOH used in the homogeneous transesterification was replaced by 0.5 g of the solid base (MgO-350-0.5h, MgO-350-1h, MgO-350-2h, MgO-350-3h, MgO-350-4h), (D-100-2h, D-200-2h, D-300-2h, D-400-2h, D-500-2h, D-600-2h, D-700-2h, D-800-2h, D-800-5min, D-800-0.5h, D-800-1h, D-800-4h, D-800-8h, D-800-12h). Sample analysis took place as described above.

IV. RESULTS AND DISCUSSION

Figure 1(a-f) shows the X-ray diffraction patterns of untreated dolomite, D-100, D-300, D-400, D-500 and D-600. All patterns are characterized by very sharp lines indicating the high crystallinity of the investigated rock samples. For phase identification purposes, the diffraction lines were compared with the stick patterns of some reference materials (drop lines in figure 9): Dolomite, $\text{CaMg}(\text{CO}_3)_2$ (JCPDS 00-036-0426), calcite, CaCO_3 (JCPDS 00-005-0586), magnesium calcite, $\text{Ca}_{0.86}\text{Mg}_{0.14}(\text{CO}_3)_2$ (JCPDS 00-043-0697), MgO (JCPDS 00-004-0829) and MgCO_3 (JCPDS 00-008-0479).

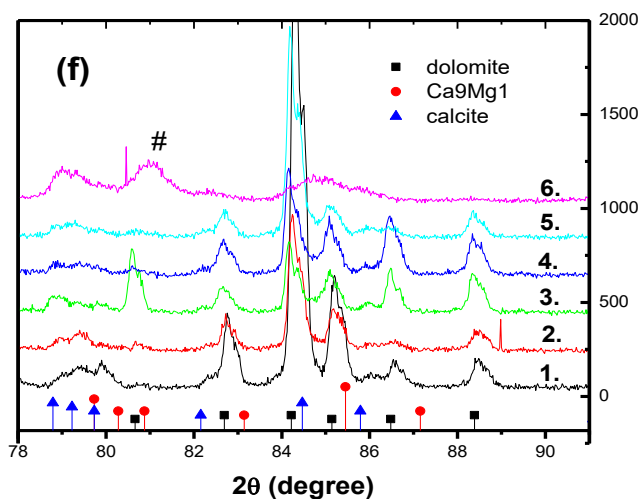
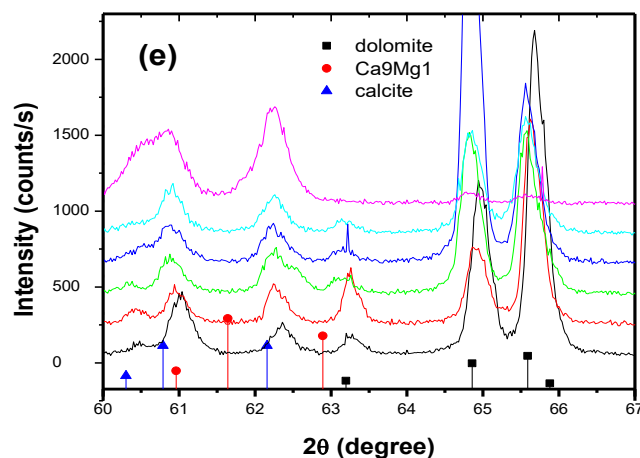
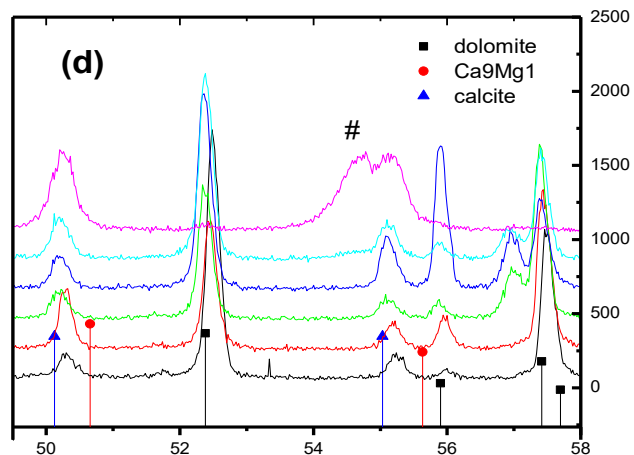
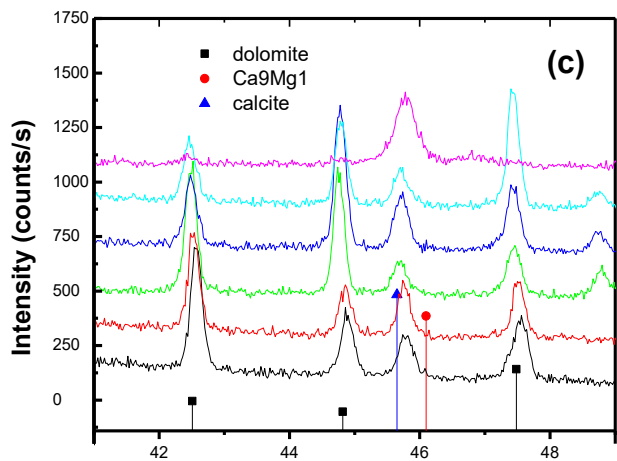
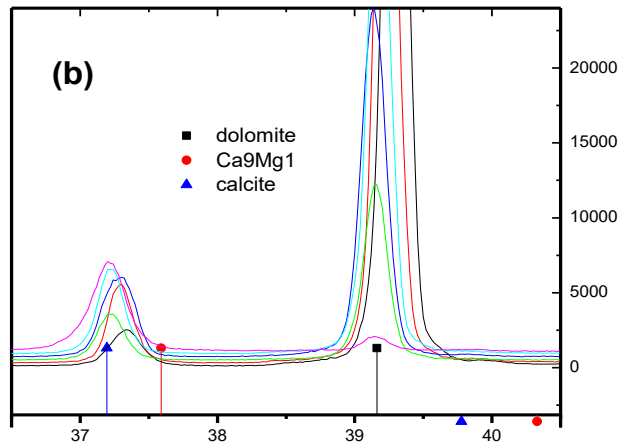
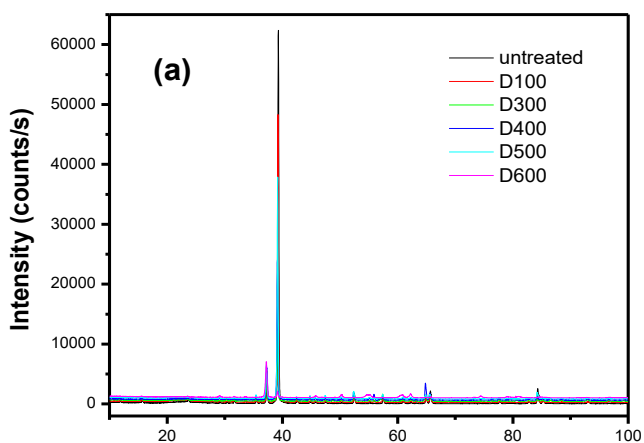


Fig 1 (A-F): X-Ray Diffraction Patterns of Dolomite Samples 1) Untreated, 2) D-100, 3) D-300, 4) D-400, 5) D-500 and 6) D-600.

Amorphous carbonates are however metastable with respect to crystalline carbonate [25].

Figure 2 shows the X-ray diffraction patterns of a) D-800-0.5h, b) D-800-2h and c) dolomite treated for two hours at 600°C then for two hours at 800°C. No dolomite structure can be recognized, this is in agreement with the results shown in the previous figure that the dolomite phase has disappeared upon thermal treatment at 600°C. Apparently,

calcium carbonate underwent decarbonation but it didn't disappear completely at this temperature. This is because the practical decomposition temperature of CaCO_3 is above 800°C [23].

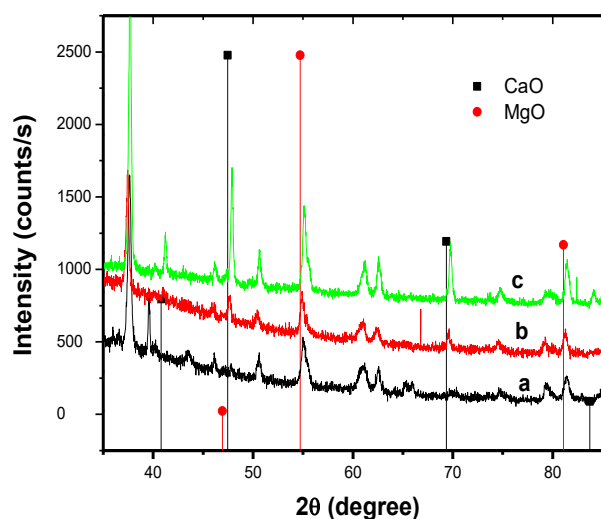


Fig 2 X-ray diffraction patterns of a) D-800-0.5h, b) D-800-2h and c) dolomite treated for two hours at 600°C then for two hours at 800°C .

➤ FTIR-spectroscopy

Figure 3 shows the FTIR spectra of the dolomite samples thermally treated for two hours at various temperatures (D-100-2h, D-200-2h, D-300-2h, D-400-2h, D-500-2h, D-600-2h, D-700-2h and D-800-2h). Carbonate characteristic bands can be recognized in figure.6. These bands include the ν_3 asymmetric stretching vibration of the carbonate species at $\sim 1430\text{ cm}^{-1}$, the sharp ν_2 bending vibration at $\sim 880\text{ cm}^{-1}$, a weak ν_1 symmetric stretching vibration at $\sim 1030\text{ cm}^{-1}$ and a sharp band that appears as a doublet at 729 cm^{-1} and 713 cm^{-1} . In addition, O-H stretching vibration can be observed as a broad band centered around 3450 cm^{-1} corresponding most probably to water crystal and hydrogen bonded OH groups. The O-H bending vibration shows a vibrational mode at $\sim 1640\text{ cm}^{-1}$.

Upon thermal treatment at 600°C and 700°C , drastic changes in the IR spectrum can be observed. First of all, the sharp band at 728 cm^{-1} disappears while that at 715 cm^{-1} persists. It was reported that the band around 710 cm^{-1} belongs to calcite [80]. Accordingly, it seems plausible to conclude that the band at 725 cm^{-1} belongs to the carbonate species in MgCO_3 since the XRD results show that the magnesium carbonate undergoes decomposition by thermal treatment at 600°C . Also, the shoulder at lower wave numbers to the 880 cm^{-1} band is observed to disappear by heating up to 600°C which can also be attributed to the decomposition of MgCO_3 .

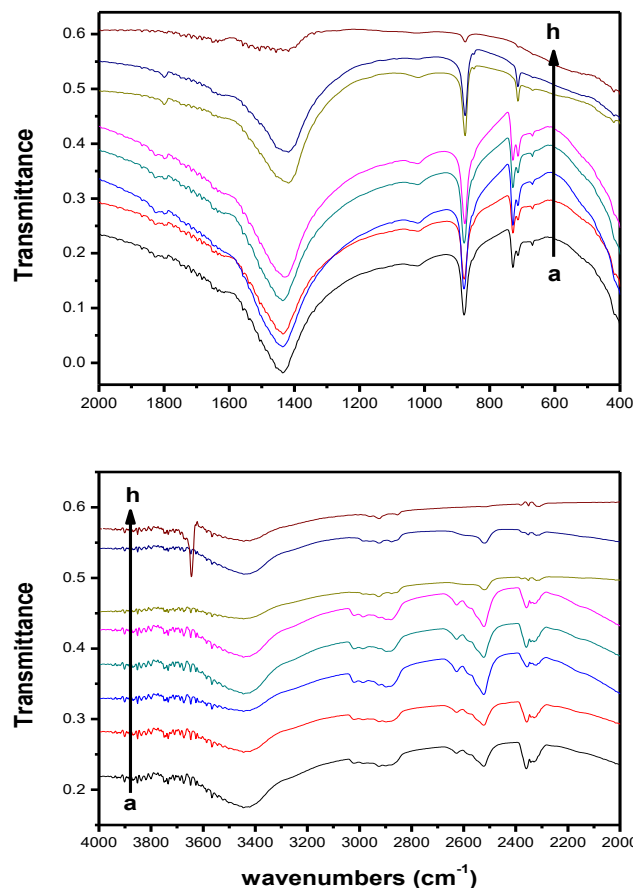


Fig 3 FTIR spectra of dolomite samples treated for two hours at various temperatures: a) D-100-2h, b) D-200-2h, c) D-300-2h, d) D-400-2h, e) D-500-2h, f) D-600-2h, g) D-700-2h and h) D-800-2h.

Thermal treatment at 800°C leads almost to the disappearance of the carbonate characteristic vibrational modes indicating that at this temperature also calcite (CaCO_3) undergoes decomposition which is in agreement with previous works which calcium carbonate undergoes thermal decomposition above 800°C [23]. The disappearance of the carbonate characteristic vibrational bands is accompanied by the appearance of a sharp band at 3645 cm^{-1} which can be assigned to free hydroxide groups. This also is consistent with the decomposition of calcium carbonate into strong basic calcium oxide which upon cooling in the oven under open atmosphere (unavoidable since the samples were heated under open atmosphere) may adsorb water vapor leading to the formation of free hydroxide groups.

The additional absorption bands in figure 6 may be explained as follows: The doublet between $2300\text{--}2400\text{ cm}^{-1}$ can be assigned to gas phase CO_2 that accumulated in the sample compartment with time. But the origin of the two bands at 2526 cm^{-1} and 2635 cm^{-1} is not very clear and we believe that they belong to some CO_2 trapped in the mineral terminally adsorbed to the surface. It also possible that, since the sample is natural carbonate rock, it contains some organic material which can also contribute to the absorption features observed just below 3000 cm^{-1} usually assigned to C-H stretching vibration.

Figure 4 shows the IR spectra of the dolomite samples thermally treated at 800°C for various time periods. It is obvious that at least one hour treatment at 800°C is necessary to appreciably decarbonate the sample. It can be also seen that the ν_3 asymmetric stretching vibration of the carbonate species (1430 cm^{-1}) that remains after extended heating at 800°C (more than 2 hours), splits after heating to 12h into two bands centered at 1485 cm^{-1} and 1425 cm^{-1} . This splitting of the carbonate band into doublet is well known in literature and is attributed to better crystallinity of the system [23,24].

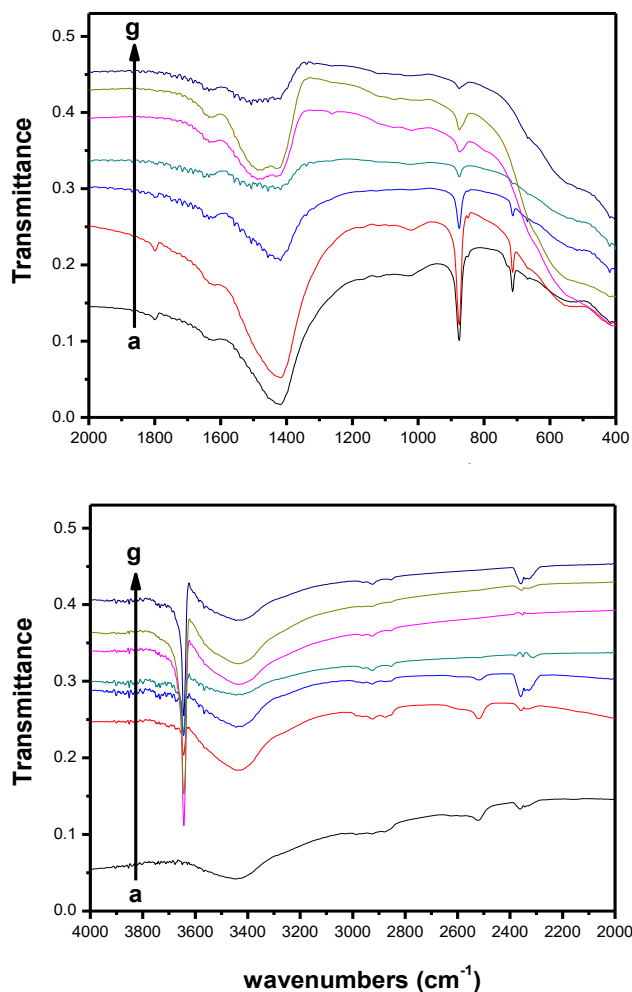


Fig 4 FTIR spectra of dolomite samples treated for different periods of time at 800°C: a) D-800-5min, b) D-800-0.5h, c) D-800-1h, d) D-800-2h, e) D-800-4h, f) D-800-8h and g) D-800-12h

➤ *¹H-NMR in biodiesel production*

¹H-NMR is an effective technique in monitoring the progress of oil transesterification in which glycerin is substituted by methanol. Figure 5 shows the ¹H-NMR spectrum of raw Jatropha oil. The various peaks are assigned to the different H atoms in the oil molecule according to the insert in figure 5. Upon preesterification, a new singlet peak appears at 3.65 ppm (j peak) corresponding to the hydrogen atoms of the methoxy group (figure 6). It appears in low intensity, obviously because of the low percentage of free fatty acids in fresh Jatropha oil. No other significant change in the spectrum of raw oil is observed.

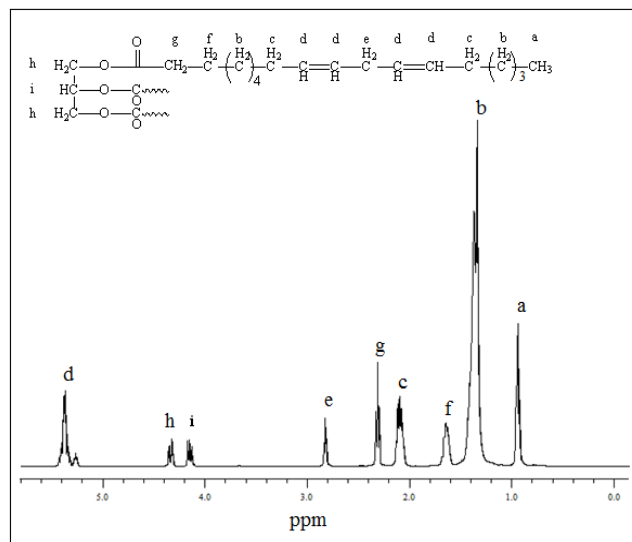


Fig 5 ¹H-NMR Spectrum of Raw Jatropha Oil

By transesterification (Figure 6), the intensity of the j-peak increases corresponding to an increase in the fraction of methyl esters, whereas the h- and i-peaks corresponding to the triglyceride hydrogen atoms are disappeared indicating complete transesterification. The intensity of the j-peak can thus be taken as a measure to the extent of reaction progress. To eliminate the effect of oil concentration in the analyzed samples, the intensity of the j-peak relative to that of the a-peak (which corresponds to terminal CH₃ groups of FAME or oil molecules) is considered. The reason why the a-peak was chosen for this purpose is; it is not supposed to undergo any change during preesterification or transesterification reactions.

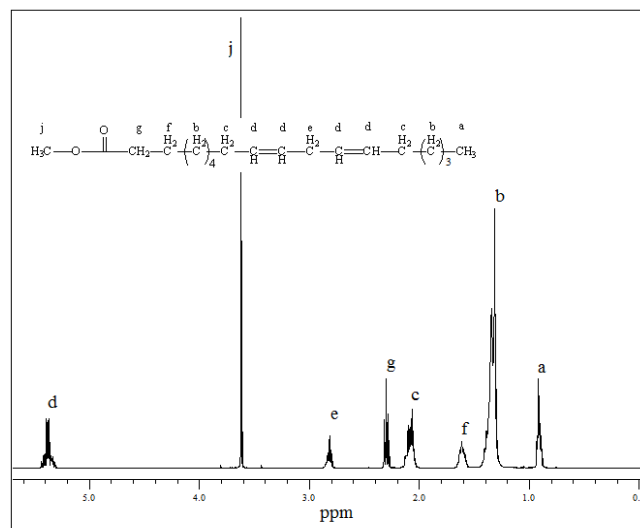


Fig 6 ¹H-NMR Spectrum of Transesterified Jatropha Oil (KOH with 1.2% w/w of Methanol Added, and 6:1 Methanol/Oil Molar Ratio).

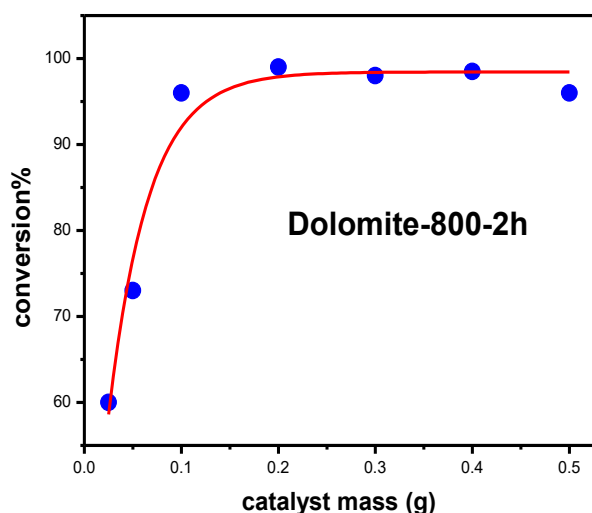


Fig 7 Conversion Achieved by Dolomite-800-2h in the Production of FAME from Preesterified Jatropha Oil as a Function of Applied Catalyst Mass. Reaction Conditions: Reaction Temperature is 60°C, the Molar Methanol-to-Oil Ratio was 6:1, and the Mass of Oil was 5 g.

From figure 7 it can be recognized that a catalyst mass of 0.10 g of D-800-2h is sufficient to almost completely transesterified (96-98%) 5g of preesterified Jatropha oil (the catalyst/oil mass ratio is thus 50/1). Higher catalyst-to-oil ratios are not only wasted amount of catalysts, they may also lead to adverse effects such as increased saponification causing separation difficulties and loss of desired product.

V. CONCLUSIONS

Heterogeneous catalysts based on natural Yemeni dolomite mineral and on magnesium oxide-hydroxide systems were tested with respect to their efficiency in the transesterification of Jatropha oil into biodiesel.

XRD measurements showed that the dolomite mineral is highly crystalline with small amounts of calcite. Temperatures as high as 800°C were found to be necessary to start the thermal decomposition of calcium carbonate, but appreciable amounts of calcite remained even after several hours of thermal treatment at 800°C. IR spectroscopy confirms the decomposition of $MgCO_3$ at 600°C and that of $CaCO_3$ at 800°C. The appearance of free hydroxide groups in the dolomite samples thermally treated at 800°C has been attributed to the interaction of strongly basic oxide species with water vapor from the atmosphere.

Raising the temperature of thermal treatment to 800°C has been clearly increased the activity to 95%-conversion, apparently due to the formation of strongly basic CaO. Further experiments were carried out to optimize the thermal treatment of dolomite at 800°C with respect to its duration. It was found that heating the mineral for at least 30 minutes at 800°C is necessary to produce a highly active system.

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