

Autothermal Reforming of Hydrocarbon Fuels

Harald Zeman, Michael Url, Hermann Hofbauer

Institute of Chemical Engineering, Vienna University of Technology
Getreidemarkt 9/166, A-1060 Vienna, harald.zeman@tuwien.ac.at

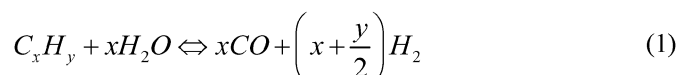
Nowadays, for many processes, high-quality-synthesis gas is required. For its generation, catalytic autothermal reforming of hydrocarbons, which is a combination of classic steam reforming (endothermic) and partial oxidation (exothermic), is a very capable method. Hence, it has been the focus of research in the past few years. The great advantage of autothermal reforming, in contrast to steam reforming or partial oxidation, is that there is no need to supply or dissipate thermal energy to or from the reaction. This feature makes it interesting for many applications, especially for smaller decentralized plants.

The aim of this work is to explore the fundamentals of that process by practical experiments. According to the results of the experiments, comparisons with the gas composition gained from thermodynamic equilibrium are drawn. It can be shown that these equilibrium values nearly can be achieved by the use of a noble metal catalyst even at low temperatures. Furthermore, noble metal catalysts feature only marginal losses of the hydrocarbon-conversion by increasing the space velocity.

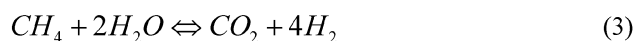
1. Introduction

Hydrogen is a major feedstock in many chemical and petrochemical industries. Due to the extreme increase in energy consumption, it is furthermore frequently considered as an attractive fuel for many energy supply applications. Reforming of hydrocarbons has been attracting great interest for generating hydrogen rich synthesis gas as future clean fuel.

There are several possibilities to generate synthesis gas (syngas) by reforming of hydrocarbons. First of all and especially for industrial hydrogen production, most applied is steam reforming (SR). Eq. 1 shows the general equation of steam reforming:



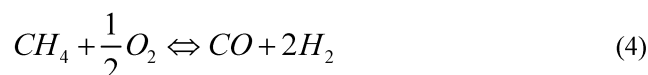
At the steam reforming process several reversible reactions Eq 2-3 proceed. For demonstration the following equations are stated for methane as feedstock:



Eq (2) points out a slight exothermic reaction, the so called water gas shift (WGS) reaction. Hence carbon monoxide in addition with water generates hydrogen and carbon dioxide. Lower temperatures favor the rate of hydrogen yield.

Eq (3) shows the degradation of methane and the formation of hydrogen and carbon dioxide. High temperatures support the procedure of this reaction based on the endothermic behavior.

Another way generating synthetic gas is partial oxidation of the feedstock. This reaction, also exemplary shown for methane, is outlined in Eq 4.



By using a SR process a syngas with a high H₂/CO-ratio (>3) can be obtained, depending on the amount of steam (S/C-ratio) and temperature. Therefore, a SR process is very useful for hydrogen production. The main disadvantage of SR is the heat consumption of the reaction. This means heat must be provided externally at a high temperature level (>1000°C).

In contrary, partial oxidation shows a slight exothermic behavior, but it features a lower H₂/CO – ratio (~2) than SR. As a kind of combination of the both reforming methods explained before, autothermal reforming (ATR) can be seen (Dias and Assaf, 2004). It takes the advantages of both; the required energy for the endothermic steam reforming is provided by the exothermic oxidation reaction at contemporaneously increasing of the hydrogen yield. In theory, this method can be totally held in heat balance, but in reality heat losses through the reactor wall occur. (Pettersson and Westerholm, 2001)

To realize this concept, the present work focuses on finding out optimal conditions of catalytic autothermal reforming at short contact times for various feedstocks. On the one hand different catalysts are investigated on their suitability for reforming hydrocarbons and on the other hand variations of reforming process parameters are carried out.

2. Test Rig

To conduct an experiment, a test rig was designed. The flow sheet is pictured in Figure 1. The test rig is designed for feeding different hydrocarbon feedstocks without any structural alteration works at the installation. To assure accurate volume flows of the gaseous feed components mass flow controllers (MFC) are applied. For the additive dosing of water, a diaphragm metering pump is utilized. The gasiform hydrocarbon and the added liquid water get heated up together, before attaining the reactor. The conceptional design of the pre-heating station makes sure, that the liquids get vaporized completely and proceeds to the reactor totally in gaseous state. Before reaching the catalyst is has to be made sure that a homogenous mixture arrives at the catalyst. The homogenization of the different gaseous media is reached by the application of a ceramic sponge. It also acts as flame trap and it protects the catalyst from erosive damaging from possible particles carried over by the fluid flow. This porous sponge has a mean pore density of 10 pores per inch. That means that there is nearly no pressure loss caused by the mixing zone. The mixing zone is directly followed by the catalyst,

where the reforming reactions take place. Afterwards the product gas is cooled down very quickly to prevent unwanted potential side reactions. For that reason, a water cooling system provided by a cryostat is installed. Hence the condensate gets separated from the gas stream. The generated synthesis gas gets analyzed by a five components measuring device continuously. This measuring device is capable to detect CO, CO₂, CH₄, H₂ and O₂. In addition, a gas chromatograph is used to detect N₂ and propane. To quantify the volume flow, a gas meter is installed after the first cooling system. So the gas volume at 15 °C can be measured. To protect the reaction from heat losses, the whole reactor is covered in heating elements.

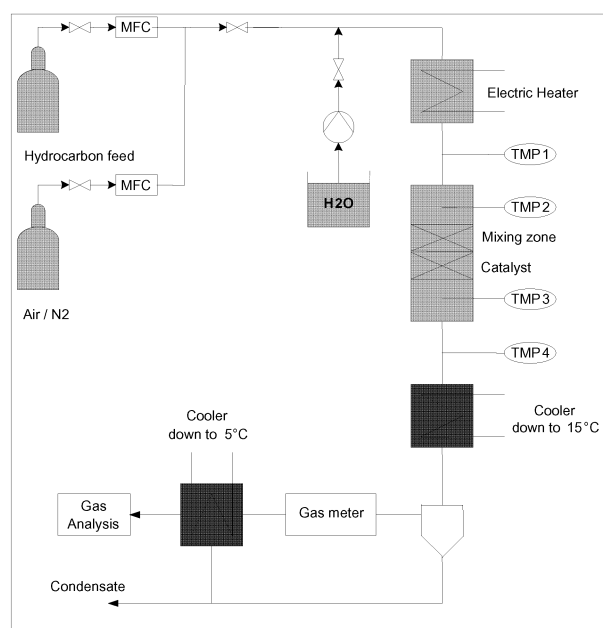


Figure 1: Flow sheet of test rig

3. Modeling and Simulation

The model used for the following simulations assumes chemical equilibrium by minimization of Gibbs free energy for the desired temperature of the reformer. The process simulation is done by a commercial steady state simulation package named IPSEpro, provided by SimTech. By varying the reformer temperature and the steam to carbon ratio for different feedstocks the necessary amount of air or ATR is calculated. Furthermore, the gas composition at equilibrium for each variation can be obtained from the simulation. The evaluation of the equilibrium data is executed to run the experiments more systematically and effectually. It also alleviates the comparison of the received results of the performed experiments. The following figures show some results of the simulation. In Figure 2 it can be clearly seen, that with increasing temperature an increasing steam to carbon ratio (S/C) higher methane conversion can be reached. To

fulfill the energy requirement of the endothermic reforming a higher amount of air is needed, which can be seen also in Figure 2. By increasing the amount of air to reach a higher temperature, the gas gets more and more diluted by nitrogen. At a certain temperature and S/C-ratio all methane is converted to syngas.

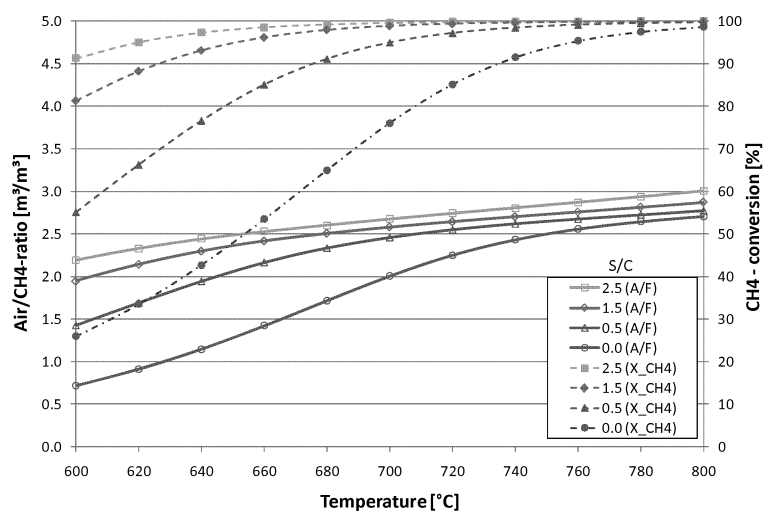


Figure 2: Air to feed ratio and methane conversion at varying temperature

To lower the amount of air process simulations have been done for heat integration and to preheat the input stream with the hot syngas. Therefore, the nitrogen dilution can be decreased and simultaneously, the efficiency of the reforming unit can be increased. In the experimental investigations all the feed streams are also preheated to a certain temperature (450°C) to simulate real process conditions.

4. Experimental

4.1 Variation of Parameters

During the test series at each tested catalyst the temperature, the steam to carbon (S/C) – ratio, the feedstock and the space velocity were varied in a way, that the expected conversion is kept high and the risk of coke formation low. The spread of the variation of temperature depends on the feedstock. Table 1 lists the used feedstocks, the temperature areas they were tested in and the field of the S/C – ratio.

Table 1: Overview of the testing parameters

Feed	Temperature [°C]		S/C - ratio		O/C - ratio	
	lowest	highest	lowest	highest	lowest	highest
Methane	650	800	0.5	2	0.8	1,2
Propane	500	700	1	3	0,1	0,9
LPG	500	700	1	3	0,1	0,9

To reach an assigned reaction temperature it is necessary to adjust the oxygen to carbon (O/C) ratio received from the simulation.

The catalysts can be classified by their main substances which are supported on ceramic monoliths. The first one contains a high amount of rhodium and the other is based on a mixture of noble metals.

4.2 Results and discussion

For methane as feedstock a comparison of the conversions of two different catalysts at varying S/C- ratios is visualized in Figure 3a.

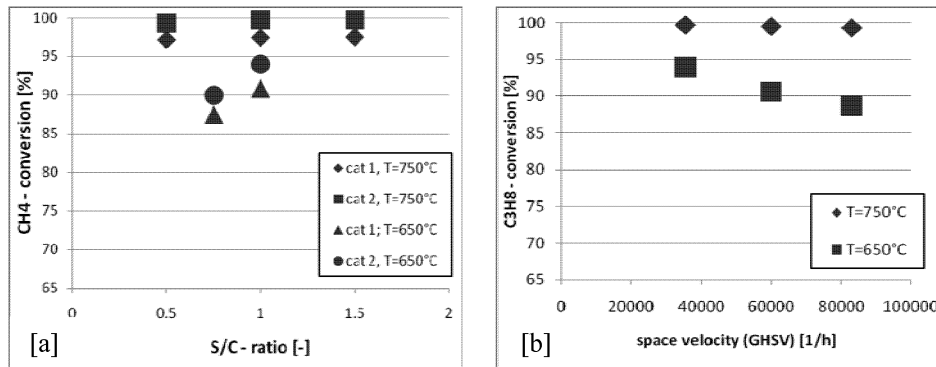


Figure 3: Methane conversion at varying S/C – ratios at 650°C and 750°C; rhodium catalyst (cat 1) compared to noble-metal-mixture catalyst (cat 2) [a]; Propane conversion at varying S/C – ratios at 500°C, 600°C and 700°C, noble metal catalyst, S/C=1 [b]

A rhodium catalyst and a noble-metal-mixture catalyst are utilized under same conditions. The experiments were carried out at two different temperatures and varying S/C – ratios. The results show that a noble-metal-mixture catalyst lead the reforming reaction closer to total feed conversion than a rhodium based. Figure 3a also illustrates the fact that reducing the temperature at low S/C – ratios decreases the conversion considerably under conditions of autothermal reforming. In Table 2 an example of the syngas composition at a reformer temperature of 700°C is compared to equilibrium data from simulation. It can be seen that these values correlates very well.

Table 2: Exp. results vs. simulation; feed CH₄; S/C=1; temperature=700°C; O/C=1,02

	H ₂	CO	CO ₂	CH ₄	N ₂	CH ₄ -conversion
experimental	41,5	11,8	6,1	1,1	39,5	94,2
simulation	43,1	12,4	6,4	0,5	37,6	97,7

Using propane as feedstock and a noble metal catalyst, experiments at different S/C-ratios were carried out. Moreover the test series were repeated at various temperatures. Figure 3b visualizes the obtained results. The diagram clarifies that at lower temperatures, the conversion decreases, especially at reduced S/C – ratio.

Varying the gas hourly space velocity (GHSV) between 30000 1/h and 80000 1/h, its influence can be stated as follows. The increase of the space velocity causes a decrease of conversion. Obviously the decrease of conversion is based on the shorter residence time available for the feedstock at the catalyst's surface.

Experiments on LPG (mixture of 95% propane and 5% butane) show nearly the same results as those on pure propane. The great divergence one more occurs at very low temperatures. The influence of sulfur, which inevitable is contained in LPG, becomes noticeable. Active centers on the catalyst surface get blocked by sulfur molecules, what leads to degrading of conversion. Besides it is essential to mention that this phenomenon of sulfur poisoning depends a great deal on the reaction temperature (Ashrafi et al., 2008). It is important to point out, that such a sulfur poisoning is only partly reversible.

Another serious problem is deactivation of the catalyst by coke formation. In that case carbon is deposited at the catalyst surface and deactivates it. There are several routes to carbon formation. Some are partly reversible, others not. (van Beurden, 2004)

5. Conclusions

At high temperatures both types of catalysts, as well the rhodium-based as the noble-metal-mixture catalyst, can reach the equilibrium gas composition very well. However at lower temperatures the conversion of the feedstock decreases by utilizing the rhodium-based catalyst.

Other important influencing factors on the success of autothermal reforming are space velocity and possibly occurring catalyst deactivating mechanisms. Their main exponents are sulfur poisoning and coke formation.

To all of these factors have to be paid attention to ensure a successful run of autothermal reforming, where lower temperatures are preferred because of the minor effort to prevent heat losses. However at these low temperatures mentioned deactivating mechanisms are more common.

References

- Ashrafi M., Pfeifer C., Pröll T., Hofbauer H., 2008, Experimental Study of Model Biogas Catalytic Steam Reforming: 2. Impact of Sulfur on the Deactivation and Regeneration of Ni-Based Catalysts, *Energy & Fuels*, 22, 4190-4195.
- Dias J.A.C., Assaf J.M., 2004, Autothermal reforming of methane over Ni/ γ -Al₂O₃ catalysts: the enhancement effect of small quantities of noble metals, *Journal of Power Sources*, 130, 106–110.
- Petterson L.J., Westerholm R., 2001, State of the art of multi-fuel reformers for fuel cell vehicles: problem identification and research needs, *International Journal of Hydrogen Energy*, 26, 243-264.
- van Beurden P., 2004, On the catalytic aspects of steam-methane reforming, ECN - Energy research Centre of the Netherlands, Petten, the Netherlands.