Simulation on Landfill Gas-Steem Reforming

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ABSTRACT

Landfill gas (LFG) is a kind of methane-rich biogas. Methane is a potent greenhouse gas with over 20 times the potential in trapping heat in the atmosphere compared to carbon dioxide over a 100-year period. In the chemical industry, methane is a source for hydrogen production. The advantage of hydrogen over methane is that in a fuel cell it can be a high efficient source of electric energy. In this paper, the LFG steam reforming is investigated by simulation. The effect of pressure, methane and steam concentrations and the effect of traces of ethane and nitrogen are analyzed at above 1000 K. The effects of small quantities of oxygen and hydrogen sulphide in landfill gas are also evaluated. The results demonstrate that the hydrogen production in reforming process is affected significantly by pressure. Traces of ethane would act as reactants in system, but nitrogen and oxygen are inert.

1. INTRODUCTION

Landfill gas (LFG) is generated through the anaerobic decomposition of organic waste present in municipal solid waste. Generation starts shortly after a landfill begins receiving waste and can last for up to 30 years after the landfill closes. The average composition of this LFG is about 54% methane (CH₄), 42% carbon dioxide (CO₂), and other gases. There are also trace amounts of non-methane organic compounds (NMOC).

LFG can be captured, converted, and used as an energy source [1-7], instead of escaping into the air directly. Utilization of LFG helps to prevent methane from migrating into the atmosphere and contributing to local smog and global climate change. LFG can be used to produce alternate fuels to offset the using of natural gas, coal or electricity generation. Recently, the most popular method is to produce hydrogen (H₂) by steam reforming as shown in Eq. (1) [8-15]. The reaction normally followed by a water gas shift as shown in Eq. (2).

\[
\begin{align*}
\text{CH}_4(g) + \text{H}_2\text{O}(g) &\rightarrow \text{CO}(g) + 3\text{H}_2(g) \\
\text{CO}(g) + \text{H}_2\text{O}(g) &\rightarrow \text{CO}_2(g) + \text{H}_2(g)
\end{align*}
\]

(1) (2)

LFG as a source of H₂ production has already been studied [16-19]. Unstable and uncontrollable gas production in landfills and a variety of catalyst poisonous trace gases are the most important aspects to be taken into account.

2. GIBBS MINIMIZATION METHOD

According to Gibbs Minimization method, the conditions for maximum H₂ were simulated by:

\[
G = \sum_{i=1}^{N} n_i \mu_i = \text{Min}
\]

(3)

It was based on the thermo physical data of the reactants [20] to calculate the compositions of substances in the reforming system. At definite temperatures T and pressures P, substances are favoured to the lower chemical potential G. In the ideal gas system, the formula becomes into:

\[
G = RT \sum_{i=1}^{N} n_i \left( \frac{G_i^0}{RT} + \ln P + \ln \frac{n_i}{n} \right)
\]

(4)

For a closed system, the total number of atoms of each component will remain constant. Then the solution of the steam reforming system equilibrium is equivalent to finding the minimum of the Gibbs function in Eq. (4) on a set of \(n_i\) satisfying the equation:

\[
\sum_{i=1}^{N} a_{ij} n_i = b_j, \ j = 1, 2, \ldots, M
\]

(5)

Generally, the Lagrange multiplier theory [21] is a classical method to such minimization model. Within this study, a non-commercial computer program described in ‘Thermodynamik der Elektrolytlösungen’ [22] was used. All the gaseous products were expressed as molar ratios.

3. RESULTS AND DISCUSSION

3.1 Steam concentration on gas production

LFG steam reforming system is endothermic. H₂ production would increase as temperature increasing,
meanwhile, the production would decrease in higher pressure [23-24]. In this simulation, steam concentrations were considered under pressure of 1 bar and 40.013 bar at respectively. Therefore, the simulated reactants were mixed as 6.0 mol CH₄ and 4.0 mol CO₂ in initial.

Fig. 1(a) shows the result of product gas compositions at different steam concentrations. At 40.013 bar and 1273.15 K, when the steam is less than 3.0 mol at the beginning, the H₂ concentrations kept around 42%. Then the H₂ production increased gradually as steam concentration increased. It reached the maximum at 47.19% with 6.0 mol steam in initial. As more steam was added into the mixed gas, H₂ production decreased.

At 1 bar, the maximum H₂ product reached to more than 55%. As Fig. 1(b) shown, H₂ is about 55.84% at 1073.15 K. It is noted, at 1273.15 K (shown in Fig. 1(c)), H₂ increased to 56.96% with 2.0 mol steam in simulation conditions. In industry processing, to prevent methane cracking, the ratio of steam to methane is kept larger than 1.0.

3.2 Header Section

Traces of hydrocarbons, which include alkyls, alkenes, alkynes and benzene, can be found in LFG. In this work, the effect of ethane (C₂H₆) on reforming system was studied.

There were two series of simulations to be calculated. In the first series, mixed gas which consists of 6.0 mol CH₄ and 4.0 mol CO₂ was simulated with 6.0 mol H₂O. It represented purified LFG reforming. In another series, with the same H₂O concentration, 5.4 mol CH₄ and 4.0 mol CO₂ was added up with 0.6 mol C₂H₆.

The results are shown in Fig. 2. From 973.15 K, the ratios of H₂ and CO are slightly higher (about 1%) than those without C₂H₆ in purified LFG. In contrast, the ratio of CO₂ decreased around 0.8% after adding C₂H₆. The traces of C₂H₆ would take part in steam reforming (Eq. (1)), giving rise to the slight increase of H₂.

3.3 Effect of oxygen on gas production

For the typical LFG, oxygen occupies about 0.8%. In this simulation, traces of oxygen were taken into account. In typical LFG, there are around 5.4 mol CH₄, 4.2 mol CO₂, and 0.08 mol O₂ with 6.0 mol H₂O in initial conditions. Compared the gas production with that from ideal LFG, which consists of 6.0 mol CH₄, 4.0 mol CO₂ with 6.0 mol H₂O in initial conditions, oxygen has almost no effect on gas composition.

As Fig. 3 shows, H₂ production is higher from ideal LFG (6.0 mol CH₄, 4.0 mol CO₂) than that from typical LFG (5.4 mol CH₄, 4.2 mol CO₂, and 0.8 mol O₂) in the same conditions. At 1073.15 K, H₂ reached the maximum 54.47% by ideal gas reforming, but for typical gas reforming process, H₂ only reached the maximum – about 51.68% at 1053.15 K. This difference is mainly caused by CH₄ concentration.

3.4 Effect of methane on gas production

As CH₄ increases, H₂ production will increase significantly. Meanwhile, methane cracking could cause catalyst deactivation in industry. As Fig. 4 shows, when steam is consumed during reforming process, methane decomposition will become a dominant reaction, and carbon deposit will occur. The reaction is shown as followed:

\[ CH_4(g) = C + 2 H_2(g) \]  (6)

3.5 Effect of hydrogen sulfide on gas production

Trace of hydrogen sulphide was studied in simulation. As Fig. 5 shows, 0.003 mol H₂S were considered into typical LFG in initial. The calculation results prove that traces of H₂S
do not react with any other components at high temperature. H₂S is able to poison catalyst, such as platinum in chemical industry. It is important to get rid of H₂S in practical LFG reforming.

4. CONCLUSIONS

In a theoretical approach the LFG reforming by computer simulation was analysed. Pressure, temperatures are vital for the methane reforming system. A wide range of steam concentration was considered for reforming reactions at 1bar and 40.013 bar. Lower pressure demonstrated a higher product ratio of H₂ from reforming system. On the other hand, the ratio of steam to methane should larger than 1. Otherwise, methane cracking would deactivate catalyst.

In addition to reaction conditions, traces of ethane as reactant were studied by simulation. It was proven by the calculation results that ethane also took part in reactions, so that H₂ production was slightly higher than that from purified LFG. Traces of oxygen, hydrogen sulphide do not change the reforming gas compositions. But the destroyed effect of hydrogen sulphide on metal catalyst for reforming process should be taken into account. A trace of nitrogen was also studied in the simulation. It is concluded that LFG reforming allows a relevant lower NOₓ releasing.

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NOMENCLATURES

- \( a \): amount of the element \( j \) in the component \( i \)
- \( b \): total amount of element \( j \)
- \( G \): Gibbs-energy
- \( G_i^0 \): standard Gibbs free energy of components \( i \) (J mol\(^{-1}\))
- \( N \): total amount of components(mol)
- \( n \): amount of components in a closed system (mol)
- \( n_i \): amount of component \( I \) (mol)
- \( p \): Pressure (kPa)
- \( T \): Temperature (K)
- \( \mu_i \): chemical potential of component \( I \) (J mol\(^{-1}\))

REFERENCES


