CHEMICAL KINETICS OF HIGH TEMPERATURE HYDROCARBONS REFORMING USING A SOLAR REACTOR

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Abstract - This study is aimed at developing a model for solar volumetric reactor for hydrocarbon reforming, operating at high temperature and pressure based on two achievements: 1. The development of the DIAPR, a volumetric receiver tested at 5000-10,000 suns, gas outlet temperature up to 1200°C and a pressure of 20 atm. 2. A laboratory scale chemical kinetics study of hydrocarbons reforming reactions with Ru base catalyst. The receiver operation is simulated using PHOENICS package. The reaction kinetics is computed, using the CHEMKIN package. A chemical kinetic simulation of a CHO system based on three elements: Definition of a computational cell in the reactor by the relevant parameters: temperature, pressure, reactant compositions, residence time, and catalyst load. Using of laboratory results at 700-1400 K and 4 atm. to find kinetic parameters for the overall CO2 reforming of CH4 and for the Reverse Water Shift Reaction. Use of CHEMKIN with kinetic parameters found and with unit cell of the DIAPR derived from the CFD model to compute the size of the DIAPR receiver for CO2 reforming of CH4. Results show that with achievable catalyst load in the cell and at 1600 K and 20 atm only 10 cm of cell matrix would be necessary to achieve 90% methane conversion. This work provides an essential step in simulating the performance of high temperature and pressure volumetric solar reformer. More computational and experimental work is needed for more accurate model.

1. INTRODUCTION

Solar reforming of methane and the complete Thermochemical Heat Pipe cycle (‘Close-Loop’ reforming–methanation) of the reaction

\[ \text{CH}_4 + \text{CO}_2 = 2\text{H}_2 + 2\text{CO} \]

have been studied at the Weizmann Institute over the last two decades. (Rosin and Levy, 1989) (Rosin and Levitan, 1989). Solar reforming at a scale of several hundred kilowatts was conducted at the Weizmann Institute using (in succession) a DLR-built volumetric reformer, and a Weizmann-built tubular reformer. Another joint project which includes a reforming high pressure reactor of DLR-Stuttgart - Germany, operating in conjunction with an electric gas turbine is presently running. Studies on developing volumetric reforming reactors has been run also in Sandia National Laboratories (Skocypec and Buck, 1994.) (Hogan and Muir, 1994) and in the Boreskov Institute of Catalysis in Novosibirsk, Russia (Funken and Kuzin, 1998).

In all of the developed systems, in the above mentioned sources, either the reforming temperature, or its pressure, or both, were below the optimum conditions, due to the limited capabilities of the solar receiver/reactor. For example, the maximum operating pressure and temperature of the WIS tubular reformer are 10-15 bars and 800-850°C, respectively; the DLR volumetric reactor is limited to 3 bars and 850-900°C, and the newly developed one is designed to higher pressure but similar temperature limits. Consequently, industrial solar reforming based on these devices would be neither as efficient, nor as cost-effective as non-solar, standard, industrial reformers.

Feasibility studies and cost analyses (Yogeif and Shemer 1996) indicate that the combination of Tower Reflector optics and the technology developed by WIS and Rotem for the DIAPR receiver can be the foundation for the development of an advanced, cost-effective solar receiver/reformer. Such a reformer will be able to operate at high sunlight concentration (1000 C 5000), temperature (800 T 1050°C) and pressure (10 p 25 bar).

The R&D studies on the DIAPR receiver proved that even without chemical reactions modeling of the performance of the receiver plays a crucial role in the parametric research. In this case the Computational Fluid Dynamic (CFD) model based on PHOENICS program package provided guidelines in different stages of the experimental work as well as for the overall system optimization, to increase energy efficiencies and to assure safe standing of materials in the high temperature and high pressure environment. The scope of this work is:

- To gather known catalytic kinetic parameters of the CHO system from results reported in the literature, reaction kinetic databases and results of local studies carried on in the WIS catalytic laboratories.
- To implement the CHEMKIN II code package in analyses of reforming and side reactions of the CHO system.

To link the kinetics model based on CHEMKIN II to the existing CFD model in order to have a complete simulation of the high temperature and high-pressure receiver-reformer reactor.

2. KINETIC PARAMETERS OF THE CATALYTIC REACTIONS

Integrating the CFD model with chemical process using CHEMKIN II, we need to define all the elementary reactions involve and the kinetics parameter for each reaction. The DIAPR CFD model without chemical reactions is very complicate and not finishes yet. Even at this stage the run time of calculation is very long. Adding a chemical process to this model is reasonable only if we reduce the system to a very few reactions. We decided to base our model on the assumption that the catalyst is very selective and we can take into account only the two main reactions:

1. \[ \text{CH}_4 + \text{CO}_2 = 2\text{CO} + 2\text{H}_2 \]
2. \[ \text{CO}_2 + \text{H}_2 = \text{CO} + \text{H}_2\text{O} \]

To find the kinetic parameters for those two reactions we used the experimental data published by Berman et al (Epstein and Karni, 1996). In this work they measured the rate of the over all reactions and not the hundreds elementary reactions involve. So
it meets our purpose. The published results are given in l/h*g units.

In order to obtain the kinetic parameters from the laboratory results we have to define a unit cell as in the CFD model. The cell composed of a central pin and four quarters of edge pins, sums to 2 pins active areas. The length of the cell is 1.56 mm the width is 0.9 mm the height is 6 cm. using the typical Ru load of 1 mgr./cm in 1-% Ru catalyst results in an overall cell load of 1.2-gr. catalyst.

2.1 Reforming Reaction

Arrhenius plots based on the measured rates for some cases of the CO2 reformerming with CH4 reaction are shown in figure 1. Each case is for different type of catalyst. The cases 5A and 5B are without catalyst.

![Figure 1: Arrhenius plots of measured rates for few catalyst cases, non-catalyst and trend line of case T13.](image)

Figure 1: Arrhenius plots of measured rates for few catalyst cases, non-catalyst and trend line of case T13.

It can be seen that within the estimate of experimental errors the Arrhenius model presents quite well the dependence of the measured rates on temperatures. Each case has different kinetic values. We chose to base our model on case named that we T13. The other cases gave lines of higher rate values but they are curved in the region of interest, the high temperatures region and meet the rate values of case T13. We assume that in those cases the system reach to equilibrium before the reactor end.

In table 1 the Arrhenius kinetic parameters are noted, based on a trend line marked in figure 1 of case T13. The 2
d row set in the table is related to non-catalyst experiments.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>T Range K</th>
<th>A[I/h]</th>
<th>Ea [cal/mole]</th>
<th>Ek* [K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru (T13)</td>
<td>700-1300</td>
<td>1050</td>
<td>12104</td>
<td>6114</td>
</tr>
<tr>
<td>Non-cat</td>
<td>1100-1300</td>
<td>5.27E+7</td>
<td>52074</td>
<td>26300</td>
</tr>
</tbody>
</table>

* R=A*exp(-Ea/RT) =⇒ R=A*exp(-Ek/T)

Table 1: Experimental Arrhenius parameters.

The reaction rate in table 1 and the unit cell define lead to the kinetics values using simple calculation.

\[ r' = - \frac{d[CH_4]}{dt} = (1.2*1050) \times \exp (-12104/RT) \quad [l(NTP)/h] \]

Eq. (1)

By basic units conversion:

\[ r' = 0.016 \times \exp (-12104/RT) \quad [\text{mol} / \text{s}] \] Eq. (2)

And considering the cell volume:

\[ V = 0.9*1.56*6 = 8.424 \, \text{cm}^3\] Eq. (3)

\[ r = \frac{r'}{V} = 0.00186 \times \exp (-12104/RT) \quad [\text{mol} / \text{cm}^3 \, \text{s}] \] Eq. (4)

Based on the assumption that the trend Arrhenius line drawn in figure 1 represents experimental results compatible to 4 atm in about feed reactant composition (CO2/CH4 = 1.3) and assuming a second order unidirectional reaction, we can calculate the rate constant coefficient from:

\[ r = k \times [\text{CH}_4] \times [\text{CO}_2] \] Eq. (5)

When:

\[ [\text{CH}_4] = 0.435 \times (\text{P}/\text{RT}) = 0.435 \times \left(\frac{4}{82.06 \, \text{T}}\right) = 0.023/T \quad [\text{mol/cm}^3] \] Eq. (5)

\[ [\text{CO}_2] = 0.565 \times (\text{P}/\text{RT}) = 0.565 \times \left(\frac{4}{82.06 \, \text{T}}\right) = 0.030/T \quad [\text{mol/cm}^3] \] Eq. (6)

And the rate constant expression, compatible with CHEMKIN II program is:

\[ k \, [\text{cm}^3/\text{mol} \, \text{s}] = 2.69 \times T^2 \times \exp (-12104 / RT) \] Eq. (7)

2.2 Reverse Water Shift Reaction (RWSR)

Kinetic Data for the RWSR in gas phase are not reported. In the NIST Database a sole reference is found (Graven and Lang, 1954) for the equilibrium reaction:

\[ \text{CO}_2 + \text{H}_2 = \text{CO} + \text{H}_2\text{O} \]

However, in reference to this source it is stated that “data too complex to abstract”.

Laboratory experiments reported by Berman et al. (1996) are the source for kinetic parameters (Epstein and Karni, 1996) in which produced H2O was measured besides the reforming reaction products. Figure 2 shows some Arrhenius plots based on measured rates for some cases of the RWSR.

![Figure 2: Arrhenius plots of measured rates of the RWSR.](image)

Figure 2: Arrhenius plots of measured rates of the RWSR.

We use the same mathematics as for the reforming and we get the Arrhenius plots in figure 3 for the case T13.
The longitudinal velocity, as found by the CFD model, is 1.5 m/s and the cell displacement along the velocity vector is 1.56 cm; these two values gave a residence time of 0.01 see.

The conversion may be increased by three ways according to the present model:

- Decreasing the flow rates.
- Increasing the catalyst load on the pins.
- Increasing the gas pressure.

Decreasing flow rates damages the reactor throughout (e.g. the windows cooling won’t be sufficient).

Increasing catalyst load decreases the needed cells number. Figure 5 shows that a tenfold increase in the catalyst load (increasing only k of the reforming by 10 times) lasts in 0.3 second reaction time for about 90% conversion; still a 47 cm long reaction zone is needed.

Figure 6 indicates that increasing the reactor pressure from 4 to 20 atm can also be considered an efficient way to increase the conversion.
Figure 6: Mole fraction and CH4 conversion vs. time for 6mg. 1%-Ru catalyst load at 20 atm.

Figure 7 shows that reasonable increase in both the pressure to 20 atm and the catalyst load 10 times leads to only 6 cells needed for a conversion of 90% (0.06 sec) which means about 10 cm long of the reaction zone.

These results indicate that it is possible to use the DIAPR receiver as a reformer.

4. CONCLUSIONS

The calculations done so far are of a very preliminary manner. Nevertheless we can already draw some conclusions, to the pursuance of the study.

- The DIAPR volumetric receiver can be used as a reformer with high load of catalyst and high pressure.
- It is most important to conduct laboratory scale experiments, to increase the present active catalyst load on the pins joint by an increase of surface area and to study the effect of the pressure on the overall reaction kinetics.
- To gradually expand the reaction to surface, gas or combined detailed elementary reactions. To consider the choice of implementing an overall reaction vis-a-vis detailed elementary reactions.
- To add desired and undesired side reactions like the carbon formation reactions and to back there kinetic parameters by laboratory scale experiments.

- To link, step by step the elementary cell concept to the CFD program and to feed the resulted kinetic affecting parameters back to CHEMKIN.
- To design the reaction area by an optimization of the available specific energy density on the surface with the area needed for chemical reaction completion.

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