

Chapter 7

A Short Review on Production of Syngas via Glycerol Dry Reforming



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Abstract Glycerol, a by-product from biodiesel production, has been widely investigated as one of the alternative feedstocks for production of synthesis gas (syngas). The production of syngas through glycerol pyrolysis, gasification, and steam reforming has been well established. However, to date, there were only a few literatures focusing on the use of glycerol dry reforming (GDR) to produce syngas. GDR offers a better pathway for the production of syngas as it converts carbon dioxide, a greenhouse gas, into a value-added product and converts the biodiesel by-product, glycerol, into an alternative source of energy. Nickel (Ni) is extensively used as a catalyst in many reforming processes due to its excellent capacity for carbon-carbon bond cleavage and because it is easily available and economically

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cheap. The major challenge faced by the application of Ni as a catalyst in GDR is mainly due to the deactivation of catalyst through carbon formation.

This review focuses on the performance of potential catalysts and operating conditions that exhibit high catalytic activity and stability in GDR. Few perspectives of catalyst properties such as catalyst dispersion, basicity and acidity, reducibility, oxygen storage capability, and interaction between support and catalyst have been included in the review, and their catalytic performances have been deliberated. Effects of reaction parameters such as reaction temperature, gas hourly space velocity, and reactants partial pressure were discussed in detail, followed by the thermodynamics study. This short review is expected to create a clear understanding on the correlation between catalytic properties and their performance in glycerol dry reforming.

Keyword Glycerol dry reforming · Syngas · Catalytic properties · Carbon formation · Operating conditions · Thermodynamic study · Dry reforming · Catalyst deactivation · Hydrogen energy · Catalyst support

Abbreviations

ASEAN	Association of Southeast Asian Nations
BET	Brunauer–Emmett–Teller
FTS	Fischer–Tropsch synthesis
GDR	Glycerol dry reforming
GHSV	Gas hourly specific velocity
GSVC	Gas space velocity per gram of catalyst
MTOE	Million ton oil equivalent
Ni-CC	Ni catalyst supported on cement clinker
RWGS	Reverse water-gas shift
WHSV	Weight hourly space velocity

7.1 Introduction

Energy has been a vital element in human life since the past centuries. Over the years, the world has been depending on fossil fuel as the main energy resource for heating, electricity, and vehicle's power generation. The energy consumption is increasing every year due to the growth in human population as well as the development of industries across the globe. The world population of 7.3 billion in 2015 is expected to rise in 2030 to 8.5 billion (Department of Economic and Social Affairs of United Nation 2015). From the projection done by International Energy Outlook

(2016) on the energy consumption from all resources from 1990 until 2040, it was found that fossil fuel remains as the primary energy resource with 78% usage from the total energy consumption. Global natural gas and coal consumption are increasing by 1.9% and 0.6%, respectively, from 2012 to 2040. Additionally, there is a rapid growth in nuclear energy consumption with 2.3% increment, and renewable energy has been projected to be the fastest to grow with 2.6% increment from 1992 to 2040 (International Energy Outlook 2016).

According to ASEAN Centre for Energy (Lean and Smyth 2010), energy consumption in ASEAN countries is predicted to rise from 200 million ton oil equivalent (MTOE) in 2000 to 580 MTOE in 2020. Transportation consumes the highest energy, which constitutes 47%, while the other sectors, such as industry, accounted for 25%, commercial and residential 14%, non-energy 12%, and agriculture 2% (Lean and Smyth 2014). In general, the surge in energy consumption especially fossil fuels will result in the fluctuating price of fossil-based energy in the market, exhaustion of fossil-based resources, and global climate change due to carbon emission. Hence, renewable energy is gaining attention as an alternative energy.

Among the alternative energies, syngas consisting of hydrogen (H_2) and carbon monoxide (CO) has appeared as the potential alternative for various downstream productions such as the production of ammonia and as the feedstock for methanol synthesis, fuel cells, and Fisher–Tropsch reaction. This hydrogen-based energy solution is also considered as a clean and environmental friendly energy due to its clean emission and high efficiency and becomes one of the potential alternatives in reducing the dependency towards the nonrenewable energy sources. Syngas is normally derived from different hydrocarbon materials and produced through the hydrocarbon reforming and electrolysis processes (Chakik et al. 2017). Both processes are commonly chosen by the industry; however, the constraints are majorly coming from the high processing cost and feed price.

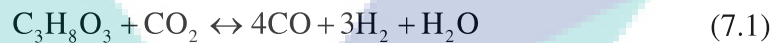
The development and utilization of renewable sources as an alternative energy is one of the solutions to resolve the issues related to the depletion of fossil fuel. Renewable source is very important as it can sustain the sources for energy demand that currently relies on nonrenewable sources. Various potential renewable feedstocks should be introduced so that the aim in replacing nonrenewable sources can be achieved. Biomass is suggested as one of the potential solutions to replace the nonrenewable sources. Biomass is a renewable source of energy that is derived from animal or plant. It is more economical compared to fossil fuels as it provides clean energy that has zero emission of carbon dioxide and less emission of soot, sulfur dioxide, and nitrogen oxide (Balat 2009). Vegetable oil, animal fat, wood, crop, and garbage are the examples of biomass that are used as raw materials or feedstocks in energy production.

Recently, the valorization of biomass particularly glycerol as the alternative feedstock for syngas production has gained substantial attentions from researchers worldwide (Charisiou et al. 2017). Glycerol, a by-product from biodiesel production, faced oversupply crisis due to the massive production of biodiesel, thus bringing down its commercial value. It is estimated that about 10% of glycerol is generated from biodiesel production, which is about 1.05 pound of glycerol pro-

duced per one gallon of biodiesel generated (Demsash et al. 2018). Hence, the production of syngas from glycerol will be a cost-effective way to boost up the potential of glycerol as the value-added by-product from biodiesel, simultaneously lowering the production cost of biodiesel.

A number of literatures found that syngas could be potentially produced using different routes of gasification processes such as steam reforming, autothermal reforming, pyrolysis, partial oxidation, dry reforming, and supercritical water reforming (Demsash et al. 2018; Charisiou et al. 2017). Steam reforming has been widely investigated for the production of H_2 and currently employed in industry for syngas production from glycerol (Harun et al. 2019). It is an attractive process since it produces higher yield of hydrogen gas, i.e., seven moles of hydrogen are theoretically produced for every mole of glycerol fed to the reactor. However, this approach suffers from carbon attack and carbon dioxide (CO_2) greenhouse gas emission and leads to various side reactions such as methanation and water-gas shift. The level of steam needs to be carefully controlled as excess steam will reduce the efficiency of the process and insufficient amount of steam will result in carbon formation. The high H_2/CO ratio also makes the process undesirable for Fischer–Tropsch synthesis (FTS) (Lee et al. 2014a).

Recently, glycerol dry reforming (GDR) has become one of the potential pathways for the syngas production through the utilization of greenhouse gas (CO_2) and biodiesel by-product, glycerol as the feedstocks. GDR can be considered as a green process since the bio-based glycerol is coming from a renewable sources and the utilization of CO_2 potentially suppresses the greenhouse impact. The overall GDR process is represented by Eq. (7.1).



Apart from the main reaction, other potential reactions are anticipated to occur, and the possible reactions are listed as follows (Tavanarad et al. 2018):

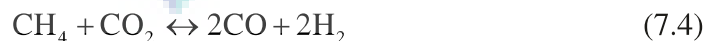
Decomposition of glycerol



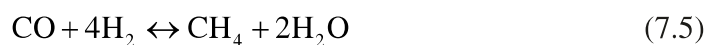
Water-gas shift reaction



Methane dry reforming

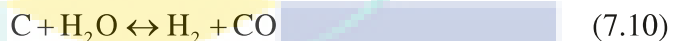


Methanation





Deposition and gasification of carbon



The nature and properties of the catalyst significantly influence the catalytic conversion of GDR. Various types of catalysts, namely, the nickel-based, cobalt-based, and noble metal-based catalysts, have been widely used in reforming studies. Nevertheless, catalysts containing Ni have always been chosen due to their excellent activity and stability, easily available, and cheapness in cost compared to noble metals such as Rh, Pt, and Pd (Thyssen et al. 2013). However, Ni-based catalysts are prone to be easily deactivated through the carbon deposition. Thus, the aim of this paper is to review the potential of various types of catalysts in GDR. Apart from that, the effect of reaction parameters, i.e., reaction temperature, gas hourly space velocity, and reactants partial pressure, and thermodynamics analysis will be elaborated in detail.

7.2 Catalysts for Glycerol Dry Reforming

One of the obstacles in the application of GDR is the rapid degradation of catalyst due to carbon formation. From thermodynamic analysis based on total Gibbs energy minimization method, Friestas and Guirardello (2014) proposed that dry reforming shows the highest susceptibility towards carbon formation among other reforming technologies for glycerol. Low temperatures below 600 °C and high pressures at above 3 bar will favor the formations of ethylene (C₂H₄) and ethane (C₂H₆), thus contributing to the significant amount of carbon during glycerol dry reforming. In another earlier work, Wang et al. (2009) evaluated glycerol dry reforming using thermodynamic analysis and suggested that Boudouard reaction is the dominant carbon formation reaction during glycerol dry reforming. The amount of carbon increases with the increase of CO₂-to-glycerol ratio which leads to the increase of CO in the system. Nevertheless, Wang et al. (2009) suggested that carbon formation could be controlled by using suitable catalysts during glycerol dry reforming.

Compared to steam reforming which has been widely explored for glycerol, it is only recent that the catalytic studies on glycerol dry reforming are available in the open literature. Among the earliest group that has worked on the glycerol dry reforming, Lee et al. (2014b) have performed the process using Ni catalyst sup-

ported on cement clinker (Ni-CC). Cement clinker composed of a mixture of CaO and SiO has been reported to release CO₂. Thus, the main reason of utilizing the particular support is to reduce the effect of catalyst deactivation due to carbon deposition. Whisker carbon was detected on the spent Ni-CC catalyst after the dry reforming of glycerol, yet the carbon is easily gasified by O₂ oxidation (Lee et al. 2014a, b). Later from the same group, Siew et al. (2014, 2015a, b) employed La-promoted Ni–Al₂O₃ catalyst for glycerol dry reforming at 650–850 °C. It is suggested that La promotion has successfully improved carbon resistance in Ni – Al₂O₃ catalyst as La offers redox properties which provides additional route for carbon removal, provides better Ni metal dispersion, and reduces the acidity of the Ni catalyst. In contrary to the earlier thermodynamic analysis, the group proposed that the high CO₂-to-glycerol ratio is essential for carbon mitigation as CO₂ effectively acts as a gasification agent in carbon gasification pathway.

Similarly, in another study using Ni catalyst supported on Al₂O₃ of a nanocrystalline structure by Tavanard et al. (2018), the increase of CO₂ content has improved the occurrence of reverse Boudouard reaction that allows more for gasification of carbonaceous species on the catalyst surface. Additionally, in a recent work using Ni – Al₂O₃ catalyst, Ag has been employed as a promoter in glycerol dry reforming. The promoted catalyst has given better glycerol conversion due to the ability of Ag to enhance the dispersion on Ni particles on the Al₂O₃ support surface. Two types of carbon were observed after 72 h of longevity study, encapsulated and whisker-type carbons, yet they were easily removed through oxidation during TPO analysis at temperatures below 680 °C (Harun et al. 2019).

Dry reforming of glycerol also has been conducted on Ni catalyst supported on ZrO₂, CaO, and La₂O₃ supports (Mohd Arif et al. 2017). Ni–CaO with 15% Ni provides the highest hydrogen yield and glycerol conversion as the catalyst shows a higher metal dispersion and smaller crystallite size of NiO species compared to that with other catalysts (Ni–ZrO₂ and Ni–La₂O₃). CaO support has been suggested to reduce the accumulation of carbon on the catalyst surface due to its basic site properties. Basic functional group on support is beneficial for CO₂ adsorption and thus assists in gasification of carbon on the catalyst surface. Further, the group has incorporated Re as a promoter on the same catalyst (Ni–CaO), and the addition of Re has been anticipated to enhance the surface adsorption of OH group of the glycerol (Mohd Arif et al. 2018). The addition of Re also has contributed to the lesser amount of carbon on the Ni–CaO catalyst during glycerol dry reforming.

Besides the Ni-based catalysts, noble catalysts such as Rh, Ru, Ir, Pd, and Pt supported on alumina-stabilized alumina (MgAl₂O₄) also have been investigated for glycerol dry reforming (Tavanarad et al. 2017). Among the catalysts, Rh – MgAl₂O₄ has displayed the highest glycerol conversion and stability for 20 h of operation. The authors attributed the decent activity of Rh catalyst to its high BET surface area and high active metal area. Similar to previous work using Ni – Al₂O₃, the presence of whisker carbon was also observed on the spent Rh – MgAl₂O₄. Additionally, the excess of CO₂ also has suppressed the carbon formation on the noble catalysts.

Rh catalyst has been further employed for dry reforming of glycerol (Bulutoglu et al. 2018). Two catalysts, Rh – ZrO₂ and Rh – CeO₂, have been investigated for

their performance and carbon deposition. Rh – ZrO₂ has displayed a higher conversion and syngas yield compared to the Rh – CeO₂ catalyst due to high specific surface area and small average Rh particle size of Rh – ZrO₂ catalyst. Rh – CeO₂ catalyst on the other hand has been suggested to have strong metal-support interaction when CeO₂ support was found encapsulating the Rh nanoparticles. The strong metal-support interaction unfortunately has partially rendered the active sites of the Rh catalyst in Rh – CeO₂, resulting in a lower catalytic activity than that of Rh – ZrO₂. Nevertheless, the presence of CeO₂ has inhibited carbon formation due to the mobility of oxygen species and oxygen vacancies of CeO₂ sites on the Rh – CeO₂ catalyst. Meanwhile, the Rh – ZrO₂ deactivated faster than the Rh – CeO₂ catalyst, which has been correlated to the sintering of Rh nanoparticles and carbon deposition.

Ni-based catalysts and Rh catalysts are the primary catalysts employed for dry reforming of glycerol. Regardless whether it is metal or noble catalyst, the aim of catalyst selection is to achieve high catalytic activity and suppression of carbon deposition during glycerol dry reforming. Additionally, supports and promoters have been critically chosen to assist on providing catalyst with high surface area, high catalyst dispersion, strong metal-support interaction, better carbon removal due to oxygen species mobility, and basic site properties. As for the future, research in glycerol dry reforming should focus on minimizing carbon deposition with more attention on development of carbon-resistance catalysts.

7.3 Effects of Operating Conditions

Apart from catalyst used in GDR, operating conditions including reaction temperature, gas space velocity per gram of catalyst, and molar ratio of reactant carbon dioxide to glycerol are also few important factors that need to be considered. In this short review, the effect of reaction conditions in controlling the glycerol and CO₂ conversion, product yield, and catalyst deactivation were discussed. Understanding the influence of operating conditions and thermodynamic behavior of the GRD are required to design an efficient reactor system and proper catalyst in maximizing the reactant conversion and product yield.

7.3.1 Effect of Reaction Temperature

Endothermic process behavior of glycerol dry reforming needs higher temperatures at above 500 °C to favor the reaction and maximizing the syngas yield (Bulutoglu et al. 2018). Glycerol reactant is likely to decompose at higher temperatures as its molecule is thermally unstable (Valliyappan et al. 2008). This aspect was often overlooked by previous GDR researchers, which in fact caused in imprecise results on the catalytic activity performance. Bulutoglu et al. (2018) have highlighted this

aspect through their study on GDR process without presence of any catalyst under various reaction temperatures to examine the non-catalytic glycerol conversion routes. They have reported that without the presence of catalyst, the glycerol was homogeneously broken down with the increase in temperature up to 750 °C. 7% of glycerol conversion was obtained at 600 °C and increased to 31% at reaction temperature of 750 °C. Contrary with glycerol, no CO₂ conversion was observed in reaction temperatures of 550–750 °C (Bulutoglu et al. 2018).

In practical reforming technologies, the production of syngas is significantly increased with the increase in the reaction temperature. From the thermodynamic analysis performed via MATLAB software using Lagrange's undetermined method focusing on the CO₂ reactant, Wang et al. (2009) reported that CO₂ possibly started to breakdown at 677 °C. Similar observations by Bulutoglu et al. (2018) showed that the CO₂ molecule starts to convert to syngas at 750 °C but the degree of conversion is also depending on the types of catalyst used. Different CO₂ conversions were observed at 750 °C over the Rh – ZrO₂ and Rh – CeO₂ catalysts with 12.6% and 7.1%, respectively; however, within the range of 600–700 °C, negligible conversion of CO₂ was obtained for both catalysts (Bulutoglu et al. 2018). Thus, it can be concluded that the process involved with CO₂ was favored at temperatures more than 650 °C due to thermodynamic limitation of CO₂. However, at reforming temperatures above 500 °C with the presence of CO₂, the reactant will favor the reverse water-gas shift (RWGS), the reverse of Eq. (7.3). This side reaction gives a significant influence to the product distribution as the excess by-product of water will inhibit the syngas production (Fernández et al. 2010; Bulutoglu et al. 2018).

As reported by Bulutoglu et al. (2018), glycerol possibly decomposes to various species at temperatures as low as 600 °C although without the presence of catalyst. This is apparently noticeable since the operation temperature itself could energize the breakdown of glycerol molecule without any assisted active sites. Further investigation on GDR was conducted over Rh – ZrO₂ and Rh – CeO₂ catalysts, and the result shows a similar increment in glycerol conversion up to ~82% in both catalysts at temperature 700 and 750 °C, respectively (Bulutoglu et al. 2018).

Reaction temperature of GDR also affects the syngas yield or practically presented in H₂/CO ratios. Hydrogen yield was reported to increase as the operating temperature increased up to 700 °C, and the trend started to decline as the temperature increased (Wang et al. 2009; Freitas and Guirardello 2014). Wang et al. (2009) found that at a reactant molar ratio CO₂-to-glycerol ratio of 1:1, 727 °C was the optimum temperature to achieve maximum hydrogen yield (Wang et al. 2009). Meanwhile, the presence of intermediate species of methane during the GDR would promote the formation of carbon monoxide and hydrogen (Bulutoglu et al. 2018). The generation of methane during the glycerol decomposition will react with readily CO₂ and subsequently form carbon monoxide and hydrogen as shown in Eq. (7.4). These gas products increase with the increase of temperature. Even though high temperatures promoted the syngas yield, coke formation and active site sintering would also favor at extremely high temperatures (Bulutoglu et al. 2018).

7.3.2 *Effect of Gas Space Velocity per Gram of Catalyst (GSVC)*

Effect of velocity of inlet gas per gram of catalyst used has not been widely studied, and only few literatures are focusing on this parameter. Mohd Arif et al. (2018) have studied the effect of gas hourly specific velocity (GHSV) over Re/Ni – CaO at 800 °C with ratio CO₂-to-glycerol of 3. They observed that an increase of GHSV favors the conversion of glycerol as well as carbon monoxide and hydrogen yield. It is mainly due to lower residence time that limits the reactant and catalyst active sites to react. From their finding, the highest glycerol conversion (61%) and yield of hydrogen (56%) over Re/Ni – CaO were found at GHSV of $3.6 \times 10^4 \text{ ml g}^{-1}_{\text{cat}} \text{ s}^{-1}$. Reaction of GDR operating at more than $3.6 \times 10^4 \text{ ml g}^{-1}_{\text{cat}} \text{ s}^{-1}$ would give a negative effect towards the reforming process ($X_{\text{glycerol}} = 28\%$, $Y_{\text{H}_2} = 16\%$, $Y_{\text{CO}} = 37\%$). In addition, it will contribute more on coke formation (Mohd Arif et al. 2018).

Harun et al. (2019) recently studied the effect of gas space velocity which is represented in weight hourly space velocity (WHSV) in the range of $14.4 \times 10 \text{ L g}^{-1}_{\text{cat}} \text{ h}^{-1}$ to $72 \text{ L g}^{-1}_{\text{cat}} \text{ h}^{-1}$ over Al₂O₃-based catalyst for GDR. It was found that the glycerol conversion increased with the increase of WHSV up to $72 \text{ L g}^{-1}_{\text{cat}} \text{ h}^{-1}$ with 41.09% of glycerol conversion. Further increase in WHSV led to decline of glycerol conversion due to the limitation of active sites as less catalyst weight was introduced. Moreover, the lowest WHSV would reduce the glycerol conversion and hydrogen yield as more metal active sites were exposed to the intermediate species of reaction which would favor the carbon formation and led to deterioration of catalyst (Harun et al. 2019; Pairojpiriyakul et al. 2014).

7.3.3 *Effect of Molar Ratio of Carbon Dioxide-to-Glycerol*

GDR is a reaction between one mole of glycerol with one mole of CO₂ to produce syngas consists of CO and H₂ and water as shown in Eq. (7.2). From the overall main reaction of GDR, CO₂-to-glycerol of 1 is an ideal thermodynamic conditions to achieve high yield of syngas. Wang et al. (2009) reported that at 727 °C of operating temperature with CO₂-to-glycerol ratio of 1 was found as the optimum condition to reach maximum yield of hydrogen. However, many researchers have been investigated the effect of CO₂-to-glycerol towards the product yield (Tavanarad et al. 2018; Bulutoglu et al. 2018; Harun et al. 2019).

Bulutoglu et al. (2018) have studied the influence of CO₂-to-glycerol ratio within 0–4 over Rh – ZrO₂ and Rh – CeO₂ catalysts at 750 °C towards the syngas product yield. From their observation, ~96% of glycerol conversion was achieved with presence of glycerol only with no CO₂ inlet was introduced (CO₂-to-glycerol = 0). Meanwhile, the glycerol conversion decreases around 30% along with the increasing CO₂-to-glycerol ratio from 0 to 4 at constant reaction temperature (Bulutoglu

et al. 2018). These results proved that higher CO₂ consumption will lead to negative impact on the glycerol conversion and hydrogen yield since the process favors the RWGS reaction (Bulutoglu et al. 2018; Wang et al. 2009).

Excessive CO₂ molecule tends to react with hydrogen that is previously produced from the main GDR reaction and from water Eq. (7.1). This leads to the limitation of glycerol conversion and hydrogen yield but favors the formation of carbon monoxide. Wang et al. (2009) reported that at CO₂-to-glycerol ratio less than 1, the hydrogen production increases with the increase of reaction temperature. Harun et al. (2019) observed that the formation rates of the hydrogen and carbon monoxide dropped as the CO₂-to-glycerol ratio increased from 3 to 5. This trend was probably due to the thermodynamic limitation of GDR itself while competing with side species of light hydrocarbon to form the syngas.

Numerous works have been conducted to study the effects of operating conditions on catalytic reforming of glycerol, and these literatures have highlighted the benefits and limitation faced by the process. However, important targets in terms of high reactant conversion and product yield as well as coking elimination have yet to be achieved. Here are some suggestions that might be considered to achieve the targets:

- (i) To design an efficient reactor structure by considering heat transfer coefficient, reaction rate, endothermic reaction, and temperature gradient of the reactor. Several reactors types can be proposed and studied to improve the catalytic gas reaction including fluidized bed reactor, catalytic wall reactor, solar reactor, and membrane reactor.
- (ii) To introduce a vacuum condition to the reactor which could potentially reduce the reaction temperature since low reaction temperature would minimize the catalyst deactivation due to coking and sintering.
- (iii) To develop kinetics model which can be further used to validate results obtained from the experimental data. From the model, an accurate reaction conditions required to achieve higher catalytic activity can be predicted.
- (iv) To develop a coke-resistance catalyst that also able to inhibit undesired side reactions, i.e., RWGS.

7.4 Thermodynamic Analysis of Glycerol Dry Reforming

Thermodynamic analysis is important to predict the behavior of syngas synthesis from glycerol dry reforming. Wang et al. (2009) have conducted a study on thermodynamic analysis of glycerol dry reforming using Gibbs free energy minimization method. In their study, reaction equilibrium constant, K_p , of Eqs. (7.2), (7.3), (7.4), (7.5), (7.6), (7.7), (7.8), (7.9) and (7.10) at different temperatures has been determined from Eq. (7.11):

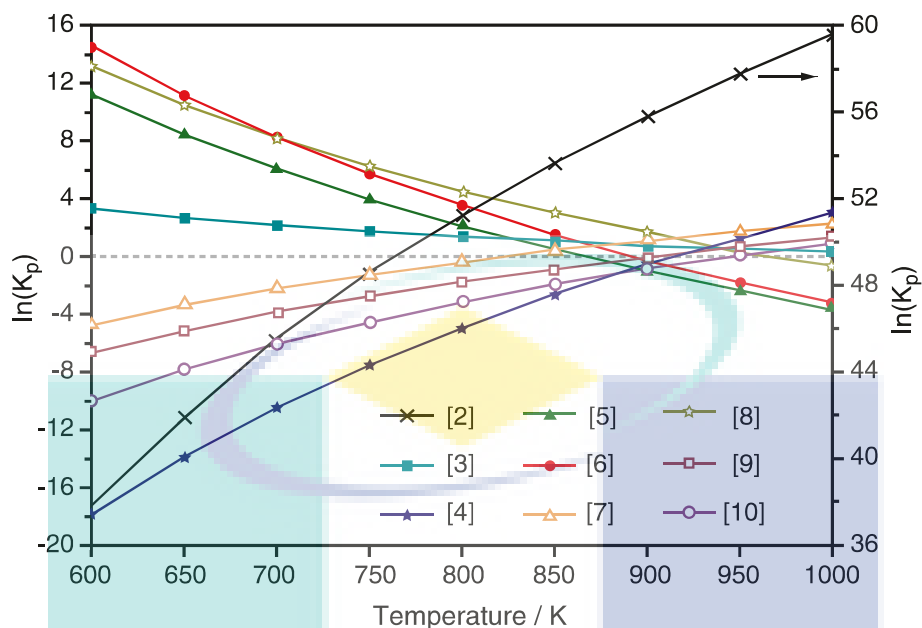


Fig. 7.1 Equilibrium constants of reactions participating in glycerol dry reforming at different temperatures. The equilibrium composition was calculated using MATLAB and Lagrange's undetermined multiplier method (Wang et al. 2009)

$$\ln K_p = \frac{-\Delta G}{RT} \quad (7.11)$$

Figure 7.1 shows the equilibrium constant at different temperatures of all reactions involved in glycerol dry reforming. It can be seen that the highest equilibrium constant was achieved through glycerol decomposition Eq. (7.2), and this result indicates that this particular reaction has become the most influential reaction pathway that determines the yield and composition of the products. Since the values of $\ln K_p$ for reactions from Eqs. (7.3) and (7.7) are close to zero, it means that both reactions are affected by equilibrium limitation for the entire temperature range. Other reactions (Eqs. 7.4, 7.5, 7.6, 7.8, 7.9, and 7.10) are reversible at temperature lower than 527 °C; however, the reactions are also affected by equilibrium limitation when the temperature is higher than 527 °C. These reactions have relatively low equilibrium constant compared to the glycerol decomposition reaction. Therefore, these reactions are easily affected by the reaction parameter such as temperature, pressure, and CO₂-to-glycerol ratio.

Reactions from Eqs. (7.7), (7.8), (7.9) and (7.10) contribute to the carbon formation. Based on equilibrium constant values in Fig. 7.1, it can be clearly seen that reaction from Eq. (7.8) is the main contributor for the carbon formation in the glycerol dry reforming process. Besides the thermodynamic analysis, the kinetic study of glycerol dry reforming is also important to provide in-depth understanding of the process. However, to the best of our knowledge, the reaction kinetics of glycerol dry reforming is not being studied yet. Therefore, the kinetics study of glycerol dry reforming could be an attractive area to be explored.

7.5 Conclusions

Glycerol dry reforming has become one of the promising routes for the syngas production. However, most of the reforming processes involve glycerol as the feedstock experiencing severe catalyst deactivation through the carbon deposition. Throughout the years, a good progress has been made to improve the glycerol dry reforming process, and it is clearly notable that few researches have successfully reduced the coking problems. These researches discover various potential catalysts that can be used to improve the process. Apparently, the addition of noble metal catalysts, i.e., Rh as the promoter, has proven to significantly reduce the carbon deposition and produces high syngas yield and glycerol conversion. The type of support does give influence on the performance of the catalyst especially in reducing the coking effect. Therefore, future development of carbon-resistance catalyst could potentially give significant impact to the yield and conversion of glycerol dry reforming. Apart from that, there is still lack of knowledge on the kinetics and mechanism of the glycerol dry reforming reaction. Thus, this scope of study could be an attractive area to be explored in the future.

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