Hydrogen or Syn Gas Production from Glycerol Using Pyrolysis and Steam Gasification Processes

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ABSTRACT

Glycerol is a waste by-product obtained during the production of biodiesel. Biodiesel is one of the alternative fuels used to meet our energy requirements and also carbon dioxide emission is much lesser when compared to regular diesel fuel. Biodiesel and glycerol are produced from the transesterification of vegetable oils and fats with alcohol in the presence of a catalyst. About 10 wt% of vegetable oil is converted into glycerol during the transesterification process. An increase in biodiesel production would decrease the world market price of glycerol. The objective of this work is to produce value added products such as hydrogen or syn gas and medium heating value gas from waste glycerol using pyrolysis and steam gasification processes.

Pyrolysis and steam gasification of glycerol reactions was carried out in an Inconel®, tubular, fixed bed down-flow reactor at atmospheric pressure. The effects of carrier gas flow rate (30mL/min-70mL/min), temperature (650°C-800°C) and different particle diameter of different packing material (quartz - 0.21-0.35mm to 3-4mm; silicon carbide – 0.15 to 1mm; Ottawa sand – 0.21-0.35mm to 1.0-1.15mm) on the product yield, product gas volume, composition and calorific value were studied for the pyrolysis reactions. An increase in carrier gas flow rate did not have a significant effect on syn gas production at 800°C with quartz chips diameter of 3-4mm. However, total gas yield increased from 65 to 72wt% and liquid yield decreased from 30.7 to 19.3wt% when carrier gas flow rate decreased from 70 to 30mL/min. An increase in reaction temperature, increased the gas product yield from 27.5 to 68wt% and hydrogen yield from 17 to 48.6mol%. Also, syn gas production increased from 70 to 93 mol%. A change in particle size of the packing material had a significant increase in the gas yield and hydrogen gas composition. Therefore, pyrolysis reaction at 800^{o}C, 50mL/min of nitrogen and quartz particle diameter of 0.21-0.35mm were optimum reaction parameter values that maximise the gas product yield (71wt%), hydrogen yield (55.4mol%), syn gas yield (93mol%) and volume of product gas (1.32L/g of glycerol). The net energy recovered at this condition was 111.18 kJ/mol of glycerol fed. However, the maximum heating value of product gas (21.35 MJ/m^{3}) was obtained at 650^{o}C, 50mL/min of nitrogen and with a quartz packing with particle diameter of 3-4mm.

The steam gasification of glycerol was carried out at 800^{o}C, with two different packing materials (0.21-0.35mm diameter of quartz and 0.15mm of silicon carbide) by changing the steam to glycerol weight ratio from 0:100 to 50:50. The addition of steam to glycerol increased the hydrogen yield from 55.4 to 64mol% and volume of the product gas from 1.32L/g for pyrolysis to 1.71L/g of glycerol. When a steam to glycerol weight ratio of 50:50 used for the gasification reaction, the glycerol was completely converted to gas and char. Optimum conditions to maximize the volume of the product gas (1.71L/g), gas yield of 94wt% and hydrogen yield of 58mol% were 800^{o}C, 0.21-0.35mm diameter of quartz as a packing material and steam to glycerol weight ratio of 50:50. Syn gas yield and calorific value of the product gas at this condition was 92mol% and 13.5MJ/m^{3}, respectively. The net energy recovered at this condition was 117.19 kJ/mol of glycerol fed.

The steam gasification of crude glycerol was carried out at 800^{o}C, quartz size of 0.21-0.35mm as a packing material over the range of steam to crude glycerol weight ratio from 7.5:92.5 to 50:50. Gasification reaction with steam to glycerol weight ratio of 50:50 was the optimum condition to produce high yield of product gas (91.1wt%), volume of gas (1.57L/g of glycerol and methanol), hydrogen (59.1mol%) and syn gas (79.1mol%). However, the calorific value of the product gas did not change significantly by increasing the steam to glycerol weight ratio.

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Last but not the least, thanks to my parents, grand parents, aunty and sisters for their enthusiastic support which encouraged me throughout my academic pursuits.

DEDICATION

This work is dedicated to

My Parents, Grand parents

and

Periamma

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NOMENCLATURE

GHSV	Gas hourly space velocity, h^{-1}
ΔH_f	Heat of formation, kJ/mol
ΔH_r	Heat of reaction, kJ/mol
ΔH_{vap}	Heat of vaporization, kJ/mol
Q	Enthalpy, kJ

1. INTRODUCTION

Fossil fuel is one of the major energy resources being widely used to meet our energy requirements. This resource is depleting fast and also, many consider that it is the major source of global warming (Wigley, 1991 and Hoel and Kverndokk, 1996). Various alternative fuels such as hydrogen, ethanol and biodiesel (eg: methyl esters) are being exploited/used currently to sustain the energy requirement.

Biodiesel has become an attractive alternative fuel because of environmental benefits such as lower emission of carbon monoxide and carbon dioxide compared to regular diesel (National Biodiesel Board, 2004). Biodiesel has been produced from vegetable sources (soybean, sunflower, canola, cotton seed, rapeseed and palm oil) and animal fats. There are four ways to make biodiesel; direct use and blending, micro emulsions, thermal cracking (pyrolysis) and transesterification (Ma and Hanna, 1999). Transesterification is the reaction of fat or vegetable oil with an alcohol to form biodiesel (esters) and glycerol using a catalyst (Sridharan and Mathai., 1974; Boocock et al., 1995; Fillieres et al., 1995; Dalai et al., 2000; Demibras, 2002; and Shah et al., 2003). For example, in the transesterification of rapeseed oil using ethanol (Peterson et al., 1996), 10wt% of glycerol is produced as by-product.

Different feedstocks such as soybean, corn, trap grease and inedible tallow are available in the world market to produce 5.8 billion litres of biodiesel (Tyson, 2003).

When biodiesel is produced in large quantity, it is important to find useful applications for the resulting large quantity of glycerol in the world market. Tyson (2003) reported that glycerol markets are limited; an increase in biodiesel production may cause glycerol prices to decline from $1/L to $0.7/L by 2010. The money invested in purifying the glycerol would also be high (Prakash, 1998). Also, Tyson, 2003 reported that net biodiesel production costs can be reduced from US$0.63/litre of B100 to US$0.38/litre of B100 by adding value to the glycerol by-product. The main objective of this research was to identify the possible ways to convert the crude glycerol into value added products.

Glycerol is a potential feedstock, for hydrogen production because one mole of glycerol can produce up to four moles of hydrogen. Hydrogen (H_2) is mostly used in refinery hydrotreating operations, ammonia production and fuel cells (Rapagna et al., 1998). When glycerol is cracked at high temperature to produce hydrogen, it is possible to get carbon monoxide as one of the gaseous products. Formation of syn gas (H_2+CO) in the ratio of H_2/CO equal to 2:1 could be used as a feedstock in Fischer Tropsch synthesis to produce long chain hydrocarbon ($-CH_2-$; green diesel) (Chaudhari et al., 2001 and Steynberg and Nel, 2004). Gases which are produced from thermal cracking of glycerol would have medium heating value and can be used as a fuel gas. Therefore, it was proposed to produce value added products such as hydrogen or syn gas and medium heating value gases from glycerol using fixed bed reactor without a catalyst.

Non-catalytic processes such as pyrolysis and steam gasification are technologies that can produce value-added products such as hydrogen and syn gas from glycerol. Pyrolysis is the high temperature thermal cracking process of organic liquids or solids in the absence of oxygen (Cutler and Antal 1987). Steam gasification produces gaseous fuel with higher hydrogen content than the pyrolytic process in the presence of oxygen and it reduces the diluting effect of nitrogen, used as a carrier gas in the pyrolysis, in the produced gas (Franco et al., 2002).

1.1 KNOWLEDGE GAP

Literature are available on converting glycerol into hydrogen rich gas using catalytic process (Xu et al., 1996, Czernik et al., 2000 and Cortright et al., 2002). However, literature based on converting glycerol into value added products such as hydrogen or syn gas using pyrolysis and steam gasification are very less. No systematic studies have been carried out on the effects of process parameters such as carrier gas flow, temperature, particle diameter of packing material and steam to glycerol weight ratio. Process conditions are needed to be optimized to maximize the production of hydrogen or syn gas and volume of the product gas. A comprehensive method should be developed for converting crude glycerol into hydrogen or syn gas.

1.2 OBJECTIVES

The objective of this research is to carry out a detailed study on pyrolysis and steam gasification of glycerol. In this investigation, process conditions will be optimized by the studying the effects of carrier gas flow rate, temperature, particle size of the packing material and steam to glycerol weight ratio on product yield, gas composition, volume and calorific value of the product gas. The specific objectives of this research are described in the following sections.

1.2.1 Pyrolysis of glycerol

Preliminary studies on pyrolysis of glycerol showed that at 700^{o}C with the carrier gas flow rate of 50mL/min in a packed bed reactor would produce 70mol% of syn gas. Therefore, process conditions will be studied over the ranges of those values. The pyrolysis of glycerol will be carried to the study the effects of carrier gas glow rate, over the range of 30mL/min to 70mL/min and temperature, over the range of 650^{o}C to 800^{o}C. Optimum carrier gas flow rate and temperatures will be chosen based on the maximum yield of gas and syn gas composition. Optimum temperature and carrier gas flow rate selected from these studies will be used to investigate the effects of particle size of the packing material.

1.2.2 Steam gasification of glycerol

A suitable temperature and particle size will be selected to study the steam gasification of glycerol by varying the weight ratio of steam to glycerol from 0:100 to 50:50. The effects of steam to glycerol weight ratio on product yield, volume of product and product gas composition will be studied. The optimal weight ratio of steam to glycerol will be chosen to study the gasification of crude glycerol.

1.2.3 Steam gasification of crude glycerol

A sample will be obtained from Agriculture and Agri-Food Canada and will be analyzed to determine the composition of crude glycerol. Steam gasification studies will be carried out on the crude glycerol and synthetic mixtures of glycerol having similar composition of crude glycerol sample.

2. LITERATURE REVIEW

Limited literature is available regarding the two possible processes, pyrolysis and steam gasification, used to convert glycerol into hydrogen and other value-added products. Literature based on these processes is discussed below. Catalytic conversion of glycerol into hydrogen is also discussed in this chapter. The potential feedstock to produce biodiesel and glycerol is also discussed. Glycerol can also be used in various applications such as tooth paste, cosmetics and food (Claude, 1999). These applications require that the glycerol has a purity of at least 99.5% (wt/wt). Claude (1999) reported that glycerol can be a potential feedstock for the production of 1,3-propanediol, polyglycerols and polyurethanes. However, glycerol is one of the potential feedstock to produce hydrogen.

2.1 FEEDSTOCK POTENTIAL IN CANADA

Prakash (1998) reported that the production of canola and soy oils in 1996 in Canada was 1,153 million tonnes and 166,000 tonnes, respectively. He assumed that 10wt% of canola and soy oil could be used for the production of biodiesel. That would result in 277 million litres of biodiesel per year. He also reported that 108 million litres of biodiesel could be obtained from tall oil (a by-product from the treatment of pine pulp). This adds up to a total biodiesel production to 385 million litres per year. This would lead to the production of 38.5 million litres of glycerol per year in the Canadian glycerol market.

The federal government of Canada has planned to produce 500 million litres of biodiesel per year by the year 2010 to meet the Kyoto protocol (Smith, 2004). With 10wt% production of glycerol, this would lead to 55.4 million litres of glycerol/year in the Canadian market. Xu et al. (1996) reported that increasing demand for biodiesel may create a glut of glycerol, which could become available as a feedstock at low or negative cost. To improve the economics biodiesel production and also to improve the glycerol market, it is important to process glycerol into value-added products. The viable processes to convert glycerol into value added products, such as hydrogen or syn gas, are pyrolysis, steam gasification and catalytic steam reforming.

2.2 PROCESSES TO PRODUCE HYDROGEN OR SYN GAS FROM GLYCEROL

Literature on pyrolysis and steam gasification of glycerol with different process conditions such as temperature and steam to glycerol ratio are discussed in this section. Also, catalytic conversion of glycerol into value-added chemicals using different catalyst such nickel, platinum, HZSM-5 and Y-Zeolite are discussed in this section.

2.2.1 Pyrolysis and Gasification of Glycerol

The pyrolysis process yields liquid fuels at low temperatures (400 to 600^{o}C) and gaseous products at high temperatures (>750^{o}C). Gasification is a process related to pyrolysis, but the major difference between is that gasification achieved in the presence of oxygen, in the form of air, pure oxygen or steam.

Value added products such as hydrogen or syn gas is produced from pyrolysis of glycerol in a fixed bed reactor (Chaudhari and Bakhshi, 2002). The pyrolysis of glycerol was carried out in two ways; pyrolysis with and without any carrier gas (nitrogen). Chaudhari and Bakhshi (2002) carried out the pyrolysis of glycerol at 400^{o}C and 500^{o}C with a glycerol flow rate of approximately 2.0g/h. They reported that the operation was quite difficult without using a carrier gas because of char formation in the feed inlet.

Chaudhari and Bakhshi (2002) carried out the pyrolysis of glycerol with a nitrogen flow rate of 50ml/min, a glycerol flow rate from 2.2 to 4g/h and over the temperature range of 350 to 700^{o}C in a packed bed reactor. They found that the complete conversion of glycerol occurred at 700^{o}C. They reported that a gas yield of 50wt% was obtained but there was no liquid product. The residue was 6.3wt% and the remaining weight percent was char. The gaseous product essentially consisted of syn gas (H_2/CO ratio: 1.77).

They also carried out steam gasification of glycerol with steam flow rate of 2.5g/h, 5g/h and 10g/h at 600°C and 700^{o}C and glycerol flow rate of 4g/h. They reported that ~80wt% of glycerol was converted when steam flow rate of 10g/h at 700^{o}C was used and producing 92.3mol% syn gas mixture of approximately H_2/CO ratio of 2. Gaseous product was around 70wt%. They reported that syn gas can be further converted to hydrogen by water-gas shift reaction and can be used as a fuel for fuel cells. Also, syn gas could be converted to green diesel using the Fischer-Tropsch reaction.

Steam gasification of glycerol was studied in a laminar flow reactor in gas phase, homogenous reaction (Stein and Antal, 1983). The main objective of the study was to produce the liquid product. Stein and Antal (1983) carried out experiments at 650-700°C with residence time of 0.1s and steam flow rate of 1g/min. Products of the gasification of glycerol using steam at 650°C and 1 atm were acrolein and acetaldehyde with yields of 52mol % and 48mol %, respectively. For a shorter residence time (i.e., 0.1s) and lower temperatures, acrolein and acetaldehyde were primary liquid products. As the temperature increased from 650 to 700°C, syn gas of 76.4mol% at 700°C (mixture of carbon monoxide 43.5mol% and hydrogen 32.9mol%) was the major gaseous product.

Carbon-catalyzed gasification of organic feedstocks was conducted using supercritical water by Xu et al. (1996). The organic feed stocks were glycerol, glucose, cellobiose, whole biomass feedstocks (bagasse liquid extract and sewage sludge) and wastes from the United State's Department of Defence. They used different carbon catalysts such as spruce wood charcoal, macadamia shell charcoal, coal activated carbon, and coconut shell activated carbon. They studied effects of temperature (500-600°C), pressure (251 atm - 340 atm), weight hourly space velocity (14.6 h^{-1}-22.2 h^{-1}) and the type of catalyst used for gasification. They carried out gasification of glycerol (2.0M) with supercritical water at 600°C, a pressure of 340atm, with and without coconut shell activated carbon catalyst in a supercritical reactor. They reported that glycerol was easily and completely gasified to a 54.3mol% hydrogen-rich gas in supercritical water without a catalyst. The presence of a catalyst had little effect on the gas composition. They found that a low yield of 2mol% of CO and high yield of 54.3mol% H_2 in these experiments. This result was in contrast to that of Stein and Antal, (1982). According to Xu et al. (1996), supercritical reaction might have different gasification chemistry than that of observed at atmospheric pressure, because, at high pressure reaction condition, ionic reaction pathway dominates.

2.2.2 Catalytic Treatment of Glycerol

Catalytic steam reforming of organic compounds is one of the processes used to produce hydrogen. Catalyst is mainly used to increase the reaction rate and to increase the selectivity of hydrogen. Steam reforming reactions of any oxygenated organic compounds such as glycerol and acetaldehdye proceeds according to the following equation 2.1 (Czernik et al., 2002):

$$C_nH_mO_k + (n-k)\ H_2O \rightarrow nCO + [(n+m/2-k)]\ H_2 \qquad (2.1)$$

Because of the excess steam used in the process, carbon monoxide further undergoes the water gas shift reaction to produce CO_2 and H_2. Research has been also carried out to produce hydrogen from biomass-derived oxygenated compounds such as methanol, glycerol and ethylene glycol using catalytic aqueous phase reforming reactions (Davda et al., 2003).

Czernik et al. (2000) carried out catalytic steam reforming of bio oil derived fractions and crude glycerine (a by-product from transesterification of vegetable oil with methanol) using a fluidized bed reactor to produce hydrogen. In experiments, 150g - 200g of a commercial nickel based catalyst was used. Catalyst was fluidized by the superheated steam. They reported that crude glycerine was a very viscous liquid and partially miscible with water. The temperature of crude glycerine was maintained at 60-80°C because of its high viscosity. They suggested that at a lower viscosity, it was easier to pump and atomize. The glycerol was fed at the rate of 78g/h, GHSV = 1600 h^{-1} and steam at a rate of 145 g/h. Therefore, the steam to carbon ratio was 2.3. Concentration of major gaseous product was found to be constant but, there was an increase in methane production from 500 parts per million (ppm) to 2200ppm when the run time increased from 0 min to 250 min. The hydrogen yield was around 77wt%. They suggested that a higher yield of hydrogen would be possible if a higher amount of steam was used in the process. Conversion of carbon monoxide in the gas through water-gas shift to CO_2 and H_2 would increase the yield to 95 wt %. These results showed that a commercial value by-product from bio-diesel production could become a viable renewable material for producing hydrogen. They suggested that integration of the water-gas shift reaction and fluidized bed technologies would enhance the production of hydrogen and make it economically feasible.

Sugar-containing hydrolysates and glycerol-containing liquors derived from residual fats can also be potential feedstock for the production of hydrogen (Chornet and Czernik, 2002). Chronet and Czernik, (2002) suggested that feedstocks should preferably be obtained from high-productivity biomass crops (for example, jatropha plant can grow even in dry land); with little or no use of synthetic fertilizers (fertilizers could act as a catalyst in the process). They suggested that the steam reforming of biomass derived oxydegenated hydrocarbon such as glycerol, sorbitol and ethylene glycol using nickel based steam reforming catalyst could maximize the production of hydrogen. They also suggested that the robustness of a nickel based catalyst guarantee this operation over thousands of hours.

Cortright et al. (2002) carried out aqueous-phase reforming of sugars and alcohols using a fixed-bed reactor at temperatures near 265^{o}C and 225^{o}C to produce hydrogen. They used platinum catalyst supported on nanofibres of γ-alumina. Alcohols such as glycerol, sorbitol, methanol and ethylene glycol were used in this study. They suggested that the reforming of more immediately available compounds such as glucose is likely to be more practical. Higher hydrogen yields were obtained using sorbitol, glycerol and ethylene glycol as a feed molecule for aqueous-phase reforming than the hydrogen yield from glucose. The hydrogen yield from glycerol reforming was 64.8mol% and 57mol% at 225^{o}C and 265^{o}C, respectively. They found that gaseous streams from aqueous phase reforming of the oxygenated hydrocarbons contained low levels of carbon monoxide (<300 ppm). Liquid products from the reactions essentially consisted of ethanol, 1,2-propanediol, ethanol, 1-propanol, acetic acid, ethylene glycol, acetaldehyde, 2 propanol, propionic acid, acetone, propionaldehyde and lactic acid.

Chaudhari and Bakhshi (2002) studied catalytic conversion of glycerol with 3 different catalysts such as HZSM-5, γ - alumina and Y – zeolite. The experiments were carried out at 400, 450 and 475^{o}C with nitrogen flow rate of 50ml/min, glycerol flow rate of 2.1-2.3 g/h/g of catalyst and catalyst loading of 1g. In this case, glycerol was completely converted to H_2, CO, CO_2, acrolein and acetaldehyde etc. Reactions using HZSM-5 catalysts produced 53-61wt % of liquid product consisting of acetaldehyde and acrolein. As a result, gaseous product (~9wt%) yield was very low in which hydrogen concentration was around 57-64mol%.

Reactions using γ-alumina produced 52-68 wt % of liquid product, essentially consisting of acrolein and acetaldehyde. Gas yield was low (5-10 wt %). Unreacted glycerol (11wt%) was more when they used γ-alumina as a catalyst when compared to the liquid yield of 0.3wt% using HZSM-5 catalyst. Reactions using Y-zeolite produced similar results to the reactions using γ-alumina as a catalyst. However, γ-alumina and Y-zeolite performed poorly when compared to HZSM-5 catalyst.

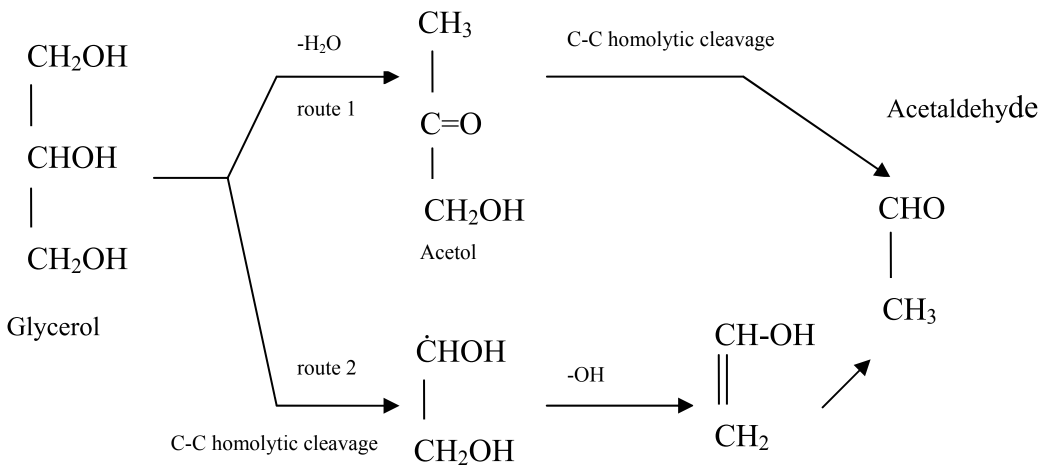
Thus, the literature review based on the three possible processes including pyrolysis, steam gasification and catalytic steam reforming studies shows that there is a potential for producing value added products from waste glycerol, obtained from biodiesel production. Very few researchers are working in the chemistry of gasification of glycerol. In the following section, the literature is reviewed regarding on the chemistry of glycerol gasification.

2.3 CHEMISTRY OF GASIFICATION OF GLYCEROL

The thermal cracking of oxygenated organic compounds, such as glycerol and acetaldehyde pyrolysis products, has complex chemistry (Wang et al., 1996). Large numbers of primary and secondary pyrolysis products are generated through many different pathways. Wang et al. (1996) reported that partial thermal cracking of oxygenated hydrocarbons would produce hydrogen, carbon monoxide, carbon dioxide, methane and coke by primary decomposition reaction as represented in the equation 2.2.

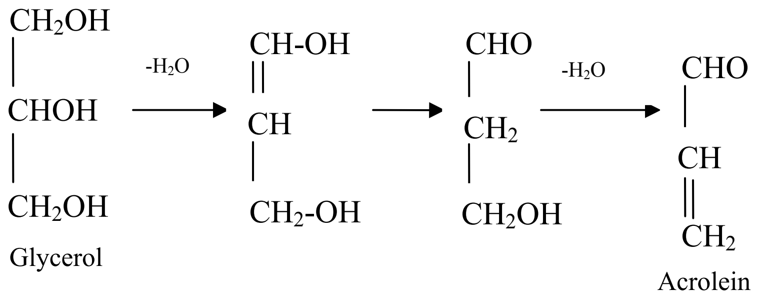
$$C_mH_nO_k \rightarrow C_xH_yO_z + \text{gas } (H_2, CO, CO_2, CH_4, \ldots) + \text{coke} \qquad (2.2)$$

Glycerol decomposes when heated in supercritical water at 500°C and 340 atm to acetaldehyde, acrolein and gaseous mixture consisting of H_2, CO, CO_2, CH_4, C_2H_4 and C_2H_6 (Antal et al., 1985). Antal et al. (1985) reported that the two possible pathways for the formation of acetaldehyde (C_2) from glycerol (C_3) are initial dehydration and homolytic cleavage of the C-C bond (C-C bond breaks without charge) as shown in the equation 2.3. Their result supported that the homolytic cleavage of the C-C bond (route 2) is responsible for the formation of acetaldehyde.



(2.3)

Antal et al. (1985) reported that acrolein could have formed from glycerol via dehydration as shown in the equation 2.4.



(2.4)

The main products from decomposition of glycerol in near and supercritical water were methanol, acetaldehyde, propionaldehyde, acrolein, allyl alcohol, ethanol, formaldehyde, carbon monoxide, carbon dioxide and hydrogen (Buhler et al., 2002). Buhler et al. (2002) reported that free radical reaction pathway dominates at lower pressures and/or higher temperatures. The formation of gaseous products is favourable at high temperatures and they follow radical reaction pathway.

From the literature review, it is clear that glycerol, a by-product from production of biodiesel process, has an ability to produce value added products using three possible processes namely pyrolysis, steam gasification and catalytic steam reforming. The results obtained by Chaudhari and Bakhshi, (2002) showed that there is no liquid product in pyrolysis of glycerol process at 700°C. This result was in contrast with those obtained by Stein and Antal (1983) who reported that pyrolysis process produced liquid products consisting of acrolein and acetaldehyde. Also, the results from Chaudhari and Bakhshi (2002) and Stein and Antal (1983) indicated that glycerol pyrolysis and steam gasification could lead to high quality hydrogen production. Thus, pyrolysis and steam gasification of glycerol processes should be revisited to understand the chemistry of the reactions and process parameters such as temperature, carrier gas flow rate and packing material. In addition, steam to glycerol weight ratio should be tuned to maximise the yield of hydrogen or syn gas. Therefore, it was proposed that detailed pyrolysis and steam gasification studies would be carried out for both pure glycerol and crude glycerol to produce value-added products.

3. EXPERIMENTAL

This chapter describes the design and construction of the experimental set up for the pyrolysis and steam gasification of glycerol. Procedures and experimental details of each phase of the research are described in this chapter. Techniques for the analysis of products from the experiments and analysis of crude glycerol are also described in this chapter.

3.1 EXPERIMENTAL SET UP

3.1.1 Droplet Size Distribution over the Bed Packing

A study on the distribution of droplets of the reactant over the bed packing was conducted with different nitrogen flow as shown in the Figure 3.1. This reactor configuration facilitates the gasification process because of formation of smaller droplets and enhances the heat transfer. Glycerol was pumped using an LDC analytical pump at the rate of 5.4 g/h and it flows from the top through a 1.58mm internal diameter pipe. Nitrogen was used as the carrier gas. Nitrogen and glycerol entered into the electric furnace maintained at approximately 300^{o}C. This temperature was similar to the temperature at the top of the reactor during pyrolysis and gasification experiments. The droplet distribution of the reactant was also studied for a water and glycerol mixture in the weight ratio of 50:50 in the absence of carrier gas flow. The wax paper was placed below the feed nozzle at a distance similar to the distance between the feed nozzle and the top surface of the reactor bed.

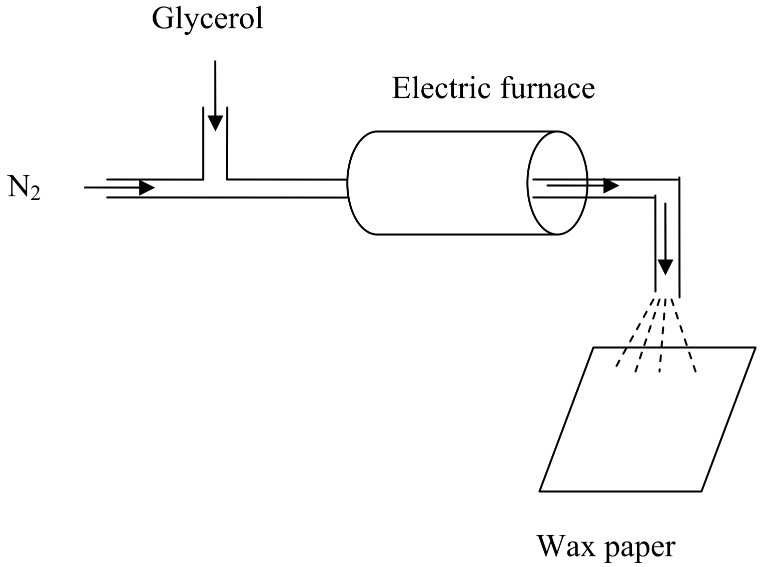


Figure 3.1: Set up for the spray studies

3.1.2 Experimental set up for the Pyrolysis and Gasification Processes

Pyrolysis and steam gasification of glycerol was carried out in a continuous down-flow fixed bed micro reactor at atmospheric pressure (see Figure 3.2). The Inconel® alloy reactor was 500mm long by 10.5mm internal diameter made of tube and was filled packing material. Quartz, silicon carbide and sand were used as packing material in order to have a plug flow and even distribution of the reactant inside the reactor. Packing material was held on a plug of quartz wool, which was placed on a supporting mesh at the center of reactor. Reactor packing height was 70 mm. The feed inlet tube was placed 40mm above the packed bed. Nozzle of the feed inlet facilitates the reactant to flow as smaller droplets because of the

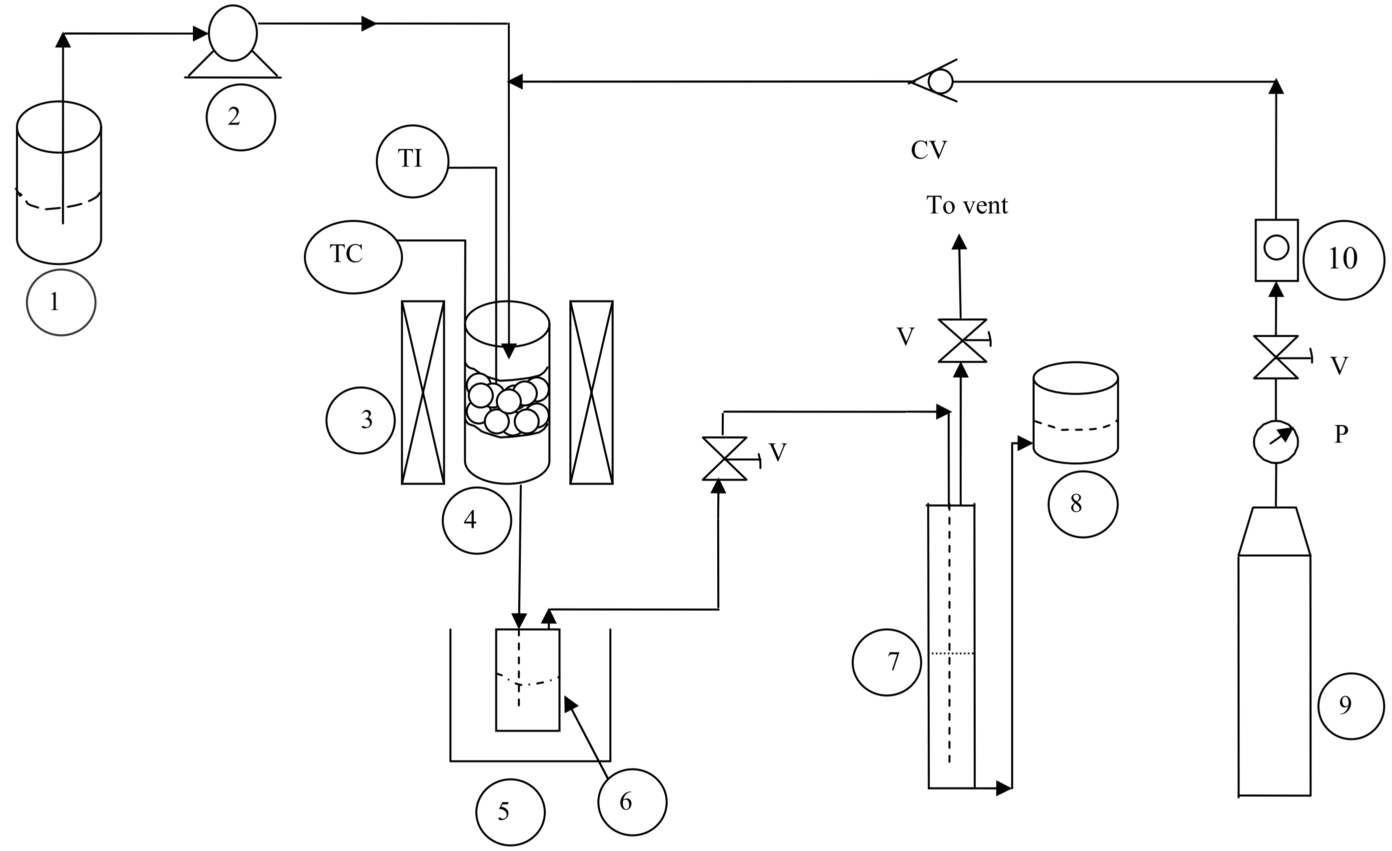


Figure 3.2 Experimental set up for pyrolysis of glycerol.
1.Reactant beaker 2.LDC Analytical pump 3.Electric furnace 4.Fixed bed reactor 5.Ice bath 6.Liquid collector 7.Gas collector 8.Brine solution 9.Nitrogen cylinder 10.Flow meter, V– Valve, P- Pressure regulator, CV- Check Valve, TC- Temperature controller and TI- Temperature indicator

carrier gas flow (nitrogen) and the temperature. Carrier gas was used to facilitate the uniform distribution of reactant in the reactor bed packing. The carrier gas flows downwards from the top of the reactor at a desired flow rate before the reactor was heated to a desired temperature (only for pyrolysis process). The flow rate of carrier gas was adjusted with a needle valve and was controlled using a mass flow meter (Sierra Instruments Inc, California, USA). Calibration of this mass flow meter was made using a calibrated bubble flow meter and was converted to the flow rates at standard temperature and pressure (STP) (see Appendix A1). Temperature was measured and controlled using a K-type thermocouple placed at the heating zone in the furnace and connected to temperature controller (Shimaden SR22, Tokyo, Japan). Another K-type thermocouple was placed inside the bed using a thermo well to measure the bed temperature. The temperature measured inside the reactor coincided with the operating temperature. The desired temperature of the reactor was reached in 45 to 75 min. Glycerol was pumped into the reactor using a LDC analytical pump (Rayonics Scientific Inc, Ontario, Canada) at the rate of 5.4 g/h. The LDC analytical pump was calibrated in the range of 2 g/h to 8g/h (see Appendix A2).

3.1.3 A typical run

The reactor was cleaned, dried, weighed with the packing material and mounted inside the furnace. Nitrogen was allowed to flow at the desired flow rate before the reactor attained the desired temperature. Glycerol was fed at 5.4 g/h at the desired reactor temperature 30 min. The product leaving the reactor was condensed and separated into liquid and gaseous fractions. The liquid product fraction was collected in a liquid trap, cooled with ice-salt bath and the gaseous product was collected over a saturated brine solution of sodium chloride. The flow of nitrogen was maintained for 2 min to flush the entire product inside the reactor after the reaction time of 30 min. The reactor was then cooled and weighed to determine the amount of char.

3.2 CRUDE GLYCEROL ANALYSIS

Crude glycerol was analyzed at the Saskatchewan Research Council (SRC). Methanol, water and potassium hydroxide were present in the crude glycerol. Methanol and glycerol were analysed using a HP (Hewlett Packard) 5890 gas chromatograph with an auto sampler and having a Flame Ionisation Detector (FID). The GC was equipped with the Nukol (15m, 0.53mm ID, 0.50 μm film thickness) fused silica capillary column. Helium was used as a carrier gas. Air and hydrogen were used to ignite the FID. The injector and detector temperature was 250^{o}C and 330^{o}C respectively. Two different programs were used to analyse the methanol and glycerol. The following GC program was used to analyze methanol: initial temperature at 30^{o}C, initial temperature hold time of 5 min, heating rate of 50^{o}C/min, final temperature at 190^{o}C and final temperature hold time of 0 min. The glycerol was analysed using the following GC program: initial temperature at 120^{o}C, initial temperature hold time of 4 min, heating rate of 8^{o}C/min, final temperature at 190^{o}C and final temperature hold time of 0 min. The potassium hydroxide was analysed using acid-base titration in which an accurately weighed sample was titrated with 0.1N hydrochloric acid using a phenolphthalein indicator until the pink color disappeared.

3.3 EXPERIMENTAL PROGRAM

Experiments were carried out in three major phases in this work and are listed below. Experiments under each phase are explained below.

1. Pyrolysis of pure glycerol
2. Steam gasification of pure glycerol
3. Gasification of crude glycerol and synthetic mixture

3.3.1 Pyrolysis of glycerol

3.3.1.1 Effects of carrier gas flow rate

Experiments in this section were carried out over the range of carrier gas flow rates of 30mL/min to 70mL/min at 800^{o}C, and with the quartz particle size of 3-4mm. By changing the carrier gas flow rate, effects of distribution of reactant inside the reactor and residence time of the reactant on the product yield, volume and composition of product gas were studied. The residence time was calculated on the basis of carrier gas flow and empty reactor volume (Appendix B1). The optimum carrier gas flow rate was chosen based on the maximum volume of the product gas, selectivity of synthesis gas produced and low char yield from these experiments. The optimum flow rate was used to the study of effects of temperature.

3.3.1.2 Effects of temperature

The main objective for changing the reaction temperature was to maximise the gas product yield, synthesis gas selectivity and volume of product gas. Experiments were carried out at the carrier flow rate of 50mL/min (chosen from the above studies) and over the temperature range between 650°C to 800°C. The optimum temperature of 800°C was chosen because glycerol was completely cracked and yielded high volume of gas.

3.3.1.3 Effects of particle size of packing material

The objective of changing particle size of the packing material (quartz, silicon carbide and sand) was to maximise the volume of the product gas and hydrogen production because of the porosity of the reactor bed and thermal conductivity of the packing material. The experiments were carried out at 800°C (optimum temperature), 50mL/min and over the different particle sizes of the packing material.

The broken quartz tube was collected from the catalysis and chemical reaction engineering laboratories and was crushed using pestle and mortal to make it into smaller particles. The particles were separated into the desired mesh size of -45+60mesh (0.21-0.35mm), -25+30mesh (0.60-0.71mm) and -5+7mesh (3.0-4.0mm) using different sieves.

Silicon carbide of different mesh size of 100 (0.15mm), 60 (0.21mm), 25 (0.71mm) and 16 (1mm) was procured from Exolon-Esk, Tonawanda, New York, USA. Ottawa sand was procured from U.S Silica, Ottawa, Illinois, USA of mesh size of -45+60 (0.21-0.35mm), -25+30 (0.60-0.71mm) and -8+16 (1.0-1.15mm).

3.3.2 Steam gasification of glycerol

Effects of steam on product yield, product gas composition and volume were studied in this section. An objective of this work was to minimize the char production, thereby increasing the selectivity of hydrogen, hydrogen to carbon monoxide ratio and volume of product gas. As water is soluble in the glycerol, it was added directly to glycerol so as to maintain water to glycerol weight ratio of 10:90, 25:75 and 50:50. Steam gasification of glycerol was carried out in the absence of carrier gas flow. The size of packing material of the reactor bed was chosen from the above studies which increase the volume of gas and synthesis gas production. Experiments were carried out at 800^{o}C and with the quartz particles of size 0.21-0.35mm. Also, steam gasification of glycerol was carried out with silicon carbide packing with the particle size of 0.15mm.

3.3.3 Gasification of crude glycerol

Experiments were carried out with crude glycerol and synthetic mixture of glycerol over the different steam to glycerol weight ratio at optimum temperature as obtained from studies on temperature effects, with the quartz packing. Experiments using synthetic mixture were carried out in the following steps. Initially, steam gasification of glycerol was carried out with steam to glycerol weight ratio of 50:50. Pyrolysis of pure methanol was carried out to study the effects of methanol in the synthetic mixture. Pyrolysis of methanol and glycerol was carried out in the weight ratio of 65:35. Water was added to the glycerol and methanol to study the effects of water in the weight ratio of 60:30:10 (glycerol:methanol:water). To study the effects of potassium hydroxide (KOH) which is the catalyst used in the transesterification of vegetable oil, was added to glycerol, methanol and water mixture in the weight ratio similar to that in crude glycerol. The objective of this study was to compare the effects of each component present in the crude sample and to maximise the product yield. Steam to crude glycerol ratios used in this study was 7.5:92.5, 25:75 and 50:50.

3.4 ANALYSIS OF PRODUCTS

The gas and liquid products from the experiments were analyzed using HP 5880), HP 5890 and Fison gas chromatograph 8000 series.

3.4.1 Product gas analysis

A HP 5890 gas chromatograph (GC) with the thermal conductivity detector (TCD) having Carbosive S II column (3 m, i.d. 3.18mm) was used to analyze H_2, CO and CO_2. Helium gas was used as a carrier gas. A 5890 GC was programmed using following conditions: initial temperature 40^oC, initial temperature hold time of one min, heating rate 12^oC/min, final temperature 200^oC, final temperature hold time of one min and detector temperature of 250^oC.

Hydrocarbons such as CH_4, C_2H_4, C_2H_6 and C_3+ were analyzed using a 5880 HP GC. A 5880 HP GC was equipped with the flame ionization detector (FID) having Chromsorb 102 Column (1.8 m, i.d. 3.18 mm). Helium gas was used as a carrier gas in a 5880 HP. Air and hydrogen was used to ignite the flame for FID. A 5890 GC was programmed using following conditions: initial temperature 40^oC, initial temperature hold time 3 min, heating rate 10^oC/min, final temperature 200^oC, final temperature hold time 2min and detector temperature of 250^oC. The GCs were calibrated using the standard gas mixtures (Appendix A3).

3.4.2 Liquid product analysis

Unknown compounds present in the organic liquid products obtained from pyrolysis and steam gasification were identified using a gas chromatograph VG-250-SE mass-spectrometer (GC-MS). The attached GC was a Fisons GC 8000 series, Model 8060, which was equipped with the stabilwax (cross bonded, 30 m long, i.d. 0.25mm) capillary column. The GC-MS was programmed using following conditions: initial temperature 40°C, initial temperature hold time 5 min, heating rate 5°C/min, final temperature 200°C, final temperature hold time 15min and the detector temperature was 250°C. Split ratio in the injector was 1:200 at 220°C. The peaks obtained in the GC-MS analysis were identified using the GC-MS component library. Also, water content of the liquid product was analysed using Karl-Fishcer titrator.

3.4.3 Typical product analysis

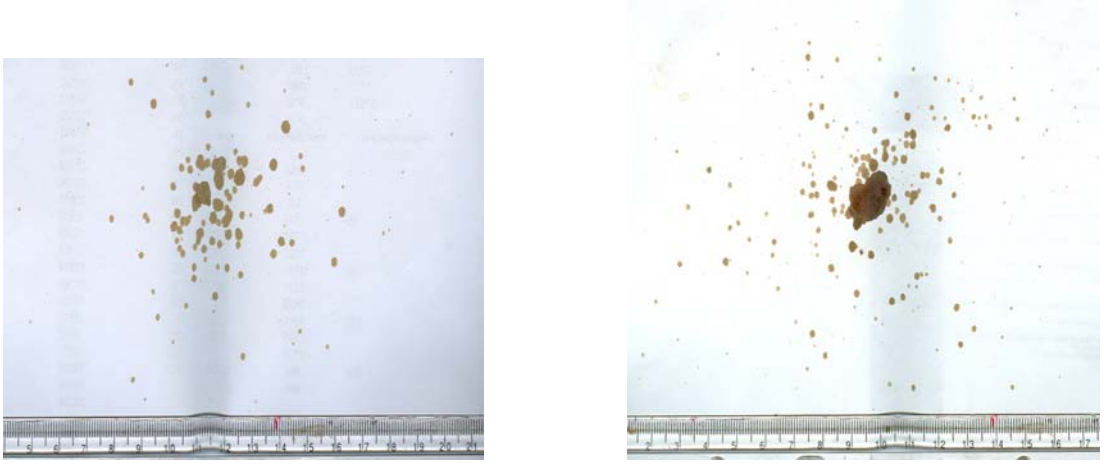
A gas sample of 500µL was injected into HP 5890 GC. It took approximately 15 min to detect the H_2, CO and CO_2. The oven was then allowed to cool down to the initial temperature of 40°C before injecting another sample. A gas sample of 300µL was injected to the FID of 5880 HP GC. The FID analysis took approximately 21 mins to elute all the gas components. During this time, all hydrocarbons including methane were analyzed. The peak area from GCs gave corresponding number of moles of each component present in the gas mixture at STP. The gas composition and volume of gas were calculated on nitrogen free basis.

4. RESULTS AND DISCUSSION

In this chapter, the effects process parameters such as carrier gas flow, temperature, and particle diameter of the packing materials (quartz, silicon carbide and sand) and steam to glycerol weight ratio on the yields of gas, liquid, char, and product gas composition are explained. Also, the droplet distribution of reactant over the reactor bed is discussed.

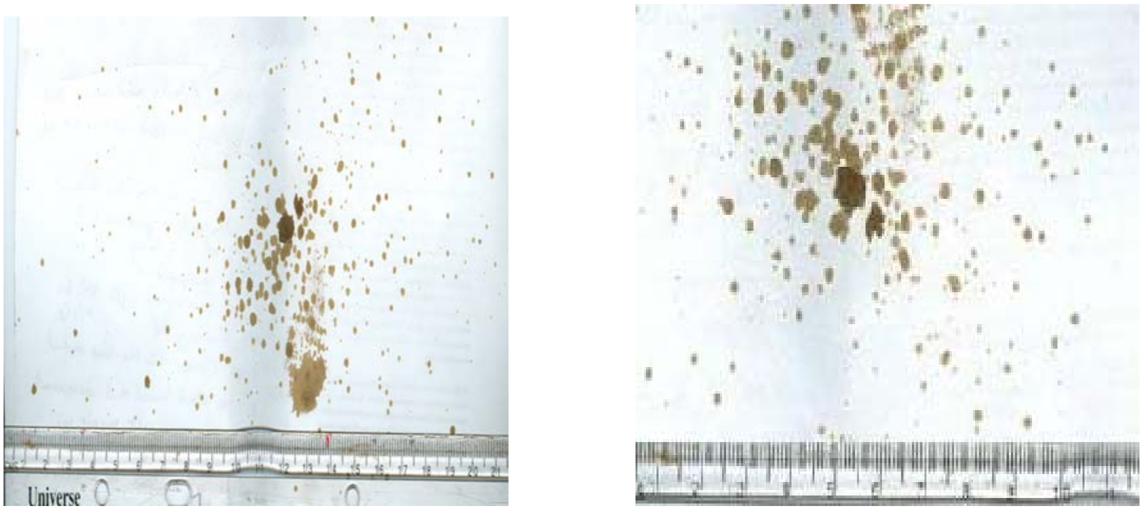
4.1 DROPLET SIZE DISTRIBUTION OF REACTANT

The reactant feed system was designed in such a way that the nozzle would spray the reactant as fine droplets. The high temperature in the furnace facilitated spraying by reducing the viscosity of glycerol. Because of the carrier gas flow and low viscosity of the liquid, the glycerol was sprayed as small droplets from the feed inlet nozzle were shown in Figure 3.1. It is observed from Figure 4.1 that the flow of carrier gas had a significant effect on spray pattern and droplet size of the reactant. When the carrier gas flow rate was increased from 30mL/min to 70mL/min, the spray droplet size decreased approximately from 2 to 0.5mm and the droplets were distributed in larger surface area on the bed as shown in Figure 4.1(a), 4.2 (b) and 4.3(c). The addition of steam to glycerol also had similar effect on the distribution and size of droplets of the reactant but the droplet size was less when compared to spray with carrier gas flow as shown in Figure 4.1(d).



a: Spray with 30mL/min

b: Spray with 50mL/min



c: Spray with 70mL/min

d: Spray with mixture of water and glycerol

Figure 4.1 Glycerol droplet size distribution as a function of flow rate of nitrogen (a to c) and without nitrogen (d)

4.2 REPRODUCIBILITY OF EXPERIMENTAL DATA

A few experiments were repeated to check the reproducibility. The standard deviations and errors for the run #1, 2, 3, 4, 32 and 33 are reported in the Table 4.1. From run #1 to 4 are the pyrolysis of glycerol with carrier gas flow rate of 30mL/min and 50mL/min. Run# 32 and 33 are the steam gasification of crude glycerol at 800°C. From Table 4.1, it is observed that the standard deviations and the percentages of errors were mostly below one and ±5% with 95% confidence respectively. Material balances for the few runs of pyrolysis and steam gasification of glycerol are given in the Table 4.2. The overall material balance for all the experiments was mostly in the range of 90-95 wt%. Sample calculations for mass balance and calorific value of the product gas are shown in the Appendix C. Also, experimental data for all the runs are given in Appendix D.

Table 4.1: Reproducibility of pyrolysis of glycerol and steam gasification of crude glycerol.

Run#	Gas wt%	H_2 mol%	CO Mol%	CH_4 mol%	C_2H_4 mol%	Volume of gas (L/g)	Calorific value of gas (MJ/m^3)
1	67.6	47.4	43.6	4.7	2.8	1.12	14.5
2	67.4	46.1	44.8	4.7	2.9	1.08	14.6
SD*	0.14	0.9	0.8	0	0.1	0.0	0.1
Error	±1.8	±11.4	±10.1	±0	±1.2	±0	±1.2
3	66.6	48.6	44.9	3.3	2	1.15	13.7
4	66.7	48.0	45.4	3.5	2.2	1.15	13.9
SD*	0.1	0.4	0.4	0.1	0.1	0	0.1
Error	±1.2	±5.08	±5.08	±1.2	±1.2	±0	±1.2
32	91.1	59.6	19.7	11.5	2.4	1.57	15.72
33	90.1	59.8	21.3	10.8	2.4	1.62	15.67
SD*	0.6	0.13	1.13	0.5	0	0.04	0.04
Error	±7.6	±1.65	±14.3	±6.3	±0	±0.5	±0.5

* Standard Deviation (SD) = $\sqrt{((n\sum X^2-(\sum X)^2)/(n \times (n-1)))}$
Error = t x SD; (distribution t=12.706 at 95% confidence and number of degrees of freedom = 1).

Table 4.2: Material balances for the pyrolysis and steam gasification of glycerol (N_2 free basis) with an inert packing bed height of 70mm, 800°C (run time 30 min).

Particle diameter (mm)	N_2 flow rate (mL/min)	Feed		Liquid Product		Product gas			Char		Total Accounted	
		Glycerol (g)	Water (g)	(g)	wt%	(L/g)	(g)	wt%	(g)	wt%	(g)	wt%
Quartz 0.21-0.35	50	2.71	0	0.49	20.5	1.32	1.74	71.3	0.2	8.2	2.44	89.0
Quartz 0.6-0.71	50	2.76	0	0.62	24.6	1.22	1.73	67.5	0.2	7.9	2.54	92.0
Quartz 3.0-4.0	50	2.67	0	0.64	26.1	1.15	1.64	66.6	0.18	7.3	2.46	92.0
Sand 0.21-0.35	50	2.79	0	0.57	21.3	1.22	1.88	71.9	0.16	6.3	2.61	93.7
Sand 0.6-0.71	50	2.71	0	0.65	25.1	1.21	1.85	70.7	0.11	4.3	2.61	96.1
Sand 1.0-1.15	50	2.78	0	0.75	28.	1.12	1.82	68.1	0.11	3.9	2.68	96.6
Quartz 0.21-0.35	0	2.39	0.27	0.63	16.8	1.55	1.62	75	0.17	7.9	2.42	91.4
Quartz 0.21-0.35	0	2.00	0.67	0.81	8.2	1.65	1.45	84.8	0.12	7.0	2.38	89.3
Quartz 0.21-0.35	0	1.31	1.31	0	0	1.71	1.11	94	0.07	6.0	2.5	95.0
SiC 0.15	0	2.68	0.03	0.41	17	1.23	1.83	75.2	0.19	7.8	2.43	90.9
SiC 0.15	0	2.03	0.68	0.24	14.3	1.33	1.32	78.5	0.12	7.2	2.36	86.8
SiC 0.15	0	1.33	1.33	0.05	4.2	1.43	1.00	89.5	0.07	6.2	2.45	92.3

4.3 PYROLYSIS OF GLYCEROL

4.3.1 Effects of carrier gas flow rate

The effect of carrier gas flow rate on product yield during pyrolysis of glycerol is shown in Figure 4.2. It is observed from the figure that with an increase in carrier gas flow from 30mL/min to 70mL/min, gas production decreased from 72 to 65wt%, liquid yield increased from 19.3 to 30.7wt% and char production decreased from 8.5wt% to 4.1wt%. This is possibly due to the distribution of the reactant as a droplet on the bed and the decrease in residence time from 4.13s to 1.8s as the carrier gas flow rate increased. As the carrier gas flow rate decreased, the liquid product had undergone significant reaction, thereby increasing the gas yield.

The effect of carrier gas flow rate on product gas composition from pyrolysis of glycerol is shown in Figure 4.3. There were no significant changes in the product gas composition for the flow rate between 30 and 50mL/min. However, H_2 and CO production changed considerably from 48.6mol% at 50mL/min to 37.9mol% at 70mL/min and from 44.9mol% at 50mL/min to 51.2mol% at 70mL/min, respectively. Methane production was slightly increased from 3.3mol% at 50mL/min to 6.0mol% at 70mL/min. As the carrier gas flow rate increased, the reactant would have distributed uniformly inside the bed and lead to the parallel reaction to produce H_2, CO, CO_2, CH_4, C_2H_4 and coke as shown in the equation 2.2. An increase in methane and hydrocarbon production was because of decrease in residence time as the carrier gas flow rate increased. The formation of syn gas remained almost constant at 93 mol% over the flow rates 30mL/min - 70mL/min.

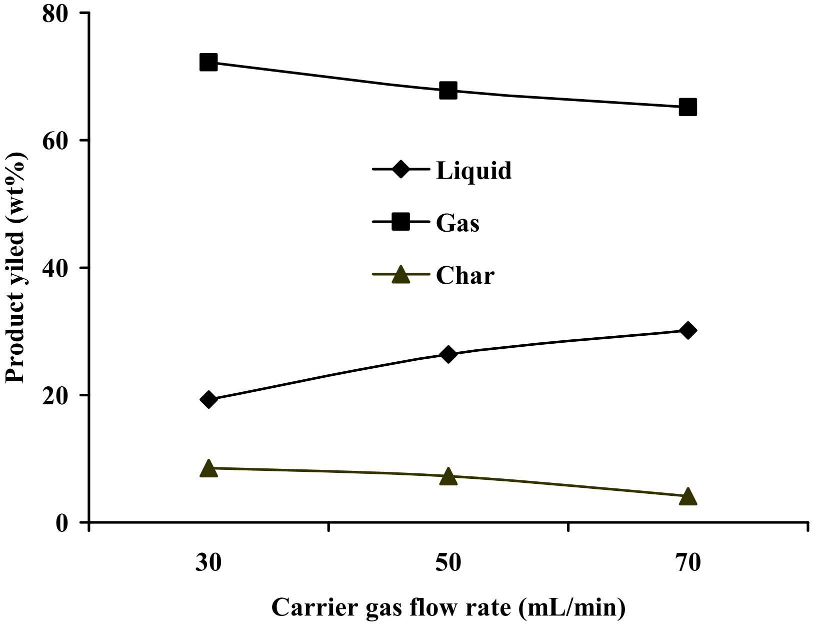


Figure 4.2 Effect of carrier gas flow (N_2) on product yield during pyrolysis of glycerol at 800°C, bed height 70mm and glycerol flow rate 5.4 g/h.

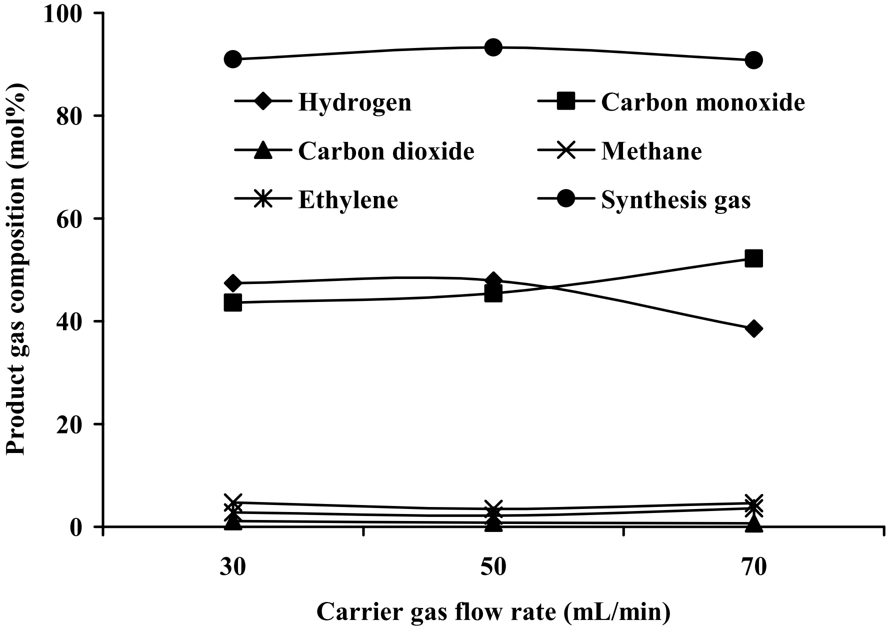


Figure 4.3 Effect of carrier gas flow (N_2) on product composition during pyrolysis of glycerol at 800°C, 70mm bed height and glycerol flow rate 5.4g/h.

The effects of carrier gas flow rate on volume of product gas and calorific value are shown in Figure 4.4. As expected, the volume of the product gas decreased from 1.2L/g of glycerol fed to 1.09L/g of glycerol fed when the carrier gas flow rate increased from 30mL/min to 70mL/min. From the figure, it can be seen that calorific value of gas increased from 14.3MJ/m^3 to 15.1MJ/m^3 as the flow rate increased from 30mL/min to 70mL/min. This increase in calorific value was due to increase in the yield of hydrocarbon production. For example, calorific value of methane (37MJ/m^3) is much higher than the hydrogen (12MJ/m^3) and carbon monoxide (11.7MJ/m^3).

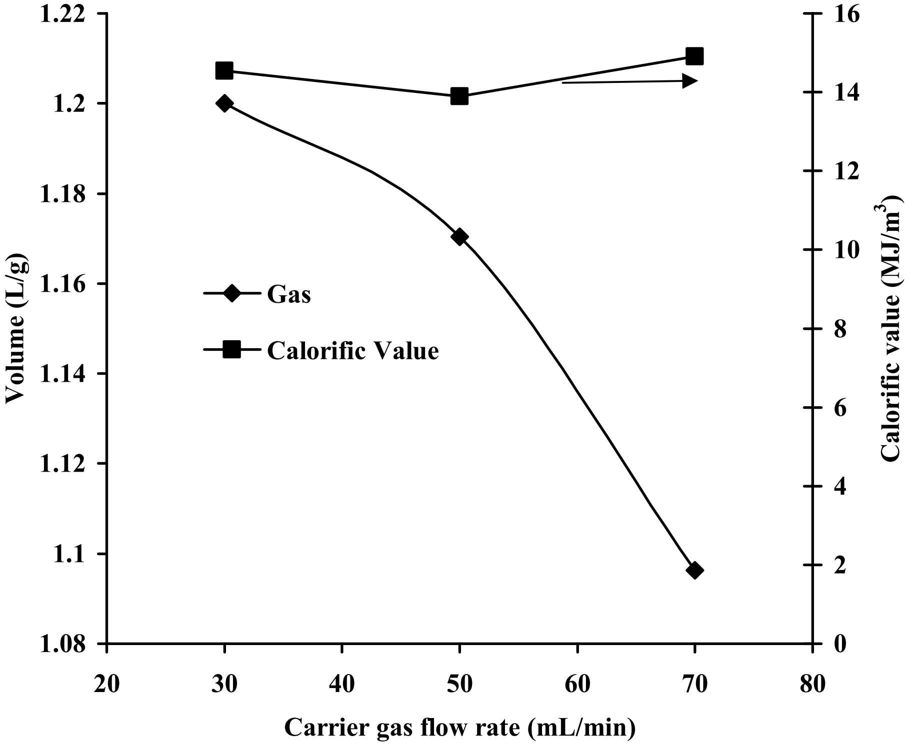


Figure 4.4 Effects of carrier gas flow (N_2) on volume and calorific value of gas during the pyrolysis at 800°C, 70mm bed height and glycerol flow rate 5.4g/h.

Carrier gas flow rates did not have significant effect on the production of syn gas. Optimum carrier gas flow rate was chosen for the further studies based on the volume of product gas produced and char yield. Effects of carrier gas flow study showed that nitrogen flow rate of 50mL/min would be optimum because char yield was 7.3wt% when compared to 8.5wt% at 30mL/min of N_2. Spray pattern was better for 50mL/min. Carrier gas flow rate of 70mL/min was not favourable for further studies because the volume of product gas (1.09L/g) obtained at this condition was less compared to that of 1.17L/g at 50mL/min of carrier gas. Therefore, 50mL/min of nitrogen flow was chosen to study the effects of temperature. At this condition, 93mol% of syn gas was obtained with H_2/CO of 1.05.

4.3.2 Effects of temperature

The effect of temperature on product yield during pyrolysis of glycerol with a carrier gas flow of 50mL/min is shown in Figure 4.5. It is observed from Figure 4.5 that the gas yield increased from 27.5wt% at 650^{o}C to 66.7wt% at 800^{o}C. As expected, the amount of liquid product decreased from 68 to 26wt% as the temperature increased from 650^{o}C to 800^{o}C. Char production was increased from 4.1 to 7.3wt% as the temperature increased from 650^{o}C to 800^{o}C. Increase in gas and char yield is due to the increase in thermal cracking of reactant as the temperature increased at the fixed carrier gas flow rate.

The effect of temperature on gas product composition during pyrolysis of glycerol is given in Figure 4.6. It is observed that production of hydrogen increased from 17 to 48.6mol% with an increase in temperature from 650^{o}C to 800^{o}C. There was a

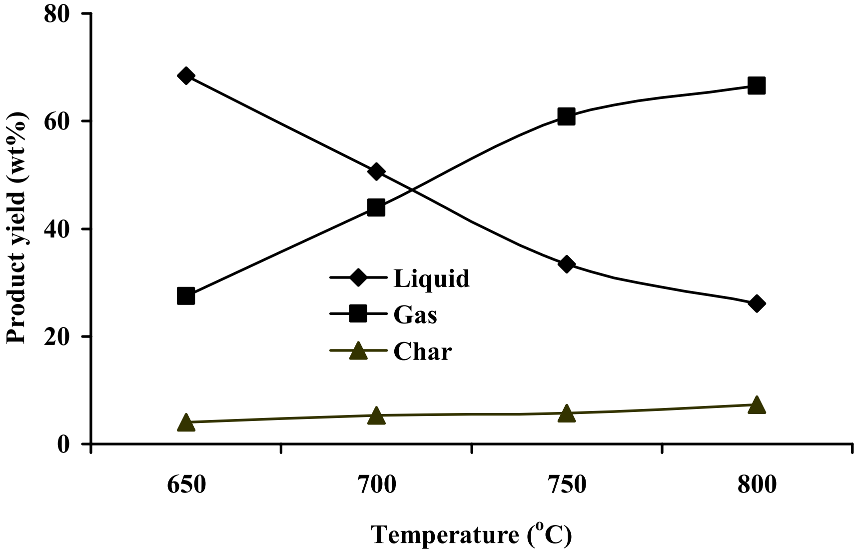


Figure 4.5 Effect of temperature on product yield during the pyrolysis of glycerol at a carrier gas flow rate of 50mL/min, 70mm bed height and glycerol flow rate 5.4g/h.

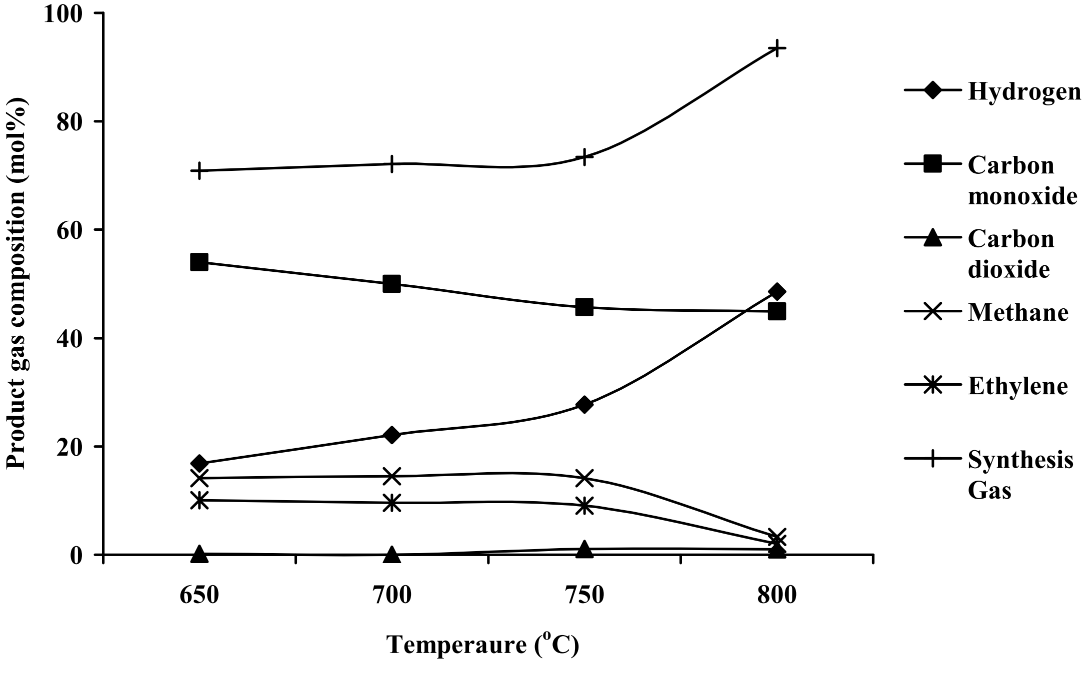


Figure 4.6 Effect of temperature on product composition during pyrolysis of glycerol at carrier gas flow rate 50mL/min, 70mm bed height and glycerol flow rate of 5.4 g/h.

sudden increase in hydrogen production from 27.7mol% at 750°C to 48.6mol% at 800°C. Also, the production of carbon monoxide decreased from 54mol% to 44.9mol%as the temperature increased from 650°C to 800°C. However, methane and ethylene production were almost constant at the range of 650°C - 750°C. But at 800°C, there was a sudden decrease of methane and ethylene concentration from 14 to 3.5 mol% and from 10 to 2mol%, respectively.

The pyrolysis of glycerol would have undergone the parallel reaction (equation 2.2) to give H_2, CO, CH_4, C_2H_4, coke and liquid product as proposed by Wang et al. (1996). As the temperature was increased from 650°C to 750°C, the yield of hydrogen only increased with temperature and those of all other compounds decreased. Liquid product would have undergone cracking to give more hydrogen and lower liquid hydrocarbon as the temperature increased from 650°C to 750°C. This is evident from Figure 4.5 that gas yield increased when the temperature increased. At 800°C, the sudden increase in hydrogen concentration may be due to aromatization of hydrocarbon (see equation 4.1) or decomposition of methane and ethylene to coke and hydrogen (see equation 4.2, Goswami 1999, Bradford 1999, Steinberg 1999 and Ferdous 2000).

$$6CH_4 \leftrightarrow C_6H_6 + 9H_2 \qquad (4.1)$$

$$C_xH_y \leftrightarrow (y/2)\, H_2 + xC_{(s)} \qquad (4.2)$$

From Figures 4.5 and 4.6, it can be seen that there was an increase in char and hydrogen production at 800°C, respectively. Therefore, it is proposed that methane and ethylene have undergone cracking at a higher temperature (800°C) to produce hydrogen and char as explained in the equation 4.2. Syn gas (H_2+ CO) production increased slowly from 70mol% at 650°C to 74mol% at 750°C. There was a sudden increase in production of syn gas to 93mol% at 800°C. This is due to the thermal cracking of hydrocarbons to hydrogen.

The effect of temperature on volume and calorific value of gas produced is shown in Figure 4.7. As expected, there was an increase in volume of gas from 0.4L/g of glycerol to 1.17L/g of glycerol with the rise in temperature from 650°C to 800°C. It is observed from the figure that the calorific value of product gas was decreased slightly from 21.35MJ/m^3 at 650°C to 20.56MJ/m^3 at 750°C. There was sudden decrease in calorific value to 13.77MJ/m^3 at 800°C. This sudden decrease in calorific value of the product gas is due to the decrease in hydrocarbon concentration, as the hydrocarbons have higher heating values.

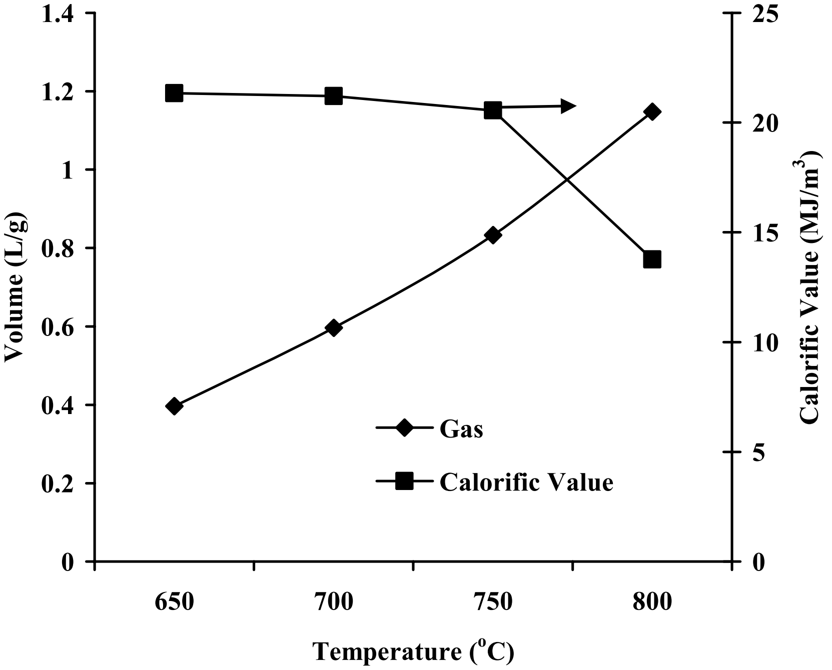


Figure 4.7 Effects of temperature on volume and calorific value of gas during pyrolysis of glycerol at carrier gas flow rate 50mL/min, 70mm bed height, quartz particle of diameter 3-4mm and glycerol flow rate 5.4g/h.

In summary, syn gas production increased from 70mol% at 650°C to 93mol% at 800°C. Also, the volume of the product gas increased from 0.4L/g to 1.17L/g. Therefore, effects of temperature studies indicated that 800°C would be the optimum temperature for hydrogen or syn gas production (H_2/CO of 1.05). This operating temperature was used to study the role of particle diameter of the packing material in the pyrolysis of glycerol process.

4.3.3 Effects of particle diameter of the packing material

Pyrolysis of glycerol was carried out with different particle diameter of the packing materials (quartz, silicon carbide and sand). Cortright et al. (2002) suggested that undesirable liquid phase reactions can be avoided by minimizing the void volume of the reactor. Therefore, changes in particle diameter of the bed packing may alter the product yield and product gas composition because of the influence of particle diameter in the porosity and permeability of the bed packing. The porosity of the reactor is the ratio of void volume of the bed to the total volume of the bed. Sometimes porosity of the bed is represented in percentage. The porosity measurements and percentage of porosity of the packing bed with different materials are shown in Appendix B2. Reduction in the particle diameter of the packing offers resistance to the flow of the reactant. It is generally defined as permeability. Permeability of the packed bed for the different particle diameter of the packing materials is given in Appendix B3. Also, changing the packing material may have an effect on the product yield because of differences in thermal conductivity of the materials. The thermal conductivity of the packing materials at 800°C were: quartz, 5W/mK (Yoon et al., 2004); silicon carbide, 25W/mK; and sand, 1.7W/mK (Shackelford et al., 1994). Pyrolysis experiments were carried out to study the effects of particle diameter of material at 800°C with 50mL/min of nitrogen.

4.3.3.1 Effects of diameter of quartz particle

The effect of particle diameter of quartz on product yield during the pyrolysis process is shown in Figure 4.8. It is observed from Figure 4.8 that when the particle diameter was reduced from 3-4mm to 0.21-0.35mm, product gas yield increased from 66.6wt% to 71wt%. Liquid product yield concurrently decreased from 26wt% to 20wt%. In addition, char production increased from 7.3 to 8.1wt% as the particle diameter decreased. This is due to the porosity of reactor bed which decreased from 75% to 44%

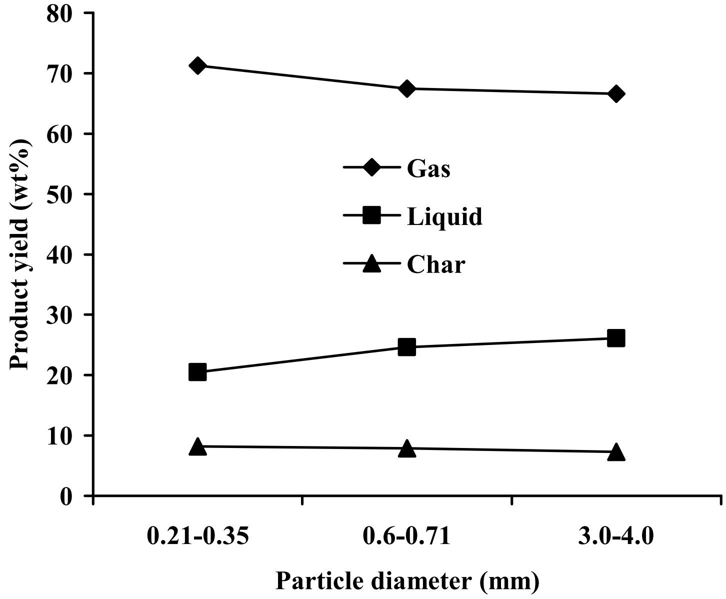


Figure 4.8 Effect of particle diameter of quartz particles on the product yield for glycerol pyrolysis at 800°C, 70mm bed height, 50mL/min of N_2 flow and glycerol flow rate of 5.4 g/h.

and permeability (resistance to the reactant flow and uniform distribution of reactant) of the packed decreased from 4.6 x 10^{-3} to 8.5 x $10^{-7}$$cm^2$ when the particle diameter decreased from 3-4mm to 0.21-0.35mm. An increase gas yield is also due to the increase in residence time of the reactant as the particle diameter of the packing material decreased. Decrease in particle diameter made the reactant to crack down to gaseous and char product completely.

The effect of particle diameter of quartz on the composition of product gas was studied and shown Figure 4.9. It is observed from Figure 4.9 that the hydrogen production increased from 48.6 to 55.4mol% as the particle diameter decreased from 3-4mm to 0.21-0.35mm. On the other hand, carbon monoxide production decreased from 44.9 to 36.9mol% as the particle diameter decreased. This is probably due to the formation of water during the pyrolysis process could have undergone water-gas shift reaction that resulted decrease in carbon monoxide production as shown in the equation 4.3 (Demirbas, 2002).

$$CO + H_2O \leftrightarrow H_2 + CO_2 \tag{4.3}$$

Furthermore, decrease in particle diameter increased the contact points between particle and reactant. Decrease in the particle diameter of the packing material increased the residence time thereby increased the production of hydrogen and char. The reduction in particle diameter does not have a significant effect on syn gas production (~93mol%).

The effects of particle diameter of the quartz on the volume and calorific value of gas produced were also studied and shown in Figure 4.10. The volume of gas produced increased from 1.15L to 1.32L per gram of glycerol fed when the particle diameter reduced. This is due to the decrease in porosity and permeability of the reactor

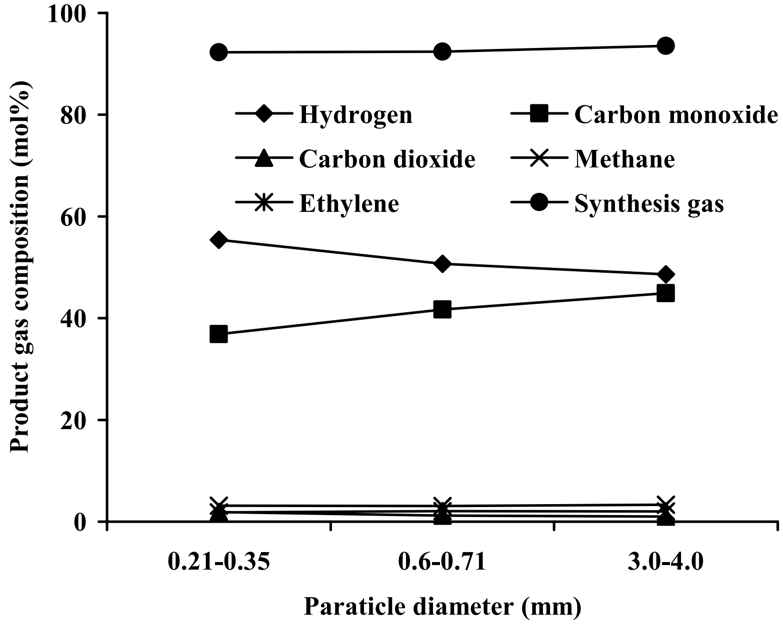


Figure 4.9 Effect of particle diameter of quartz particles on the product gas composition for glycerol pyrolysis at 800°C, 70mm bed height, 50mL/min of N_2 flow and glycerol flow rate of 5.4 g/h.

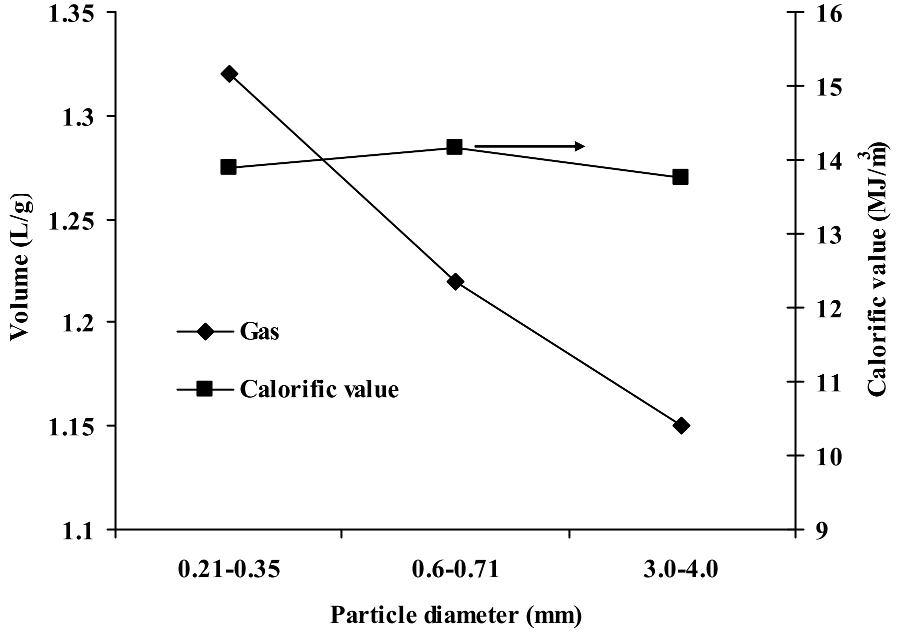


Figure 4.10 Effects of particle diameter of quartz particles on the volume and calorific value of gas for glycerol pyrolysis at 800°C, 70mm bed height, 50mL/min of N_2 flow and glycerol flow rate of 5.4 g/h.

bed as the particle diameter of the packing material decreased. It is observed that the particle diameter of quartz does not have a significant effect on calorific value of product gas because there was not a significant change in the production of hydrocarbons.

4.3.3.2 Effects of diameter of silicon carbide particle

The effect of particle diameter of silicon carbide on yields of gas, liquid and char is shown in Figure 4.11. It is observed from the Figure 4.11 that when the particle diameter was reduced from 1mm to 0.15mm, product gas yield increased from 73wt% to 77wt% whereas liquid product yield decreased from 23wt% to 16wt%. On the other hand, char production increased from 3.6wt% to 6.3wt% as the particle diameter decreased. More liquid was converted to gaseous compound and char due to decrease in porosity of the reactor bed from 65% to 49% as the particle diameter decreased from 1mm to 0.15mm. Higher the thermal conductivity (25W/mK) of silicon carbide particle, higher the heat transfer rate. Also, decrease in particle diameter of the packing material increased the residence time of the reactant.

The effect of particle diameter of silicon carbide on the composition of product gas was studied and shown in Figure 4.12. It is observed from the Figure 4.12 that syn gas production increased from 80 to 93mol% as the packing material diameter decreased from 1mm to 0.15mm. It can also be seen that with the decrease in particle diameter from 1mm to 0.15mm, hydrogen and carbon monoxide production increased from 39 to 49.7mol% and from 40.2 to 44mol%, respectively. On the other hand, hydrocarbon production decreased as the particle diameter decreased. Hydrogen production increased

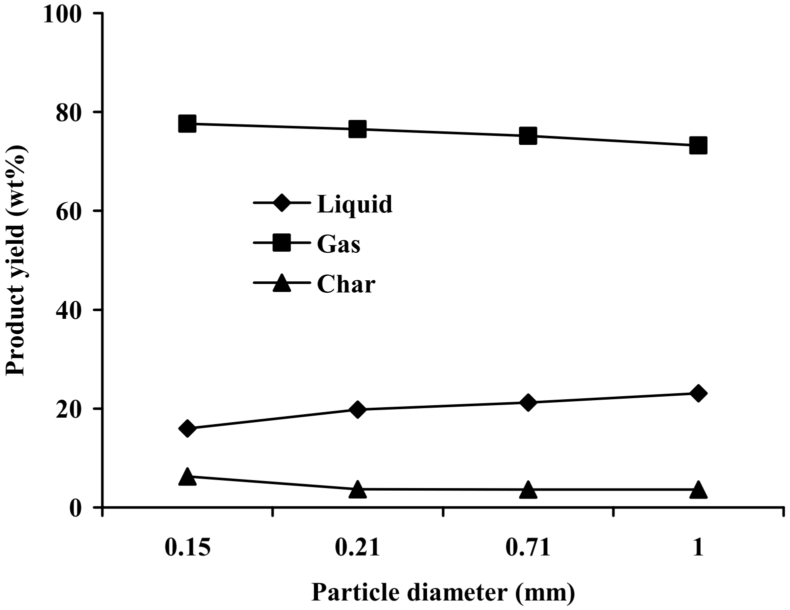


Figure 4.11 Effect of particle diameter of silicon carbide on product yield during pyrolysis of glycerol at 800°C, 70mm bed height, at carrier gas flow rate 50mL/min and glycerol flow rate 5.4 g/h.

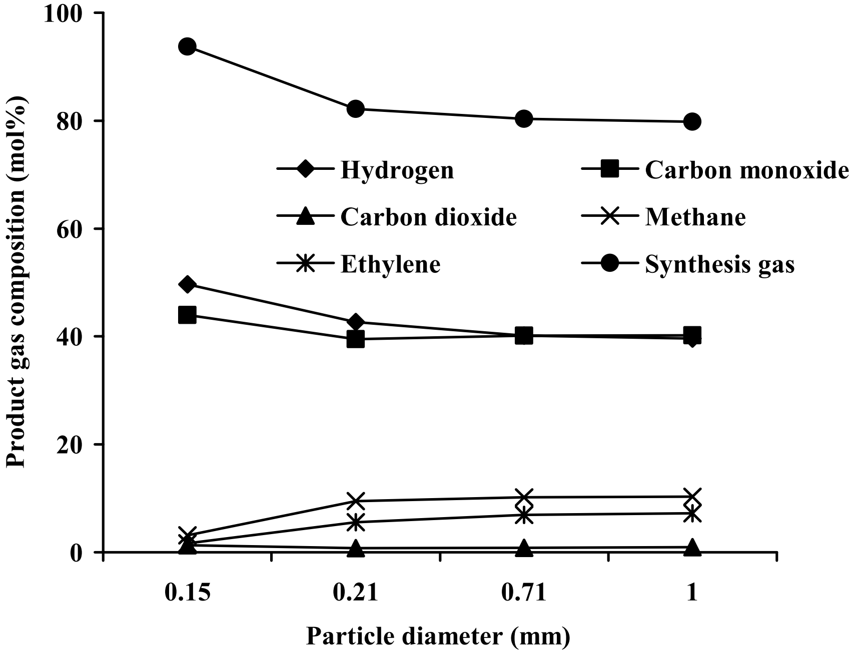


Figure 4.12 Effect of particle diameter of silicon carbide on product composition during pyrolysis of glycerol at 800°C, 70mm bed height, at carrier gas flow rate 50mL/min and glycerol flow rate 5.4 g/h.

due to the thermal cracking of hydrocarbon as the particle diameter decreased (see equation 4.2). It is evident from the Figure 4.10 that thermal cracking of hydrocarbon increased the char yield as the particle diameter decreased. Also, steam reforming reaction of hydrocarbon could have increased the hydrogen and carbon monoxide production as shown in the equation 4.4 (Moenne et al., 1995, Specht et al., 2000 and Cipriani et al., 1998). This steam reforming reaction could be possible because water was one the products in the liquid.

$$CH_4 + H_2O \leftrightarrow 3H_2 + CO \tag{4.4}$$

The effects of particle diameter on the volume of gas produced and calorific value are presented in Figure 4.13. The volume of gas increased from 1.17L/g to 1.27L/g of feed when the particle diameter reduced from 1 to 0.15mm. This is probably due to the decrease in porosity from 65 to 49% and permeability from 1.2×10^{-4} to 5.7×10^{-7} cm^2 of the packed bed as the particle diameter decreased. Decrease in permeability would allow the reactant to distribute uniformly and also increase the residence time. The calorific value also decreased from 18.46MJ/m^3 to 13MJ/m^3 as the particle diameter decreased from 1mm to 0.15mm. This is due to a decrease in the production of hydrocarbon as the particle diameter decreased.

4.3.3.3 Effects of diameter of sand particle

The effect of particle diameter of sand on product yield during pyrolysis reaction is shown in Figure 4.14. From Figure 4.14, it is observed that when the particle diameter was reduced from 1-1.15mm to 0.21-0.35mm, product gas yield increased from 68 wt% to 72 wt% whereas liquid product yield decreased from 28wt% to 22wt%. On the other

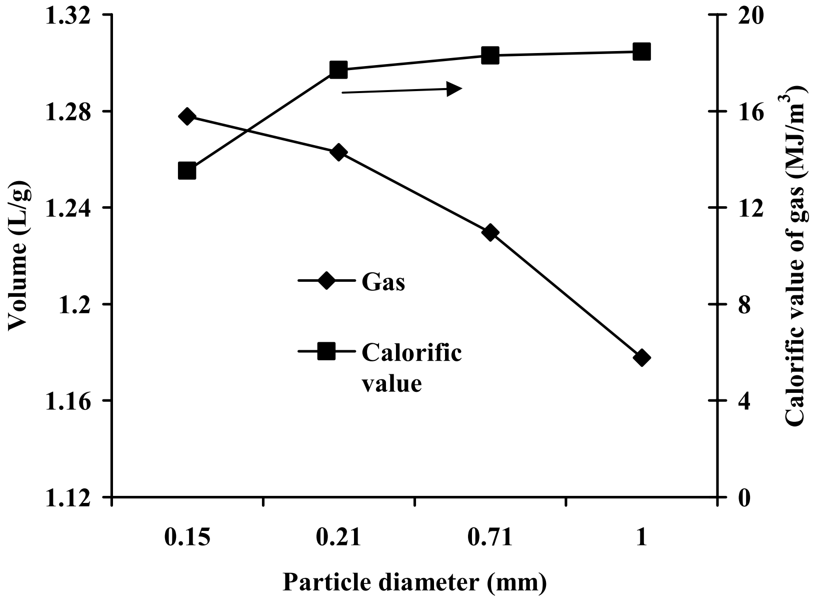


Figure 4.13 Effects of particle diameter of silicon carbide on volume and calorific value of gas during pyrolysis of glycerol at 800°C, 70mm bed height, at carrier gas flow rate 50mL/min and glycerol flow rate 5.4 g/h.

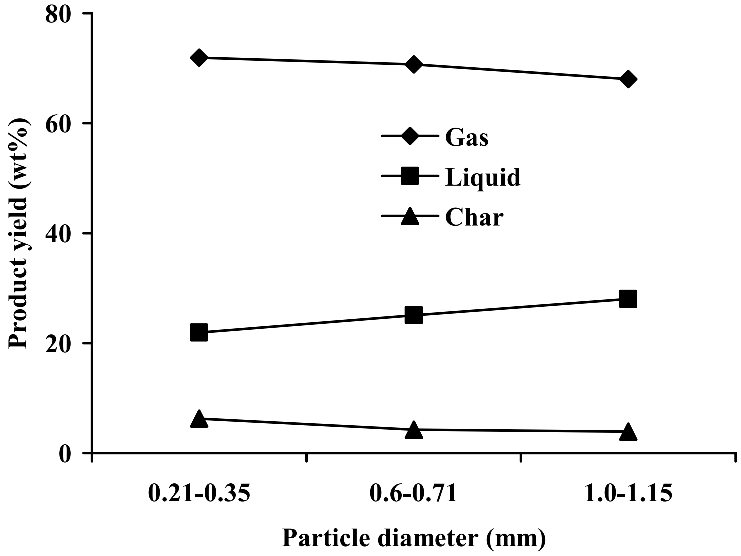


Figure 4.14 Effect of particle diameter of sand on the product yield of glycerol pyrolysis at 800°C, 70mm bed height, 50mL/min of N_2 flow and glycerol flow rate of 5.4 g/h.

hand, char production increased from 3.9wt% to 6.3wt% as the particles decreased. Increase in gas and char yield is due to the decrease in the porosity of the reactor bed from 55% to 35% and increase in the residence time of the reactant as the particle diameter decreased from 1-1.15 to 0.20-0.35mm. A decrease in porosity and permeability of the reactor bed would allow the reactant to distribute uniformly inside the bed.

Figure 4.15 shows that the hydrogen production increased from 40mol% to 46.7mol% as the particle diameter decreased from 1-1.15mm to 0.21-0.35mm. In addition, the reduction in particle diameter does not have any effect on production of carbon monoxide. It is observed from the figure that syn gas production increased from

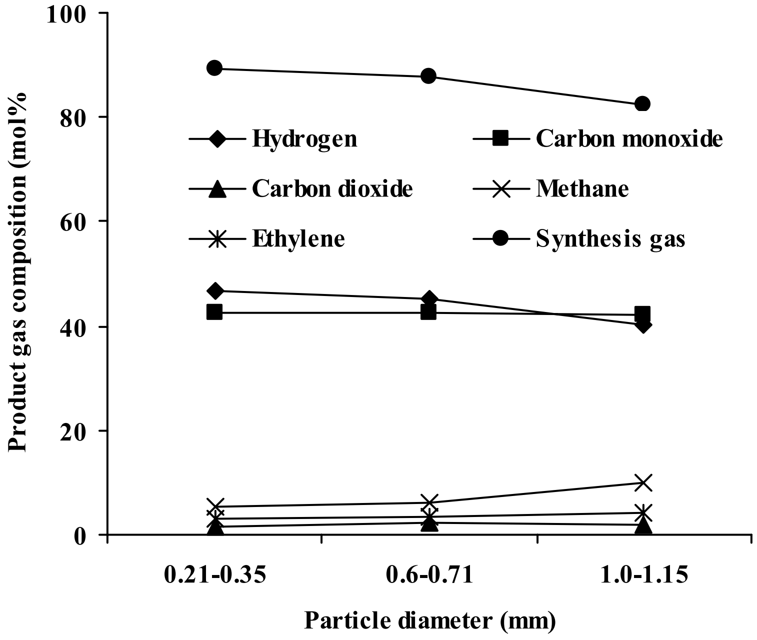


Figure 4.15 Effect of particle diameter of sand on the product gas composition for glycerol pyrolysis at 800°C, 70mm bed height, 50mL/min of N_2 flow and glycerol flow rate of 5.4 g/h.

82 to 89mol% as the particle diameter decreased. Also, hydrocarbon production decreased when the particle diameter of sand decreased. Hydrocarbons such as methane and ethylene had undergone cracking to give more hydrogen and char when the particle diameter was reduced as shown in the equation 4.2. It is evident from Figure 4.14 that the char yield is increasing as the particle diameter of sand decreased.

Figure 4.16 shows the effect of particle diameter of sand on the volume and calorific value of produced gas. The volume of gas produced increased from 1.12L to 1.22L per gram of glycerol fed when the particle diameter reduced from 1-1.15mm to 0.21-0.35mm. This is due to the decrease in the porosity of the reactor bed as the particle diameter decreased and thermal conductivity of 1.7 W/mK. Calorific value of the product gas increased from 15.1MJ/m^3 to 17.2MJ/m^3 when the particle diameter increased from 0.21-0.35mm to 1-1.15mm. This decrease in calorific value is due to the decrease in the production of hydrocarbon as the particle diameter of sand decreased.

The effects of particle diameter of different packing material showed that porosity, permeability and thermal conductivity of the packing material had a significant effect on product yield, product gas composition and volume of product gas produced. It is possible to maximise the volume of product gas and syn gas production if the lowest particle diameter of all the packing material was used in the pyrolysis studies. When a quartz particle diameter of 0.21-0.35mm was used, the volume of gas produced was much higher when compared to the volume of gas produced with the lowest particle diameter of the other packing materials (see Figure 4.10, 4.13 and 4.16). This is probably due to the better porosity (44%) and thermal conductivity (5W/mK) of the quartz bed when compared with the other packing materials. Effects of quartz with 0.21-

0.35mm and silicon carbide with 0.15mm particle diameter on syn gas production (~93mol%) are quite comparable. Therefore, it was decided to use the lowest particle diameter of quartz and silicon carbide to maximise the volume of the product gas and syn gas production in the steam gasification of glycerol process.

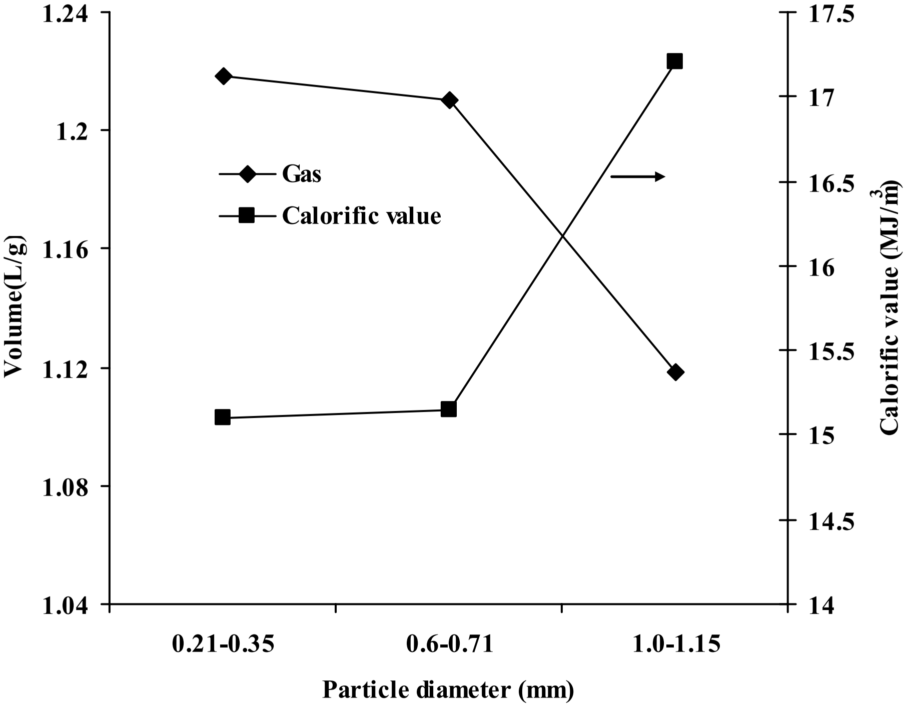


Figure 4.16 Effects of particle diameter of sand on volume and calorific value of gas for glycerol pyrolysis at 800°C, 70mm bed height, 50mL/min of N_2 flow and glycerol flow rate of 5.4 g/h.

4.4 STEAM GASIFICATION OF GLYCEROL

Steam gasification of glycerol was carried out with the different packing materials (quartz and silicon carbide) and over different steam to glycerol weight ratios of 10:90 25:75 and 50:50 at 800°C. No carrier gas was used in the steam gasification studies.

4.4.1 Effects of steam using quartz as a packing material

Steam gasification of glycerol was carried out with quartz particle diameter of 0.21-0.35mm to study the effects of steam on product yield (see Figure 4.17). It is observed from Figure 4.17 that gas yield increased from 71.3 wt% to 94wt% when the weight ratio of steam to glycerol increased from 0:100 to 50:50. The liquid yield decreased from 20.5wt% to 0wt% as the steam to glycerol ratio increased. Glycerol was completely gasified when 50:50 weight of ratio of steam to glycerol was used. Liquid product yield was calculated on the basis that the steam, formed during the reaction, was completely gasified. Also, char production decreased from 8.2wt% to 6wt% as the steam to glycerol weight ratio increased. Probably, the addition of water to the glycerol could have enhanced the gasification process by distributing the reactant uniformly through out the reactor bed.

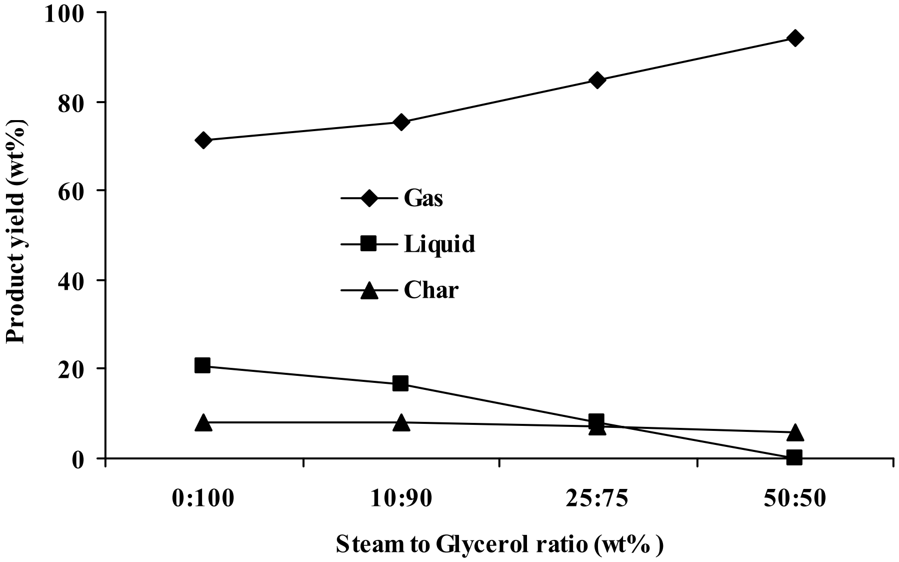


Figure 4.17 Effect of steam on the product yield of glycerol gasification using quartz of diameter 0.21-0.35mm as a packing material at 800°C, 70mm bed height and glycerol flow rate of 5.4 g/h.

The effect of addition of steam to glycerol on product gas composition was studied and shown in Figure 4.18. Figure 4.18 shows that there was increase in hydrogen production from 55.4mol% to 64 mol% when the steam to glycerol ratio changed from 0:100 to 25:75. Probably, the addition of steam improved the distribution of reactant through out the bed and also enhanced the cracking of glycerol. Then, there was a slight decrease in the hydrogen production to 58 mol% when the steam to glycerol weight ratio increased to 50:50. This is probably due to a decrease in residence time from 3s to 1.7s when the steam to glycerol ratio increased from 25:75 to 50:50. It is evident from Figure 4.18 that methane and ethylene increased from 3.5 to 4.8mol% and 0.47 to 1.3mol%, respectively. It is observed from Figure 4.18 that hydrogen selectivity

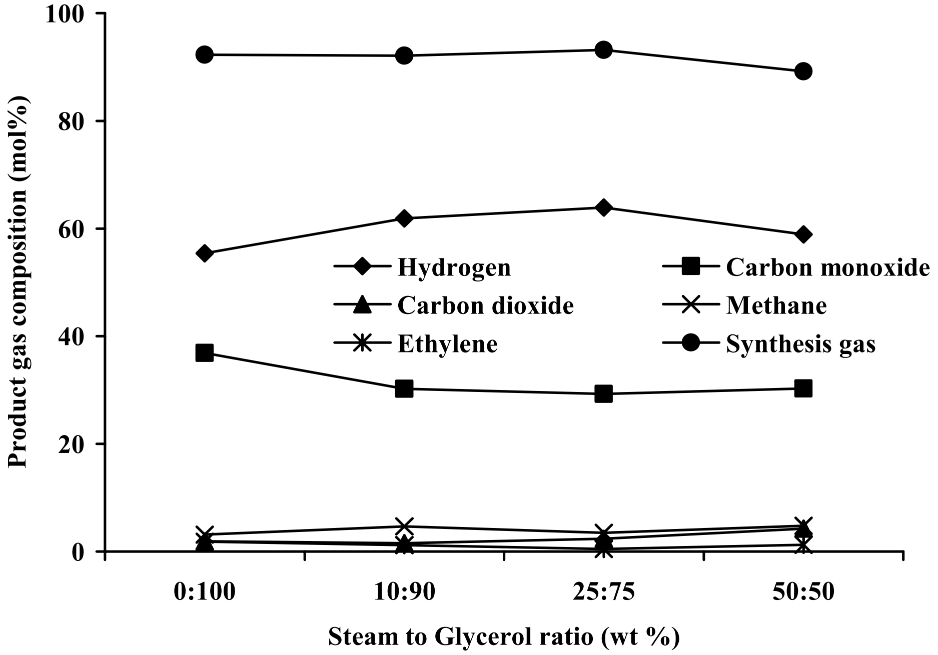


Figure 4.18 Effect of steam on the product gas composition of glycerol gasification using quartz of diameter 0.21-0.35mm as a packing material at 800^{o}C, 70mm bed height and glycerol flow rate of 5.4 g/h.

increased by 10mol% at 25:75 weight ratio of steam to glycerol when compared with the pyrolysis of glycerol at 800°C, 50mL/min and 0.21-0.35mm of particle diameter of quartz. Carbon monoxide production decreased from 36 to 30mol% when the steam to glycerol ratio increased from 0:100 to 10:90. This is probably due to the water gas shift reaction when carbon monoxide reacts with steam which is formed during the reaction to give hydrogen and carbon dioxide as shown in the equation 4.3. There was not a significant change in the production of carbon monoxide when the steam to glycerol ratio was increased from 10:90 to 50:50. It is observed from Figure 4.18 that there was an increase in the production of carbon dioxide from 1.9 to 4mol% when the steam to glycerol weight ratio increased. It is also possible that gasification of char would have increased the production of carbon dioxide as reported by Demirbas (2002). It is evident from Figure 4.17 that char production decreased as the steam to glycerol ratio increased. Addition of steam did not have any significant effect on syn gas production (~92mol%) and hydrocarbon production. However, the addition of steam, increased H_2/CO from 1.5 (absence of steam) to 2.1 (steam to glycerol ratio weight of 25:75).

Figure 4.19 shows the effects of steam on the volume and calorific value of product gas. The volume of gas produced increased from 1.32L to 1.71 L per gram of glycerol fed when the steam to glycerol weight ratio increased from 0:100 to 50:50. The increase in volume of gas produced was due to the addition of steam that improved the uniform distribution of the reactant on the reactor bed. The calorific value of the product gas did not change significantly because the production of hydrocarbon did not change much.

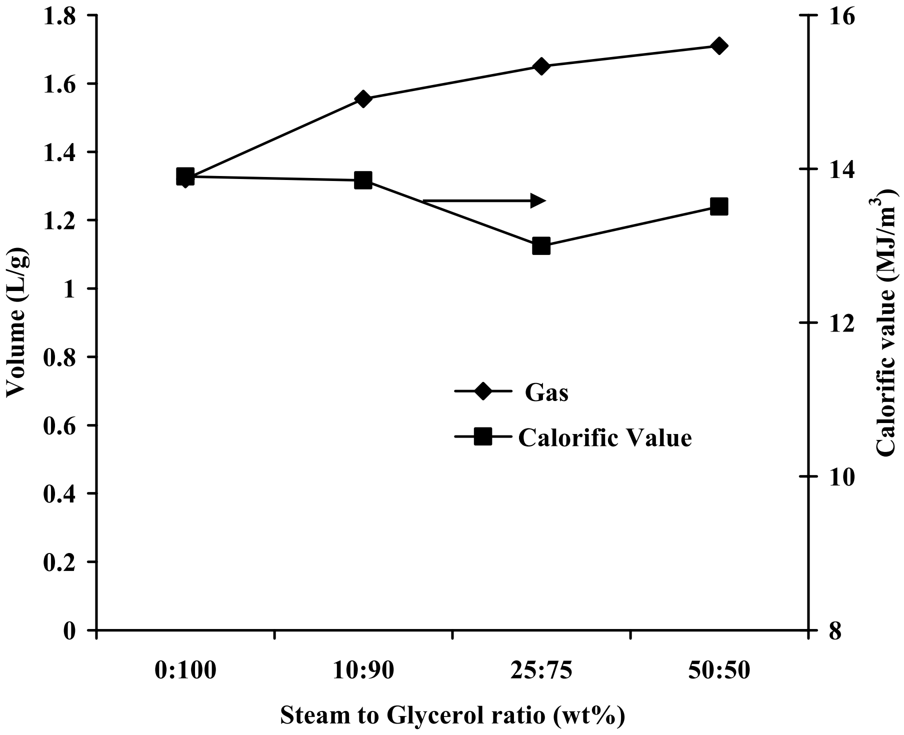


Figure 4.19 Effects of steam on the volume and calorific value of gas during glycerol gasification using quartz of diameter 0.21-0.35mm as a packing material at 800°C, 70mm bed height and glycerol flow rate of 5.4 g/h.

4.4.2 Effects of steam using silicon carbide as a packing material

The effect of steam gasification of glycerol using silicon carbide of diameter 0.15mm as a packing material was studied on product yield (see Figure 4.20). It is observed from Figure 4.20 that when the steam to glycerol weight ratio was increased from 0:100 to 50:50, product gas yield increased from 77.6wt% to 89.5wt% whereas liquid product yield decreased from 16wt% to 4.2wt%. This is probably due to the addition of steam to glycerol which could have enhanced the steam gasification process. It may be possible that the addition of steam might increase the uniformity of the distribution of reactant inside the bed. The addition of steam to glycerol does not have any significant effect on char production.

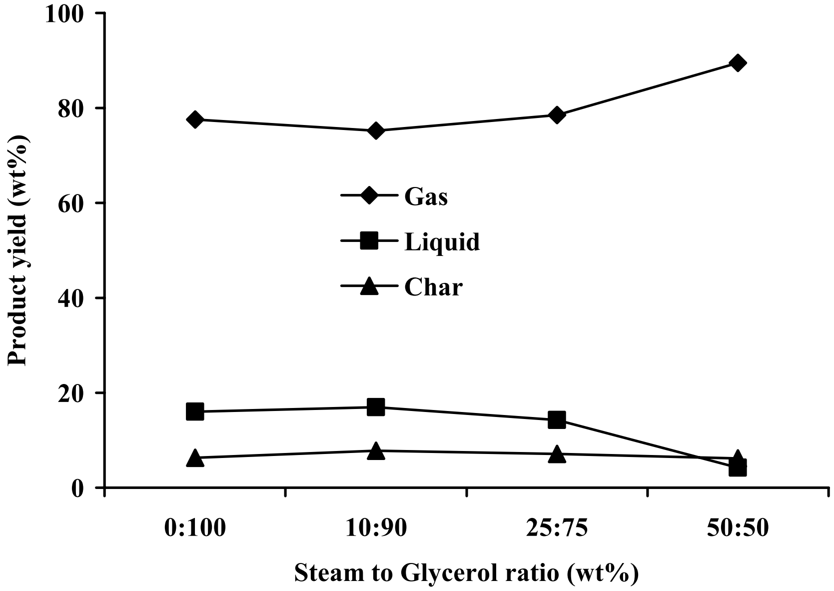


Figure 4.20 Effect of steam on the product yield of glycerol gasification using silicon carbide of diameter 0.15mm as a packing material at 800^oC, 70mm bed height and glycerol flow rate of 5.4 g/h.

The effect of steam on the composition of product gas obtained from steam gasification process was studied and shown in Figure 4.21. It is observed from Figure 4.21 that the hydrogen production increased from 49.7 to 57.8mol% and carbon monoxide production decreased from 38 to 33mol% when the steam to glycerol weight ratio increased from 0:100 to 25:75. The addition of steam enhanced the uniform distribution of reactant in the bed and thermal cracking process lead to an increase in hydrogen production. Furthermore, there was decrease in hydrogen production to 54 mol% and increase in carbon monoxide production to 37.5mol% at 50:50 weight ratio of steam to glycerol. This decrease in hydrogen production is probably due to a decrease in residence time from 3s to 1.7s. A similar trend was also observed during the studies on the effect of steam gasification of glycerol using quartz chips as a packing material. It is observed from figure that the addition of steam does not have any effect on syn gas (~92mol%). Methane and ethylene production increased from 3.2 to 6.6mol% and 1.3 to 3.2mol%, respectively as the steam to glycerol weight ratio increased from 0:100 to 10:90. Then, hydrocarbon production decreased as the steam to glycerol weight ratio increased from 10:90 to 50:50. This is probably due to the steam reforming reaction of hydrocarbons as shown in the equation 4.4.

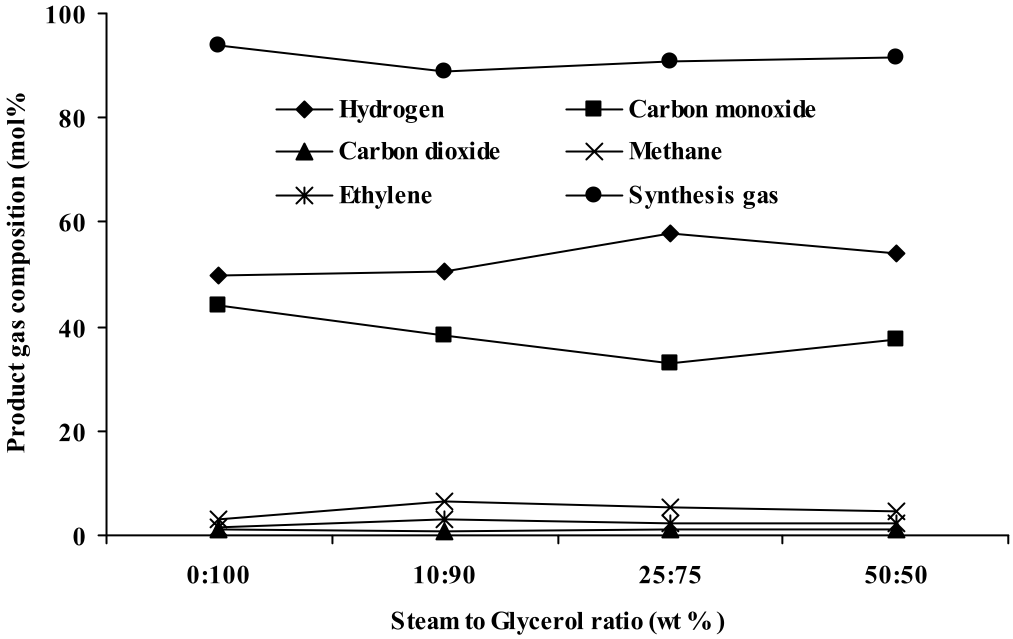


Figure 4.21 Effect of steam on the product gas composition of glycerol gasification using silicon carbide of diameter 0.15mm as a packing material at 800°C, 70mm bed height and glycerol flow rate of 5.4 g/h.

The effect of steam gasification of glycerol on the volume and calorific value of the gas produced is shown in Figure 4.22. It is observed from Figure 4.22 that the volume of the gas produced decreased from 1.27L/g to 1.23L/g of glycerol when the steam to glycerol ratio increased from 0:100 to 10:90. This decrease in volume may be due to the experimental error. When the steam to glycerol weight ratio increased from 10:90 to 50:50, the volume of the product gas increased from 1.23L/g to 1.43L/g of glycerol. Probably, the addition of steam could have enhanced the thermal cracking process to produce more volume of gas. Calorific value of the product gas increased from 13.5 to 15.4MJ/m^3 as the steam to glycerol ratio increased from 0:100 to 10:90. This is due to the increase in hydrocarbon production (see Figure 4.21). When the steam to glycerol weight ratio increased from 10:90 to 50:50, calorific value of the product gas decreased from 15.4 to 14.3MJ/m^3.

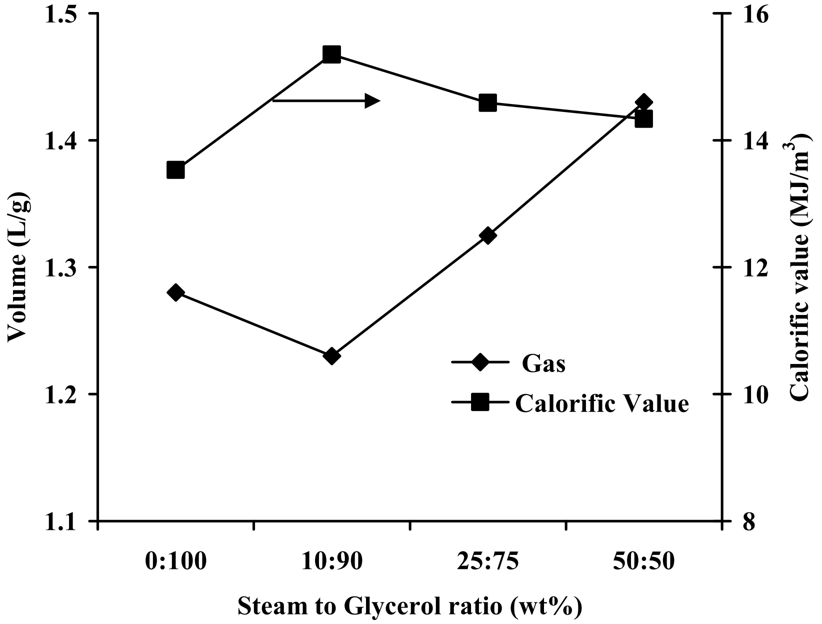


Figure 4.22 Effects of steam on the volume and calorific value of gas during glycerol gasification using silicon carbide of diameter 0.15mm as a packing material at 800°C, 70mm bed height and glycerol flow rate of 5.4 g/h.

The effects steam gasification of glycerol using different packing material studies shows that the addition of steam to glycerol and porosity of the packing bed had significant effects on product yield, volume of product gas produced and its composition. It is possible to produce 94wt% of product gas using quartz diameter 0.21-0.35mm as a packing material which is higher than 89wt% of product obtained using silicon carbide of diameter 0.15mm for steam to glycerol ratio 50:50. This is probably due to the porosity of the reactor bed. Porosity of the reactor bed using quartz was 44% whereas silicon carbide packing bed had 49%. Glycerol was completely gasified to gas and char, when the steam to glycerol weight ratio 50:50 was used for quartz packing whereas for the silicon carbide packing, the liquid yield was 4.2wt%. Steam gasification of glycerol using different packing material does not have a significant effect on the syn gas production (~92mol%). However, volume of the gas produced using quartz particles (1.71L/g) was more than volume of gas (1.43L/g) using silicon carbide packing for the steam to glycerol ratio of 50:50. In summary, using quartz particles as a packing material increased the volume of the product gas and its yield. Therefore, it was proposed to use the quartz particles as a packing material to study the steam gasification of synthetic mixture and crude glycerol.

4.5 GASIFICATION OF CRUDE GLYCEROL

Steam gasification of crude glycerol, produced during the transesterification of vegetable oil, was carried out in this work. The intent of this work was to study the effects of each compounds present in the crude glycerol on product yield, gas product composition and volume of gas produced. Crude glycerol was analysed in the analytical laboratories of the Saskatchewan Research Council. It was found that crude glycerol had 60wt% of glycerol, 31wt% of methanol, 7.5wt% of water and 1.5wt% of potassium hydroxide. Synthetic mixtures of glycerol were prepared based on the reported composition of crude glycerol to compare the effect of steam gasification of synthetic mixtures of glycerol with crude glycerol on product yield, gas composition and volume of gas.

4.5.1 Studies on synthetic mixtures of glycerol

Gasification experiments were carried out by preparing synthetic mixtures of glycerol, similar to the crude glycerol, at 800^{o}C, with the packing having quartz particles diameter of 0.21-0.35mm. No carrier gas was used in this study. Various mixtures of glycerol, water, methanol and potassium hydroxide were used for the studies (see Table 4.3). Pure methanol was completely gasified to produce gaseous products and char. Gasification of methanol produced 97mol% of syn gas and 65.7mol% of H_2. The volume of gas collected was 2.4L/g of methanol fed.

Gasification of the mixture (glycerol - 65wt% and methanol - 35wt%) produced 80.8wt% of gas and 91.1mol% of syn gas. Liquid product was about 16.6wt%. From Table 4.3, it is observed that addition of steam to glycerol and methanol mixture increased the production of gas from 80.8wt% at 0wt% of steam to 90.92wt% at 10wt% of steam, thereby decreasing the production of liquid from 16.51 wt% to 6.56 wt%. However, the addition of steam does not have a significant effect on the hydrogen, carbon monoxide and syn gas production. Hydrogen and carbon monoxide production was in the range of 57 to 54.4mol% and 34.1 to 34.6mol%, respectively. The syn gas

Table 4.3: Material balance and product gas composition for gasification of synthetic mixtures at 800°C using quartz packing with particle diameter 0.21-0.35mm.

Feed				Product liquid		Product gas			Char	Composition of product gas (mol%)				
Glycerol wt%	Steam wt%	Methanol wt%	KOH wt%	(g)	wt%	(L/g)	g	wt%	(g/g of organic mixutre)	H_2	CO	CO_2	CH_4	H_2+CO
50	50	-	-	-	-	1.71	1.1	94	0.05	58.9	30.3	4.4	4.8	89.2
-	-	100	-	-	-	2.4	2.7	98.9	0.01	65.7	32.1	1.1	1.16	97.7
65	-	35	-	0.3	16.5	1.63	1.5	80.8	0.03	57.1	34.1	3.9	3.6	91.2
60	10	30	-	0.1	6.6	1.66	1.5	90.9	0.03	54.4	34.6	4.3	4.85	89.0
60	7.5	31	1.5	0.2	8.3	1.48	2.1	88	0.04	52.0	29.8	7.7	8.8	81.8

production ranged between 88.9 to 91.1mol%. From this study, it is observed that the addition of steam to the mixture of glycerol and methanol had a significant effect on the product yield. Also, the addition of steam increased the volume of gas produced from 1.63L/g to 1.66L/g of mixture of glycerol and methanol.

Gasification of the mixture (glycerol, water, methanol and KOH) produced 88wt% of product gas, 52mol% of hydrogen and 29.8mol% of carbon monoxide. Probably, the addition of potassium hydroxide to the mixture of glycerol, methanol and water could have decreased the hydrogen and carbon monoxide production. Therefore, syn gas production decreased from 89 mol% to 81 mol% and H_2/CO was ~1.75. The production of char and liquid did not have a significant effect for the addition of potassium hydroxide to the mixture. The volume of gas produced decreased from 1.66L/g of mixture to 1.48L/g of mixture when potassium hydroxide is added to the mixture. With the addition of water, methanol and KOH to the glycerol did not have a significant effect on the production of hydrocarbons. Therefore, the calorific value of product gas ranged between 13.1 and 13.7MJ/m^3.

From the steam gasification of synthetic mixture study, it was observed that there is a strong potential that crude glycerol can be converted into value added products such as hydrogen or syn gas by optimizing the process parameters such as temperature, amount of steam and particle diameter of reactor packing.

4.5.2 Steam gasification of crude glycerol

To study the effects of steam gasification of crude glycerol at 800°C with packing of quartz particle of diameter 0.21-0.35mm, steam was added to crude glycerol in the weight ratio of 25:75 and 50:50. The gasification of crude glycerol (as obtained) was also carried out without adding excess water i.e., 92.5 wt% crude glycerol and 7.5wt% water. Material balance and composition of the product gas of the steam gasification of crude glycerol experiments are presented in Table 4.4.

From Table 4.4, it is observed that the production of product gas from gasification of glycerol increased from 78 to 91.1wt% when steam was increased from 7.5 to 50wt% in the crude glycerol. There was no liquid product obtained when crude glycerol was gasified at the steam to crude glycerol weight ratio of 50:50. Furthermore, the addition of steam had significant effect on the product gas composition. Hydrogen selectivity increased from 52 to 59mol% when the steam to crude glycerol weight ratio increased from 7.5:92.5 to 50:50. On the other hand, production of carbon monoxide decreased from 31 mol% to 19.7 mol% due to water gas shift reaction. Syn gas production decreased from 83 mol% to 79 mol% when steam was added to the glycerol.

From Table 4.4, it is observed that the volume of the product gas increased from 1.33L/g to 1.57L/g of crude glycerol fed. This increase in volume was due to the increase in steam to glycerol weight ratio. And the crude glycerol was completely gasified to gaseous product when the steam to glycerol weight ratio was 50:50 wt%. There was no significant change in the composition of product gas during the steam gasification of synthetic mixture and crude glycerol (60 wt% glycerol; 31 wt%; methanol; 1.05 wt% KOH and 7.5 wt% water) processes. There was, however, a significant change in the product yield in the steam gasification of crude glycerol when compared to steam gasification of synthetic mixture. The gaseous product yield decreased from 88wt% to 78wt% and thereby increasing the liquid product yield from

Table 4.4: Material balance and product gas composition for gasification of crude glycerol at 800°C using quartz particle of diameter 0.21-0.35mm.

Feed		Product liquid		Product gas			Char	Composition of Product gas (mol%)				
Water wt%	Crude Glycerol wt%	(g)	wt%	(L/g)	(g)	wt%	(g/g of crude glycerol)	H_2	CO	CO_2	CH_4	H_2+CO
7.5	92.5	0.45	15.9	1.33	2.22	78.1	0.08	52.1	31.2	5.1	9.5	83.3
25	75	0.13	9.8	1.46	1.12	81.6	0.07	57.3	22.1	4.7	12.4	79.4
50	50	-	-	1.57	0.81	91.1	.04	59.1	19.7	6.	11.5	79.1

8.3 to 15.9wt% when compared with steam gasification of a synthetic mixture of glycerol. The volume of gas produced in steam gasification of a synthetic mixture was 1.48L/g glycerol and methanol which is more than the volume of gas produced in steam gasification of crude glycerol (1.33L/g of mixture of glycerol and methanol in crude).

4.6 LIQUID PRODUCT ANALYSIS

Acetaldehyde, acetone, methanol, ethanol, water and acetic acid were the major liquid products obtained during the pyrolysis of glycerol carried out over the temperatures 650^{o}C, 750^{o}C and 800^{o}C (see Table 4.5). Acrolein and unreacted glycerol were also found in the liquid product for the pyrolysis runs at 650^{o}C and 750^{o}C. Acetaldehyde, methanol and acrolein could have formed by the radical mechanism as reported by Buhler et al. (2002) and Antal et al. (1985). Reaction pathways for the formation of acetaldehyde and acrolein were shown in equations 2.3 and 2.4, respectively. It is observed from Table 4.5, the water was one of the liquid products in the pyrolysis of glycerol. Water content in the liquid product was analyzed using Karl-Fischer titrator. Amount of water produced during the pyrolysis reaction increased from 38 wt% at 650^{o}C to 97 wt% 800^{o}C. It is in agreement with the Buhler et al. (2002) and Antal et al. (1985) findings.

Liquid products from the steam gasification of glycerol process with the weight ratio of steam to glycerol of 10:90 and 50:50 were analyzed and presented in Table 4.5. Amount of water in the liquid product during steam gasification of glycerol was in the range of 98 to 99.5 wt%. However, a trace amount of methanol and acetic acid was produced during the steam gasification reactions.

Table 4.5: Components present in the liquid product in the pyrolysis and steam gasification processes.

Pyrolysis at 650^{o}C, 50mL/min, 3-4mm Quartz chips	Pyrolysis at 750^{o}C, 50mL/min, 3-4mm Quartz chips	Pyrolysis at 800^{o}C, 50mL/min, 3-4mm Quartz chips	Steam gasification at 800^{o}C, 0.21-0.35mm Quartz chips, wt ratio 10:90	Steam gasification at 800^{o}C, 0.21-0.35mm Quartz chips, wt ratio 50:50
Formaldehyde	Formaldehyde			
Acetaldehyde	Acetaldehyde	Acetaldehyde		
Propanal	Propanal			
Acetone	Acetone	Acetone	Acetone	
Acetic acid, methyl ester	Acetic acid, methyl ester			
Acrolein	Acrolein			
Methanol	Methanol	Methanol	Methanol	Methanol
Ethanol	Ethanol	Ethanol		
Water (38 wt%)	Water (74 wt%)	Water (97 wt%)	Water (98 wt%)	Water (99.5 wt%)
Allyl acohol		Acetic acid	Acetic acid	Acetic Acid
Acetic acid	Acetic acid			
Propanoic acid	Propanoic acid			
Glycerol	Glycerol			

4.7 NET ENERGY RECOVERY

The energy balance calculations for pyrolysis and steam gasification of glycerol are shown in Appendix E1 and E2 respectively. The assumption made in calculating energy balance was that one mole of glycerol would be converted into 4 moles of hydrogen and 3 moles of carbon monoxide at 800^{o}C, 50 mL/min of nitrogen flow and 70mm of packing bed height of quartz particle of diameter 0.21mm-0.35mm. Energy supplied to crack one mole of glycerol during the pyrolysis reaction was 547.4 kJ (see Appendix E). One mole of hydrogen will have the heating value of 282.4 kJ. If hydrogen selectivity for this reaction is 100%, then output heat energy will be 1129.6 kJ. The net heat energy recovered will be 582.22 kJ/mol of glycerol fed.

Hydrogen production during the pyrolysis reaction at 800^{o}C, 50 mL/min of nitrogen flow and 70mm of packing bed height of quartz particle of diameter 0.21mm-0.35mm was 2.33 moles/mole of glycerol fed. Therefore, the heating value of the produced hydrogen during pyrolysis reaction was 658.56 kJ. The net energy recovered was 111.18 kJ/mol of glycerol fed. For the breakeven value of energy, the minimum hydrogen yield should be 1.94 moles of hydrogen/mol of glycerol fed.

The total energy input to heat one mole of glycerol and 5.2 mol of water in steam (50:50 steam to glycerol weight ratio) gasification process at 800^{o}C and 70mm of packing bed height of quartz particle of diameter 0.21mm-0.35mm was 910.2 kJ. The hydrogen produced during steam gasification of glycerol was 3.64 moles/mole of glycerol fed. Therefore, the heating value of the produced hydrogen during this reaction was 1027.35 kJ. The net energy recovered was 117.19 kJ/mol of glycerol fed.

5. CONCLUSIONS AND RECOMMENDATIONS

In this chapter, conclusions derived from the pyrolysis and steam gasification of pure and crude glycerol processes are reported. Also, recommendations for the further studies in converting glycerol into value-added chemicals are reported in this chapter.

5.1 CONCLUSIONS

1 The optimum conditions to produce maximum gas yield (71wt%), volume of gas (1.32L/g of glycerol), syn gas composition (93mol%) and minimum amount of char (8.1wt%) and liquid (21.9wt%) in pyrolysis of glycerol process were at 800°C, 50mL/min of nitrogen and quartz packing with the particle diameter 0.21-0.35mm.

2 Glycerol was completely converted to gas which was mostly syn gas of 93mol% (mole ratio of H_2/CO is 2) and a small amount of char when 50:50 weight ratio of steam to glycerol was used with the quartz packing of particle diameter of 0.21-0.35mm at 800°C. The addition of steam enhanced the gasification of glycerol process to produce large volume of gas and hydrogen yield.

3 The crude glycerol was completely gasified into gaseous product when the steam to crude glycerol weight ratio of 50:50 was used at 800°C with quartz packing having particle diameter of 0.21-0.35mm. The gas product yield and synthesis gas production was 91.1wt% and 79mol% respectively. There was no significant

change in the product gas composition for the steam gasification synthetic mixture and crude glycerol.

4 Net energy recovered from pyrolysis and steam gasification processes were 111.7 kJ/mole of glycerol fed and 117 kJ/ mole of glycerol, respectively. Thus, the present study shows that there is a strong potential for making syn gas, methane, ethylene, and high-heating value gas from the pyrolysis of glycerol.

5 Overall conclusion from this research is that a waste by-product glycerol from biodiesel production can be completed converted to gaseous products such as hydrogen or syn gas and medium heating value gas in the range of 21MJ/m^3-13.9 MJ/m^3.

5.2 RECOMMENDATIONS

1 Steam gasification of glycerol using nickel supported on alumina would be the ideal catalyst for producing hydrogen rich synthesis gas.

2 Thermal cracking of glycerol using HZSM-5, Y-zeolite and γ-alumina catalysts should be performed to get other value added products such as acrolein, 1,3-propanediol and methanol etc.,

3 Char yield can be reduced by using fluidized bed reactor. Fluidized bed reactor would help in uniform heat transfer and increases the gas yield.

4 Cost estimation and feasibility study of the present work should be carried out.

5 Steam gasification of crude glycerol can be performed after distilling methanol from the crude because methanol can be reused for the transesterification process.

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7. APPENDICES

Appendix – A: Calibration of Mass flow meter, LDC analytical pump, HP5890 GC and HP5880 GC

Appendix A1: Calibration of mass flow meter

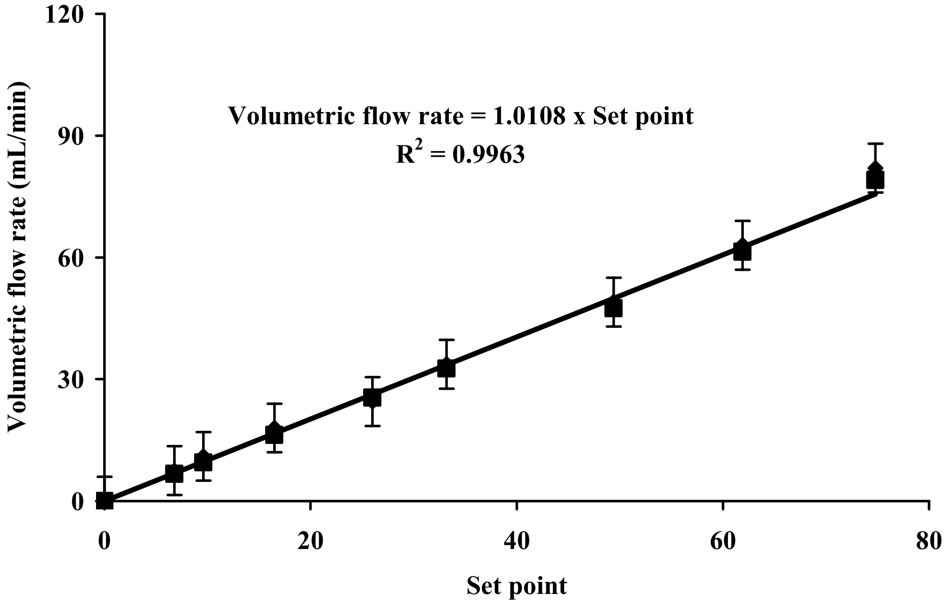

Figure A1: Calibration of Mass flow meter.

Appendix A2: Calibration of LDC analytical pump

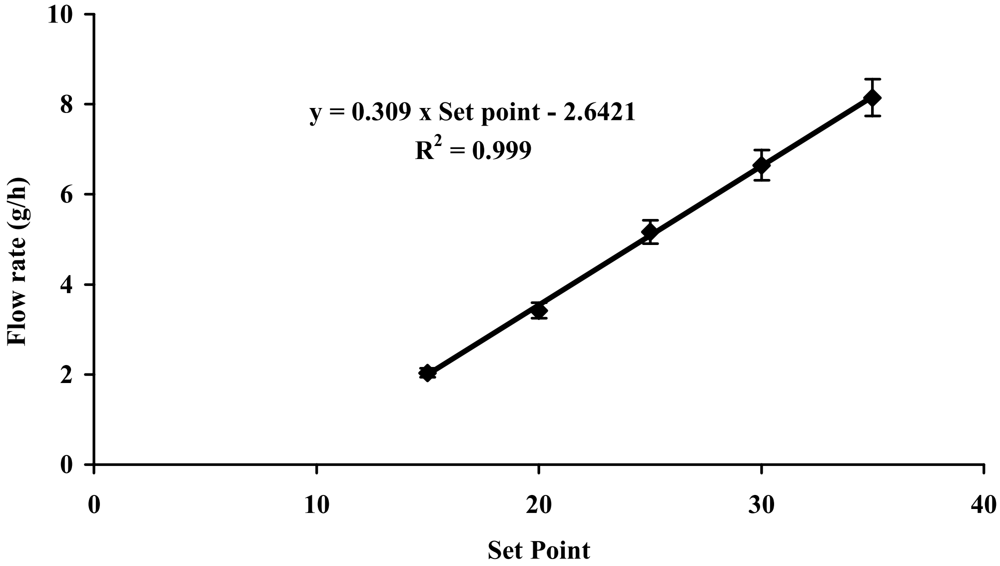

Figure A2: Calibration of LDC pump for glycerol.

Appendix A3: HP 5890 GC and HP 5880 GC Calibration Curves for the Gaseous Product

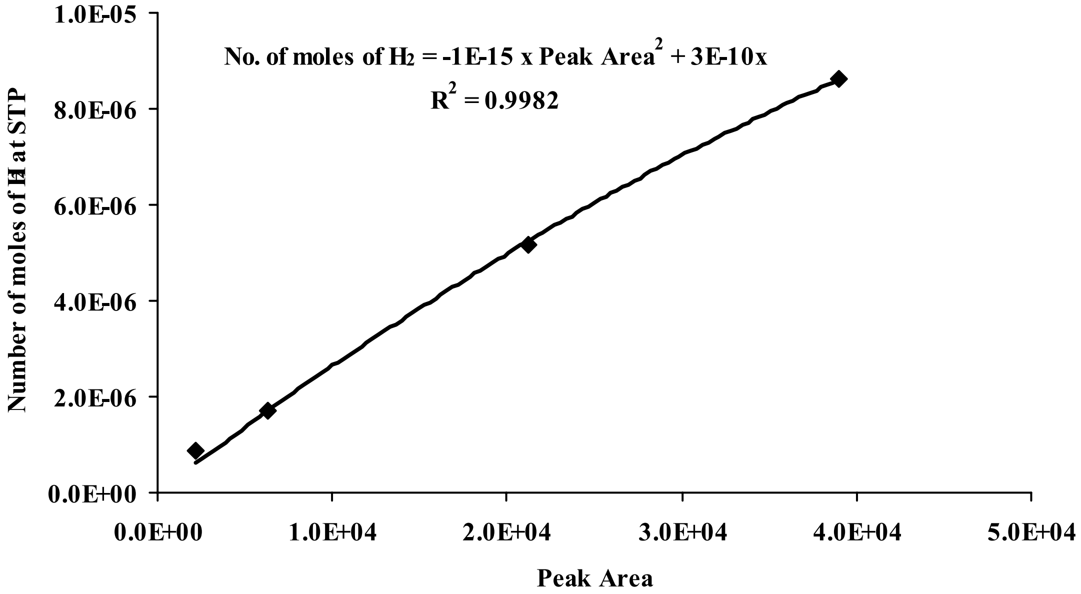

Figure A3.1: Calibration curve for hydrogen.

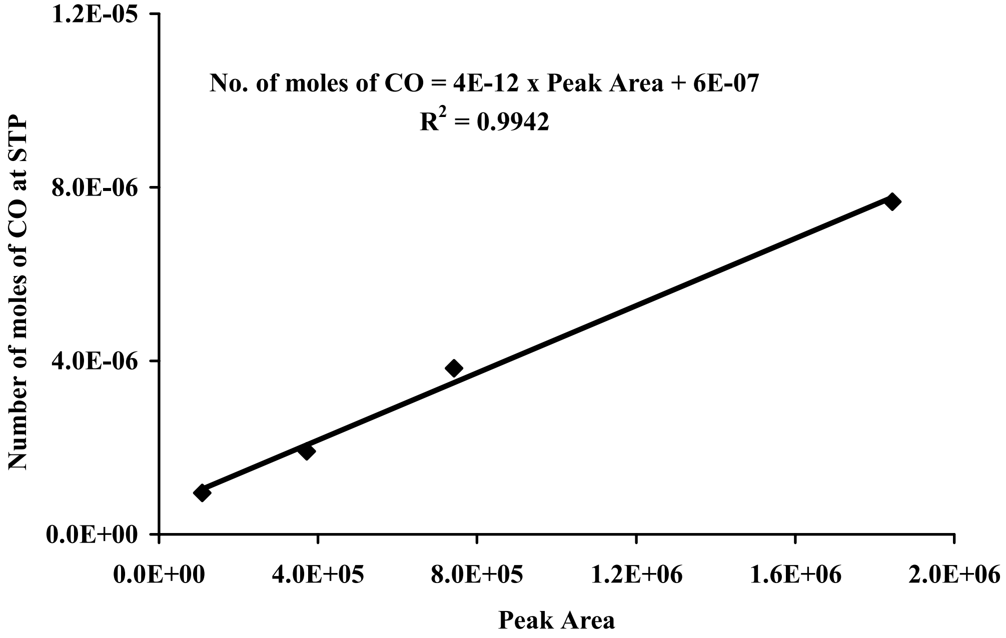

Figure A3.2: Calibration curve for carbon monoxide.

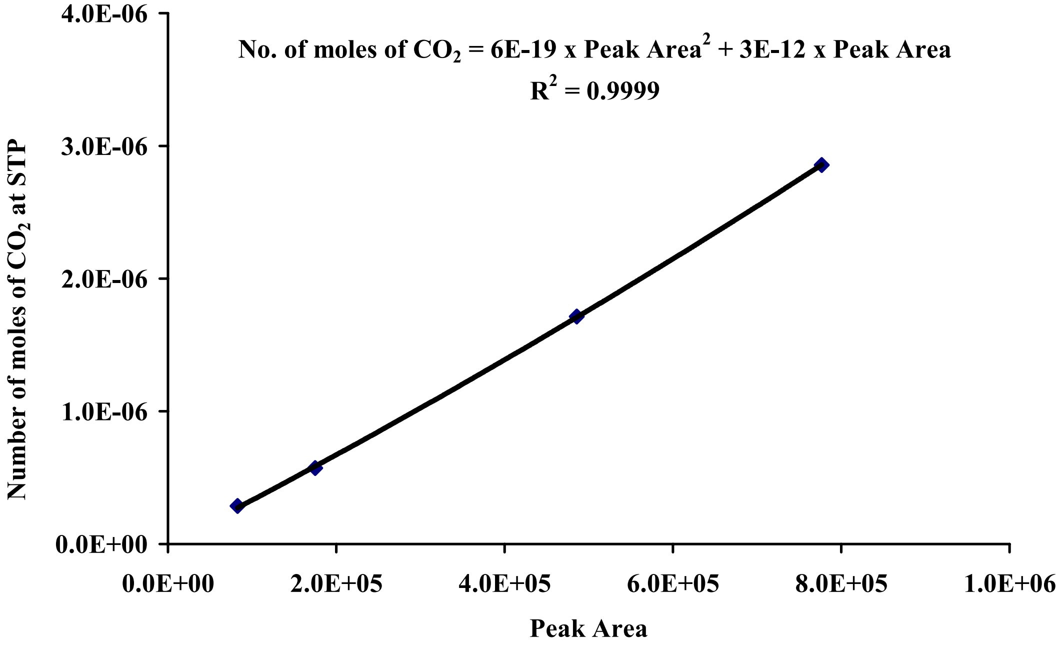

Figure A3.3: Calibration curve for carbon dioxide.

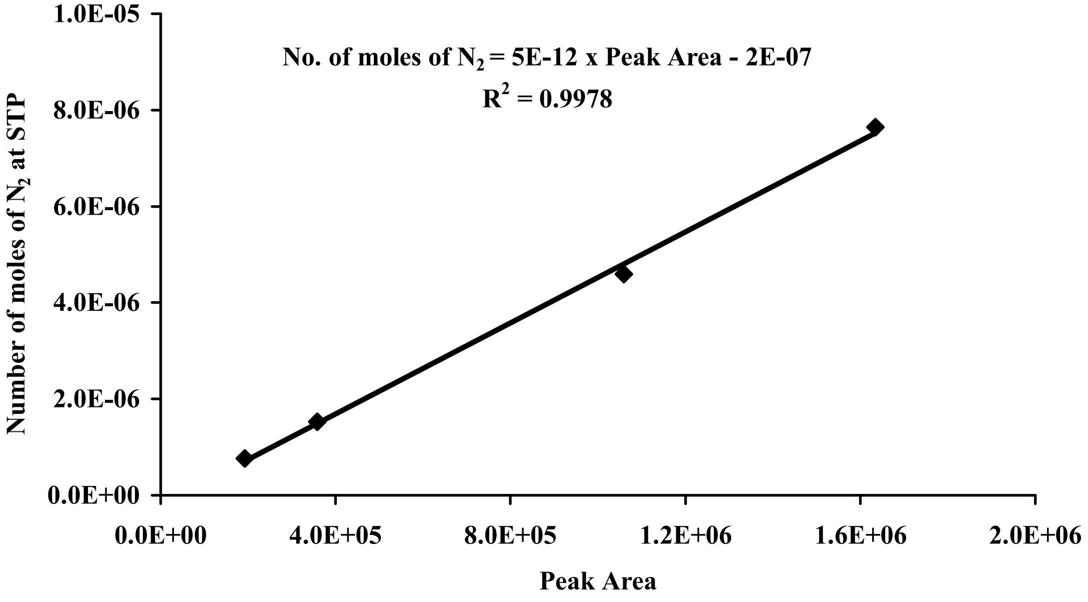

Figure A3.4: Calibration curve for nitrogen.

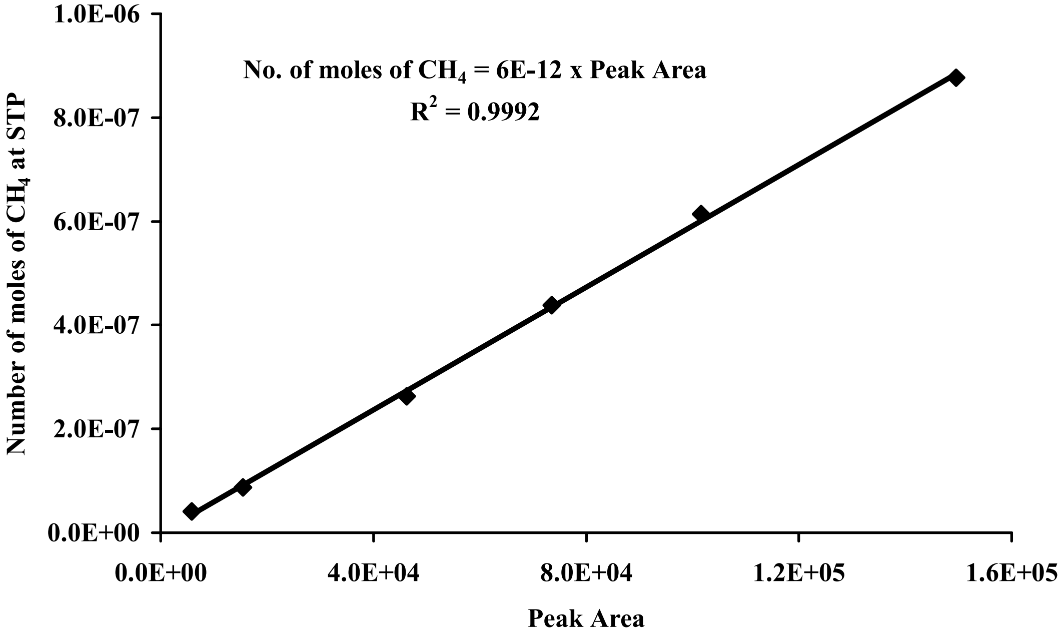

Figure A3.5: Calibration curve for methane.

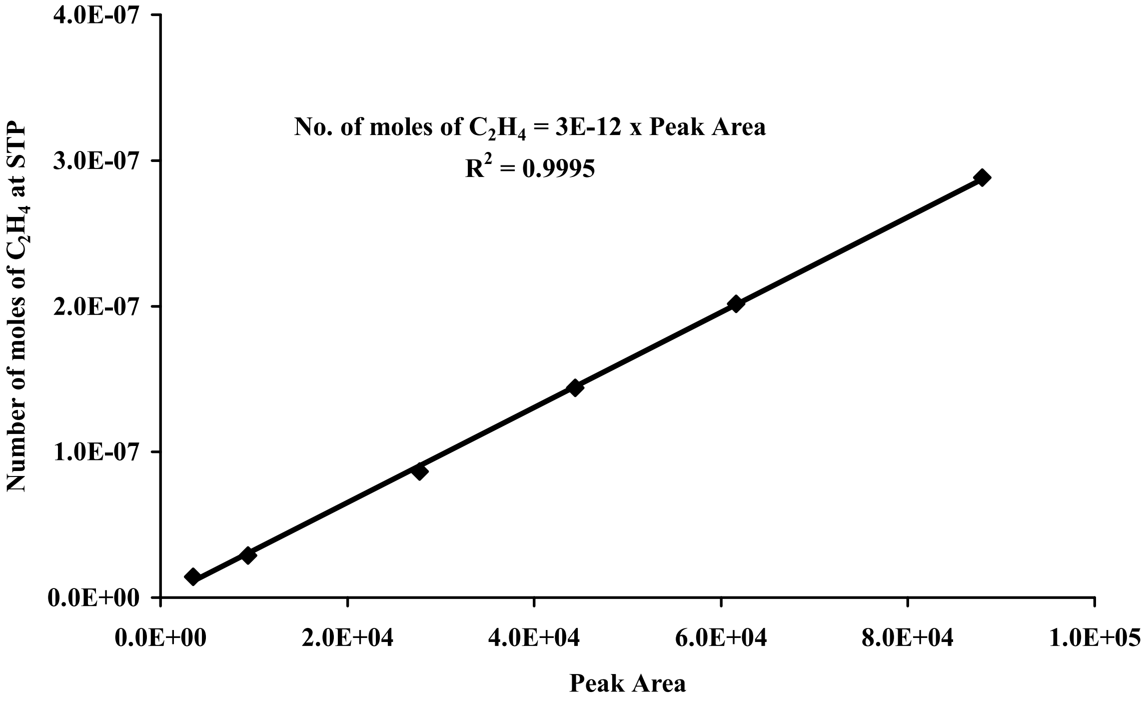

Figure A3.6: Calibration curve for ethylene.

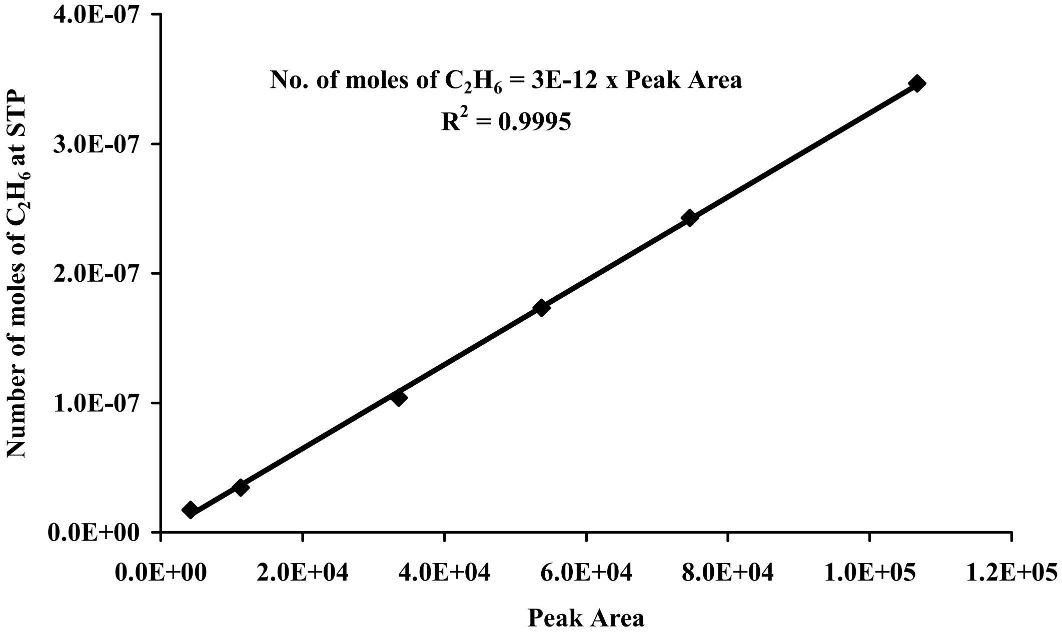

Figure A3.7: Calibration curve for ethane.

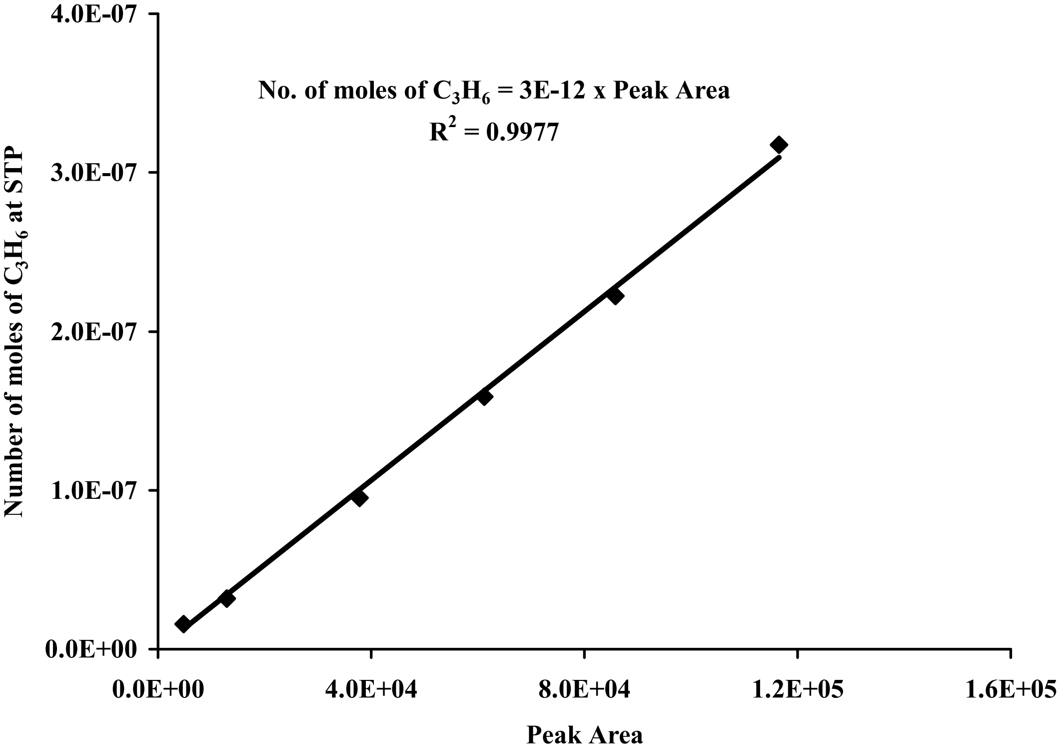

Figure A3.8: Calibration curve for propylene.

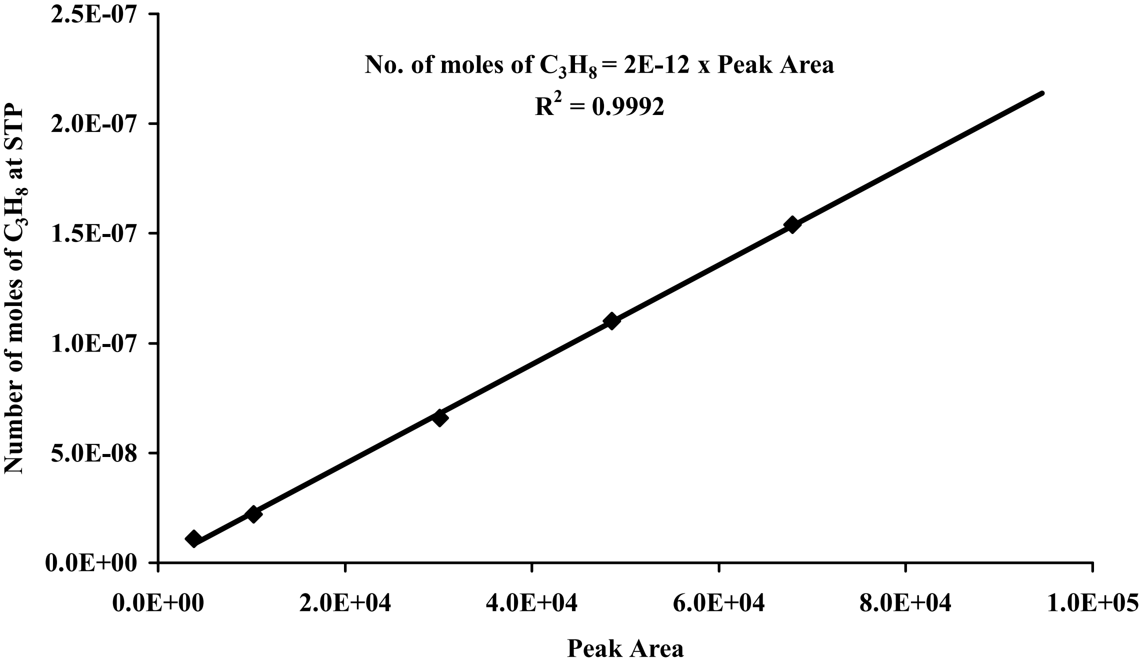

Figure A3.9: Calibration curve for propane.

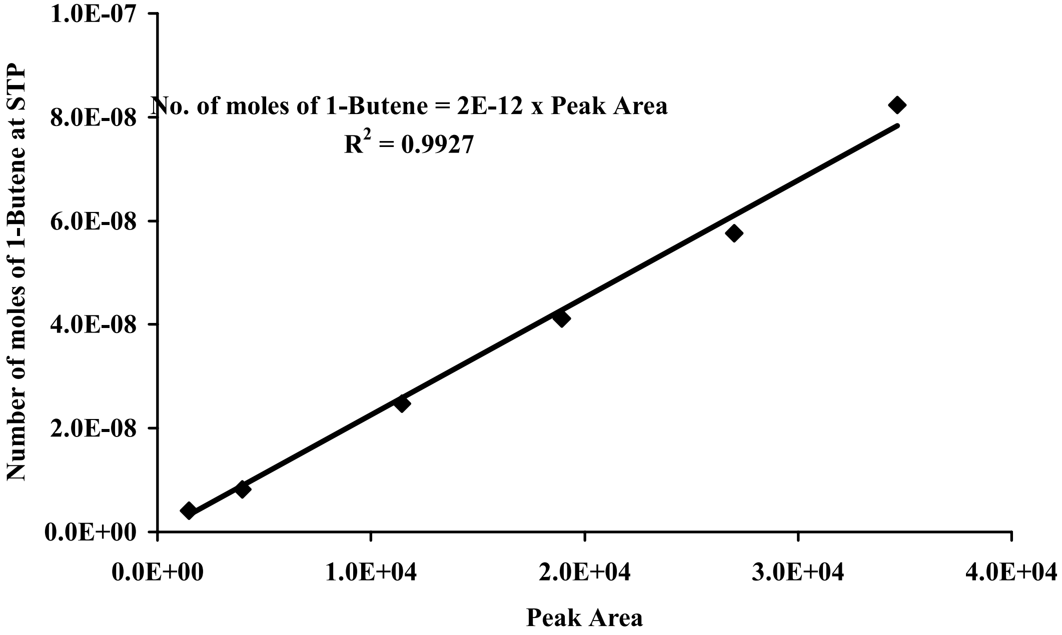

Figure A3.10: Calibration curve for 1-butene.

Appendix – B: Residence Time Calculations, Porosity and Permeability of the Packed Bed

Appendix – B1: Residence Time Calculations

Assumptions for calculating residence time of the reactant in the pyrolysis process :

1. Residence time of the reactant was calculated based on the flow rate of carrier gas
2. Reactor bed volume was calculated on the basis of empty bed

Height of the bed = 70mm

Radius of the reactor = 5.25mm

Volume of the reactor = $6058 mm^3$

Example

Volumetric flow rate of nitrogen = 30mL/min

At T = 800^oC, Volumetric flow rate of nitrogen = (30*800)/273 = 87.91 mL/min

Residence time t = Volume of the bed / Volumetric flow rate (s)

Table B1.1: Residence time of the reactant during pyrolysis process

Carrier gas flow rate mL/min	Residence time s
30	4.1
50	2.5
70	1.8

Assumptions for calculating residence time of the reactant in the steam gasification process:

1. Residence time of the reactant was calculated based on the flow rate of steam
2. Reactor bed volume was calculated on the basis of empty bed

Volume of the reactor = $6058 mm^3$

Example

Steam to Glycerol weight ratio = 10:90

0.27gms of steam/30 min was pumped into the reactor

Specific volume of the water at 800°C and atm pressure = 4.8872m^3/kg

Volumetric flow rate of steam = 43980 mm^3/min

Residence time = 8s

Table B1.2: Residence time of the reactant during steam gasification process

Steam to glycerol weight ratio	Residence time s
10:90	8
25:75	3
50:50	1.7

Appendix – B2: Porosity of the reactor bed

The porosity of the reactor bed is the ratio of void volume of the packing material to the total volume of the bed including void volume. Usually porosity is given in the percentage. Measurement of porosity with different particles of the packing material is explained below.

A dry graduated cylinder was filled with the desired particle size of the packing material to the known volume (V_s). An empty beaker was weighed and filled with water. Again, the beaker was weighed with water to calculate the weight of the water. From the weight of the water, the volume of water (V_1) can be calculated by keeping the density of the water as 1g/mL. Water was poured into the measuring cylinder up to the top surface of the packing material. If the water crosses the height of the bed, the above procedure should be repeated to maintain the level of the water. The beaker containing the water was weighed again to measure the volume of the water (V_2). Void volume of the bed (V_o) was calculated by (V_1-V_2). Percentage of the porosity of the reactor bed can be calculated by the following formula.

Porosity (%) of the reactor bed $\varepsilon = (V_o/V_s) \times 100$.

Porosity of the reactor bed packed with different particle size of the packing material is given in the Table B2

Appendix - B3: Permeability of the packed bed

Presence of the packing material in the reactor creates resistance to the reactant flow. It is more difficult for the reactant to flow in a packed bed than in an open tube. Resistance to the flow in a packed bed can be defined as permeability (B_o). B_o is usually given in units of cm^2. Permeability of the packed bed with different particle diameter of the packing material is given Table B2.

$$B_o = d_p^2 \times \varepsilon^2/(180 \times (1-\varepsilon)^2)$$

where
d_p – diameter of the particle, cm
ε – porosity of the packed bed

Table B2: Porosity and permeability of the packed bed with different particle size of the packing material

Packing material	Particle size mm	Porosity (ε) (%)	Permeability (B_o) cm^2
Quartz	0.21-0.35	44	$8.5*10^{-7}$
Quartz	0.6-0.71	60	$3.2*10^{-5}$
Quartz	3.0-4.0	75	$4.6*10^{-3}$
SiC	0.15	49	$5.7*10^{-7}$
SiC	0.21	54.5	$1.9*10^{-6}$
SiC	0.71	61.7	$4.5*10^{-5}$
SiC	1.0	65	$1.2*10^{-4}$
Ottawa sand	0.21-0.35	35	$4.4*10^{-7}$
Ottawa sand	0.6-0.71	40	$4.2*10^{-6}$
Ottawa sand	1-1.15	55	$4.6*10^{-5}$

Appendix – C: Sample Calculations for Mass Balance

Pyrolysis of glycerol

The calculations are based on the data collected for experimental Run#04

Feed:

Glycerol = 2.67g

Mass balance calculations:

Total volume of gas collected excluding nitrogen = 3.08L

Gas analysis from GC

Volume of gas injected into GCs was 500µL. Table C1 represents the calculations for the gas composition and weight of the product gas.

Table C1: Calculations for the product gas composition and weight

Components	Peak area from GCs	Number of moles in 500µL	Total Number of moles in 3.08L	mol% (excluding N_2)	Weight g
H_2	17687	5.4E-06	0.0515	48	0.10
CO	1030954	5.1E-06	4.88E-02	45.4	1.37
CO_2	35313	8.8E-08	8.39E-04	0.8	0.04
CH_4	239800	4.0E-07	0.0037	3.5	0.06
C_2H_4	350750	2.4E-07	0.0023	2.2	0.07
C_2H_6	39127	8.6E-09	8.15E-05	0.1	0.0
C_3H_6	30058	9.8E-09	9.31E-05	0.1	0.0
C_3H_8	0	0.0E+00	0.00E+00	0.0	0.0
1-Butene	9729	3.6E-09	3.431E-05	0.03	0.0
Nitrogen	1490875	7.9E-06	0.0749		
Total number of moles		1.9E-05	0.1824	100%	
Total number of moles excluding nitrogen			0.1075	**Total weight**	1.64

Calculations for finding calorific value of the product gas:

Calorific value of the ideal gas in MJ/m^3 can be calculated from the mole fractions at 15°C and atm pressure. The ideal gas calorific value is given by (Wrobel and Wirght, 1978)

$CV = x_1*CV_1 + x_2*CV_2 + \ldots\ldots\ldots\ldots$

where x_1, x_2….. are mol fractions, CV_1,CV_2………. are the calorific values. Calorific value of the product gas is presented in the Table C2

Table C2: Calculations for the calorific value of product gas

Components	Calorific value at 15°C and atm pressure MJ/m^3	Mole fractions	Calorific value MJ/m^3
H_2	12.1	48	7.13
CO	11.97	45.4	3.62
CH_4	37.71	3.5	1.82
C_2H_4	59.72	2.2	0.75
C_2H_6	66.07	0.1	0.19
C_3H_6	87.09	0.1	0.9
C_3H_8	93.94	0.0	0
1-Butene	114.98	0.03	0
		Total	13.5

Weight of the liquid product collected in the condenser = 0.638 g

Weight of the char collected in the reactor = 0.18 g

Weight of the product gas = 1.64 g

Total product = 2.46 g

Mass balance = [(input-output)/input] * 100 = [(2.67-2.46)/2.67] * 100 = 91.9%

Appendix – D: Experimental Results

	Run01	**Run02**	**Run03**	**Run04**	**Run05**
Packing material	Quartz	Quartz	Quartz	Quartz	Quartz
Size (mm)	3.0-4.0	3.0-4.0	3.0-4.0	3.0-4.0	3.0-4.0
Run time (min)	30	30	30	30	30
Reaction temperature (^oC)	800	800	800	800	800
Reactant flow rate (g/h)	5.4	5.4	5.4	5.4	5.4
Crude glycerol	No	No	No	No	No
Glycerol in feed (g)	2.67	2.67	2.67	2.67	2.67
Water in feed (g)	0	0	0	0	0
Methanol in feed (g)	0	0	0	0	0
Potassium hydroxide in feed (g)	0	0	0	0	0
Nitrogen flow rate (mL/min)	30	30	50	50	70
Steam to glycerol (wt ratio)	N/A	N/A	N/A	N/A	N/A
Product gas (mol%)					
H_2	47.4	46.1	48.6	48.0	38.6
CO	43.6	44.8	44.9	45.4	52.2
CO_2	1.1	1.2	1.0	0.8	0.7
CH_4	4.7	4.7	3.3	3.5	4.6
C_2H_4	2.8	2.9	2.0	2.2	3.6
C_2H_6	0.2	0.2	0.1	0.1	0.1
C_3H_6	0.1	0.1	0.1	0.1	0.1
C_3H_8	0.0	0.0	0.0	0.0	0.0
1-Butene	0.0	0.0	0.0	0.0	0.1
Total product gas (moles)	0.107	0.104	0.108	0.108	0.09
Calorific value (MJ/m^3)	14.5	14.6	13.7	13.9	14.9
Volume of gas(L/g)	1.12	1.08	1.15	1.15	1.05
Products yield (g)					
Gas	1.64	1.61	1.64	1.64	1.62
Liquid	0.58	0.58	0.58	0.64	0.74
Char	0.21	0.2	0.18	0.18	0.1
Product yield (wt%)					
Gas	67.6	67.4	66.6	66.7	65.7
Liquid	23.7	24.3	26.1	26	29
Char	8.7	8.3	7.3	7.3	4.1
Mass balance (wt%)	90.8	89.5	91.7	91.9	92.3

	Run06	**Run07**	**Run08**	**Run09**	**Run10**
Packing material	Quartz	Quartz	Quartz	Quartz	Quartz
Size (mm)	3.0-4.0	3.0-4.0	3.0-4.0	3.0-4.0	0.6-0.71
Run time (min)	30	30	30	30	30
Reaction temperature (^oC)	800	650	700	750	800
Reactant flow rate (g/h)	5.4	5.4	5.4	5.4	5.4
Crude glycerol	No	No	No	No	No
Glycerol in feed (g)	2.67	2.67	2.67	2.67	2.67
Water in feed (g)	0	0	0	0	0
Methanol in feed (g)	0	0	0	0	0
Potassium hydroxide in feed (g)	0	0	0	0	0
Nitrogen flow rate (mL/min)	70	50	50	50	50
Steam to glycerol (wt ratio)	N/A	N/A	N/A	N/A	N/A
Product gas (mol%)					
H_2	41.5	16.9	22.1	27.7	50.7
CO	49.9	54.0	50.0	45.7	41.3
CO_2	0.6	0.2	0.0	1.1	1.2
CH_4	4.7	14.2	14.5	14.1	3.1
C_2H_4	3.2	10.1	9.6	9.1	2.1
C_2H_6	0.1	2.2	2.0	1.5	1.1
C_3H_6	0.1	2.4	1.7	0.8	0.6
C_3H_8	0.0	0.0	0.0	0.0	0.0
1-Butene	0.1	0.1	0.1	0.0	0.0
Total product gas (moles)	0.1	0.030	0.052	0.076	0.115
Calorific value (MJ/m^3)	14.7	21.4	21.2	20.6	14.17
Volume of gas (L/g)	1.07	0.41	0.61	0.85	1.19
Products yield (g)					
Gas	1.68	0.68	1.08	1.5	1.7
Liquid	0.75	1.66	1.2	0.8	0.62
Char	0.1	0.08	0.11	0.14	0.2
Product yield (wt%)					
Gas	66.4	28.1	45.2	60.8	67.7
Liquid	29.6	68.7	50.1	33.4	24.4
Char	4	3.3	4.7	5.8	7.9
Mass balance (wt%)	95.4	91.5	89.2	91.2	92.3

	Run11	**Run12**	**Run13**	**Run14**	**Run15**
Packing material	Quartz	SiC	SiC	SiC	SiC
Size (mm)	0.21-0.35	1	0.71	0.21	0.15
Run time (min)	30	30	30	30	30
Reaction temperature (^oC)	800	800	800	800	800
Reactant flow rate (g/h)	5.4	5.4	5.4	5.4	5.4
Crude glycerol	No	No	No	No	No
Glycerol in feed (g)	2.67	2.67	2.67	2.67	2.67
Water in feed (g)	0	0	0	0	0
Methanol in feed (g)	0	0	0	0	0
Potassium hydroxide in feed (g)	0	0	0	0	0
Nitrogen flow rate (mL/min)	50	50	50	50	50
Steam to glycerol (wt ratio)	N/A	N/A	N/A	N/A	N/A
Product gas (mol%)					
H_2	55.4	39.6	40.2	42.6	49.7
CO	36.9	40.2	40.1	39.5	44.0
CO_2	1.9	1.0	0.8	0.8	1.3
CH_4	3.1	10.3	10.2	9.6	3.2
C_2H_4	1.9	7.2	6.9	5.6	1.6
C_2H_6	0.8	1.0	1.1	1.3	0.1
C_3H_6	0.0	0.6	0.7	0.6	0.0
C_3H_8	0.0	0.0	0.0	0.0	0.0
1-Butene	0.0	0.0	0.0	0.0	0.0
Total product gas (moles)	0.13	0.110	0.12	0.12	0.12
Calorific value (MJ/m^3)	13.9	18.5	18.3	17.7	13.5
Volume of gas (L/g)	1.32	1.18	1.2	1.23	1.28
Products yield (g)					
Gas	1.74	1.89	1.9	1.9	1.8
Liquid	0.5	0.6	0.56	0.51	0.4
Char	0.2	0.1	0.1	0.1	0.15
Product yield (wt%)					
Gas	71.2	73	75.1	76.3	77.6
Liquid	20.5	23	21.2	19.98	16
Char	8.2	3.7	3.6	3.7	6.4
Mass balance (wt%)	89.7	98	98	92.9	92.1

	Run16	**Run17**	**Run18**	**Run19**	**Run20**
Packing material	Sand	Sand	Sand	Quartz	Quartz
Size (mm)	1.0-1.15	0.6-0.71	0.20-0.35	0.2-0.35	0.2-0.35
Run time (min)	30	30	30	30	30
Reaction temperature (^oC)	800	800	800	800	800
Reactant flow rate (g/h)	5.4	5.4	5.4	5.4	5.4
Crude glycerol	No	No	No	No	No
Glycerol in feed (g)	2.7	2.7	2.7	2.39	2
Water in feed (g)	0	0	0	0.27	0.67
Methanol in feed (g)	0	0	0	0	0
Potassium hydroxide in feed (g)	0	0	0	0	0
Nitrogen flow rate (mL/min)	50	50	50	0	0
Steam to glycerol (wt ratio)	N/A	N/A	N/A	10:90	25:75
Product gas (mol%)					
H_2	40.3	45.1	46.6	61.9	64.0
CO	42.3	42.6	42.5	30.2	29.3
CO_2	1.9	2.2	1.7	1.6	2.4
CH_4	9.8	6.3	5.3	4.7	3.6
C_2H_4	4.3	3.6	3.0	1.2	0.5
C_2H_6	1.4	0.1	1.0	0.4	0.2
C_3H_6	0.1	0.1	0.0	0.1	0.0
C_3H_8	0.0	0.0	0.0	0.0	0.0
1-Butene	0.0	0.0	0.0	0.0	0.0
Total product gas (moles)	0.105	0.120	0.12	0.14	0.13
Calorific value (MJ/m^3)	17.1	15.1	15.1	13.8	13
Volume of gas (L/g)	1.11	1.21	1.22	1.51	1.65
Products yield (g)					
Gas	1.83	1.85	1.88	1.62	1.45
Liquid	0.75	0.64	0.57	0.36	0.14
Char	0.11	0.11	0.16	0.17	0.12
Product yield (wt%)					
Gas	68	70.9	71.9	75.3	84.8
Liquid	28.1	24.8	21.9	16.8	8.2
Char	3.9	7.2	6.1	7.9	6.99
Mass balance (wt%)	96.5	96	93.7	91.4	91.4

	Run21	**Run22**	**Run23**	**Run24**	**Run25**
Packing material	Quartz	SiC	SiC	SiC	Quartz
Size (mm)	0.2-0.35	0.15	0.15	0.15	0.2-0.35
Run time (min)	30	30	30	30	30
Reaction temperature (^oC)	800	800	800	800	800
Reactant flow rate (g/h)	5.4	5.4	5.4	5.4	5.4
Crude glycerol	No	No	No	No	No
Glycerol in feed (g)	1.31	0.03	0.69	1.33	0
Water in feed (g)	1.31	2.68	2.03	1.33	0
Methanol in feed (g)	0	0	0	0	2.75
Potassium hydroxide in feed (g)	0	0	0	0	0
Nitrogen flow rate (mL/min)	0	0	0	0	50
Steam to glycerol (wt ratio)	50:50	10:90	25:75	50:50	N/A
Product gas (mol%)					
H_2	58.9	50.6	57.8	54.1	65.7
CO	30.3	38.3	33.0	37.5	32.1
CO_2	4.4	0.8	1.1	1.1	1.1
CH_4	4.8	6.6	5.3	4.7	1.2
C_2H_4	1.3	3.3	2.4	2.3	0.0
C_2H_6	0.3	0.3	0.2	0.3	0.0
C_3H_6	0.1	0.1	0.1	0.1	0.0
C_3H_8	0.0	0.0	0.0	0.0	0.0
1-Butene	0.0	0.0	0.0	0.0	0.0
Total product gas (moles)	0.09	0.130	0.11	0.07	0.25
Calorific value (MJ/m^3)	13.5	15.4	14.6	14.3	12.22
Volume of gas (L/g)	1.71	1.23	1.33	1.4	2.4
Products yield (g)					
Gas	1.11	1.83	1.32	1	2.7
Liquid	0	0.41	0.24	0.05	0
Char	0.07	0.19	0.12	0.07	0.03
Product yield (wt%)					
Gas	94	75.2	78.6	89.5	98.9
Liquid	0	17	14.3	4.2	0
Char	6	7.8	7.1	6.3	1.1
Mass balance (wt%)	95	90.8	86.8	92.3	99

	Run26	**Run27**	**Run28**	**Run29**	**Run30**
Packing material	Quartz	Quartz	Quartz	Quartz	Quartz
Size (mm)	0.2-0.35	0.2-0.35	0.2-0.35	0.2-0.35	0.2-0.35
Run time (min)	30	30	30	30	30
Reaction temperature (^{o}C)	800	800	800	800	800
Reactant flow rate (g/h)	5.4	5.4	5.4	5.4	5.4
Crude glycerol	No	No	No	No	Yes
Glycerol in feed (g)	1.31	1.26	1.1	1.7	1.94
Water in feed (g)	1.31	0	0.18	0.21	0.24
Methanol in feed (g)	0	0.68	0.54	0.88	1
Potassium hydroxide in feed (g)	0	0	0	0.04	0.05
Nitrogen flow rate (mL/min)	0	50	0	0	0
Steam to glycerol (wt ratio)	50:50	N/A	10:60	10:60	7.5:91.5
Product gas (mol%)					
H_2	58.9	57.0	54.4	52.1	52.1
CO	30.3	34.1	34.5	29.8	31.2
CO_2	4.4	3.9	4.3	7.7	5.1
CH_4	4.8	3.6	4.9	8.8	9.5
C_2H_4	1.3	0.9	1.4	1.2	1.5
C_2H_6	0.3	0.3	0.5	0.5	0.6
C_3H_6	0.1	0.0	0.1	0.0	0.1
C_3H_8	0.0	0.0	0.0	0.0	0.0
1-Butene	0.0	0.0	0.0	0.0	0.0
Total product gas (moles)	0.09	0.110	0.1	0.15	0.16
Calorific value (MJ/m^3)	13.5	13.12	13.7	14.2	14.8
Volume of gas (L/g)	1.71	1.63	1.66	1.5	1.4
Products yield (g)					
Gas	1.11	1.5	1.5	2.1	2.22
Liquid	0	0.31	0.28	0.2	0.45
Char	0.07	0.05	0.04	0.09	0.17
Product yield (wt%)					
Gas	94	80.8	90.9	88.02	78.1
Liquid	0	16.5	6.6	8.27	15.9
Char	6	2.7	2.5	3.7	6
Mass balance (wt%)	95	95.5	98.4	93.4	95.6

	Run31	**Run32**	**Run33**
Packing material	Quartz	Quartz	Quartz
Size (mm)	0.2-0.35	0.2-0.35	0.2-0.35
Run time (min)	30	30	30
Reaction temperature (^{o}C)	800	800	800
Reactant flow rate (g/h)	5.4	5.4	5.4
Crude glycerol	Yes	Yes	Yes
Glycerol in feed (g)	1.6	1.33	1.3
Water in feed (g)	0.53	1.11	1.1
Methanol in feed (g)	0.13	0.69	0.68
Potassium hydroxide in feed (g)	0	0.03	0.03
Nitrogen flow rate (mL/min)	0	0	0
Steam to glycerol (wt ratio)	25:75	50:50	50:50
Product gas (mol%)			
H_2	57.3	59.6	59.7
CO	22.1	19.7	21.3
CO_2	4.7	6.0	5.0
CH_4	12.4	11.5	10.9
C_2H_4	2.6	2.4	2.4
C_2H_6	0.7	0.6	0.6
C_3H_6	0.2	0.2	0.2
C_3H_8	0.0	0.0	0.0
1-Butene	0.0	0.0	0.0
Total product gas (moles)	0.09	0.070	0.07
Calorific value (MJ/m^3)	16.3	15.7	15.7
Volume of gas (L/g)	1.47	1.63	1.66
Products yield (g)			
Gas	1.1	1.5	1.5
Liquid	0.13	0	0
Char	0.12	0.05	0.04
Product yield (wt%)			
Gas	81.5	91.05	90.9
Liquid	9.8	0	6.6
Char	8.7	8.9	9.8
Mass balance (wt%)	89.2	90.1	90.5

Appendix – E: Energy Balance Calculations for Hydrogen Production from Glycerol

Specific heat capacity, heat of formation and enthalpy of formation of components such as glycerol, water, hydrogen and carbon monoxide were taken from Chemical Properties Handbook, Yaws, 1999.

E1: Energy balance for the pyrolysis of glycerol process:

The energy calculations are based on the following thermal cracking of glycerol reaction in the absence of water and conditions

$C_3H_8O_3 \rightarrow 4H_2 + 3CO$

Feed at 25°C and Product at 800°C

Basis : 1 mol of glycerol in feed

Boiling temperature of glycerol is 290°C

Energy required to take liquid glycerol from 25°C to boiling temperature (290°C):

$$Q_1 = \int_{25}^{290} mC_p dT$$

$$Q_1 = 1 * \int_{25}^{290} (132.145 + 8.6007 * 10^{-1} T - 1.9745 * 10^{-3} T^2 + 1.8068 * 10^{-6} T^3) dT$$

$$Q_1 = 68.9kJ$$

Heat of vaporization (H_{vap}) of glycerol at 290°C is 66.13KJ/mol

Energy required to vaporize the liquid glycerol at 290°C

$$Q_2 = H_{vap} * 1mol = 66.13kJ$$

Energy required to take glycerol vapor from 290°C to 800°C

$$Q_3 = 1 * \int_{290}^{800} (9.656 + 4.2826 * 10^{-1} T - 2.6797 * 10^{-4} T^2 + 3.1794 * 10^{-8} T^3 + 2.7745 * 10^{-11} T^4) dT$$
$$Q_3 = 106.494 kJ$$

Total energy required for the feed at reaction temperature:

$Q_F = Q_1 + Q_2 + Q_3$

$Q_F = 241.52$ kJ

Calculation for the heat of reaction of the following reaction:

$C_3H_8O_3 \rightarrow 4H_2 + 3CO$

$$\Delta H_r(H_2) = 4 * (\Delta H_f(H_2) + \Delta C_p dT)$$
$$= 4 * (0 + \int_{25}^{800} (25.399 + 2.0178 * 10^{-2} T - 3.8549 * 10^{-5} T^2 + 3.1880 * 10^{-8} T^3 - 8.7585 * 10^{-12} T^4) dT)$$
$$= 89 kJ$$
$$\Delta H_r(CO) = 3 * (\Delta H_f(CO) + \Delta C_p dT)$$
$$= 3 * (-110.54 + \int_{25}^{800} (29.556 - 6.58 * 10^{-3} T + 2.013 * 10^{-5} T^2 - 1.2227 * 10^{-8} T^3 + 2.2617 * 10^{-12} T^4) dT)$$
$$= -262.21 KJ$$
$$\Sigma(\Delta H_r)_{products} = \Delta H_r(H_2) + \Delta H_r(CO) = -173.2 kJ$$

$$\Delta H_r(C_3H_8O_3) = 1 * (\Delta H_f(C_3H_8O_3) + \Delta C_p dT)$$
$$= 1 * (-582.8 + \int (9.656 + 4.2826 * 10^{-1} T - 2.6797 * 10^{-4} T^2 + 3.1794 * 10^{-8} T^3 + 2.7745 * 10^{-11} T^4) dT)$$
$$= -479.06 kJ$$
$$\Sigma(\Delta H_r)_{reac\tan t} = -479.06 kJ$$
$$(\Delta H_r)_{reaction} = Q_R = \Sigma(\Delta H_r)_{product} - \Sigma(\Delta H_r)_{reac\tan t} = 305.86 kJ$$

Total energy required for the reaction:

$Q = Q_F + Q_R = 547.38$ kJ

Energy Output

Heating value of H_2 = 282.24 kJ/mol

If hydrogen selectivity for the pyrolysis reaction is 100%

The total heating value of produced H_2 is

4*282.24 = 1129.6 kJ

The net energy gain is

1129.6-547.38=582.22 kJ/mol of glycerol reacted

Energy balance for the Run#11

Basis: Run time =1 h

Moles of glycerol fed = 5.43/92 = 0.06 moles

Moles of H_2 produced = 0.1422 moles

Therefore, 2.33 moles of H_2 produced from one mole of glycerol fed.

Heating value of the produced H_2 = 2.33*282.24 = 658.56kJ

Total energy input for the reaction = 547.38kJ

Net energy recovered = 658.56-547.38=111.18kJ/mol of glycerol fed

For the breakeven value of energy, the minimum hydrogen yield needed is:

547.38/282.24 = 1.94 moles H_2/mol of glycerol feed.

E2: Energy balance for the steam gasification of glycerol:

The energy calculations are based on the following steam gasification of glycerol reaction and conditions

$C_3H_8O_3 + 5.2H_2O \rightarrow 4H_2 + 3CO + 5.2H_2O$

Steam to glycerol weight ratio 50:50.

Feed at 25°C and product at 800°C.

Calculations shown here for the Run#21

Heat required for feed glycerol

$Q_{glycerol}$ = 241.52 kJ

Heat required for feed water

Boiling temperature of water is 100°C

Specific heat capacity of water = $75.5*10^{-3}$ kJ/(mol.K)

Energy required to take liquid water from 25°C to 100°C

$$Q_{w1} = mC_p dT = 5.2*75.4*10^{-3}*(100-25) = 29.41kJ$$

Heat of vaporization of water at 1 atm is 39.5 KJ/mol

$$Q_{w2} = m*H_{vap} = 205.4kJ$$

Energy required to take water vapor from 100°C to 800°C

$$Q_{w3} = m\int_{100}^{800} C_p dT$$

$$= 5.2*\int_{100}^{800}(33.933 - 8.4186*10^{-3}T + 2.9906*10^{-5}T^2 - 1.7825*10^{-8}T^3 + 3.693*10^{-12}*T^4)dT$$
$$= 127.98kJ$$

Total heat energy required for the feed water

$Q_{water}=Q_{w1}+Q_{w2}+Q_{w3}$=362.78kJ/mol of water fed

Assuming steam is not taking part of the reaction.

Total heat energy required for the feed water and glycerol in steam gasification process:

$Q_F = Q_{glycerol} + Q_{water}$ = 604.3 kJ

Total heat energy required for the reaction

$Q=Q_F+Q_R$= 604.3 + 362.78 = 910.16 kJ

Energy Output

Moles of glycerol fed = 1.31/92 = 0.014 moles

Moles of water fed = 1.31/18 = .073 moles

Moles of H_2 produced = 0.051 moles

Therefore, 3.64 moles of H_2 produced from one mole of glycerol fed.

Heating value of the produced H_2 = 3.64*282.24 = 1027.35kJ

Total energy input for the reaction = 910.16kJ

Net energy recovered = 1027.35-910.16=117.19kJ/mol of glycerol fed

For the breakeven value of energy, the minimum hydrogen yield needed is:

910.16/282.24 = 3.22moles H_2/mol of glycerol feed.