Comparisson of reforming process between different types of biogas reforming reactors

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ABSTRACT
This report contains a small comparison of the different chemical reactions that occur in a fixed- and fluidized bed reactor with and without following carbon monoxide shift reactors. It also presents the chemical reactions during plasma reforming. Finally a short presentation of the advantages and drawbacks with membrane reactor reforming is done.

NOMENCLATURE

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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</thead>
<tbody>
<tr>
<td>$H_2$</td>
<td>Hydrogen</td>
</tr>
<tr>
<td>$CH_4$</td>
<td>Methane</td>
</tr>
<tr>
<td>$CO$</td>
<td>Carbon monoxide</td>
</tr>
<tr>
<td>$CO_2$</td>
<td>Carbon dioxide</td>
</tr>
<tr>
<td>$H_2O$</td>
<td>Water, Steam</td>
</tr>
<tr>
<td>$NH_3$</td>
<td>Ammonia</td>
</tr>
<tr>
<td>$H_2S$</td>
<td>Hydrogen sulfide</td>
</tr>
<tr>
<td>$C_2H_2$</td>
<td>Acetylene</td>
</tr>
<tr>
<td>$NiO$</td>
<td>Nickel monoxide</td>
</tr>
<tr>
<td>$\Delta H$</td>
<td>External heat</td>
</tr>
<tr>
<td>$S/C$</td>
<td>Steam to methane ratio</td>
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Greek Symbols

<table>
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<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>$\varepsilon$</td>
<td>Membrane porosity</td>
</tr>
<tr>
<td>$\tau$</td>
<td>Membrane tortuosity</td>
</tr>
<tr>
<td>$\mu$</td>
<td>Dynamic viscosity</td>
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Subscripts

<table>
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<tr>
<th>Symbol</th>
<th>Description</th>
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</thead>
<tbody>
<tr>
<td>$r_p$</td>
<td>Effective membrane pore diameter</td>
</tr>
<tr>
<td>$R$</td>
<td>Universal gas constant</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature</td>
</tr>
<tr>
<td>$M_i$</td>
<td>Molecular weight of species i</td>
</tr>
<tr>
<td>$N_i$</td>
<td>Flux of species i</td>
</tr>
<tr>
<td>$D_{i,eff}$</td>
<td>Effective diffusivity of species i</td>
</tr>
<tr>
<td>$x_i$</td>
<td>Mole fraction of species i</td>
</tr>
<tr>
<td>$P$</td>
<td>Pressure</td>
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INTRODUCTION
The purpose of reforming biogas is to create a gas with a high concentration of hydrogen. This gas can be used as fuel in gas engines or in fuel cells for power production or vehicle propulsion.

Different reactors produce gas suitable for different purposes and the composition of the effluent gas is depending on which reforming method being used.

This report will compare how the effluent gas composition differs and how the different chemical reactions occur between steam reforming in fixed- and fluidized-bed reactors, with and without carbon shift reactors, and between plasmatron reformers and membrane reactors.

The biogas used for reforming in all the different reactors is of typical composition with 50-60 % $CH_4$, 40 % $CO_2$, 1 % $H_2O$ and small traces of $NH_3$ and $H_2S$. [1]

FIXED- AND FLUIDIZED-BED STEAM REFORMING
In a fixed- or fluidized bed reformer, the $H_2S$ has to be removed prior to the reforming not to cause poisoning of the process catalyst. This is done in an activated carbon filter.

The chemical reactions that take place during steam reforming are [2]:

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \quad \Delta H = +206kJ / mol$$

This reaction is highly endothermic, that is, the reaction needs a large addition of external heat.

If there is a shortage of water, dry reforming occurs and the chemical reaction for this is:

$$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2 \quad \Delta H = +247kJ / mol$$

The equation shows that this reaction is highly endothermic too.

The reaction temperature and steam to methane ratio has a high influence on the $CH_4$ conversion rate and
H₂ yield in the effluent gas. The CH₄ conversion to H₂ increases steeply when raising the reactor temperature and thereby raises the H₂ yield and concentration in the effluent gas. Although after 750°C the gain in conversion is very low and after 800°C the H₂ concentration even decreases. The optimum temperature is in the range of 700-750°C.

By adding steam during the reaction the H₂ selectivity increases and that leads to a lower concentration of CO in the effluent. The increase of S / C always lead to an improved methane conversion rate and thus H₂ yield and concentration but the evaporation and superheating of water results in a high energy demand. [2]

The maximum concentration of H₂ in the effluent from steam reforming in a fluidized bed reactor is 60-62 %. The CH₄ conversion during those conditions are >98 %. A fixed bed reactor have 7-15 % lower conversion grade of CH₄ and CO₂ and thereby the effluent gas contains a lower concentration of H₂. This is due to inferior heat distribution in the fixed bed reactor that gives cold spots. The heat transfer rates in a fluidized bed reactor are also much higher than those in a fixed bed reactor.

The effluent gas contain CO, CO₂ and H₂. Any excessive steam is removed by condensation and the conversion to methane is almost complete. [1]

**CO SHIFT REACTIONS**

The effluent gas from the steam reforming contains a high concentration of CO that improves the performance in gas engines, although when the gas is addressed as fuel in a fuel cell this CO₂ has to be minimized not to poison the fuel cell.

To minimize the CO concentration, the steam reforming in fixed- or fluidized-bed reactors is followed by CO shift reactions in one low- and one high-temperature CO shift reactor.

\[
\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2 \quad \Delta H = -41 \text{kJ} / \text{mol}
\]

This reaction is exothermic and the temperature of the effluent gas from the fluidized bed reactor is reduced before entering the HT- and LT-shift reactors to optimize the performance of the reactors.

The reactor temperature and steam addition have a similar influence on the reaction as it had during steam reforming. The only difference is that the temperature needs to be lower for optimum performance. The optimum temperatures in the HT- and LT-reactors are 300 °C and 200 °C respectively. The HT-reactor increases the H₂ concentration and the LT-reactor decreases the CO concentration. This gives a product gas with a H₂ concentration of 68 % and a CO concentration as low as 0,2 %.

The additional reforming makes the process more expensive and more complex but the low CO concentration makes the product gas suitable for fuel cells. [3]

**BIOGAS REFORMING USING PLASMATRON**

Plasmatron is the name of the high temperature reforming method using a plasma flame that is generated by air and arc discharge in the reforming reactor. The purpose of using this method is to overcome the drawbacks of conversion using conventional reforming, e.g. Steam reforming.

Conventional reforming methods need an external high temperature source because of the highly endothermic reactions. They also suffer from slow ignition characteristics and catalytic poisoning by a small amount of sulphur in the fuel gas.

Fig. 2. shows an experimental apparatus for plasma reforming:

![Fig. 2. Schematic of experimental plasmatron apparatus. [4]](image-url)

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The reactions during plasma reforming are very diverse and complex but some of the reactions are the same that occurs during steam reforming with CO shift reactions:

Partial oxidation reforming reaction:
\[ CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2 \] (1)

Carbon dioxide reforming reaction:
\[ CH_4 + CO_2 \rightarrow 2CO + 2H_2 \] (2)

Steam reforming reactions:
\[ CH_4 + H_2O \rightarrow CO + 3H_2 \] (3)
\[ C + H_2O \rightarrow CO + H_2 \] (4)

Plasma (cracking) reforming reactions:
\[ CH_4 \rightarrow C + 2H_2 \] (5)
\[ 2CH_4 \rightarrow C_2H_2 + 3H_2 \] (6)
\[ 2CO \rightarrow C + CO_2 \] (7)

Water-gas shift reaction:
\[ CO + H_2O \leftrightarrow CO_2 + H_2 \] (8)

CO oxidation:
\[ CO + \frac{1}{2}O_2 \rightarrow CO_2 \] (9)

Catalytic surface reactions:
\[ CH_4 + NiO \rightarrow C + H_2 \] (10)
\[ C + O \rightarrow CO \] (11)

The superior reactions are the partial oxidation reforming (1) and the plasma reforming of eq. (5) and (6). When changing the \( CH_4 \) concentration in the feed gas, the CO concentration varies comparatively little. This is because the CO created during the partial reforming reaction is continuously converted into \( CO_2 \) through plasma reforming (7) and CO oxidation (9). The maximum \( H_2 \) concentration after the reforming is 45.4 % and the corresponding CO concentration is 6.9 %.

By adding steam during the process, the \( H_2 \) concentration in the effluent gas increases as with previously reforming methods. This is because the steam reforming reactions (3) and (4) and water-gas shift reaction (8) progress strongly. The maximum \( H_2 \) concentration with steam addition is 50.4 %. The CO concentration also decreases more than 50 %. [4]

The concentration of \( H_2 \) is lower in the effluent gas from the plasma reforming than from the conventional steam reforming. The reforming method is however relatively new and not so well developed yet.

**BIOGAS REFORMING WITH MEMBRANE REACTORS**

Membrane reforming has a great advantage in that the reactions are not limited to thermodynamic equilibrium. This means that the produced effluent gas can achieve very high concentration of \( H_2 \). Another practical advantage is that the reaction and separation process is performed in the same unit.

**Fig. 3. Membrane autoreformer.** [5]

There are two different types of membrane that both have certain qualities. Dense metallic membranes have very high \( H_2 \) selectivity but suffer from relatively poor permeability because of the dense material. This leads to the need of membranes with large areas, and thereby large costs and high energy demands, to produce gas in a commercially feasible rate. These dense membranes also have some fatigue problems due to hydrogen embrittlement and they are very sensitive to sulphur poisoning like the steam reforming method.

One way to avoid these problems is to use porous ceramic membranes which have better thermal and mechanical stability and permeability. The drawback of this porous material is that it allows other gases than \( H_2 \) to permeate through the membrane. The bigger pore size of the ceramic membranes leads to Knudsen separation factors in the membrane. This means that the mass transfer is inversely proportional to the square root of molecular weight.

Knudsen diffusivities:
\[
D_{i,k} = \frac{4 \epsilon \left( r_p \right)}{3 \pi} \sqrt{\frac{8RT}{\pi M_i}}
\]

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The mass transfer of the various species in the gas mixture across the membrane can be calculated using a modified Fick’s formula:

\[
N_i = -\frac{1}{RT} \left( D_{i,eff} \frac{\partial (x_i P)}{\partial r} + \frac{B}{\mu} x_i P \frac{\partial P}{\partial r} \right)
\]

In addition to the advantage with very high \( H_2 \) concentration in the effluent, membrane reforming reactors may also benefit from lower energy input. The most important factor for low energy requirement is high permeance but the membranes selectivity toward hydrogen also influence on the energy requirement.

The membrane reforming method suits small scale production of hydrogen rich gas better because of the slow process when high \( H_2 \) selectivity is addressed. The membranes are also highly appropriate for \( CO_2 \) separation. [5]

CONCLUSIONS

The different reforming methods show different advantages for hydrogen rich gas production. The reforming with fixed- and fluidized bed reactors is a well known technique but the thermodynamic limits makes it desirable to develop the membrane reforming methods further. The plasmatron could be a future alternative to membrane reforming but the method is still new and need much research and development.

REFERENCES


