Effect of microwave irradiation on the etherification of biodiesel-derived glycerol in a solvent free process

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Abstract. This study revolves mainly about the effect of etherification of glycerol to polyglycerols using a heterogeneous catalyst under microwave radiation. Microwave radiation serves as a purpose to shorten the reaction time of the procedure. Cerium Nitrate and Lithium Nitrate was used to modify montmorillonite K-10 clay (MK-10) which was then used to catalyze the etherification process. They were several reaction parameters that were observed for this study which were: catalyst concentration and reaction time. The parameter that played a vital role was the catalyst concentration which affected the percentage conversion of glycerol, selectivity of pentaglycerols, selectivity of cyclic diglycerols and undesired cyclic diglycerols. It was observed that with a high temperature and high reaction time, the amount of undesired cyclic glycerol was increased. Optimum amount of catalyst conversion promoted higher amount of desired cyclic glycerol. Longer reaction time is needed to produce higher yield and selectivity. The production of undesired cyclic diglycerol can be removed with the help of vacuum distillation. The highest glycerol conversion was found of 94% with highest yield of desired products of 70% polyglycerol at 260 °C and 5 h of reaction time. The selectivity towards undesired high order polyglycerol was found 24% at same reaction conditions.

Keywords-component: glycerol; etherification; heterogenous; microwave irradiation

1. Introduction

The market for glycerol started picking up with some fluctuations occasionally just few decade ago during 90’s. It was the time for biodiesel to introduced as alternative energy of fossil fuel as a quest for sustainable growth [1,2]. Due to continuous demand and production of biodiesel, an overproduction of crude glycerol was led as by-product. The excessive production of crude glycerol scarred the price of glycerol in the market due to the amount of impurities in the glycerol produced from the biodiesel transesterification [3-7]. On the other hand, the refining industry took a turn and the equipment to refine and purify gycerine became very expensive and unaffordable [5,8]. This became a liability to
the manufacturers as the price of glycerol dropped drastically and the equipment to purify glycerol was too expensive. Researchers work to find out economical active process for conversion and utilization of this crude glycerol [6,9]. The etherification process of glycerol with a suitable catalyst to produce polyglycerol was found one of the most feasible and economical process for conversion of crude glycerol [10,11]. This process can also be an attribution to the biodiesel industry to utilization of a waste crude glycerol to valuable product. As for glycerol, they can also utilize to form polyglycerols in the form of mono-, di- and triether [8]. Polyglycerol consists of glycerol in smaller compounds of different molecular weights and increasing number of hydroxyl group. The most common and has many applications in the industry is the di-glycerol and tri-glycerol [9,12]. Low degree polyglycerols such as the diglycerols and triglycerols have become a very useful applicant in the industry targeting food industries and as a fuel additive [13-15]. The most essential characteristics for polyglycerols are its light colored, good odor and sweet in taste. Polyglycerol has greater flexibility and functionality compared to glycerol [16-18]. Catalyst is a compound that is added to chemical reactions to speed up the reaction without having to change the reactants and product chemically and physically [19]. The main two different type of catalyst, homogenous and heterogeneous catalyst were studied by many researchers and elaborated their behaviour according to their application. The conventional method used for the conversion of glycerol to polyglycerols was over homogenous alkaline catalyst with the production of significant amount of polyglycerol. This etherification process was done by conventionally heated at a very high temperature of 270 °C at a pressure of normal or reduced level [20-23]. Water removal was done with flowing a stream of inert gas as blanket during the process.

Conventional heating usually requires a very long reaction time [24]. Bookong and his research group worked on heating system and found that the use of microwave irradiation compared to conventional heating as a method to heat organic reactions leads to an efficient green chemistry procedure and provides simple and safe conditions [25]. Additionally, the Joint Expert Committee on Food Additives (JECFA) have set a rule for polyglycerols used as food additives to have a mixture of di-, tri- and tetra- of not less than 70-75% and not more than 10% hepta - or bigger compound in the specifications of polyglycerols allowed [16,26].

The main objective of this research work was to determine the effect of the usage of microwave radiation on etherification of glycerol in a solvent free process using a heterogeneous solid catalyst. The scope of the study however mainly compromises on the parameters studied for the overall process of etherification of glycerol to produce polyglycerol using the new methods introduced compared to the conventional methods which serves as a greater advantage. The reaction time and the catalyst concentration were main studied parameters. The reaction temperature was observed to play the most vital role in this project because of a slight increase or decrease in temperature, alter the oligomerization production results. Additionally, the reaction temperature was also found having severe effect on the amount percentage of glycerol converted and desired diglycerol produced.

2. Materials and Methods

A. Materials

Anhydrous glycerol (>99%) was obtained from R&M Chemicals, Ltd., Malaysia while lithium hydroxide (99%) was purchased from BDH, UK. Meanwhile, the catalyst support i.e. montmorillonite K10 clay was supplied by Sigma–Aldrich. All the received chemicals were used as received.

B. Preparation and characterization of clay catalyst

A 250 mL round bottom flask equipped with a reflux condenser was charged with 10 g of MK-10, measured amount of Cerium nitrate and Lithium Nitrate and 100 mL of deionized water. This mixture was heated under reflux for 12 h and the slurry was allowed to cool to room temperature. The solid part was then separated from the liquid by centrifugation and it was washed by resuspending it in 500 mL of deionized water followed by centrifugation. This whole procedure was repeated for two more
times to ensure complete removal of any soluble species. The solid was then calcined in a furnace at 450 °C for 4 h. The clay was then named Clay Ce/MK-10, Li/MK-10 and CeLi/MK-10 based on the metal used to modify the clay and was subsequently characterized FTIR, surface analyser (BET) and Scanning Electron Micrography (SEM). The base strength of the catalyst (Hₗ) was determined using Hammett indicators. For comparison, the original MK-10 was also characterized using the same methods.

C. Microwave radiation
The etherification of glycerol was experientially set up. The clay was added to glycerol in a round bottom flask. The etherification took place in a microwave reactor with reaction temperature of 260 °C, catalyst concentration of 1% and 4%, microwave power of 2.45 Ghz and 300 W, atmospheric pressure and reaction time of 1 h to 4 h with and interval of every 30 minutes. To prevent re-entering of water, a bump trap and a condenser was connected to a glass reactor. The products taken at every interval of time were analysed using a High-Performance Liquid Chromatography (HPLC). The parameters that were tested under the influence of microwave were the reaction time of the etherification of glycerol process and the effect of catalyst metal weightage on the polyglycerols produced during etherification process. Not only that the different types of method used for etherification process were analysed and the suitable catalyst was studied using microwave radiation.

![Figure 1. Schematic diagram of reactor setup](image)

D. Catalyst weightage
In catalyst preparation, calculations based on Cation Exchange Capacity were calculated. This was to understand how much capacity the clay can withstand. Some catalyst used can damage the capacity and porosity of the clay which is why prior calculations based on the Cation Capacity Exchange of the soil with molecular weight and valency of the catalyst used to modify the clay. First, an assumption was made to how many percentage of Cerium Nitrate, Ce(NO₃)₃·6H₂O that can be used. The assumption made was 5% of catalyst to modify the clay.

\[
\frac{x}{x + \text{Amount of clay, g}} = \text{Catalyst weightage(%)}
\]

\[
\text{Amount of metal (g)} = \frac{x}{\text{molecular weight of Metal (g mole)}} \times \text{molecular weight of solution (g mole)} \times \text{purity of the solution (g mole)}
\]
Table 1 shows the amount of metal deposited for each catalyst weightage that was tested in the microwave reactor for a constant 260 °C and 4 h reaction time to study the effect of different amount of metal loading on the surface of the catalyst.

| Weightage (%) | x-value for 5g of clay | Cr metal (g) | Li Metal (g) |
|---------------|------------------------|--------------|--------------|
| 1             | 0.05                   | 0.157        | 0.507        |
| 2             | 0.102                  | 0.319        | 1.034        |
| 3             | 0.155                  | 0.485        | 1.571        |
| 4             | 0.208                  | 0.651        | 2.108        |
| 5             | 0.263                  | 0.823        | 2.67         |

E. Reaction time
Normal conventional method for the glycerol to convert took place up to 8 h and sometimes it took up to 12 h for a full conversion. The microwave reaction was tested for a full conversion of glycerol. The time of the microwave was tested for a period of 7 h and the glycerol sample is collected every 1 h to study the percentage of glycerol converted and the percentage of desired polyglycerols produced. The desired polyglycerols are the diglycerol and triglycerol component in the polyglycerol produced.

3. Results and Discussion

A. SEM images
The other catalyst prepared was Cerium Nitrate, Ce(NO$_3$)$_3$·6H$_2$O with montmorillonite clay MK-10. Cerium metal will intercalate with the clay and nitrate will burn to the air during the catalyst preparation technique. As for the SEM Images of Ce/MK-10, the structure shows a very narrow distribution among each other which is the opposite of our objectives, but the structure possesses a cloud like structure which proves the ability of a catalyst. Cerium metal still can be used but there is a need of another metal to intercalate together with the clay to make the catalyst a strong and powerful catalyst suitable for etherification process. As for Lithium Nitrate (LiNO$_3$) modified on montmorillonite clay MK-10, the catalyst produced is Li/MK-10. The picture illustrated in Figure 2, 3 and 4 show that each sample seems like molecule which proves that it has incorporated successfully with the metal Lithium. Not only that, the structure has wider distribution among the each other compared to Ce/MK-10 which shows it has higher surface area. The aim was to produce a mesoporous catalyst with a large surface area and thus lithium intercalated with clay shows a better result compared to Ce/MK-10. From the topography collected for modified clay CeLi/MK-10, it can be observed that the structure of the clay remained in sponge like characteristics which proves it to be a heterogenous catalyst with a good porous structure. There was a slight change in the structure compared to the other two modified catalyst in this experiment. The layer in this CeLi/MK-10 became thicker which proves there were no organic compound and the less presence of water due to evaporation process. The catalyst also was orderly mannered crystal structure which will result in a good selectivity of polyglycerols.
Figure 2. SEM images of Li/MK-10

Figure 3. SEM images of Ce/MK-10
Figure 4. SEM images of CeLi/MK-10

B. Fourier-Transform Infrared Spectroscopy (FTIR)
The FTIR Spectra obtained for the clays ranged from a wave number of 450 and 4000 cm$^{-1}$ as shown in Table 2. As can be observed from the three different graphs is Cerium modified clay had the most intense band of 1051 cm$^{-1}$ compared to lithium which was 1035 cm$^{-1}$ which proves that Cerium modified clay has decline Si-O in-plane stretch. Nevertheless, comparing Lithium modified clay had two new bands compared to the parent clay and cerium modified clay. This presence proves the existence of acid in the clay and formation of Li molecules. FTIR spectra is usually studied to prove that the clay has been modified and how it effects the parent clay and how the component and bond changes and shifts. The maximum band wavenumber increased with the loading of metals on its surface. For example, in our case study, the metals Lithium and Cerium was loaded on the clay, the band which is associated with H-O-H bond which is wavenumber from 1600 cm$^{-1}$ to 1700 cm$^{-1}$, increased and shifted compared to the parent clay.

Table 2. Peak Values of FTIR Spectra

| No. | Peak value spectra of MK-10 Clay & Modified MK-10 claysamples |
|-----|-------------------------------------------------------------|
|     | Samples | 3400 – 3500 cm$^{-1}$ | 1600 – 1700 cm$^{-1}$ | 1000-1100 cm$^{-1}$ | 300-400 cm$^{-1}$ |
| A   | MK-10   | 3423             | 1695               | 1035               | 460              |
| B   | Li/MK-10| 3440             | 1640               | 1080               | 460              |
| C   | Ce/MK-10| 3440             | 1637.1             | 1051               | 474              |

For band 3400 cm$^{-1}$ to 3500 cm$^{-1}$, it attributes to the absorption of water molecules and stretching modes of the H- O-H bond molecules into the parent clay. From the peaks that can be absorbed, our parent clay had a wavenumber of 3423 cm$^{-1}$ but increased to 3440 cm$^{-1}$ when intercalated with metals. This band can read the stretching, bending and vibrations of the presence of water molecules in the
clay. The band from 1000 cm\(^{-1}\) to 1100 cm\(^{-1}\) proves how poor the component was resolved. 1035 cm\(^{-1}\) band attributes that the Si-O bending vibrations are in plane with the oxygen O\(_2\) atom. This concludes that the vibrations cannot be oxidized whereas for metal intercalated clay, the Si-O plan vibrations were at 1050 cm\(^{-1}\) and 1080 cm\(^{-1}\) which means that the silicon molecules were out of plane with the oxygen atom and made the oxygen atom ready to react and can easily oxidize.

C. Surface Analyzer (BET)
The surface area and pore size results from four sample that was being tested which was the parent montmorillonite clay, MK-10 and three modified clay using Lithium metal, Li/MK-10, Cerium metal, Ce/MK-10 and Cerium and Lithium metal modified on clay, CeLi/MK-10. Comparing the tabulated results, the basic strength of the clay after modification was obvious especially the changes made due to the presence of the water. The clay had previously some acid base on it due to the presence of aluminum molecule but after the modification of clay and surface implantation of metal on it, the acid was modified and neutralized by the introduction of base conjugate on it. During the calculation of the amount of metal loading on the clay, we will have to consider the cation exchange because intercalation impregnates the clay with cations compared to the parent clay.

Comparing the surface area of the clay was observed and main characteristics added in Table 3. According to BET surface area results, the surface area of the impregnated clay was decreased compared to the parent clay because metals had successfully loaded on the clay surface decreasing the surface area of the clay. The surface area of Li/MK-10 was 422.79 m\(^2\)/g which is the highest compared to the other samples and showed the nearest of surface area compared to MK-10. Other than that, CeLi/MK-10 was also decreased subsequently from the parent clay from 494.81 m\(^2\)/g to 369.38 m\(^2\)/g. The Ce/MK-10 surface area was decreased the worse from the parent clay and this was due to the blockage or deterioration of some layers in the clay due to the intense strength of the metal. As for pore size results, the volume of samples tested shows that when lithium was modified on the clay, there was a very small indefinite change of the cumulative volume of the molecule. The cerium metal was the most affected with a decrease in surface area and volume of the modified clay.

**Table 3. Surface area results**

| Sample   | BET surface area (m\(^2\)/g) | Mesoporous area (m\(^2\)/g) | P/P\(^0\) initial final value |
|----------|-------------------------------|-------------------------------|--------------------------------|
| MK-10    | 494.81                        | 443.81                        | 0.05-0.33                     |
| Li/MK-10 | 422.76                        | 396.76                        | 0.05-0.33                     |
| Ce/MK-10 | 294.81                        | 345.81                        | 0.05-0.33                     |
| CeLi/MK-10 | 369.38                     | 453.73                        | 0.05-0.33                     |

As for the pore size range is important parament for measuring pore size of the prepared material. Figure 5 and 6 seem to not have any visible changes other than the adsorption-desorption curve shape significantly changed. This was because of the treatment of acidity towards the clay creates a large pore volume but the micro porosity did not change according to this principal. According to the table results, the best modified clay that can be studied further was the Lithium modified clay, Li/MK-10.
D. Microwave irradiation

1. Etherification method
Microwave radiation uses radiation with power of 2.45 GHz and 300 W whereas conventional heating uses very high temperature reaction to achieve maximum conversion of glycerol to polyglycerols. To find out the best method according to the objectives, an experiment was carried out by reacting glycerol with homogenous catalyst NaCO₃ for a total reaction time of 8 h at the same temperature of 260 °C as shown in Figure 7. According to the graph plotted on the glycerol conversion compared for the suitable method to etherify glycerol, the best method which took a lesser reaction time was
microwave radiation method. This was because the glycerol was 98% converted into polyglycerols in 4 h compared to the conventional method which only converted 96% of glycerol to polyglycerols in a total of 8 h reaction time.

2. Effect of catalyst used
The effect of catalyst was tested with only glycerol reaction in the microwave, homogenous catalyst Sodium Carbonate, (Na$_2$CO$_3$) with glycerol and Heterogenous catalyst, Cerium Lithium modified on montmorillonite clay, CeLi/MK-10 with glycerol. The reaction took place in a microwave with output power of 2.45 GHz and 300 W. 100 g of glycerol and 2 g of catalyst was added in a three-necked glass reactor vessel on a hot stirring plate at 260 °C constant temperature and 4 h reaction time as shown in Figure 8. The glycerol alone reacting in the microwave can convert up to 40% of glycerol to polyglycerol with diglycerol selectivity only at 2.5%. Though the conversion rate of simple glycerol was low, the microwave radiation worked as a best platform to convert glycerol to polyglycerol. Comparing the homogenous and heterogenous catalyst, the best was Li/MK-10 which converted 93% of glycerol up to 35% of diglycerol selectivity. This was proven that heterogenous catalyst aids this reaction better yielding better results.
The best heterogenous catalyst was further assisted to microwave radiation process of etherification of glycerol with different metal loadings as shown in Figure 9. According to the catalyst characterization, there were three different types of catalyst prepared. The results of these three catalysts proved that the best catalyst under the reaction of microwave was the Lithium Modified clay (Li/MK-10). Cerium modified clay (Ce/MK-10) showed the worst results as only 50% of glycerol was converted but only has 9% of polyglycerols were diglycerol. The LiCe/MK-10 showed slightly better results but lithium modified clay proved to yield better results.

![Percentage Converted of Different Heterogenous Catalyst tested under Microwave Radiation](image)

**Figure 9.** Types of heterogenous catalyst experimented

3. **Effect of catalyst weightage**

The effect of catalyst weight effect on etherification was observed and shown in Figure 10. The reaction occurred when the catalyst weightage was 1%, 2% and 3% loads on the surface of the clay was the glycerol molecules losses it water component when the metal on the catalyst attacks the glycerol component. The radiation of the microwave promoted attack on the structure of glycerol leaving it to be dehydrated. This process split the glycerol molecule into diglycerol and further attacked on the glycerol component to further split the glycerol into smaller components. According to this result, at 3% metal impregnation on clay proved to have better conversion and selectivity of polyglycerols produced. The metal on this clay was equally and well distributed at 3% and did not destroy or deteriorate the clay instead it increased the stability of the clay causing a higher surface area and increasing the stability of the mesoporous structure of the catalyst.
4. Reaction time

The constant time taken for a microwave assisted etherification reaction was 4 h and this theory was put up to the test to lengthen the microwave reaction up to 7 h and the glycerol sample was tested every 1-h interval for 7 h straight. After the reaction time of 4 h, the glycerol conversion was slightly increased at the 5th hour and the diglycerol and triglycerol selectivity increased subsequently. The percentage selectivity of desired polyglycerols was decreased gradually from 66% to 60% from 5 to 6 h and decreased beyond this time as shown in Figure 11. This may be due to other by-products which is undesired released during this reaction. The diglycerol and triglycerol is produced when the glycerol molecule is dehydrated, therefore excessive dehydration may result in the formation of unwanted products such as acrolein. Higher component of oligomers was produced which was undesired polyglycerols. This may happen because the bigger the component of the polyglycerols produced, it will block the catalyst reaction reducing the number of active sites available to produce desired polyglycerols. As a conclusion the reaction time of 5 h produced a slightly better result compared to 4 h reaction time. The microwave reaction for the etherification of glycerol assisted with heterogenous catalyst at reaction time of 5 h and temperature 260 °C generated a better yield result.
5. Overall Performances

The overall performances proves that Lithium modified clay was the best proven catalyst compared to Cerium clay (Ce/MK-10) and CeLi/MK-10 as shown in Figure 12. The most optimum reaction time was 5 h in a microwave assisted reaction and the best catalyst weightage tested was 3% of metal loading on the clay. The temperature according to literature review was set constant to 260 °C because it proves to the best temperature to provide ambient surrounding for the etherification process to take place. The number of desired polyglycerols which was the diglycerol and triglycerol produced was the best compared to the other catalyst which was tested. The results below show the trend of the desired polyglycerols produced in a total of 7 h reaction in a microwave.

![Figure 12. Overall polyglycerol fraction of Li/MK-10 on the microwave assisted etherification](image)

4. Conclusion

The conversion of crude glycerol produced as a by-product from the biodiesel transesterification to a value-added polyglycerol product benefits many industries to utilize their by-product in an economical way especially the biodiesel industry. Furthermore, this process was done using a heterogeneous catalyst providing a solvent free system together by adding microwave radiation which was proven to shorten the reaction time of this process. The montmorillonite clay modified using Cerium Nitrate and Lithium Nitrate did not only increase the base strength of the catalyst but also increased mesoporous capability enhancing the etherification process facilitating it to provide better diglycerol yields. The analysed and report study of the process with parameters such as: reaction time and catalyst concentrations proved that the optimum condition for etherification to take place to produce high selectivity to diglycerol and high glycerol conversion percentage at a constant temperature of 260 °C after 5 hr reaction time. These analysed parameters produced the highest glycerol conversion of 94%, highest yield of desired products of 70% and selectivity towards undesired large polyglycerol at 24%. These results suggested that modified Clay Li/MK-10 can be used as catalyst for the etherification of glycerol with microwave radiation to produce a better yield of value-added polyglycerol.

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