

# Kinetics of Vegetable Oil Transesterification Catalyzed by Magnesium Oxide Supported on Cashew Nut Shell Liquid Templated Mesoporous Silica

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**Abstract-**In this work, Cashew Nut Shell Liquid Templated Mesoporous Silica support (MTS (CNSL)) was synthesized. Limited works were reported on the use of natural templates in synthesis of mesoporous silica. Heterogeneous catalysis of transesterification using MgO/MTS (CNSL) catalysts was utilized to produce biodiesel from *Jatropha curcas* oil and methanol. Different ratios of Si/Mg were employed. Among all catalysts, 3MgO/MTS (CNSL) showed the highest activity achieving higher conversion of 98.71% at optimal conditions: 200 °C, 4 h, 6.0 %wt and the molar ratio of methanol to oil being 36:1. The effects of reaction temperature, catalyst concentration, and reaction time on the conversion to methyl ester were studied with temperature being the most significant parameter. This study has explored the possibility of using CNSL as a natural catalyst support in the transesterification of *Jatropha curcas* oil using MgO.

**Keywords-** Cashew Nut Shell Liquid; Mesoporous Silica; Characterization

## I. INTRODUCTION

In the past, traditional sources of energy such as fuel wood, charcoal, and dung were the only sources of energy used for all types of applications. It is only during the last 250 years that fossil fuels such as coal, oil and gas and electricity have emerged as major sources of energy in most developed countries. However, nearly 75% of the world's population which lives in the developing countries continues to depend on the traditional sources of energy for most of their energy requirements [1]. Depletion of the world petroleum reserves and increasing environmental concerns has stimulated the search for renewable fuels, such as biodiesel, in recent years. Meanwhile the gap between the production and demand continues to rise; economies of many developed countries suffer significant disruption. From an environmental point of view, combustion of petroleum fuels is a main contributor of an increasing global CO<sub>2</sub> atmospheric concentration, a driver of global warming. These concerns have driven significant investment into alternative energy sources for internal combustion engines [1]. Currently, there are two major types of liquid biofuels that can be used in the transportation industry. These include: (i) bioethanol which is produced out of plant starch, sugar, and more recently but still on an experimental basis, cellulose, and (ii) biodiesel which is made out of vegetables or grain oil and recycled cooking oil.

Triglyceride vegetable oils are a renewable and potentially inexhaustible source of energy with energetic content close to diesel fuel [2]. At present, the most common process for converting vegetable oils or animal fats into biodiesel fuel is transesterification, most often using a catalyst intermediately [1]. Three main synthetic approaches have been used for biodiesel production that includes alkali catalyzed transesterification, acid-catalyzed transesterification, and noncatalytic conversion via transesterification and esterification under supercritical alcohol conditions [3-6]. Base catalyzed transesterification is commonly used for large large-scale or commercial productions for its faster rate and is less corrosive as when using the acid-catalyzed process [7].

However, the use of homogeneous base catalysts require neutralization from the final reaction mixture leading to a series of environmental problems related to the use of high amounts of solvents and energy [8]. Heterogeneous basic catalysts, able to catalyze the transesterification of alkyl esters could solve such problems; they can be easily separated from the reaction mixture by simple filtration, without the use of solvent, they are easily regenerated leading to safer, cheaper and more environment-friendly operations [8]. Solid base catalysts are widely used catalysts in the synthesis of biodiesel because of their high activity compared to solid acid catalysts. Heterogeneous catalysts that are reported in literature to be active include alkali-earth-metal compounds, sulphated zirconia, calcium carbonate, zeolites and alumina loaded with alkali-metal salts [1].

As compared to the homogeneously catalyzed process, the transesterification with solid catalyst occurs at harsher reaction conditions, i.e., at higher temperatures and pressures. This is because the solid catalyzed process is a three-phase system (oil,

methanol, and catalyst) and, for mass transfer reasons, it protracts the transesterification [9]. One way of minimizing the mass transfer problems is the use of catalyst supports. A catalyst support is a material on which the catalyst is deposited or is a skeletal or binding material for the active component and its mass is normally greater than that of an active component, and its catalytic is slight, or non-existent in the reaction of interest [10].

Mesoporous materials are among the known catalysts supports. These materials have pore diameter of 2-50 nm. They possess large surface area which make them being of great importance in the study of catalyst supports. These materials have been of great interest in the view of the fact that, small changes in the procedure can result in large changes in the morphology.

Micelle Templated Silica (MTS) is a generic name for silica prepared using sol-gel methodology, but with a micelle template. Mobil researchers Kresge and Beck in 1992 were the first to prepare a family of highly ordered mesoporous molecular sieves M41S similar to MTS [11]. The most popular MCM materials are MCM-41 and MCM-48, which possess hexagonal and cubic ordered structures respectively. The general synthesis strategy involves the condensation of an appropriate monomer in the presence of a templating agent. The templating agent (surfactant) is later removed from the composite material by Soxhlet, hot filtration or calcination revealing a network of mesopores. The pore size of the resulting mesoporous material can be controlled by the choice of a template. In most studies, charged (cationic and anionic) and neutral surfactants have been employed as templates that direct the mesophase formation based on the electrostatic and hydrogen-bonding interactions respectively [12].

Two major general methods are widely used in the preparation of MCM-type of materials. These are (post-functionalization) grafting and one-pot co-polymerization [13]. In this work, the latter was used. Tetraethoxysilane (TEOS) was used as a source of silica when organosilane was copolymerized. SBA-15 is another type of mesoporous silica studied by many researchers. SBA stands for Santa Barbara Amorphous. Martins et al. [14] used Mg/Al hydrotalcite as a basic catalyst solid, synthesized using the co-polymerization method with Mg/Al molar ratio of 3.0 in the transesterification of soybean oil to produce biodiesel. At a molar ratio of 20:1 (methanol:oil) and with a reaction time 10 h, the highest ester content was 94.8%. The study showed satisfactory catalytic activity for biodiesel production.

Another study was by Xie et al. [15]. They prepared a heterogeneous solid catalyst SnO<sub>2</sub> and supported it using WO<sub>3</sub> by impregnation method. The supported catalyst was used in the transesterification of soybean with methanol. With loading of 30% WO<sub>3</sub> and calcined at a temperature of 1173 K, it showed a high catalytic activity with maximum conversion to FAME of 79.2% after 5 h at 383 K and 5 wt.% of catalyst employed. The solid catalyst was reused for four runs without significant deactivation. Investigations on the transesterification of sunflower oil with methanol over MoO<sub>3</sub> (8%) supported on SiO<sub>2</sub>, SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> was carried out in order to elucidate the effects of the support on the nature of the supported MoO<sub>3</sub> species and transesterification activity. This was carried out by Sankaranarayanan et al. [16]. The catalyst support was found to have much influence on the stability of the MoO<sub>3</sub> species during the reaction.

An additional work was done on the transesterification of sunflower oil to biodiesel using ZrO<sub>2</sub> supported La<sub>2</sub>O<sub>3</sub> as a catalyst. ZrO<sub>2</sub> supported La<sub>2</sub>O<sub>3</sub> catalyst was prepared by impregnation method and was examined in transesterification reaction of sunflower oil with methanol to produce methanol [17]. The crystalline size of support was shown to decrease after loading the catalyst. Moreover, this might be because the catalyst had occupied some pores. Most solids of high surface area are to some extent porous. The texture of such materials is defined by the detailed geometry of the void and pore space. Porosity is a concept related to texture and refers to the pore space in a material [18].

This present work was targeted on using cashew nut shell liquid (CNSL) as a natural template in synthesizing mesoporous silica support. MTS materials prepared with CNSL template possess more desirable properties, such as large pores into which a catalyst can be supported, cheap and easy to prepare, than those prepared using commercially available surfactants like cetyltrimethylammonium bromide (CBA) and polyoxyethylene hexadecylether. MgO was impregnated into the support and used in the transesterification of jatropha curcas oil. Catalyst characterization on the basis of their surface area, basic site strength, and basicity was performed.

Many reported studies have conducted using prepared surfactants that are normally expensive. The main objective of this study was to develop natural template using CNSL. Natural templates are cheap and easy to prepare. MTS-CNSL produce large pores and they can also withstand high temperatures without being damaged. The supported catalyst can be reused without deactivation.

## II. EXPERIMENTAL SECTION

### A. Reagents and Materials

Jatropha oil was purchased from Diligent Tanzania Limited (Arusha, Tanzania) and Cashew nut shells from Uvungi Cashew Nut Processing Industry (Kibaha, Tanzania). Methanol, hexane, aqueous ammonia (33%), absolute ethanol (95%), absolute methanol (95%), tetraethyl-orthosilicate (TEOS), sodium hydroxide and magnesium nitrate were purchased from Sigma Aldrich Malaysia. All solvents were AR grade and were used without purification.

### B. Catalyst Preparation

Preparation of the support involved two steps: preparation of the MTS (CNSL) support; followed by wetness impregnation of MgO catalyst at different ratios.

#### 1) Synthesis of MTS Support Using CNSL:

Tetraethoxysilane (TEOS, 36.67 g) was added to a stirred solution containing a mixture of 5g CNSL in 104 ml aqueous ethanol and 106 ml of distilled water. The mixture was adjusted to pH of 10.5 by addition of ammonia solution dropwise. The mixture was initially clear, but increasingly became cloudy. The thick paste was filtered and was washed with 100 ml hot methanol and 100 ml distilled water after 24 h of continuous stirring. The final powder was then left to dry at room temperature overnight for 12 h, and calcined at 450 °C for 6h at the rate of 5 °C/minute.

#### 2) Impregnation of MgO onto MTS Support:

A mixture containing 1.5 g of the freshly calcined MTS support, a calculated amount of salt [Mg (NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O based on a Si/Mg<sup>2+</sup> ratio of 1:1, 1:2 and 1:3], and 25 g of methanol were mixed and stirred at room temperature for 2 h. The solvent was then evaporated, and the solid calcined at 550 °C for 4 h at a rate of 5 °C/minute. The impregnated samples were denoted as 1MgO/MTS (CNSL), 2MgO/MTS (CNSL), and 3MgO/MTS (CNSL) whereby they stand for impregnated catalyst at ratio of 1:1, 1:2, and 1:3 respectively.

### C. Catalyst Characterization

The specific surface area, pore volume and pore size distribution properties of the catalyst were measured by nitrogen adsorption isotherm at 77 K using an ASAP 2020 Micromeritics instrument by Brunauer-Emmett-Teller (BET) method. Scanning electron microscopy/energy dispersive x-ray (SEM/EDX) using QUANTA FEG 250 operated at 5.0 kV was used to carry out analysis on the catalysts to study its surface morphology. The ratio between cations for each sample was calculated by measurements of energy dispersive x-ray spectra (EDX), obtained by the ISIS Oxford Microanalysis facility of the system. The crystalline structure of the catalysts was characterized by XRD Philip PW 1820 diffractometer using Cu K $\alpha$  radiation ( $\lambda=1.5418$  Å). Fourier transform infrared (FT-IR) analysis was applied on the same catalysts to determine the surface functional groups using Shimadzu FT-IR infrared spectroscope. The spectra were recorded from 4000 to 400 cm<sup>-1</sup>.

### D. Catalytic Test

Thirty grams (30 g) of jatropha oil, methanol 39.68 g corresponding to the molar ratio of 36:1 of alcohol to oil, and nMgO/MTS (CNSL) catalyst in various concentrations were mixed in a high-pressure autoclave batch reactor with a magnetic stirrer (n stands for 1, 2, or 3 Mg/Si ratio). Heating was achieved by means of a heating mantle controlled by a proportional integrated derivative (PID) temperature controller. Experiments were conducted in different temperatures under continuous stirring of 500 rpm. At different intervals of time, the reaction was stopped, cooled to room temperature. After cooling, the catalyst was separated from the product mixture by filtration. The product and by-product were left to separate overnight and upper layer which is the methyl ester was taken for analysis.

### E. Sampling and Analysis

The sample preparation was done by taking 12.5  $\mu$ L of biodiesel feedstock into 250  $\mu$ L of internal standard. Methyl heptadecanoate was used as the internal standard, and the injection volume was 1  $\mu$ L. Helium was used as the carrier gas with the flow rate of 10 ml/min (Pressure 4.8 psi). Oven temperature was held at 110 °C (0.5 min) and was then heated at a rate of 10 °C/min to 220 °C (8 min). The temperature of injector and detector was set at 220 °C and 250 °C, respectively. Using Design-Expert 7.1 software, on the basis of Central Composite Design (CCD) statistical analysis of variance (ANOVA) was conducted to study the effect of individual and interactions of catalysts.

## III. RESULTS AND DISCUSSION

### A. Catalyst Characterization

The Brunauer-Emmett-Teller (BET) specific surface area, pore volume and mean pore diameter calculated from the adsorption branch by the Barrett-Joyner-Halenda (BJH) model, are presented in Table 1. The nitrogen adsorption-desorption isotherms (Fig. 1) obtained for all developed mesoporous catalysts tested in this study were type IV with H1 hysteresis loops, indicative of large channel-like pores in a narrow range size. According to International Union of Pure and Applied Chemistry (IUPAC) classification, type IV isotherms are commonly observed for mesoporous solids in which capillary condensation takes place at higher pressures of adsorbate in addition to multilayer adsorption at lower pressure [19]. 3MgO/MTS (CNSL) was observed to have larger mean pore diameter compared to other catalysts, this may be due to the existence of the higher amount of Mg<sup>2+</sup> ion that has larger ion radius. This is also proved by XRD results of 3MgO/MTS (CNSL) catalyst whereby, the reflection (1 0 0) tend to shift to a higher angle, indicating a lower d100 spacing with the introduction of Mg<sup>2+</sup>. This was also supported by Lin and Rudolph [1] that the introduction of Mg<sup>2+</sup> caused lower d100 spacing. In addition to that, SEM/EDX results also confirmed the presence of higher MgO atomic ratio compared to other catalysts.

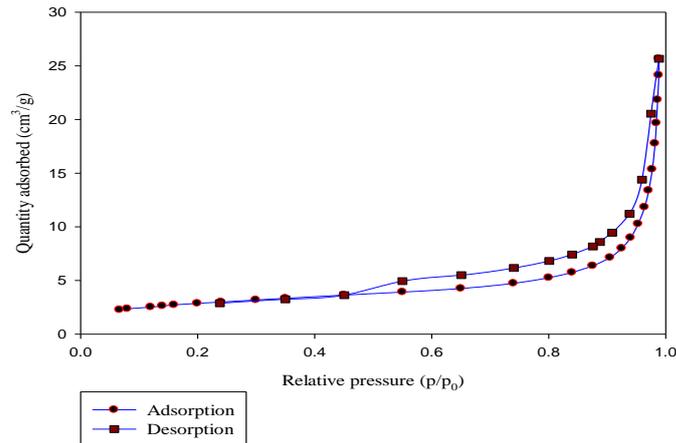


Fig. 1 Nitrogen adsorption/desorption isotherms of 3MgO/MTS (CNSL)

TABLE 1 CHARACTERISTICS OF THE DEVELOPED MESOPOROUS CATALYSTS

Catalyst	Specific surface area (BET)/ m <sup>2</sup> g <sup>-1</sup>	Volume of pores (cm <sup>3</sup> /g)	Mean pore diameter (nm)
1MgO/MTS (CNSL)	176.35	0.04	8.16
2MgO/MTS (CNSL)	135.52	0.01	2.33
3MgO/MTS (CNSL)	69.23	0.04	23.11

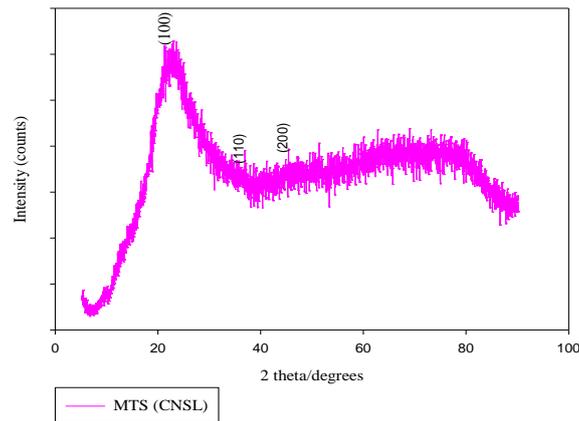
However, 3MgO/MTS (CNSL) though it possesses lower surface area, it was observed to have the higher methyl ester conversion compared to other catalysts. The reason to that may be due to the reason that, higher area materials necessarily comprise a high proportion of tiny pores and thus will lead to severe diffusion limitations in this complex three-phase reaction. Moreover, solid metal oxides as catalysts in oil transesterification depend on their catalytic activities, and it has been reported that the base sites over heterogeneous catalysts are active centers for transesterification [19].

The developed catalysts when examined using titration method according to [20], showed to have almost similar base site concentration. However, 3MgO/MTS (CNSL) appeared to have a slightly higher basicity of 2499.3  $\mu\text{mol/g}$ . Furthermore the catalyst was found to have a positive effect on transesterification reaction as it was enriched with 13.01% atomic MgO becoming a substantially basic catalyst. The strongest base sites promoted the transesterification reaction at very low temperature while the basic sites of medium strength required higher temperatures to promote the same reaction [21]. It was observed also that, there is strong correlation between activity of the catalyst and its surface Mg concentration, as observed earlier by Li and Rudolph [1]. The higher surface Mg concentration, point out the more availability of Mg for the catalysis. When the same catalyst support was used, the activity of the catalyst was attributed to its surface Mg concentration, which was determined by the catalyst loading. 3MgO/MTS (CNSL) was found to have higher surface Mg concentration (see Table 2) compared to other prepared catalysts.

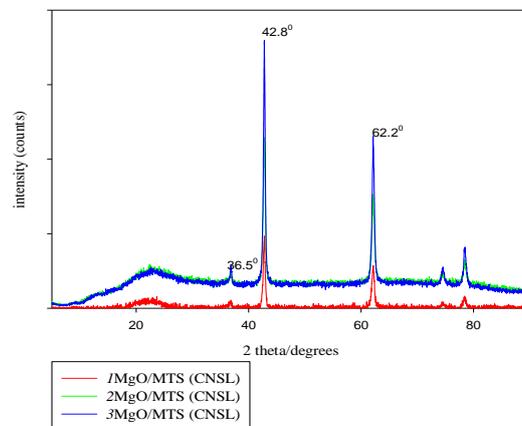
TABLE 2 ATOMIC PERCENTAGE OF MAGNESIUM AND BASICITY

Catalyst	Mg (atomic %)	Basicity ( $\mu\text{mol/g}$ )
1MgO/MTS (CNSL)	4.54	2498.7
2MgO/MTS (CNSL)	12.09	2499
3MgO/MTS (CNSL)	13.01	2499.3

XRD shows (Fig. 2) that the mesostructure of all catalysts were maintained after MgO loading. MTS (CNSL) showed Bragg plane pattern (1 0 0), (1 1 0) and (2 0 0) reflections, which are characteristic of a two-dimensional (2D) hexagonal ( $p6mm$ ) structure [12]. However, increasing the amount of the loading Mg, the two weak diffraction peaks of (1 0 0) and (2 0 0) became indistinct, indicating the decrease of the order of mesoporous structure. Increasing impregnation ratio of MgO increased the intensity of the peaks, indicating the presence of cubic MgO into the MTS (CNSL). However, the reflection (1 0 0) of the impregnated catalysts have a tendency to shift to a higher angle, indicating a lower  $d_{100}$  spacing with the introduction of Mg<sup>2+</sup> [1]. These results keep up a correspondence to SEM/EDX results which showed the increase in MgO in the 3MgO/MTS (CNSL) sample. Peaks  $2\theta$  at  $42.8^\circ$  and  $62.2^\circ$  corresponds well with the (2 0 0) and (2 2 0) reflections of MgO in periclase structure [2].



(a)



(b)

Fig. 2 (a) XRD of MTS (CNSL); (b) supported catalysts

Fig. 3 shows the FT-IR transmission spectrum of the MTS (CNSL) and the supported catalysts. A prominent peak was observed at 3400-3500  $\text{cm}^{-1}$  as a strong OH band. This O-H band absorption was not totally attributed to the stretching vibration of the water molecule but partly assigned to the absorption of surface hydroxyl groups.

The intensity of the band at 1650  $\text{cm}^{-1}$  is predicted to be the bending vibration of water molecule physisorbed. The absorption band at 1080  $\text{cm}^{-1}$  is attributed to anti-symmetric stretching of the silica framework. By comparing with the MTS (CNSL) sample, the band slightly shifted to higher wavenumbers in MgO/MTS (CNSL) samples. Reason to that could probably be attributed to the increase of Si-O distance caused by substitution of the small ionic radii of silicon by the larger ionic radii of magnesium.

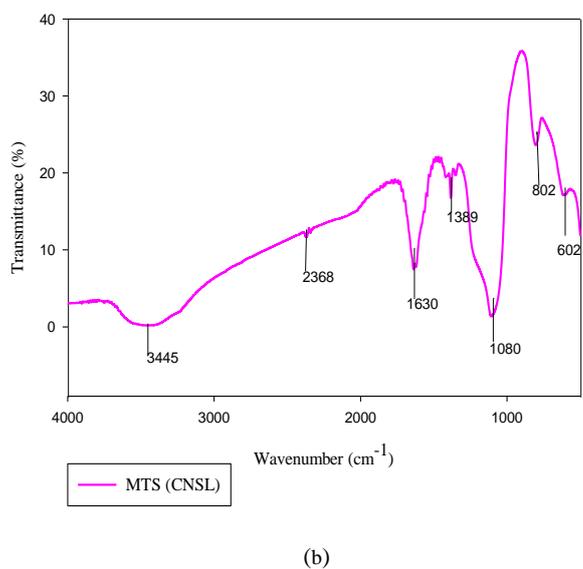
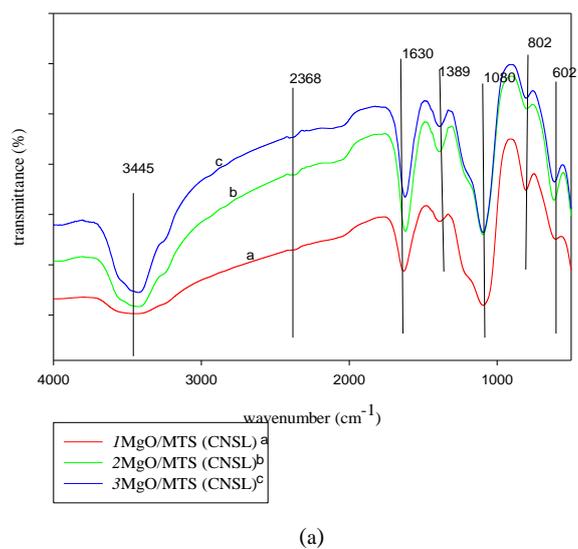
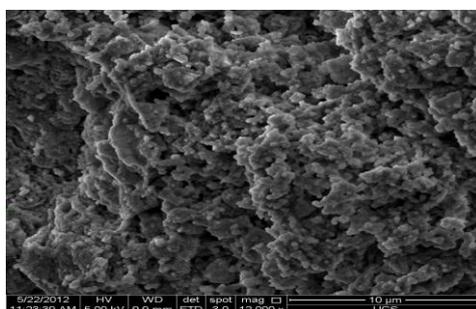
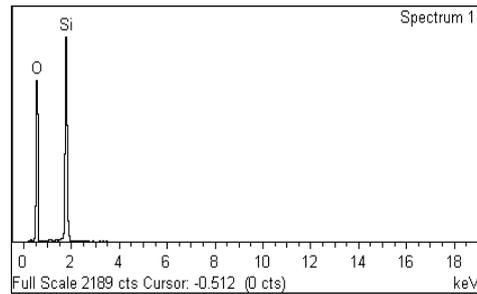


Fig. 3 FT-IR transmission spectrum of: (a) MgO/MTS (CNLS) catalysts; (b) MTS (CNLS) support

SEM images (Fig. 4) show the presence of spherical particles and flaky surface of silica and this is also evident with the EDX results (Table 3).



(a)



(b)

Fig. 4 SEM image of (a) MTS (CNSL); (b) EDX results of MTS (CNSL)

TABLE 3 ELEMENTAL COMPOSITION OF MTS (CNSL)

Element	App Conc.	Intensity Corn.	Weight%	Weight% Sigma	Atomic%
O K	4.32	1.7136	2.53	0.06	64.89
Si K	2.66	1.1081	2.4	0.04	35.11
<b>Totals</b>			<b>4.93</b>		

The cubical structure of the MgO can be observed from the micrographs (Fig. 5) which are evident with XRD results. The composition of MgO in 3MgO/MTS (CNSL) as shown in the EDX Table 4 results was of the higher amount due to an increase in impregnation ratio. For the 3MgO/MTS (CNSL), the Mg/Si distribution was more heterogeneous, suggesting the formation of separated silica and silica-magnesia domains [2].

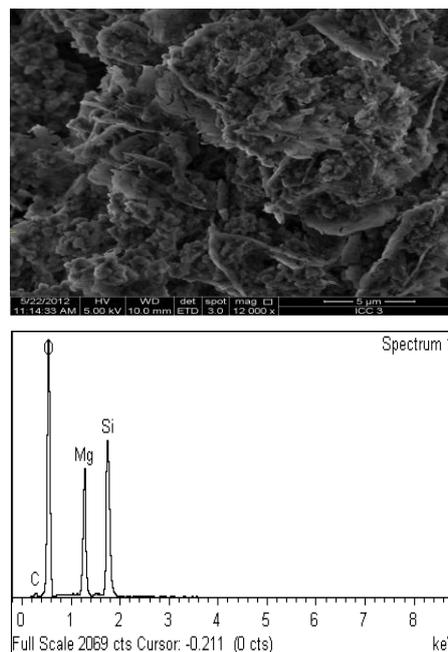


Fig. 5 SEM/EDX images of 3MgO/ MTS (CNSL)

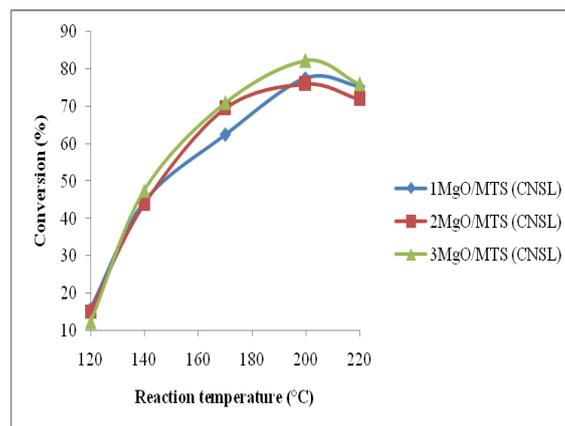
TABLE 4 ELEMENTAL COMPOSITION OF 3MGO/MTS (CNSL)

Element	App Conc.	Intensity Corn.	Weight%	Weight% Sigma	Atomic%
C K	0.09	0.531	0.17	0.04	4.57
O K	5.76	1.8367	3.13	0.07	63.31
Mg K	1.13	1.1543	0.98	0.03	13.01
Si K	1.7	1.0282	1.66	0.04	19.1
<b>Totals</b>			<b>5.94</b>		

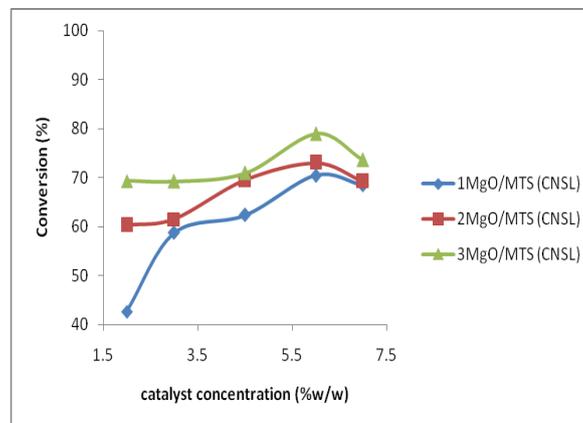
## B. Transesterification Reaction

### 1) Effect of Reaction Parameters

The Effects of reaction temperature, catalyst concentration, and reaction period on transesterification of jatropha oil were investigated using the supported catalyst (Figs. 6 and 7). Mixing rate and methanol to oil ration was set at 500 rpm and 36:1 respectively. The reaction temperature showed to have more influence on the reaction rate and the methyl ester yield because the intrinsic rate constants are strong functions of temperature [5]. In this work, the effects of the reaction temperature on conversions of jatropha oil and methyl ester yield were investigated at five different reaction temperatures 120, 140, 170, 200, and 220 °C based on the Central Composite Design (CCD) experimental design. Each experiment was run at 3.25h with 4.5% wt catalyst. The results indicated in the Fig. 6(a) shows that initially, at 120 °C both of them had a very little effect on the transesterification but methyl ester yield increased sharply as reaction temperature rose, and reached 82.27% at 200 °C with 3MgO/MTS (CNSL) catalyst. However, the yield decreased as temperature increased further, probably due to vaporization of methanol and formed many bubbles, which could inhibit reactions on the three-phase interface [6]. Using a five-level-three-factor CCD the optimized temperature was found to be 200 °C.



(a)



(b)

Fig. 6 Effect of: (a) Reaction temperature (3.25h, 4.5% wt catalyst conc.); (b) Catalyst concentration (170 °C, 3.25h) on Methyl ester yield

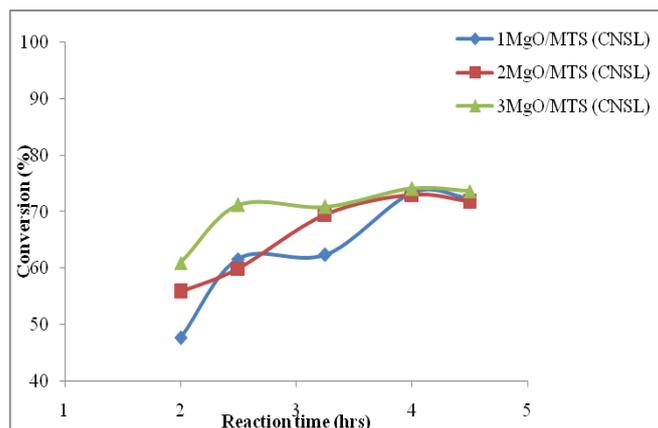


Fig. 7 Effect of reaction time [170 °C, 4.5% wt catalyst conc.] on methyl ester yield

The supported catalysts also had an effect on the methyl ester conversion since they exhibit high activity because they possessed strong basic sites and large surface area. On the basis of Central Composite Rotatable design (CCRD), multiple regressions using Design-Expert 7.1 software, methyl ester yield showed to vary significantly among the catalysts tested with 3MgO/MTS (CNSL) demonstrating the highest conversion. The effect of catalyst concentration used to study the methyl ester conversion was 2.0, 3.0, 4.5, 6.0, and 7.0 %wt referenced to the starting oil weight. It can be seen from Fig. 6(b) conversion of methyl ester increased as the catalyst concentration was raised from 2.0 to 6.0 %wt. The reason was that catalyst concentration increase contact between reactants and catalyst.

However, conversion decreases at 7.0 %wt because it is believed that, high catalyst concentrations in the mixture will lower the effect of mixing that is also considered as a significant factor for the transesterification process [22]. Furthermore, when excessive catalyst was used, the transesterification process was easily emulsified and resulted in hard separation of products. So the optimized catalyst concentration was 6.0 %wt using CCD method.

Methyl ester yield was observed to increase with time (Fig. 7). In the beginning, the reaction was slow due to the mixing and dispersion of alcohol into the oil. After a while, the reaction proceeded very fast because sufficient time was needed for the diffusion of molecules between the three different phases i.e., oil-methanol-catalyst to take place. However, when reaction time was longer, the yield decreased. This was probably due to the occurrence of reversible reaction [23].

## 2) Catalyst Screening

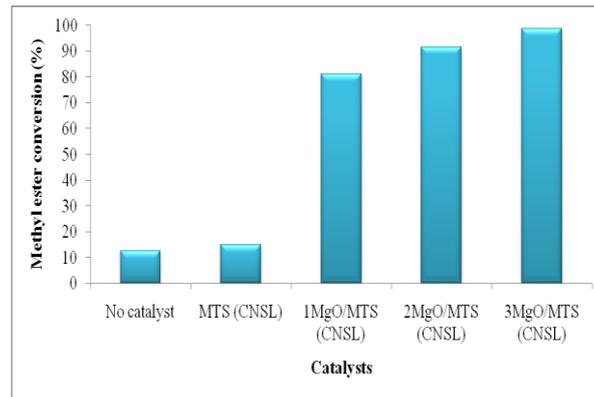
Catalytic screening of the supported catalysts used in the transesterification process was done by comparing their conversions. The same reaction conditions (170 °C, 3.25 h, and 4.5 % wt.) were employed in each experiment for direct comparison among the catalysts as summarized in Fig. 8(a). The ester conversions of the reactions catalyzed by pure silica without loading showed almost similar conversion to that of the control experiment, where no catalyst was used.

## 3) Kinetic Parameters

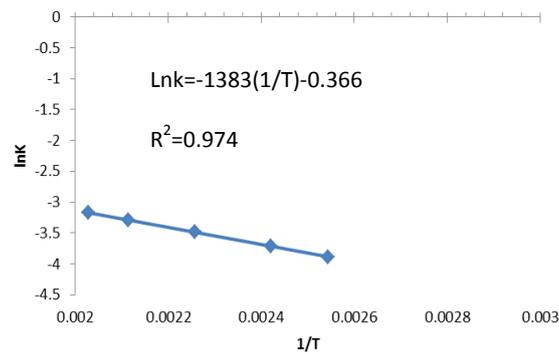
The kinetic study was done based on the reactions conditions that gave the paramount yields of methyl esters during the optimization studies of MgO-MTS (CNSL) as a heterogeneous catalyst. Transesterification process usually proceeds in three steps, whereby, triglyceride reacts with methanol to produce diglycerides, which further reacts with methanol to give monoglycerides that finally reacts with methanol to produce methyl esters and glycerol [23, 24]. Eq. (1) shows the overall chemical reaction from triglycerides to methyl esters.



Where, TG and GL stand for triglyceride and glycerol respectively.



(a)



(b)

Fig. 8 (a) Methyl ester conversions of transesterification reactions; (b) first order reaction rate constant in Arrhenius plot [1MgO/MTS (CNLS)]

With the whole reaction assumed to proceed in first order as a function of concentration of methyl esters [24], a simple first order differential equation (shown in Eq. (2)) expresses the first order rate constant of the reaction with respect to percentage methyl esters, which increases as a function of reaction time.

$$-Rate = \frac{-d(ME)}{dt} \quad (2)$$

where,  $ME$  stands for percentage methyl esters.

Introducing the rate constant ( $k$ ), the first order rate equation can as well be written as:

$$-Rate = k(ME)$$

Then, Eq. (2) can be modified as:

$$\frac{-d(ME)}{dt} = k(ME)$$

Defining the initial concentration of methyl esters as  $ME_0$  at time  $t=0$  and the concentration of methyl esters at a time,  $t$ , as  $ME_t$ , integration of the above equation gives:

$$\int_{ME_0}^{ME_t} \frac{d(ME)}{(ME)} = k \int_0^t dt$$

Then finally,

$$k = \frac{\ln(ME_t) - \ln(ME_0)}{t} \quad (3)$$

where  $k$  is the rate constant, for 3MgO/MTS (CNLS) was higher (Table 5) because higher methyl esters were obtained compared to other catalysts, probably due to availability of more active sites for reactants to attach.

Eq. (4) presents the Arrhenius equation which includes the rate constant,  $k$ , the frequency factor,  $A$ , and the activation energy,  $E_a$ .

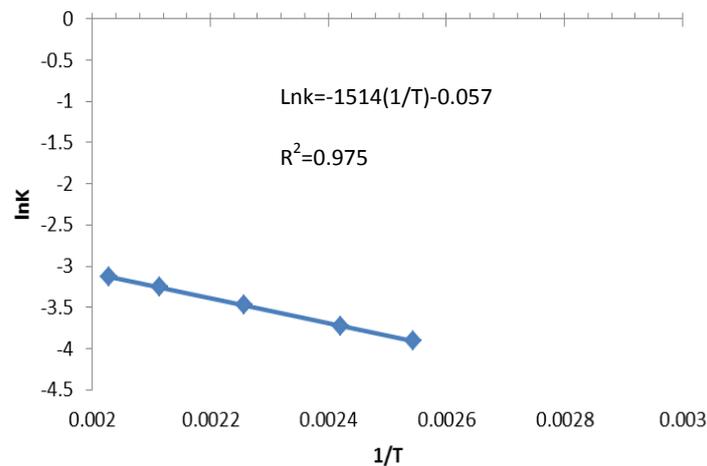
$$k = Ae^{-E_a/RT} \quad (4)$$

Where,  $R$  and  $T$  stand for universal gas constant and temperature respectively.

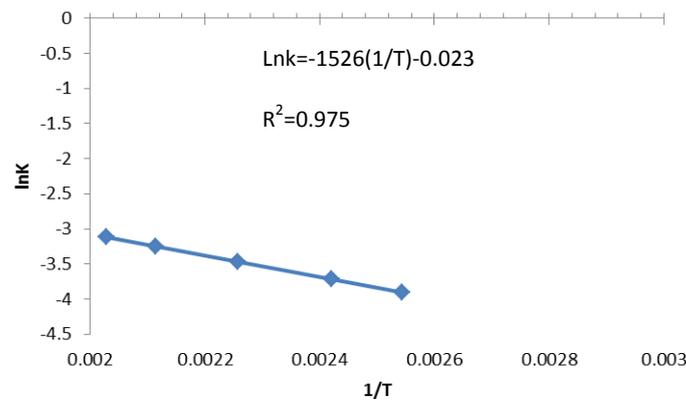
Eq. (4) can be rearranged as:

$$\ln k = \ln A - E_a / RT \quad (5)$$

It can be shown in Figs. 8 (b), 9 (a) and (b) the three tested catalysts had linear plots. It signifies that, the reactions were first order reactions. From the plots activation energies were obtained as shown in Table 5. Among the catalysts, 3MgO/MTS (CNSL) has higher rate constant indicating higher reaction rate of reaction and higher methyl ester yields.



(a)



(b)

Fig. 9 First order reaction rate constant in Arrhenius plot: (a) 2MgO/MTS (CNSL); (b) 3MgO/MTS (CNSL)

TABLE 5 RATE CONSTANTS AND ACTIVATION ENERGIES

	Reaction constant ( $\text{min}^{-1}$ )	Activation energy (J/K.Mol)
1MgO/MTS (CNSL)	0.02831	11499
2MgO/MTS (CNSL)	0.02886	12588.2
3MgO/MTS (CNSL)	0.02896	12687.9

#### IV. CONCLUSION

In this study, three mesoporous catalysts prepared using different Mg/Si ratios had varying selectivity toward the transesterification reaction of jatropha oil with methanol depending on their basicity, base site strength, and surface area. When reaction was carried out in a batch reactor 3MgO/MTS (CNSL) was found to be the most effective among all, reaching a high conversion of 82.27 %. The optimized conditions were as follows: 200 °C, 4 h, 6.0 %wt catalyst concentration with molar ratio of methanol to oil and stirring speed being set at 36:1 and 500 rpm respectively.

It was found that the activity of a catalyst does not depend solely upon its basic properties or any isolated determining factors, such as surface area, porosity, and surface Mg concentration. It suggests that the activity of a catalyst to be a result of the combined effects of the multiple attributes of its support material. The surface Mg concentration determined the amount of catalysts available for catalyzing the transesterification reaction, which appeared to be dominated over other physical properties of the support material.

In general, among the catalysts used, MTS (CNSL) support impregnated with MgO was the promising catalyst for the transesterification of vegetable oil for biodiesel production, indicating that it has the potential to be utilized as a heterogeneous catalyst for such reactions.

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