Thermodynamic Analysis of Aqueous Phase Reforming of Sorbitol

By

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Dissertation submitted in partial fulfillment of
the requirements for the
Bachelor of Engineering (Hons)
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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
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(CHEMICAL)

Approved by,

_____

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NOVEMBER 2014

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.

_____

MUHAMAD ZAAIM ZHAFRI BIN ZAKARIA

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Abstract

Demand for energy is getting higher every year and consumption of petroleum-based product also has reached the peak level. Many people come with other alternative to replace the uses of fossil fuel with another sustainable resource such as hydrogen. Aqueous phase reforming process has been discovered by Dumesic and co-worker (2002) as a way to produce hydrogen from biomass-derived oxygenated compound such as glycerol, sugar and sugar alcohols. These compounds are easy to find in bulk with incredibly at low price especially in Asian region where the countries solely plantation industry is palm oil or corn. This study is imperative in the way that it helps to discuss thermodynamic importance in aqueous phase reforming. Fundamentally, thermodynamic analysis is a crucial section in any field of chemical engineering study since it embodies the characteristic and effect of the particular reaction. Behavior of each species can be determined by studying their thermodynamic during the reaction to know what kind of parameters do the reaction favor the most. In order to understand the thermodynamic of the aqueous phase reforming, there are few parameters need to be tested using commercial modeling software. Each of the parameters has their own ranging value for the best APR process which can only be found using simulation software. The thermodynamic final result from this study will characterized optimum parameters values, and becomes useful to be used as guidelines to perform aqueous phase reforming of sorbitol. At the end of this research, all the relationship of the parameters with the product selectivity will be analyzed and recorded.

Acknowledgement

I am using this chance and opportunity to express my gratitude to everyone who helped and guided me throughout this final year project. Finally I am able to complete the final report for 'Thermodynamic analysis of aqueous phase reforming of sorbitol'.

I would like to thank my parents for giving me the support and strength to pursue my study particularly in Chemical Engineering. Their hope is the source of my strength to keep moving forward in my study. Not to forget, my supervisor, Dr Mohammad Tazli for guiding me on how to do research and analysis for this project. He has been a great help in this project by putting his effort to teach me a lot of things, knowledge on research field.

Finally, I want to thank my friends and colleagues who had been helping me to finish this project. A lot of help regarding simulations and compilation of project comes from them.

1.0 INTRODUCTION

1.1 Background

Demands for energy in this world have increased significantly, and this pressure has put together researchers all around the globe to develop a new method of recovering new hydrocarbon resources. When one is found, this technology must be able to withstand economic change and capable to perform sustainable production. Aqueous phase reforming (APR) is first introduced in 2002 by Dumesic and co-worker (Cortright, Davda, & Dumesic, 2002). Main prospect of APR process is, to produce hydrogen from water-soluble oxygenated compound such as glycerol, sugar and sugar alcohols.

This APR method is very economic since it does not use volatize water (steam) in the process. Throughout this paper, thermodynamic of APR of sorbitol is analyzed in details for more understanding. The target of this analysis is to discover the best parameters (i.e. temperature, pressure) for APR process. Basically, every parameter has different effect to APR process and by altering this value, the conclusion of relationships in between parameters and thermodynamic can be achieved.

Sorbitol is one of the sugar alcohols where it is mainly used in many food industries as sweetener, laxative for bowel treatment and medical applications. This glucose alcohol can be produced by the reduction of glucose, and mainly found in fruits (Teo, et al., 2006). On the other hand, sorbitol has high potential to be produced in a big amount in Malaysia due to large tapioca industries where the starch is converted into glucose and then sorbitol.

1.2 Problem Statement

Wyman reported that over past 50 years, technologies have been developed and built to find efficient way of producing hydrogen from petroleum-based stock. But, it is still a challenge to everyone to produce hydrogen from biomass-derived resources. Dumesic et al. reported, hydrogen can be produced using aqueous phase reforming of renewable biomass (glycerol, sorbitol, glucose). Although a few studies are encountered for APR process, thermodynamic analyses for this process are rarely found.

The purpose of thermodynamic analysis on APR is to understand affect of certain variables and parameters to this process and find the ideal way to produce higher yield of hydrogen with lower yield of undesired product (Adhikari et al, 2007).

1.3 Objective

This work is to study thermodynamic of aqueous phase reforming process for production of hydrogen from sorbitol. The main objective of this study is to find the best and ideal condition, parameters for APR process so that the production of hydrogen can be maximized with low production of carbon monoxide. Other than that, the objective of this simulation is also to discover another formation of synthetic gas.

1.4 Scope of Study

This work main focus is to study the thermodynamics of aqueous phase reforming of hydrogen from sorbitol. The study is on the thermodynamic of APR for using Gibbs energy minimization method. Modeling software such as iCon, and Hysis is the best approach to analyze thermodynamic by altering and modify the parameters and then analyze the results. For this particular case, modeling software iCon is used to simulate the whole APR process and calculate each data for different parameters and compare parameter's value to find the most optimum result. By using this iCon, the cause and effect on thermodynamic system can be easily recorded and analyzed.

2.0 LITERATURE REVIEW

2.1 Hydrogen

. Hydrogen really has the potential to be used as source energy since it can be generated from clean and green resources (Dutta, 2013). Main point of this study is to do analysis thermodynamic on aqueous phase reforming on a particular substance that is sorbitol.

Hydrogen is accepted in the world wide as clean energy carrier and it is source independent (Satyapal, 2007). It can be produced from biomass which can be getting at low cost. Mohammed et al. (2010) reported, Malaysia is one of the world's largest producers and exporter of palm oil where at the same time of production, abundant of biomass from palm oil is created. This side product (biomass) produced from palm oil industries are best to be used as the source of clean energy.

2.2 Aqueous Phase Reforming of Glycerol

Over a decade fossil fuels starts to depleting and finding alternatives for fossils fuel has been the concern of many organization or researcher. Lately, the raise of awareness of turning biomass into energy resources induces many people to find technique of converting these unlimited resources as another form of energy. Dumesic and co-worker have come with new approach by introducing aqueous phase reforming to produce hydrogen from biomass.

On the other hand, the biomass is predicted to produce 20% of transportation fuel and 25% of chemicals by 2030 due to huge shift or energy resources from petroleum-based to carbohydrate-based economy (George W & Dumesic, 2006).The main concern of producing sustainable energy from biomass such as hydrogen gives a huge impact to research and development all around the world. A few researchers found a promising way of producing hydrogen from biomass-derived oxygenates i.e., glucose, sorbitol, glycerol and ethylene glycol using APR (Guo et. al, 2011).However, in order to find the most suitable operating parameters to carry out this process, thermodynamic analysis plays an important role. Thermodynamic analysis of give the full prospect and looking on what are the best parameters and values for variables.

2.3 Hydrogen Production by Aqueous Phase Reforming of Sorbitol

Tanksale and co-worker (2009) produced hydrogen by aqueous phase reforming method from sorbitol. They reaction is carried out with 10 %(w/w) of sorbitol with addition of mono and bi-metallic Ni-Pt supported on alumina nano-fibre(Alnf), mesoporous ZrO_2 and mixed oxides of (CZxS). CZxS stands for ceria-zirconia-silica and the small letter x represent the concentration of silica. The selectivity of the hydrogen is highest when using co- impregnated Ni-Pt/Alnf. Different combination of catalyst and support is used in this study to determine and find relationship in between them with hydrogen selectivity. Presence of high concentration of silica in mixed oxide lower the reducibly of NI which is a favor to this reaction. Tanksale et al. (2009) reported that addition of noble metal such as Ni increase the rate of hydrogen production by 3-5 times in APR reaction. The set of graph below shows different catalyst and support combination and their outcome of hydrogen selectivity.

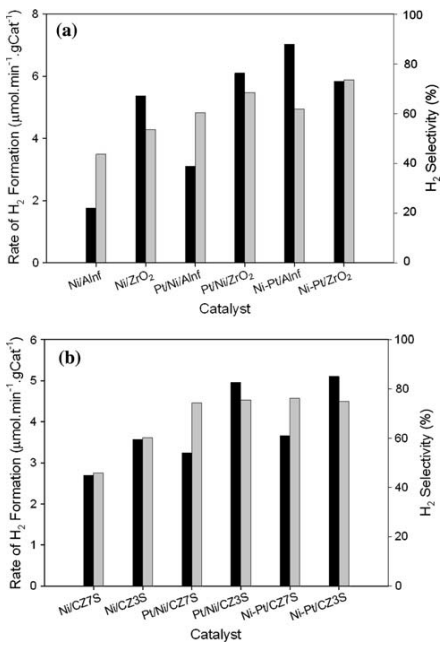


Figure 1: A set of graft showing different combination of catalyst and the hydrogen selectivity

2.4 Thermodynamic Analysis of Aqueous Phase Reforming of Glycerol

Authayanun et al. (2010) has carried out thermodynamic study of hydrogen production from crude autothermal reforming for fuel application. This research can be used as the guideline to set up the parameters and as the method of approach for doing APR modeling. From this article, the research particularly focused on crude glycerol derived from biodiesel production process.

Methodology:

Authayanun and co-worker investigate the thermodynamic of APR using advanced modeling software HYSYS. HYSYS help to generate and calculate any input formulae and reactions faster and much more accurate compared to manual ways.

Thermodynamic analysis of glycerol is to consider the following parameters in the APR as recorded by Authayanun et al.:

1. Reformer Temperature(K)
2. Pressure (Atm)
3. Steam to crude glycerol ratio
4. Oxygen to crude glycerol ratio
5. Inlet Feed Temperature
6. Thermo neutral Condition

Authayanun and co-worker have prepared a few ranges of parameters to understand the effect of each parameter to the thermodynamic of APR. The ranges of parameters prepared by the team are as in table 1:

Table 1: Operating Condition for Autothermal Reforming of Crude Glycerol Proposed by Authayanun et al. (2010)

OPERATING CONDITION FOR AUTOTHERMAL REFORMING OF CRUDE GLYCEROL		
Parameters	**Standard Condition**	**Operational Range**
Reformer Temperature(K)	1000	600-1200
Pressure(atm)	1	-
Steam to crude glycerol ratio	3	1-9
Oxygen to crude glycerol ratio	0.6	0.1-0.8
% of glycerol in crude glycerol	-	40-100

These parameters are used to investigate their impact to the production of hydrogen at specific inlet feed temperature, 550 K. It is reported by Authayanun et al. that the yield of hydrogen increases if the amount of the glycerol content in the crude glycerol is higher. It means that the amount of glycerol in the crude glycerol is directly perpendicular to the amount of hydrogen produced.

Increasing the operating temperature will increase the molar fraction and the molar flow of hydrogen. However, the amount of hydrogen molar flow at the end of the reaction depends more on the presence of glycerol in crude glycerol. If the amount of methanol in crude glycerol increases, the amount of hydrogen will decreases as matter of fact that the hydrogen produced from methanol is much less compared from glycerol: refer to equation below:

$C_3H_8O_3 + 3H_20 \leftrightarrow 7H_2 + 3CO_2$

$CH_3OH + H_2O \leftrightarrow 3H_2 + CO_2$

Usually, excess steam is used to counter equilibrium limitation and at the same time enhancing the amount of hydrogen. Even though the molar flow rate of hydrogen increases with increasing steam rate, the drawback to the fraction of the hydrogen is big since unreacted steam dilutes the product that is hydrogen (Authayanun et al., 2010). Authayanun et al. (2010) reported that increased amount of oxygen favors the oxidation reaction and significantly reduces the reforming of carbon monoxide in the process. But, the drawback of the reaction causes depletion of hydrogen fraction. On the other hand, Adhikari et al. (2007) says ideal temperature to produce hydrogen though APR is more than 900 K and at the same time inhibit carbon formation. Hence maximum yield of hydrogen is possible to be produced.

Adhikari et al. (2006) use different approach by calculating number of moles of hydrogen produced by using minimized Gibbs energy. He uses different parameters to analyze the formation of hydrogen from glycerol. The parameters used by Adikhari are:

1. System pressure
2. System temperature
3. Water to glycerol feed ratio (WGFR)

The ranges for variables are, pressure 1-5 atm, temperature 600K-1000K, WGFR 1:1-1:9. From his study, Adhikari concludes that high temperature that is more than 900K favors the reaction. At high WGFR, the mole fraction of hydrogen becomes lower due to high amount of water content. However, Adhikari and co-worker (2006) found that, hydrogen yield can be increased if they increase WGFR with optimum value of temperature. With higher WGFR, the formation of methane can be minimized and carbon formation is inhibited. Low pressure does favor the reaction rather than high pressure. The results from Adhikari and his team research are expressed in figure below:

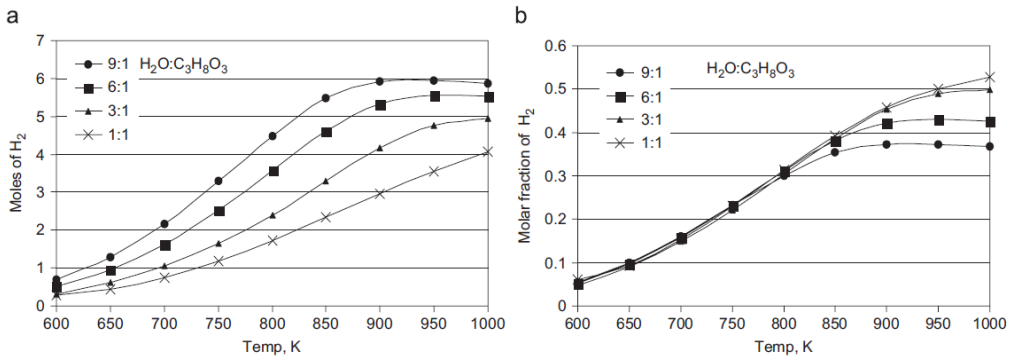


Figure 2: (a) Hydrogen moles vs temperature at different WGFRs at *P* = 1 atm, (b) mole fraction of hydrogen vs temperature at different WGFRs at *P* = 1 atm.

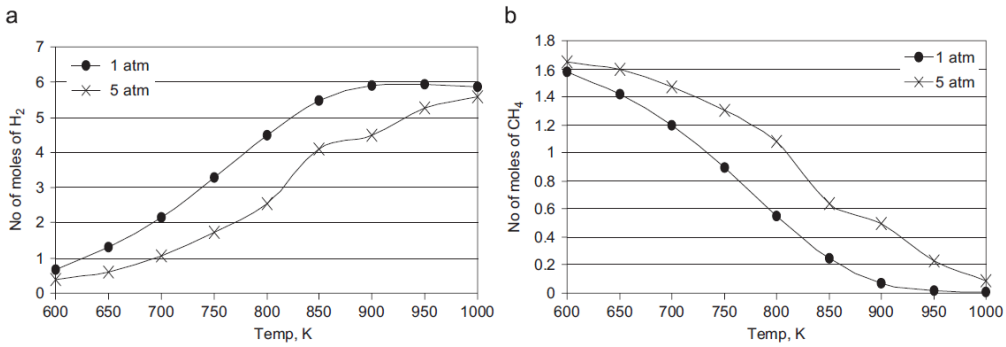


Figure 3: (a) Hydrogen and (b) methane moles produced at selected pressure and WGFR = 9:1.

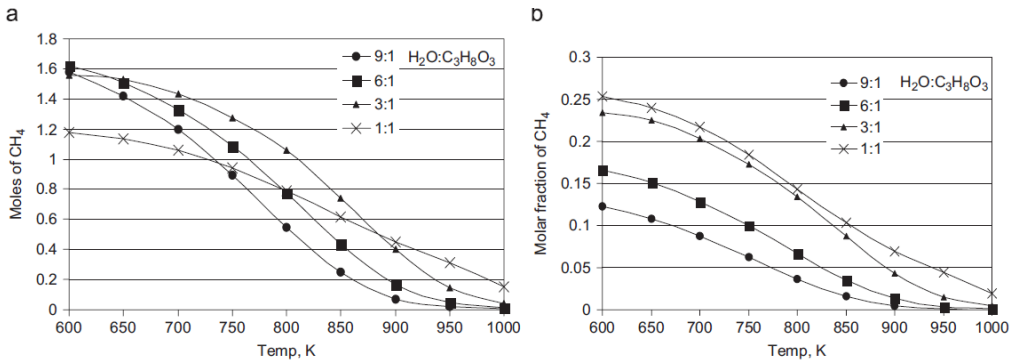
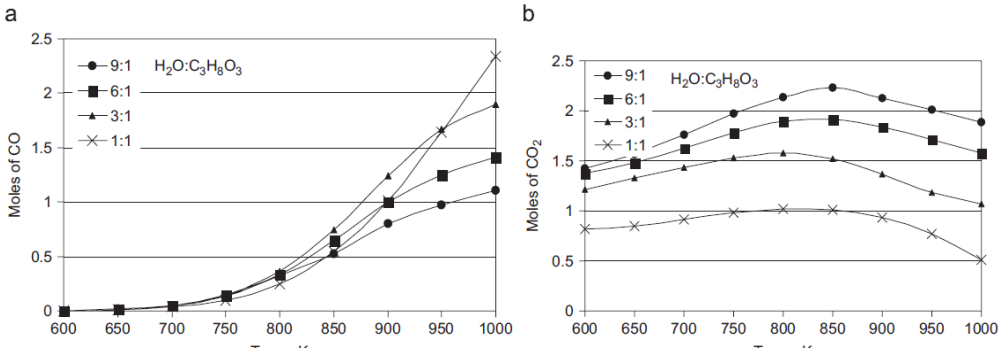


Figure 4: (a) Moles of methane vs temperature at different WGFRs at *P* =1 atm, (b) mole fraction of methane vs temperature at different WGFRs at *P* =1 atm.



: (a) Moles of CO vs temperature at different WGFRs at *P* = 1 atm, (b) moles of CO2 vs temperature at WGFRs at *P* = 1 atm.

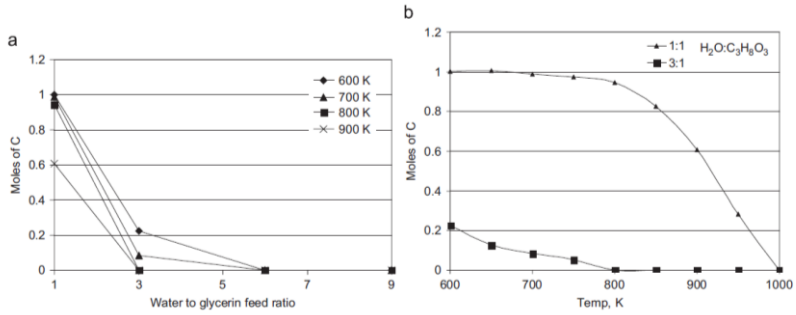
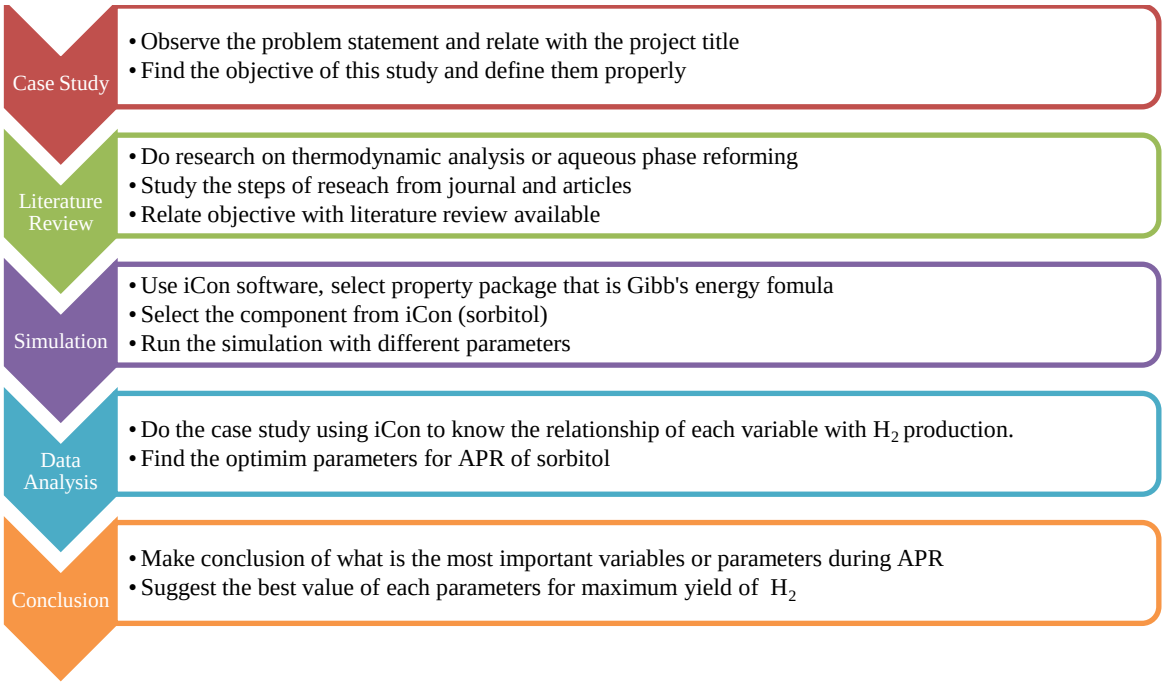


Figure 5: (a) Moles of carbon formation at different WGFRs at selected temperatures at *P* = 1 atm, (b) moles of carbon formation at different temperatures at selected WGFRs at *P* = 1 atm.

3.0METHODOLOGY

3.1 Project Flow Chart



3.2 Gantt Chart & Key Milestone

WEEKS / ACTIVITY	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Project Title Selection & Meeting With Project Supervisor														
Preliminary Research Work and Proposal Preparation														
Extended Proposal Submission & Proposal Defense														
Project Work Continue														
Submission of Interim Draft Report														
Submission of final Interim Report														

Week 1-2: Discussion and meeting with supervisor regarding the ideal topic for the final year project (FYP). Analysis of thermodynamic of aqueous phase reforming of sorbitol has been selected. Dr. Tazli guidelines are to prepare the information needed for simulation purpose.

Week 3-7: Internet and reading research for available journal, articles that have connection with the FYP title. The research is done through internets and library. Most of the research is more to process and experiment on autothermal reforming, aqueous phase reforming of glycerol. Only a few available journals contain the analysis of the thermodynamic. Through these weeks, meeting is scheduled with Dr. Tazli to discuss outcomes of the research and verify information gathered. The most crucial part is to find the exact component present in the sorbitol reaction in APR process. These components are one of the functions needed in creating simulation.

Week 7-8: Preparation of proposal defense slides for presentation. The slides must compromise every single explanation of this project but at the same time need to be simple. 20 minutes is given to each student for presentation.

Week 8-13: Correction of earlier report. More information and data must be added into literature review section to support this case study. Explanation of methods on how to carry out simulation is crucial for readers understanding and verifies this work can be done within time frame.

Week 13: Submission of interim draft report to supervisor for final look and correction. Any mistakes or lack of data is recorded for further improvisation.

Week 14: Submission of final interim report to supervisor for marking and review.

3.3 Experiment Methodology

3.3.1 Simulation

For thermodynamic analysis, there are two options to solve phase equilibrium problems. The options are stoichiometric and non stoichiometric thermodynamic approaches. Stoichiometric approach requires the system to be described by stochiometrically independent reactions (Fishtik et al., 2000). Oppositely, non stoichiometric approaches use direct method of Gibbs free energy formula to find the equilibrium composition which is why it is used in this study.

$$G = \sum_{i=1}^{K} \mu_i n_i \qquad (1)$$

Equation 1 can be expressed into:

$$G = \sum_{i=1}^{K} n_i \, \Delta G_i^0 + RT \sum_{i=1}^{K} n_i \ln y_i + RT \sum_{i=1}^{K} n_i \ln P \qquad (2)$$

Main important steps before proceed with APR simulations are, to find the correct property package and check the reliability of iCon software for this particular process. Hence, works done by Authayanun et al., 2010 entitled 'Thermodynamic study of hydrogen production from crude glycerol autothermal reforming for fuel cell applications' and Adhikari et al., 2006 entitled 'A thermodynamic analysis of hydrogen by steam reforming of glycerol are tested using three different property packages as listed below:

1. Advanced Peng Robinson
2. Wilson
3. Gasification

(Note: all the property packages listed above are subjected to iCon software)

Different property package means different approach of calculating the reaction mechanism Property package that yields the most accurate result with respect to the literatures is chosen.

Table 2: Operating Condition for aqueous phase reforming of sorbitol

OPERATING CONDITION FOR AQUEOUS PHASE REFORMING OF SORBITOL	
Parameters	**Value**
Operating Pressure	29-60 bar(sorbitol)
Operating Temperature	250-1000 ^{o}C(sorbitol)
Concentration of sorbitol	1%-30%
Carbon formation	-

Reference:

1. Kirilin, A.V., Tokarev, A.V., Kustov, L.M., Salmi, T., Mikkola, J.P. and Murzin, D.Y. (2012) Aqueous Phase Reforming of Xylitol and Sorbitol: Comparison and Influence of Substrate Structure. Applied Catalysis A: General, 435-436, 172-180.
2. Davda, R.R. and Dumesic, J.A. (2004) Renewable Hydrogen by Aqueous-Phase Reforming of Glucose. Chemical Communication, Issue 1, 36-37.

The first step to create a simulation is by opening icon software and selects the desired property package. When creating a new simulation, a new tab as shown in the figure 7 will pop up. After the desired property package is selected, components available in the reaction are added. However, if there is no preferred component in the lists, user can add a new one by inserting density, boiling point or other properties of that precise compound. The components are listed in the table 3. Then, drag equilibrium reactor into the layout and add inlet and outlet stream. Double click the reactor to open up properties form and change the reactor specification into Gibb's reactor. After all is set, the simulation can be carried out to analyze the effect of different parameters value to the thermodynamic reaction. User may also use case study feature in iCon, where it allow user to make different set of value range for each parameters, determine the dependent variable, and independent variable. Throughout this way, the results for simulation can be extracted easily and it is time saving.

Table 3: List of components for simulations

Component for 1st set of simulation
1.Sorbitol
2.Water
3.Hydrogen
4.Carbon
5.Carbon dioxide
6. Methane
7. Ethane
8.Propane
9.Propane
10. Butane
11. Pentane
12. Hexane
13. Ethylene
14. Propylene

Reference:

1. Cortright, R.D., Davda, R. R. & Dumesic, J. A. Hydrogen from catalytic reforming of biomass-derived hydrocarbons in liquid water.*Nature* 418. 964-967 (2002)
2. Huber, G. W.: Cortright, R.D.: and Dumesic, J.A.: Renewable Alkanes by Aqueous-Phase Reforming of Biomass Derived Oxygenates, Angewandte Chemie International Edition, 43, 1549-1551(2004)

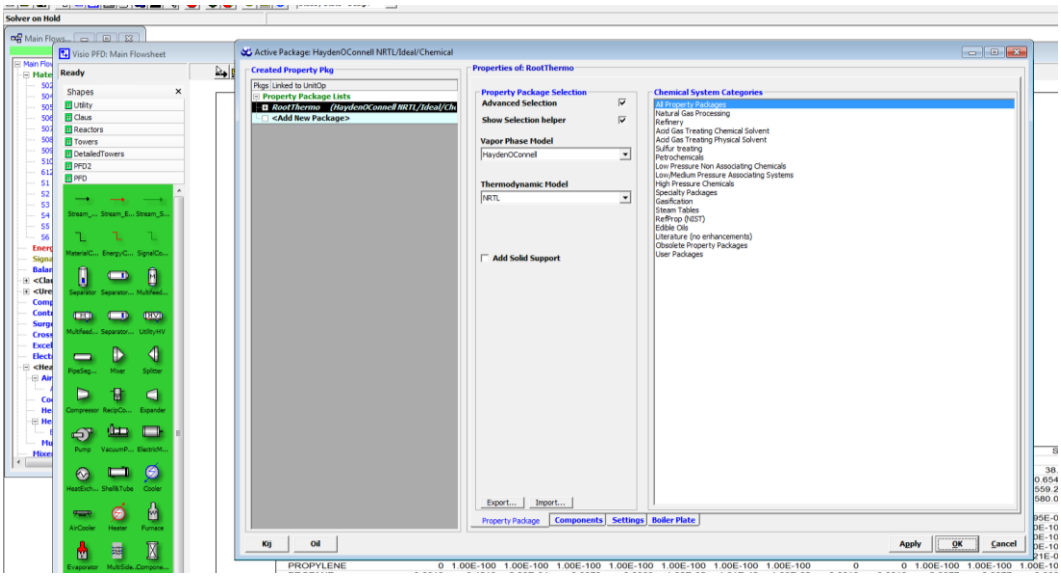


Figure 7: Property package and components tab in iCon software

4.0 RESULT AND DISCUSSION

4.1 Finding Reliable Property Package for Aqueous Phase Reforming

4.1.1 Property Package Test & Cross Reference with Authayanun et al., 2010

In this section, work done by Authayanun et al., 2010 and Adhikari et al., 2006 is tested using different property package to find out the most effective and reliable one. In other hand, the main goal of this test is also to check the reliability of iCon software by cross checking results from literature review with the results obtained from actual simulation. The property package which gives the most accurate result with respect to the literature review is considered precise enough and reliable for simulation in this study. Below are the comparisons data from the literature review and results from simulation. Result recorded by Authayanun et al. is displayed in figure 8 whereby result from simulation is in figure 9. In his report, Authayanun uses Peng-Robinson-Stryjeck-Vera equations of state as his property package. Comparisons with two literature review are essential to determine the right equation of state for aqueous phase reforming. In this section, simulation is done by replicating data from literature and run them using iCon to see how the final results look like whether it is the same or opposite with original results from literature.

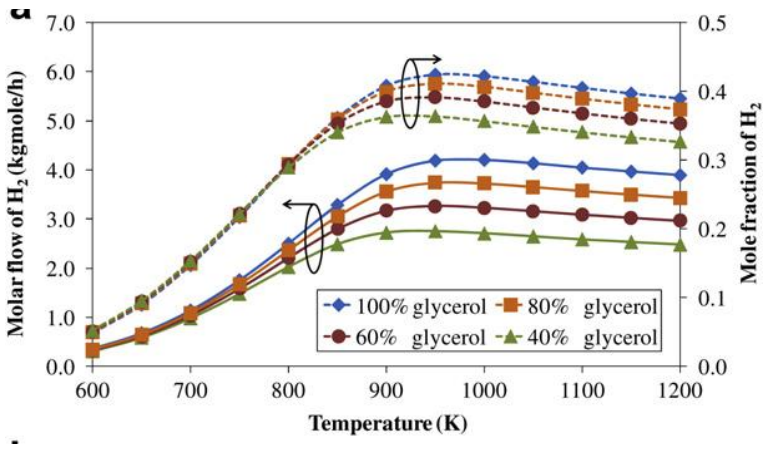


Figure 8 : Effect of temperature towards Molar Flow of H_2 and Mole fraction of H_2

(Source: Authayanun et. al. 2010. Thermodynamic study of hydrogen production from crude glycerol autothermal reforming for fuel cell apllications)

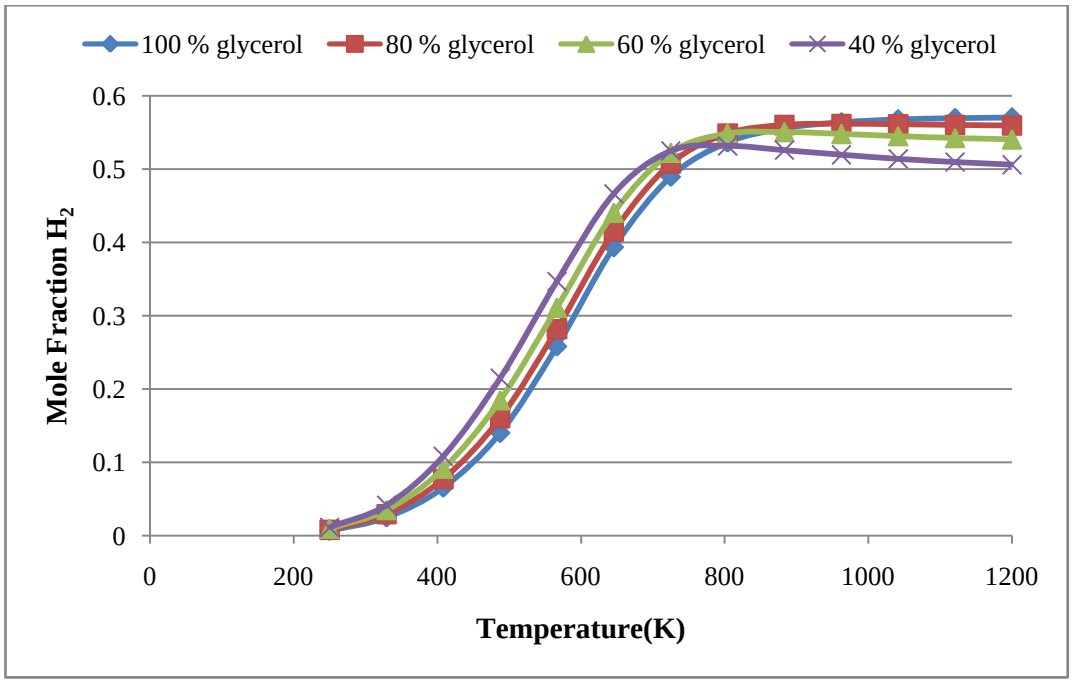


Figure 9: Test using Advance Peng Robinson

In the test simulation, the inlet temperature is kept constant at 550K while temperature inside reactor is manipulated in range of 250K- 1000K by varying output temperature. Pressure in the reactor is constant at 29 bar. There are 4 different compositions of glycerol in the simulation which is represented by different color in the graphs. Correlations of hydrogen mole fraction with the reactor temperature can be seen clearly in the graphs, when temperature is increased then the mole fraction also increases until they reach at certain level where the mole fraction drops; except for Gasification property package. Different property package gives out different result since they use different approach of calculation and constraint. Simulation using Advance Peng Robinson property package yield almost the same result as recorded by Authayanun and co-worker. From test using Advance Peng Robinson, mole fraction of H_2 is the highest and keeps increasing when amount of glycerol is at the lowest, 40% followed by 60%, 80% and 100%. However, when temperature rises in range of 800K to 1000K, graph starts to show turning points. At the end, opposite finding is obtained where highest yield of H_2 is when amount of glycerol is the highest, 100% followed by 80%, 60% and 40%. From the comparisons, simulation generated using Advance Peng Robinson property package has the closest data distribution to the results reported by Authayanun et al., 2010.

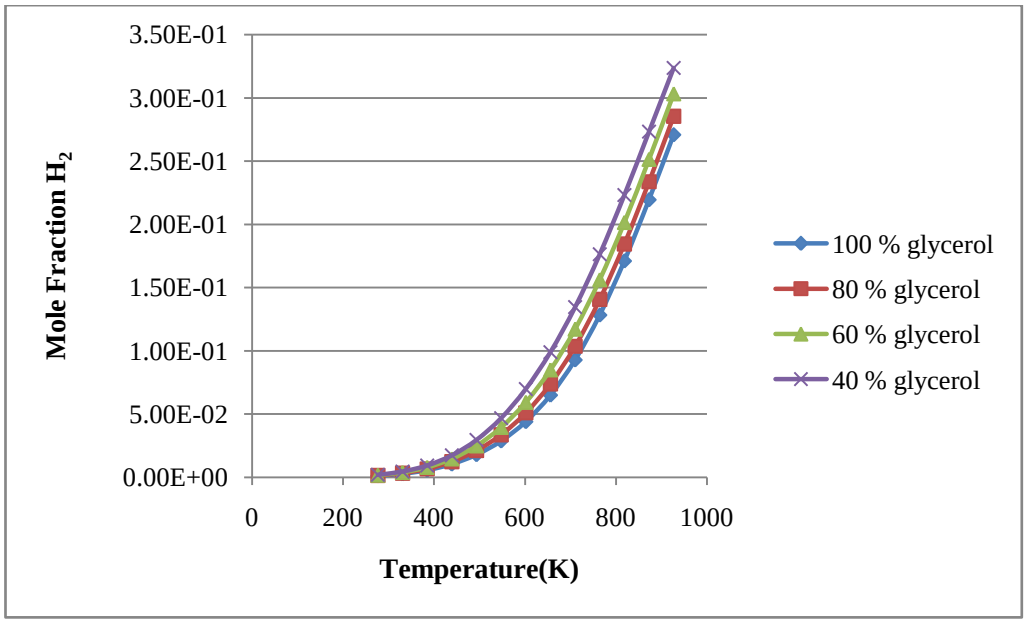


Figure 10: Test using Gasification

The second test is carried out with same parameters by Authayanun et. al but with Gasification property package. Fig. 10 shows mole fraction of hydrogen increase steeply without any drop as the temperature increases. Basically, any reaction carried out using iCon, the result will be more biased to gaseous phase and the final data usually calculated based on the presence of gases. In a simulation with gaseous property package, the formation of liquid product becomes lesser or in this case liquid product is almost zero. The reason mole fraction of H_2 does not drop when temperature is high is, due to the presence of gases (oxygen, carbon dioxide, hydrogen, methane) in the model itself. Conclusion is made that Gasification property package is not suitable and not accurate enough to simulate APR process, which is a process that is suppose to consist of liquid and gas phase.

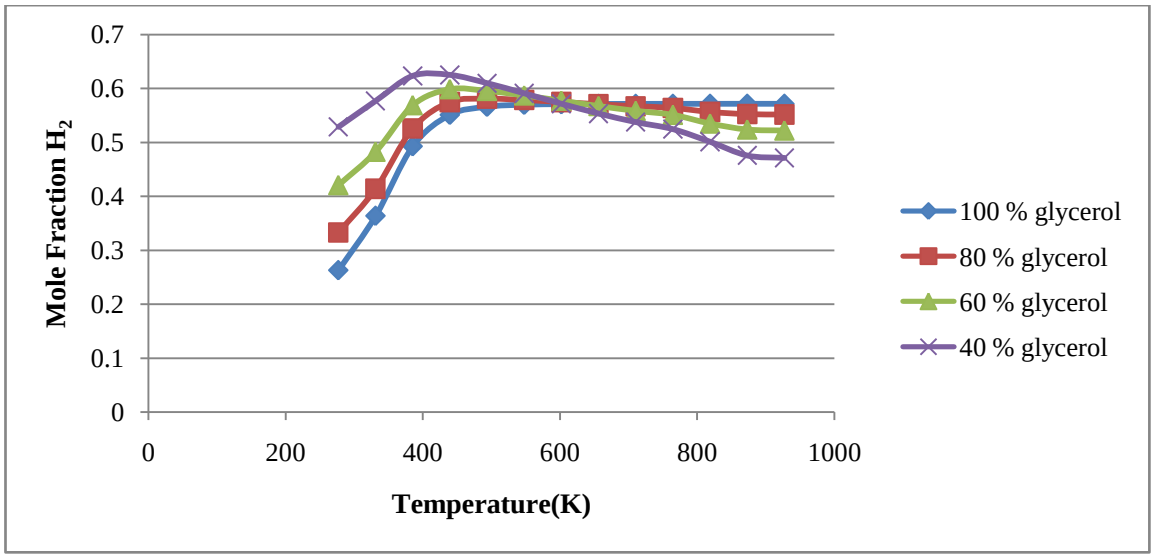


Figure 11: Test using Wilson

Third test is carried out using Wilson property package and the result is surprisingly different in many ways compared to literature review. The inlet temperature for this test is set for 250K since the reaction is fast and happened at high rate when temperature is low. The production of hydrogen falls down in even when temperature is below 500K. Mole fraction of H_2 is at its highest level when reactor is heated up from 250K- 400K. Hence, Wilson equation of state is not suitable to be used as the basis of this study due to significance difference of simulation result (when using Wilson property package) compared to the result from literature review. As can be seen, Wilson is not the best property package to be selected as the result yielded from this simulation is so much different from the literature review. Wilson equation of state is not suitable to be used for aqueous phase reforming simulation.

4.1.2 Property Package Test & Cross Reference with Adhikari et al., 2007

In order to ensure the right property package is selected, second set of test is made using research paper prepared by Adhikari and his team. The parameters, procedure are duplicated from that literature entitled 'A thermodynamic analysis of hydrogen production by steam reforming of glycerol' (Adhikari et al., 2007). Basis of methodology is to compare results and analysis from literature with results from simulations. Figure 11 is the results extracted from Adhikari and co-worker's journal.

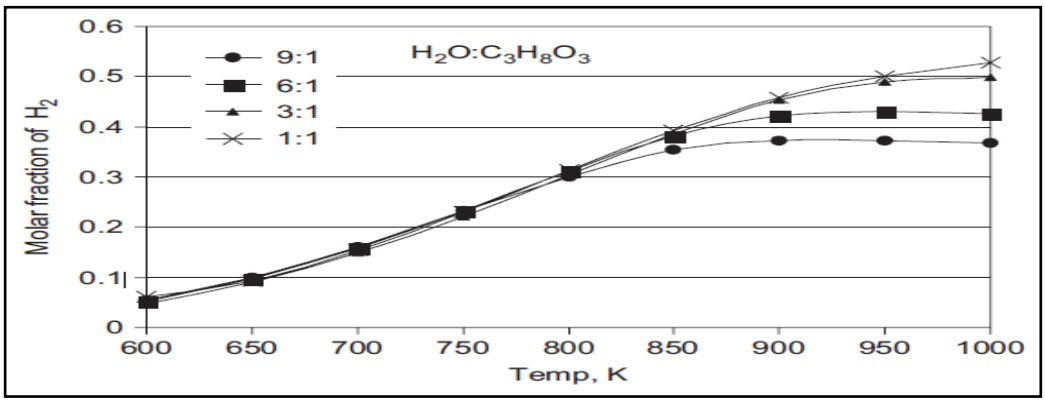


Figure 12: Effect of temperature to Molar fraction of H_2 with different composition of water-glycerol ratio

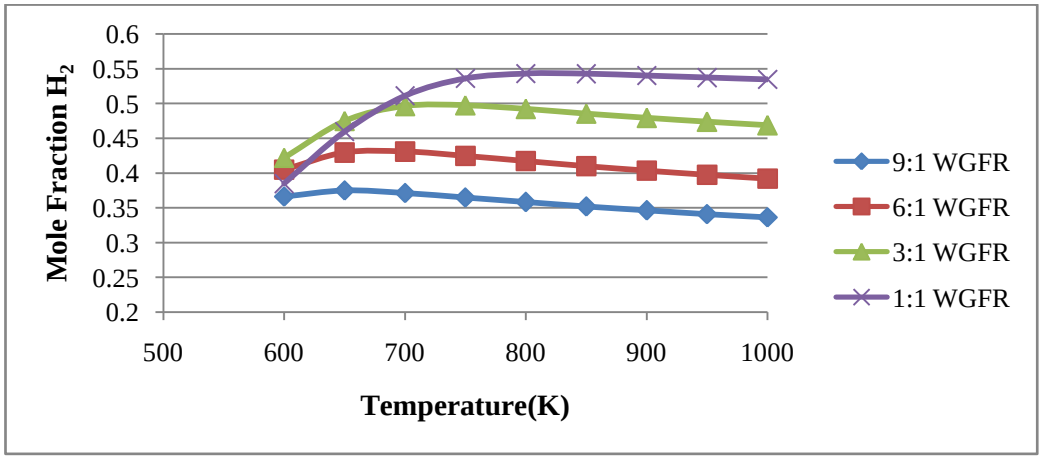


Figure 13: Test using Advanced Peng Robinson

Figure 13, 14 & 15 depict the hydrogen molar fraction at different temperature and water to glycerol feed ratio (WGFR). The only graph which is consistent with result yield from literature review is figure 13 (test using Advance Peng Robinson property package). Both of the figures above share same characteristic and data distribution. Mole fraction of hydrogen is the lowest for highest WFGR.

This condition is related to suggestion by Adhikari suggesting that unreacted water reduces molar fraction of hydrogen (Ahikari et al., 2007). Dissimilar outcome acquired from test using Gasification and Wilson property package in figure 14 and 15 where. The results imply that they are not dependable for APR process. These 2 sets of test already proved Advance Peng Robinson is the only equation of state that correlates with two literature reviews mentioned earlier (journal by Adhikari, 2007 & Authayanun, 2010). As can be seen from both set of tests, Advance Peng Robinson gives the unsurpassed result which indicates it is reliable for continuation of this project. Since the best property package as so called Advance Peng Robinson equation of state is confirmed, analysis of thermodynamic of aqueous phase reforming of sorbitol is continued.

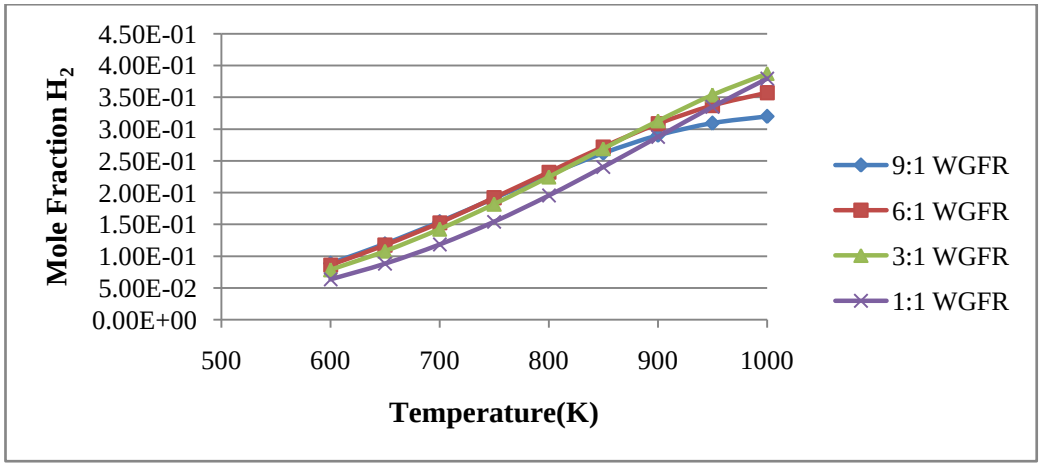


Figure 14: Test using Gasification property package

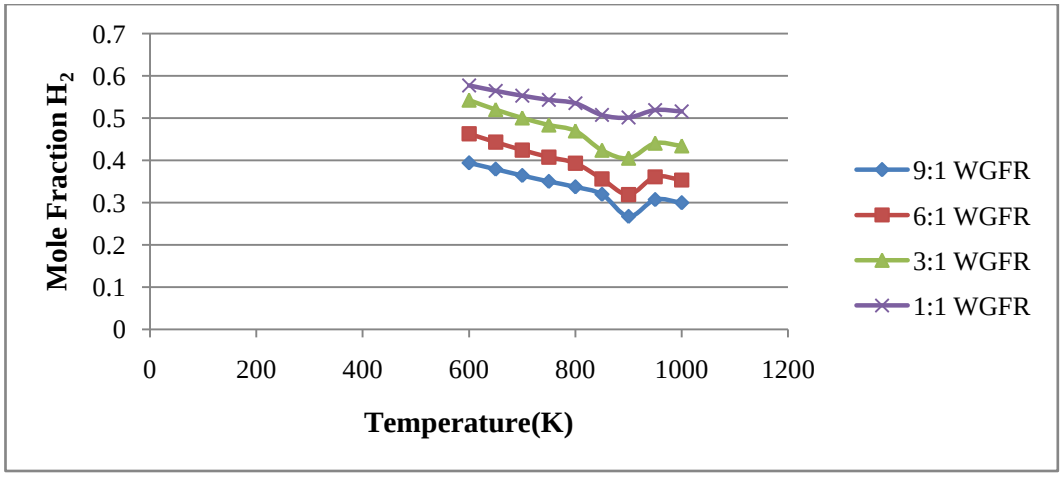


Figure 15: Test using Wilson property package

4.2 Effect of Temperature on Aqueous Phase Reforming of Sorbitol

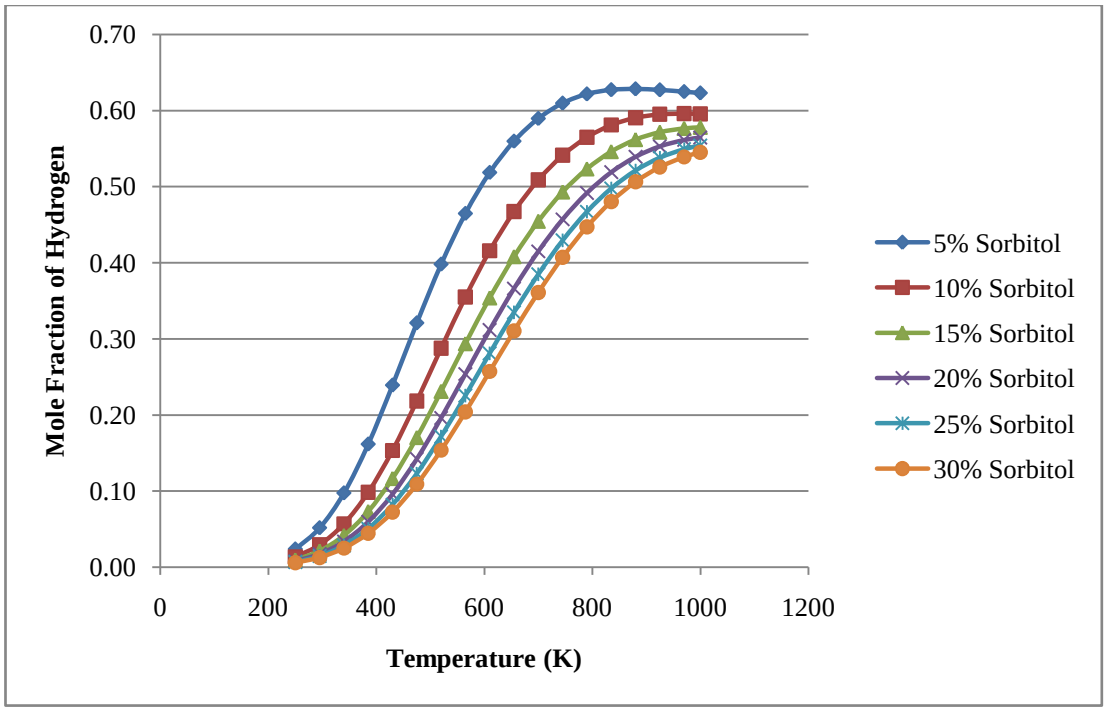


Figure 16: Aqueous phase reforming of sorbitol-Temperature effect on Mole Fraction of H_2

The graph above shows the mole fraction distribution of hydrogen with respect to different temperature and sorbitol concentration. The concentration of sorbitol denotes the amount of sorbitol in water content. Example, inlet feed is having 30% of sorbitol indicates the rest 70% of the content is water. In this study, 5 different concentration of sorbitol is used to analyze the effect of water-sorbitol composition, temperature to the production of hydrogen. Clearly by increasing temperature, formation of hydrogen becomes more favorable until at some point the yield production rate starts to slow down. The hydrogen yield is the highest when amount of water contest is high. This is due to condition where molecular bond of water, H_2O breaks apart into O_2 and H_2.

This condition can be explained through:

$$C_6H_{16}O_6 + H_2O \rightarrow 26H_2 + 6CO_2$$

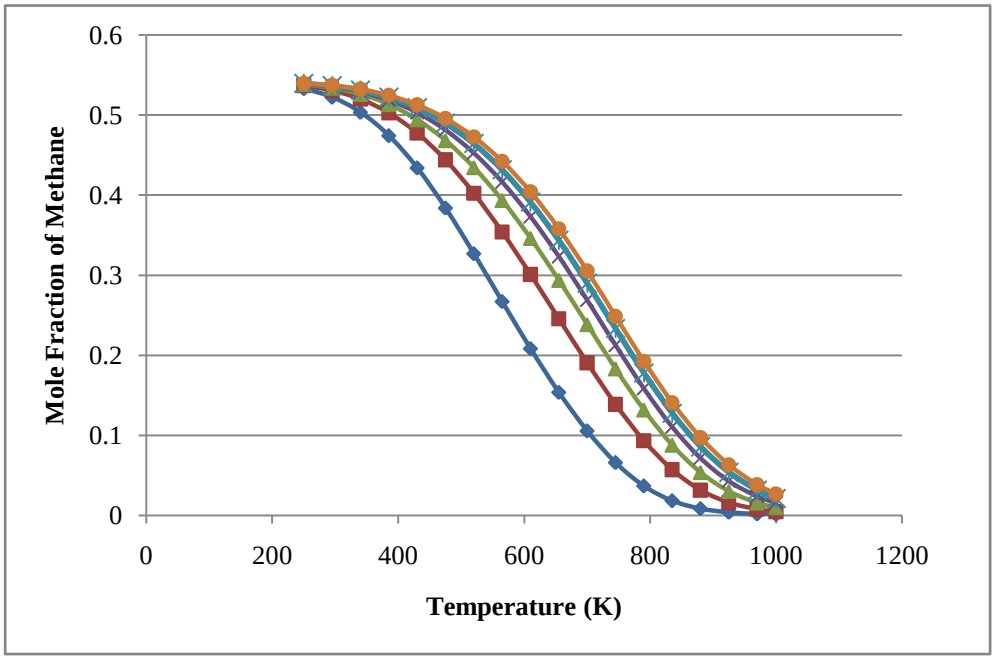


Figure 17: Mole fraction of Methane with respect to temperature

Increasing temperature increases the amount of hydrogen yield but decreases the production of methane. This is because the methane selectivity competes with hydrogen selectivity. Hence, when the production of hydrogen is high, then production of methane is low. This case can also be defined based on the carbon monoxide and carbon dioxide yield. As the temperature increases, the amount of carbon monoxide and carbon dioxide becomes high. Following equation relates the production of CO and CO_2 with methane selectivity:

$$CH_4 + 2H_2 \leftrightarrow CO_2 + 4H_2$$

$$CH_4 + H_2O \leftrightarrow CO + 3H_2$$

4.3 Effect of Pressure on Aqueous Phase Reforming

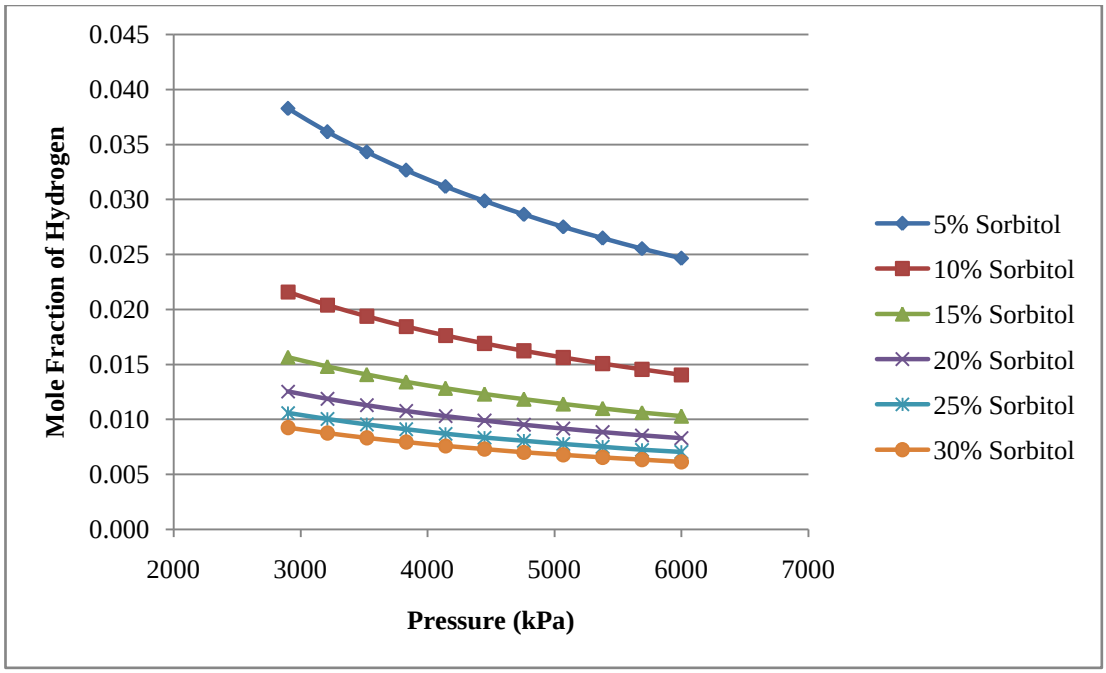


Figure 18: Aqueous phase reforming of sorbitol- Pressure effect on Mole Fraction of H_2

Mole fraction of hydrogen decreases when pressure increases indicating formation of hydrogen is more favorable at lower pressure. High pressure usually compresses gases into liquid where this case; it suppresses hydrogen formation in the system. Other than that increasing composition of sorbitol does not help selectivity of hydrogen for both temperature and pressure profiles. Hydrogen mole fraction reaction for pressure profile is similar with temperature profile in term of sorbitol concentration. It can be seen that high concentration of sorbitol lowers the mole fraction of hydrogen in both profiles. One of the main purposes of using high pressure is because it is the main characteristic of aqueous phase reforming compared to autothermal reforming. The pressure used in autothermal reforming is much lower than in APR. Typically, APR main objectives are to minimize production of carbon monoxide and reduce cost since it does not use heating mechanism.

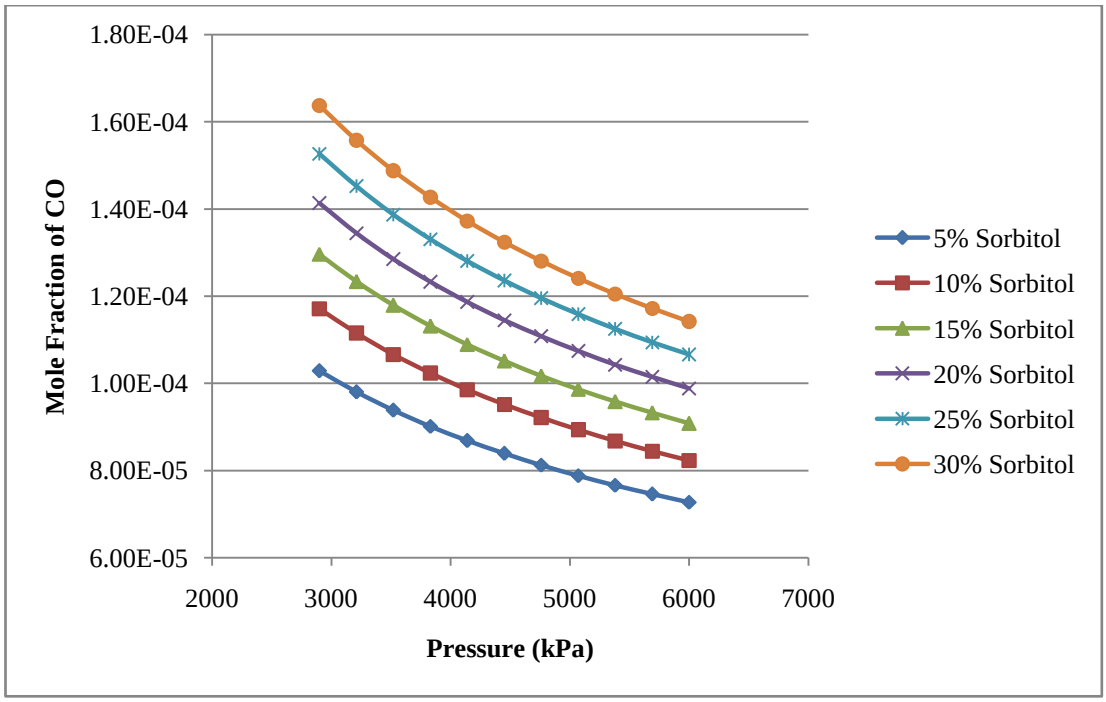


Figure 19: Mole fraction of carbon dioxide with respect to pressure

Production of carbon monoxide is particularly low when pressure increases. Mole fraction of hydrogen, carbon monoxide and carbon dioxide decreases with increasing of pressure. However, the methane produced becomes higher. Higher amount of methane produces in APR lowers the possibility and selectivity of another carbon component to form.

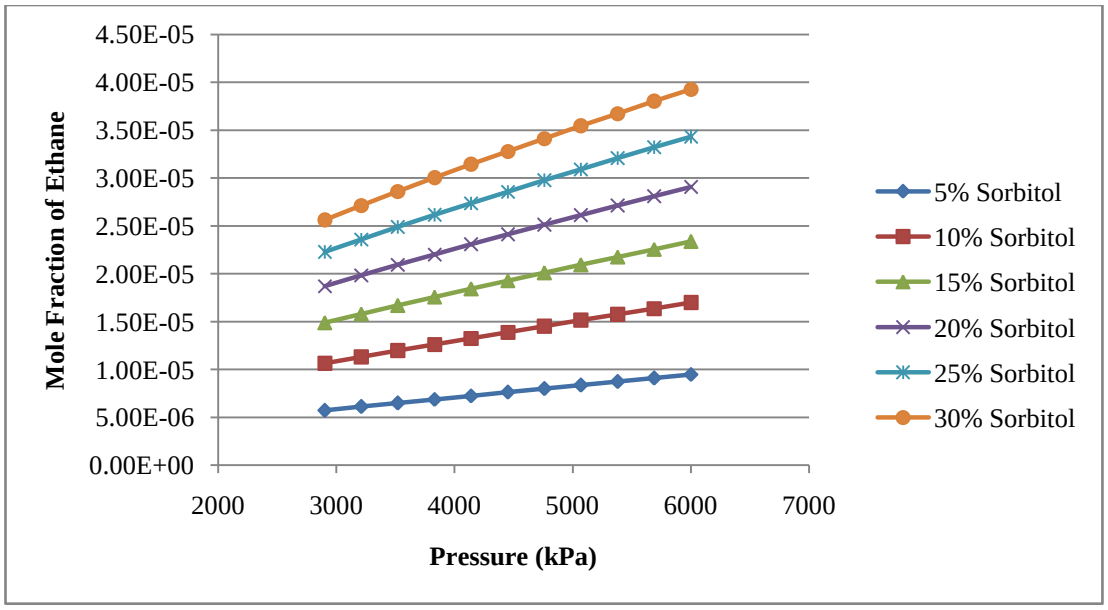


Figure 20: Mole fraction of ethane with respect to pressure

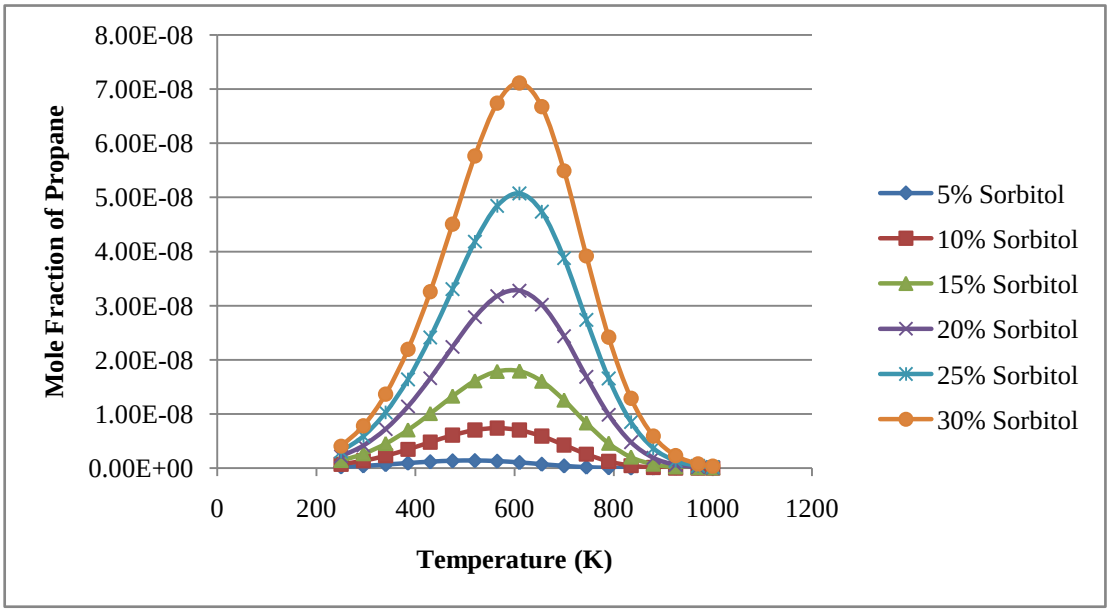


Figure 21: Mole fraction of propane with respect to temperature

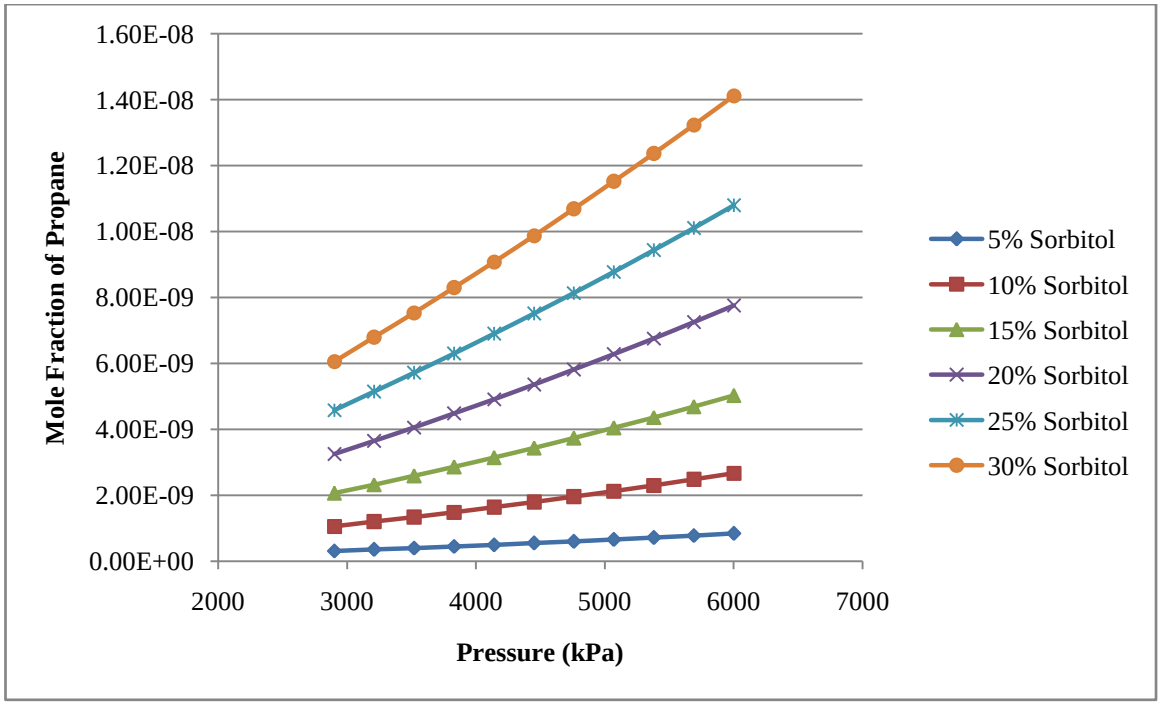


Figure 22: Mole fraction of propane with respect to pressure

Figure 20, 21, 22 shows the formation of another synthetic gas during aqueous phase reforming. However, the formation of these gases is quite small. Apart from ethane and propane, other substances also formed during APR of sorbitol. The lists of these components are summarized in the table below:

Table 4: Component list of product

Component	**Range of Mole fraction**
Ethane	$2 \times 10^{-9} – 1.98 \times 10^{-5}$
Pentane	$1.4 \times 10^{-14} – 3.42\ 10^{-10}$
Butane	$8.9 \times 10^{-20} – 3.59 \times 10^{-13}$
Methane	0.001 – 0.539
n-propylene	$2.35 \times 10^{-15} – 2.16 \times 10^{-6}$
n-ethylene	$1.65 \times 10^{-12} – 1.89 \times 10^{-6}$

4.6 Carbon Formation

The thermodynamic results of carbon formations were studied as a function of temperature and pressure. Both studies show a there is a sign of carbon formation. However, the amount of carbon formed in the system during APR is very small ranging from 3×10^{-45} to$1 \times 10^{-4-23}$. Carbon formation may occur through series of reactions between gas products:

$CO + H_2 \rightarrow C + H_2O$

$CO_2 + 2H_2 \rightarrow C + 2\ H_2O$

$C\ H_4 \rightarrow C + 2\ H_2$

Solid carbon formed in the process consumes hydrogen, hence reducing the selectivity of hydrogen (Xie J. et al, 2011). Hence, it can be concluded that the higher the temperature used, the higher the formation of carbon. In the figure below, the amount of carbon starts to increase steeply when temperature is more than 800 K which signifies that the carbon formation is high when hydrogen yield is not favorable. At temperature more that 800K the hydrogen production if not favored.

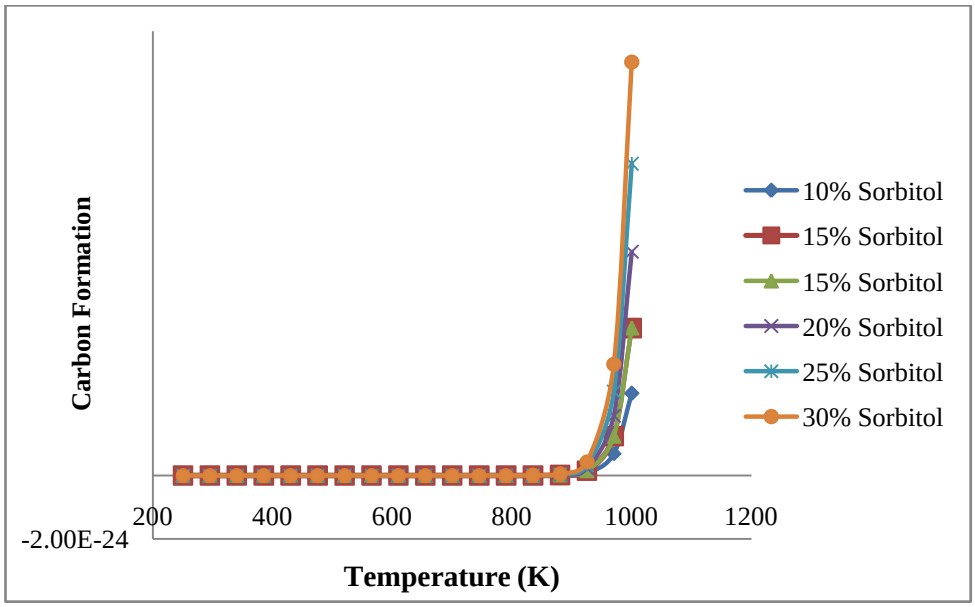


Figure 23: Aqueous phase reforming of sorbitol-Temperature effect on Carbon formation

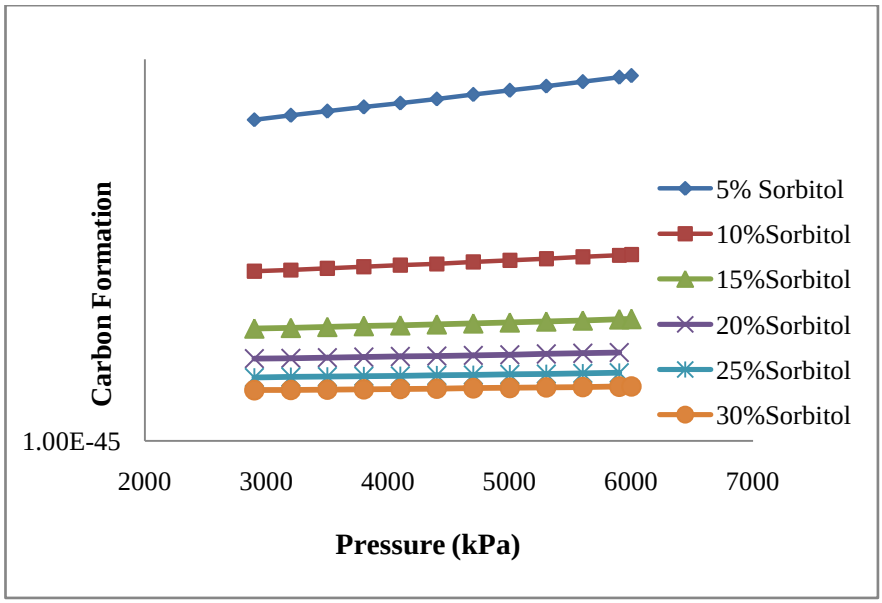


Figure 24: Aqueous phase reforming of sorbitol-Pressure effect on Carbon formation

Based on the figures above, higher temperature and pressure resulted in higher carbon formation. But the rate of the formation is much smaller for pressure graph. By controlling maximum temperature and pressure, unwanted product such as solid carbon can be minimized. Presence of carbon in reactor may induce problems in future. As time goes by, the carbon will deposit to the surface of reactor and altering optimum function of equipment.

5.0 CONCLUSION AND RECOMMENDATION

In conclusion, increasing temperature causes the mole fraction of hydrogen to increase gradually. Minimum yield of hydrogen is at highest concentration of sorbitol, 30% specifically when temperature is at 250 K. Maximum mole fraction of hydrogen is obtained is 0.62 at temperature 925K with concentration of 10%. At some point, the hydrogen mole fraction will drop when temperature increases but vary based on the concentration of sorbitol. Hydrogen selectivity for concentration 10%, 15%, 20%, 25%, 30% start to fall when temperature is more than 1000K. However, it goes differently for the pressure parameters where the yield of hydrogen drops as soon as the reaction occurs. This indicates aqueous phase reforming process is better at low pressure. In the pressure profile, the amount of hydrogen yield is highest when concentration of sorbitol is lowest. Production of hydrogen change with respect to pressure, temperature and concentration is strongly related to Le Chatelier's principle where he indicates the equilibrium state in a reaction will move to counteract or reverse the act of parameters change. Carbon formation has been proved happened during aqueous phase reforming process. Carbon is formed the most when temperature is high. Besides that, formation of the solid carbon is obviously small in this simulation and the formation occurs when temperature is high and hydrogen yield is low. This discovery is important since it signify that there is presence of carbon along the process and determines the most optimum temperature, pressure, concentration for aqueous phase reforming of sorbitol. Hence, the yield of hydrogen can be increased with minimum production of carbon monoxide and solid carbon.

In the future, this simulation can be improved by back testing a few more property package (equation of state) to find the most precise and reliable package for aqueous phase reforming. Since this aqueous phase reforming reaction occur at gaseous state with various components, a few more considerations such as polar components, component reactivity must be taken into account when selecting property package. On the other hand, thermoneutral condition also needs to be tested in future research. Thermoneutral is a condition of increasing oxygen to sorbitol molar ratio in order to decrease external heat requirement. Hence, there is high possibility to control the aqueous phase reforming process by using oxygen feed.

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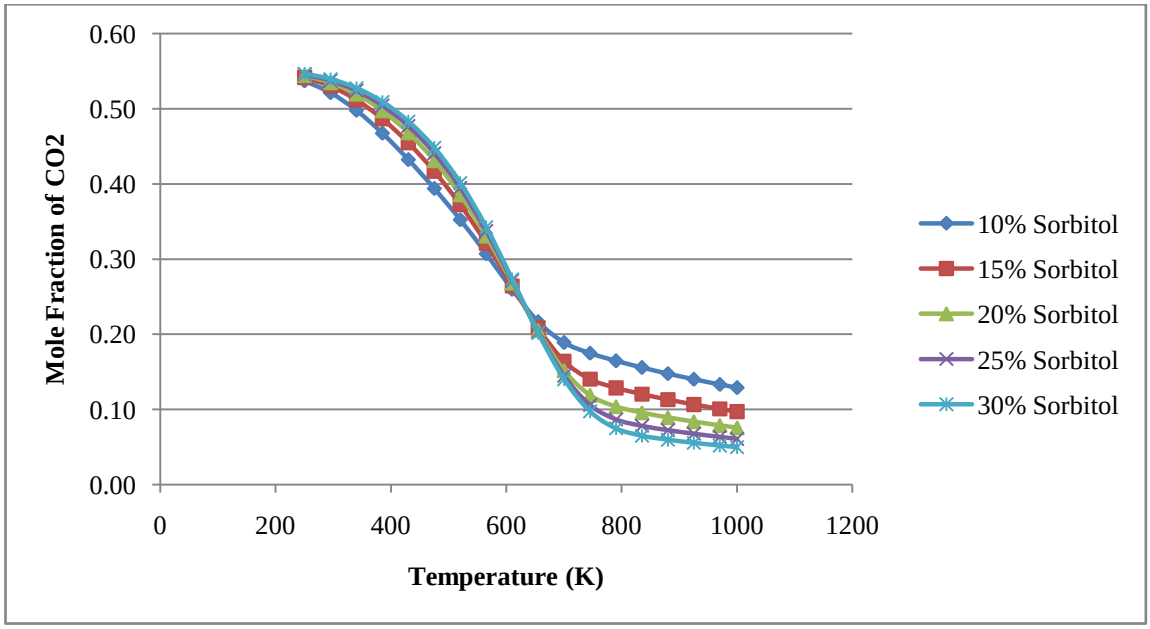
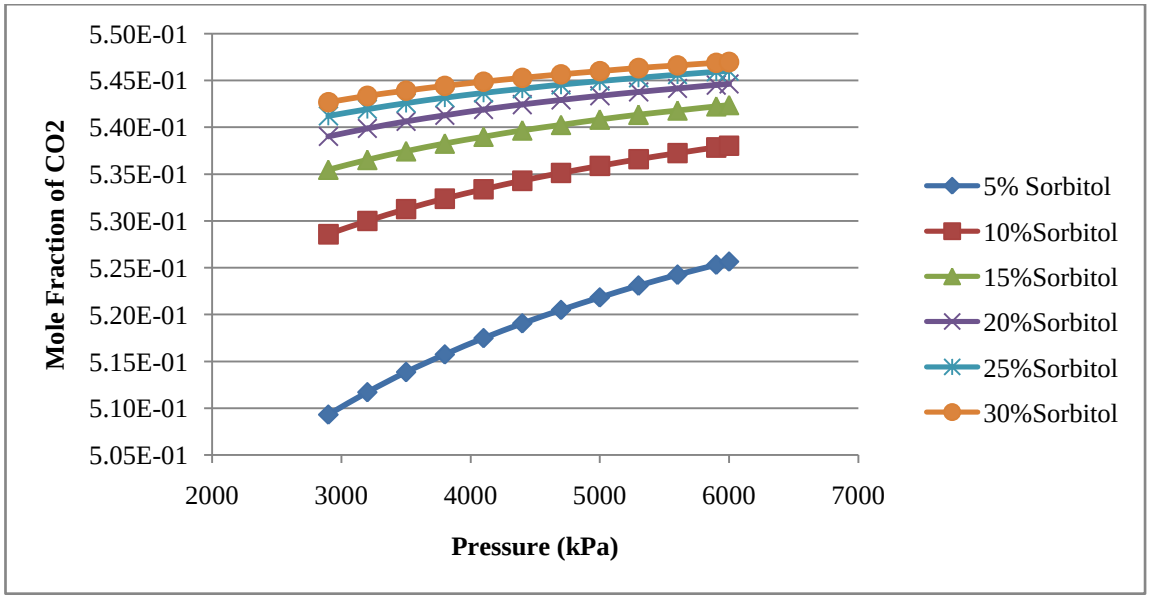
Appendices



Appendix 1: Effect of temperature towards mole fraction of CO_2



Appendix 2: Effect of pressure towards mole fraction of CO_2