EXPERIMENTAL STUDIES OF GASIFICATION OF GLYCEROL FOR THE PRODUCTION OF HYDROGEN

Muhammad Ayoub*, Sanjeev Sathiaseelan, Siti Aminah Mohd Johari

Department of Chemical Engineering, Universiti Teknologi PETRONAS, Malaysia

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ABSTRACT

In this study, pure glycerol and crude glycerol conversion to hydrogen gas was investigated using a fixed-bed reactor. The gasifying agent utilised for this research is steam. The efficiency of the reaction was based on the results data of the H_2 yield obtained. The reaction was conducted using two different packing materials, which were silicon carbide and quartz. The effect of packing material was investigated. Next, steam-to-glycerol ratios were varied in the range of 0:0, 10:90, 25:75 and 50:50 to study the influence of the ratios on the product hydrogen gas. The effect of the catalyst and the amount of catalyst loading was investigated using a Ni/Al_2O_3 catalyst. The effect of temperature on the yield of product was studied in the range of 650 - 800°C. Product gasses H_2, CO_2, CO and CH_4 were analysed using TCD and NDIR analysis. The highest purity of H_2 was 65 mol% at the optimised condition of 25:75 steam to glycerol ratio and 800°C.

Keywords: *glycerol, crude, hydrogen, gasifying, fixed bed reactor pyrolysis*

INTRODUCTION

In the past few decades, fossil fuel has become one of the dominant energy resources that is widely used to cope with our energy requirements [1]. Fossil fuel is classified as a non-renewable form of energy due to the timeline that is required for it to form. The formation of fossil fuels requires several centuries to millions of years [2]. This resource is also classified as a major factor in global warming. This is because fossil fuel combustion produces energy in the forms of hydrogen gas, syngas, methane, and others, releasing carbon dioxide as the byproduct. The emission of CO_2 gas to the atmosphere increases the temperature of the environment, thus leading to global warming [3]. After many years of studies, researchers have found several alternative energy forms to fossil fuels, such as hydrogen, ethanol, and biodiesel. Alternative forms of energy are widely applied to the present day in maintaining sustainable energy production.

One of the alternative fuels that have gained attention in recent decades is biodiesel as its contribution to the sustainable production of energy [4]. In biodiesel production, carbon monoxide and carbon dioxide emissions are lower when compared to normal diesel production. Biodiesel is produced from animal fats and vegetables. There are several methods of biodiesel production, such as transesterification, thermal degradation and emulsion [5]. Biodiesel demand has increased significantly in the last two decades, as shown in Figure 1, due to the vast benefits of the production of biodiesel.

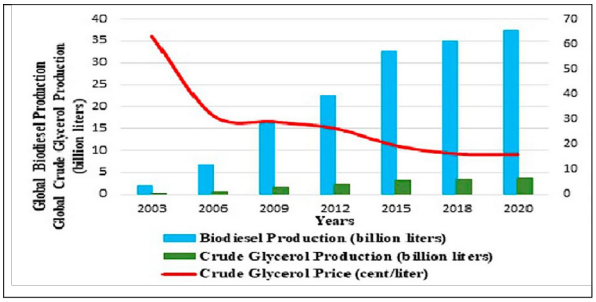

Figure 1 Price of biodiesel and glycerol against production [6]

Glycerol, also known as glycerine or glycerin, is a byproduct from the transesterification process during the production of biodiesel [7]. Based on previous studies, it can be said that for every 100 kg of biodiesel produced, 10 kg of glycerol is produced [7]. Due to the excess supply of glycerol that exceeded the demand for glycerol, glycerol price has plunged significantly. In achieving sustainable production of biodiesel, byproduct glycerol must be properly utilised [8]-[9].

Hydrogen gas, H_2, is known to be a clean source of fuel and is being widely developed as an alternative to oil and other fuels. This is because of its good energy storage capacity. Currently, the primary method of hydrogen production is by cracking natural gas or waste oil at high temperatures. Hydrogen gas could be converted to various forms of energy, such as heat and electricity, by combustion or electrochemical reactions. Hydrogen production from biomass waste has overwhelming attention due to its environmental sustainability, social, and economic benefits. This report focuses on hydrogen production by decomposition of biomass such as glycerol. The steam reforming process is the most commonly used method to convert crude glycerol into hydrogen gas [10].

Fossil fuels happen to be the major source of hydrogen in industries. The cracking of crude glycerol at high temperatures (>600°C) can yield major gas products, hydrogen and carbon monoxide [10]. Renewable resource-based hydrogen production is a sustainable option to utilise the glycerol that is produced from biodiesel production. Based on a study, it can be said that 1 mol of glycerol is able to produce up to 4 moles of hydrogen, making it a potential feedstock for hydrogen production [11]. The main objective of this study is to study the parameters that influence the steam gasification of glycerol. The ratios of glycerol-steam were tested for 0:0, 10:90, 25:75 and 50:50. The catalytic and non-catalytic experiments were carried out in the temperature range of 650°C to 800°C.

*Corresponding author.
E-mail address : muhammad.ayoub@utp.edu.my

EXPERIMENTAL

Material

Nickel (II) nitrate hexahydrate (Ni $(NO_3)2{\bullet}6H_2O$) with 99.99% of purity, aluminium oxide (Al_2O_3) with 99.99% purity were purchased from Sigma-Aldrich, pure glycerol (85%) was purchased from R&M, deionised water and crude glycerol were obtained from biodiesel production of waste cooking oil.

Preparation of Ni/Al_2O_3

Different quantities of nickel nitrate hexahydrate were dissolved in deionised water to make a precursor solution for nickel loading 0.2 g, 0.4 g, 0.6 g and 0.8 g. The nitrate solution was added to support particles Al_2O_3. The solution was then stirred for 3 hours and dried in an oven at 110°C before calcination for 5 hours at 500°C.

Characterisation of Feed

The TGA analysis was used to study the pure and crude glycerol's thermal stability and the composition of ash and volatile compounds present. This can be observed by monitoring the weight change that happens to the glycerol when it is heated at a constant rate.

Glycerol Steam Reforming

Steam gasification of pure and crude glycerol was conducted in a continuous down-flow fixed bed micro reactor at atmospheric pressure. Packing materials were used to provide a plug flow and even distribution of reactant in the reactor. The packing materials used for this experiment were quartz and silicon carbide. Nitrogen gas was used as a carrier gas to facilitate the distribution of components or reactants. The mixture of steam to glycerol ratio was changed from 0:0, 10:90, 25:75 and 50:50. The catalytic and non-catalytic experiments were carried out in the temperature range of 650°C to 800°C with an increase of 17°C/min, which was measure using a K-type thermocouple placed at the heating zone in the furnace and connected to a temperature controller. 70 mm reactor packing height was used. The water and glycerol were fed into the reactor using an LDC analytical pump at the rate of 5.4 g/min.

Catalytic steam gasification was performed using a commercial Ni/Al_2O_3 catalyst with a particle size of 0.15 mm. The catalyst loading used was 0.2 g, 0.4 g, 0.6 g and 0.8 g.

The product leaving the reactor was condensed and separated into liquid and gaseous fractions. The liquid product fraction was collected in a liquid trap and cooled with an ice-salt bath, and the gaseous product was collected over a saturated brine solution of sodium chloride. The reactor was then cooled and weighed to determine the amount of char. The volume of gas was measured at room temperature 25°C and 1 atm pressure.

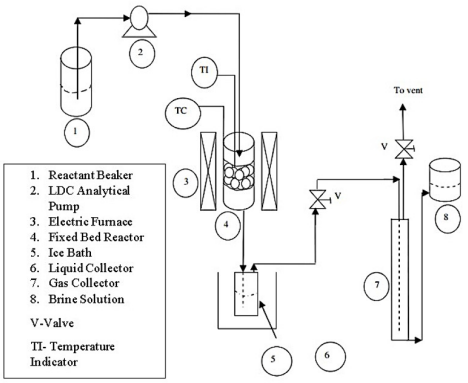

Figure 2 Experimental Diagram of Project

Composition of Pure and Crude Glycerol

Table 1 Composition of different types of glycerol

Glycerol type	Glycerol (wt%)	Methanol (wt%)	KOH (wt%)	Water (wt%)
Pure	100	0	0	0
Crude	60	31	1.05	7.5

Table 1 shows the crude glycerol consists of approximately 1% potassium hydroxide, 31% methanol, 7.5% water and 60% glycerol in wt. % respectively. The presence of potassium and methanol has no significant effect on the product yield.

Steam Gasification of Pure Glycerol

The gasification process using steam as the gasifying agent was carried out to determine the effects of process parameters on products such as liquid, gas and solid yields. The gasification process was done to produce hydrogen with steam as the gasifying agent. Different steam-to-glycerol weight ratios were used during this experiment, as tabulated in Table 2.

Table 2 Steam to glycerol ratio with packing material silicon carbide and quartz

Run Number	Steam (wt%)	Glycerol (wt%)	Packing Materials
Run 1 Run 2	0	100	Quartz Silicon Carbide
Run 3 Run 4	10	90	Quartz Silicon Carbide
Run 5 Run 6	25	75	Quartz Silicon Carbide
Run 7 Run 8	50	50	Quartz Silicon Carbide

The reaction was carried out at 800°C in a fixed bed reactor with a stainless-steel supporting mesh. The mesh is inert during the gasification process. The reaction was conducted using different packing materials at different particle diameters. The selected packing materials were silicon carbide and quartz. In this experiment, the product yields were defined as gram product/100g of feed glycerol.

Product Characterisation

The gas produced from the reaction is pumped into the TCD-GC for analysis purposes. The TCD determines the composition of respective gases produced during the reaction by measuring the thermal conductivity of the gas. The TCD measured the difference in conductivity of carrier has N_2 and carrier gas containing product gas H_2, CO, CO_2, and CH_4 components.

RESULTS AND DISCUSSION

Steam Gasification of Pure Glycerol

Analysis was conducted, and the results have been organised into Tables 3 and 4. A noticeable increase in the gas yield when the steam-to-glycerol ratio was increased with quartz as the packing material. Liquid product and solid product, mainly char yield, decreased as the ratio of steam increased in the reaction. Based on the literature review conducted, we know that glycerol decomposes to form hydrogen, carbon monoxide, carbon dioxide, methane, ethylene, acetic acid, acetone, methanol, acrolein, ethanol, water, and char.

Table 3 Effect of packing material quartz with different steam to glycerol ratios at 800°C

	Quartz particle (0.21-0.35 mm)			
Steam to glycerol ratio (wt%)	0:100	10:90	25:75	50:50
Gas (wt%)	71.2	75.3	84.8	94.0
Liquid (wt%)	20.6	16.8	8.2	0.0
Char (wt%)	8.2	7.9	7.0	6.0
Volume (L/g)	1.32	1.51	1.65	1.71
Calorific value (MJ/m^3)	13.9	13.8	13.0	13.5

Table 4 Effect of packing material silicon carbide with different steam to glycerol ratios at 800°C

	Silicon Carbide particle (0.15 mm)			
Steam to glycerol ratio (wt%)	0:100	10:90	25:75	50:50
Gas (wt%)	77.6	75.2	78.6	89.5
Liquid (wt%)	16.0	17.0	14.3	4.2
Char (wt%)	6.4	7.8	7.1	6.3
Volume (L/g)	1.28	1.23	1.33	1.4
Calorific value (MJ/m^3)	13.5	15.4	14.6	14.3

Gas product hydrogen and solid product char are formed from the dehydration and cracking reactions of glycerol. The reactions that take place in the process are described in Equations 1 to 10:

Steam Reforming of Glycerol

$$C_3H_8O_3 \xrightarrow{H_2O} 3CO + 4H_2 \quad (1)$$

Water Gas Shift Reaction

$$CO + H_2O \Leftrightarrow CO_2 + H_2 \quad (2)$$

Overall Reaction

$$C_3H_8O_3 + 3H_2O \rightarrow 3CO_2 + 7H_2 \quad (3)$$

Steam Reforming of Methane

$$CH_4 + H_2O \Leftrightarrow CO_2 + 3H_2 \quad (4)$$

Steam Reforming of Alchohol

$$C_2H_5OH + H_2O \rightarrow CO_2 + CH_4 + 2H_2 \quad (5)$$

Steam Reforming of Aldehyde

$$CH_3CHO + H_2O \rightarrow CO_2 + CH_4 + 2H_2 \quad (6)$$

At temperature >700°C Steam and Carbon Dioxide Reforming

$$C(S) + H_2O \rightarrow CO + H_2 \quad (7)$$

$$C(S) + 2H_2O \rightarrow CO_2 + 2H_2 \quad (8)$$

$$2C(S) + 2H_2O \rightarrow CH_4 + CO_2 \quad (9)$$

$$(CS) + CO_2 \rightarrow 2CO \quad (10)$$

Carbon in the form of solid C(s) are char residues that are formed during the process. From the analysis done, as the steam-to-glycerol ratio increases, the amount of char produced decreases considerably.

When quartz is replaced with silicon carbide in the reaction (Table 4), the trend of the gas yield remains almost similar, whereby it increases the gas yield as the steam to glycerol ratio is increased except for a ratio of 10:90. The gas yield obtained for the ratio of steam to glycerol for Run 4 was lower than the gas yield for gasification of glycerol 100 wt% feed.

Gas yield for both packing materials is highest at steam to glycerol ratio of 50:50, which is 94 wt% for quartz particles and 89.5 wt% for silicon carbide. However, the char produced did not have a large variance for the process where silicon carbide is used as the packing material. From the table obtained, the char produced when quartz material is used is lower than that of silicon carbide at a 50:50 ratio of steam to glycerol, where the highest gas yield was achieved. For both packing. The addition of steam enhanced the decomposition reaction by heat transfer. This is due to the higher thermal conduction and uniform distribution of reactants.

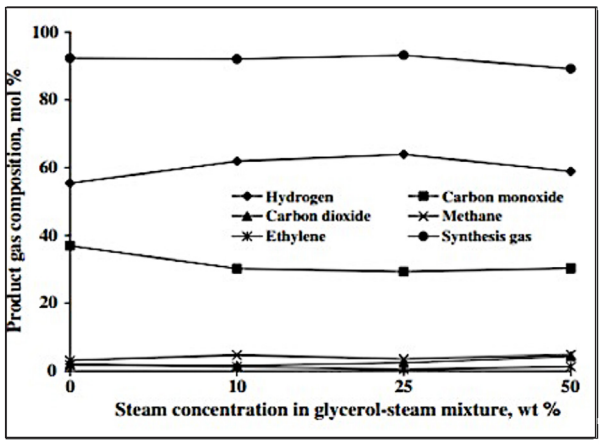

Figure 3 Result of component distribution against glycerol-steam ratio using quartz diameter 0.21-0.35 mm as packing material at 800°C

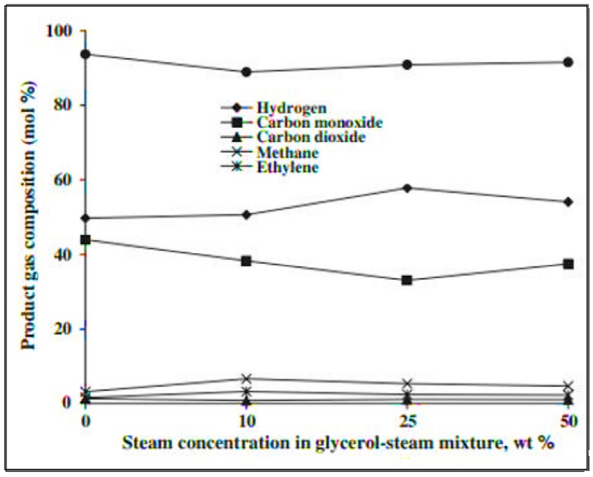

Figure 4 Result of component distribution against glycerol-steam ratio using silicon carbide diameter 0.15 mm as packing material at 800°C

The effects of increasing the amount of steam in the reaction with quartz and silicon carbide as the packing materials can be interpreted based on the obtained results (Figures 3 and 4). For H_2 produced, it can be seen as the amount of steam is being increased in the feed, the hydrogen produced increases, and the CO produced decreases. This situation is contradicted by the previous study [12], where hydrogen production decreased when the feedstock flow rate increased, most probably due to different types of catalysts applied. The reason H_2 increased is due to the water gas shift (WGS) reaction and reforming reactions of methane. A higher ratio of steam favours the WGS, hence increasing the H_2 yield. The CO yield decreases due to the partial utilisation of CO in the WGS reaction. The addition of steam did not influence the yield of syngas by a huge variance. However, the quality of syngas obtained was higher. This is because when the hydrogen yield is higher, the H_2/CO ratio increases. At a 50:50 ratio of steam and glycerol, a small decrease in H_2 yield is noticed. This indicates that the optimum steam-to-glycerol ratio for the steam gasification process will be at the ratio of 25% steam to 75% glycerol. Based on an earlier study by Haider and Chaturvedi [13], they reported lower hydrogen yield when increasing the glycerol flow rate and thus, their optimum molar ratio of water to glycerol was 2.33. For the packing material silicon carbide (Figure 4), on the other hand, a similar trend to the packing material quartz is observed. Therefore, similar justifications were applied for both packing materials. The volume of gas yield increases as the amount of steam ratio increases. This is because steam improves the uniform distribution of the reactant in the bed packing. This experiment shows that using quartz as the packing material increases the volume of the gas yield. This could be due to the difference in the porosity of the packing material. The porosity of the reactor bed was 44% for quartz and 49% for silicon carbide. For reaction with quartz as packing material, there were no significant changes in the calorific value. However, for the process with silicon carbide as the packing material, the calorific value increased from 13.5 to 15.4 MJ/m^3 and then decreased to 14.3 MJ/m^3 as the steam to glycerol ratio changes. This is due to the change in hydrocarbon production.

Therefore, parameters such as the ratio of steam to glycerol and the characteristics of the packing material, such as porosity and conductivity, influence the product yield during the reaction. The gas yield that is produced highest is at a 50:50 ratio for steam to glycerol. However, the highest H_2 yield was obtained at the ratio of 25:75 of steam to glycerol. The gas yield was higher when quartz was used as the packing material. Therefore, quartz was selected to be used to study other parameters of the gasification process.

Steam Gasification of Crude Glycerol

The steam gasification of crude glycerol was carried out to be compared with the gasification of pure glycerol in terms of the composition of the product and hydrogen yield. The process was carried out 50:50 ratio of steam to glycerol at 800°C with the packing material quartz. The LHSV remained constant at 1.3 h^{-1} for all the experiments. The product distribution is tabulated as in Table 5.

Table 5 Product and component distribution of steam gasification of pure glycerol and crude glycerol at steam to glycerol ratio 50:50 at 800°C

	Glycerol	
	Pure	Crude
Gas (wt%)	94.0	91.1
Liquid (wt%)	0.0	0.0
Char (wt%)	6.9	8.9
Total gas (L/g)	1.76	1.57
Gas composition (mol%)		
H_2	54.1	59.1
CO	37.5	19.7
CO_2	1.1	6.0
CH_4	7.4	11.5
C_{2+}	4.7	3.7

Based on the obtained results obtained, the amount of gas product at the end of the reaction is higher for crude glycerol when compared to pure glycerol. There is no liquid yield in both reactions, where there is a small deviation in the char yield. However, the H_2 yield for the process with feed crude glycerol was higher than for

pure glycerol. This is due to the composition of crude glycerol. The presence of KOH in crude glycerol increases the selectivity of H_2. Char produced for the process with crude glycerol is higher due to the deposition of KOH at higher temperatures.

Catalytic Steam Gasification of Pure Glycerol and Crude Glycerol

Table 6 Product distribution of gasification of pure glycerol and crude glycerol in the presence of catalyst Ni/Al_2O_3 at 0.2 g catalyst loading with steam to glycerol ratio 50:50 at 800°C

Yield (%)	Pure Glycerol		Crude Glycerol	
	Non-catalytic	Catalytic	Non-catalytic	Catalytic
Gas	89.5	89.6	91.1	92.2
Liquid	4.2	6.5	0	0
Char	6.2	3.9	8.9	7.8
Total gas (L/g)	1.7	2.4	1.6	2.3
Gas composition (mol%)				
H_2	54.1	68.2	59.1	67.7
CO	37.5	19.9	19.7	19.6
CO_2	1.1	7.4	6	5.8
CH_4	7.4	4.1	11.5	5.4
C_{2+}	4.7	0.5	3.7	1.4

Based on the results obtained, the gas yield and hydrogen yield have a significant increment with the presence of catalyst Ni/Al_2O_3. This is due to the small size of Ni-particles, higher dispersion, and catalytic surface area. The catalyst plays a pivotal role in determining the reaction pathway and component distribution of products formed. Catalyst Ni/Al_2O_3 assists the reaction in breaking of carbon bonds, improving the WGS reaction and increasing the H_2 yield due to its favourable selectivity towards H_2.

The total gas yield of the reactions without the catalyst was 89.5 % and 91.1% for pure glycerol and crude glycerol, respectively (Table 6). In the presence of a catalyst, higher conversion of steam to glycerol products is achieved. The gas yield obtained with the presence of a catalyst was 89.6% and 92.2% for pure glycerol and crude glycerol, respectively. As for the major product, H_2 yield, both reactions with the presence of a catalyst yielded a higher wt% of H_2 when compared to the reaction without the catalyst.

Table 7 Effect of catalyst loading on component distribution of steam gasification process

Catalyst Loading (g)	Gas Composition				
	H_2	CO	CO_2	CH_4	C_{2+}
0	55.4	36.9	1.9	3.1	1.9
0.2	64.1	21.2	6.9	5.9	1.7
0.4	67.8	22.5	6.5	2.9	0.8
0.6	67.4	20.2	7.7	3.9	0.7
0.8	68.3	22.2	6.4	2.4	0.72

The increase in catalyst loading led to a significant increment in the H_2 product yield (Table 7). This can be related to the kinetic theory; as the amount of catalyst is increased, the rate of reaction increases with the condition of sufficient active sites for reactions to take place. The presence of more catalysts provides a higher number of collision sites for the reaction to take place. From the results obtained, the highest yield of H_2 was obtained when catalyst loading was at 0.8 g, which was 67.8%.

Effect of Temperature on Steam Gasification Process

The effect of temperature on the yield of product was studied by carrying out the pyrolysis of the glycerol process from 650°C to 800°C [2]. The process was carried out with a carrier gas flow rate of N_2 at 50 mL/min and a glycerol flow rate of 5.4 g/hr.

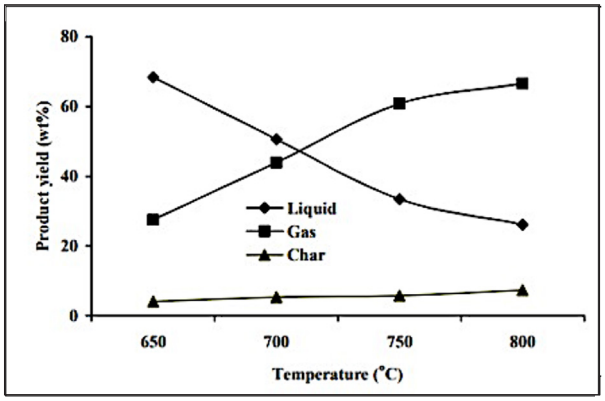

Figure 5 Results of product yield (%) against temperature

The influence of temperature on the yield of the product can be observed in Figure 5. The gas yield for the reaction increases consistently from 27.5 wt% to 66.7 wt% as the temperature is increased from 650°C to 800°C which is similar to a study by Maiceras et al. [12] where the hydrogen yield was the highest (55% purity) at high temperature (900°C). The liquid product yield decreased as temperature increased, whereas the char residues increased due to the increase in temperature. The increase in temperature enables higher efficiency of thermal cracking of the reactants such as methane and char.

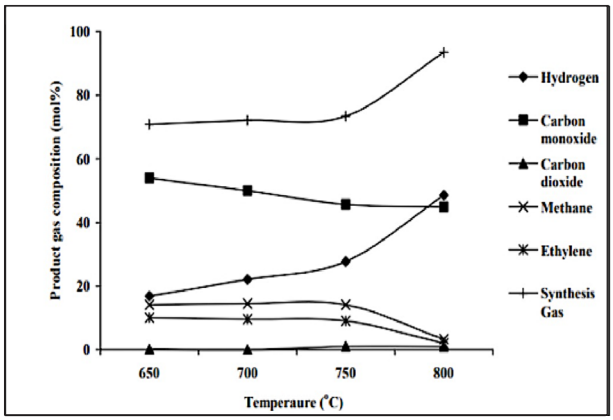

Figure 6 Results of product gas composition (mol%) against temperature (°C)

The influence of temperature on the composition of the final product is described in the results obtained. Hydrogen yield increases as the temperature of the reaction increases from 650°C to 800°C. Hydrogen yield is at its peak when the temperature of the reaction is at 800°C. The trend of carbon dioxide and syngas from the results states the gas obtained has a higher H_2/CO ratio, which means that the hydrogen gas produced is more than the CO gas. Meanwhile, the preceding analysis reported that 658°C was the optimum temperature for the highest hydrogen production, most probably due to different conditions in terms of the feedstock ratio [13]. Therefore, it can be concluded that the optimum temperature to obtain the maximum yield of H_2 would be more than 800°C.

Contributions

The optimum parameters to carry out the steam gasification process of glycerol to produce hydrogen gas were identified. First and foremost, the selection of the type of glycerol is very crucial. This is due to the cost of obtaining the feedstock. Pure glycerol, which has undergone a purification process, is proven to be more expensive when compared to crude glycerol. Besides that, the hydrogen gas yield from the reaction using pure glycerol is lower than that of crude glycerol. An investment in an expensive feedstock to obtain a less efficient product is not a feasible process. Therefore, the selection of the type of glycerol used plays a pivotal role in this process.

Next, the steam-to-glycerol ratio which influences the water gas shift reaction. Based on the studies done, it has been proven that the optimum steam-to-glycerol ratio should be set at 25:75. By doing so, maximum gas yield is obtained.

Packing material for the reactor greatly influences the reaction as well. Two different packing materials were studied in this research, which are silicon carbide and quartz. The difference in characteristics of packing materials, such as porosity and thermal conductivity, contributes to a variance in the gas yield in the process. Based on this study, the suitable packing material will be quartz. This is due to its lower porosity and higher thermal conductivity compared to silicon carbide.

The type of catalyst and the amount of catalyst loading play a pivotal role in the gasification reaction. Many studies have shown the advantages of nickel-based catalysts in gasification reactions to obtain hydrogen gas as the major product. This is due to the selectivity towards hydrogen and the ability to promote the water gas shift for reaction. Ni/AL_2O_3 had the best performance in the gasification process to produce hydrogen gas [6]. From the research, we can see as the catalyst loading is increases, the amount of hydrogen gas yield increases. Therefore, the proposed catalyst loading will be at 0.8 g.

Lastly, the influence of temperature on the product H_2 yield. Based on the study, we can conclude that the optimum temperature to carry out the steam gasification process should be higher than 800°C . This is because at high temperatures, the higher efficiency of thermal cracking of the reactants such as methane and char.

CONCLUSION

In this study, steam reforming of crude glycerol and pure glycerol was studied alongside parameters that influence the process and yield of product hydrogen. Based on the observation, it was clear that crude glycerol would be the suitable feedstock for hydrogen production when compared to pure glycerol. This is due to the impurities present in it, such as potassium hydroxide (KOH), that increase the selectivity of hydrogen. Besides that, the cost of purification of glycerol to obtain pure feedstock of glycerol would increase the cost of production despite providing a lower yield of the desired product. Optimum parameters to carry out the steam gasification process are identified. Steam to glycerol ratio of 25:75, increased catalyst loading to obtain maximum yield of hydrogen, and the temperature of process at a range of >800°C to ensure char and tar decompose. The objectives of the research were achieved.

Several recommendations can be suggested to improve the efficiency of the steam gasification process. Firstly, using nickel supported on alumina would be the recommended catalyst for producing hydrogen-rich gas. Next, the char yield can be reduced by using a fluidised bed reactor. A fluidised bed reactor would help in uniform heat transfer and increase the gas yield. Besides that, the cost estimation to carry out the process with pure and crude glycerol should be carried out to determine the feasibility of the process economically. Lastly, the process should be carried out at higher than 800°C to determine the potential for higher H_2 yield.

ACKNOWLEDGEMENT

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REFERENCES

[1] R. Zhang, G. Guo, Y. Gao, L. Wang, N. Zhang, and J. Cai, "Compared study on the bentonite supported nickel-based catalysts materials," *Mater. Lett*., vol. 113, pp. 146–148, 2013, doi: 10.1016/j.matlet.2013.09.019.

[2] T. Valliyappan, N. N. Bakhshi, and A. K. Dalai, "Pyrolysis of glycerol for the production of hydrogen or syngas," *Bioresour. Technol*., vol. 99, no. 10, pp. 4476–4483, 2008, doi: 10.1016/j.biortech.2007.08.069.

[3] B. V. Ayodele, T. A. R. B. T. Abdullah, M. A. Alsaffar, S. I. Mustapa, and S. F. Salleh, "Recent advances in renewable hydrogen production by thermo-catalytic conversion of biomass-derived glycerol: Overview of prospects and challenges," *Int. J. Hydrogen Energy*, vol. 45, no. 36, pp. 18160–18185, 2020, doi: 10.1016/j.ijhydene.2019.08.002.

[4] A. Tamošiūnas, P. Valatkevičius, D. Gimžauskaitė, V. Valinčius, and M. Jeguirim, "Glycerol steam reforming for hydrogen and

synthesis gas production," *Int. J. Hydrogen Energy,* vol. 42, no. 17, pp. 12896–12904, 2017, doi: 10.1016/j.ijhydene.2016.12.071.

[5] J. Iyyappan, G. Baskar, B. Bharathiraja, and R. Saravanathamizhan, "Malic acid production from biodiesel derived crude glycerol using morphologically controlled Aspergillus niger in batch fermentation," *Bioresour. Technol*., vol. 269, pp. 393–399, 2018, doi: 10.1016/j.biortech.2018.09.002.

[6] N. A. Roslan, S. Z. Abidin, A. Ideris, and D.-V. N. Vo, "A review on glycerol reforming processes over Ni-based catalyst for hydrogen and syngas productions," *Int. J. Hydrogen Energy*, vol. 45, no. 36, pp. 18466–18489, 2020. doi: 10.1016/j.ijhydene.2019.08.211.

[7] J. Chen, S. Yan, X. Zhang, R. D. Tyagi, R. Y. Surampalli, and J. R. Valéro, "Chemical and biological conversion of crude glycerol derived from waste cooking oil to biodiesel," *Waste Manag*., vol. 71, pp. 164–175, 2018, doi: 10.1016/j.wasman.2017.10.044.

[8] L. R. Kumar, S. K. Yellapu, R. D. Tyagi, and X. Zhang, "A review on variation in crude glycerol composition, bio-valorisation of crude and purified glycerol as carbon source for lipid production," *Bioresour. Technol*., vol. 293, p. 122155, 2019, doi: 10.1016/j.biortech.2019.122155.

[10] N. H. Zamzuri, R. Mat, N. A. Saidina Amin, and A. Talebian-Kiakalaieh, "Hydrogen production from catalytic steam reforming of glycerol over various supported nickel catalysts," *Int. J. Hydrogen Energy*, vol. 42, no. 14, pp. 9087–9098, 2017, doi: 10.1016/j.ijhydene.2016.05.084.

[11] S. J. Yoon, Y. M. Yun, M. W. Seo, Y. K. Kim, H. W. Ra, and J.-G. Lee, "Hydrogen and syngas production from glycerol through microwave plasma gasification," *Int. J. Hydrogen Energy*, vol. 38, no. 34, pp. 14559–14567, 2013, doi: 10.1016/j.ijhydene.2013.09.001.

[12] R. Maceiras, J. Feijoo, V. Alfonsín, L. Pérez, M. A. Álvarez-Feijoo, P. Falcón, and J. P. Vallejo, "Influence of alumina fixed-bed in steam reforming of glycerol for hydrogen production," *Energy Reports*, vol. 9, pp. 309–315, 2023, doi: 10.1016/j.egyr.2023.08.092.

[13] M. A. Haider and N. D. Chaturvedi, "An energy-efficient and cleaner production of hydrogen by steam reforming of glycerol using Aspen Plus," *Int. J. Hydrogen Energy*, 2023, doi: 10.1016/j.ijhydene.2023.09.089.