Applied Chemistry Project

Project title	Catalytic conversion of glucose to ethyl lactate over zeolite

Student names	Miss Panipuk Maneethai	ID	6033826223

Program Bachelor of Science in Applied Chemistry

Academic year 2020

Faculty of Science, Chulalongkorn University

Catalytic conversion of glucose to ethyl lactate over zeolite

by

Miss Panipuk Maneethai

In Partial Fulfillment for the Degree of Bachelor of Science

Program in Applied Chemistry (International Program)

Department of Chemistry, Faculty of Science

Chulalongkorn University

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Accepted by Department of Chemistry, Faculty of Science, Chulalongkorn University in Partial Fulfillment of the Requirements for the Degree of Bachelor of Science Program in Applied Chemistry (International Program)

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Abstract

Conversion of glucose to ethyl lactate was conducted using retro-aldol reaction using various types of catalysts. In this report conversion of glucose *via* retro-aldol reaction was conducted with different catalysts. Beta and other catalysts were synthesized and impregned with a direct and wet impregnation method with Niobium as metal oxide for the supported catalyst in order to increase Lewis acid. All catalysts were investigated for their identity and presence of Niobium using X-ray diffraction (XRD). The reaction was conducted mainly at 200 ^{o}C in a 25 mL Parr reactor for 1 hour. Gas chromatography (GC) was used to investigate carbon based yield of the ethyl lactate which is the main product of reactions. The result showed the reaction that conducted with impregnation zeolite uses less metal oxide than separately add metal oxide for 4.4 times and still gives higher percent of carbon based yield. As a result Nb-MCM-22 gives out 26% yield of ethyl lactate and the catalyst that gives the highest yield is Nb-Beta zeolite which gives out 32%.

Acknowledgement

I would like to express my special thanks of gratitude to my advisor Assistant Professor Dr. Duangamol Tungasmita for providing me with all the facilities that were required and giving me advice. I would also extend my gratitude to Uratsaya Kunanonvorakun and other lab members for their able guidance and support in completing my project. Lastly, I would be thankful for my friend, Naomi Knol, who always supports me during this rough year.

Table of Content

Lists of figures

Chapter 1

Introduction

1.1 Introduction to the research problem and significance

Nowadays the world's energy market mostly uses fossil fuel coal, natural gas and petroleum oil as sources for thermal energy for fuel. However, those are limited and non renewable. The renewable carbon substances that persist all over the world and can be used instead of fossil fuel is biomass[1]. Biomass is the organic substance that also can be used for providing renewable fuel. It comes from living organisms such as plants and animals and also appears in non living organisms as well. The examples of biomass include cellulose and chitin. The cost of production can be reduced, if transforming biomass was done in an efficient and green way. Currently, the use of biomass is widespread in many industries including cosmetic industry, food industry and plastic industry. Glucose is the most abundant monosaccharide and known as simple sugar. It mostly comes from photosynthesis of algae and plants. Glucose can be found in all organisms, fruit as an energy source. Glucose is also an energy source of plants and animals[2]. Glucose can be converted into many compounds including ethyl lactate, ethyl levulinate, and lactic acid depending on the paths of catalytic reactions[4]. The conversion of sugar such as glucose or fructose can be catalyzed by a homogeneous catalyst. Metal-containing catalysts can be used to improve performance of sugar conversion [5]. Ethyl lactate is one of the products of glucose. It consists of two main components which are lactic acid and alcohol. Ethyl lactate can be used in many fields of work such as production of nitrocellulose, preparation in pharmaceutical, food flavor addictive, or be replaced for conventional solvent such as halogenated hydrocarbon due to its low toxicity[4]. Also, the better performance of the reaction can be used to reduce cost of production of the industry and lead to more environmentally friendly substitution of sources of non-renewable thermal energy[1].
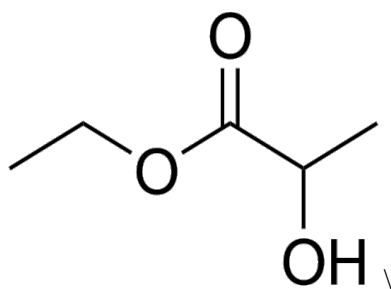
figure 1. Structure of ethyl lactate

1.2 Research objectives

The objective of this project is to study the systematic performance of zeolite and Niobium modified zeolite with regard to the conversion of glucose to ethyl lactate in ethanol. The performance of catalytic activity was done and investigated by retro-aldol reaction followed by dehydration and 1,2-hydride shift.

1.3 Literature search

1.3.1 Heterogeneous catalyst

Heterogeneous catalyst is the catalyst that have differ phase between catalyst and reactant or product. Meanwhile homogeneous catalysts have all the same phase in reactant, product, and catalyst. The usage of catalyst is to increase the rate of reaction without being consumed and also reusable. This leads to cheaper production cost and more environmentally friendly for catalytic reaction [6]. Currently, because of its ability, catalyst was used in many industries. The examples of porous material that can be used as heterogeneous catalysts are zeolite, metal-organic framework (MOFs), and mesoporous silica. Zeolite was one of the useful heterogeneous catalysts usually used in petroleum industries and conversion of renewable energy[7]. Zeolite are inert, microporous crystalline hydrated aluminosilicates with well-defined structure. Alumino silicate is aluminium and silicon oxide connected with oxygen bonding with ratio more than 1. Zeolite has many 3D-connected frameworks that were created from the connection of Si/Al[8]. Today there are more than 237 types of zeolite framework present in the

Structure Commission of International Zeolite Association (IZA-SC). Each zeolite has a different framework depending on the aluminosilicate and surface area of porous material[8]. For example, MCM-22 have MWW framework type which is the framework that consists of 10 membrane rings that connect with 12 membrane rings, ZSM-5 have MFI framework type which consisting of a straight 10-membered ring channel that intersected with sinusoidal 10-membered ring channel, and Beta zeolite have BEA framework type that consists of 12 membrane rings system. According to the article framework of the zeolite can directly affect the catalytic activity in the reaction. Pore size and surface area of mesoporous material can increase yield of the product. From the study from the last year senior project, Miss Uratsaya Kunanonvorakun , the higher pore diameter can give higher surface area and higher surface area can improve catalytic activity because more active catalytic sites in the reaction or in other word it is a pore selection process of catalyst[7], [10].

1.3.2 MCM-22

MCM-22 is one of the heterogeneous catalysts with MWW framework. MCM-22 was reported from last year's study from Miss Uratsaya as a highly active catalyst for conversion of trioses to methyl lactate in methanol and water. This is because MWW consists of 10 membrane rings that connect with 12 membrane rings which help in pore selection for size of glucose. This type of framework could help involve larger molecules inside the pore structure during the reaction[7].
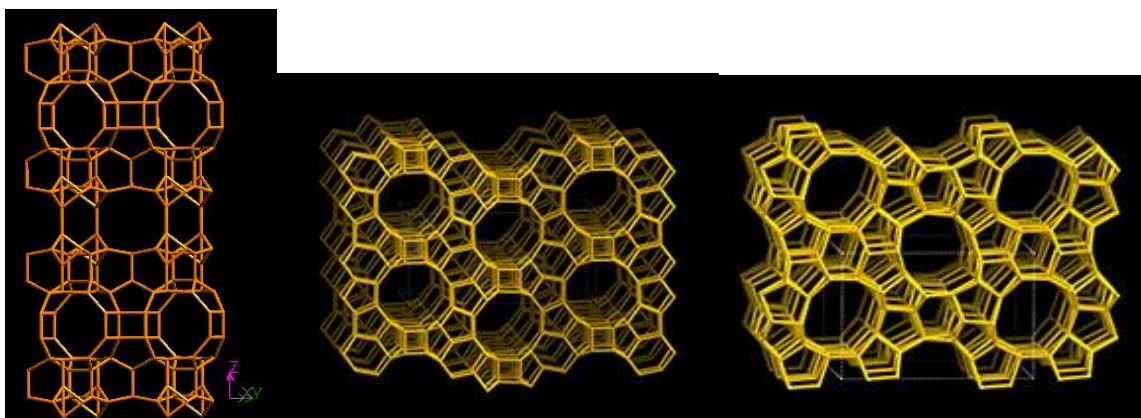
figure 2. Framework types MWW, BEA, MFI

1.3.3 Physical combination of zeolite.

1.3.3.1 Metal oxide

Metal oxide is a crystalline solid that reacts with water and contains metal cation with balancing of oxide anion. Metal oxide usually reacts with water from bases and acid from salt. Besides, metal oxide plays an important role as a support metal for catalysts for changing acid sites. The combination of metal oxide with zeolite was used in catalytic performance[11]. Niobium is one of the active retro-aldol reactions of glucose by previous study. Besides, metal oxide was observed to change reversibly bronsted acid and lewis acid sites in the presence of water which can affect conversion of sugar[12], [21].

1.3.3.2 Wet impregnation method

Wet impregnation method is one of the popular methods that are used for modification of zeolite. This method can be used in many solvents such as water, methanol, and ethanol to improve performance of heterogeneous catalysts[13]. Currently, metal oxide such as copper and Niobium was used as a support metal in this method. This can lead to changing acid sites in the catalytic reaction to improve catalytic activity. Impregnation method was conducted by stirring metal oxide with zeolite in the solvent. Then heat the zeolite in the oven until it dries to coat metal oxide on the surface of the zeolite.

1.3.4 Retro-aldol reaction

Retro-aldol reaction is the reaction that beta hydroxy ketone is decomposed to aldehyde or ketone. In another word, retro-aldol reaction is the reversible reaction of aldol reaction[14]. Retro-aldol reaction has been used as a step for converting biomass-derived hexoses and pentose into C4 to C2 products. From the previous study retro-aldol with acidic or basic conditions in alcoholic solvent can produce ethyl lactate as a product depending on the pathway of the reaction. In this study retro-aldol reaction was studied after glucose is isomerized to fructose and conduct the retro-aldol reaction in ethanol the product that would be received is ethyl lactate. The path of the reaction is going to be as in the figure 2[4]. Besides, different pathways from glucose can produce other products based on concentration of lewis acid. In a high acidic reaction the product is going to be ethyl levulinate and in absence of lewis acid the product is going to be acetaldehyde diethyl acetal[4].
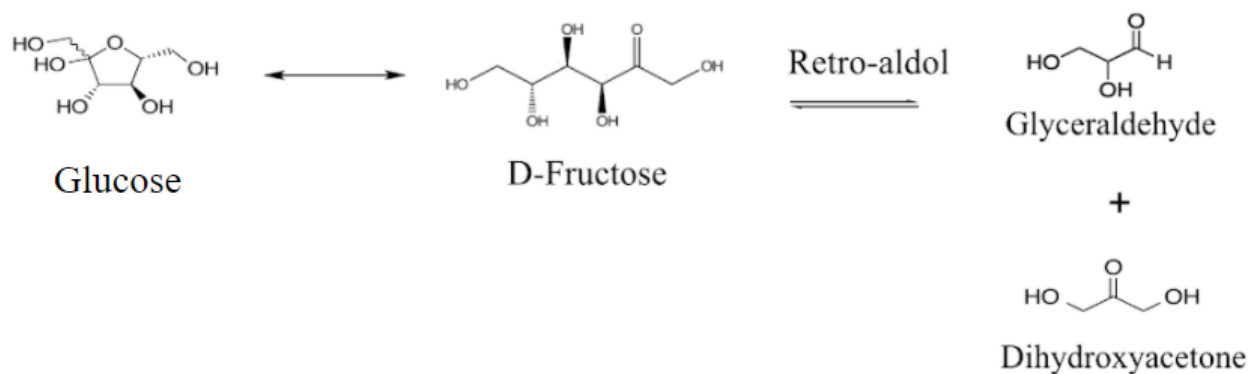
figure 3. Retro-Aldol reaction of Glucose
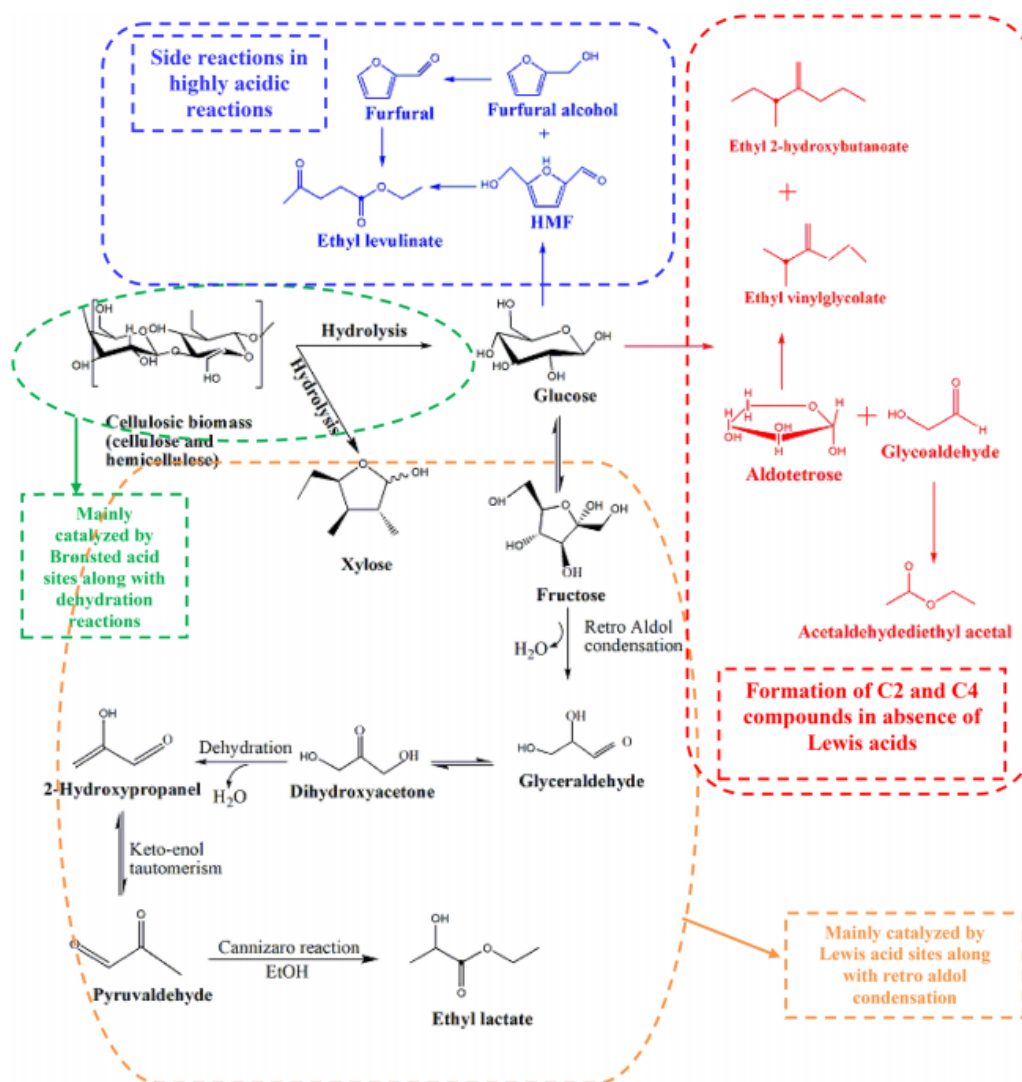
Figure 4. Glucose path of reaction [4]

1.3.5 Product of glucose

The product that is received from conversion of glucose in ethanol could result in many substances depending on the path of reaction. From figure 4, Lewis acid sites play an essential role in conversion of glucose. Also glucose can be isomerized to fructose. With a retro-aldol reaction in ethanol it can give out ethyl lactate as a product. Besides, with side reactions in highly acidic reactions Glucose can change to hydroxymethylfurfural (HMF) and give out ethyl levulinate. Moreover, with

formation of C2 and C4 compounds in absence of lewis acid g;ucose can give out Ethyl vinyl glycolate with ethyl 2-hydroxybutanoate or acetaldehyde diethyl acetal as a product[4].

1.3.5.1 Usage of products

Many products can be produced from glucose conducting reactions in ethanol. Ethyl lactate is one of the products that can be produced in high percentage compared to others. Ethyl lactate was used as a solvent with various types of polymer. Also, it was used in many fields of industries including pharmaceutical, cosmetic, or even food industries. It is considered as a compound degradable in natural forms. ethyl lactate also known as green biomass with reusable characteristic. This product was considered environmentally friendly because of its low toxicity[15].

1.3.5.2 Previous studies

Study of biomass conversion using the aldol-retro reaction has been studied by many researchers. Combination of heterogeneous catalyst and metal oxide in order to improve the conversion performance by controlling the lewis acid site also studied to increase the desired yield of the product. The examples of this study are the previous research on Production of Ethyl Lactate from rice straw[4] which study yields ethyl lactate using various zeolites and conditions.

Another previous study is the study that is conducted by conversion of fructose to ethyl lactate. The reaction was done in autoclave for 3 hours at 160 $^{\circ}$C with several catalysts[26].

Chapter 2

Experiment

2.1 List of equipment and instrument

Gas Chromatography (GC) Varian CP-3800, Scales Precisa XT 220A, Scales Precisa 6800 CSCS, Heater IKA C-MAG HS 7 Control, Parr 4843 controller, Zebron ZB-FFAP column.

2.2 Chemicals

D(+)- Glucose monohydrate Sigma‑Aldrich company, Ammonium niobate(V) oxalate hydrate 99.9% trace metals basis Sigma‑Aldrich company, Dihydroxyacetone Merck company, Niobium(V) oxide 99.9% trace metals basis Sigma‑Aldrich company, Ethyl Lactate >98% TCI, Methyl lactate >98% TCI, methanol Merck, ethanol Merck, Hexamethyleneimine 99% Sigma‑Aldrich company, Beta zeolite (Si/Al = 28), MCM-22 (Si/Al = 14.1), ZSM-5 zeolite, Sodium hydroxide > 97% Sigma‑aldrich company, Sodium aluminate Sigma‑aldrich company, Hydrophilic fumed silica Sigma‑aldrich company. Niobium(V) oxide 99.99% Sigma‑aldrich.

2.3 Materials

2.3.1 Synthesis and Modification of Heterogeneous Catalyst

2.3.1.1 MCM-22

MCM-22 was synthesized using hexamethyleneimine (HMI) as an organic template[16]. From the article 3.50 g of sodium hydroxide was dissolved with 150 g of distill water. Then dissolved it by using a magnetic stirrer at 50 rpm until it becomes a homogenous solution. After receiving the clear

solution, add 25.04 g of fumed silica and stir it for 1 hour. After receiving the white solution dropwise under vigorous 37.19 g hexamethyleneimine and stirred for another 1 hour the product that is going to be received is going to be a mixed solution. Then add 2.71 g of sodium aluminate with 150 g distilled water dropwise under vigorous then stirred for 1 hour. Then the product that we received from this method is gel. After receiving the gel, crystallized it at 140 ^{o}C in autoclave for 7 days using Parr reactor at speed 70 rpm. After that filtered and washed white precipitate until pH below 9 and dried at 80 ^{o}C overnight. After receiving the product, it was calculated at 550 ^{o}C for 5 hours. The product is going to be MCM-22 with ratio equals to SiO_2/Al_2O_3 = 28.2, Si/Al = 14.1.

2.3.1.2 Ion-exchange of Niobium species by directly adding Niobium during synthesis of MCM-22.

MCM-22 was directly exchanged with Niobium species with Na+ in the zeolite by synthesizing MCM-22 again with different Niobium oxide and changing the ratios of chemicals. In this time 3.50 g sodium hydroxide was dissolved in 150 mL of distilled water then stirred it by using a magnetic stirrer until it became a homogenous solution. After receiving a clear solution add 22.50 g fumed silica and stirred it for 1 hour. After receiving the white solution dropwise under vigorous 37.15 g hexamethyleneimine and stirred for another 1 hour the product that is going to be received is going to be a mixed solution. Then add 2.71 g of sodium aluminate with 62.74 g distilled water dropwise under vigorous. Meanwhile add 9.15 Ammonium niobate(V) oxalate hydrate with exact 87.26 mL of distilled water dropwise under vigorous and then stirred for 1 hour. Then the product that we received from this method is gel. After receiving the gel, crystallized it at 140 ^{o}C for 7 days using Parr reactor at speed 70 rpm. After that filtered and washed white precipitate until pH below 9 and dried at 80 ^{o}C overnight. After receiving the product, calcined at 550°C for 5 hours. The product that was received from this method is going to be 10wt% Nb-MCM-22.

2.3.1.3 Ion-exchanged of Niobium species using wet impregnation method

Pure MCM-22 was used for Ion-exchange of Niobium species using impregnated methods. 1.8 g of MCM-22 was prepared and mixed with 0.65 g aluminium niobate(V) oxalate hydrate. Then slowly drop 7 mL distilled water to the solid and stirred for 2 hours and 30 minutes. After receiving the white mixture, dry it at 100 $^{\circ}$C overnight. Then, calcined at 550 $^{\circ}$C for 5 hours. The product that was received from this method is going to be 10wt% Nb-MCM-22. which is the Niobium that covers the surface of the zeolite. After that calcined the product at 550 $^{\circ}$C for 5 hours.

ZSM-5 zeolite was prepared by calcined at 550 $^{\circ}$C for 5 hours. Then, add 0.65 g aluminium niobate(V) oxalate hydrate with the zeolite and slowly drop 12 mL distilled water to the solid and stir for 2 hours and 30 minutes. After receiving the white mixture dry it at 100 $^{\circ}$C overnight. Then, calcined at 550 $^{\circ}$C for 5 hours. The product that was received from this method is going to be 10wt% Nb-ZSM-22. which is the Niobium that covers the surface of the zeolite. After that calcined the product at 550C for 5 hours.

Beta zeolite was prepared by calcined at 550 $^{\circ}$C for 5 hours. Then, add 0.65 g aluminium niobate(V) oxalate hydrate with the zeolite and slowly drop 7 mL distilled water to the solid and stir for 2 hours. After receiving the white mixture dry it at 100 $^{\circ}$C overnight. Then, calcined at 550 $^{\circ}$C for 5 hours. The product that was received from this method is going to be 10wt% Nb-Beta-22. which is the Niobium that covers the surface of the zeolite. After that calcined the product at 550 $^{\circ}$C for 5 hours.

2.4 Catalytic Reactions

2.4.1 Catalytic reaction from fructose to methyl lactate

The Retro-Aldol reaction was conducted using different zeolite and Niobium species that directly and impregly with the zeolite. This was to study how different zeolite and metal oxide in zeolite affect the result of the product or in other word, the percent production of methyl lactate from fructose. Also, before conducting the reaction all zeolite and metal oxide was prepared by calcined at 550 $^\circ$C for 5 hours.

Firstly, the studied conditions were done using the same condition as the previous report in order to test the difference between the preceding one which was conducted in Japan by one of the lab members, Miss Uratsaya Kunanonvorakun, last year. The only difference between the report and this experiment is the ratio of substance which because of bigger containers the ratio of the substances have to be 3 times higher. Thus, as mentioned before, The 150 mg of fructose, 240 mg of Niobium, 300 mg MCM-22, and 18.36 mL of methanol that was measured using micropipette was mixed in a 100 mL Parr stainless steel reactor. The reaction was conducted at 160 $^\circ$C for 1 hours at 545 rpm. After receiving the product with precipitate. filter the precipitate and collect the remaining liquid in a 10 mL glass bottle.

The second reaction was conducted by using MCM-22 that synthesized from the method 2.3.1.1 as a zeolite in 100 mL Parr. The 150 mg of fructose, 240 mg of Niobium, 300 mg MCM-22, and 18.36 mL of methanol was mixed in a 100 mL Parr stainless steel reactor. The reaction was conducted at 160 $^\circ$C for 1 hours at 545 rpm. After receiving the product with precipitate. Filter the precipitate and collect the remaining liquid in a 10 mL glass bottle. In total, the reactions that were received from fructose using 100 mL parr is 2 reactions.

For reaction in a 25 mL Parr reactor for fructose in a sand bath. In this part retro-aldol reactions of fructose and glucose were conducted using 25 mL Parr in sand baths and were done using different zeolite and Niobium species that directly and impregly with the zeolite. The ratio of the chemical was reduced to 50% according to *Orazov, M. and Davis, M. E. (2015)* due to smaller capacity of the parr.

From the first experiment in 25 mL parr 50 mg of fructose, 80 mg of metal oxide, 100 mg of MCM-22 that synthesized last year and have used in the previous study last year in Japan and 6.12 mL methanol was prepared and mixed together in the 25 mL Parr teflon-lined stainless steel reactor. The reaction was conducted in the sand bath with the temperature at 200 ^{o}C outside the stainless parr and inside the stainless parr at 100 ^{o}C. After receiving the product with precipitation, filter the precipitate and collect the remaining liquid in a 10 mL glass bottle.

For the second experiment in 25 mL parr 50 mg of fructose, 80 mg of metal oxide, 100 mg of MCM-22 that synthesized from method 2.3.1.1 and 6.12 mL methanol was prepared and mixed together in the 25 mL Parr teflon-lined stainless steel reactor. The reaction was conducted in the sand bath with the temperature at 200 ^{o}C outside the stainless parr and inside the stainless parr at 180 ^{o}C. After receiving the product with precipitation, filter the precipitate and collect the remaining liquid in a 10 mL glass bottle. In total the reaction that was received from fructose using 25 mL parr in a sand bath is 2 reactions.

2.4.2 Catalytic reaction from glucose to ethyl lactate

For reaction in 25 mL Parr reactor for glucose in sand bath. In this part retro-aldol was conducted using several zeolites and modified zeolites. This reaction was conducted in order to find the effect that zeolite and metal oxide affect to the production of ethyl lactate that is received from the conversion of glucose. From the experiment 50 mg of fructose, 80 mg of metal oxide, 100 mg of zeolite and 6.12 mL methanol was prepared and mixed together in the 25 mL Parr teflon-lined stainless steel reactor. The reaction was conducted in the sand bath with the temperature at 200 ^{o}C outside the stainless parr and inside the stainless parr at 180 ^{o}C. After receiving the product with precipitation, filter the precipitate and collect the remaining liquid in a 10 mL glass bottle. The zeolite that use for this experiment are ZSM-5, modification of ZSM-5 with neobrium by impreging method, MCM-22 that synthesized last year, MCM-22 that received from method 2.2.1.1, MCM-22 modification of MCM-22 with neobrium by impreging method, Beta zeolite, and Beta modification of MCM-22 with Niobium by impreging method. There are 7 reactions for fructose conducting in a 25 mL Parr reactor.

2.5 Calibration of products for quantitative analysis.

2.5.1 Internal standard calibration method

Internal standard was tested to find the yield and concentration of ethyl lactate and methyl lactate which is the product of the reaction. Because two types of reaction which are conversion of fructose to methyl lactate and conversion of glucose to methyl lactate were done separately, two collections of solutions were prepared and checked using gas chromatography (GC) in order to plot two sets of calibration curves.

For the first reactions which are conversion of fructose to methyl lactate. 0.256 g of naphthalene was prepared in 100 mL flask and mixed with methanol in order to receive 0.02 M of naphthalene solution. This solution would be used as an internal standard. After that methyl lactate was prepared in various concentrations starting from mixing 5.9 g of methyl lactate in a 25 mL flask with methanol. Then dilute it into 10 mL flasks and the concentration of methyl lactate that received from this step are 0.5 M, 0.1 M, 0.5 M, 0.025 M, and 0.0125 M respectively in order to obtain 5 points in the calibration curve.

For the second reaction which is conversion of glucose to ethyl lactate. The preparation was the same as the previous one but this time 5.20 g of ethyl lactate was prepared and mixed with ethanol in 100 mL flask. After that ethyl lactate was prepared in various concentrations starting from mixing 5.2 g of ethyl lactate in a 25 mL flask with ethanol. Then dilute it into 10 mL flasks and the concentration of methyl lactate that received from this step are 0.5 M, 0.1 M, 0.5 M, 0.025 M, and 0.0125 M respectively. The calibration curve in this chromatogram also uses 5 points.

The two sets of solutions with internal standard was injected into GC with Zebron ZB-FFAP column. The temperature program was set as in the figure 3 the rate of the program was set at 60 $^{\circ}$C then held for 5 minutes. After that temperature would rise with the rate of 5 $^{\circ}$C/min. Then the maximum temperature will be 230 $^{\circ}$C.
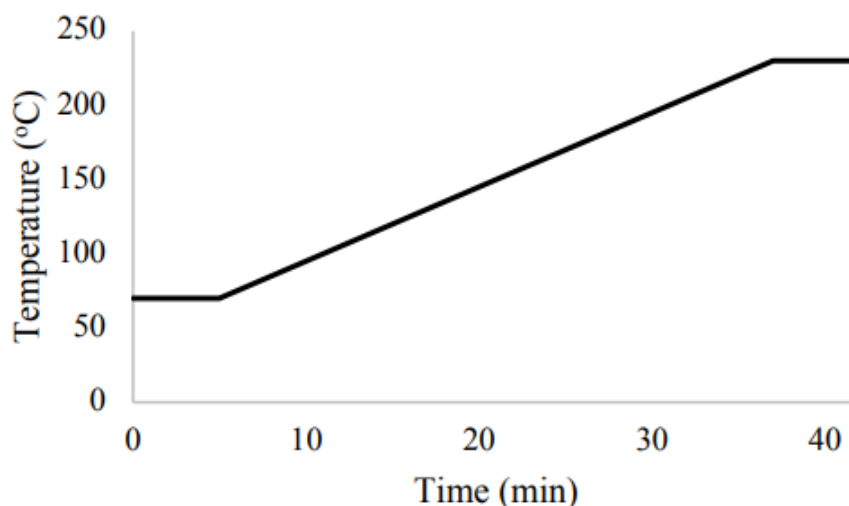
Figure 5. Temperature program of gas chromatography analysis

2.6 Characterization

2.6.1. XRD

For characterization XRD was used to analyze the catalysts and compare with international centres for diffraction data in order to confirm the identity. Moreover, to confirm the ion‑exchange of Niobium species using impreg and direct methods. All catalysts were characterized by this method including MCM‑22, MCM‑22 with impreg Niobium, MCM‑22 with direct synthesized with Niobium, ZSM‑5, ZSM‑5 with impreg Niobium, Beta, Beta with impreg Niobium. XRD patterns were obtained over the 2θ range.

2.6.2 Product analysis

Gas chromatography (GC) was used for analysis of the methyl lactate and ethyl lactate which are the products of fructose and glucose. GC was used with a packed column Zebron ZB‑FFAP using naphthalene as an internal standard. The solution for analysis was prepared by adding 0.1 mL of

naphthalene to 1 mL of reaction mixture. The temperature program was set as the same as in the method 2.5 and the percentage of carbon based yield was calculated according to the equations below.

The percentage of carbon based yield was calculated by using concentration of the ethyl lactate that received from calibration curve times the number of carbon of the product which is 4 for methyl lactate and 5 for ethyl lactate. Then divided by concentration of reactant which are concentration of fructose and glucose and times with number of carbon of the reactant which are 6 for both reactants.

$$\text{Carbon Based Yield (\%)} = \left(\frac{(Concentration\ of\ Product \times n_p)}{(Initial\ Concentration\ of\ Reactant \times n_r)}\right) x\ 100$$

n_p = number of carbon of the product
n_r = number of carbon of the reactant

Chapter 3

Result and discussion

3.1 Catalyst characterization

3.1.1 XRD analysis

3.1.2.1 Identification of MCM-22 and its modified form

The identification of MCM-22 and its modified form was confirmed from the database. From the result the synthesis of MCM-22 was successfully synthesized as a crystalline phase according to the method from 2.3.1.1. For the post MCM-22 which is prepared using a wet impregnation method with aluminium niobate(V) oxalate hydrate. According to XRD machine, the diffraction of catalyst showed peaks appear with a crystalline phase at the region of 23, 28, 36 and 46 which is the same as a peak that is observed from Niobium oxide. But for the MCM-22 that was synthesized using a direct method the result appeared as a non-crystalline material without a peak. The phenomena could occur because of Niobium in mother gel.
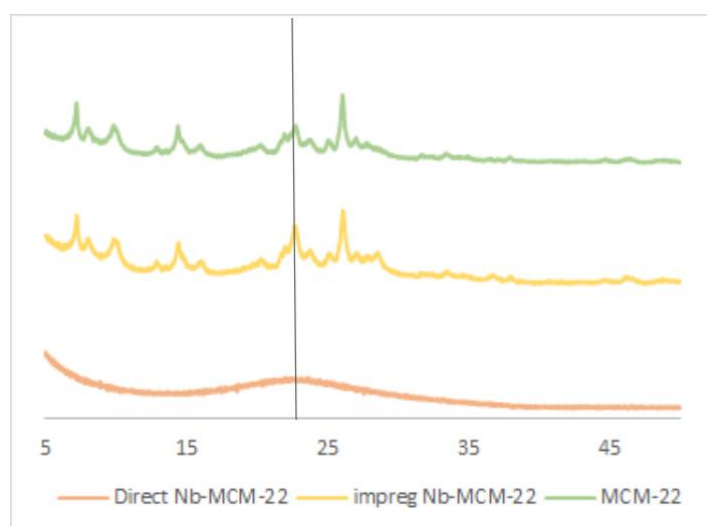

Figure 6. XRD patterns of MCM-22 and its modified form

3.1.2.2 Identification of ZSM-5 and its modified form

Identification of ZSM‑5 was confirmed from the database. The peaks were observed at $2\theta =$ 8, 9, 23, 24 which is the characteristic of ZSM‑5 that reported as a MFI structure [17]. From the result, ZSM‑5 was successfully impregnated with Niobium(V) aluminate oxalate. According to XRD machine the diffraction of catalyst showed peaks appear with a crystalline phase at the region of 23, 28, 36 and 46 which is the same as a peak that is observed from Niobium oxide[22].

Figure 7. XRD patterns of ZSM‑5and its modified form

3.1.2.3 Identification of BETA and its modified form

Identification of Beta was confirmed from the database. The peaks were observed at $2\theta = 7, 22.5$ which is the characteristic of Beta Zeolite[18]. From the result, Beta also successfully impregnated with Niobium(V) aluminate oxalate. According to XRD machine the diffraction of catalyst showed peaks appear with a crystalline phase at the region of 23, 28, 36 and 46 which is the same as a peak that is observed from Niobium oxide[22].
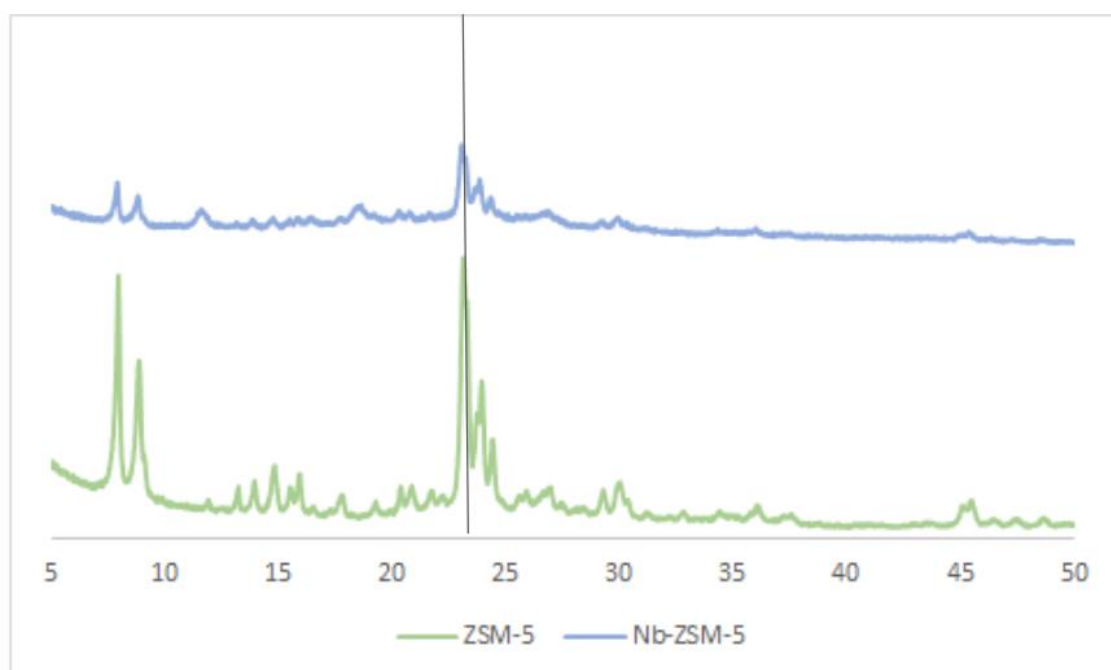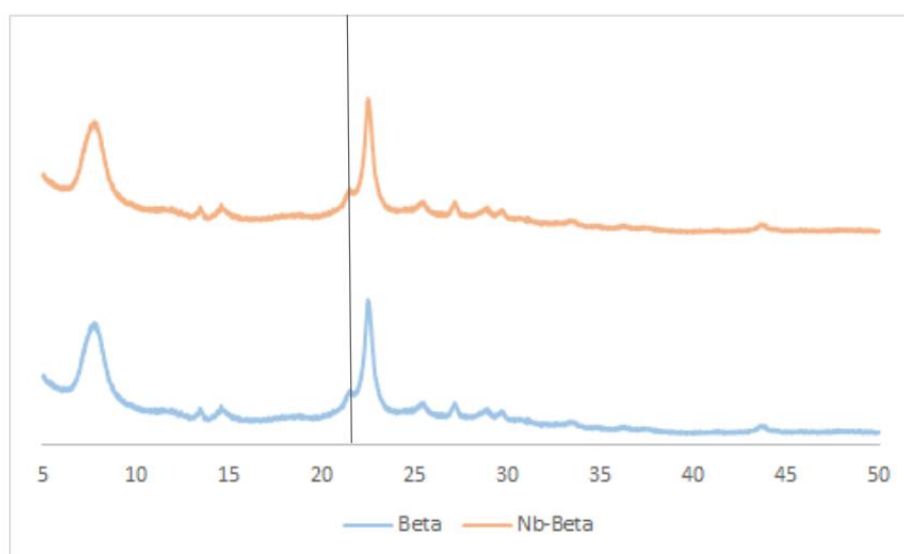

Figure 8. XRD patterns of Beta and its modified form

3.2 Retro-Aldol reaction

3.2.1 Product analysis

The calibration of the product was conducted by Gas chromatography (GC). The analysis was based on ratio of molar ratio and area ratio between analyst and internal standard which is naphthalene. The internal standard appeared at 21.3 minutes on the chromatogram. For the product, firstly, methyl lactate appeared at 9.6 minutes. The peak position was confirmed by mixing 1 mL of methyl lactate

with 0.1 mL of naphthalene. The equation that is received from the calibration curve is y = 0.1105 + 0.0604 with R² equals to 0.9984.

Next, for the ethyl lactate, the position was appeared at 10.2 minutes on chromatogram and was confirmed by mixing 0.1 mL naphthalene with 1 mL ethyl lactate the equation that received from calibration curve was y = 0.0798x+0.0101 with R² equals to 0.9993.
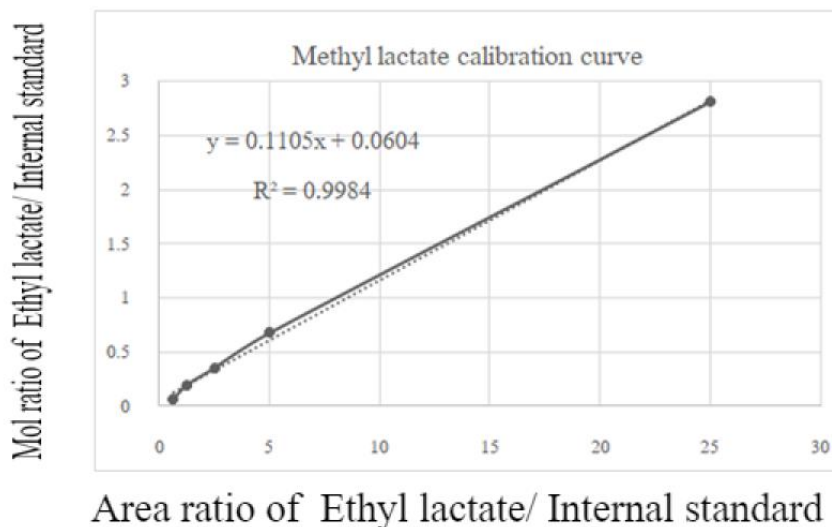
Figure 9. Calibration of Methyl lactate

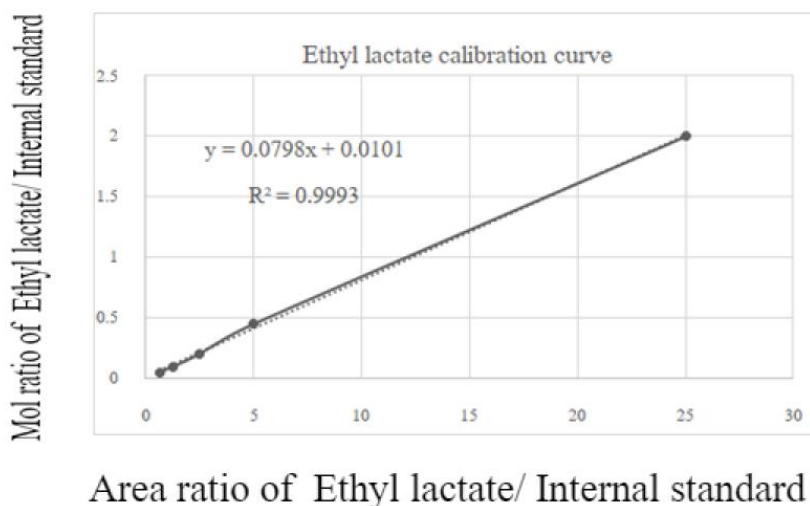Figure 10. Calibration of Ethyl lactate

3.2.2 Overall effect of catalyst on product formation

The reaction was conducted by using several zeolites and modified zeolites. The ratio of chemical substance was adapted in order to match with the equipment which are 100 mLParr reactor and 25 mL Parr reactor.

For the production of methyl lactate from fructose in methanol. Both 100 mL Parr reactor and 25 mL Parr reactor were used in order to test the most efficient way of producing the product. For 100 mL Parr reactor 150 mg of fructose, 240 mg of metal oxide, and 300 mg zeolite was prepared with 18.36 mL methanol the time and temperature are 1 hr with 160 ^{o}C. The ratio of chemical substance was three times larger than the original method from William N. P. Van Der Graaff et al. (2017). For the 25 mL Parr reactor the amount of chemical substance was reduced to half of the original one. 50 mg of Fructose, 80 mg of metal oxide and 100 mg of zeolite was prepared and mixed with 6.12 methanol the reaction was conducted in 1 hr with 200 C sand bath.

The percent of carbon based yield was calculated by using concentration of the ethyl lactate that received from calibration curve times the number of carbon of the product which is 4 for methyl lactate and 5 for ethyl lactate. Then divided by concentration of reactant which are concentration of fructose and glucose and times with number of carbon of the reactant which are 6 for both reactants.

According to the result the most condition that gives out methyl lactate is the reaction that uses MCM-22 that was by Miss Uratsaya Kunanonvorakun in a 25 mL Parr reactor. The carbon based yield is equal to 51.18%. After that the second condition that gives out most methyl lactate yield is MCM-22 that conducts the reaction in a 25 mL Parr reactor. the result gives out 48.67% yield. MCM-22 that was synthesized last year in 100 mL Parr and MCM-22 in 100 mL Parr reactor give out 45.99% and 46.76% respectively.

From the result size of Parr reactor and temperature have significant impact in giving out methyl lactate products. It is clearly seen that in the same condition the reaction that conducts in a 25 mL Parr reactor gives out most yield compared to 100 mL reactor. This could happen because the 25 mL parr reactor could have better flow of heat during reaction. According to the previous experiment

of one of the lab members high heat in a short time can lead to significant increase of product of methyl lactate.
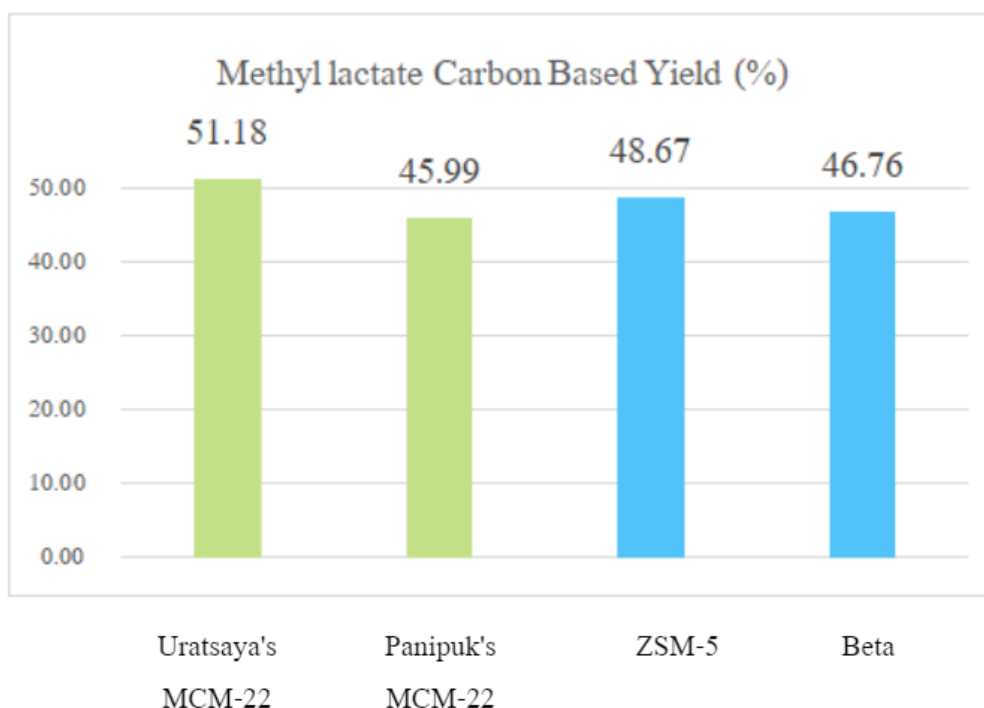

Figure 11. Methyl lactate Carbon based yield

For ethyl lactate the same method as methyl lactate reaction was used. but instead of fructose, glucose was used as a reactant to produce ethyl lactate in methanol. All reaction was conducted in a 25 mL Parr reactor knowing that it would be more efficient to increase percent of carbon based yield. From the result, beta with impregnation of Niobium give out highest yield which is 32.5% Then Nb-ZSM-5, ZSM-5, Nb-MCM-22, Beta, MCM-22 that synthesized last year, and MCM-22 which are 28.90%, 28.30%, 25.84%, 25.17%, 25.09%, and 22.91% respectively. From the result we can see that impregnation of Niobium has a significant impact on product yield. The reaction that uses zeolite with impregnation of Niobium has a higher yield compared to the one that adds bare metal oxide before the reaction. This might be because a great amount of water using an impregnation method can change acid site from bronsted acid reversibly to lewis acid[12]. So impregnation mental oxide can change the lewis acid site. This can lead to improving production of sugar conversion.
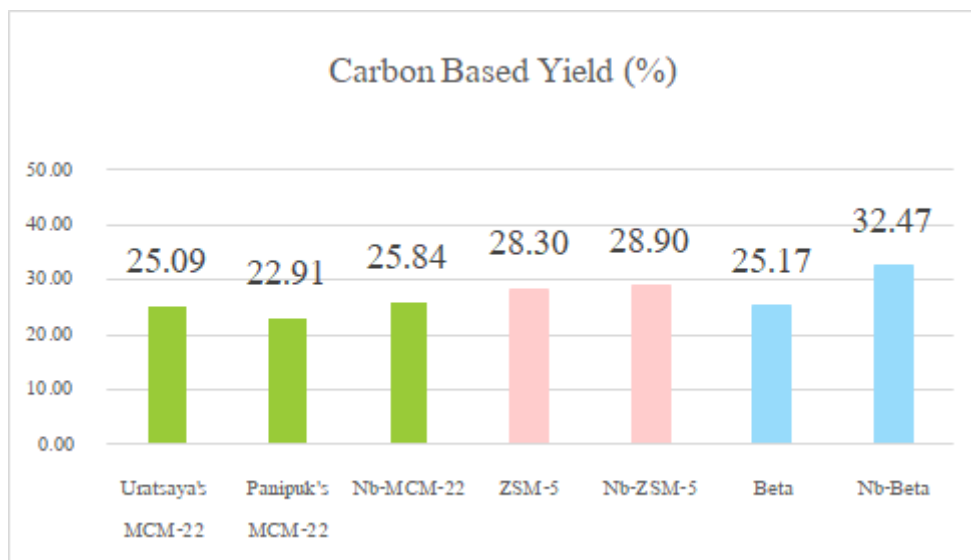
Figure 12. Results for ethyl lactate Carbon based yield

3.2.2.1 Product from reaction using metal oxide

Niobium oxalate was known as active metal oxide for catalytic conversion[24]. Thus, various reactions were done in order to observe the ability of this metal oxide. According to the experiment of converting glucose to methyl lactate the reaction of MCM-22 that was synthesized last year in 25 mL Parr gives out the highest carbon based yield which is 51.18%. Compared to the previous study MCM-22 that was used as a catalyst without mental oxide could have only 4.1% yield. Thus, the result tells us that Niobium can help improve yield of the methyl lactate. This might be because Lewis acid that might be turned by using various metal oxide is important for conversion of triose to methyl lactate.
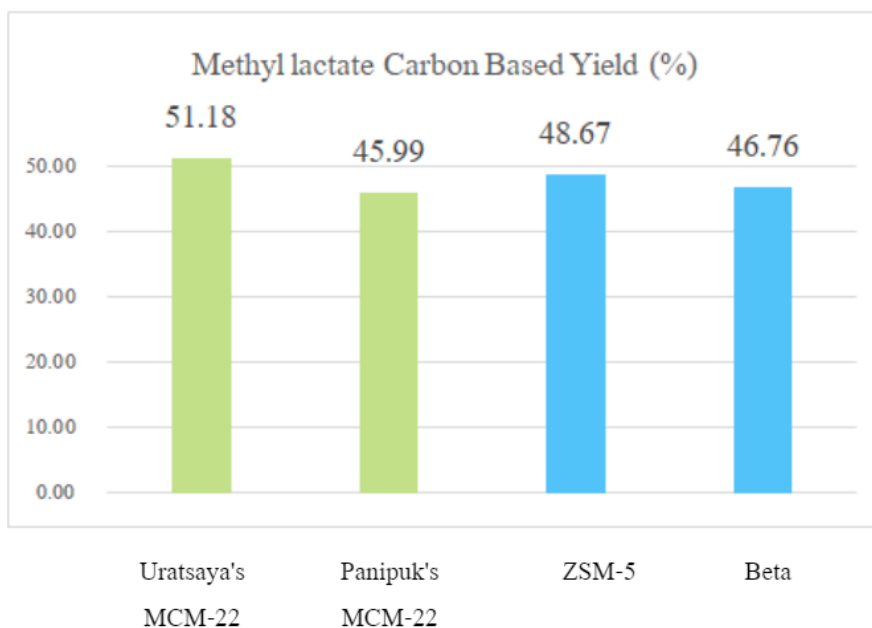
Figure 13. Carbon based yield of methyl lactate using metal oxide

For the conversion of glucose to ethyl lactate using separately metal oxide, the highest yield came from ZSM-5 which equals to 28.30%, Then Beta which is 25.17%, after that is MCM-22 which is 25.09% and 22.91% respectively. it happens that zeolite with smaller pore size which is ZSM-5 can give out the most yield. This might happen because s large pore size of MCM-22 might include glucose in pore and catalyze other side reactions[7].
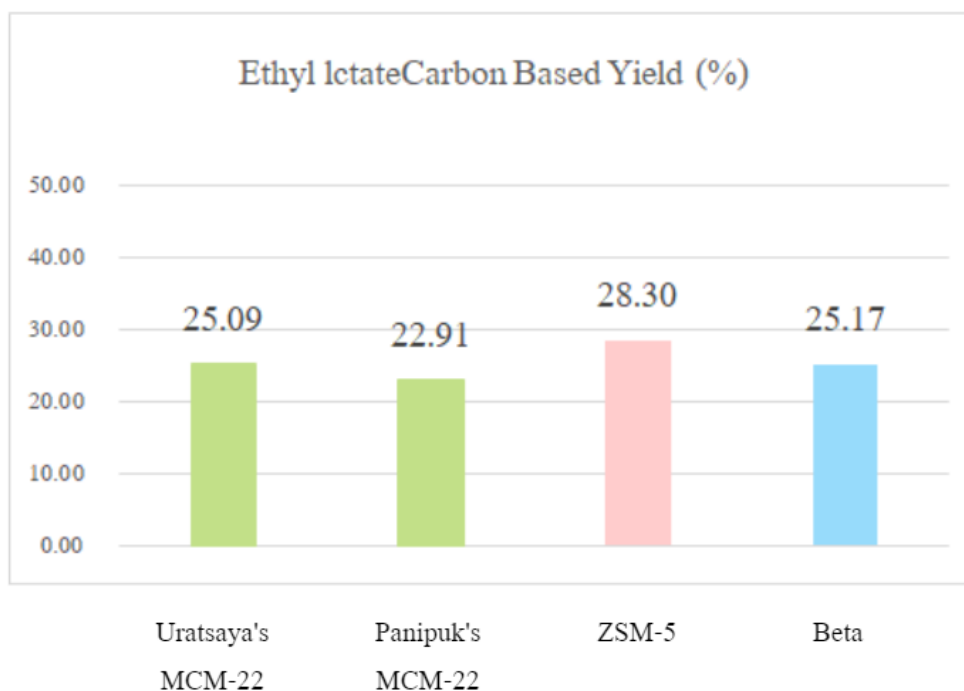
Figure 14. Carbon based yield of ethyl lactate using metal oxide

3.2.2.2 Product from reaction using impregnated metal oxide

For the conversion of glucose to ethyl lactate using impregnation metal oxide, the highest yield also came from ZSM-5, Then Beta , and MCM-22 which is the same as reaction that is done with separately mixed metal oxide. However, it happens that yield got from impregnation method is better than other method. the percent is equal to 32.47%, 28.90%, and 25.84% respectively.

Figure 15. Carbon based yield of ethyl lactate using metal oxide by impregnation

3.2.2.3. Amount of Niobium in reaction

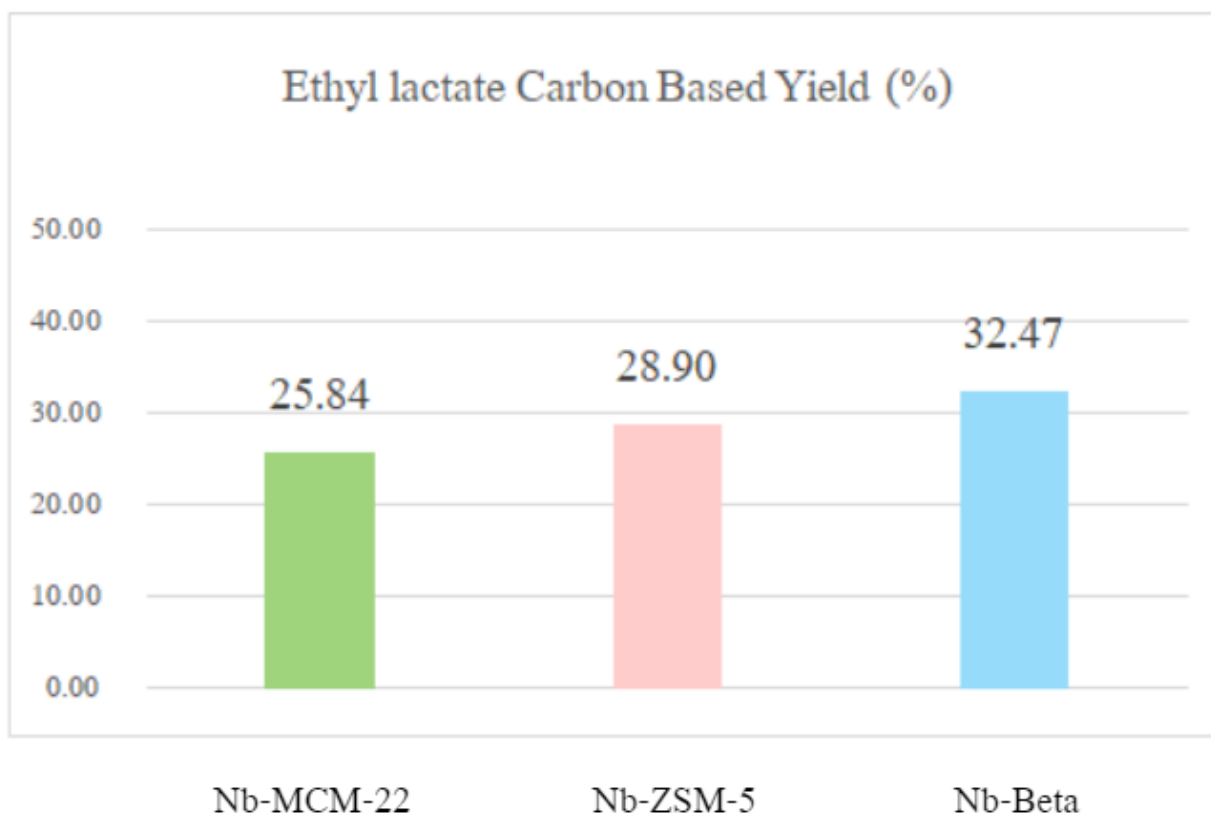After comparing the result between two conditions of the reaction in percentage as in picture below. Adding Niobium by impregnation method can significantly increase carbon based yield of ethyl lactate. On the first reaction that separately adds Niobium for 80 mg and zeolite for 100 mg. The second reaction uses 180 mg of 10 wt% Nb-zeolite. From the result the second method can increase more yield than the first one. Compared with the first method the amount of Niobium used in reaction is 80 mg, but for the second reaction, calculated from weight percent, impregned Niobium was used for only 18 mg. This result means that the second method uses less Niobium than the first one for 4.44 times. Also, even though it used less Niobium, the percent of carbon based yield is better than other methods.
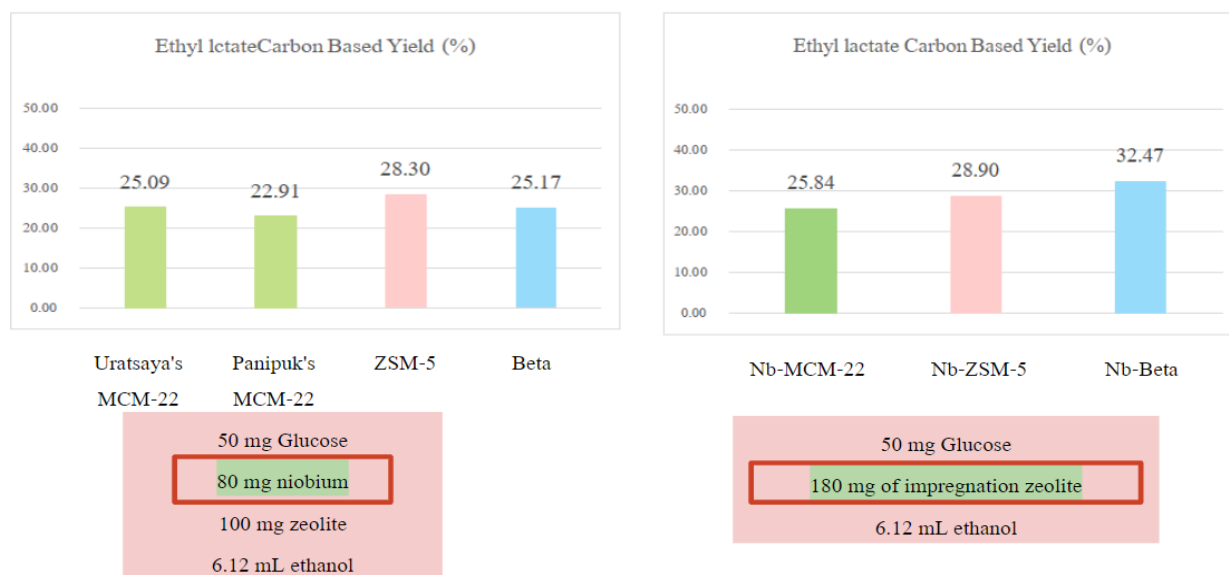
Figure 16. Comparison of niobium usage

3.2.2.4 Result comparison with literature review from the previous study

The conversion of glucose to ethyl lactate was conducted in previous study that were done from rice straw to ethyl lactate[4]. The reaction was using $SnCl_2/SnCl_4$ and $SnCl_2/ZSM$-5 as Catalyst. The reaction was done in 220 ^{o}C for 4 hours. The results of ethyl lactate are 21.8% and 20.0% respectively. Knowing from the previous report from Japan by Miss Uratsaya that high temperature in a short time will give out more yield, the experiment in this report was conducted at 200 ^{o}C for 1 hours with different zeolites. According to metal-containing catalysts can be used to improve performance of sugar conversion [5]. In this case, Niobium was selected and used in order to observe the performance. The result said that Niobium can significantly increase the carbon base yield of the product. From separately adding metal oxide with ZSM-5, Then Beta, and MCM22 the product was 25.09%, 25.17%, and 28.30% and for impregnation method yield were increased to 32.47%, 28.90%, and 25.84% respectively. Another previous study is the study which conduct by conversion of fructose to ethyl lactate. The reaction was done in autoclave for 3 hours at 160 ^{o}C with several catalysts. The result said that the highest yield of ethyl lactate was 55% using SnO_2-ZnO/Al_2O_3 as a catalyst[26]. Compared with the experiment that uses glucose as a reactant with Nb-Beta catalyst that

conducts for 1 hour at 200 ^{o}C Nb-Beta give out only 32.47%. This might happen because of the reaction path. Which glucose is not fully isomerized to fructose can conduct other side reactions.

Chapter 4

Conclusion

The conversion of glucose to ethyl lactate was investigated using MCM-22 and its motifined form. Besides, others catalyst with smaller pore size were used to compare the result of the product in the reaction. Firstly, MCM-22 and its modified form was successfully synthesized along with other zeolites. However, the second time that MCM-22 with direct Niobium was synthesized it's turn out that direct Nb-MCM-22 was turned to amorphous confirming by XRD. This might happen because there is not high enough thermal temperature to change Niobium from amorphous to crystalline or not collect ratio of synthesizing due to human error. However, All zeolites except direct Nb-MCM-22 identified through XRD were successfully confirmed. After that a catalyst was used and set the reaction at 160 ^{o}C for 1 hours in a 100 mL Parr reactor. The carbon based yield was investigated by Gas chromatography. It was calculated using the concentration of product and reactant. The result of carbon based yield was good. However to conduct the reaction with a 100 mL Parr reactor takes a long time and is inconvenient due to the heater. So the 25 mL Parr reactor was used instead. The result shows that a 25 mL Parr reactor can give out more yield than 100 mL Parr. This might be because higher heat that can flow inside the reactor. After that various zeolites with mental oxide were investigated. The result shows that zeolite impregnated with Niobium can give out better yield than zeolite that separately adds Niobium into the reaction. This might be because impregnation mental oxide can change the Lewis acid site. This can lead to improving production of sugar conversion. Compared with previous study Niobium played an essential role in increasing yield in the conversion of sugar. This is because Lewis acid that might be turned by using various metal oxide is important for conversion of triose to methyl lactate. From the result compared with others, zeolite Nb-MCM-22 can give out only 25.9% which is lower than Nb-Beta and Nb-ZSM-5. This might be because of larger pore size that might include glucose in pore and catalyze other side reactions. Moreover, impregnation zeolite uses less Niobium than separately used in reaction for 4.4 times and still gives higher yield. This might be used for reducing the cost of conversion in the future. To conclude, the highest

conversion of glucose to methyl lactate is conducted in 25 mL Parr impregnation with Niobium oxide at 160 $^{\circ}$C and reaction time at 1 hr. However, the limitation that came from the larger pore of zeolite can limit the ability of conversion. MCM-22 might not be the best zeolite for converting glucose to ethyl lactate. Anyhow, impregnation method can lead to study reduction of cost in sugar conversion in the future.

Future Plan

It is obvious that niobium as a metal oxide can increase the yield of ethyl lactate. However, MCM-22 might not be the best zeolite that can conduct the reaction due to the larger pore. In the future smaller pore zeolite might be used and studied as a zeolite for ethyl lactate conversion. Moreover, in the future acid sites in zeolite might be detected in order to know the effect of Lewis acid.

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Biography

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