Aqueous Phase Reforming of Sorbitol for Value Added Chemicals Production

by

Nur Fatin Dariah binti Mohamad Daud

15668

Dissertation submitted in partial fulfillment of
the requirements for the
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CERTIFICATION OF APPROVAL

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(CHEMICAL ENGINEERING)

Approved by,

____
(Dr. Mohammad Tazli Bin Azizan)

UNIVERSITI TEKNOLOGI PETRONAS

BANDAR SERI ISKANDAR, PERAK

September 2015

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

NUR FATIN DARIAH BINTI MOHAMAD DAUD

ABSTRACT

Biomass has been considered as the only sustainable source of energy and organic carbon for our industrial society. Biomass is a highly useful and renewable resource countless potential for utilization as a basis for hydrogen production. The behaviour of polyol (sorbitol) from hemicelluloses was investigated in aqueous phase reforming over supported Ni/Alumina catalysts. The effects of metal loading on the Ni/Alumina support on the catalytic performance were also studied. The objectives of this project which are to synthesize and characterize Ni/Alumina catalyst promoted by Ca for aqueous phase reforming (APR) of sorbitol and to conduct APR of sorbitol in order to identify the value added chemical that produced are investigated. The catalysts were synthesized by using several techniques such as Thermogravimetric Analysis (TGA), Scanning Electron Microscopy (SEM), and H_2-Temperature Programmed Reduction (H_2-TPR) to distinguish its characteristics. The TGA results shows that the optimum calcination temperature for all the catalysts is at 500^{o}C. Prior the catalytic activity test, all the catalysts were reduced in hydrogen flow by using the Tubular Furnace Reactor (TFR). The catalytic activity test was carried out in a batch-type reactor, PREMEX Autoclave reactor at 230^{o}C, 10 bar and 450 rpm. Last but not least, the most important element that makes this project different and interesting is the addition of the cheap promoter (Ca) that will be added to study the effect of each of them in Ni/ɣ- Al_2O_3. The liquid products produced from the catalytic activity test of sorbitol are analyzed by using Gas Chromatography Mass Spectrometry (GCMS) and High Performance Liquid Chromatography (HPLC) analysis.

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LIST OF ABBREVIATIONS

γ-Al_2O_3	Gamma Alumina
APR	Aqueous Phase Reforming
BET	Brunauer-Emmet-Teller method
Ca	Calcium
$CaCl_2.2H_2O$	Calcium Chloride Dehydrate
CO	Carbon Monoxide
CO_2	Carbon Dioxide
H_2	Hydrogen
H_2SO_4	Sulphuric Acid
HPLC	High Performance Liquid Chromatography
Mg	Magnesium
$Mg(NO_3)_2.6H_2O$	Magnesium Nitrate Hexahydrate
Ni	Nickel
$Ni(NO_3)_2.6H_2O$	Nickel NitrateHexahydrate
SEM	Scanning Electron Microscopy
TGA	Thermogravimetric Analysis
TFR	Tubular Furnace Reactor
TPR	Temperature Programmed Reduction
WGS	Water-Gas Shift

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Energy acts as the backbone of every modern society. However, the production of energy is one of the main contributors toward the global climate change which lead to global warming. Based on the future forecast for the economic growth in Asia Pacific and industrial development in Africa indicate that the total world energy demand will rise up from 462 quadrillion British Thermal Units (BTU) in 2005 up to 695 quadrillion BTU by 2030. The increment of CO_2 emissions to around 30 Gt per year from utilization of fossil fuel can lead to the global warming (Ribeiro, 2007). Therefore, incentives have been taken to find alternatives fuels which are from renewable sources such as biomass. In the "Roadmap for Biomass Technologies", report that authored by 26 leading experts has predicted that 20% of transportation fuel and 25% of chemicals will be produced from biomass by 2030 (Thompson, 2003).

Biomass is a highly useful and renewable resource countless potential for utilization as a basis for hydrogen production. The potential of biomass materials can be used as a feedstock for hydrogen production includes agricultural and forestry products and waste residues, livestock effluents, waste from the food processing industry, waste from the pulp and paper industry, sewage sludge and consumer wastes (Florin & Harris, 2007). Graham et al., mentioned that there are various method for producing hydrogen from biomass (Graham, 1984).

However, this project will focus on the aqueous phase reforming (APR)of sorbitol. Sorbitol is selected as one of the 12 biomass derived molecules that can be used for the production of fuels and chemicals as transformation of sorbitol into hydrocarbons is currently considered to be as a promising technology for the production of second-generation biofuels. In this project, the characterization of catalyst Ni/Alumina promoted by Ca/Mg for aqueous phase reforming of sorbitol and the value added chemical that will be produced is investigated.

1.2 Problem Statement

The increment of global demand for energy, chemicals and materials combined with the environmental issues in our current society had led to the efforts to develop low environmental effect technologies from renewable sources. Since the interest of alternatives raw materials to conventional fossil raw materials have increasing over recent years, it has been contributing to the foundation of a new paradigm which is the bio refinery concept. Basically, a bio-refinery is a similar concept to the conventional refinery which aims to maximize the outputs for energy, fuels, chemicals and materials from the processing of the raw materials. In this case, biomass and waste are selected as the renewable feed stocks and converted into valuable markets products by using a series of sustainable and low environmental impact technologies.

The bio refinery concept have encouraged a major concern of interaction between scientists from different fields including bio chemistry, biology, environmental sciences, economics and bio-chemical engineering in an attempt to shift to a bio-based industry that can make use of renewable resources for an increased competitiveness. The improvement of a more integrated approach to resource management based sustainable strategies along the whole supply chain to valorize residues, by products and waste in order to maximize the ratio products/feedstock is essential.

Therefore, approaches have to be made to process the waste residues aiming to produce high added value end products which can be implemented into current markets. Recently, a new pathway was proposed for bio-fuels production. It is the direct transformation of biomass derived-product, which is sorbitol into liquid hydrocarbon in aqueous medium over a heterogeneous acid-metallic bi-functional catalyst (Carol, 2013). Another way in the aim to change the mentality and perception in society on the waste instead as an issue, this project have make biomass derived product which is sorbitol as a resource to produce the value added chemical by using the aqueous phase reforming (APR) method.

1.3 Objectives

The objectives of this project are:

1. To synthesize and characterize Ni/Al_2O_3 catalyst promoted by Ca/Mg for APR of sorbitol.
2. To conduct aqueous phase reforming of sorbitol to identify the value added chemical that has been produced.

1.4 Scope of Study

The scopes of study of this project are:

1. Setting up a laboratory scale experiment to prepare Ni/Al_2O_3 catalyst using incipient wetness impregnation method.
2. Studying the effect of promoting the catalyst with Ca/Mg.
3. Characterization of catalysts using TGA, SEM, SEM-EDS, and H_2-TPR.
4. Evaluating the performance of catalysts.
5. Identification of value added chemical produced with its product distribution.

CHAPTER 2

LITERATURE REVIEW & THEORY

2.1 General Issue

Today, as petroleum is playing one of the main role in the world economy, global energy crisis nowadays is led by the rapid growth consumption of fossil fuels and depletion of total crude-oil reservations. Due to the fossil fuel pollutant gas emission, it has caused a huge bad impact on environment and public health. One of the biggest environmental issues in human history is global warming that caused by the increasing emission of greenhouse gas that was introduced by burning of fossil fuel (Wei, 2014).

As stated by Cortright & Davda, the continuous increment of energy demands and the depletion of fossil fuels reserves make the hydrogen an attractive alternative energy source. Hydrogen is currently derived from nonrenewable natural gas and petroleum but also can be produced from renewable resources such as biomass or water (Cortright, 2002).

Fuel cells based on hydrogen are environmentally clean, quiet and efficient in energy conversion and power generation. However, most mature hydrogen methods require high-temperature steam to reform non-renewable resource such as fossil fuel and natural gas (Davda, 2005). In order to achieve a full environmental friendly generating power from hydrogen fuel cells, hydrogen must be produced from renewable sources for example biomass. Biomass is said to be the promising sources to sustain the production of hydrogen in the era of dropping fossil fuels assets.

On the other hand, biomass has great potential as a substitute for fossil feedstock for the renewable production of transportation fuels and industrially important chemicals. Biomass is a plant material resulting from the reaction between carbon dioxide, CO_2 in the atmosphere, water and sunlight through the photosynthesis process to produce carbohydrates that form the structure blocks of biomass (Kendry, 2002).

Efforts on the production of new fuels from biomass have been focused which is called "biofuels". It can give good distribution over the surface of the earth and important potential for development. The carbon emitted from the biomass sources can be recycled which reabsorbed by the plants or crops for photosynthesis process (Janssen, 2014).

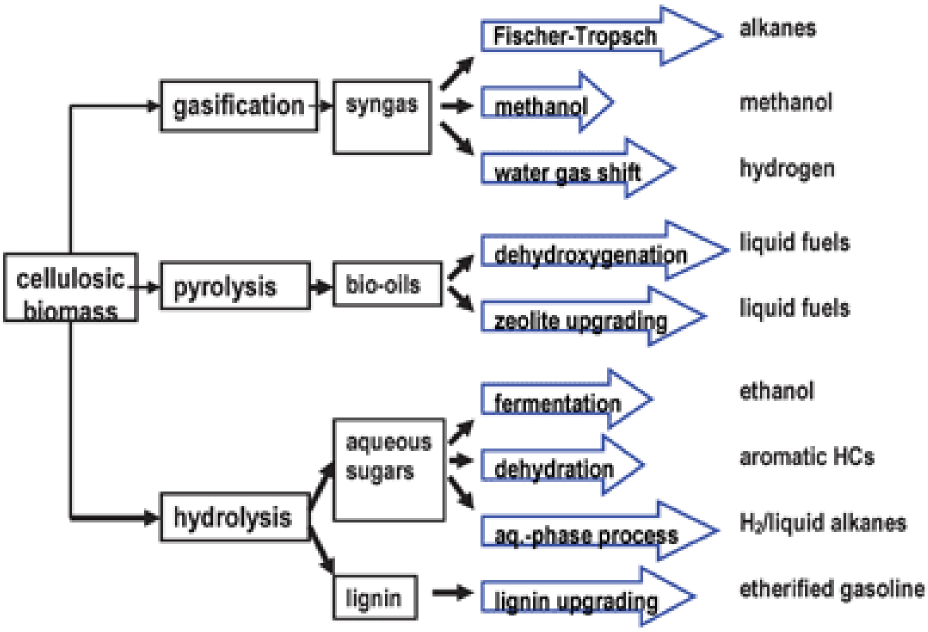


FIGURE 2.1 Possible cellulosic biomass utilization pathways (Navarro, 2007)

On the other hand, He and Chen mentioned that chemical energy in biomass is mostly stored in the form of glucose. The major constituents of biomass such as starch, cellulose, lactose and sucrose which are the complex sugars can be degrading to obtain glucose by fermentation process. The conversion of biomass to hydrogen by processing glucose to hydrogen production plays an important role (He, 2012).

Since the petrochemical technologies that have been well developed over the last decade are not valid to process the biomass-derived compounds, the shift from a petroleum-based economy to one based on biomass needs new strategies. As biomass-derived platform molecules are known to have a high oxygen content that gives them low volatility, high solubility in water, high reactivity and low thermal stability, catalytic aqueous-phase technologies fulfill the properties of these resources at moderate temperatures (Serrano-Ruiz, 2011). Industrial feasibility of the aqueous-phase reforming process is supported by a successful process startup for APR by Virent Energy Systems21 and developing of Bio-reforming Platform combining APR and conventional chemical methods for production of diesel, gasoline, jet-fuel and chemicals.

2.2 Technologies Used

However, the conversions of biomass to hydrogen still a challenge because the processes produce low production rates and require complex processing. Several types of hydrogen technologies have been identified for the purpose of hydrogen conversion from biomass.

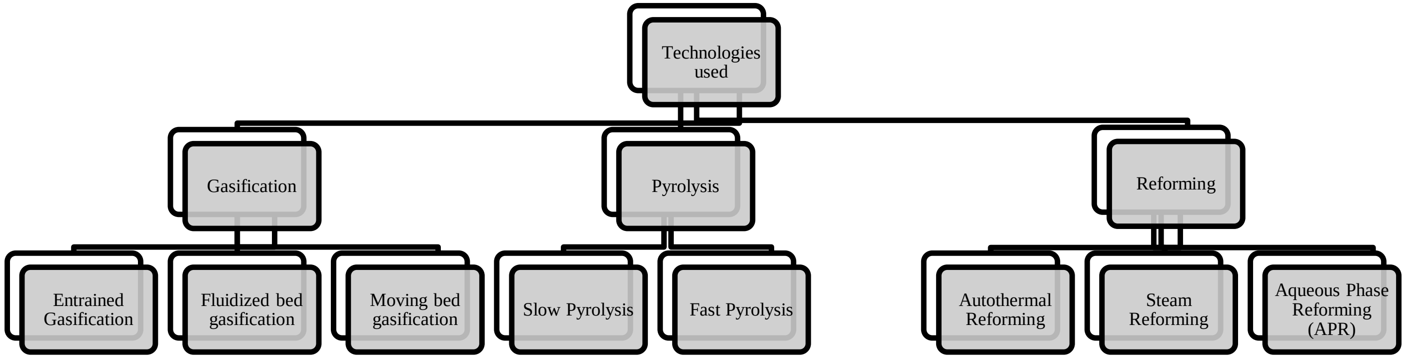
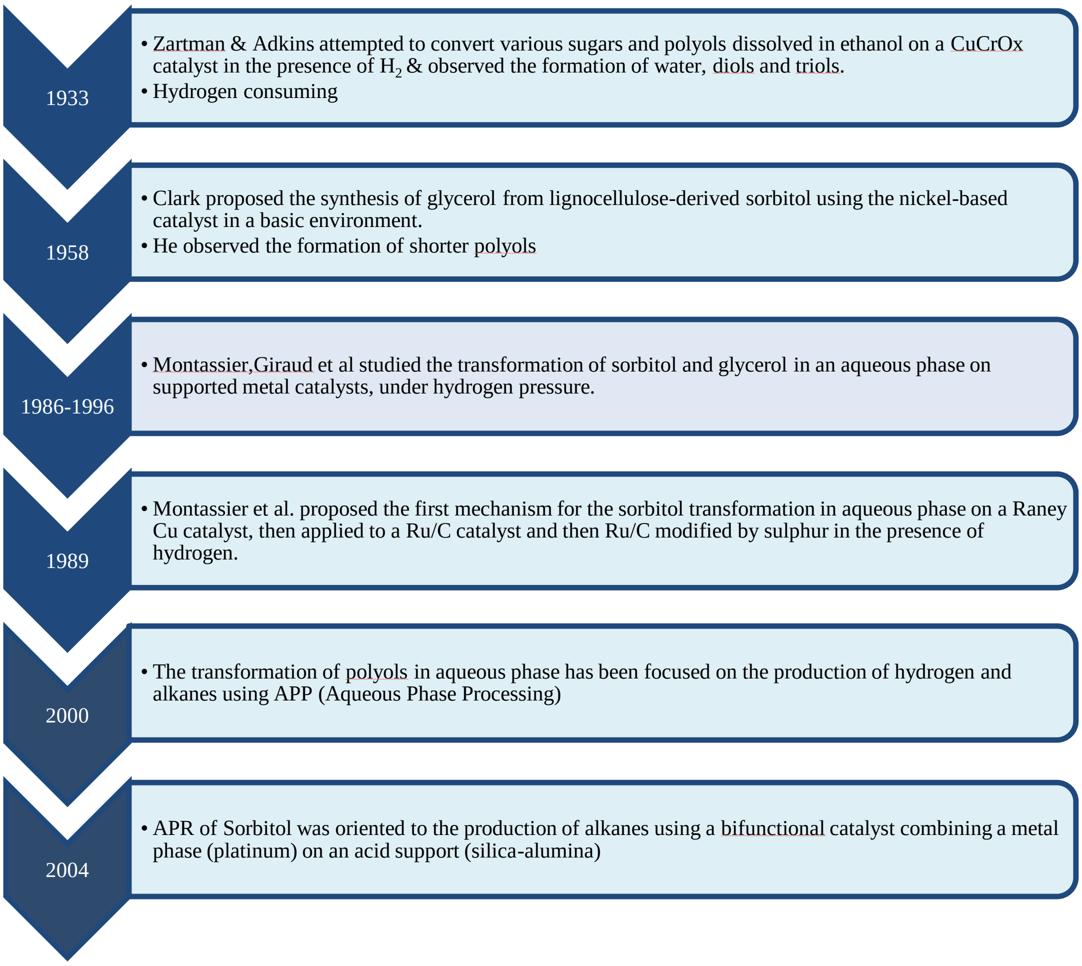


FIGURE 2.2 Types of Hydrogen technologies

2.3 Aqueous Phase Reforming of Polyols

The aqueous phase reforming was first introduced by Dumesic and co-workers in 2002. It is a catalytic transformation of biomass-derived oxygenates which allows production of both hydrogen and hydrocarbons. The transformation of sugars and polyols into hydrogen in aqueous phase at low temperature (220-260°C) using the heterogeneous catalyst was first studied by Cortright et al. From this study, they got a mixture of hydrogen, carbon dioxide CO_2, and gaseous alkanes together with the products in aqueous phase. This process is named Aqueous Phase Reforming (APR). Flowchart below shows the chronology of APR since year 1933 until the latest development.



1933

- Zartman & Adkins attempted to convert various sugars and polyols dissolved in ethanol on a CuCrOx catalyst in the presence of H_2 & observed the formation of water, diols and triols.
- Hydrogen consuming

1958

- Clark proposed the synthesis of glycerol from lignocellulose-derived sorbitol using the nickel-based catalyst in a basic environment.
- He observed the formation of shorter polyols

1986-1996

- Montassier,Giraud et al studied the transformation of sorbitol and glycerol in an aqueous phase on supported metal catalysts, under hydrogen pressure.

1989

- Montassier et al. proposed the first mechanism for the sorbitol transformation in aqueous phase on a Raney Cu catalyst, then applied to a Ru/C catalyst and then Ru/C modified by sulphur in the presence of hydrogen.

2000

- The transformation of polyols in aqueous phase has been focused on the production of hydrogen and alkanes using APP (Aqueous Phase Processing)

2004

- APR of Sorbitol was oriented to the production of alkanes using a bifunctional catalyst combining a metal phase (platinum) on an acid support (silica-alumina)

FIGURE 2.3 The Chronology of aqueous phase reforming (Kirilin, 2014)

Interests in using APR process to produce hydrogen have developed strongly due to its significantly advantages over other techniques. The advantages of hydrogen production using APR of carbohydrates are as below:

1. The need to vaporize both water and the oxygenated hydrocarbon is eliminated which will reduce the requirements of energy for hydrogen production.
2. The nonflammable and non-toxic oxygenated compounds of interest allow them to be stored and handled safely.
3. The water-gas shift reaction of APR occurs in favorable conditions that make it possible to generate hydrogen with low amounts of CO in a single chemical reactor.
4. Undesirable decomposition reactions that usually occur when carbohydrates are heated to high temperature can be minimized as APR occurs at low temperature.
5. By using pressure-swing adsorption or membrane technologies, APR is conducted at pressures (normally 15-50 bar) where the hydrogen-rich effluent can be effectively purified and carbon dioxide can be effectively separated.
6. Accomplished in a single-step and low temperature process in production of hydrogen and carbon dioxide.

As in the reaction shown below, alkane is transformed into hydrogen (H_2) and carbon monoxide (CO). Then, the carbon monoxide reacts further in the present of excess water through the water-gas shift (WGS) reaction to produce carbon dioxide (CO_2) and more hydrogen.

Equation (1): Transformation of Alkane into Hydrogen and Carbon Monoxide

$$\mathrm{C_nH_{2n+2} + nH_2O \leftrightarrow nCO + (2n + 1\,)H_2} \tag{1}$$

Equation (2): Water-gas shift reaction (WGS)

$$\mathrm{CO + H_2O \leftrightarrow CO_2 + H_2} \tag{2}$$

2.4 Sorbitol

Sorbitol is broadly used in food and medicine. Sorbitol also referred as a nutritive sweetener since it is often used in diet food as sugar substitute. This is because, compared to sugar and starch, sorbitol provides fewer calories to the diet while retaining 60% of the sweetness**.** Silveira.MM and Jonas.R (2002) also stated that sorbitol has been act as an increasing industrial interests which polyol that is found in many fruits as a sweetener, humectant, texturizer and softener.

Besides, sorbitol also known as glucitol. It is a sugar alcohol that human body metabolizes slowly. Most of sorbitol is made from corn syrup. On the other hand, it is a polyol found in a lot of fruits such as apples, pears, peaches, and prune. However, sorbitol not only can be produced chemically. It also can be produced biotechnologically.

TABLE 2.1 Characteristics of sorbitol (Wei, 2014)

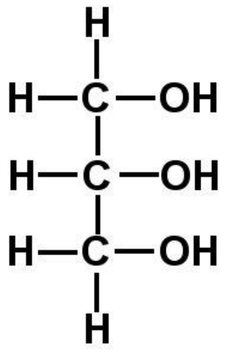
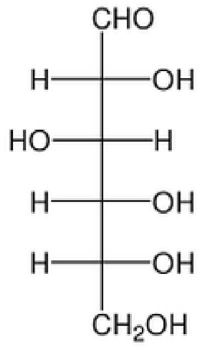
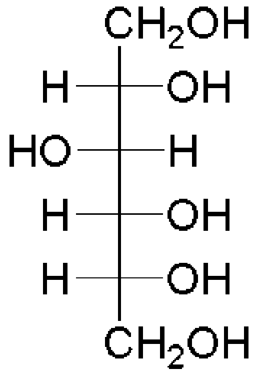
Systematic name	D-glucitol
Metabolism	Partially absorbed in the upper gastrointestinal tract where it undergoes digestion, and non-absorbed part is metabolized by colonic bacteria
Biological Activities	• Non-cariogenic • Reduced calorie value • Very low glycemic index
Industrial Manufacturing	Catalytic hydrogenation of sugar, starch or glucose syrups, at high temperature (typically, 100–150 ° C) and high pressure [100–150 bar]
Reported side effects	Osmotic diarrhea as a result of intestinal mal-absorption when ingested dose is greater than 50 grams per day

Nowadays, sorbitol is not only produced chemically, but also by biotechnologically using the bacterium Zymomonasmobilis as catalyst for production of sorbitol and gluconicacid. This is possible in a one-step reaction through a glucose-fructose oxidoreductase so far only known from Z. mobilis.

Sorbitol has been chosen as one of the 12 biomass-derived molecules that can be used for the production of fuels and chemicals as stated by the US Department of Energy because it has been considered as a high potential reagent. On the other hand, sorbitol is one of the most attractive biomass derived resources for APR process since last decade. As mentioned by S. Ramaswamyetal.,sorbitol is a potential key chemical intermediate from biomass resources for deriving a number of intermediates and chemicals such as propylene glycol, ethylene glycol, glycerol, lactic acid, and isosorbide.

Sorbitol have molecular formula of $C_6H_{14}O_6$ which is double the carbon bond from Glycerol which having molecular formula$C_3H_8O_3$. The molar mass of sorbitol is 182.17 g/mol which is approximately double the Glycerol which having molar mass of 92.02 g/mol.Comparisonof Glycerol ($C_3H_8O_3$), Glucose ($C_6H_{12}O_6$) and Sorbitol ($C_6H_{14}O_6$) chain as per below:

TABLE 2.2 Structures of Glycerol, Glucose and Sorbitol chain

Molecular structure	 Glycerol ($C_3H_8O_3$)	 Glucose ($C_6H_{12}O_6$)	 Sorbitol ($C_6H_{14}O_6$)

Sorbitol can be obtained by the reduction of glucose, which changes the aldehyde group to a hydroxyl group though the process called hydrogenation of glucose. Figure 2.4 shows the hydrogenation of glucose to produce sorbitol:

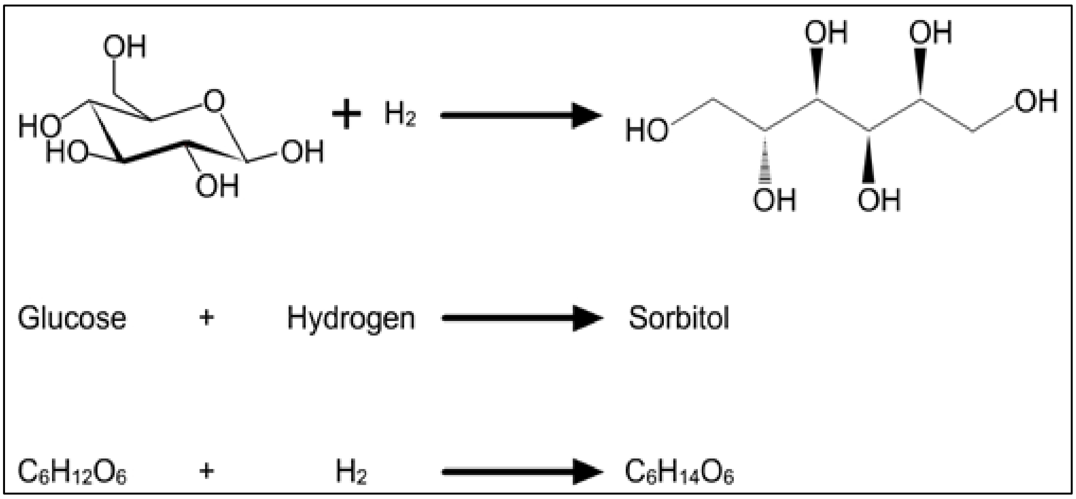


FIGURE 2.4 Hydrogenation of glucose to produce sorbitol

As National Institute of Starch stated that the annual production of sorbitol is 800,000Mt encouraged this project to carry out because of the availability of natural and renewable sources for sorbitol. In the figure below shows the primary conversion routes for sorbitol.

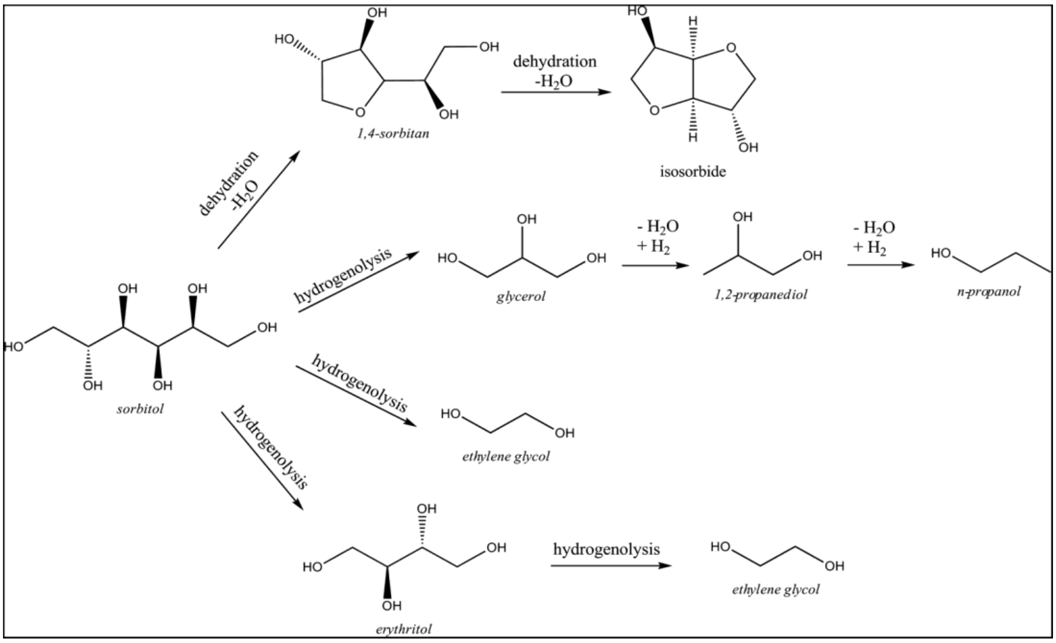


FIGURE 2.5 Primary conversion routes for sorbitol (Q. Zhang, 2014)

2.5 Aqueous Phase Reforming of Sorbitol

During aqueous phase reforming of sorbitol, the main products that are formed are hydrogen, carbon dioxide and a mixture of alkanes in the gas phase and also oxygenated products which mainly present in liquid phase. Figure below shows the illustration of the distribution of products in the APR of sorbitol that consists a mixtures of hydrogen, carbon dioxide, alkanes and oxygenated products.

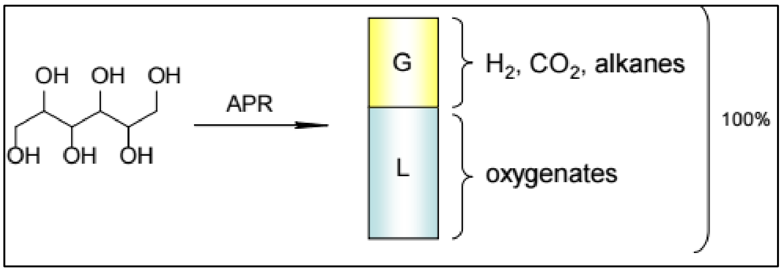


FIGURE 2.6 Distribution of products in APR of sorbitol

In theory, APR consist of two steps which the sorbitol is first undergoes reforming into hydrogen and CO. Then, the CO produced will be transformed into $CO_2$and hydrogen by the Water Gas Shift (WGS) reaction. Typically, those two reactions are catalyzed by a supported metal catalyst at elevated temperature (210-250°C) and pressures of 30-50 bars.

Equation 3: Reforming of sorbitol:

$$C_6H_{14}O_6 \leftrightarrow 6CO + 7H_2 \tag{3}$$

Equation 4: Water Shift Gas Reaction (WGS):

$$6CO + 6H_2O \leftrightarrow 6CO_2 + 6H_2 \tag{4}$$

Equation 5: Aqueous Phase Reforming (APR):

$$C_6H_{14}O_6 + 6H_2O \leftrightarrow 6CO_2 + 13\,H_2 \tag{5}$$

The pathway of APR process of sorbitol is said to be similar as glucose. Whenever C-C bond cleavage occurs, one molecule of carbon monoxide and hydrogen are formed with directly formed one molecule of carbon dioxide and extra hydrogen molecules. Aiouache et al. have studied another reaction mechanism which presented an intermediate during APR process of sorbitol. Sorbitol is said was converted to generic intermediates ($C_xH_yO_z$) then formed hydrogen and carbon through water-shift gas reaction. The homogeneous side reactions of sorbitol are claimed have been successfully reduced which becomes the utmost advantage of sorbitol over glucose feedstock (Y.Wei, 2014).

Besides, Y. Wei et al. has stated that the result of Davda's investigation of APR process using sorbitol and glucose as feedstock gave 13-60% of hydrogen selectivity under the same reaction conditions. Figure below shows the main pathways of sorbitol transformations during APR that have been chosen for mathematical modeling of kinetics.

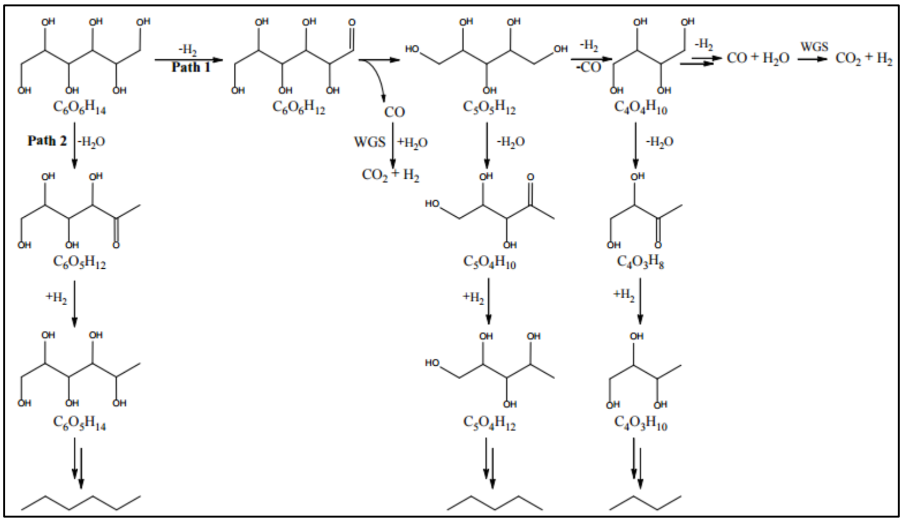


FIGURE 2.7 The main pathways of sorbitol transformations during APR chosen for mathematical modeling of kinetics (Wei, 2014)

As shown in the main pathways of sorbitol transformations during APR above, the path 1 shows the part of sorbitol to alcohols, $C_nO_nH_{2n+2}$ with n<6, starting with dehydrogenation on the metal sites leading to a corresponding aldehyde.

In Path 2, sorbitol undergoes dehydrogenation on acidic sites to a ketone followed by hydrogenation to a C_6 alcohol with one hydroxyl group less than the starting sorbitol (Kirilin, 2013). Kirilin also stated that this initial step of dehydration is considered to be the rate determining one, while the following steps of hydrogenation - dehydration - hydrogenation were merged together.

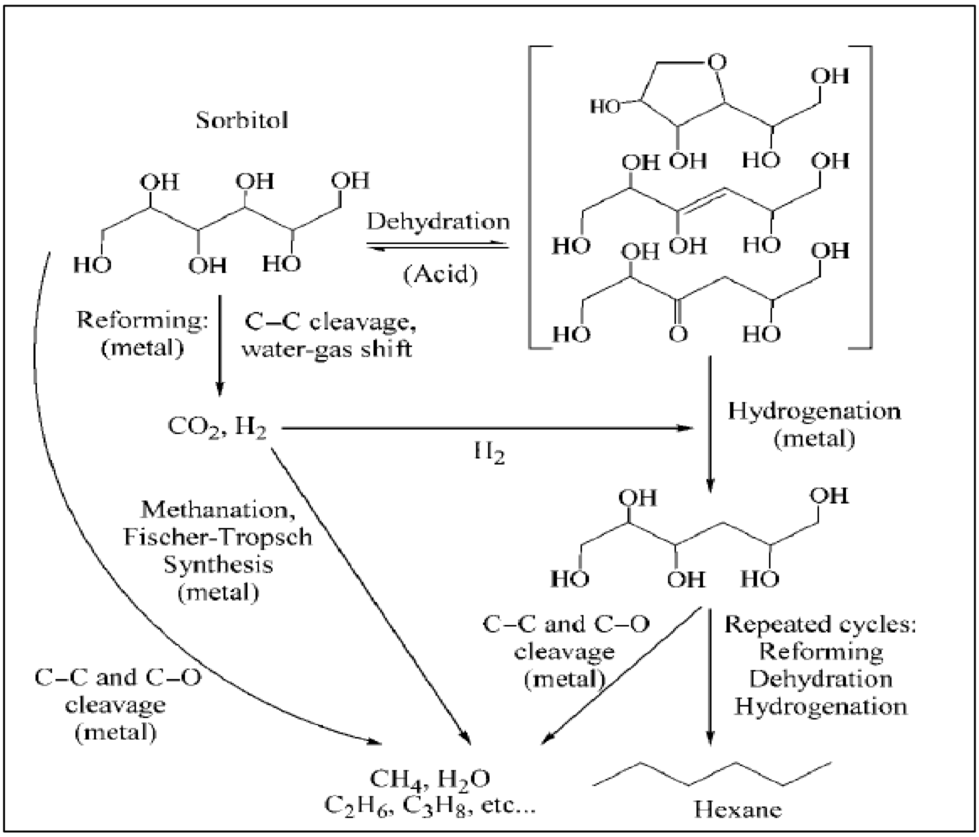


FIGURE 2.8 Bi-functional reaction pathways for the production of alkanes from sorbitol over catalysts with metal and acidic components

Huber (n.d) studied that aqueous phase hydro-deoxygenation of carbohydrates to produce a wide range of products including C1-C6 alkanes, C1-C6 primary and secondary alcohols, cyclic ether and polyols. It has been reported that Ni is one of the metals that favors the production of alkanes from polyols (sorbitol) over hydrogen due to the fact that C-O bond cleavage is favored more than C-C bond cleavage over these metals.

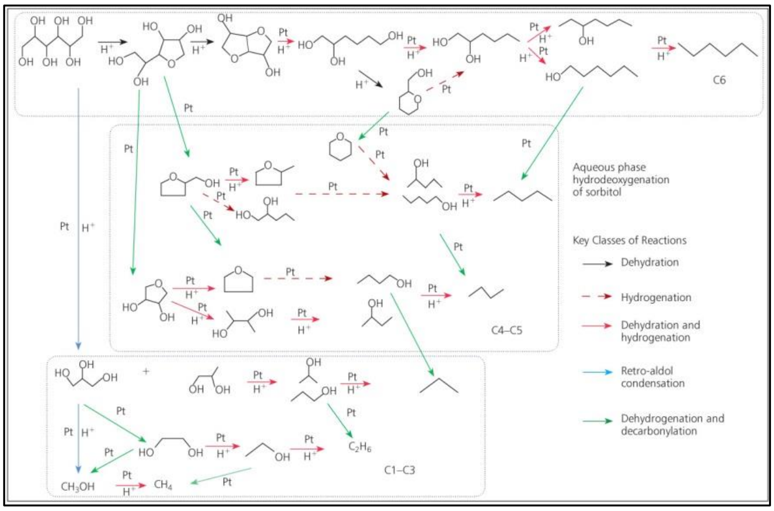


FIGURE 2.9 Reaction pathways for hydro-deoxygenation of sorbitol over a platinum bi-functional catalyst (Huber, n.d)

Sorbitol has more limitations for APR process compared with other biomass derived polyols. However, as glucose derived polyols, sorbitol has great potential in APR process of hydrogen production.

2.5.1 Catalysts Selection for Sorbitol Transformation

Modification of the catalyst and/or the temperature of the process modifies the composition of the resulting gas. For example, in earlier work Virent founders discovered that the aqueous-phase reforming of sorbitol, glycerol, and ethylene glycol solutions produced an effluent gas stream composed of 50-70 mol% H_2, 30-40 mol% CO_2, and 2–11 mol% alkanes (dry basis) at high conversion.

As stated by Huber, the selectivity towards alkanes can be adjusted by modifying the catalyst composition, pH of the feed, reaction conditions and the reactor design. For example, the selectivity towards heavier alkanes can be increased when a solid acid catalyst (SiO2/Al_2O_3) is added to Pt/Al_2O_3, whereas the selectivity towards hydrogen decreases from 43% to 11%. This behavior indicates that the majority of the hydrogen production by reforming reaction is consumed by the production of alkanes when the catalyst contains sufficient number of acid sites.

Nickel catalysts have gained tremendous attention because they are active in hydrogenation, hydro-treating and steam reforming reactions. The idea of supporting nickel catalysts on high surface area ceramic substrates like alumina is to increase the surface area of the catalyst.

2.5.2 Catalytic Activity Test of Sorbitol

Q.Zhang stated that the catalytic activity test of the catalyst was carried out in a batch-type autoclave reactor with a capacity of 250 ml. Oxygen in the reactor was removed by purging it with hydrogen for three times the reaction was performed at 240^{o}C and 4.0Mpa for 1 hour under the stirring speed of 200r min^{-1} (Q. Zhang, 2012).

Kirilin have performed aqueous phase reforming of sorbitol at 225^{o}C and 29.3 bar in a continuous reactor over supported Pt/Al_2O_3. Products such as isosorbide and organic acids (100–500 ppm) were observed in the liquid products from an empty reactor with a feed of 5 wt% sorbitol heated at 538 K and 57.5 bar, whereas negligible amounts of liquid products were observed at 498 K and 36.5 bar. The conversion and the alkanes selectivity were measured by the formulas below:

Equation 6: Sorbitol Conversion Formula

$$\text{Sorbitol conversion}(\ \%) = \frac{\text{Sorbitol}_{\text{m}} - \text{Sorbitol}_{\text{residue}}}{\text{Sorbitol}_{\text{m}}} \times 100 \qquad (6)$$

TABLE 2.3 Comparison study for catalysts used for APR of sorbitol

Reference	**Catalyst**		**Reaction Conditions**	**Sorbitol conversion (%)**	**H_2 Selectivity (%)**	**Products**
	Metal	Support				
Kirilin et al., 2014	Pt	Al_2O_3	T= 498 K P = 29.3 bar	100 %	43%	H_2, CO_2, and a mixture of alkanes.
Aiouche et al.	Zeolite	Ni	T= 498 K P = 29.3 bar	Not reported	Not reported	Not reported
Davda et al.	Pt	Al_2O_3	T= 498 K P = 29.3 bar	Not reported	13-60%	Not reported
Huber et al.	Pt	Al_2O_3	-	Not reported	60%	Not reported
Q. Zhang et al., 2012	HZMS-5	Ni	T= 500C	Refer appendix A	Not reported	47.6% of bio gasoline yield
Dumesic, 2004	Pt/SiO_2	Al_2O_3	T= 498 K P = 39.6 bar	58-89%	Not reported	Not reported

TABLE 2.4 Research on the experimental activity aqueous phase of sorbitol

Who	**Title of Article**	**Catalyst Preparation**	**Catalytic activity test**	**Products**
Kirilin et al, 2002	Kinetic Modeling of Sorbitol Aqueous-Phase Reforming over Pt/Al_2O_3	Incipient wetness impregnation method.	Used a batch-type autoclave reactor	Isosorbide
Qing Zhang et.al., 2011	Isoparaffin production by aqueous phase processing of sorbitol over the Ni/HZSM-5 catalysts : Effect of the calcination temperature of the catalyst	Incipient wetness impregnation method.	Used a batch-type autoclave reactor.	Iso-paraffin
Qi Zhang et. al., 2012	Aqueous phase reforming of sorbitol to bio-gasoline over Ni/HZXM-5 catalysts	Incipient wetness impregnation method.	Batch-type high pressure autoclave	Bio-gasoline
Qing Zhang et.al., 2014	Production of liquid alkanes by controlling reactivity of sorbitol hydrogenation with a Ni/HZXM-5 catalyst in water	Incipient wetness impregnation method.	Used a batch-type autoclave reactor.	Liquid alkanes

CHAPTER 3

METHODOLOGY

3.1 Research Methodology

This chapter comprises of the project research methodology and experimental activities. Figure below illustrated the project flow for this study.

FIGURE 3.1 Project Flow

In the beginning, the author identified the objectives of this research project and understanding the problem statement. The author has gathered all the relevant information from several trusted sources such as journals, books and websites.

On the other hand, method to conduct the experimental activities has been studied and identified properly. The chemicals, apparatus and equipment needed are listed as well as the data needed to collect from experiments. Experimental activities are conducted once all the important matters are prepared.

Then, the author analyzed and interpreted the findings and comparison has been made from the literature studies that have been made earlier. Last but not least, the findings are documented and reported in detail and some recommendation for future improvement also discussed in this report.

For experimental activities are divided into three main parts that is illustrated as below:

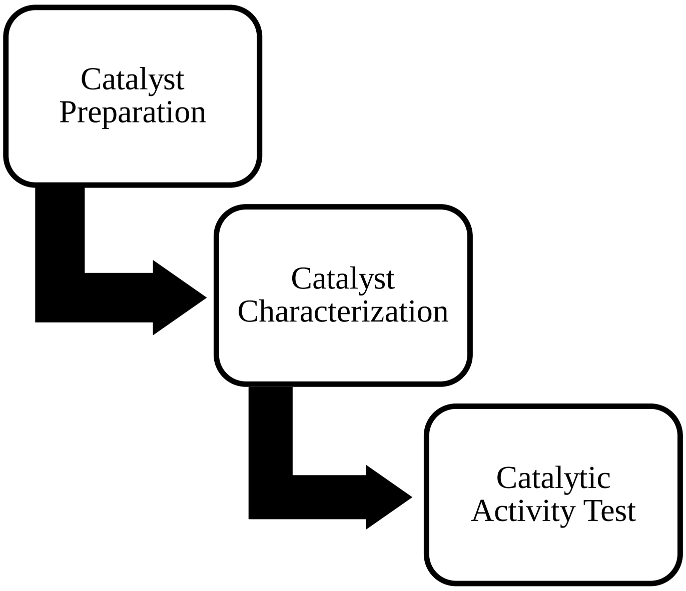


FIGURE 3.2 Experimental Activities

First of all, the author prepared 9 nickel based catalysts promoted of bimetallic pair with calcium and magnesium salts through wetness impregnation method. Once the catalysts have been synthesized, they undergo catalysts characterization to know the physiochemical properties through several techniques such as TGA, H_2-TPR and SEM analysis.

Lastly, these catalysts are evaluated in a reactor under nitrogen flow to study their performances in aqueous phase reforming reaction with sorbitol. The liquid product produced from this reaction is analyzed with Gas Chromatography Mass Spectrometry (GCMS) and High Performance of Liquid Chromatography (HPLC) equipment to know the value added chemicals produced.

3.2 Gantt Chart and Key Milestones for FYP

TABLE 3.1 Gantt Chart

		FYP 1														FYP 2													
#	**Detail**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**
1	Selection of Project Topic	▨	▨																										
2	Critical literature review of aqueous phase reforming		▨	▨	▨	▨	▨																						
3	Requisition of chemicals and laboratory apparatus			▨																									
4	Research methodology and Project Activities					▨	▨	▨																					
5	Submission of Extended Proposal to Supervisor							🟡																					
6	Proposal Defense									▨																			
7	Project Work Continue								▨	▨	▨	▨	▨																
8	Submission of Interim Draft Report													🟡															
9	Submission of Final Interim Report														🟡														
10	Synthesis of catalyst													▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨					
11	Characterization of catalysts and evaluation of catalytic activity of the catalysts																		▨	▨	▨	▨	▨	▨	▨	▨	▨		
12	Submission of Progress Report																						🟠						
13	Pre-Sedex																									🟠			
14	Submission of Draft Report																									🟠			
15	Submission of Dissertation (soft bound)																										🟠		
16	Submission of Technical Paper																										🟠		
17	Viva																											🟠	
18	Submission of Project Dissertation (Hard Bound)																												🟠

Legend ▨ Duration Interval 🟡 FYP I Key Milestone 🟠 FYP II Key Milestone

3.3 Chemicals, Apparatus and Equipment

The chemicals, apparatus and equipment that was used for this project are listed in the table below:

TABLE 3.2 List of chemicals and apparatus

Chemicals/Apparatus	Quantity	Purpose
Gamma Alumina	1 kg	Catalyst Synthesis
Nickel Nitrate Hexahydrate	500 g	Catalyst Synthesis
Magnesium Nitrate Hexahydrate	500 g	Catalyst Synthesis
Calcium Chloride Dehydrate	500 g	Catalyst Synthesis
Sorbitol	1 kg	Catalytic Activity Test
0.005 M Sulphuric Acid	1 L	Mobile Phase for High Performance Liquid Chromatography
Parr Batch Reactor	1	Catalytic Activity Test
Beaker 200 ml	2	Catalyst Synthesis
Beaker 500 ml	2	Catalyst Synthesis
Crucible	6	Catalyst Synthesis
Hot Plate Stirrer	1	Catalyst Synthesis
Magnetic Bar	1	Catalyst Synthesis
Spatula	2	Catalyst Synthesis

TABLE 3.3 List of equipment needed for catalysts preparation

Equipment	Function
Drying Oven	For drying purpose.
Furnace	To remove the moisture in the catalyst.

3.4 Catalyst Preparation

Based on the literature review and researches that have been made, the method used to prepare the catalyst for this project is by incipient wetness impregnation (IWI) method to investigate the hydrogenation of sorbitol in the liquid phase. For this project, nine (9) samples will be prepared by using nickel nitrate hexahydrate, Ni $(NO_3)_2.6H_2O$, magnesium nitrate hexahydrate, $Mg(NO_3)_2.6H_2O$ and calcium chloride dehydrate $CaCl_2.2H_2O$ on gamma alumina, γ-Al_2O_3 support. However, gamma alumna (γ-Al_2O_3) is prepared as a base only.

TABLE 3.4 Catalysts Composition

	Sample	Composition of Al_2O_3:Ni:Ca:Mg
1.	10% Ni/ γ-Al_2O_3	90 : 10 : 0 : 0
2.	0.5% Ca + 10% Ni/ γ-Al_2O_3	89.5 : 10 : 0.5 : 0
3.	3% Ca + 10% Ni/ γ-Al_2O_3	87 : 10 : 3 : 0
4.	5% Ca + 10% Ni/ γ-Al_2O_3	85 : 10 : 5 : 0
5.	0.5% Mg + 10% Ni/ γ-Al_2O_3	89.5 : 10 : 0 : 0.5
6.	3% Mg + 10% Ni/ γ-Al_2O_3	87 : 10 : 0 : 3
7.	5% Mg + 10% Ni/ γ-Al_2O_3	85 : 10 : 0 : 5
8.	0.5% Ca + 0.5% Mg + 10% Ni/ γ-Al_2O_3	89 : 10 : 0.5 : 0.5
9.	5% Ca + 5% Mg + 10% Ni/ γ-Al_2O_3	80 : 10 : 5 : 5

Based on the composition in the table above, calculation is made to formulate the solution as attached in Appendix B.

The procedure to prepare Ni/ γ-Al_2O_3 catalyst, promoted by Ca/Mg using the incipient wetness impregnation method as follows:

1. γ-Al_2O_3 was placed into crucible and calcined at 500°C in furnace for 24 hours.

FIGURE 3.3 γ-Al_2O_3 in furnace for calcination process

2. $Ni(NO_3)_2.6H_2O$salt was weighted and diluted in distilled water to become aqueous solution.

FIGURE 3.4 Dilution of $Ni(NO_3)_2.6H_2O$ salt solution

3. Calcined Al_2O_3 was mixed with $Ni(NO_3)_2.6H_2O$solution. The mixture was stirred for 4 hours.

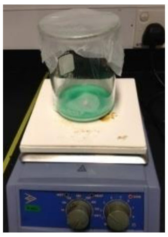


Figure 3.5 $Ni(NO_3)_2.6H_2O$ solution was stirred with calcined Al_2O_3

4. The mixture was dried in oven for 24 hours. Figure below shows the difference in color for addition of Ca and Mg in the mixture that was dried. The dried mixture was crushed using mortar and strained to get fine powder.

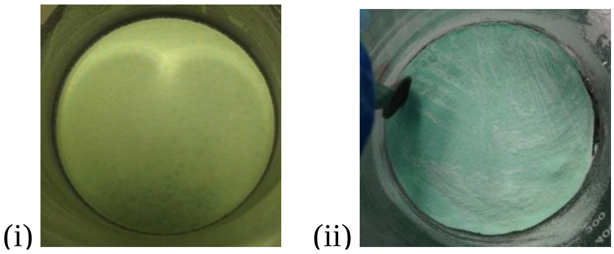

(i) (ii)

FIGURE 3.6 Addition of (i) Ca and (ii) Mg into solution

FIGURE 3.7 Crushing process using mortar

5. For promoted catalysts preparation, the calcium and magnesium salt was added into $Ni(NO_3)_2.6H_2O$ solution. Step 3 to 5was repeated.

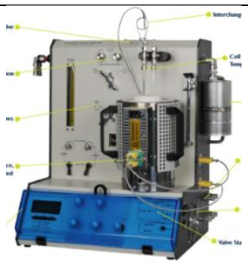
6. The catalysts were sent for thermogravimetric analysis to know the most suitable calcination temperature before it is calcined in a muffle furnace for 16 hours.

7. The catalysts were sent for characterization.

3.5 Catalyst Characterization

Table below shows the list of equipment that is used for the catalyst characterization.

TABLE 3.5 List of equipment for catalyst characterization

Method of Characterization	Equipment	Function(s)
Brunauer-Emmett-Teller (BET) analysis		To measure the surface area and structural properties of the samples by N_2 multilayer adsorption.
Temperature programmed reduction (TPR)		To distinguish the reducible species existence, their interaction and degree of reducibility.
Scanning Electron Microscopy (SEM)		Characterization of nano-structure, to observe the real surface structures with optimum contrast.
X-Ray Diffraction (XRD)		1. To identify the crystalline material and unit cell dimensions.(Dutrow, 2015) 2. To analyze the minerogical of solid materials for phase determination.
Thermogravimetric Analysis (TGA)		1. To identify the catalysts' thermal stability and composition. 2. To know the calcination temperature of the catalysts.

3.5.1 Thermogravimetric Analysis (TGA)

To know the suitable calcination temperature, the catalysts were sent for thermogravimetric analysis. The catalysts were analyzed by using a computerized TGA equipment, Perkin Elmer Model PYRIS 1. The temperature was increased from 30ºC until 800ºC with the heating rate of 5ºC/min in oxygen-free nitrogen gas as the carrier.

3.5.2 Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy was performed to obtain the microscopy images in order to observe the real surface structure of the catalysts. The catalysts were analyzed under magnification of 500X, 1500X and 3000X with the scale of 100µm, 50µm and 20µm respectively by using the PhenomProXdekstop scanning microscope. Sample structures can be physically examined and their elemental composition can determined from the Phenom ProX that is a fully integrated designed EDS detector.

3.5.3 H_2-Temperature Programmed Reduction (H_2-TPR)

20 mg of each catalyst was used to be analyzed with TPDRO 1100 Equipment to determine the reducibility of the catalysts by temperature programmed reduction. The catalyst firstly pretreated at 250ºC in a pure nitrogen (N_2) stream for 1 hour with the flow rate 30 ml/min and heating rate of 10ºC/min. After cooling to room temperature, the sample was introduced with 5% H_2/N_2 flow at the heating rate 5ºC/min for 1 hour.

3.6 Catalytic Activity Test

The catalysts will be evaluated in PREMEX autoclave reactor (batch type reactor) with a capacity of 250ml. 0.05 mol of sorbitol and catalyst is stirred together and the reaction is fed with Nitrogen gas. Further experimental procedure is explained in Section 3.6.2.

3.6.1 Sorbitol Preparation

The desired amount of 0.05 mol sorbitol in 150 ml of distilled water is calculated as below:

$$\text{Mole needed (n)} = \frac{\text{Mass of sorbitol needed}}{\text{Molar Mass of sorbitol}} \tag{7}$$

Data available:

Molar mass of sorbitol	= 182.17 g/mol
Mole needed (n)	= 0.05mol

After substituting the data into Equation (7), the mass of sorbitol needed is 9.1 gram. This sorbitol is diluted with 150 ml distilled water.

3.6.2 Experimental Procedure

In conducting the experiment, all the operating parameter such as temperature and pressure are fixed. The type of catalysts is been varied. Each type of catalysts will be tested with 0.05 mol of sorbitol to see the effect of metal loading (Ca) catalyst. Table 3.6 shows the experimental variables that will be used throughout of the experiment.

TABLE 3.6 Experimental Variables

Constant Variable	Temperature: 230°C Pressure: 20 bar Speed of rotation: 450 rpm Amount of sorbitol : 0.05 mol in 150 ml distilled water
Manipulated variable	Type of catalysts
Responding variable	The types of value added chemicals that are produced.

The procedure of catalytic activity test as below:

1. 1g of catalyst is weighed using a weigh balance.
2. Sorbitol solution and catalyst are put together in the reactor.
3. Autoclave reactor is switch on.
4. All the parameters are set as the details in the table above.
5. After 30 minutes, the reforming liquid is been taken out from discharge vessel.
6. The liquid is analyzed using High Performance Liquid Chromatography(HPLC) to know the existence of the value added chemicals been produced.
7. All steps are repeated by using different catalyst.

3.6.3 GCMS Operating Conditions

In conducting the GCMS Analysis, a few parameters need to be setup. Acetonitrile is used as solvent during the sample analysis. The inlet temperature will be 280°C with the injection volume of 1µL. The split ratio is 50:1, with the initial temperature 40°C (5°C/min) and hold time, 10 minutes. The temperature is raised further until 200°C with the rate 10°C/min and hold time 10 minutes.

3.6.4 HPLC Operating Conditions

HPLC is used to determine the retention time of sorbitol with different concentration without any catalyst and the value added chemicals produced from the different type of catalysts. A proper operation conditions for HPLC is very important to examine the accurate retention time. Table 3.7 shows the operating conditions for HLPC equipment.

TABLE 3.7 HPLC Operating Conditions

Injection Volume: $30\mu L$	Detector: UV
Flow rate: 0.6 mL/min	Column: Eclipse XDB C18,
Pressure: 48 bar	$5\ \mu m, 46\ x\ 150\ mm,$ Agilent
Temperature: 30^{o}C	Runtime: 35 minutes
Mobile Phase: 0.005M of H_2SO_4	Signal: 215 nm and above

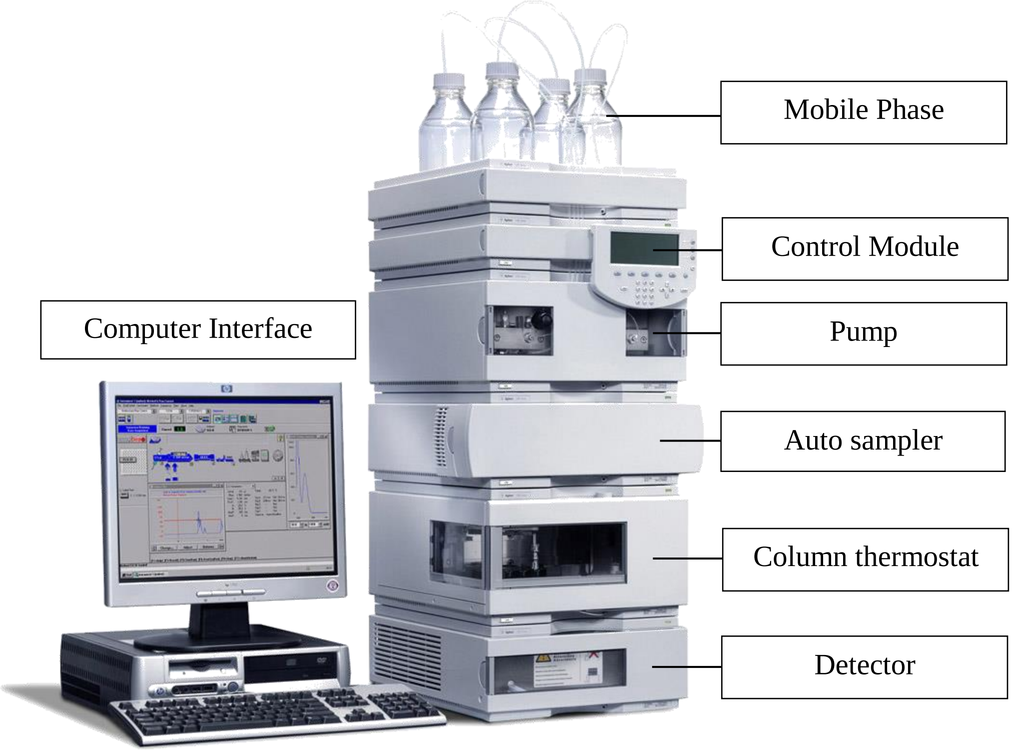


FIGURE 3.8 HPLC Equipment

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Introduction

In this chapter, the author discussed the results of the catalysts characterization and the reaction discussion. All the calculations involved in the catalysts formulation also will be explained in this chapter. Besides calculation, this chapter will explain the results of catalyst characterization from TGA, SEM, SEM-EDS and H_2-TPR. Last but not least, the catalytic activity of the catalysts with sorbitol also will be discussed in detail.

4.2 Catalyst Preparation

The weight of catalyst that is prepared is 25g each. The percentage of nickel loading is kept constant at 10% for each catalyst. The composition of supported metal, Ca and Mg is varied to 0.5%, 3% and 5% loading. Nine samples with different compositions are prepared based on the calculation in Appendix C.

4.3 Catalyst Characterization

The catalysts are characterized and analyzed from the results of TGA, SEM, SEM-EDS, H_2-TPR.

4.3.1 Thermogravimetric Analysis (TGA)

The purpose of doing the thermogravimetric analysis is to determine the most suitable calcinations temperature of each catalyst. The weight loss, thermal behavior and the structural of the catalysts also can be investigated from this analysis (Zangouei, 2010). For this project, TGA measures weight changes for each catalyst as a function of temperature in minute under a controlled atmosphere. The graph shows the weight percent (%) and derivative weight percent (%/min) versus temperature of Ni/Al_2O_3 respectively.

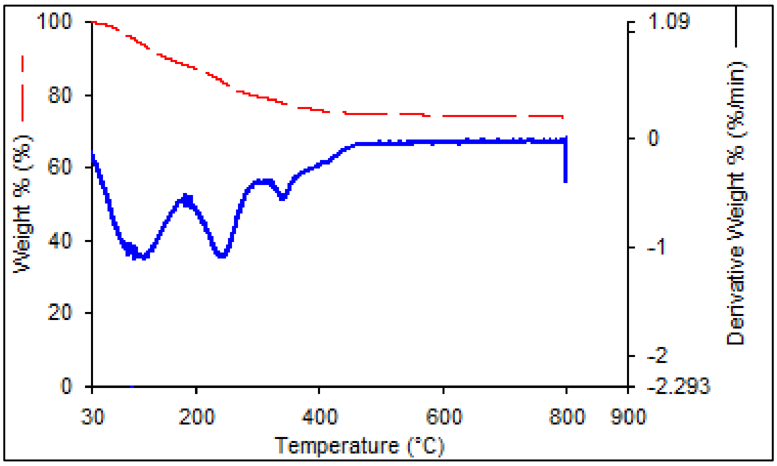


FIGURE 4.1 TGA profiles for 10% Ni/Al_2O_3

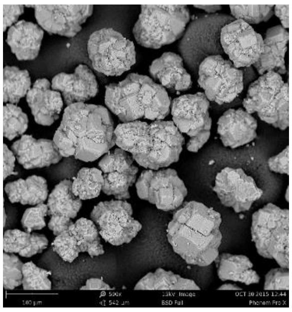
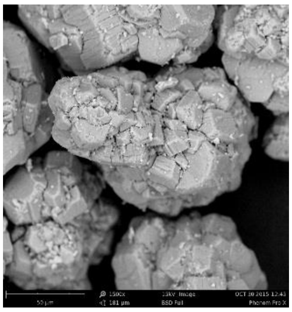
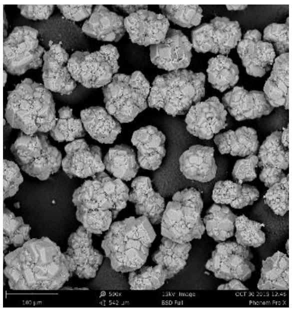
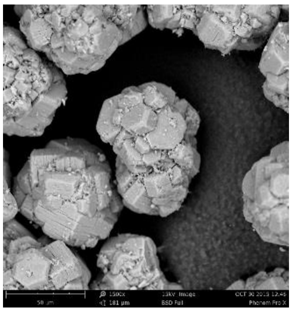
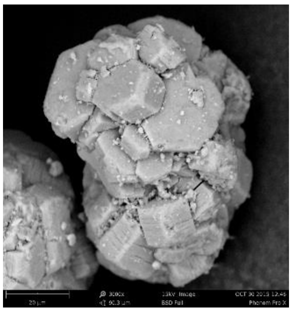
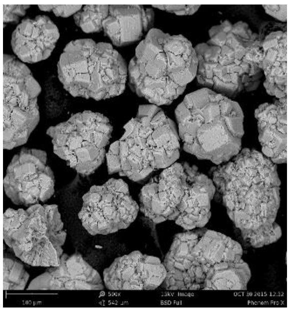
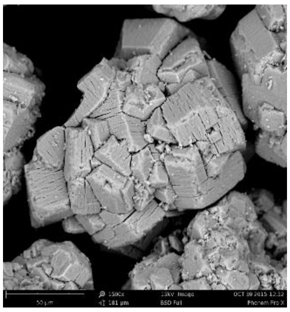
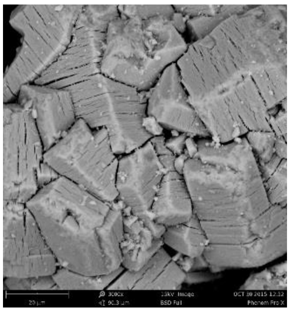
As show in the graph, the weight percentage slowly decreases as temperature increase. The derivative weight percent indicates the weight loss per minute. The weight loss per minute progressively happened as the temperature increase to 500°C. The most suitable temperature for calcination is where the graph shows the weight loss starts to be constant which is approximately within the range of 450 to 550°C.

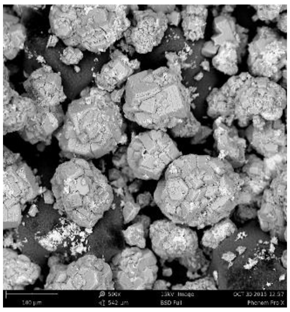
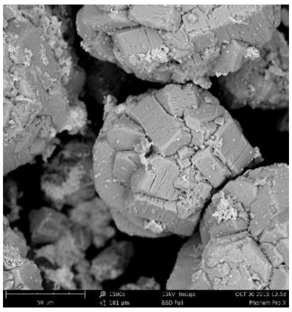
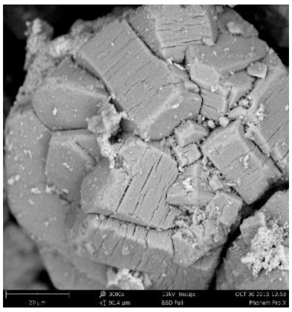
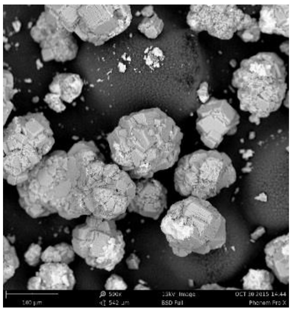
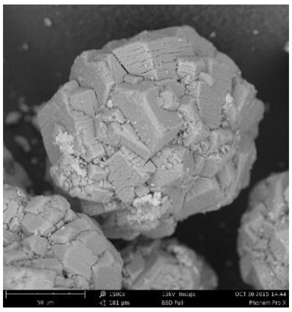
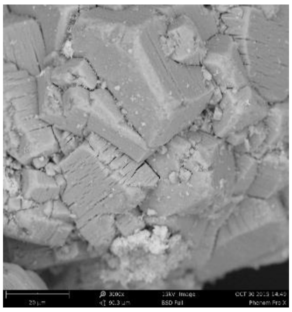
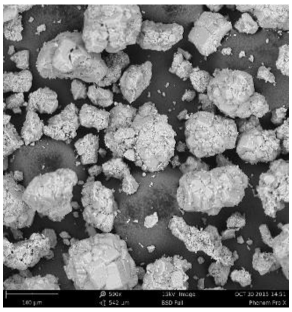
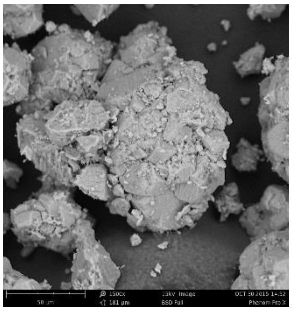
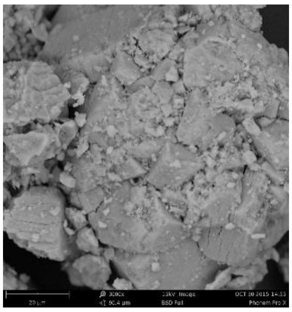
The results obtained similar with the TGA investigation from Zangouei and friends in year 2010. From all the TGA results obtained, the suitable temperature for all of the catalysts for calcination is concluded to be similar, which is approximately 500°C. For this project, the calcination temperature of the catalyst is kept constant at 500°C. The results of TGA for promoted catalysts are attached in the Appendix D.

4.3.2 Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM) was used to investigate the morphology of the catalyst. Each catalyst undergoes 500X, 1500X and 3000X magnifications. Table 12 shows the micrographic images of the catalysts.

TABLE 4.1 SEM Images of catalysts at 500X, 1500X and 3000X magnifications

Catalyst	500X	1500X	3000X
$\gamma - Al_2O_3$			
10% Ni/Al$_2$O$_3$			
0.5% Ca + 10% Ni/Al$_2$O$_3$			

3% Ca + 10% Ni/Al$_2$O$_3$			
5% Ca + 10% Ni/Al$_2$O$_3$			
0.5% Mg + 10% Ni/Al$_2$O$_3$			

The morphology of the catalysts clearly shows that nickel, calcium and magnesium particles are visibly dispersed on the catalyst. By using the incipient wetness impregnation method, with the addition of Ca/Mg on the Alumina support, the researcher can see that the elements are dispersed on the surface of the support.

TABLE 4.2 SEM-EDS, catalyst elemental distribution

Catalyst	Composition (%)
1 $\gamma - Al_2O_3$	Aluminium – 43.7
	Oxygen – 55.4
	Yytrium – 0.9
2 10% Ni/Al_2O_3	Aluminium – 20.9
	Nickel – 65.6
	Oxygen – 13.5
3 0.5% Ca + 10% Ni/Al_2O_3	Aluminium – 42.5
	Nickel – 48.2
	Oxygen – 9.3
4 3% Ca + 10% Ni/Al_2O_3	Aluminium – 43.0
	Nickel – 11.4
	Oxygen – 35.9
	Calcium – 9.7
5 5% Ca + 10% Ni/Al_2O_3	Aluminium – 21.1
	Nickel – 25.9
	Oxygen – 47.8
	Calcium – 5.2
6 0.5% Mg + 10% Ni/Al_2O_3	Aluminium – 19.1
	Nickel – 67.7
	Oxygen – 12.1
	Magnesium – 1.0

From the SEM-EDS, the composition of elements distributed on each catalyst can be identified. For 0.5% Ca + 10% Ni/Al_2O_3 catalyst, the composition of calcium cannot be detected due to the small amount of composition on the support. However, for 0.5% Mg + 10% Ni/Al_2O_3, the amount of Mg can be detected is very low which only 1.0%.

4.3.3 H_2-Temperature Programmed Reduction (TPR)

To distinguish the reducible species existence, the interaction and degree of reducibility, H_2-TPR was conducted. The graphs of detector versus temperature of all the catalysts are attached in Appendix E. From the graphs, the suitable temperature for reduction with hydrogen flow before the catalytic reaction is conducted can be determined. The temperature for reducibility that is chosen is the highest temperature that showing peaks in the detector readings.

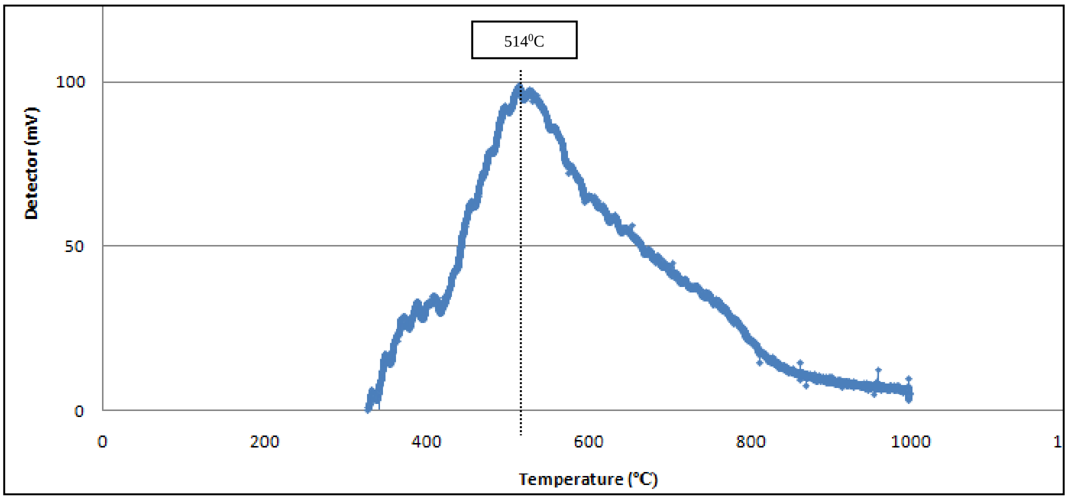


FIGURE 4.2 H_2-TPR analysis for 10% Ni/Al_2O_3

From the graph of H_2-TPR analysis of 10% Ni/Al_2O_3, the highest peak is at 514^{o}C. It is the temperature where a Ni oxide is removed from the catalyst to form metal state. The reduction temperature to be reduced in hydrogen flow must be higher than the stated temperature or else, the amount of hydrogen flow need to be increased or increase the reduction period in order to ensure all the Ni oxide is removed from the catalyst.

The H_2-TPR patterns of 10% Ni/Al_2O_3 which added with different composition of calcium are exhibited in Figure 4.2.As shown in the figure, the TPR pattern of 0.5% Ca+ 10% Ni/Al_2O_3 sample showed one broad reduction peak in the range of 497-600^{o}C and one small peak in the range 750-800^{o}C representing the reduction of calcium.

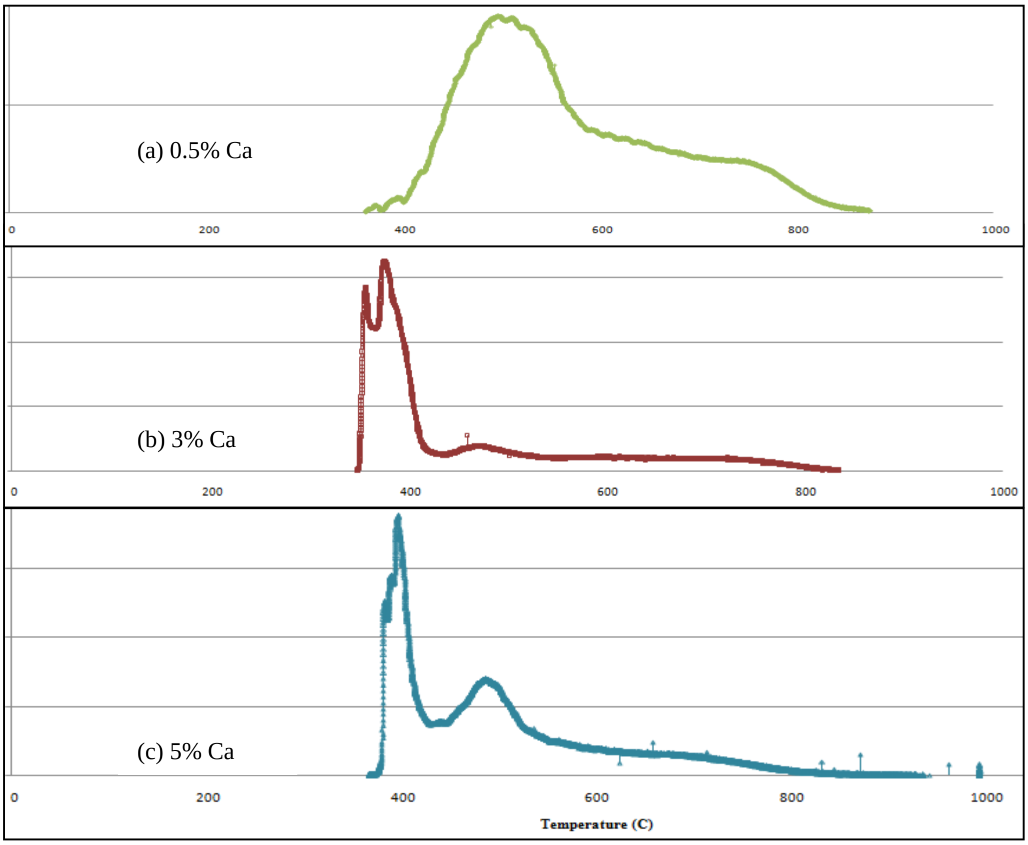


FIGURE 4.3 H_2-TPR patterns for 10% Ni/Al_2O_3 with the addition of: (a) 0.5% Ca, (b) 3% Ca, (c) 5% Ca

From the patterns showing that the Ni oxides are reduced at temperature 497ºC for all the catalysts with calcium loading on Ni/Al_2O_3 which is lower temperature than Ni/Al_2O_3 without any metal (514ºC). This shows that the calcium loading into the Ni/Al_2O_3 had reduced the temperature needed for the reduction of Ni oxide. This clarify that the calcium loading will make the energy required will be lower. The result of H_2-TPR analysis for 10% Ni/Al_2O_3 is similar from what have been found by Li, G., et al. (2006).where the Ni/Al_2O_3 was reduced between 500 and 920 °C.

As shows in appendix E, for 10% Ni/Al_2O_3, different calcium loading and 0.5%Ca+0.5%Mg loading on 10% Ni/Al_2O_3support showing the suitable temperature for reduction is similar, which is at 500ºC. Different magnesium loading and 0.5%Ca+Mg loading on 10% Ni/Al_2O_3 support shows that the suitable reduced temperature is at 800ºC and 450ºC respectively.

Hence, from the H_2-TPR analysis, the suitable reduction temperature for the catalysts is determined. All calcium loadings catalysts are reduced with purified hydrogen flow at 500°C for one hour prior to the catalytic activity testing.

4.4 Aqueous Phase Reforming Performance of Sorbitol

The liquid products from the aqueous phase reforming of sorbitol with different composition of catalysts are analyzed by using Gas Chromatography Mass Spectrometry (GCMS) and High Performance Liquid Chromatography (HPLC) analysis. Figure below is the liquid products from the APR of sorbitol with different calcium loading in 10% Ni/Al_2O_3.All the reacted products have pungent smell.

4.4.1 Gas Chromatography-Mass Spectrometry (GCMS) Analysis

From GCMS analysis, only liquid products obtained from 3% Ca with 10% Ni/Al_2O_3 is successfully determined that is Hexadecane. As shown in the graph below, the retention time of Hexadecane is 24.445.

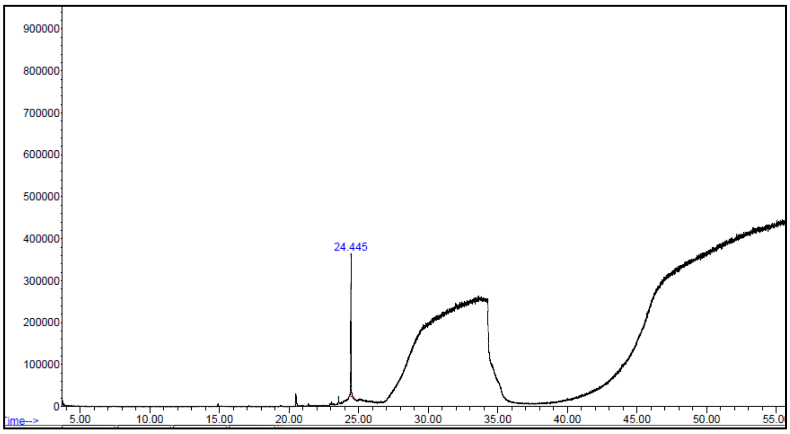


FIGURE 4.4 GCMS analysis for APR with 3% Ca + 10% Ni/Al_2O_3

For other catalysts are not able to be detected by GCMS. This may caused by the unavailable standard of the product in the GCMS system.

4.4.2 High Performance Liquid Chromatography (HPLC) Analysis

First of all, 0.05 mol of sorbitol is analyzed to know the retention time of sorbitol without any catalyst. From the graph obtained, it can be deduced that the highest and only peak, 6.3641 mAU is belongs to sorbitol. The retention time of sorbitol is 4.032 minutes.

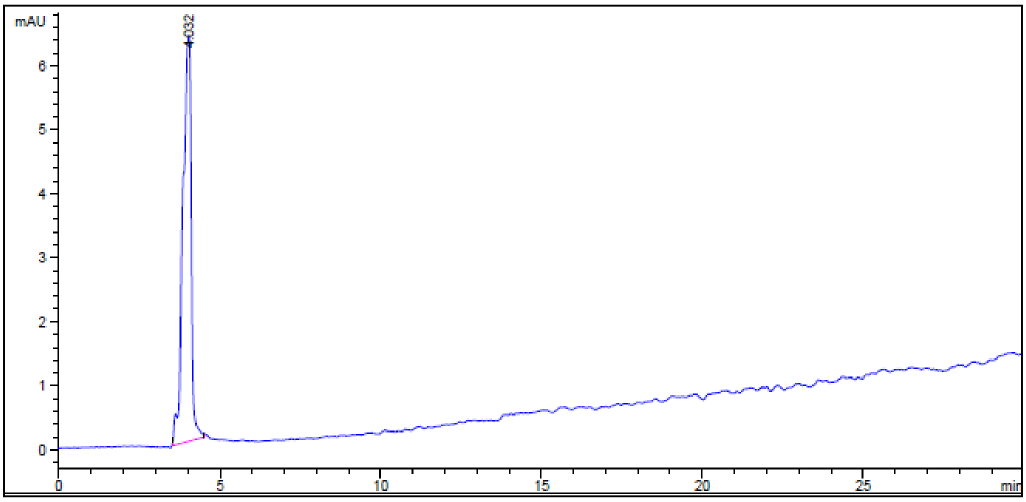


FIGURE 4.5 HPLC Result of 0.05 mol of sorbitol solution

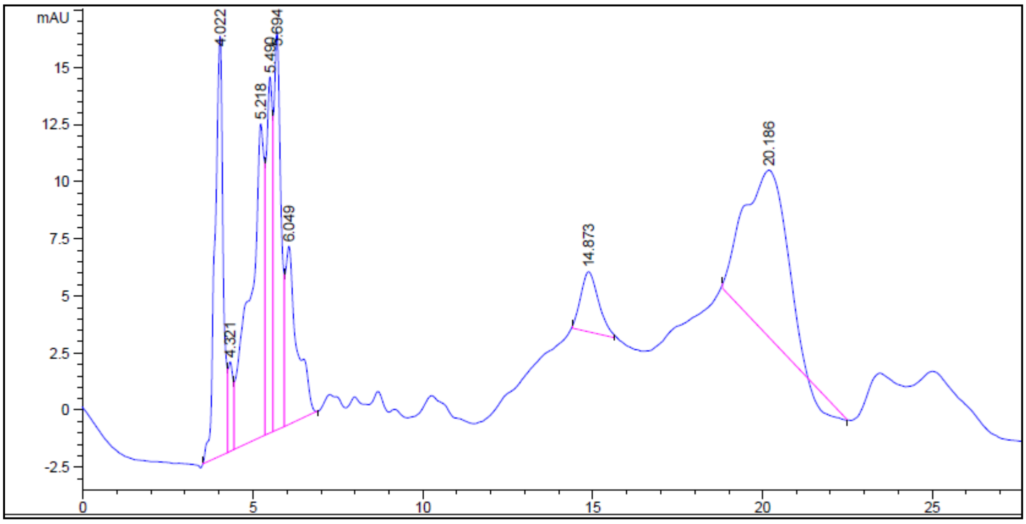


FIGURE 4.6 HPLC Result of 0.05 mol of sorbitol using 10% Ni/Al_2O_3

From the reaction of 10% Ni/Al_2O_3 with sorbitol, eight peaks are produced from the HPLC analysis. Figure 4.5 shows the highest peak is belongs to sorbitol at retention time of 4.022 minutes with the height of 18.39 mAU.

The area under the sorbitol peak is 308.02 mAU*s. Another 7 peaks are unable to identify because their retention time do not fall in the value of the retention time of HPLC for standard solution provided.

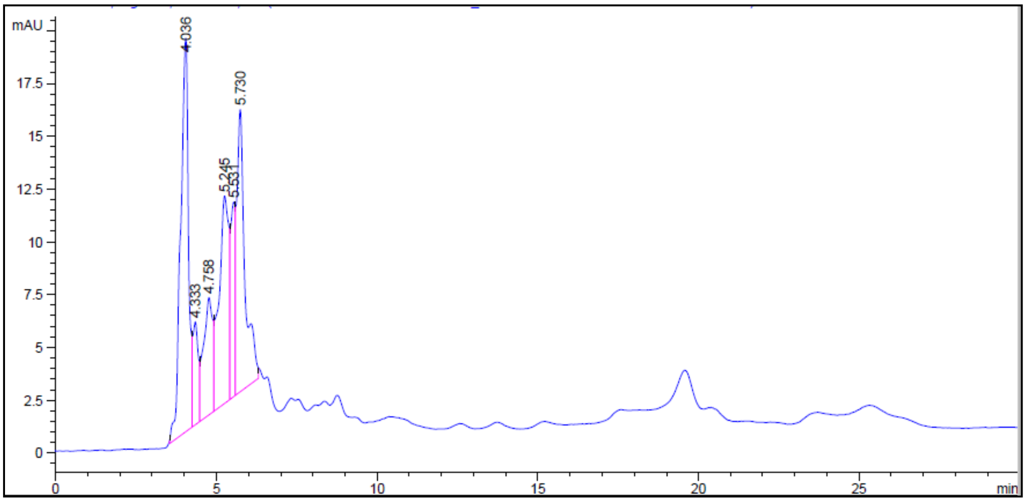


FIGURE 4.7 HPLC Result of 0.05 mol of sorbitol using 0.5% Ca + 10% Ni/Al_2O_3

APR of sorbitol by using 0.5% Ca + 10% Ni/Al_2O_3 catalyst managed to produce six (6) peaks that may indicate 6 different components. The first peak is belong to the unconverted sorbitol, that having the retention time of 4.036 minutes. One peak with the retention time of 5.245 minutes is close to the value of retention time of ethanol, at 5.251 minutes. Therefore, this peak is assumed belongs to ethanol.

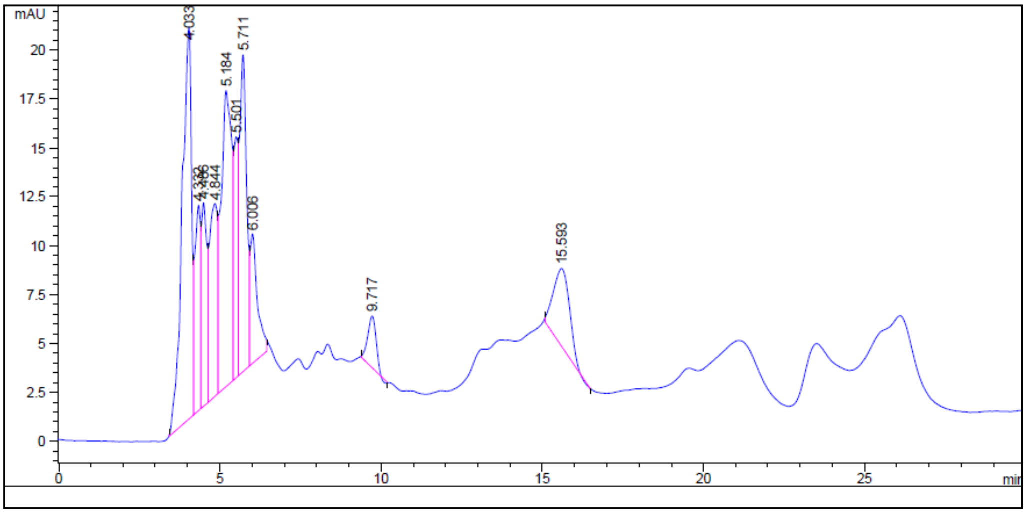


FIGURE 4.8 HPLC Result of 0.05 mol of sorbitol using 3% Ca + 10% Ni/Al_2O_3

On the other hand, ten (10) peaks have been produced for reaction with 3% Ca + 10% Ni/Al_2O_3. However, only a few peak able to identified. The first peak is sorbitol that having the retention time of 4.033 minutes. Propanol has been detected in the reaction of sorbitol with 3% Ca + 10% Ni/Al_2O_3, that having the retention time of 4.844 minutes.

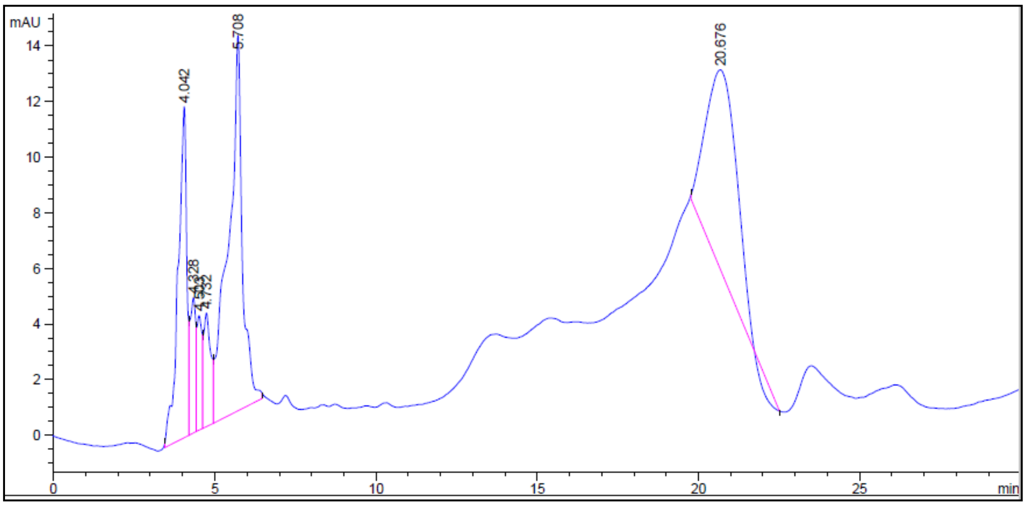


FIGURE 4.9 HPLC Result of 0.05 mol of sorbitol using 5% Ca + 10% Ni/Al_2O_3

Last but not least, six (6) peaks are produced for 5% Ca loading on the catalyst. The first peak is the unconverted sorbitol solution. The value added chemicals produced from this catalyst is propionaldehyde since the retention time is very close to the retention time provided from standard solution, 4.745 minutes.

The conversion of sorbitol is calculated by using the formula as below:

$$\text{Peak Area} = \text{height X width X 0.5} \tag{8}$$

$$\text{Total area} = \text{Peak area 1} + \text{Peak area 2} + \ldots. \tag{9}$$

$$\text{Mole \% for Peak Area 1} = (\text{Peak area 1} / \text{Total area}) \text{ X 100} \tag{10}$$

From the peaks that are identified, some calculations have been done by using above formula. Table 4.3 is the tabulated sorbitol conversion and value added chemicals produced.

TABLE 4.3 The conversion of sorbitol with respect to the value added chemicals produced

Samples	Conversion of Sorbitol (mol %)	Value added chemicals produced
Sorbitol	-	-
10% Ni/Al_2O_3	85.25	Unknown liquid products
0.5% Ca, 10% Ni/Al_2O_3	69.09	Ethanol + other liquid products
3% Ca, 10% Ni/Al_2O_3	77.76	Propanol + other liquid products
5% Ca, 10% Ni/Al_2O_3	82.46	Propionaldehyde + other liquid products

On the other hand, sorbitol solutions with concentration of 1 wt.%, 5 wt.% and 10 wt.% is tested with HPLC to know the retention time without any catalysts. The HPLC result for these concentrations are attached in Appendix F. Table below is the data extracted from the HPLC results of sorbitol.

TABLE 4.4 Data from HPLC for Sorbitol

Species	**Concentration (wt%)**	**Area (mAU*s)**	**Retention Time (min)**
Sorbitol-1	1%	116.1097	4.168
Sorbitol-2	5%	242.14	4.169
Sorbitol-3	10%	339.2267	4.1

From the data obtained from HPLC, the researcher manages to tabulate them as shows in the Table 4.4 and construct a calibration curve Area versus Concentration as attached in Appendix G. From the graph obtained, gradient of the graph can be determined from the graph. The equation obtained, $y = 2457.1x + 101.45$ can be used to calculate the concentration (x) by using the same gradient, $m=2457.1$. This calibration curve is very useful for future to determine the unknown concentration (x) of sorbitol with given area (y) under the curve from HPLC analysis. However, the calibration curve that has been plotted is only valid for the concentration within 1 wt.% until 10 wt.%.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The transformation of lignocellulose-derived polyols in aqueous phase reforming creates an interesting, emerging way to produce high-value compounds for the fuel or chemistry industries. The main objectives of this project are to synthesize and characterize Ni/Al_2O_3 catalyst promoted by metal (Ca) for aqueous phase reforming of sorbitol are achieved. On the other hand, the value added chemical that will be produced by the aqueous phase reforming of sorbitol with the prepared catalysts will be studied with the appropriate methodology and planning.

In conducting this project, ten samples with different composition of nickel and promoter which are calcium and magnesium on alumina support are prepared and synthesized by using the incipient wetness impregnation method. The characterizations of the catalysts are conducted using few techniques which are TGA, SEM, and H_2-TPR. From the TGA results, the best temperature for the catalysts for calcination has been identified, along with the thermal degradation of the catalysts. From the SEM results, the difference of the crystal growth and morphology of the catalyst has been identified with and without the promoter of Ca/Mg on the alumina support. The reducibility of each catalyst is determined by the variations of graph Detector (mV) versus Temperature (ºC) that are produced from the H_2-TPR analysis.

Before the catalytic activity test of sorbitol is performed, calibration curve graph are developed from the HPLC results of sorbitol from different concentration. From the calibration curve, it can be useful for the researcher in the future to know the unknown concentration of sorbitol within the range of 1wt.% to 10 wt.% by knowing the area under the curve obtained from the HPLC results. The linear equation obtained from the calibration curve is $y= 2457.1x + 101.45$.

The catalytic activity will be done in the PREMEX Autoclave reactor under nitrogen flow for one hour with temperature 230°C. The product produced from the reaction is analyzed by the GCMS and HPLC analysis. One of the achievable products produced is Hexadecane ($C_{16}H_{34}$) from 3% Ca + 10% Ni/Al_2O_3 catalysts with sorbitol. This proves that cheap metal (Ca) also can be used to produce something brand new or expensive materials like alkanes products. However, from the HPLC analysis, Ethanol, Propanol and Propionaldehyde are detected.

The scopes of study, the objectives that need to achieved and all the experimental researches are relevant within the time frame. All the objectives of this project which is to synthesize and characterize Ni/Al_2O_3 catalyst promoted by Ca/Mg has been achieved and to investigate the value added chemicals production from the aqueous phase reforming of sorbitol are achieved.

5.2 Recommendations

In this research, there are some limitations occurred in completion of this project:

1. The equipment unavailability in the laboratory led to the time consuming. Before the catalytic activity test is conducted, the catalysts need to be reduced in hydrogen flow by using Temperature Programmed Desorption/ Reduction/ /Oxidation (TPD/R/O) equipment. However, the equipment is malfunctioned thus alternative way was identified to reduce the catalysts. Alternative way was, the catalysts will be reduced with hydrogen flow in the reactor for 30 minutes before adding the sorbitol solution for the catalytic activity test.

2. Purified hydrogen is highly flammable. Gas mixture of 5% H_2/N_2 is not available in the laboratory. Since purified hydrogen is highly flammable, the reaction may cause hazards to safety thus it was not permissible to run the reaction by using the purified oxygen. Hence, a suggestion to use gas mixture of 5% H2/N2 was proposed, however it is not available in the laboratory.

3. It is recommended to conduct the HPLC analysis for all the standards solution which may become the possible value added chemicals that will be produced from the catalytic reaction of sorbitol. This is to ensure the unknown produced chemicals can be identified by referring to the retention time from the HPLC analysis. Besides, it is recommended to conduct the experiment repetitively to ensure accurate results can be obtained.

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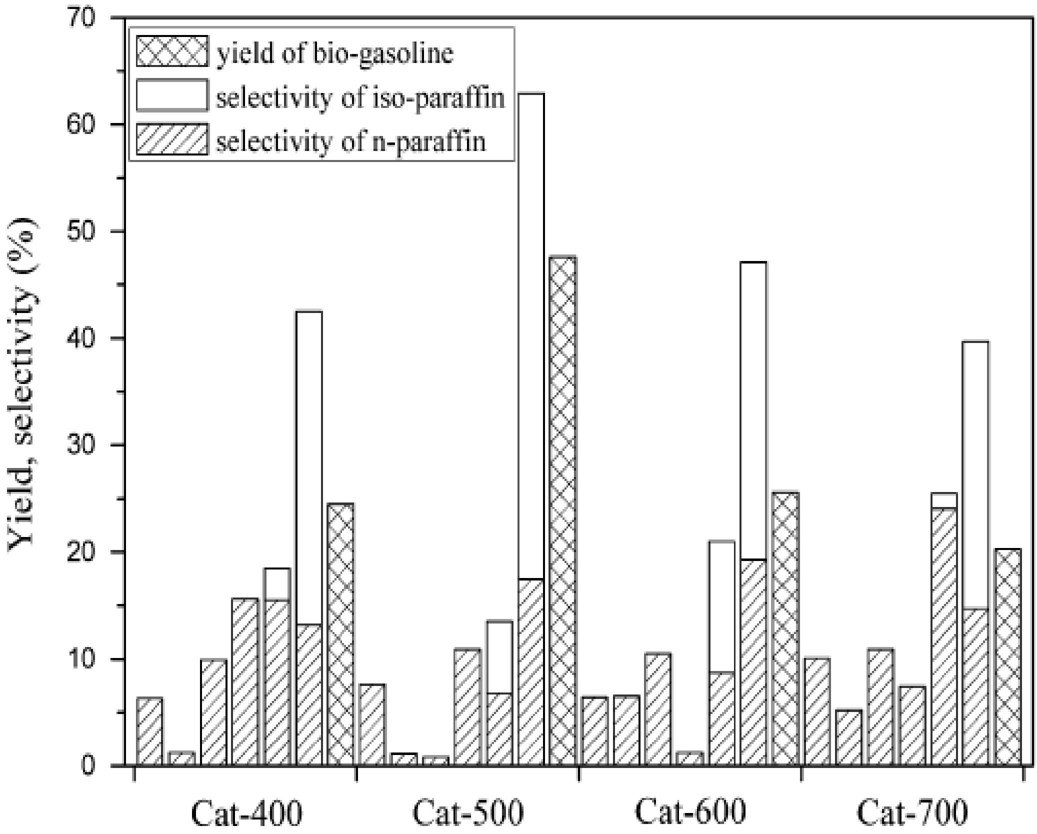
Zhang, Q., Wang, T., Li, B., Jiang, T., Ma, L., Zhang, X., & Liu, Q., (2012). Aqueous phase reforming of sorbitol to bio-gasoline over Ni/HZSM-5 catalysts, *Applied Energy*. *97*, 509-513.

APPENDICES

Appendix A: Graph the effect of calcination temperatures of the Ni/HZSM-5 catalyst on the catalytic performance for APR of sorbitol(Left to right: 6 intervals corresponding to C1-C6) (Q. Zhang et.al, 2012).



Graph A.1 the effect of calcination temperatures of the Ni/HZSM-5 catalyst on the catalytic performance for APR of sorbitol

Appendix B: Catalyst Formulation

Mass of catalyst: 25 gram

Mass of catalyst = mass of metal + mass of support

TABLE B.1 Composition of catalysts

#	Sample	Composition of Al_2O_3:Ni:Ca:Mg
1.	10% Ni/ γ-Al_2O_3	90 : 10 : 0 : 0
2.	0.5% Ca + 10% Ni/ γ-Al_2O_3	89.5 : 10 : 0.5 : 0
3.	3% Ca + 10% Ni/ γ-Al_2O_3	87 : 10 : 3 : 0
4.	5% Ca + 10% Ni/ γ-Al_2O_3	85 : 10 : 5 : 0
5.	0.5% Mg + 10% Ni/ γ-Al_2O_3	89.5 : 10 : 0 : 0.5
6.	3% Mg + 10% Ni/ γ-Al_2O_3	87 : 10 : 0 : 3
7.	5% Mg + 10% Ni/ γ-Al_2O_3	85 : 10 : 0 : 5
8.	0.5% Ca + 0.5% Mg + 10% Ni/ γ-Al_2O_3	89 : 10 : 0.5 : 0.5
9.	5% Ca + 5% Mg + 10% Ni/ γ-Al_2O_3	80 : 10 : 5 : 5

TABLE B.2 Compound and its molecular weight

Compound	Molecular weight
Nickel Nitrate Hexahydrate	290.81 g/mol
Calcium Chloride Dehydrate	147.02 g/mol
Magnesium Nitrate Hexahydrate	256.41 g/mol

TABLE B.3 Metal and its atomic mass

Element/Metal	Atomic mass
Nickel	58.7 g/mol
Calcium	40.1 g/mol
Magnesium	24.3 g/mol

General formula used:

$$Mass\ of\ metal\ loading = \frac{Percentage\ (\%) of\ metal\ loading}{100\%} \times Mass\ of\ catalyst$$

$$Mass\ of\ salt\ needed\ = \frac{Molecular\ mass\ of\ salt}{Atomic\ mass\ of\ metal} \times Mass\ of\ metal\ loading$$

Calculation for 10% Nickel loading:

$$\text{Mass of Nickel loading} = \frac{10}{100} \times 25\text{g of catalyst} = 2.5\text{ g of Nickel}$$

$$\text{Mass of Nickel Nitrate Hexahydrate needed} = \frac{290.81 \frac{\text{g}}{\text{mol}}\ \text{Ni(NO}_3\text{)}_2.6\text{H}_2\text{O}}{58.7 \frac{\text{g}}{\text{mol}}\ \text{Ni}} \times 2.5\text{g Ni}$$

$$= 12.39\text{g Ni(NO}_3\text{)}_2.6\text{H}_2\text{O}$$

Calculation for $\gamma - \mathrm{Al_2O_3}$ needed in 10% Ni/γ - $\mathrm{Al_2O_3}$

$$\text{Mass } \gamma\text{ - }\mathrm{Al_2O_3} \text{ needed} = \frac{90}{100} \times 25\text{g of catalyst}$$

$$= 22.5\text{g } \gamma\text{ - }\mathrm{Al_2O_3}$$

or

$$\text{Mass } \gamma\text{ - }\mathrm{Al_2O_3} \text{ needed} = 25\text{g} - 2.5\text{g of Nickel}$$

$$= 22.5 \text{ g } \gamma\text{ - }\mathrm{Al_2O_3}$$

TABLE B.4 Calculated mass of metals in catalysts for different composition

#	Sample	γ-Al_2O_3 (g)	$Ni(NO_3)_2.6H_2O$ required (g)	$CaCl_2.2H_2O$ required (g)	$Mg(NO_3)_2.6H_2O$ required (g)
1	γ-Al_2O_3	25.0	-	-	-
2	10% Ni/Al_2O_3	22.5	12.38	-	-
3	0.5% Ca + 10% Ni/Al_2O_3	22.38	12.38	0.46	-
4	3% Ca + 10% Ni/Al_2O_3	21.75	12.38	2.75	-
5	5% Ca + 10% Ni/Al_2O_3	21.25	12.38	4.58	-
6	0.5% Mg + 10% Ni/Al_2O_3	22.38	12.38	-	1.32
7	3% Mg + 10% Ni/Al_2O_3	21.75	12.38	-	7.91
8	5% Mg + 10% Ni/Al_2O_3	21.25	12.38	-	13.19
9	0.5% Ca + 0.5% Mg + 10% Ni/Al_2O_3	22.25	12.38	0.46	1.32
10	0.5% Ca + 0.5% Mg + 10% Ni/Al_2O_3	20	12.38	4.58	13.19

Appendix C: TGA Results

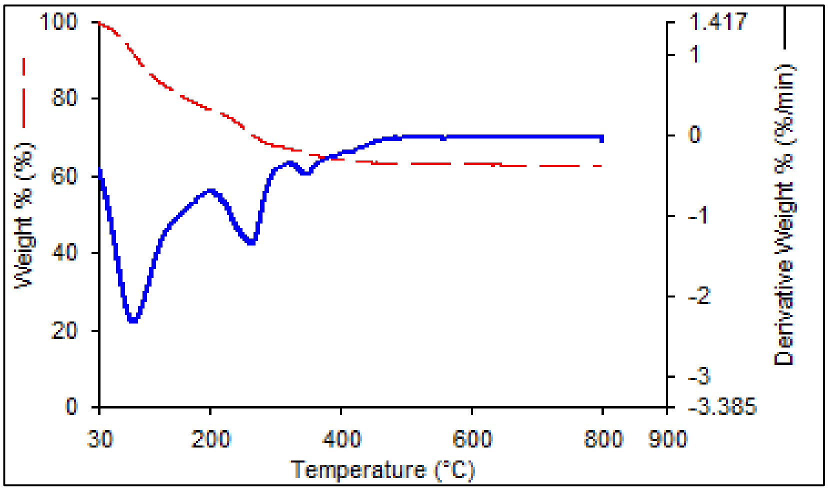


FIGURE C.1 TGA Profiles for 0.5% Mg + 10% Ni/Al_2O_3

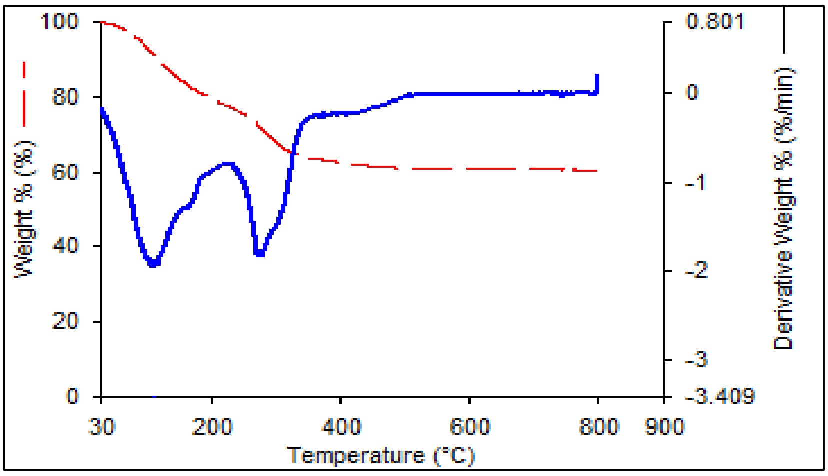


FIGURE C.3 TGA Profiles for 3% Mg + 10% Ni/Al_2O_3

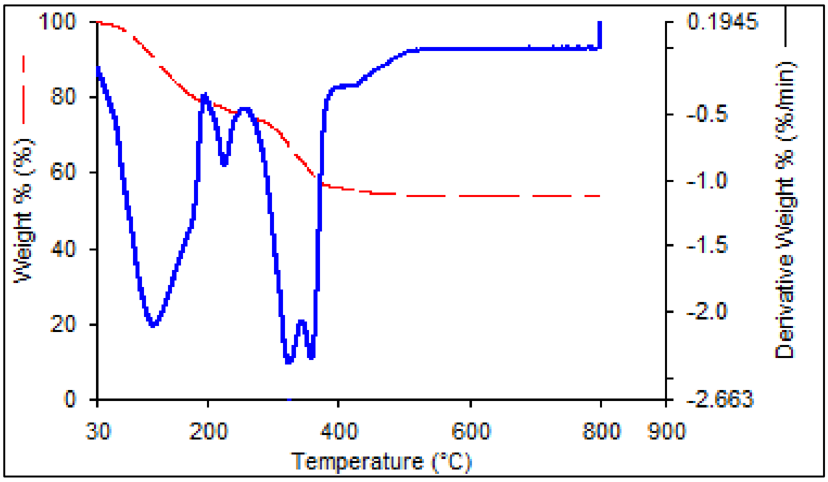


FIGURE C.4 TGA Profiles for 5%Mg + 10% Ni/Al_2O_3

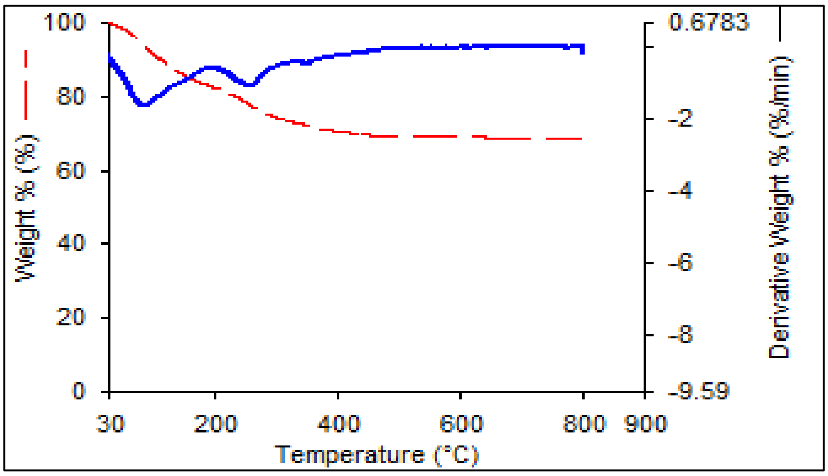


FIGURE C.5 TGA Profiles for 0.5%Ca + 0.5% Mg + 10% Ni/Al_2O_3

Appendix D: H_2-TPR Profiles

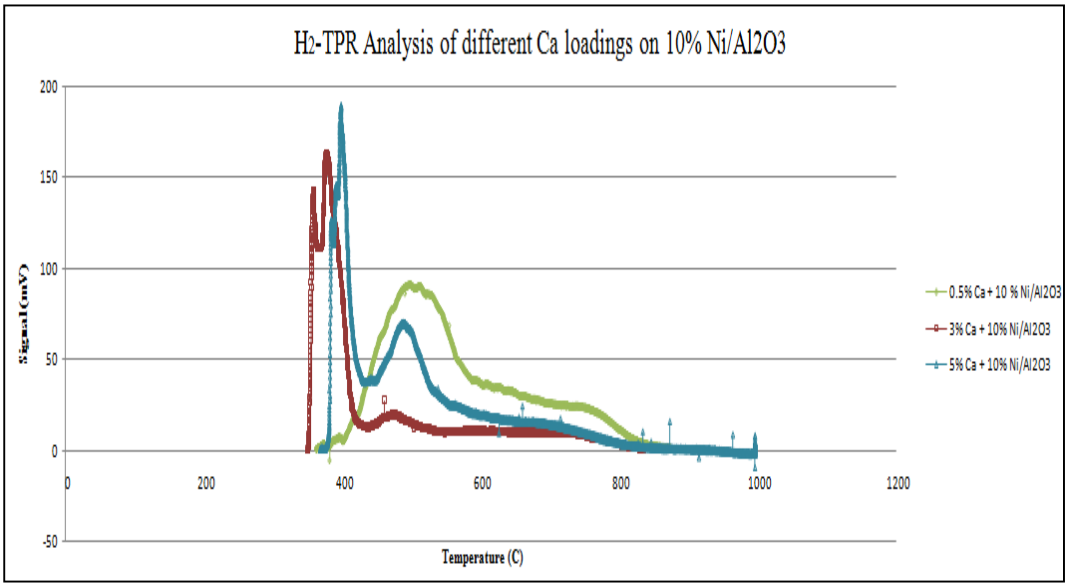


FIGURE D.1 H_2-TPR Profiles for different Ca loading on impregnated 10% Ni/Al_2O_3 catalyts calcined at 500^{o}C: (a) 0.5%Ca; (b) 3% Ca; (c) 5%Ca.

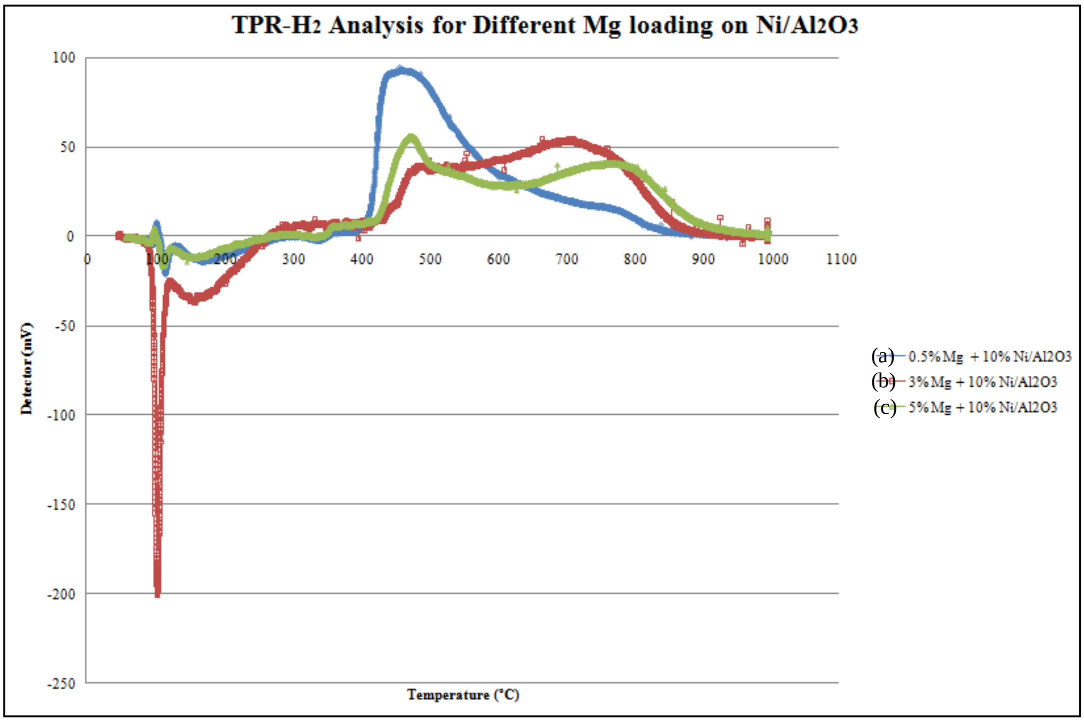


Figure D.2 H_2-TPR Profiles for different Mg loading onimpregnated10% Ni/Al_2O_3 catalystscalcined at 500^{o}C: (a) 0.5%Mg; (b) 3% Mg; (c) 5% Mg.

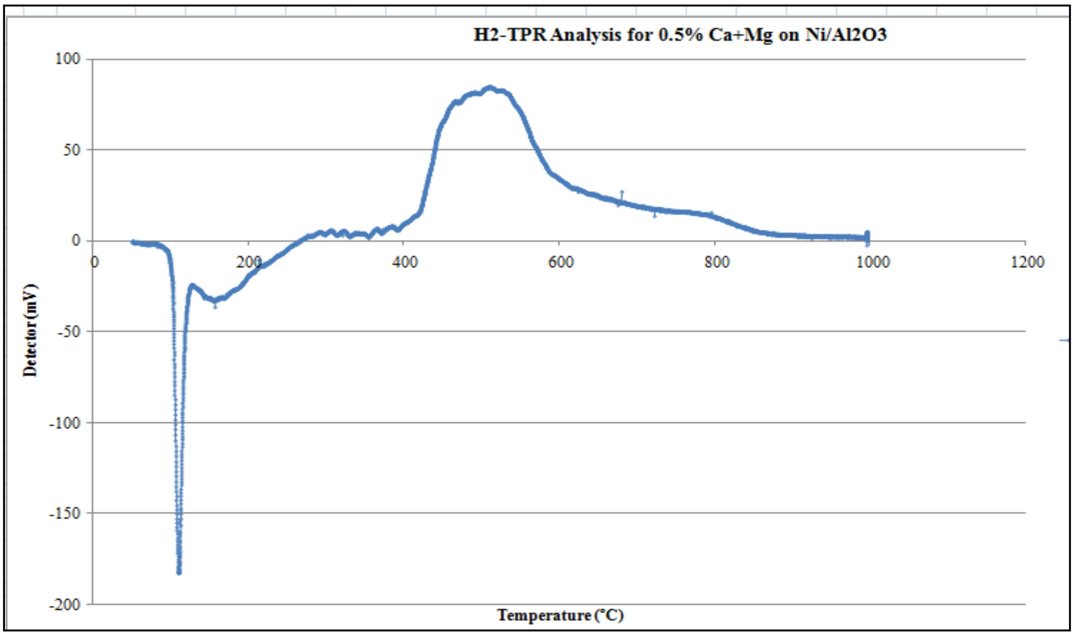


FIGURE D.3 H_2-TPR Profiles for different 0.5%Ca and Mg loading onimpregnated10% Ni/Al_2O_3 catalysts calcined at 500°C

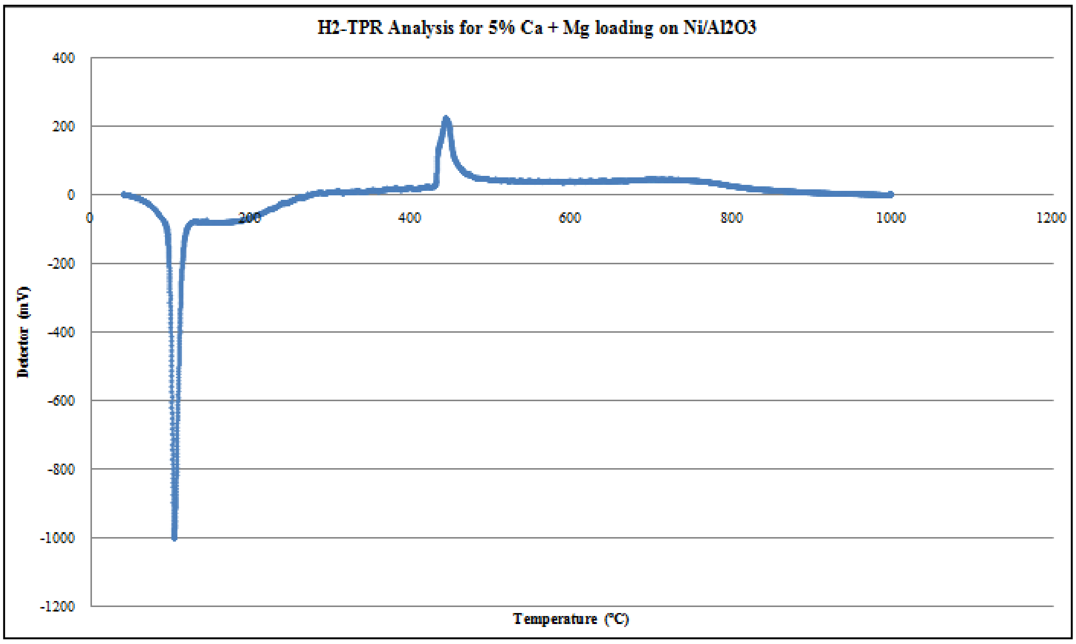


FIGURE D.5 H_2-TPR Profiles for 5% Ca and Mg loading onimpregnated10% Ni/Al_2O_3 catalysts calcined at 500°C

Appendix E HPLC Results for Standard Solution

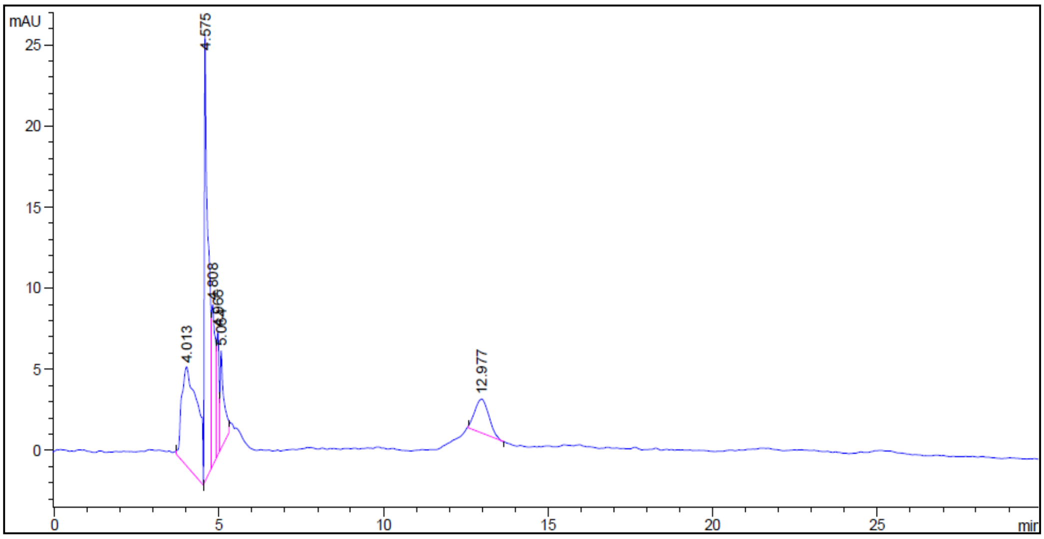


FIGURE E.1 HPLC Result for 1,3 - Propanediol

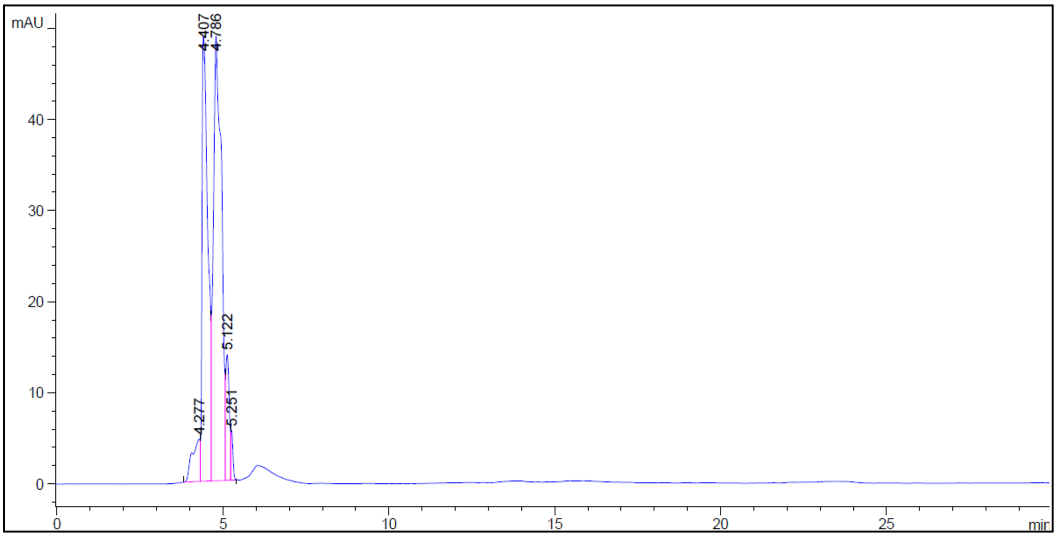


FIGURE E.2 HPLC Result for Ethanol

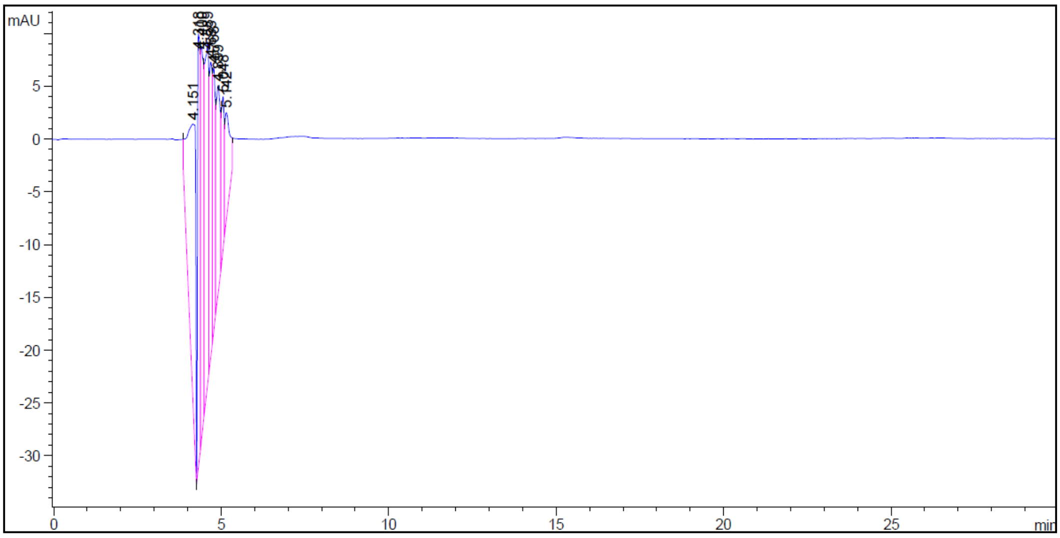


FIGURE E.3 HPLC Result for Ethylene Glycol

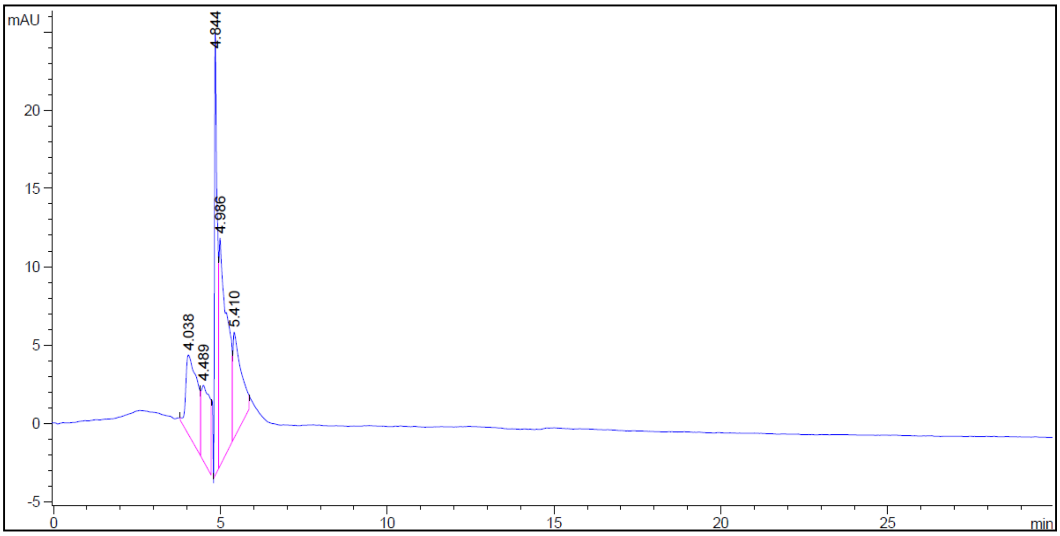


FIGURE E.4 HPLC Result for Propanol

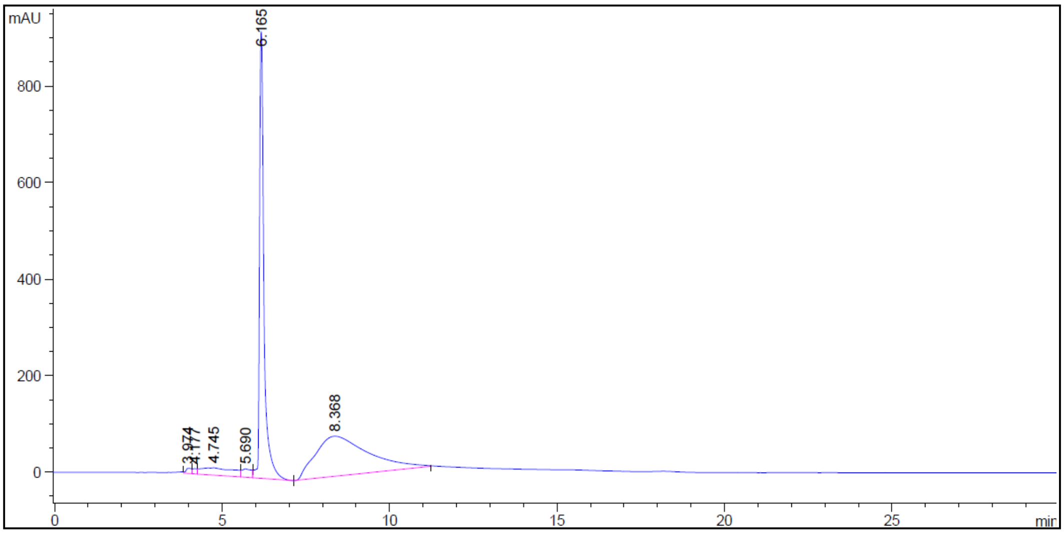


FIGURE E.5 HPLC Result for Propionaldehyde

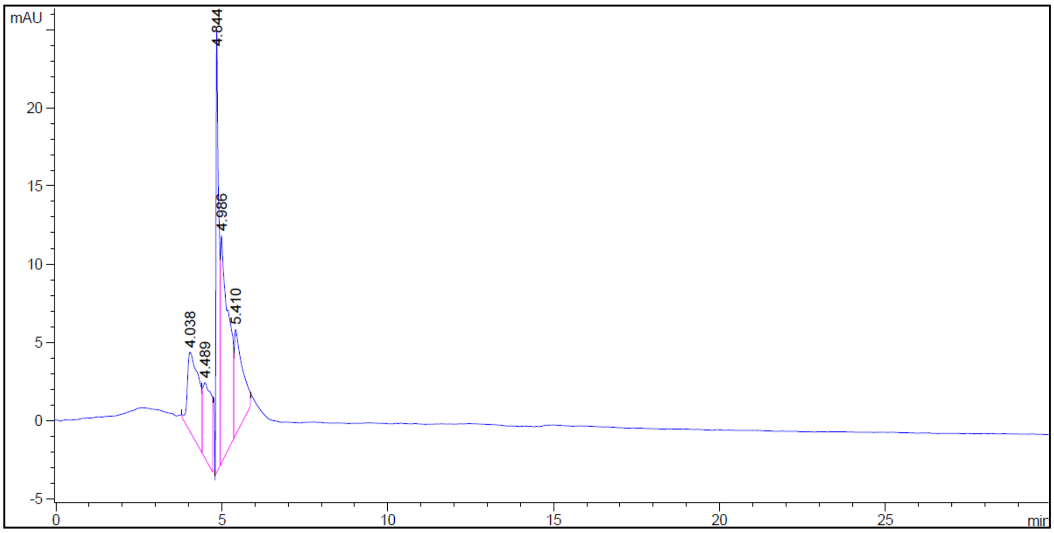


FIGURE E.6 HPLC Result for Propylene Glycol

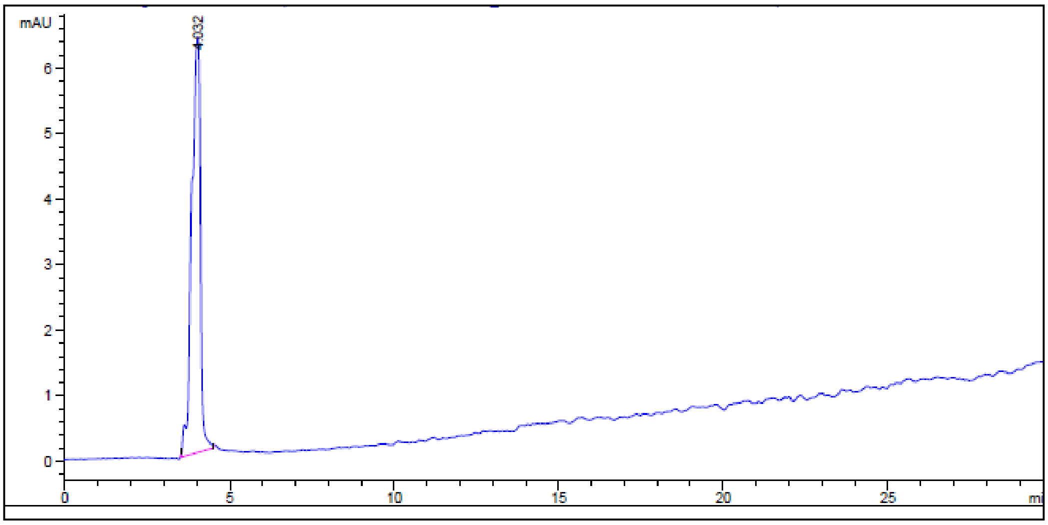


FIGURE E.7 HPLC Result for 0.05 mol sorbitol

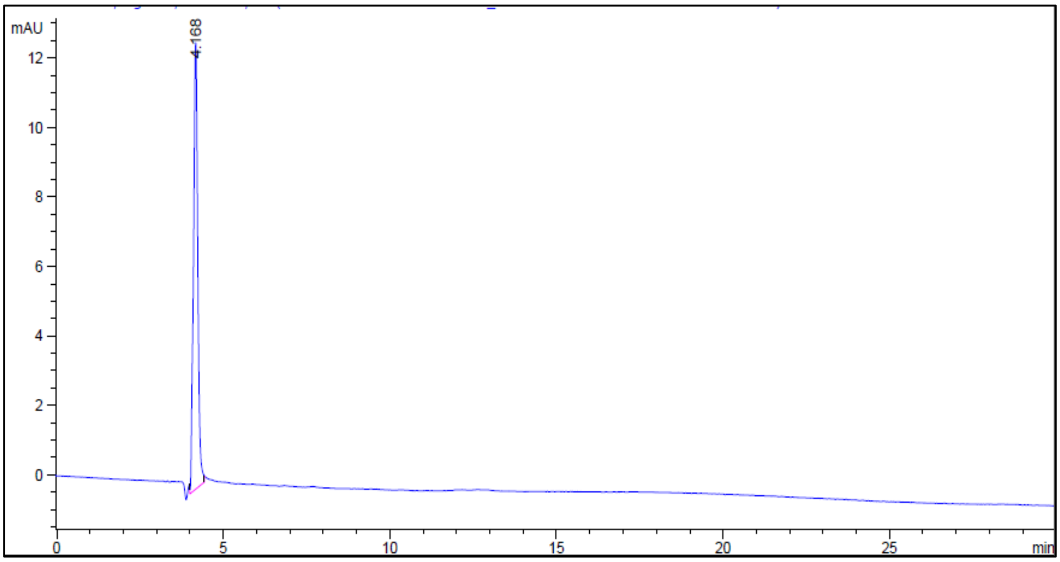


FIGURE E.8 : HPLC Result of 1 wt. % Sorbitol Solution

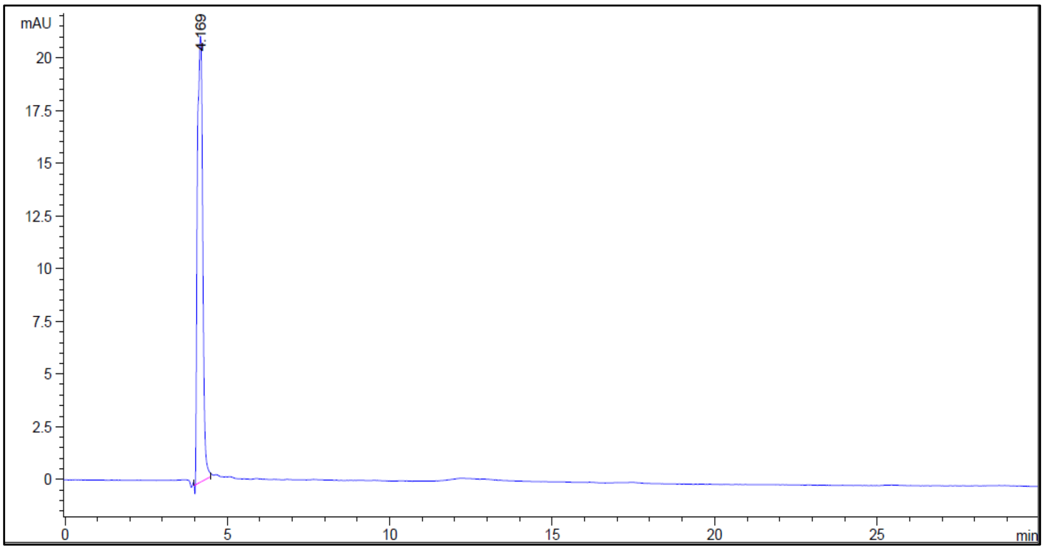


FIGURE E.9 : HPLC Result of 5 wt. % Sorbitol Solution

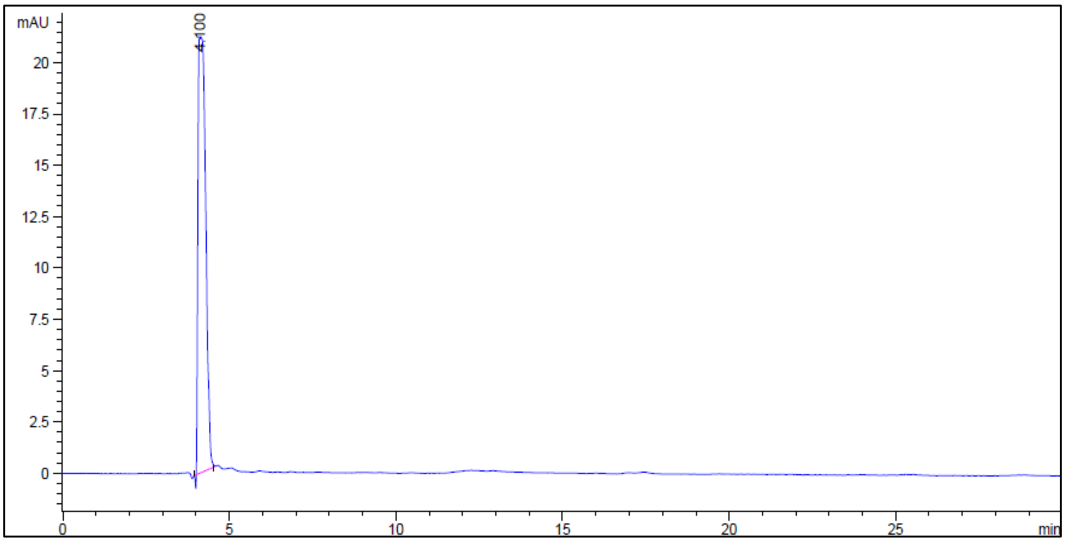


FIGURE E.10 HPLC Result of 10 wt. % Sorbitol Solution

Appendix F: Calibration Curve of Sorbitol (Area vs Concentration)

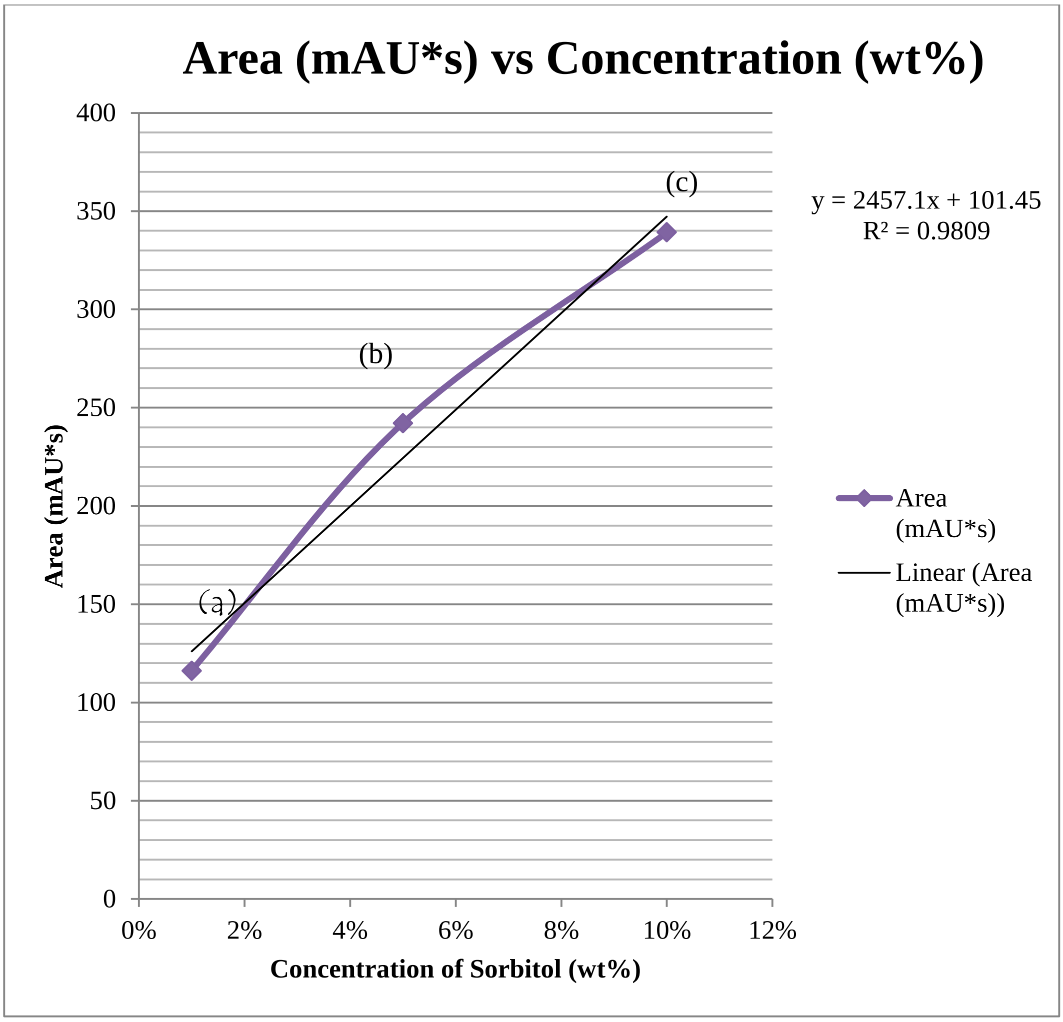


FIGURE F.1: Calibration curve of sorbitol at different concentrations. (a) 1 wt.%; (b)5wt.%; (c)10wt.%