

THERMODYNAMIC ANALYSIS OF GLYCEROL DRY
REFORMING

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THERMODYNAMIC ANALYSIS OF GLYCEROL DRY REFORMING

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ANALISIS TERMODINAMIK GLISEROL MELALUI PEMBAHARUAN KARBON DIOKSIDA

ABSTRAK

Permintaan yang semakin meningkat untuk tenaga hidrogen memerlukan bahan-bahan mentah yang boleh diperbaharui untuk pengeluaran. Khususnya, pengeluaran bahan api alternatif seperti biodiesel dan etanol telah meningkat sejak beberapa tahun kebelakangan ini seterusnya output gliserol meningkat hasil sampingan daripada transesterifikasi. Oleh itu, menggunakan gliserol serta pengeluaran hidrogen adalah satu alternatif untuk meningkatkan pengeluaran biodiesel. Hidrogen dihasilkan dengan menggunakan beberapa proses seperti stim pembaharuan, pembaharuan autothermal, akueus fasa pembaharuan dan supergelling air pembaharuan. Sebelum ini, kajian lebih fokus dengan pengeluaran hidrogen melalui proses stim pembaharuan. Maka, kajian mengenai penghasilan hidrogen melalui gliserol dan karbon dioksida diperlukan untuk menghasilkan gas sintesis. Gliserol mempunyai atom karbon lebih daripada etanol, ia mungkin lebih cenderung untuk menghasilkan nanofilaments karbon (CNF) yang merupakan hasil sampingan yang berpotensi untuk dipasarkan. Penelitian ini mengkaji beberapa gas sintesis yang dihasilkan dalam jangka waktu analisis termodinamik seperti metana, karbon, hidrogen karbon dioksida, dan karbon monoksida. Analisis kajian dengan menggunakan gliserol dan karbon dioksida sebagai substrat dengan tujuan menghasilkan gas sintesis pada tekanan atmosfera, suhu 500-1000 Kelvin dan purata karbon gliserol yang berbeza. Kajian ini telah menghasilkan sintesis gas iaitu hidrogen sebanyak 1.5 mol, karbon monoksida 7.6 mol, karbon dioksida 5 mol, metana 1.5 mol dan karbon 3 mol.

THERMODYNAMIC ANALYSIS OF GLYCEROL DRY REFORMING

ABSTRACT

The growing demand for hydrogen energy requires renewable raw materials for its production. In particular, production of alternatives fuels such as biodiesel and ethanol has increased over the last few years culminating in increased glycerol output, a byproduct of transesterification. Due to the increased production of biodiesel, it is imperative to find alternative uses for glycerol such as for hydrogen production. Hydrogen is produced by using several processes such as steam reforming, autothermal reforming, aqueous-phase reforming and supercritical water reforming. Most of studies concern with hydrogen production via steam reforming process. To date, few works have been dedicated to produce hydrogen from glycerol dry reforming. Significantly, since glycerol has more carbon atoms than ethanol, it may be more likely to produce carbon nanofilaments (CNF) which is a potential marketable byproduct. This research reviews the several of synthesis gas produced in term of thermodynamic analysis such as methane, carbon, carbon dioxide, hydrogen and carbon monoxide. This research analysis by using glycerol as substrate with the aim of investigating the thermodynamics of glycerol dry reforming at atmospheric pressure and reforming temperature from 500 to 1000 K. Moles of each synthesis gases is shown with different of temperature and CGRs. On the basis of thermodynamic analysis with optimized operational condition, gaseous product distributions and coke formation behavior was obtained at different CGRs with different temperature. Based on this research, the synthesis gas have been produced which is hydrogen 1.5 moles, carbon monoxide 7.6 moles, carbon dioxide 5 moles, methane 1.5 moles and carbon 3 moles.

CHAPTER I

INTRODUCTION

1.1 Background of Study

For the past decade, hydrogen has been touted as the energy for the future as it is green and does not pose detrimental effects to the environment. Coincidentally, the continuous depletion of fossil fuels also has triggered a seismic shift towards finding greener and renewable alternative sources to substitute the use of hydrocarbon. Currently, more than 60% of the world's feedstock for hydrogen production originates from natural gas [1]. Fortunately, this issue can be resolved using renewable raw material such as biomass. Glycerol, which is generated as major by-product of biodiesel is expected to inundate the commodity market once biodiesel technology becomes mature. An approximately 10 wt% of glycerol is being produced during vegetable oils and animal fats transesterification [2]. Significantly, from thermodynamic perspective, glycerol can be effectively converted into hydrogen or even hydrogen-rich synthesis gas. Furthermore, glycerol is a green chemical that exhibits properties of non-flammable, involatile and also non-toxic.

Hence, it becomes clear that glycerol can be employed as potential biofuel-production pre-cursor. For a very long time, production of synthesis gas or hydrogen by hydrocarbon steam reforming has been widely investigated [3, 4, 6]. Nevertheless, the production of synthesis gas by glycerol dry (CO_2) reforming is relatively unknown. CO_2 is commonly known as a greenhouse gas and presents readily in our atmosphere. Therefore, it can be employed to assist hydrogen production for securing the energy for the future. By doing so, adverse environmental effects that closely associated with CO_2 can also be reduced. The aim of this research is to study the thermodynamic system of glycerol dry reforming for the purpose of synthesis gas hydrogen production. The results will be shown for reaction parameters such as reactant ratios, reaction temperatures, gaseous product formations, and carbon deposition.

1.2 Problem Statement

The rising global demand for fuels has led to the search for alternative energy sources for hydrogen production. Steam reforming processes have been traditionally employed for synthesis gas production; however it is an energy-intensive process. Dry reforming process is a relatively new technique in the hydrogen production, thus it can become an excellent candidate for reaction with glycerol. The overall reaction is more environmental-friendly and probably is more economic compared to steam reforming. Water (H_2O) is the main reactant in steam reforming process while carbon dioxide (CO_2) is used in dry reforming process. CO_2 can be alternatively used to replace H_2O with minimal costs in production. Therefore, various investigations such

as thermodynamic analyses are required to provide a fundamental study into glycerol dry reforming process for fuel industry in future.

1.3 Research Objectives

The primary objective of the current research is to investigate the thermodynamics of glycerol dry reforming at atmospheric pressure and reforming temperature from 500 to 1000 K.

1.4 Scopes of Study

In order to achieve the objective of this work, the outline of research scopes for the current research are as follows:

- (i) To identify all possible reactions during glycerol dry reforming.
- (ii) To study the effect of temperature on equilibrium constants and standard reaction heat for all the possible reactions.
- (iii) To compute and obtain gaseous product distributions and coke formation behavior as function of reactant ratios and reaction temperatures at atmospheric condition.

1.5 Significance of Study

- (i) To apply the concept of thermodynamic equilibrium studies into glycerol dry reforming system.

- (ii) Analyzing the effect of different temperatures and equilibrium constants to the hydrogen and other gaseous product distributions.
- (iii) Carbon deposition and formation by CO₂ with glycerol in addition to the total hydrogen produced.
- (iv) Polymath software has been employed to carry out thermodynamic analysis of glycerol dry reforming.

1.6 Outlines of Thesis

This thesis consists of five chapters which are introduction, review of literature, methodology, results and discussion as well as conclusions and recommendations. Chapter 1 consists of background of the study, problem statement, research objectives, scope of study and significance of study. Chapter 2 (literature review) reviews the glycerol and its application, hydrogen production methods, glycerol dry reforming process and thermodynamic analysis. For Chapter 3, it discusses about the method employed for this research including thermodynamic analyses by using related formulae. Finally the main contributions of the thesis will be highlighted in Chapter 4 followed by some recommendations in Chapter 5 for future work.

CHAPTER II

LITERATURE REVIEW

2.1 Introduction

This chapter provides a literature review for the current research on thermodynamic analysis of glycerol dry reforming. It is divided into four sections in which the first section discusses about glycerol and its application. Second section provides the methods to produce hydrogen while the third section is devoted for glycerol dry reforming. Finally, the last section is about thermodynamic analysis of glycerol dry reforming.

2.2 Glycerol

2.2.1 Properties of Glycerol

Glycerol is a commercial tri-OH alcohol employed in various industries. It is the simplest form of polyol compound. The formula symbol for glycerol is C_3H_8OH or

also known as glycerin. Other synonymous names for glycerol include glycerin, glycerine, propane-1,2,3-triol, 1,2,3-propanetriol, 1,2,3-trihydroxypropane, glyceritol, and glyceryl alcohol [1]. Fig. 2.2.1 shows the structure of glycerol. By definition, glycerol is a sugar alcohol. The atomic weight is 92.09, melting point is 18.17°C and boiling point is 290°C under normal atmospheric pressure. In addition, the heat of formation is -669.6 kJ/mol. In terms of physical appearance, it is a clear, colourless, odorless and viscous liquid, derived from both natural and petrochemical feedstocks. Glycerol is completely soluble in water in all proportions and alcohol. It is slightly soluble in ether, ethyl acetate, and dioxane and insoluble in hydrocarbons. In particular, glycerol has useful solvent properties similar to those of water. Glycerol has three hydroxyl groups that are responsible for its solubility in water and its hygroscopic nature. Because of its energy content and high solubility index in water, it is widely utilized in cosmetics, foods and pharmaceutical industries.

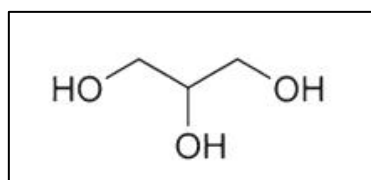


Figure 2.1 : Figure illustrates the structure of glycerol

Table 2.1 shows the physicochemical properties of glycerol at 20 °C [7]. The data in this table is useful for thermodynamic calculation. Overall, it possesses a combination of physical and chemical properties. Glycerol has over 1500 known end uses, almost two third industrial uses of glycerol are in food and beverage (23%), personal care (24%), oral care (16%), and tobacco (12%), stated by Adhikari et al.

[11]. In addition, glycerol is highly stable under normal storage conditions, compatible with many other chemical materials. It also has no known negative environmental effects with various uses.

Table 2.1 : Physicochemical properties of glycerol at 20 °C

Chemical formula	$C_3H_5(OH)_3$
Molecular mass	92.09 g mol ⁻¹
Melting point	18.17 °C
Boiling point	290 °C
Density	1.261 g cm ⁻³
Viscosity	1.5 Pa.s
Refractive index	1.474
Flash Point	160°C
Vapor pressure	0.3333 Pa at 50°C
Heat of vaporization	88174 J/mole at 55°C
Heat of combustion	1662 kJ/mole
Heat of fusion	18.3 kJ/mole
Thermal conductivity	0.29 W/m°K

2.2.2 Application of Glycerol

Glycerol is commonly used as an ingredient or processing aid in cosmetics, toiletries, personal care products, pharmaceutical formulations and foodstuffs. Currently, about 10 wt% of glycerol is obtained as a by-product in soap production as well as biodiesel fuel via catalytic transesterification process, while the amount of glycerol that goes annually into technical applications is around 160 000 tonnes, expected to grow at an annual rate of 2.8% [7]. Figure 2.2 demonstrates the traditional commercial use for glycerol.

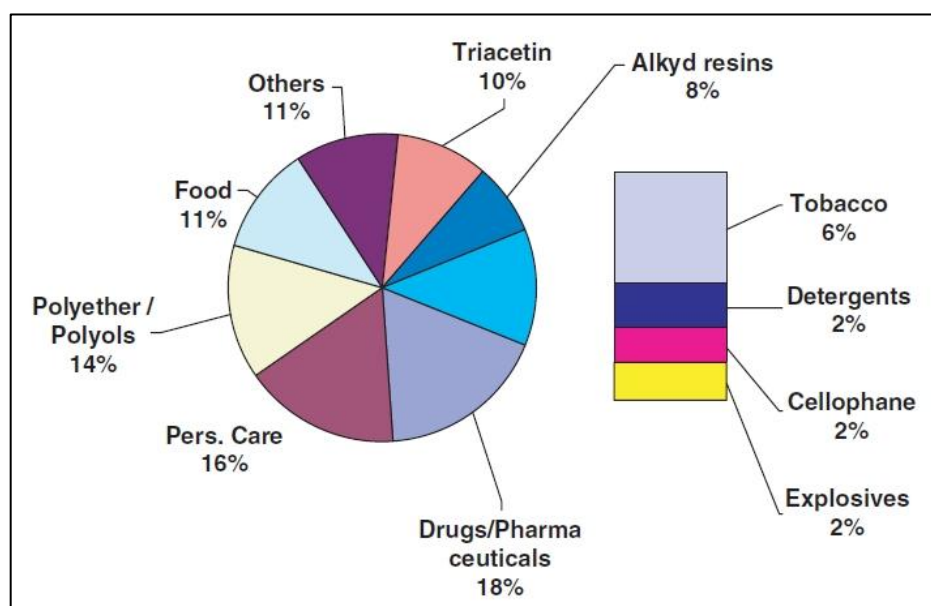


Figure 2.2: Figure illustrates the traditional commercial for glycerol (volumes and industrial uses). Sources; M. Pagliaro and M. Rossi [7].

It shows that glycerol is being used in drugs and pharmaceuticals industry, followed by personal care including toothpaste and cosmetics in using of glycerol. Glycerol is also widely used in polyether/polyols production which is for flexible foams and to a

lesser extent, rigid polyurethane foams. This is followed closely by food industry. Glycerol commonly used in alkyd resins and regenerated cellulose as a softener and plasticizer to impart flexibility, pliability and toughness in surface coatings and paints. The other application that using glycerol on industry is triacetin, detergent, tobacco and cellophane.

2.2.2.1 Food industry

Glycerol as a sugar alcohol is widely used in foods and beverages. It serves as a solvent, humectant, sweetener and helps to preserve foods. It also acts as filler for low-fats food preparations such as cookies. Glycerol and water are used to preserve certain types of leaves. Glycerol is also used to manufacture mono- and di-glycerides for use as emulsifiers. It is also used as a humectant (along with propylene glycol labelled as E1520 and/or E422) in the production of snus, a Swedish-style smokeless tobacco product. In food applications, glycerol is categorized by the American Dietetic Association as carbohydrate.

2.2.2.2 Pharmaceutical and personal care applications

Glycerol is widely used in medical and personal care preparations including for improving smoothness, providing lubricant and as a humectant. It can be found in allergen immunotherapies, cough syrups, elixirs and expectorants, toothpaste, mouthwashes, skin care products, shaving cream, hair care products, soap and water-based lubricants. In solid dosage forms like tablets, glycerol is used as tablet holding agent. For human consumption, glycerol can be classified as a caloric macronutrient.

Besides that, glycerol is a component of glycerin soap which is made from denatured alcohol, glycerol, sodium castorate (saponified castor bean oil), saponified cocoa butter, saponified tallow, sucrose, water and sodium laureth sulphate. It is a kind of essential oil which be added for fragrance.

2.2.2.3 Drugs and cosmetics

In drugs and medicine industries, glycerol is an ingredient of many tinctures and elixirs of starch for used in jelly and ointments. It is employed in cough medicine and anesthetics such as glycerin phenol solution, ear treatment, and in bacteriological culture media. Its derivatives are used in tranquilizers and nitroglycerine. For cosmetics industry, glycerin widely used in many creams and lotion production to keep the skin soft and replace skin moisture. It is the basic media which toothpaste is formed, maintaining desired smoothness and lendig a shine to paste.

2.3 Hydrogen production pathways

Hydrogen production is the first step toward a larger goal which is closer to a hydrogen economy. It is emerging as a future replacement fuel for the traditional fossil fuels that will capable of aiming our energy needs. Hydrogen may enable future energy systems and could be made to be a clean, more reliable, and more efficient; hence securing our future energy needs. Hydrogen production serves as an alternative energy source for fossil and biomass fuels. This can be achieved through

the use of hydrogen energy derived from fossil and biomass sources with carbon captures. One of the major challenges of future hydrogen economy is the reduction in the production cost, storage issue and hydrogen transportation.

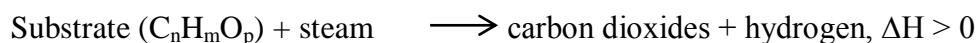
2.4 Hydrogen production from glycerol

Adhikari et al. [11] mentioned about development of 16 rigorous process simulation models for multiple reformation strategies; steam reformation (SR), partial oxidation (POX), auto thermal reformation (ATR), supercritical methanol reformation (SC), and dry methane reformation (DR). The various hydrogen production schemes were investigated for three different fuels: natural gas (approximated by methane), diesel (approximated by dodecane), and methanol. The models included all the feed pretreatment steps along with the reforming reactors and effluent treatment including the water gas shift reactors. By using advanced computer-aided tools and process integration techniques, the systems can be optimized and the economic potential of the technologies is evaluated. This work provides a comparison of reformation strategies based on the equipment requirement, energy usage, fuel complexity, economical level and challenging the previous research.

There is four ranking obviously researched for hydrogen production over the last few years which is via steam reforming, partial oxidation (gasification), autothermal reforming, aqueous-phase reforming (APR) and supercritical water reforming [12]. Currently, the dominant technology for direct production is steam reforming from hydrocarbons. But, dry reforming process is a relatively new research area compared to others.

2.4.1 Steam reforming

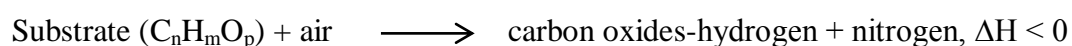
The steam reforming process is highly endothermic. In general, the process can be shown as follows :



The steam reforming of hydrocarbons has been the preferred method for industrial-scale hydrogen production. Reforming process mainly involves splitting of hydrocarbons in the presence of water and water-gas shift reaction. Overall, steam reforming process is an endothermic process. Thermodynamically, steam reforming process favours high temperatures and low pressure where as water-gas shift reaction is inhibited by high temperatures and independent of pressure. Excess steam condition is normally employed in methane steam reforming. Steam reforming process can produce higher selectivity of hydrogen when the catalyst was added into the process [12].

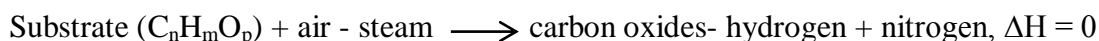
2.4.2 Partial oxidation (POX)

In the partial oxidation process, a substrate is reacted with oxygen at sub-stoichiometric ratios. The oxidation reaction results in heat generation and high temperature. The aim of reforming process in the presence of the air is to balance the energy required for the process by oxidizing some of the substrate. If excess air is added, all the substrate will be oxidized and produce mainly carbon dioxide and water. The process can be shown as follows :



2.4.3 Autothermal reforming

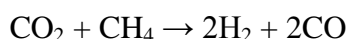
This process combines the effect of partial oxidation and steam reforming by feeding fuel, air, and water together into the reactor. The process is carried out in the presence of catalyst [12]. The steam reforming process absorbs the heat generated by the partial oxidation process. The process can be shown as:



The main benefit of the autothermal process is it does not require any energy for reaction to occur. Although the autothermal steam reforming process had advantages over conventional steam reforming, the amount of hydrogen produced from autothermal reforming would be less (on a thermodynamic basis).

2.4.4 Dry reforming

Dry reforming also known as carbon dioxide reforming is a method of producing hydrogen which is synthesis gas (mixtures of hydrogen and carbon monoxide) from reaction between carbon dioxide and hydrocarbon such as methane. In recent years, the increasing concerns on greenhouse gases jeopardizing global warming have reignited the replacement of steam as reactant with carbon dioxide. The methane carbon dioxide reforming reaction may thus be represented by:



Two-stage process of producing hydrogen by the reforming of natural gas has been developed. This process consists of a two-stage reformer. In the first reformer (dry reformer), methane or natural gas reacts with CO_2 to produce H_2 and CO while in the

second reformer (water gas shift reformer), CO reacts with steam to produce additional H₂ and CO₂ as the end products.

2.5 Glycerol dry reforming

The rising demand of fuels and biodiesel may lead to supply of glycerol as an alternatives to hydrogen production. Glycerol, which is generated as major by-product of biodiesel is expected to inundate the commodity market once biodiesel technology becomes mature. Significantly, from thermodynamic perspective, glycerol can be effectively converted into hydrogen or even hydrogen-rich synthesis gas.

Therefore, glycerol dry reforming (CO₂) process need to involve in this case. Several reasons tend to choose dry reforming process instead of steam reforming process is production by using CO₂ can totally lead to new materials such as syngas, methane, dimethyl carbonate (DMC), and carbonic esters. Besides, CO₂ is a non-toxic feedstock that can replace toxic chemicals. It is a new routes to existing chemical intermediates and the product could be safer, more efficient and economical than current methods which is steam reforming process [12].

Many challenges need to be faced by doing this process including sufficient conversion where high temperature is needed and carbon formation problem when the catalyst resistive of carbon or regeneration is formed. Zenczak et al. [28] found that the synthesis gas in the equilibrium mixture increases with the temperature.

Therefore, this research will analyse the thermodynamic behaviour in high temperature regime for higher hydrogen yield. Significantly, in steam reforming of glycerol, synthesis gas rich in hydrogen can be produced. In contrast, during the dry reforming process, the carbon monoxide may predominate in the equilibrium mixture.

2.5 Thermodynamic analysis

Thermodynamic analysis is required to provide a fundamental study into glycerol dry reforming process for H₂ production. Thermodynamic can be applied to a wide variety of topics in science and engineering such as phase transition, chemical reaction and transport phenomena. It is a branch to define macroscopic variables such as temperature, pressure, enthalpy, entropy and heat that describe how they are related. Hence, thermodynamic analysis can be manipulated to identify the operating conditions and limitations of dry reforming reaction. The effects of temperature, pressure and CO₂ as a reactant are evaluated.

The production of synthetic fuels is an interesting prospect for CO₂ employment. Indeed, the Gibbs free energy minimization method can be employed to identify thermodynamically optimal operating conditions for dry reforming as well as mixed reforming [12]. Other types of analysis also include investigation of the process's endothermicity and exothermicity. Significantly, thermodynamic computation is useful towards identifying the carbon formation and deposition as a function of reaction temperature and reactant molar ratios. Subsequently,

thermodynamic calculations will demonstrate the optimal operating conditions for the production of syngas which is the maximum H₂ yield at the achieved temperature.

From the previous study, many works have been done for glycerol steam reforming process [12]. The parameters employed (temperature and pressure) were identical to the glycerol dry reforming process. Most of the prior studies into glycerol steam reforming focused on the maximum hydrogen production at optimum temperature and pressure. Surprisingly to the best of existing knowledge, there is only one literature regarding the glycerol dry reforming. Adhikari et al. [13] found that the number of hydrogen moles increases with temperature and inversely with pressure. Moreover, the effect of the pressure on the glycerol steam reforming process is found to be consistent with methanol and ethanol steam reforming process [13].

The greatest quantity of hydrogen is produced at excess water at all temperatures. The best conditions to produce hydrogen will be with excess water. Adhikari et al [13] also mentioned that the upper limit of the moles of hydrogen produced per mole of glycerol is 6 at 960 K, water-glycerol-feed ratio of 9 and P = 1 atm. From the result, the coke formation is not desirable in the steam reforming process due to the contribution of greenhouse effect. In addition, the process might be higher cost attributed to steam generation

From Dou et al. [18] studies, sorption-enhanced steam reforming of glycerol was found to be an effective means for achieving hydrogen purity exceeding 90% and decreasing CO₂ concentration. The effect of temperature in the 400-700°C on the products selectivity is strong, with a H₂ selectivity that increases with increasing the