

Calcination Temperature of Nano MgO Effect on Base Transesterification of Palm Oil

Abdul Rahim Yacob, Mohd Khairul Asyraf Amat Mustajab, and Nur Syazeila Samadi

Abstract—Nano MgO has been synthesized by hydration and dehydration method by modifies the commercial MgO. The prepared MgO had been investigated as a heterogeneous base catalyst for transesterification process for biodiesel production using palm oil. TGA, FT-IR and XRD results obtained from this study lie each other and proved in the formation of nano MgO from decomposition of $Mg(OH)_2$. This study proved that the prepared nano MgO was a better base transesterification catalyst compared to commercial MgO. The nano MgO calcined at 600°C had gives the highest conversion of 51.3% of palm oil to biodiesel.

Keywords—Hydration-dehydration method, nano MgO, transesterification, biodiesel.

I. INTRODUCTION

THE world energy supply had relied to non-renewable fossil crude oil for more than two centuries. Energy generation for transportation was a major player of about 90% from total world energy consumed. Highly dependence on this energy have a negative impacts such as released of green house gases which comprise of carbon dioxide, carbon monoxide, nitrogen oxides, unburned hydrocarbon and sulphur-containing residues. This on the other hand can cause global warming and other environmental problems such as pollutions and acid rains [1]. The World Energy Forum has predicted less than 10 decades more; all these energy supplies will be exhausted [2]. Added by the uncertainty in crude oil price and limited resources of fossil oil makes the situation worsens. As a solutions, identifying and channeling renewable raw materials into the manufacture of liquid fuel as an alternatives had been the main focus for researches to cater new technology and keep in pace with society's need for new renewable power for the future [1]

Research on biodiesel or monoalkyl ester of long-chain fatty acids has become more attractive recently, for its environmental friendly and the fact that it can be produce from renewable resources, such as vegetables oil, animal fats, algae and waste cooking oils. Biodiesel has a tremendous potential in reducing the level of pollutants and carcinogen agents, because it produces less exhaust emissions in term of unburnt hydrocarbon, carbon monoxide, carbon dioxide, particular matter and sulphur-containing particles [3]-[4].

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Biodiesel can be applied on modern diesel engines without any modification required, thus offer the same performance and engine durability as petroleum-based diesel [5]-[6]. Usage of biodiesel will give positive approach in term of stability between agriculture, economic development and positive impact to the environment [7].

Transesterification is a process of displacement of an alcohol group from an ester by another alcohol [8]. Vegetable oils consist of triglycerides, a bulk molecule that has 3 molecules of fatty acids with high viscosity. Biodiesel on the other hand, is the transesterification process or reaction of a fat or oils with an alcohol to form straight chain of ester and glycerol molecules. This is demonstrated by schematic reaction Fig. 1. Normally for this reaction methanol or ethanol was used. This reaction however, required a catalyst to promote the reaction, such as acid catalyst, sulphuric acid [9], base catalyst such as sodium hydroxide, sodium methoxide [10]-[11] and magnesium oxide [12] and lipases [13]-[15].

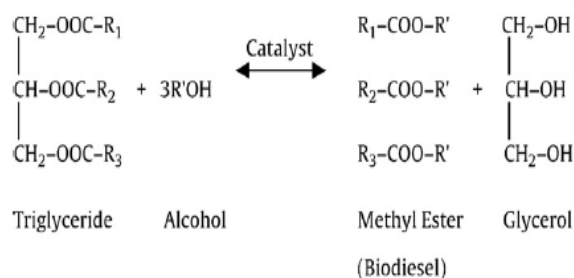


Fig. 1 General equation transesterification of vegetable oil to biodiesel

Production of biodiesel using base catalyst has become more favorable compared to other catalysts and has been up scale applied to industries. Even though faster with percentage of conversion around 95 % after 90 min, they had several drawback such as need extra neutralization by mineral acids, washing of the product biodiesel and glycerol. Here the catalyst cannot be reutilized, large amounts of wastewater and the process becomes costly [14]. To overcome this problem heterogeneous base catalyst was introduced. Heterogeneous base catalysts bring several advantages such as the catalyst can easily be separated from the reaction mixture, easy regeneration, less corrosive character of products, no washing required and leading to safer, cheaper and more environmental friendly approach [5]. The total cost of biodiesel production using heterogeneous base catalyst was more economical with a higher quality of methyl ester [15].

This research will be conducted to study the transesterification reaction of palm oil to biodiesel using prepared nanosized MgO as a heterogeneous base catalyst. Study will be focused on the preparation of nanosized MgO via different heating temperatures and their effect towards the basic catalytic activity for the transesterification of palm oil.

II. EXPERIMENTAL

A. Preparation of Nano Magnesium Oxide via Hydration-Dehydration Method

About 12.0 g of commercial MgO was dispersed in 150 mL distilled water and refluxed at about 100°C for 24 h to yields magnesium hydroxide, Mg(OH)₂. The Mg(OH)₂ precipitate was then collected by filtration and dried in oven of 100 ± 5°C for overnight to remove any excess water. Dried Mg(OH)₂ was grinded using mortar and pastel and this process is named hydration method. For dehydration method, the formation MgO, about 0.2 to 0.5 g of the prepared sample was then transferred into a quartz tube attached to a vacuum line system of 10⁻³ mbar. The sample in the quartz tube is then heated at selected temperature of 100, 200, 300, 400, 500, 600, 700 and 800 °C respectively using a heating mantel. This activation steps will be carried out for 4 hours to study the decomposition of Mg(OH)₂.

B. Characterization of Prepared Nano MgO

The prepared nanosized MgO will characterize using several methods. Thermal decomposition of Mg(OH)₂ was analyzed using Mettler-Toledo Q100 with heating rate 10°C/min in air condition FTIR spectra were recorded using Thermo Nicolet Avatar 370 DTS in the range of 400 to 4000cm⁻¹. The XRD analysis was carried to determine the crystallinity and the particle size for the prepared MgO while commercial MgO and Mg(OH)₂ for comparison. The XRD diffractograms were acquired on a Siemens D5000 powder instrument using Cu-K_α radiation (λ = 0.15148nm, kV = 40, mA = 40).

C. Transesterification Reaction

About 0.1 g of the prepared nanosized MgO and 10-15g of methanol added into two-neck round bottle flask. Reaction mixture will be refluxed at 65 ± 5 °C for 30 minutes. About 20g of palm oil was added into the reaction vessel and continued refluxed for 4 hours to completing the transesterification reaction. Upon completion, cool the mixture at room temperature and centrifuged at 6000 rpm for 30 minutes to separate the product biodiesel or fatty acid methyl esters with the byproduct of glycerol and any excess of methanol. After centrifugation, 3 layers will be obtained which comprised of the upper layer of excess methanol, middle layer the biodiesel and the bottom layer the prepared MgO and glycerol. The first and second layer will be collected and transferred into separation funnel and allow for better separation of biodiesel and methanol. As for comparison, commercial MgO will also be used to study the activity and reactivity in the transesterification process. The gas chromatogram was recorded using a Hewlett Packed Gas Chromatography model 6890. Helium gas was used as the

mobile phase and column DB-Wax with specification 0.25μm thicknesses, 30 m length and 0.20 mm internal diameter as the stationary phase with Flame Ionization Detector (FID). The percentage conversion of biodiesel was calculated using the following equation:

$$\frac{\text{Peak area of Oil} - \text{Peak area of Methyl Ester}}{\text{Peak area of Oil}} \times 100$$

III. RESULTS AND DISCUSSIONS

A. Thermogravimetry Analysis

This analysis was done in order to determined the temperature profile for the formation of MgO via dehydration of Mg(OH)₂ at different temperatures. Fig. 2 shows the total weight lost with different temperature regions.

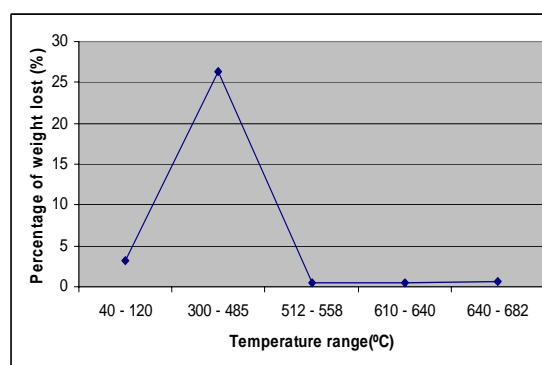
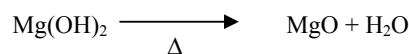


Fig. 2 Percentage of weight lost at different temperature regions from TGA

Based on this graph, first region of weight lost occurred at temperature 40 to 120 °C, around 3.2%, correlative to the removal of adsorbed water molecule. The major weight lost happens at temperature 300 to 485 °C; with almost 26.4% indicating the decomposition of magnesium hydroxide to magnesium oxide. This decomposition steps may be illustrated as starting point for the formation of MgO from their hydroxide with water molecules as the by-product. The chemical equation of the decomposition process may be describe below:



For the temperature regions of about 512 to 682 °C, less than 1 % of weight lost took place and this might be associated to the complete decomposition of Mg(OH)₂ to form MgO. Following on the TGA thermogram, the total weight lost for the decomposition Mg(OH)₂ from temperature 40 to 700°C, approximately 31.2% is the formation of water. This result was very close to the stoichiometric value for the decomposition of magnesium hydroxide to magnesium oxide of about 30.8% [16].

B. FTIR Spectra

Fig. 3 shows the FTIR spectra for $\text{Mg}(\text{OH})_2$ and the prepared MgO which was heated at temperature 400 to 600°C in vacuum. There are two types of OH bonding exist in these spectra. First, is the O-H stretching and bending bonded with Mg and secondly, O-H stretching and bending attached at the surface of the samples. The O-H stretching bonded with Mg will be appeared as a sharp peak at 3702.62cm^{-1} , bending bond at 1490.38cm^{-1} . For the second, O-H stretching appears as a broad band at $3600 - 3200\text{cm}^{-1}$ while the bending at 1639.70cm^{-1} . These bands had been previously characterized by several researchers [17]. As the temperature was raised, the peak intensity of O-H stretching bonded with Mg become smaller at temperature 400°C and finally disappears when the temperature reaches 600°C.

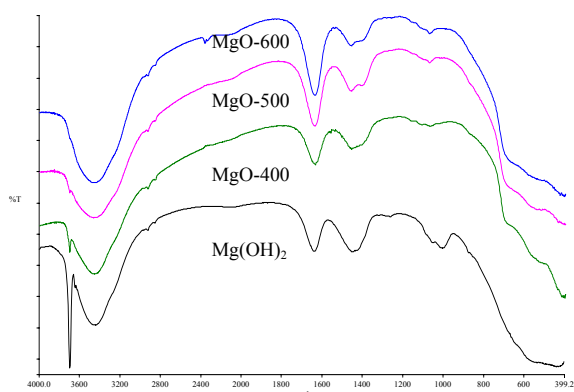


Fig. 3 FT-IR spectrum of $\text{Mg}(\text{OH})_2$ and the prepared MgO which heated at temperature 400 to 600 °C

The spectra also show water molecules adsorbed at surface MgO and this is proven by the present of broadband at $3600 - 3200\text{cm}^{-1}$ representative to O-H stretching band and bending band of O-H at 1639.70cm^{-1} . This occurrence happens due to the special characteristic of MgO, which may adsorb moisture from the environment. These FT-IR spectra also support the TGA thermogram (Fig. 1) which designates the formation of MgO from the decomposition of $\text{Mg}(\text{OH})_2$ which begin at 300°C and completed at temperature 500°C and above.

C. X-Ray Powder Diffraction

X-Ray Powder Diffraction (XRD) gives information of the structure transformation on crystallization. Powder XRD patterns were collected in order to investigate diversification before and after heating process to the sample. The diffractogram were useful to determine the type of crystallite as well as the purity of the sample. Fig. 4 (a)-(d) show the XRD diffractogram of $\text{Mg}(\text{OH})_2$ and the prepared MgO.

Based on Fig. 4 (a), there are seven typical diffraction peaks at 18.582° , 38.059° , 51.009° , 58.707° , 61.965° , 72.157° and 81.400° which may be assigned to the characteristic peak of hexagonal $\text{Mg}(\text{OH})_2$ crystals. As the temperature increased (b)-(d), decomposition begins, with all the previous peaks become smaller, whilst cubic MgO crystal start to appears. This result again supports those of TGA and FTIR.

The particle size for the prepared surface modified MgO was calculated using Sherrer's equation [18] and the resulting particle size was of approximately 10 nm. Thus, the prepared surface modified MgO was actually at nano size [19].

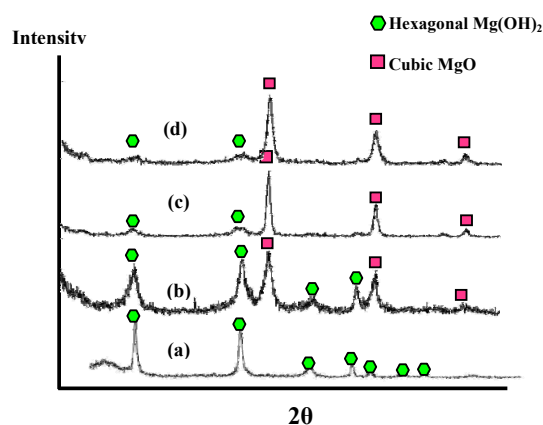


Fig. 4 XRD diffractogram for (a) $\text{Mg}(\text{OH})_2$ (b) MgO-400, (c) MgO-500 and (d) MgO-600

D. Biodiesel Yield

The heterogeneous base catalysis transesterification reaction using various temperatures of calcinations of nano MgO is shown by Fig. 5. The production of biodiesel or also known as FAME from palm oil was successfully plotted. In this experiment no saponification was observed and proved that the catalyst is free from any absorbed water. Fig. 5 also depicts the percentage conversion of palm oil to biodiesel for all catalysts.

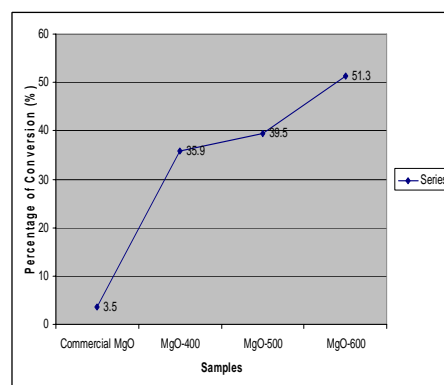


Fig. 5 Percentage conversion of biodiesel using different prepared MgO

From this line graph Fig. 5, the percentage conversion was increase when the temperature of preparation nano MgO increases. The MgO-400 only manages 35.9% conversion of palm oil to biodiesel, while the percentage increases to 39.5% when using nano MgO-500. The highest conversion was recorded when MgO-600 took place as the catalyst, with 51.3% conversion. Commercial MgO however managed only 3.5% [14]. This finding proved that this base catalyst had a

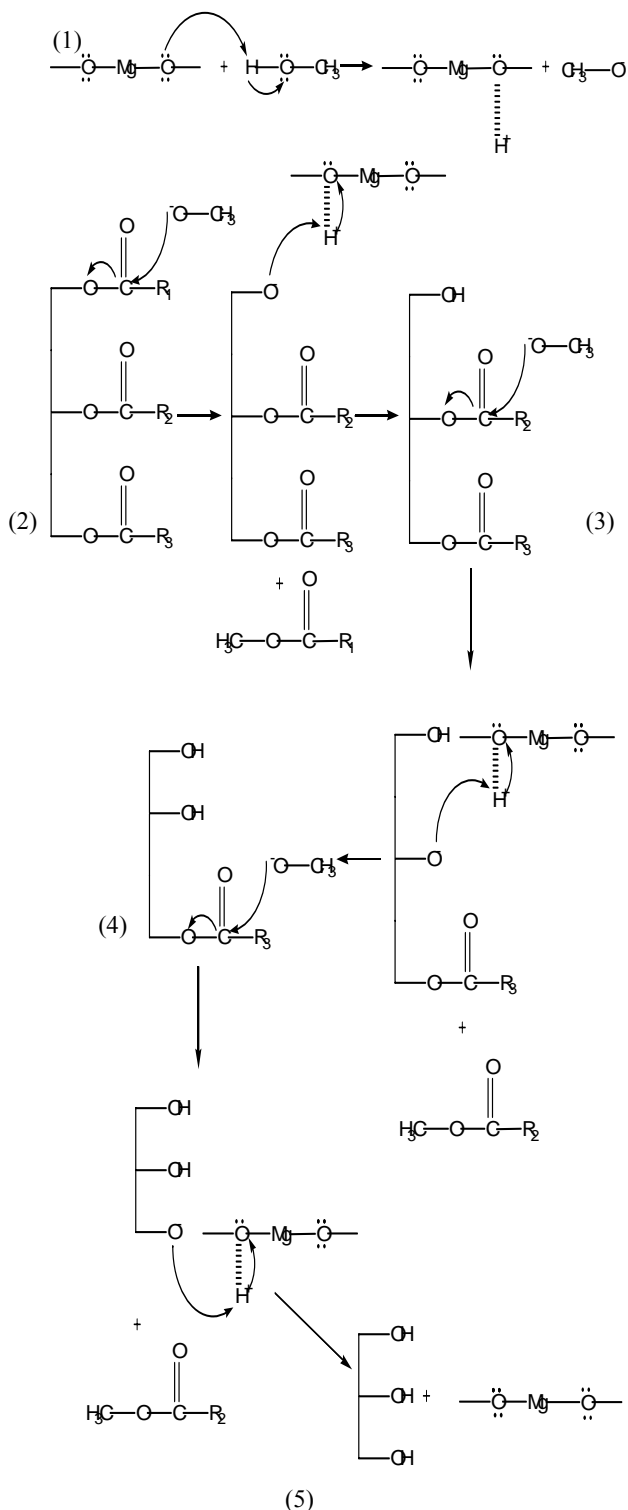


Fig. 6 Proposed mechanism reaction for transesterification of palm oil to biodiesel using the prepared nano MgO

better activity, compared to work done by Wang *et al.*, [20]. The ability of the prepared MgO to abstract H^+ from methanol to produce anionic intermediates was the basic idea for the transesterification process. The proposed schematic

reaction is as shown by Fig. 6. Another advantage in using this nano MgO is the reaction took place at mild condition, safe, easy to upscale and low cost-production compared to supercritical conditions of high temperature and pressure [21]-[23]. As in theory, the catalysts can act as a base toward the reactants, either by abstraction of proton from the reactants as in Bronsted base, or by donation of an electron pair to the reactants as in Lewis base, to form anionic intermediates, which undergo catalytic cycle and start the reactions [24]. Initially, the mechanism started by abstraction of H^+ from methanol to produce anionic intermediates, known as the methoxide ion. The carbonyl group of the fatty acids will then be attacked by the methoxide and breaks the bonds between fatty acids and glycerol, which produce fatty acid methyl ester and diglyceride. O^- at diglyceride will then abstract a proton from MgO to form $-\text{OH}$ group. This reaction will continue till completion when three moles of fatty acid methyl ester and glycerol were formed.

IV. CONCLUSION

The results obtained proved that nano MgO was successfully prepared via hydration and dehydration method using commercial MgO. The XRD, TGA and FT-IR data shows the optimum temperature for the decomposition $\text{Mg}(\text{OH})_2$ to form nano MgO. Calculation from XRD proved the formation of nano MgO with particle size *ca* 10 nm. The percentage of conversion palm oil to biodiesel was about 51.8% when applied MgO-600 as a heterogeneous base catalyst.

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REFERENCES

- [1] A. Ishizaki, K. Sonomoto, G. Kobayashi, C. Nolasco-Hipolito and E. Crabbe. "Biodiesel production from crude palm oil and evaluation of butanol extraction and fuel properties". *Process Biochemistry*, vol 37 (1), pg 65 – 71.2001.
- [2] Y.C. Sharma, B. Singh and S.N. Upadhyay. "Advancements in Development and Characterization of Biodiesel: A review". *Fuel*, vol 87, pg 2355 – 2373.2008.
- [3] E.G. Shay. "Diesel Fuel from Vegetable Oils: Status and Opportunities". *Biomass and Bioenergy*, vol 4,pg 227 – 242. 1993.
- [4] T. Krawczyk. "Biodiesel – Alternative Fuel Makes Inroads but Hurdles Remain". *INFORM*, vol 7, pg 801 – 829. 1996
- [5] T.F. Dossin, M.F. Reyniers and G.B. Marin. "Kinetics of Heterogeneously MgO-Catalyzed Transesterification." *Applied Chemistry B: Environmental*, vol 61, 35 – 45. 2006
- [6] T.F. Dossin, M.F. Reyniers, R.J. Berger and G.B. Marin. "Simulation of Heterogeneously MgO-Catalyzed Transesterification for Fine-chemical and Biodiesel Industrial Production". *Applied Chemistry B: Environmental*, vol 67, pg 136 – 148. 2006.
- [7] L.C. Meher, D. Vidya Sagar and S.N. Naik. "Technical Aspects of Biodiesel Production by Transesterification – A Review". *Renewable and Sustainable Energy Reviews*, vol 10, pg 248 – 268. 2006.
- [8] A. Srivastava and R. Prasad. "Triglyceride-based Diesel Fuels". *Renewable and Sustainable Energy Reviews*, vol 4, pg 111 – 133. 2000.
- [9] S. Zheng, M. Kates, M.A. Dube and D.D. McLean. "Acid-Catalyzed Production of Biodiesel from Waste Frying Oil". *Biomass and Bioenergy*, vol 30, pg 267 – 272. 2006.

- [10] F. Ma and M.A. Hanna. "Biodiesel Production: A Review". *Bioresource Technology*, vol 70. pg 1 – 15. 1999.
- [11] A.K. Dalai, A. D'Cruz, M.G. Kulkarni and L.C. Meher. "Synthesis of Biodiesel from Canola Oil using Heterogeneous Base Catalyst". *J. Am. Oil Chem. Soc.*, vol 84. pg 937 – 943. 2007.
- [12] J.M. Marchetti, V.U. Miguel and A.F. Errazu. "Possible Methods for Biodiesel Production". *Renewable and Sustainable Energy Reviews*, vol 11. pg 1300 – 1311. 2007
- [13] L.A. Nelson, T.A. Foglia and W.N. Marmer. "Lipase-Catalyzed Production of Biodiesel". *Journal American Oil Chemistry Society*, vol 8(73), pg 1191 – 1195. 1996.
- [14] G. Arzamendi, E. Arguñarena, I. Campo, S. Zabala and L.M. "Gandia. Alkaline and Alkaline-earth Metals Compounds as Catalysts for the Methanolysis of Sunflower Oil". *Catalysis Today*, vol 133 - 135. pg 305 – 313. 2008.
- [15] E. Santacesaria, R. Tesser, G. Minutillo, M. Cozzolino, M.Ledda and M.Di Serio. "From Homogeneous to Heterogeneous Catalysts in Biodiesel Production". *Ind. Eng. Chem. Res.*, vol 46. pg 6379 - 6384. 2007.
- [16] M.S. Mel'gunov, V.B. Felonov, E.A. Mel'gunova, A.F. Belido, and K.J. Klabunde. "Textural Changes during Topochemical Decomposition of Nanocrystalline $Mg(OH)_2$ to MgO ". *The Journal of Physical Chemistry B*, vol 107(11). pg 2427 – 2434. 2003.
- [17] H.S. Jung, J.K. Lee, J.Y. Kim and K.S Hong. "Crystallization Behaviors of Nanosized MgO Particles from Magnesium Alkoxides". *Journal of Colloid and Interface Science*. vol 259. pg 127 – 132. 2003.
- [18] K. Itatani, M. Nomura, A. Kishioka, and M. Kinoshita. "Sinterability of Various High-purity Magnesium Oxide Powders". *Journal of Materials Science*. vol 21. pg 1429 – 1435. 1986.
- [19] G. Duan, X. Yang, J. Chen, G. Huang, L. Lu, and X. Wang. "The Catalytic Effect of Nanosized MgO on the Decomposition of Ammonium Perchlorate". *Powder Technology*. vol 172. pg 27 – 29. 2007.
- [20] Y. Wang, S. Zhu, H. He and X. Liu. "Transesterification of Soybean Oil to Biodiesel using SrO as a Solid Base Catalyst". *Catalysis Communications*. vol 8. pg 1107 -1111. 2007.
- [21] L. Wang, and J. Yang. "Transesterification of Soybean Oil with Nano- MgO or Not in Supercritical and Subcritical Methanol". *Fuel*. vol 86. pg 328 – 333. 2007.
- [22] S. Ngamprasertsith, R. Sawangkeaw, S. Makmee and K. Bunyakiat. "Continuous Production of Biodiesel via Transesterification from Vegetable Oils in Supercritical Methanol". *Energy and Fuels*. vol 20. pg 812 – 817. 2006.
- [23] A.K. Singh and S.D. Fernando. "Transesterification of Soybean Oil Using Heterogeneous Catalysts". *Energy Fuel*. vol 22(3). pg 2067 – 2069. 2008.
- [24] H. Hattori. "Solid Base Catalysts: Generation of Basic Sites and Application to Organic Synthesis". *Applied Catalysis A: General*. vol 222. pg 247 – 259. 2001.