Effect of Impurities on Bioethanol Steam Reforming Process for Hydrogen Production

Thanyawat Kaewsuk and Paravee Vas-Umnuay*

Center of Excellence in Particle and Material Processing Technology, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok 10330, Thailand

*E-mail: Paravee.v@chula.ac.th

Abstract:
Bioethanol has been recognized as a potential alternative to petroleum- and natural gas-derived fuels. Bioethanol can be a suitable feedstock for a production of hydrogen via steam reforming process. Generally, hydrogen selectivity and ethanol conversion are significantly dependent on reaction temperature, steam to ethanol ratio and impurities in the feedstock. In the past, many researchers have already investigated the effects of temperature and steam to ethanol ratio on the conversion, selectivity and yield extensively. However, not many researches have reported the effect of impurities in the feedstock. Therefore, this work is to investigate the effects of different impurities (1 mol% of acetone, 1-propanol and propyl amine each which are obtained from a variety of agricultural products) on the conversion, selectivity and yield in the steam reforming process via Aspen Plus 8.8. The aim of this study is to find the amount of product distribution as a result of addition of different impurities in the feed under following conditions; atmospheric pressure, temperature ranging from 300-600°C, steam to ethanol ratio ranging from 2-3. The simulated results can be useful for prediction under various conditions and used for the design of the experimental ethanol steam reforming process.

1.Introduction
A majority of energy to supply human’s consumption is produced from petroleum and natural gas, which are non-renewable energy. However, the burning process of these resources causes a major issue of global warming. For this reason, many researchers have been searching for a renewable energy to be used an alternative energy. Bio-ethanol, one of the renewable energy resources, has a lot of advantages such as low cost, low toxic, environmentally friendly and has a potential as a feedstock for many applications e.g. fuel cell.1-2 Therefore, bio-ethanol has been receiving more attentions. So far, bio-ethanol has shown to be one of the most sustainable feedstocks for hydrogen production via steam reforming process. There were several reports that show a high conversion and high selectivity.3

In previous studies, steam reforming process from bio-ethanol for hydrogen production has been focused on the investigation of catalyst, coke formation, temperature and ratio of feed water and pure ethanol in order to obtain the optimal conditions. In general, bio-ethanol is derived from biomass. Therefore impurities are always present depending on a variety of agricultural products. These impurities, even in very small amount of less than 1 mol%, can have a significant impact on hydrogen production. The impurities that are mostly found in bio-ethanol consist of an alcohols such as 1-propanol, 2-propanol and methanol. Others are ketones such as acetone and nitrogen based compounds such as propyl-amine.4-5 Therefore in this work, we focused on 1-propanol, acetone and propyl-amine as representative impurities of alcohol, ketone and nitrogen-based compounds, respectively.

According to a previous study investigating the effect of impurities on bio-ethanol steam reforming process using Rh/Al2O3 as a catalyst by Bilal et al., they
have proposed pathway reactions of bio-ethanol steam reforming process with a presence of 1 mol% of each impurity. The reactions are shown in the following equations (1)-(13). 

\[
\begin{align*}
C_2H_5OH + 3H_2O & \rightarrow 2CO_2 + 6H_2 \\
C_2H_5OH + H_2O & \rightarrow 2CO + 4H_2 \\
C_2H_5OH + 2H_2 & \rightarrow 2CH_4 + H_2O
\end{align*}
\]

Dehydrogenation reaction

\[
C_2H_5OH \rightarrow C_2H_4O + H_2
\]

Dehydration reaction

\[
C_2H_5OH \rightarrow C_2H_4 + H_2O
\]

Ethanol decomposition

\[
\begin{align*}
C_2H_5OH & \rightarrow CO + CH_4 + H_2 \\
2C_2H_5OH & \rightarrow C_3H_6O + CO + 3H_2 \\
C_2H_5OH & \rightarrow 0.5CO_2 + 1.5CH_4
\end{align*}
\]

Water gas shift reaction

\[
CO + H_2O \rightarrow CO_2 + H_2
\]

Ethylene polymerization

\[
C_2H_4 \rightarrow \text{coke}
\]

Decompositions of ethane and ethylene

\[
\begin{align*}
CH_4 & \rightarrow C+2H_2 \\
C_2H_4 & \rightarrow 2C+2H_2
\end{align*}
\]

Boudouard reaction

\[
2CO \rightarrow CO_2+C
\]

It can be seen in the reactions that coke is a major problem for this process because it restrains the reaction, decreases the efficiency and life span of catalysts. Therefore, it could cause low selectivity of hydrogen and low conversion. Furthermore, when the feed contains the impurities like acetone and propyl amine, these compounds were reacted to produce methane as a major by-product, as shown in equations (14) and (15). While ethylene is produced as a major by-product when the feed contains 1-propanol as impurity, as shown in equations (16). As a consequence, coke can be formed as a result of methane and ethylene decomposition.

\[
\begin{align*}
10C_2H_3OH + 4H_2O & \rightarrow 4CO + 9CH_4 + 14H_2 + 5CO_2 + C_2H_4 \\
4C_2H_5OH + 3H_2O & \rightarrow CO + 4CH_4 + 7H_2 + 3CO_2 \\
23C_2H_3OH+5H_2O & \rightarrow 2CO + 4CH_4 + 10H_2 + 4CO_2 + 16C_2H_4 + 2C_2H_6+ 18H_2O
\end{align*}
\]

So far, none of the related work has been reported on the effect of coke formation during the reaction zone with impurities in the feedstock. Therefore, this work aimed to investigate the effect of impurities including 1 mol% of acetone, 1-propanol and propyl amine on the conversion of bio-ethanol via reforming process by using Aspen Plus 8.8. The suitable temperature and steam/ethanol ratio conditions were obtained.

2. Materials and Methods

Aspen plus 8.8 was used to calculate products from bio-ethanol steam reforming process at equilibrium when the feed consisted of 1% of each impurity. RGibbs was used as a reactor and the products were separated based on the phase in Flash2, as shown in Figure 1. The calculation was based on PENG-ROB as an equation of state. The operating temperature studied was ranging from 300 to 600 °C, while steam to ethanol molar ratio was ranging from 2 to 3, at atmospheric pressure.

3. Results & Discussion

3.1 Pure Ethanol

Figure 2 shows a result from Aspen Plus 8.8 of the case of pure ethanol without impurities at various operating temperatures. The ethanol and steam conversions of 100% were obtained for this condition. At low
temperature, the reaction produces high methane, but when temperature increases, methane decreases to the lowest at 3.32%. On the other hand, hydrogen increases with increasing temperature, where the highest selectivity of 69.65% was obtained when temperature was at 600°C. According to the endothermic reaction shown in equation (1), it was expected that increasing reaction temperature beyond 600°C would result in higher selectivity of H₂.

From Figure 3, coke formation was investigated when low steam/ethanol ratio was applied at any temperature. Within the low steam/ethanol ratios from 2-2.6, coke formation appears to be lower at higher temperature. This is because of high methane generation at lower temperature, which then generates coke as a result of methane decomposition, as shown in equation (11). When steam/ethanol ratio is more than 2.7, ethanol completely reacts with steam into hydrogen and carbon dioxide, therefore the coke formation approaches zero, as expressed in equation (1).

![Figure 2](image)

**Figure 2.** Productions from ethanol steam reforming (Steam/Ethanol=3) without impurities at various operating temperatures and at 1 atm.

![Figure 3](image)

**Figure 3.** Coke formation from pure ethanol steam reforming without impurities at 1 atm.

### 3.2 Effect of impurities

Figure 4 shows the effect of each impurities on selectivity of hydrogen at different temperatures. Similarly, the ethanol and steam conversions of 100% were obtained for this condition. It can be seen that all of the impurities have similar effect on hydrogen selectivity. Moreover, it is obvious that the selectivity of hydrogen obtained from the pure feed is higher than those with impurities. This could be attributed to the fact that these impurities change the reaction pathway and produce more by-products. Similarly, Figure 5 shows the effect of each impurities on the selectivity of methane at different temperatures. It can be obviously seen that methane selectivity obtained from the feed with each impurity is higher than that with pure ethanol. However, ethylene, which is another by-product, shows no effect on the reaction. It could be attributed to a reversible Boudouard reaction, as shown in equations (12) and (13). Ethylene was produced and decomposed into coke. Then, coke and carbon dioxide react to form carbon monoxide, which is shown as a result in Figures 6 and 7. Carbon dioxide was lower when the feed contained impurities, while carbon monoxide was higher, compared to that of the feed with no impurities.
Figure 4. Hydrogen selectivity obtained from the feed with various impurities at different temperatures (steam/ethanol = 3).

Figure 5. Methane selectivity obtained from the feed with various impurities at different temperatures (steam/ethanol = 3).

Figure 6. CO selectivity obtained from the feed with and without impurities at various temperatures (steam/ethanol = 3).

Figure 7. CO$_2$ selectivity obtained from the feed with and without impurities at various temperatures (steam/ethanol = 3).

Figure 8 shows coke formation from ethanol steam reforming reaction when various steam/ethanol ratios were applied. Different impurities of 1-propanol, acetone and propylamine have similar result of coke formation. It is shown that high coke formation occurred at low steam/ethanol ratio because water limited the reactants and remaining ethanol decomposed into coke. It can be summarized that when the operating temperature is at 600°C, coke formation occurs at steam/ethanol ratio from 2.7 to 2.9. At 300°C, coke formation occurs at steam to ethanol ratio from 2.5 to 2.7. High formation of coke is a result of the presence of impurities. That mean impurities causes decompositions which consequently generates coke. It also inhibits the main pathway reaction, resulting in lower selectivity of the products.
was suggested to be as follows: temperature at 600°C and steam/ethanol ratio of more than 2.6.

References