RESEARCH NOTE

DETERMINATION OF SUITABLE CONCENTRATIONS OF H_2O AND CO_2 IN THE FEED OF SYNGAS PRODUCTION

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Abstract Modeling and optimization of synthesis gas production via the non-catalytic partial oxidation of methane (NCPO) were studied by minimizing of Gibbs free energy, and comparison studies were carried out to analyze the mechanism of syngas production. For this purpose, concentrations of CO_2 and H_2O in the feed were optimized in specified pressure and temperature, such that the hydrogen to carbon monoxide ratio in the product was set between 1.98 and 2.02 (suitable ratio for FT and methanol synthesis process) and concentration of CH_4 in the product was less than 1.5%. The predictions obtained by this simulator were in agreement with the experimental data as well as the AspenPlus® package results.

Key Words SynGas, Simulation, Equilibrium, Noncatalytic

چکیده در این مقاله فرآیند تولید گاز سنتز به روش اکسیداسیون جزیی غیر کاتالیستی از طریق به حداقل رساندن انرژی آزاد گیبس مطالعه و مدلسازی شده و شرایط گوناگون برای افزایش عملکرد و بهینه سازی این واکنش بررسی و ارائه شده است. برای این منظور تعداد زیادی محاسبه به ازای غلظتهای مختلفی از H_2O و CO_2 در خوراک ورودی به ازای فشار و دماهای مختلف انجام شده است به طوری که نسبت H_2 به CO در محصول بین ۱/۹ تا ۲/۱ (نسبت مناسب برای فرآیند FT و سنتز متانل) و غلظت CH_4 کمتر از ٪۱/۵ باشد. نتایج این شبیه سازی با داده های تجربی و نتایج نرم افزار AspenPlus® بخوبی تطبیق دارد.

1. INTRODUCTION

Syngas (a mixture of CO and H_2) is a versatile feedstock mainly used in methanol, ammonia and Fischer-Tropsch synthesis processes and for carbonylation, hydroformylation, hydrogenation and reduction processes. Since last decade, worldwide efforts have been made for the conversion of methane (which is the main constituent of the natural gas) in too easily transportable and valuable products like methanol, liquid hydrocarbon fuels and petrochemical feedstocks (e.g. ethylene and other lower olefins). Table 1 shows the volumetric ratio usage of synthesis gas components for important final products.

There are two main important reactions for conversion of natural gas to synthesis gas. The first is steam reforming, a highly endothermic reaction of methane and steam over special catalyst under very severe conditions:

$$CH_4 + H_2O \rightarrow CO + 3H_2 \quad (1)$$

The second reaction is the partial oxidation of methane with oxygen. This reaction is exothermic:

$$CH_4 + 0.5O_2 \rightarrow CO + 2H_2 \quad (2)$$

In the non-catalytic partial oxidation process, oxygen and natural gas are preheated, mixed thoroughly and ignited. The principal Reaction 2 is an ideal description of what is going on. With no catalyst the peak

TABLE 1. Volumetric Ratio of Components in Synthesis Gas for Particular Processes.

Synthesis gas for Production of	Volume Ratio (stoichiometric)		
	H_2	CO	N_2
Ammonia	3	0	1
Methanol	2	1	0
Fischer-Tropsch	2	1	0
OXO	1	1	0

temperature has to be high to obtain complete conversion. Complete combustion to CO_2 and H_2O can take place, afterwards endothermic reactions like steam- reforming also take place, such that the outlet temperature is in the order of 1000-1100°C. The gas at this stage is near thermodynamic equilibrium. Recently a number of studies [1,2] have been reported on the simulation of non-catalytic partial oxidation of methane.

In this study we determine acceptable range of CO_2 and H_2O in the feed for syngas production, and also compare our simulation predictions with those of AspenPlus®[2] and experimental results [1,2,4] concluding a good agreement behavior.

2. THEORY

Minimization of Gibbs Energy The general condition that the Gibbs energy of a system at a given temperature, T, and pressure, P, must be minimum at equilibrium state can be applied directly to find the equilibrium composition of a reacting mixture without prior specification of any stoichiometric relations. The only information needed is the Gibbs energy of formation of all the chemical species expected to be present at equilibrium as well as their fugacity or activity coefficients when they cannot be assumed unity. The method is flexible with respect to possible species, since redundant ones will be seen to have negligible concentrations when the calculation is completed.

The basic equations:

Total Gibbs energy of mixture is:

$$nG_i = \sum n_i[G_i^\circ + RT\,Ln(y_i.\hat{\varphi}_i.p)] \qquad (3)$$

or, more compactly (fugacity coefficients assumed unity):

$$g = \frac{nG}{RT} = \sum n_i[g_i^\circ + Ln(\frac{n_i P}{n})] = \sum n_i[c_i + \ln(\frac{n_i}{n})] \qquad (4)$$

where $c_i = g_i^\circ + \ln P$

The material balances on the m chemical elements are:

$$b_j - \sum a_{ij} n_i = 0 \qquad j = 1,2,..., \qquad (5)$$

For m elements and c components, a_{ij} is the number of atoms of element j in molecule i, and b_j is the total amount of element j in the mixture. In terms of Lagrange multipliers, the constrained function to be minimized is:

$$f = g + \sum_{j=1}^{m} \lambda_j (b_j - \sum_{i=1}^{c} a_{ij} n_i) =$$

$$\sum_{i=1}^{c} n_i[c_i + Ln(\frac{n_i}{n})] + \sum_{j=1}^{m} \lambda_i (b_j - \sum_{i=1}^{c} a_{ij} n) \qquad (6)$$

The derivatives with respect to compositions are:

$$\frac{\partial f}{\partial n_i} = c_i + Ln(\frac{n_i}{n}) - \sum_{k=1}^{m} a_{ik} \lambda_k = 0 \qquad (7)$$

This derivative together with the material balances,

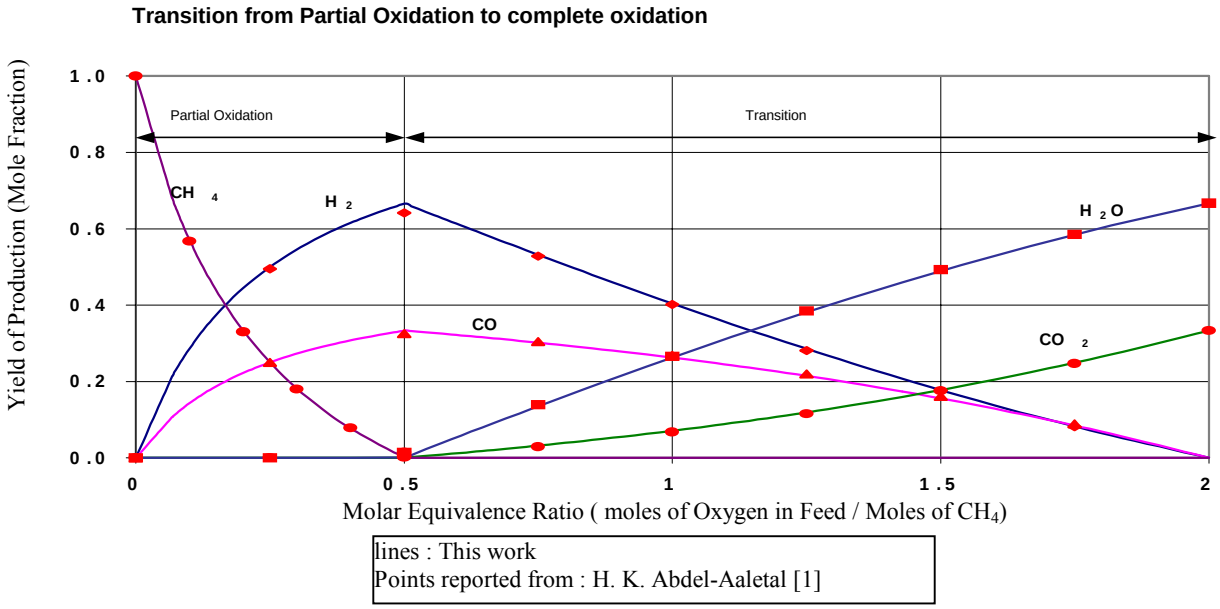

Figure 1. Concentration of some important species in partial oxidation of methane in 1477 K and 1 atmosphere.

Equation 2, and $\sum n_i = n$, constitute a system of c+m+1 equations from which n_i, λ_k and n can be evaluated in principle.

Any procedure for solving a system of nonlinear equations numerically requires starting estimated figures for the unknowns. However, we applied specific technique on Newton-Raphson method, which did not require starting estimates.

3. RESULTS AND DISCUSSION

Comparison Between Experimental and Simulated Data A comparison between this work (simulated predictions) and experimental data [1] on the dependency of the yield of production on molar equivalence ratio is depicted in Figure 1. It was noted that the simulated results were much closer to experimental data.

In Figure 1 the reaction between methane and oxygen is assumed as follows:

$$CH_4 + n\,O_2 \rightarrow CO_2 + H_2O + CO + H_2 + O_2 + CH_4\ ,$$
$$\varphi\,(\text{equvalence ratio}) = 2/n$$

Table 2 shows the comparison between the predictions of this work and AspenPlus® results [2]. It shows that, there isn't significant difference between the mole fractions of main components but there is a slight difference between other minor components. This might be due to the different value of Gibbs free energy utilized in this work (JANAF Table [6] data) and AspenPlus® package. Product components are O_2, CO_2, H_2O, H_2, OH, CO, H, O, CH_4, N_2, NO, HO_2, NO_2, N_2O, CN, HNO, N, HCO, CH, HCN, HN, C_2H_6, C_3H_6, iC_4, nC_4, NH_3, CH_2O, CH_2 and C.

It is observed that mass balance is satisfied by both software, but because of a lower minimized Gibbs energy in this work, its results seem to be more accurate than those of AspenPlus®.

Acceptable Range for Pressure of CO_2 and H_2O in the Feed As explained in the introduction, reaction 2 is an ideal description of what is going in the partial oxidation of methane, while other reactions have possibility to take place, such as:

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \qquad (8\text{-a})$$

$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad (8\text{-b})$$

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (8\text{-c})$$

TABLE 2. Comparison of the Results of This Work by M. Khoshnoodi and Y.S. Lim [2].

	Elements				From JANAF	Moles in the product	
	C	O	H	N	Gibbs Energy	This Work	ASPEN +
O_2	0	2	0	0	0	6.08212E-11	3.0815E-10
CO_2	1	2	0	0	-396356.203	49.1274769	44.59996
H_2O	0	1	2	0	-159207.767	242.5035195	240.3262
H_2	0	0	2	0	0	1378.383094	1385.204
OH	0	1	1	0	14853.83351	9.42606E-05	0.000241124
CO	1	1	0	0	-251503.65	826.0342214	837.2721
H	0	0	1	0	131187.3285	0.013669985	0.0288121
O	0	1	0	0	148865.4803	7.55192E-10	3.7462E-09
CH_4	1	0	4	0	84729.25163	4.565754855	2.258513
N_2	0	0	0	2	0	7.508721043	7.518757
NO	0	1	0	1	70249.23052	1.05877E-07	3.1969E-07
HO_2	0	2	1	0	96662.44417	2.04869E-13	5.1284E-12
NO_2	0	2	0	1	133252.0153	9.52798E-16	5.325E-15
N_2O	0	1	0	2	198658.3032	2.3914E-12	6.9848E-12
CN	1	0	0	1	275262.6176	1.50854E-09	4.60935E-09
HNO	0	1	1	1	174794.8592	1.96589E-10	6.0882E-10
N	0	0	0	1	372682.811	1.20211E-11	5.4259E-11
HCO	1	1	1	0	-29715.7289	0.00021818	0.000377905
CH	1	0	1	0	415938.1529	4.95027E-13	2.3118E-12
HCN	1	0	1	1	83077.05977	0.015262523	0.015922
HN	0	0	1	1	344670.9894	4.9907E-10	1.74175E-09
C_2H_6	2	0	6	0	238093.5421	8.46467E-05	2.38524E-05
C_3H_8	3	0	8	0	523264.1725	7.42835E-14	6.6818E-10
iC_4	4	0	10	0	1220427.626	1E-30~0	6.3269E-15
nC_4	4	0	10	0	940237	1E-30~0	1.898E-14
NH_3	0	0	3	1	131305.7037	0.125105284	0.1043728
CH_2O	1	1	2	0	-64485.3342	0.015092797	0.00922636
CH_2	1	0	2	0	302524.694	1.30328E-08	2.98888E-08
C	1	0	0	0	0	4.397924046	1.441E-14
SUM						2512.690239	2517.338507

Atom Balance	C	H	O	N	G_{total} (J / mol)
Feed	884.15612	3260.47145	1166.80806	15.15781	----------
This work	884.15612	3260.47150	1166.80810	15.15781	-172917246.4
ASPEN+	884.15615	3260.47152	1166.80807	15.15781	-172845251.8

$$CO_2 + H_2 \rightarrow CO + H_2O \quad (8\text{-d})$$

According to Reactions 3 to 6, addition of CO_2 and H_2O to the feed causes change of CO to H_2O ratio in the product. Therefore, we must determine acceptable ranges of CO_2 and H_2O concentrations in the feed in order to for suitable H_2 to CO ratio in the product stream with almost complete conversion of methane.

Figures 2-6 show acceptable ranges of CO_2 and H_2O concentration in the feed for different pressures and temperatures. In these figures, we obtained suitable amounts of CO_2 and H_2O with following conditions:

A. Mole fraction of CH_4 in the product to be less than 0.015.

B. H_2 to CO molar ratio in the product is 1.9 to 2.1 (suitable ratio for FT and Methanol processes).

For obtaining these figures, we have done about 1.2 million runs. Figures 2-6 are applied to determine the best (or desired) conditions of syngas reaction completion. The technical constraints such as the maximum pressure and temperature or H_2/CO ratio are

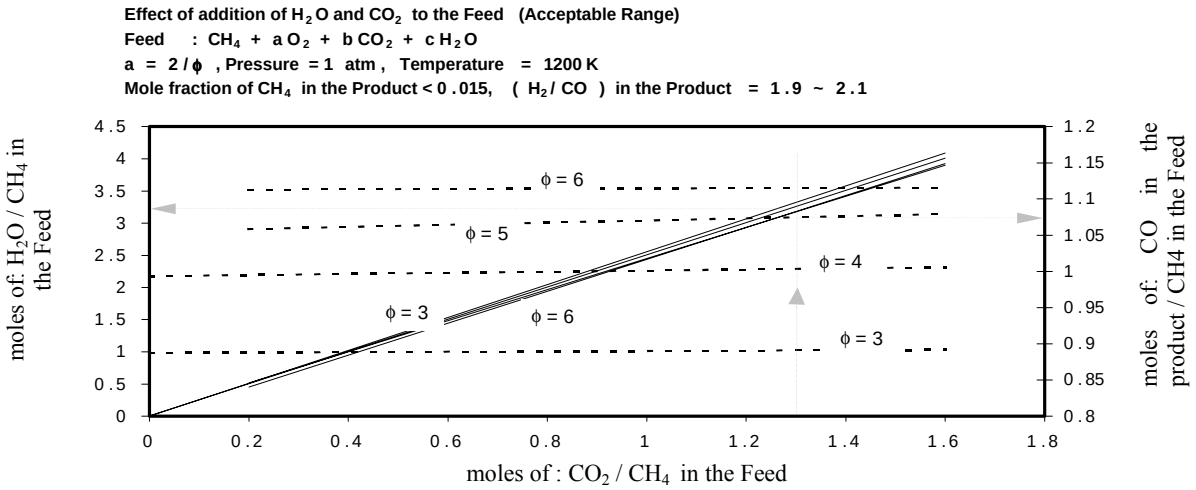

Figure 2. Yield of syngas reaction respect to the feed composition at 1 atm, 1200 K. (All of proportionalities are in mole ratio)

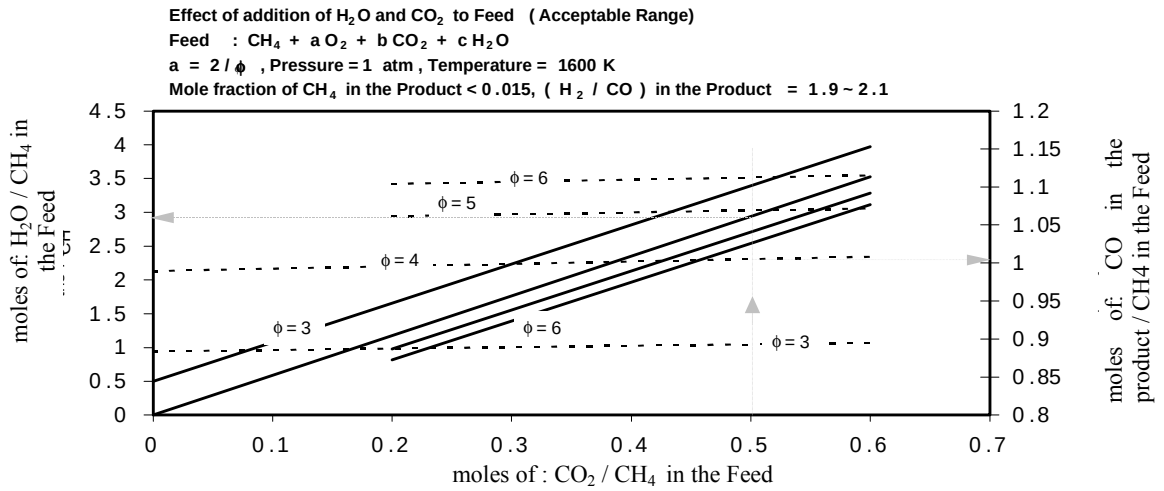

Figure 3. Yield of syngas reaction respect to the feed composition at 1 atm, 1600 k. (All of proportionalities are in mole ratio)

adjusted at first. Then by specifying the minimum required parameters such as equivalence ratio and/or CO_2/CH_4 in the feed the desired parameters will be calculated.

4. THE PROCEDURE FOR APPLICATION OF FIGURES 2 TO 6

Figures 2 to 6 are the result of many calculations with regard to several restrictive limits and conditions. These conditions and limits are printed on the top of each figure and are about predefined pressure and temperature of the reaction, maximum conversion of methane and maintaining the ratio of H_2/CO about 1.9~2. This means that any value or result that is read form these figures is a depiction of equilibrium concentration of CO in the product stream versus initial concentrations and overall permanent limits (pressure, temperature and constant ratio of H_2/CO in the product). The lines and curves on these figures cannot be extrapolated and are valid in the regions that are drawn.

Thus we can search, find and apply many

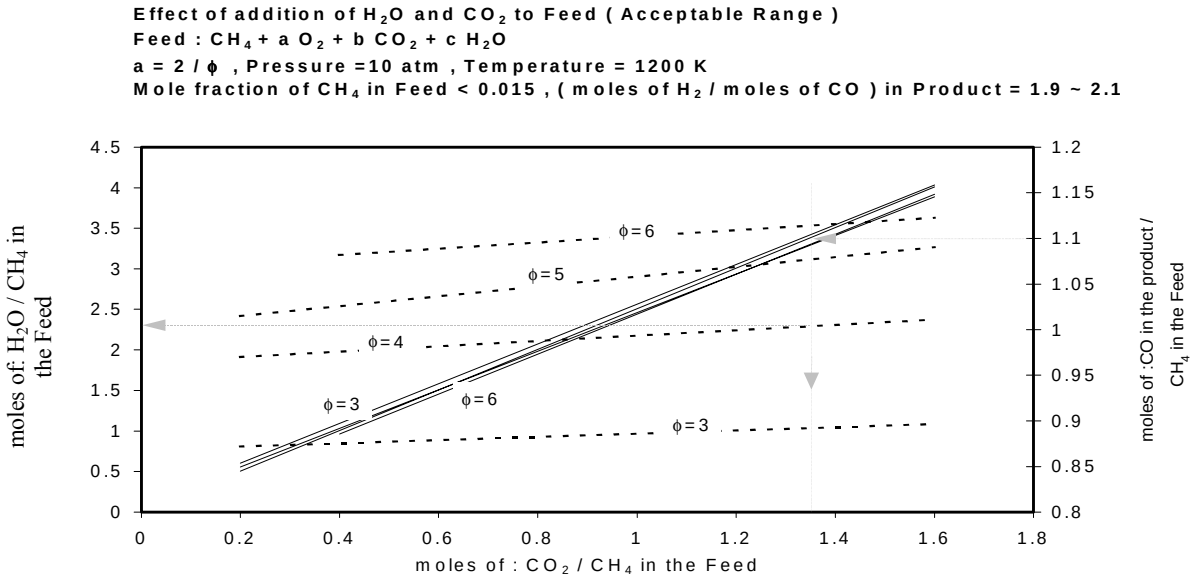

Figure 4. Yield of syngas reaction respect to the feed composition at 10 atm, 1200 K (All of proportionalities are in mole ratio).

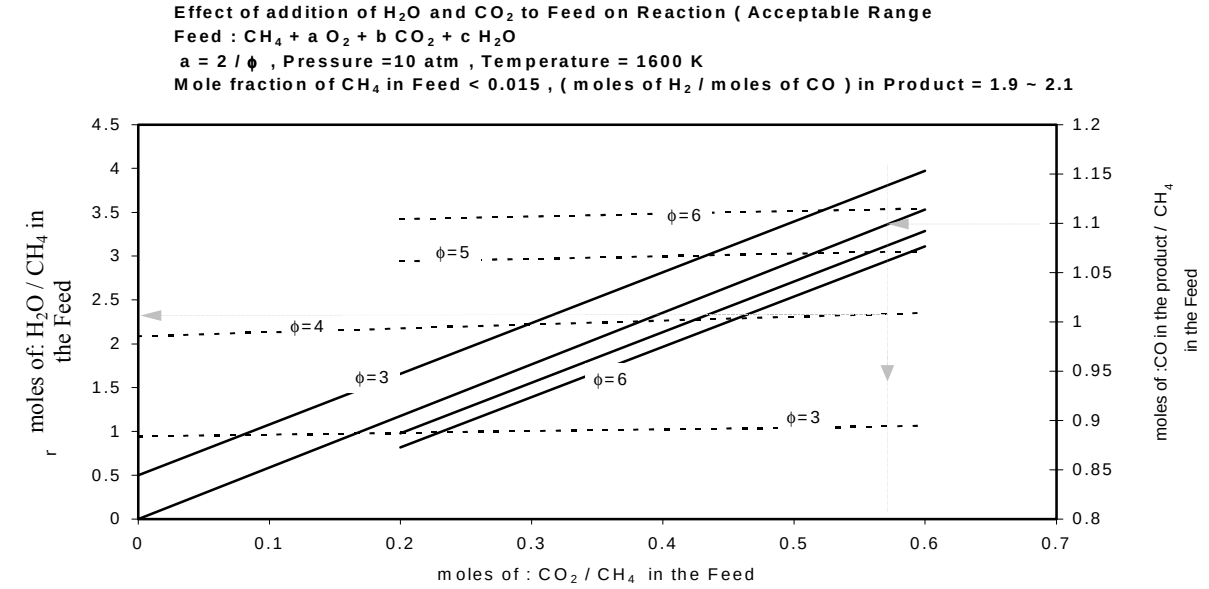

Figure 5. Yield of syngas reaction respect to the feed composition at 10 atm, 1600 K (All of proportionalities are in mole ratio).

different values for this reaction by using these figures without worrying about the violation of primitive conditions.

All figures have two vertical axes and a single horizontal axis. The left vertical axis shows the mole fraction of H_2O to methane in the feed stream and the right vertical axis shows the ratio of moles of CO in the product stream to moles of methane in the feed stream (mole fraction). Also, The horizontal axis shows the mole fraction of CO_2 to methane in the feed stream. The values on both vertical axes are tied to horizontal axis and by

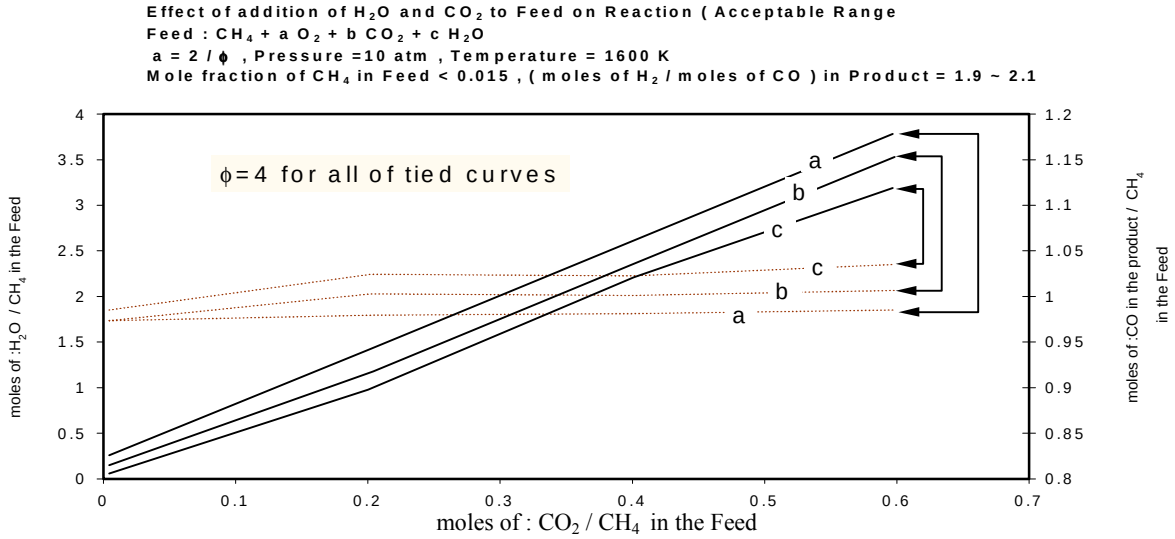

Figure 6. Yield of reaction in more detailed view on boundary lines (All of proportionalities are in mole ratio).

TABLE 3. Application of Figure 5 for Reading the Required Amount of CO_2 and H_2O in the Feed.

Predefined conditions and limits		**Assumptions and readings**	
Pressure (atm)	10	ϕ	4
Temperature (K)	1600	Moles of CO_2 in the feed	0.57
H_2/CO in the product Stream	1.9 ~ 2.1	Moles of H_2O in the feed	2.3
Moles of CH_4 in the feed	1		
Moles of CO in the product	1.1		

selection of a value on horizontal axis (CO_2/CH_4) and a value for ϕ, the values on vertical axes will be read as described below.

There are two sets of lines on the plot area of each figure. One set of lines is solid and another set is doted. These lines are parametric and vary versus the equivalence ratio. The solid lines relate the values on the left vertical axis and doted lines relate the values on the right vertical axis to the values on the horizontal axis. These lines represent the intersection of each value on the right and left vertical axes by a value on the horizontal axis with respect to a specified value of the equivalence ratio.

The amount of CO_2 and H_2O that can be injected to feed stream are not independent and are tied together with solid lines. As mentioned above, by determining two values from the three parameters of CO_2/CH_4, ϕ and H_2O/CH_4, the third value can be read from figures (E.g. from Figure 3 for CO_2/CH_4 = 0.5 and ϕ=4, H_2O/CH_4 is read about 2.9). There is a similar description for the right vertical axis. (E.g. from Figure 3 for CO_2/CH_4 = 0.5 and ϕ=4, CO_2/CH_4 is read about 1.01)

Based on the above explanations it is possible to attain 1.1 mole CO in the product stream by applying 1 mole CH_4 in feed stream in the specified conditions. The results of this case are read from Figure 5 and are printed in Table 3.

5. DISCUSSION

Figures 2 to 6 present the results of thermodynamic

simulation of noncatalytic syngas reaction at its equilibrium state under predefined conditions. A number of topics that can be found from these figures are as follow:

1- For keeping the ratio of H_2/CO in the product around the value of 2, without the injection of CO_2 and H_2O to the feed, ϕ about 4 should be selected the value of as noted in other references [1].

2- By the addition of CO_2 and H_2O to the feed, the value of equivalence ratio in a wide range of magnitudes may be to varied and selected. However, this range in a specified pressure and temperature is confined to a restricted region.

3- By increasing the magnitude of ϕ, the yield of reaction for production of CO will increase but the interval of concentration of H_2O and CO_2 that can be added to the feed will decrease. So, there is an ultimate maximum value for the equivalence ratio for each pressure and temperature that can be applied for the reaction.

4- The reaction is more sensitive to addition of H_2O with respect to CO_2. It seems that the initial amount of added CO_2 increases the production of CO, but the excess value of CO2 has the role of an inert component. However, H_2O has an effective influence on varying the yield of reaction in its entire concentration range in the feed stream.

5- In the low temperatures, the yield of reaction (amount of CO in the production) shows a little dependency to the values of ϕ with respect to the variation of CO_2. It means that at low temperatures, to control the yield of reaction at a constant value, it is possible to keep the amount of CO2 constant in the feed and adjust the value of concentration of H_2O in the feed with regard to the variation of ϕ.

6- All solid and doted lines in each figure are fitted on a narrow band of results that those have the same value of ϕ. Figure 6 is a more detailed redraw of Figure 5 that its original tied lines are showed. As shown in Figure 6, this graph is relatively complicated. In Figure 5, for every value of ϕ there is a unique line for interconnection of vertical axes to horizontal axis. But actually for ach value of ϕ there are many of these lines that are tied together. These tied lines are shown with double letters a, b and c on the Figure 6. These lines have lower and upper limits that makes possible to show all of them by a unified fitted line as presented in the Figures 2 to 6. The method of reading the data from Figure 6 is similar to that of Figures 2 to 6 as explained earlier.

6. SUGGESTIONS

It is apparent that Figures 2 to 6 are not suitable for numerical calculations, especially in the iterative cases. In continuation of this work it is a good idea to find an overall algebraic equation to fit all of parameters. This equation, if found, can be applied to design optimized noncatalytic syngas reactors.

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