



## STEAM REFORMING COMPUTER PROGRAM

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### ABSTRACT

*Steam reformer, which converts light hydrocarbons and steam to hydrogen and carbon oxides, is an important part of a hydrogen plant. Steam reforming catalysts are required in the conversion. The nature of feedstock determines which type of steam reforming catalysts used. Regardless of the type of catalyst, sulfur, coking, and other poisons can deactivate steam-reforming catalysts. To ensure a good hydrogen plant operation, selection of a suitable steam reforming catalyst and monitoring the activity of steam reforming catalyst is a must.*

*Saudi Aramco has recently developed a computer program to facilitate catalyst selection and activity monitoring of steam reforming catalyst. This computer program can calculate equilibrium compositions of steam reforming and approach toward equilibrium. Non-ideality of gas mixture is considered in the programming to simulate the actual reaction conditions. This paper discusses how the computer program was developed, validated and applied.*

**Keywords:** *Steam Reforming, Catalyst Activity, Water-Gas Shift, Approach to Equilibrium, Program Validation.*

(equilibrium compositions)

## 1. INTRODUCTION

Saudi Aramco has developed a computer program coded in C++ language, which can calculate product equilibrium compositions at steam reformer outlet conditions, product rates at equilibrium, approach to equilibrium, and steam/carbon molar ratio.

This developed computer program has been validated since approach temperatures toward equilibrium derived from this computer program and those obtained from vendor computer programs are very similar. We can apply this developed computer program in monitoring the activity of the current steam reforming catalyst to ensure the smooth steam reformer operation. We also can apply this computer program to select the most suitable steam reforming catalyst.

We recommend that refining process engineer apply this program to monitor the activity of steam reforming catalyst, and that catalyst proposal evaluators apply this computer program to select the steam reforming catalysts. The estimated saving from the catalyst selection alone is estimated at \$10,000/yr, based on a saving of 5% of catalyst cost.

## 2. COMPUTER PROGRAM

### 2.1 Development of the Computer Program

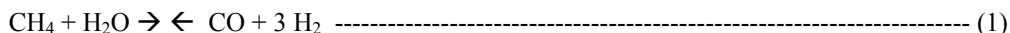
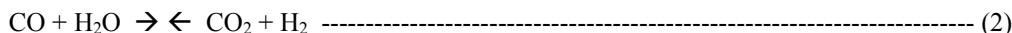
#### 2.1.1 Mass Balances

Steam reformer is normally operated at a very high temperature and a moderate pressure. The steam reformer outlet temperature range is 750-850 °C and outlet pressure is about 22 atm(g). At these conditions, all heavier hydrocarbons, except methane, are converted to carbon oxides and hydrogen. Only methane, carbon monoxide, carbon dioxide, hydrogen, and steam exist at the outlet of steam reformer.

Because hydrocarbon feed flow rate, compositions, and steam flow rate are known, we can obtain three equations from doing mass balance for C, H, and O between feed and steam reforming products. We still need two equilibrium equations in order to solve the problem since there are five unknowns.

#### 2.1.2 Equilibrium Equations

There are many reactions occurring in steam reformer, i.e., hydrocarbon reacts with steam to form carbon oxides and hydrogen; carbon monoxide can react with steam to form carbon dioxide and hydrogen; and hydrogen reacts with steam to form carbon and steam, etc. We chose methane-steam reforming reaction and water-gas shift reaction as the needed two equations since they are important reactions in steam reforming. These two reactions are shown in equations (1) and (2) below:

Methane-Steam ReformingWater-Gas Shift

The equilibrium constants for equations (1) and (2) can be expressed as a function of fugacity, as shown in equations (3) and (4), respectively.

$$K_{\text{ms}} = (f_{\text{CO}} * f_{\text{H}_2}^3) / (f_{\text{CH}_4} * f_{\text{H}_2\text{O}}) \text{-----} (3)$$

$$K_{\text{wg}} = (f_{\text{CO}_2} * f_{\text{H}_2}) / (f_{\text{CO}} * f_{\text{H}_2\text{O}}) \text{-----} (4)$$

where:  $f$ , fugacity of a reactant or a product. Fugacity of a component is equal to fugacity coefficient multiplied by partial pressure of that component, as shown in equation (5).

$$f(i) = \text{fugacity coeff.}(i) * p(i) \text{-----} (5)$$

where:  $p(i)$  is partial pressure of component  $i$ , which is equal to total pressure multiplied by molar fraction of component  $i$  in the mixture.

The relationship between equilibrium constant and Gibbs free energy of formation is indicated by the following equation:

$$K = \exp(-\Delta G / RT) \text{-----} (6)$$

where:  $R$ , gas constant; and  $T$  in  $^{\circ}\text{K}$ .  $\Delta G$  is Gibbs free energy of formation for the particular equilibrium equation. Gibbs free energy of formation for a component can be found from literature [1].

*2.1.3 Consideration of Non-Ideal Mixture*

In order to simulate the actual situations, non-ideality of the mixture was considered. Fugacity coefficient can be calculated from an equation of state. Soave-Redlich-Kwong equation of state was chosen since it is suitable for rich hydrogen and high temperature environment. The equation for fugacity coefficient calculation is shown as below:

$$\text{fugacity coeff.}(i) = \exp\{ (Z-1) * B_i/B - \ln(Z-B) - A/B * (2A_i^{0.5}/A^{0.5} - B_i/B) * \ln((Z+B)/Z) \} \quad (7)$$

where:

$$A_i = 0.42747 a_i P_{r(i)} / T_{r(i)}^2,$$

$$B_i = 0.08664 P_{r(i)} / T_{r(i)},$$

$$a_i = [1 + m_i(1 - T_{r(i)}^{0.5})]^2,$$

$$m_i = 0.48 + 1.574 w_i - 0.176 w_i^2,$$

$$A = \text{sum}[\text{sum}(y_i y_j A_{ij})],$$

$$A_{ij} = (A_i A_j)^{0.5},$$

$$B = \text{sum}(y_i B_i),$$

$$Z^3 - Z^2 + Z(A - B - B^2) - A * B = 0.$$

$P_r$  and  $T_r$  are reduced pressure and temperature, respectively;  $w_i$  is the acentric factor of component  $i$ ;  $y_i$  is molar fraction of component  $i$  in the mixture.

#### 2.1.4 Equilibrium Compositions

We have three mass balance equations for C, H, and O, and two equilibrium equations for methane-steam reforming and water-gas shift reactions. We can use these five equations to solve five unknowns, i.e., equilibrium compositions for CH<sub>4</sub>, CO, CO<sub>2</sub>, H<sub>2</sub>, and H<sub>2</sub>O at steam reformer outlet conditions. Computing algorithm for calculating equilibrium compositions is summarized in Appendix 1.

#### 2.1.5 Approach to Equilibrium

Since actual dry compositions at steam reformer outlet are known, equilibrium constant of methane-steam reforming can be calculated using equation (3). We can obtain equilibrium temperature for methane-steam reforming by solving for  $T$  in equation (6). The approach to equilibrium is the difference between reformer outlet temperature and equilibrium temperature for methane-steam reforming.

## 2.2 Input and Output of the Computer Program

### 2.2.1 Input

Input information for the computer program includes steam reformer outlet pressure in atmospheric pressure absolute, steam reformer outlet temperature in °C, hydrocarbon feed rate in Nm<sup>3</sup>/hr, hydrocarbon feed compositions, steam feed rate in kg/hr, and actual dry gas composition in vol% at reformer outlet.

### 2.2.2 Output

The output includes steam/carbon molar ratio, equilibrium compositions at reformer outlet conditions and equilibrium flow rate for each component, approach to equilibrium, and actual gas flow rate for each component.

## 2.3 Validation of the Computer Program

The approach temperatures toward equilibrium derived from this program and from vendor's programs are summarized in Table 1 as below:

**Table 1: Approach to Equilibrium Comparison, °C**

<b>This Program</b>	<b>Vendor's Program</b>	<b>Difference</b>
-12.6	-11.4	1.2
1.5	2.3	0.8
0.6	2.0	1.4

Approach to equilibrium should always be positive. The reasons we have two negative approach temperatures toward equilibrium, i.e., -12.6 and -11.4 °C, are that plant data were used in calculation and there are some discrepancies between actual and measured variables, i.e., temperature, pressure, and compositions.

The differences between approach temperatures derived from this computer program and those from vendors' are only 0.8 to 1.4 °C. We can conclude that the developed computer program is validated since the difference is small.

## 2.4 Applications of the Computer Program

### 2.4.1 Evaluation of Steam Reforming Catalyst

We can apply this computer program to evaluate the steam reforming catalyst proposal. Tables 2,3, and 4 summarize equilibrium compositions calculated from the computer program and performance data provided by vendors A, B and C in their proposals, respectively. The same hydrocarbon feed rate and compositions, and steam feed rate are used for comparison.

**Table 2: Vendor A vs. the Developed Computer Program**

	<b>Vendor A</b>	<b>Developed Computer Program</b>
<b>P<sub>out</sub>, atm.</b>	23	23
<b>T<sub>out</sub>, °C</b>	821	821
<b>CH<sub>4</sub>, vol% dry</b>	2.9	2.89
<b>CO, vol% dry</b>	7.1	7.09
<b>CO<sub>2</sub>, vol% dry</b>	7.0	6.95
<b>H<sub>2</sub>, vol% dry</b>	83.0	83.07
<b>T<sub>ap</sub>, °C</b>	0.6	

**Table 3: Vendor B vs. Developed Program**

	<b>Vendor B</b>	<b>Developed Computer Program</b>
<b>P<sub>outs</sub>, atm.</b>	22.8	22.8
<b>T<sub>outs</sub>, °C</b>	815	815
<b>CH<sub>4</sub>, vol% dry</b>	3.20	3.11
<b>CO, vol% dry</b>	6.96	6.92
<b>CO<sub>2</sub>, vol% dry</b>	6.93	7.00
<b>H<sub>2</sub>, vol% dry</b>	82.91	82.97
<b>T<sub>ap*</sub>, °C</b>	1.5	

**Table 4: Vendor C vs. Developed Program**

	<b>Vendor C</b>	<b>Developed Computer Program</b>
<b>P<sub>outs</sub>, atm.</b>	23	23
<b>T<sub>outs</sub>, °C</b>	825	825
<b>CH<sub>4</sub>, vol% dry</b>	3.27	2.72
<b>CO, vol% dry</b>	--	7.21
<b>CO<sub>2</sub>, vol% dry</b>	--	6.92
<b>H<sub>2</sub>, vol% dry</b>	--	83.15
<b>T<sub>ap*</sub>, °C</b>	12.7	

--: Data not provided.

Table 2 shows that dry gas compositions, predicted by Vendor A, are almost the same as those equilibrium compositions calculated from the computer program, resulting in a very low approach to equilibrium, 0.6 °C. Table 3 indicates that the differences between performance and equilibrium data for Vendor B are a little larger, reflected by a little higher approach to equilibrium of 1.5 °C. As shown in Tables 2 and 3, catalyst activities for steam reforming catalysts A and B are very similar, with 1 °C advantage for catalyst A over catalyst B.

On the other hand, the methane slip predicted by Vendor C is much larger than equilibrium methane composition, as shown in Table 4. As a result, the approach to equilibrium for catalyst C, which is 12.7 °C, is much higher than those for catalysts A and B.

The above example demonstrates that this program can be applied to compare steam reforming catalyst activities stated in proposals and we can use it to facilitate catalyst selection. The benefit from the catalyst selection alone is estimated at \$10,000/yr, based on a saving of 5% of catalyst cost.

### 2.4.2 Monitoring of Steam Reforming Catalyst Activity

We can plot approach to equilibrium, which can be calculated from this computer program, vs. days on stream. Such a plot shows how catalyst deactivates as a function of time. When steam-reforming catalysts can't produce enough hydrogen to meet refinery's needs, it is the time to replace them. By monitoring the trend of approach to equilibrium vs. days on steam, together with pressure drop, methane slip, and tube wall temperature, we can identify the best time to replace steam-reforming catalyst.

## 3 CONCLUSION AND RECOMMENDATION

We have developed a computer program in C++ language for calculating equilibrium compositions at steam reformer outlet, and approach to equilibrium. We recommend that refining process engineer apply this program to monitor the activity of steam reforming catalyst, and that catalyst proposal evaluators apply this computer program to select the steam reforming catalysts.

## 4 REFERENCES

1. I. Barin, "Thermochemical Data of Pure Substances", VCH Publishers, New York.

## APPENDICES

Appendix 1: Computing algorithm for calculating equilibrium compositions

1. Input feed rate, compositions,  $P_{out}$  and  $T_{out}$
2. Calculate equilibrium constant at  $T_{out}$
3. Initial guess CO and  $CO_2$  compositions and calculate  $CH_4$ ,  $H_2O$  and  $H_2$  compositions
4. Calculate fugacity coefficient and  $CH_4$  composition
5. Adjust  $CH_4$  composition stepwise and do mass balance for other components
6. Calculate fugacity coefficient and CO composition
7. Adjust CO composition stepwise and do mass balance for other components
8. Repeat steps 4-7 until converge
9. Calculate individual flow rate at equilibrium