

# An Investigation of Phenol Steam Reforming for Hydrogen Production: Thermodynamic Analysis

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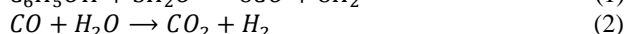
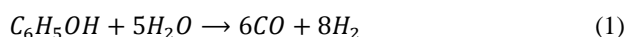
## ABSTRACT

In this work, the thermodynamic equilibrium involved in the steam reforming of phenol to produce hydrogen has been examined. The mole fraction of the hydrogen depends on several process variables, such as system pressure, temperature, and ratio of reactants. The first step to understanding the effects of the aforementioned variables is a complete thermodynamic analysis. In this study, a thermodynamic equilibrium analysis has been performed for the steam reforming process of phenol over the following variable ranges: pressure 1atm, temperature 100–1200 °C and phenol concentration in the feed ratio 2%–20%. The non-stoichiometric formulation has been used. The equilibrium concentrations of different compounds were calculated by the method of direct minimization of the Gibbs free energy. The results show that the phenol conversion and the hydrogen mole fraction increased at lower phenol concentration in the feed. The best condition for coke production was at 10% phenol concentration which produced less coke.

**KEY WORDS:** *phenol steam reforming, hydrogen production, thermodynamic analysis.*

## 1.0 INTRODUCTION

Due to the environmental concerns, production of hydrogen via the steam reforming of bio-oil components is considered as one of best ways for providing hydrogen future. The steam reforming of bio-oil is considered as an interesting route for hydrogen production with low CO<sub>2</sub> emission [1]. Among the bio-oil one of the most promising is bio-oil, which production has grown sharply in recent years. In bio-oil, around 38% wt. [2] of the bio-oil converts to the phenolic compounds. The steam reforming of phenol can reduce CO<sub>x</sub> which is the main greenhouse gases [3-5]. The reaction product of biomass pyrolysis typically contains a high molecular weight of hydrocarbon, phenolic compounds, acid, and water. Phenol was further recognized as the main component of tar formed following wood-biomass gasification by steam in a fluidized bed reactor in the low temperature range (600–700 °C) [5-7]. Phenol also can be obtained from industrial wastewater and is considered as toxic waste for many aquatic organisms. Due to its high solubility in water, it can directly convert to highly valuable gas hydrogen via steam reforming. The steam reforming of phenol, Reaction (1) and water gas shift reaction, Reaction (2), are two major side reactions that contribute to the deposition of carbon on the catalyst surface. These lead to deactivation of the catalysts and subsequently plugged the catalyst bed [8]:



Significant research has been reported for hydrogen production by carbon dioxide reforming and partial oxidation [9]. The sustainable production of hydrogen can be accomplished by the conversion of biomass through steam reforming (SR), gasification

combined with pyrolysis, partial oxidation (POX), oxidative steam reforming (OSR), and autothermal reforming (ATR) from renewable carboxylates, such as glycerol, bio-ethanol, bio-oil and carbohydrates [10].

In this study, the possibility of water-rich phase reforming of bio-oil is discovered through thermodynamic analysis. A wide range of the previous researches discovered thermodynamic analysis of ethanol and methane as a form of renewable energy production [11-14], dimethyl ether [11, 15] and methanol [11]. These researches focus on converting carbonated compounds to hydrogen. However, little effort has been expended for practically understanding the efficient thermodynamic analysis of phenol.

The aim of this work is thermodynamic analysis of steam reforming of oxygenated hydrocarbons of phenol for hydrogen production via thermodynamic design of Aspen V8.6 software. The resulting molar fractions are explored as a function of parametric variables such as pressure, phenol concentration and temperature. The production mole fractions for all of the variables were plotted.

## 2.0 METHODOLOGY

Aspen plus 8.6 software has been used for the analysis. The R-Gibbs reactor (Figure 1) with Peng–Robinson property method has been chosen for the thermodynamic analysis. Phenol is the main component with the maximum composition of the mixture chosen to simulate the reforming of the phenol steam reforming. H<sub>2</sub>, CO, CO<sub>2</sub>, and C as well as the residual fuel and H<sub>2</sub>O were measured as the reforming based products on experimental result for Aspen Plus code requirement of product definition. The phenol concentration, reaction temperature and the pressure as a part of reactants condition must be stated. The input parameter set in the steam reforming is because the reactor temperature in the steam reforming for thermodynamic analysis is controlled by external heat transfer to the reactor and not the reactor itself [16]. The range of 100-1200 °C and 2-20% were varied for temperature and phenol concentration respectively and the result was shown by molar fractions of gas products. Coke formation was defined as solid carbon formation in the oxygenated feed.

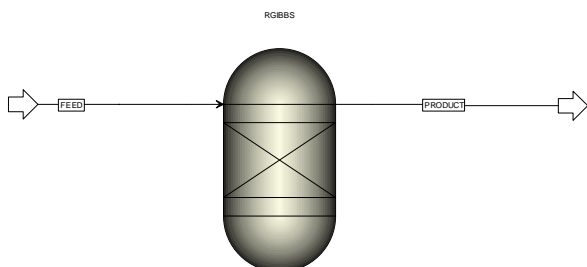


Figure 1 Schematic representation of the thermodynamic R-gibbs reactor

## 3.0 RESULTS

### 3.1 Effect of temperature on phenol conversion

Temperature is the most important influencing factor in the steam reforming of hydrocarbons. Figure 2 shows the effect of temperature on phenol conversion in various concentration of phenol in water in the feed stream. The figure shows that the phenol conversion is increased by temperature in all concentration of phenol. This tendency of positive effect of temperature on phenol steam reforming reaction is consistent with results obtain for other experimental results too [7, 8, 17-21]. As the temperature increased from 100 °C to 700 °C, the phenol conversion increased from 5% to 100% for all phenol concentrations except for 18% and 20%. Based on this thermodynamic result, it indicated that the increase of phenol concentration had a negative effect on phenol steam reforming reaction and low concentration was favorable for the phenol steam reforming reaction.

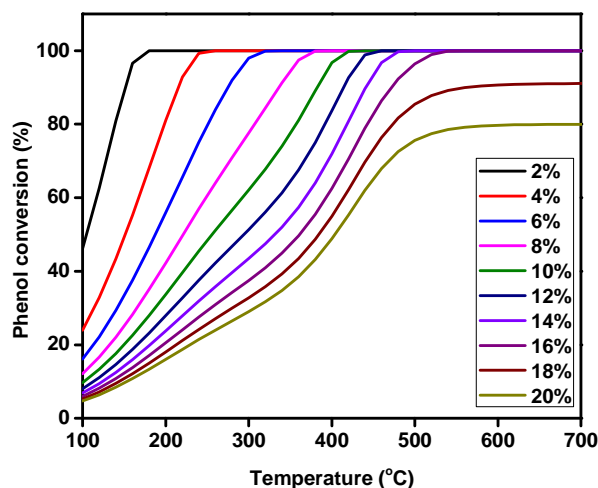


Figure 2 Effect of temperature on phenol conversion in different concentration of phenol in water

### 3.2 Effect of temperature on hydrogen molar fraction

Effect of temperature on hydrogen production was investigated at 2 to 20% concentration of phenol and 1 atm pressure at the temperature range of 100 to 1200 °C. Figure 3 shows the effect of phenol concentration and temperature on hydrogen production. In general, the molar fraction of hydrogen decreased with the increase of temperature at specified concentration. However, the molar fraction of hydrogen was higher at lower concentration. As the concentration increased from 2 wt.% to 20 wt.%, the molar fraction of hydrogen decreased gradually. It indicated that low temperature and low concentration were favourable for hydrogen production, which could enhance the steam-reforming and water-gas shift reaction better.

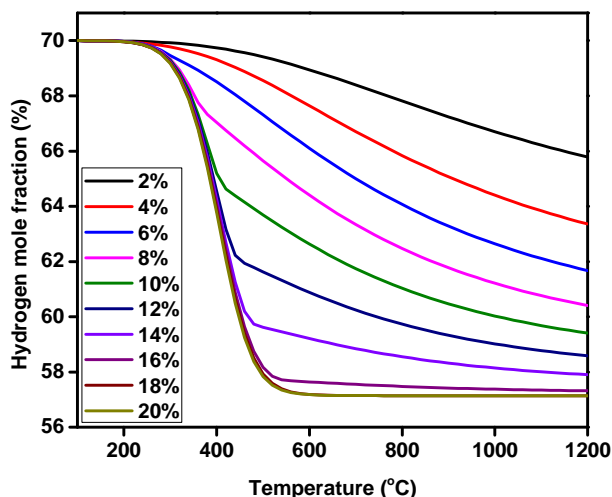


Figure 3 Effect of temperature on hydrogen molar fraction in different concentration of phenol in water

### 3.3 Effect of temperature on carbon monoxide molar fraction

Figure 4 shows the effect of temperature on carbon monoxide (CO) production at 2 to 20% concentration of phenol and 1 atm pressure at the temperature range of 100 to 1200 oC. In general, the CO molar fraction decreased with increasing the temperature from 100 to 1200 oC. As it can be seen, the phenol concentration affects the CO molar fraction at the area of 200 to 550 oC only. However, the CO contents produced are initially low due to the water gas shift reaction.

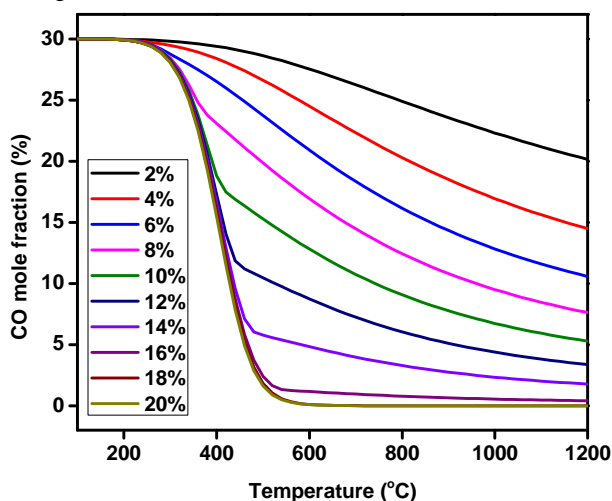


Figure 4 Effect of temperature on carbon monoxide molar fraction in different concentration of phenol in water

### 3.4 Effect of temperature on carbon dioxide molar fraction

Effect of temperature on CO<sub>2</sub> production during all concentration of phenol and temperature range is shown in Figure 5. As it can

be seen, at low temperature ranges low amounts of CO<sub>2</sub> is produced. The CO<sub>2</sub> molar fraction is increased by increasing in temperature from 100 to 1200 °C due to the reverse water gas shift reactions. Unlike above mentioned results, the low concentration is not favorable to CO<sub>2</sub> production.

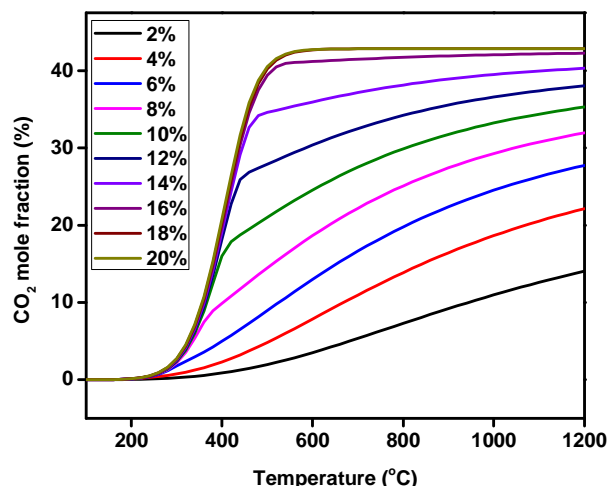


Figure 5 Effect of temperature on carbon dioxide molar fraction in different concentration of phenol in water

## 3.0 CONCLUSION

In conclusion, the temperature and the phenol concentration are playing a very significant role in the activity of phenol steam reforming. It was found that the phenol steam reforming reaction is favourable with low concentration of phenol in water rather than high concentrations. At low concentration, higher phenol was converted to product, higher hydrogen and carbon monoxide and lower carbon dioxide were produced.

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