Demonstrative Study on the Production of Hydrogen and Aromatic Compounds Originated from Biogas in the Dairy Area

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\section*{ABSTRACT:}

The biogas yielded by methane fermentation of cow slurry was provided for the experimental facilities and the refined methane was introduced to the methane direct reformer. Dehydrogenation and aromatization of methane generated hydrogen and aromatic compounds, such as benzene. In order to keep the conversion rate, pre-treatment and regeneration of the catalysts were carried out and in order to control coking at the catalysts, hydrogen was added to the material methane. Moreover a part of the un-reacted methane was introduced to the steam reformer and 99.99\% pure hydrogen was produced by the pressure swing adsorption (PSA). With the result that, it was supposed that pre-treating by methane and hydrogen, repeating regeneration by hydrogen, and more than 9\% hydrogen addition were needed to stabilize the formation of hydrogen and benzene. And furthermore, material balance of the experimental facilities was clarified.

\textbf{KEYWORDS :} biogas, hydrogen, methane direct reforming, aromatic compounds, benzene

\section*{1. Introduction}

The large-scale dairy farming is performed in Hokkaido, where is cold and snowy area. While “The Biomass Nippon Strategy” is promoted in Japan, the livestock feces and urine which generated in the dairy area are noticed as the carbon neutral energy source. Civil Engineering Research Institute for Cold Region (CERI) has carried out the development of the centralized biogas plant which is 1,000 dairy cow scale in the east Hokkaido area\textsuperscript{(1)(2)}. Moreover, aiming at the technical establishment for the efficient energy supply and the demonstration of greenhouse effect gas reduction by using hydrogen and fuel cells, the demonstrative plant which generated and stored hydrogen energy originated from biogas (Biogas to Hydrogen; BTH-Plant) was placed in 2003\textsuperscript{(2)(3)} and the research about engineering components was taken place\textsuperscript{(4)(5)}. In this research, the experimental production of hydrogen and aromatic compounds, such as benzene, from biogas by methane direct reforming and steam reforming were carried out.

\section*{2. Experimental procedure}

The demonstrative plant consists of the pre-treatment facility, the methane direct reforming facility and the steam reforming facility. In this research, 200 Nm$^3$/d of biogas was provided from the Betsukai biogas plant, as shown in Figure 1. Figure 1 also shows the appearance of the facilities.

Figure 2 shows the schematic diagram of the experimental facilities. The provided biogas contained hydrogen sulfide, methyl-mercaptan, oxygen etc. Table 1 shows the typical composition of the biogas at the Betsukai biogas plant. Because these trace chemicals degraded the catalyst performance for methane direct reforming\textsuperscript{(5)(6)} and should be reduced, the pre-treatment facility had the desulfurizing reactor, the desulfurizing absorber, the desulfurizing absorber, the gas-liquid separator and the methane renyl. Carbon dioxide which accounted for 40\% of the biogas was removed with this poly-imide membrane module.

The methane direct reformer was provided with 108 Nm$^3$/d of the refined methane. 7.5 kg of 6wt\% Mo added ZSM-5 type zeolite catalysts were used for the direct reforming reactor. The reaction of the methane direct reforming is shown by the following formula.

\[ 6\text{CH}_4 \quad \square \quad \text{C}_6\text{H}_6 \quad + \quad 9\text{H}_2 \]
Figure 1. The Bird’s-eye view of the Betsukai biogas plant and the appearance of the facilities in the BTH-plant

Figure 2. The schematic diagram of the experimental facilities
Figure 3 shows the schematic diagram of methane direct reforming reaction in the catalyst. Hydrogen and benzene are generated by the dehydrogenation and aromatization of methane. Before the reforming, the catalysts were pre-treated at 650 ºC under the pressure of 0.4MPa for 1 hour by using only the refined methane gas. Methane direct reforming was performed at 750 ºC under the pressure of 0.4MPa. Space velocity of the material methane was about 3000 L/kg-zeolite/h. In order to keep the conversion rate of methane direct reforming, pre-treatment and regeneration of the catalysts were carried out. And moreover, in order to control coking at the direct reforming catalysts and to stabilize reforming reaction for a long time, 7% to 9% hydrogen was added to the material methane (7). The product aromatic compounds were quenched and absorbed by alpha-methyl- naphthalene solvent in the absorbing tower. Benzene was distilled from this solvent.

The product gas which consisted of hydrogen, un-reacted methane and trace olefin passed through the olefin separator. Furthermore, at the methane membrane separator, a part of un-reacted methane was recycled and was added to the material methane. The other part of un-reacted methane with hydrogen was provided to the steam reformer. Steam reforming was performed at 750 ºC under the pressure of 0.36MPa. After the CO shift conversion, the product hydrogen was purified by pressure swing adsorption (PSA).

Table 1. The typical composition of the biogas at the Betsukai biogas plant

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>61.7%</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>38.1%</td>
</tr>
<tr>
<td>Oxygen</td>
<td>0.05%</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.13%</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>&lt;1ppm</td>
</tr>
<tr>
<td>Ammonia</td>
<td>&lt;0.01ppm</td>
</tr>
<tr>
<td>Methyl mercaptan</td>
<td>&lt;0.01ppm</td>
</tr>
<tr>
<td>Hydrogen sulfide</td>
<td>&lt;0.01ppm</td>
</tr>
<tr>
<td>Methyl sulfide</td>
<td>&lt;0.05%</td>
</tr>
<tr>
<td>Sulfur oxide</td>
<td>&lt;1ppm</td>
</tr>
<tr>
<td>Nitrogen oxide</td>
<td>&lt;1ppm</td>
</tr>
<tr>
<td>Alkanoic acids</td>
<td>&lt;0.5ppm</td>
</tr>
<tr>
<td>(Acetic acid,Propionic acid,etc.)</td>
<td></td>
</tr>
<tr>
<td>Amine</td>
<td>&lt;0.5ppm</td>
</tr>
<tr>
<td>(Diethyl amine, Triethyl amine,etc.)</td>
<td></td>
</tr>
</tbody>
</table>

Figure 3. The schematic diagram of methane direct reforming reaction in the catalyst
3. Results and discussion

3.1 Material balance

Figure 4 shows the schematic diagram and table of the typical material balance. The refined methane was almost 99.9% of purity and contained a trace of carbon dioxide. It was introduced into the methane direct reformer. In the case of 9% hydrogen addition of the supplied material methane, the volume of hydrogen increased to about 16% in the reformed gas. And moreover aromatic compounds, such as benzene, naphthalene and toluene, and olefin compounds were detected. After removing aromatic compounds, olefin compounds and the recycled methane, the gas which was introduced into the steam reformer consisted of about 48% hydrogen and about 52% un-reacted methane. When the conversion ratio of the steam reforming was about 86% and the refining ratio of PSA was 73%, more than 99.99% purity of hydrogen was obtained and was amounted to 140 Nm$^3$/d, except the hydrogen which was used by hydrogen addition for the methane direct reforming. Furthermore, the off-gas occurred from the pre-treatment (methane refining), the methane direct reforming and the steam reforming (PSA) facilities, with the result that the composition showed about 17% methane, 48% carbon dioxide, 34% hydrogen and 1% carbon monoxide.

![Schematic diagram and table of the typical material balance of 9% hydrogen addition case](image)

3.2 Methane direct reforming property

3.2.1 Hydrogen generating

Figure 5 shows the formation rate of hydrogen in methane direct reforming. The Hydrogen addition rate was taken from the formation rate. In the case of 7% hydrogen addition, the formation rate of hydrogen was higher in the early time. The formation rate of hydrogen showed 2500-3200 nmol/g-zeolite/s, but the tendency to fall was shown in progress of the reaction time. With the increase in the amount of hydrogen addition, the tendency to become more stable was shown at the formation rate of hydrogen, though it became lower. Especially in the case of 9% hydrogen addition, the formation rate of hydrogen did not fall greatly at 50 hours of the reaction time because coking of the catalysts was controlled.

3.2.2 Aromatic compounds generating

Figure 6 shows the formation rates of hydrogen and benzene in the direct reforming. In the case of 8% hydrogen addition, the formation rates of benzene were higher between 15 hours and 65 hours of reaction time. The formation rate of benzene showed 200-300 nmol/g-zeolite/s, but the tendency to fall was shown in progress of the reaction time. With the increase in the amount of hydrogen addition, the tendency to become more stable was shown at the formation rates of benzene, though these became lower.
3.3 Improvement of methane direct reforming

The reason why the tendency to fall was shown in the formation rate of benzene and hydrogen was because coking was taken place at the direct reforming catalysts. It was supposed that carbon generation by methane reduction became the causes of coke generation and the stoppage of micro pore especially. In order to control coking enough and to stabilize the formation rate of hydrogen and benzene, the reformation of pre-treatment and the repeated regeneration by hydrogen were needed. Figure 7 shows the patterns of pre-treatment and regeneration for the direct reforming catalysts. (a) shows the conventional pattern and (b) shows the reformed pattern. Figure 8 shows the formation rates of hydrogen and benzene in the case of the
reformed pattern. The formation rate of benzene and hydrogen recovered whenever regeneration by using hydrogen flow and especially the formation rate of benzene was kept at 200-350 nmol/g-zeolite/s.

Figure 7. The patterns of pre-treatment and regeneration for the direct reforming catalysts

Figure 8. The formation rates of hydrogen and benzene in the case of the reformed pattern
4. Conclusion

In this present work, the demonstrative examinations for the production of hydrogen and aromatic compounds, such as benzene, from biogas which was generated from the large-scale centralized biogas plant were carried out by methane direct reforming and steam reforming. In order to keep the conversion rate of methane direct reforming, pre-treatment and regeneration of the catalysts were carried out and in order to control coking at the direct reforming catalysts, hydrogen addition which was 7% to 9% of the material gas was carried out. As the result of these experiments, it was supposed that more than 9% hydrogen addition, the reformation of pre-treatment and repeated regeneration by hydrogen were needed to stabilize the formation rate of hydrogen and benzene.

Furthermore, a part of un-reacted methane with generated hydrogen was introduced to the steam reformer and 99.99% pure hydrogen was produced by pressure swing adsorption. With the result that the material balance of the experimental facilities was clarified.

Acknowledgements

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