Optimization of SynGas Production in Noncatalytic Auto Thermal Partial Oxidation of Methane Proccess

Mohammad Khoshnoodi[1], Mahmoud Din Mohammad[2]

Department of Chemical Engineering, University of Sistan and Baluchestan,
P.O. Box 98164-161, Zahedan, Iran
dinmohammadm@yahoo.com

Abstract

General modelling and optimization of syngas production via noncatalytic auto thermal partial oxidation (NGSAPO) of methane are carried out using our developed scientific software which was based on the minimization of the total Gibbs energy. In this work, a novel application of the direct search and Newton-Raphson methods was introduced to apply for optimization of a complex chemical reaction. Sensitivity analysis was done to investigate the effect of several parameters on the quality of syngas and the production yield. The acceptable concentrations of CO_2 and H_2O injected into the methane feed are optimized in the specified temperature and pressure range, while H_2/CO ratio in the product stream is set to remain at 1.5 or 2, methane slip in the syngas is to be less than 1.5% and staying in the non endothermic conversion area of reaction, simultaneously. This facilitates monetizing CO_2 in the petrochemical and steel industries. The output from this software is comparable both with the experimental results, cited in Ref. [1], and with that from ASPEN PLUS in simulating the experiments mentioned in Ref.[2]

Keyword: syngas, modelling, noncatalytic, auto thermal, partial oxidation

1- Introduction

Synthesis gas (syngas, a mixture of CO and H_2) is a versatile feedstock mainly used in ammonia, methanol, oxo-alcohol and in the Fischer-Tropsch (FT) processes. It is also used with different composition in carbonylation, hydroformylation, hydrogenation in petrochemical plants as well as for iron ore reduction in the steel industry. Since last decade, worldwide efforts are being made for economical conversion of natural gas into valuable and easily transportable products such as liquid hydrocarbon fuels, methanol, dimethyl ether, and petrochemical feed stocks like ethylene and other lower olefins.

Table 1 shows the synthesis gas mixture ratio for utilization in some important final products.

Table 1- Mixture composition for industrial Syngas

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-Alcohol	1.5	1	0

2- Syngas from natural gas

There are several commercial methods for conversion of natural gas to synthesis gas. The different technologies applied depending on various applications are:

- Steam Methane Reforming (SMR)
- Steam Methane and Oxygen Reforming (SMR /O2)
- Partial Oxidation (POX)
- Catalytic Partial Oxidation (CPO)
- Auto Thermal Reforming (ATR)
- Carbon dioxide Reforming
- Combined Auto Thermal Reforming (CAR)
- Sulfur Passivated Reforming (Sparg)
- Combined Reforming with or without pre-Reforming

---

1 PH.D of Chemichal Engineering
2 MS.D of Chemichal Engineering

▪ Gas Heated Reforming (GHR)

International companies including, Texaco, Shell, Lurgi, Topsoe, Foster Wheeler, Kellogg and Midrex have commercialised these methods under their own licenses.

The most conventional process is SMR, which is a highly endothermic reaction of methane and steam over a special catalyst:

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \qquad \Delta H_{298} = 49.3 \, \text{kcal/mol} \tag{1}$$
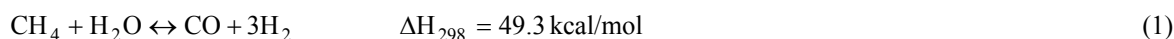
Today the promising method for syngas production is the partial oxidation of methane with pure oxygen.

$$CH_4 + 0.5O_2 \leftrightarrow CO + 2H_2 \qquad \Delta H_{298} = -8.53 \, \text{kcal/mol} \tag{2}$$
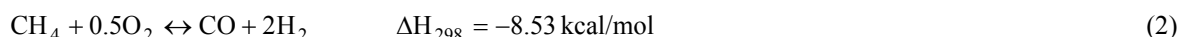
In this non-catalytic partial oxidation (NCPO), desulfurized natural gas is preheated, mixed thoroughly with oxygen, and then ignited. Because the reaction is exothermic, a considerable amount of steam or electrical power may be generated while cooling the reactor. With no catalyst, the peak reaction temperature has to be high (1100-1500 $^{\circ}$C) to achieve equilibrium conversion. Complete combustion to CO_2 and H_2O can take place if oxygen is supplied in sufficient amount.

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \qquad \Delta H_{298} = -192 \, \text{kcal/mol} \tag{3}$$
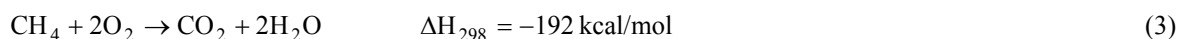
3- Simulation of Syngas Production

Recently a number of studies have been reported on the simulation of noncatalytic partial oxidation of methane and natural gas with various compositions [1,2,3,4,5]. Optimum reaction temperature for maximization of CO content of the syngas, effect of some additives and reactor pressure changes, as well as equilibrium concentration of more than twenty species in the product stream were investigated using the ASPEN PLUS simulator [2].

In the present work an advanced software was developed, to simulate auto thermal partial oxidation of natural gas combined with CO_2 and H_2O reforming of methane. To accelerate the calculation, in this method, a modified Newton-Raphson method accompanied by direct search was employed. This is a too complicated problem and has no mentioned analytic solution or popular numerical method. To find the optimum condition, each parameter was allowed to change in an appropriate range. These intervals were divided into small divisions. A large number of different parameter combinations as unique input data were generated using employed nested Do-Loops. As the number of parameters and/or divisions increases, the total number of independent inputs that must be solved grow very rapidly.

All of the inputs are generated in the first lines of software and the output is saved in a database. Through searching the records in the database, the optimum condition can be easily determined. At the end of run, it was found that about 15,450,000 independent inputs must be considered in order to have a continuous and meaningful answer to find the optimum conditions. The result of this work can be applied as a major guideline in the industrial applications so that tedious and expensive experimental works can be avoided.

A through investigation of CO_2 and H_2O addition has not been seen in previous works. The package is supported by a thermo chemical data bank from JANAF Tables [6] and is capable of optimization, design specification, and different sensitivity analysis calculations. Recalling that in most petrochemical plants a low cost source, or even a discharge, of CO_2 is available, dilution of the natural gas feed with CO_2 is of prime economic importance. This also prevents emission of a greenhouse gas into the atmosphere.

In this work, the acceptable mole ranges of O_2 ($n_{O2,f}$), CO_2 ($n_{CO2,f}$) and H_2O ($n_{H2O,f}$) injection into the feed per one mole CH_4 are explored under several imposed technical limitations of syngas quality and operational specified constraints.

The capability of the developed software for precise simulation of the considered problem is approved by repetition of the previous theoretical and experimental work results [7,8,9,10], concluding satisfactory agreement.

4- Theory

The total Gibbs energy of a single-phase mixture is expressed as:

$$G_{T,P}^t = G(n_1, n_2, n_3, ..., n_N) \tag{4}$$

n_i's are the number of chemical species moles and N is the number of components in the product. For specified T and P the set of n_i's are determined by minimizing G^t, while regarding the material balance constraints. Atomic mass balance for each element is presented by:

$$\sum n_i a_{ik} = A_k \qquad (k = 1, 2, ..., \varepsilon) \qquad (5)$$

A_k is the total number of atomic masses of kth element, a_{ik} is the number of atoms of the kth element present in the each molecule of chemical species, i, and G is the number of elements that exist in the system.

For each element balance, one Lagrange multiplier, λ_k, is introduced. By applying the Lagrange method and a short mathematical manipulation on equations 4 and 5 the final set of equations is derived as follows:

$$\Delta G_{f_i}^0 + RT \ln(y_i \hat{\phi}_i P) + \sum \lambda_k a_{ik} = 0 \qquad (i = 1, 2, 3, ..., N) \qquad (6)$$

$\Delta G_{f_i}^0$ is the Gibbs energy for each product component at the reaction temperature condition. All of $\hat{\phi}_i$ are set to unity. All of n_i and λ_k will be found by solving the set of equation 5 and 6 with a specified T, P and A_k, simultaneously [11].

In the present work, the feed of reaction is considered as a mixture of CH_4, O_2, H_2O and CO_2 with variable concentration. By applying the "direct search" and "Newton-Raphson" method for variable pressure and temperature, the appropriate concentration of O_2, H_2O and CO_2 for one mole of CH_4 is determined. The depicted flowchart in Figure 1 shows the applied algorithm for solving the proposed problem.

Any numerical procedure used for solving a system of equations requires starting estimate figures as much as possible close to the final answers to meet convergence criteria and to reduce the number of iterations. However, a specific technique based on the Newton-Raphson method, which was applied here, is capable of leading the calculation to the final answer no matter what is the initial guess. The value of 0.5 was used for all initial guess and for each independent case it took 0.05 second for calculations to be completed.

5- Results and discussion

5-1- Validity of the software output

In order to examine the validity of the software output, we started with resolving the reported data [1]. The dependency of the production yield on molar equivalence ratio, n, is illustrated in Figure 2. The simulator output (the lines) pass closely through the previous observations (the points). The figure shows transition from partial oxidation to complete combustion. In Figure 2 the reaction between methane and oxygen is represented by a general formula:

$$CH_4 + n O_2 \rightarrow CO_2 + H_2O + CO + H_2 + O_2 + CH_4 \qquad (10)$$

The numbers of moles of oxygen provided to the number of moles of CH_4 in the feed is defined as the molar equivalence ratio, n.

Another comparison is carried out with the simulation results already obtained by one of these authors using ASPEN PLUS [2]. The operational data from SGP reactor in the Shell MDS Malaysia, Sarawak plant are used in both simulators. 14946 kg per hour natural gas from South China Sea (87.97% CH_4, for complete composition see Ref. [2]), 17783 kg per hour pure oxygen and 57 kg per hour hydrogen are fed to the reactor at 1390 °C and 46-bar pressure producing 32787 kg per hour synthesis gas. Equilibrium concentration of 29 species in the syngas stream is compared in Table 2.

Slight differences between the two simulation results are due to the accuracy of the Gibbs energy values utilized from different sources. Although the material balance is satisfied in the both software, a lower value is calculated for the total Gibbs energy in the present work showing a more accurate result.
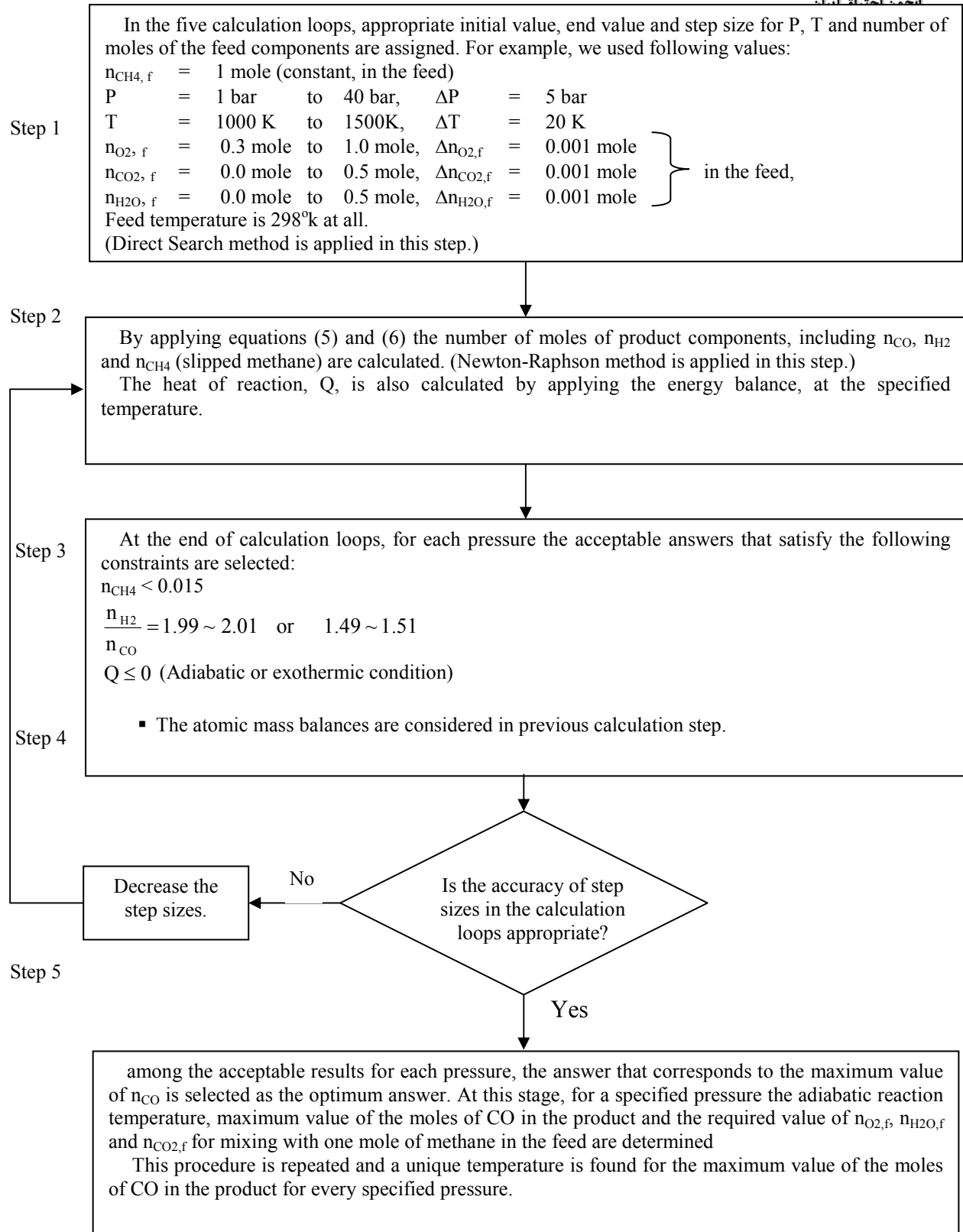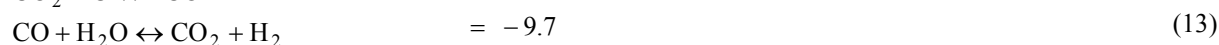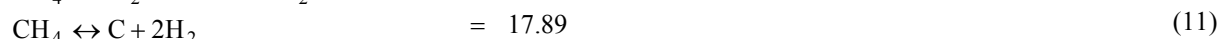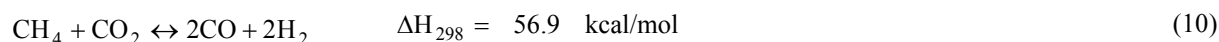
Step 1

In the five calculation loops, appropriate initial value, end value and step size for P, T and number of moles of the feed components are assigned. For example, we used following values:

$n_{CH4, f}$ = 1 mole (constant, in the feed)

P = 1 bar to 40 bar, ΔP = 5 bar

T = 1000 K to 1500K, ΔT = 20 K

$n_{O2, f}$ = 0.3 mole to 1.0 mole, $\Delta n_{O2,f}$ = 0.001 mole

$n_{CO2, f}$ = 0.0 mole to 0.5 mole, $\Delta n_{CO2,f}$ = 0.001 mole ⎫ in the feed,

$n_{H2O, f}$ = 0.0 mole to 0.5 mole, $\Delta n_{H2O,f}$ = 0.001 mole ⎭

Feed temperature is 298°k at all.

(Direct Search method is applied in this step.)

Step 2

By applying equations (5) and (6) the number of moles of product components, including n_{CO}, n_{H2} and n_{CH4} (slipped methane) are calculated. (Newton-Raphson method is applied in this step.)

The heat of reaction, Q, is also calculated by applying the energy balance, at the specified temperature.

Step 3

At the end of calculation loops, for each pressure the acceptable answers that satisfy the following constraints are selected:

$n_{CH4} < 0.015$

$\dfrac{n_{H2}}{n_{CO}} = 1.99 \sim 2.01$ or $1.49 \sim 1.51$

$Q \leq 0$ (Adiabatic or exothermic condition)

Step 4

- The atomic mass balances are considered in previous calculation step.

Decrease the step sizes.

No

Is the accuracy of step sizes in the calculation loops appropriate?

Step 5

Yes

among the acceptable results for each pressure, the answer that corresponds to the maximum value of n_{CO} is selected as the optimum answer. At this stage, for a specified pressure the adiabatic reaction temperature, maximum value of the moles of CO in the product and the required value of $n_{O2,f}$, $n_{H2O,f}$ and $n_{CO2,f}$ for mixing with one mole of methane in the feed are determined

This procedure is repeated and a unique temperature is found for the maximum value of the moles of CO in the product for every specified pressure.

Figure 1- Flowchart of the algorithm

Table 2- Comparison the outputs of the developed software with Ref. [2]

	Elements				Gibbs Energy From JANAF	Moles in the product	
	C	O	H	N		This Work	ASPEN PLUS
O_2	1	2	0	0	0.00E+00	6.08E-11	3.08E-10
CO_2	1	2	0	0	-3.96E+05	4.91E+01	4.46E+01
H_2O	0	1	2	0	-1.59E+05	2.43E+02	2.40E+02
H_2	0	0	2	0	0.00E+00	1.38E+03	1.39E+03
OH	0	1	1	0	1.49E+04	9.43E-05	2.41E-04
CO	1	1	0	0	-2.52E+05	8.26E+02	8.37E+02
H	0	0	1	0	1.31E+05	1.37E-02	2.88E-02
O	0	1	0	0	1.49E+05	7.55E-10	3.75E-09
CH_4	1	0	4	0	8.47E+04	4.57E+00	2.26E+00
N2	0	0	0	2	0.00E+00	7.51E+00	7.52E+00
NO	0	1	0	1	7.02E+04	1.06E-07	3.20E-07
HO_2	0	2	1	0	9.67E+04	2.05E-13	5.13E-12
NO_2	0	2	0	1	1.33E+05	9.53E-16	5.33E-15
N_2O	0	1	0	2	1.99E+05	2.39E-12	6.98E-12
CN	1	0	0	1	2.75E+05	1.51E-09	4.61E-09
HNO	0	1	1	1	1.75E+05	1.97E-10	6.09E-10
N	0	0	0	1	3.73E+05	1.20E-11	5.43E-11
HCO	1	1	1	0	-2.97E+04	2.18E-04	3.78E-04
CH	1	0	1	0	4.16E+05	4.95E-13	2.31E-12
HCN	1	0	1	1	8.31E+04	1.53E-02	1.59E-02
HN	0	0	1	1	3.45E+05	4.99E-10	1.74E-09
C_2H_6	2	0	6	0	2.38E+05	8.46E-05	2.39E-05
C_3H_8	3	0	8	0	5.23E+05	7.43E-14	6.68E-10
iC_4	4	0	10	0	1.22E+06	0.00E+00	6.33E-15
nC_4	4	0	10	0	9.40E+05	0.00E+00	1.90E-14
NH_3	0	0	3	1	1.31E+05	1.25E-01	1.04E-01
CH_2O	1	1	2	0	-6.45E+04	1.51E-02	9.23E-03
CH_2	1	0	2	0	3.03E+05	1.30E-08	2.99E-08
C	1	0	0	0	0.00E+00	4.40E+00	1.44E-14
SUM						2512.7	2517.3

	Atom Balance				Total Gibbs Energy (J / mol)
	C	H	O	N	
Feed	884.15612	3260.47145	1166.80806	15.15781	----------
Product, This work	884.15612	3260.47150	1166.80810	15.15781	-172917246.4
Product, ASPEN PLUS	884.15615	3260.47152	1166.80807	15.15781	-172845251.8

5-2- Acceptable mole range of O_2, CO_2 and H_2O in the feed

Reaction (2) is an ideal description of the partial oxidation process. Some other relevant reactions are

$$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2 \qquad \Delta H_{298} = 56.9 \quad kcal/mol \tag{10}$$
$$CH_4 \leftrightarrow C + 2H_2 \qquad\qquad\qquad = 17.89 \tag{11}$$
$$CO_2 + C \leftrightarrow 2CO \qquad\qquad\qquad = 41.2 \tag{12}$$
$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad\qquad = -9.7 \tag{13}$$
$$C + H_2O \leftrightarrow CO + H_2 \qquad\qquad = 31.4 \tag{14}$$
$$CH_4 + 1.5O_2 \leftrightarrow CO + 2H_2O \qquad = -123.6 \tag{15}$$

According to these reactions, addition of CO_2 and H_2O into the feed stream changes the H_2/CO ratio in the syngas. For this reason acceptable ranges of CO_2 and H_2O concentrations in the feed should be determined in order to maintain desired H_2/CO ratio with almost complete conversion of methane. Dilution of natural gas with carbon dioxide is commercially important in reforming processes.

Figures 3 to 5 are the simulation outputs for molar variations of O_2, CO_2 and H_2O in the feed as functions of reaction temperature at specified pressures (1, 5, 10, 20, 40bar). In the whole outputs, the amount of CH_4 in the feed is considered constant and equal to one mole, the ratio of H_2 to CO equal to 2, auto thermal reaction (exothermic or adiabatic conversion) and maximum methane slip (mole fraction of CH_4 in the syngas) of 0.015

When the pressure and temperature for the partial oxidation process combined with the reforming reactions are chosen and set on the figures 3 to 6, the acceptable number of moles of O_2, CO_2 and H_2O which can be mixed with one mole of CH_4 in the feed are read respectively.

For example, temperature is assumed at 1100 ^{o}K and pressure of reactor equal to 1 bar. The required moles of O_2, CO_2 and H_2O that must be mixed with one mole of methane to produce suitable syngas with specification of $H_2/CO=2$, methane slip less than 1.5% and reaction take place at auto thermal condition, are read From figures 3, 4 and 5 as equal to 0.582, 0.047 and 0.071 mole, respectively. In this case, the amount of CO in product is 0.936 mole (figure 6).

5-3- Optimization of CO yield

The produced moles of CO versus temperature in the product for various pressures are reported on figure 6 at the presumed conditions as described before. For each pressure, there is a maximum value of CO in the production and it is the most important result of this work. These maximum points show unique temperature for each pressure that the value of CO in the syngas reaches to its maximum possible value at predefined conditions.

For example, the maximum moles of CO in the syngas at the pressure of 5 bar, is produced only in 1270 ^{o}K (Figure 6), witch requires 0.617 mole of O_2 (Figure 3), 0.0012 mole of CO_2 (Figure 4) and 0.075 mole H_2O (Figure 5) to be mixed with one mole methane. General constraints are an H_2/CO equal to 2 and $y_{CH4}<0.015$ in the product and Feed temperature is 298 ^{o}K.

5-4- Simulation results for industrial applications

For each pressure, the maximum value of CO in the figure 6 is selected as optimum condition and the corresponding Temperature and mole value of O_2, CO_2, H_2O (from figures 3 to 5) are drawn versus pressure in the figures 7 to 11 accompanied with an excess condition which it is $H_2/CO = 1.5$.

Figure 11 shows the optimum operation for syngas reaction at conditions of $H_2/CO=2$ and $H_2/CO=1.5$. Figure 10 shows the maximum mole value of CO in the product versus the reactor pressure. This figure shows that as pressure increased, the yield of production of CO decreases rapidly and with lower slop after 10 bars.

Figures 7 to 9 show the required mole value of O_2, CO_2 and H_2O to mix with 1 mole methane versus reactor pressure correspond to optimum mole value of CO in the product (figure 10) and reactor temperature (figure 11).

The developed equations for the pressure curves are also indicated on each diagram. These results may be utilized for design and operation of the reactors for non-catalytic auto thermal partial oxidation of natural gas combined with CO_2 and H_2O reforming.

6- Conclusion

The developed software is capable of simulating the complex reactions of auto thermal partial oxidation of natural gas for production of synthesis gas. The effect of CO_2 and H_2O addition into the feed stream is investigated while imposing technical constraints of reaction temperature, pressure, H_2/CO ratio, auto thermal conversion and methane slip in the product stream. Optimization, design specification and sensitivity analysis tools incorporated into the simulator. The results may be report as different tables or graphical presentations. The simulator is especially helpful to study monetizing CO_2 surplus in the petrochemical and steel industries [12].
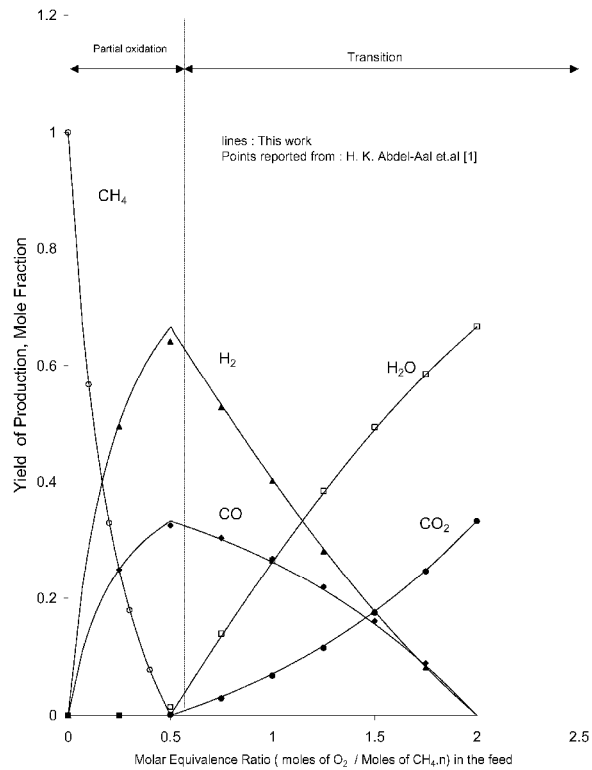
Figure 2- Concentration of some important species in partial oxidation of methane at 1477 Kand 1 bar
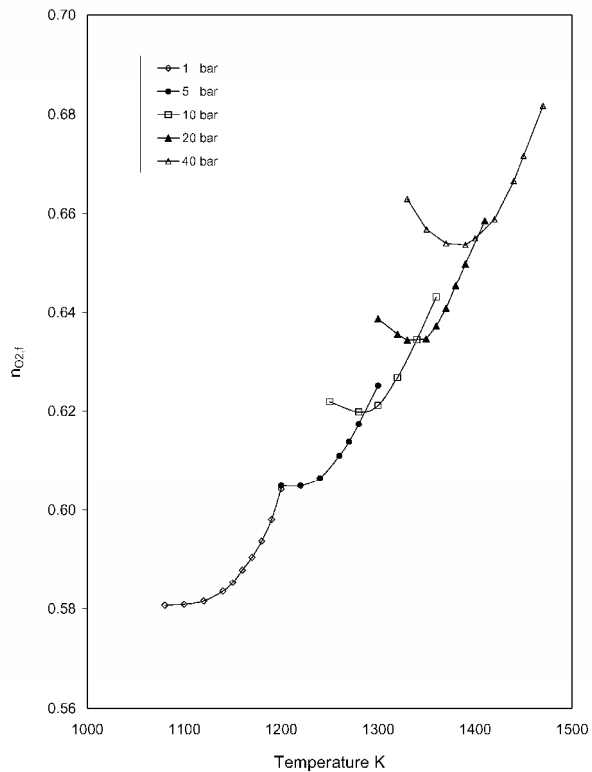

Figure 3- Acceptable moles of O_2 addition into the feed per one mole of methane as function of reaction temperature for $H_2/CO=2$
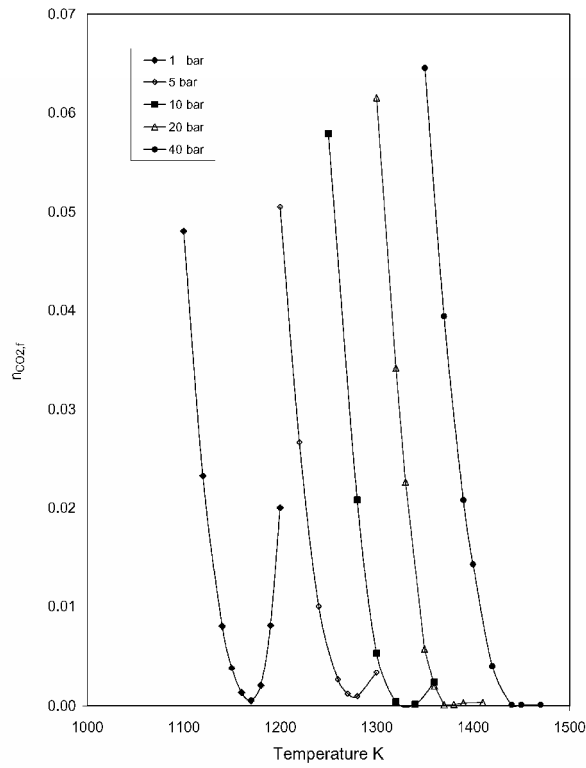
Figure 4- Acceptable moles of CO_2 addition into the feed per one mole of methane as function of reaction temperature for $H_2/CO=2$
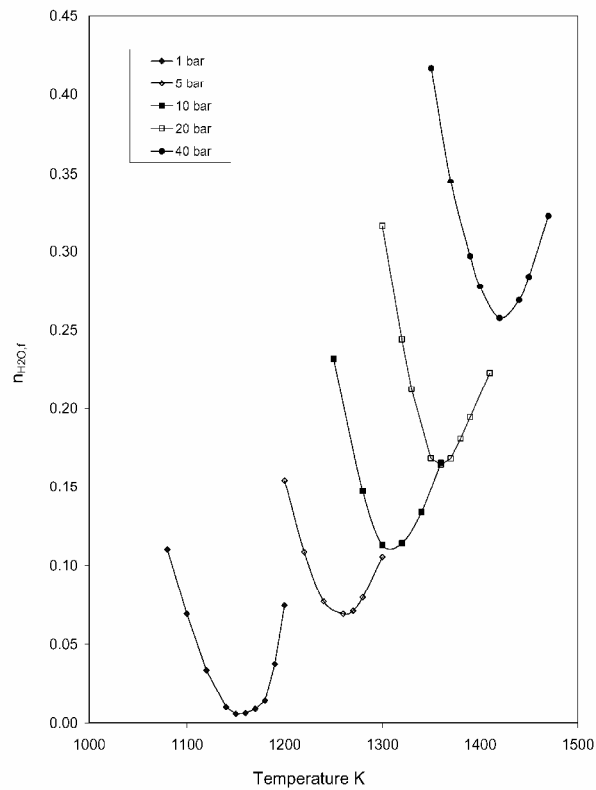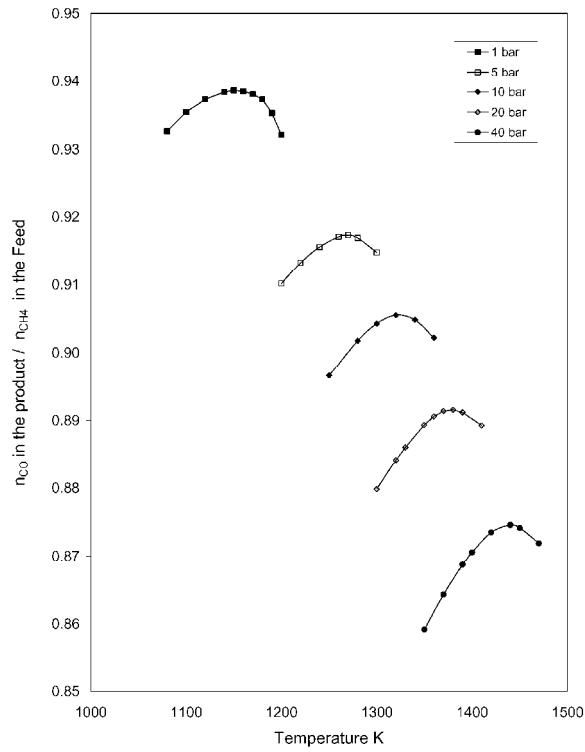

Figure 5- Acceptable moles of H_2O addition into the feed per one mole of methane as function of reaction temperature for $H_2/CO=2$

Figure 6- Maximum CO production as a function of reaction temperature for $H_2/CO=2$
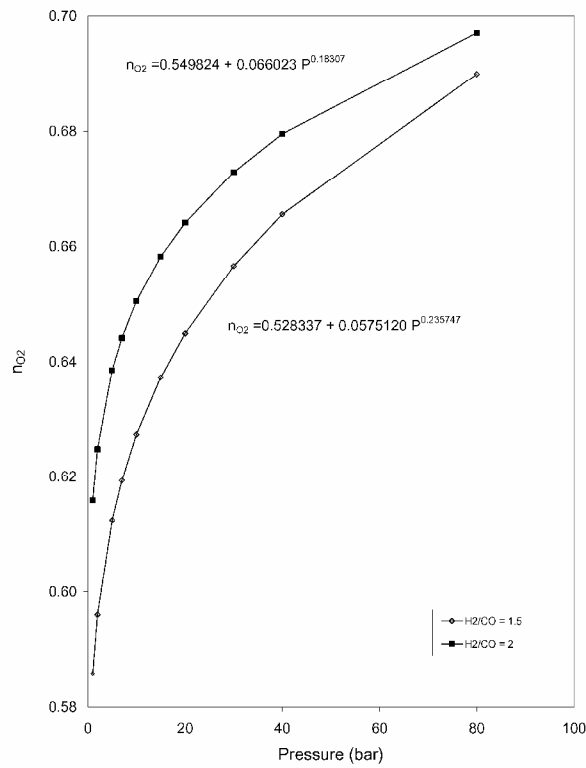
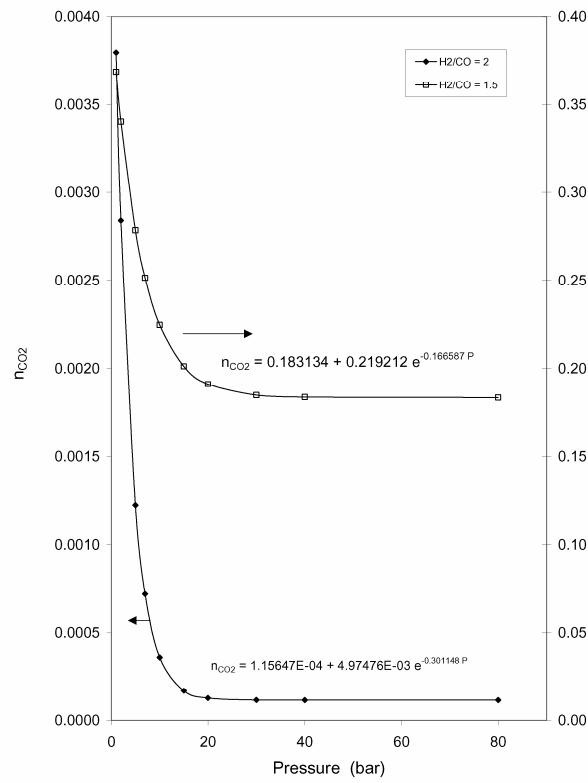**Figure 7- Optimum mole addition of O_2 to the feed per one mole of CH_4**

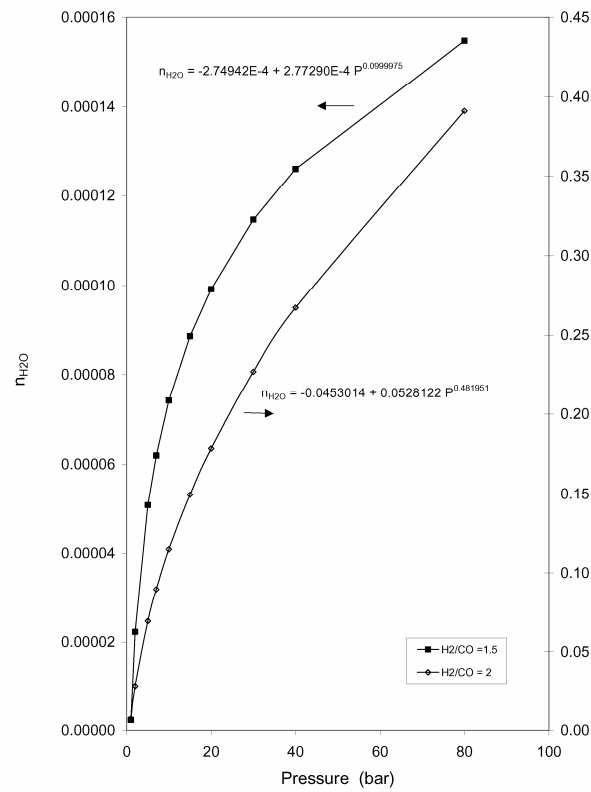**Figure 8- Optimum mole addition of CO_2 to the feed per one mole of CH_4**

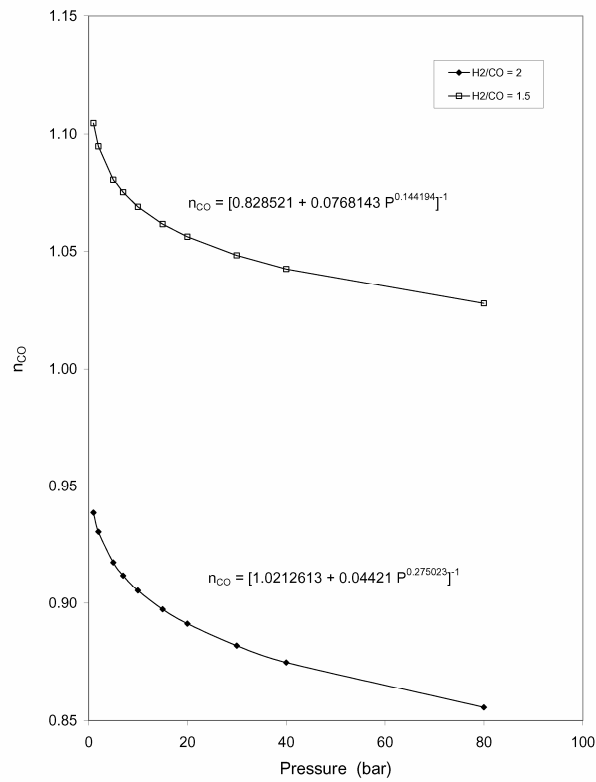**Figure 9- Optimum mole addition of H_2O to the feed per one mole of CH_4**

$$n_{CO} = [0.828521 + 0.0768143\ P^{0.144194}]^{-1}$$

$$n_{CO} = [1.0212613 + 0.04421\ P^{0.275023}]^{-1}$$

Figure 10- Optimum Yeild of CO production

$$T = 462.531 + 627.139\ P^{0.126094}$$

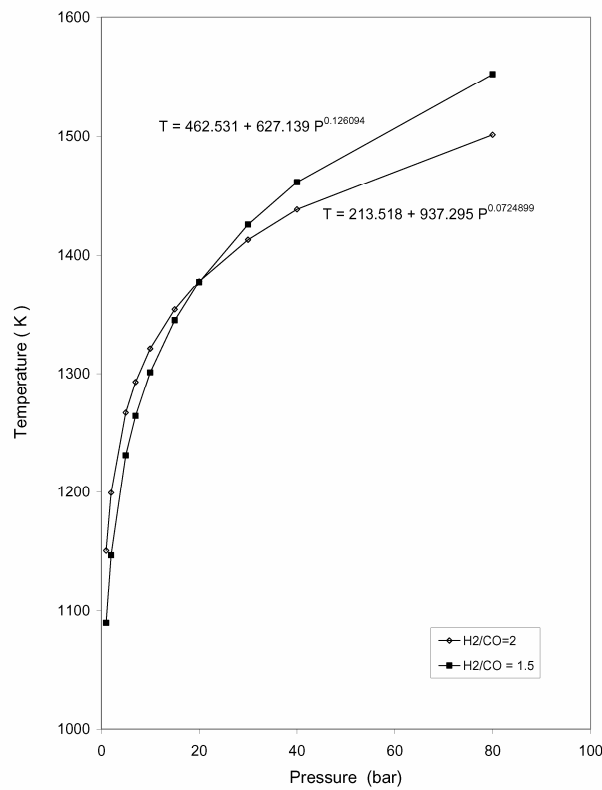$$T = 213.518 + 937.295\ P^{0.0724899}$$

Figure 11 Optimum Operating Condition for Maximization of CO

Literature Cited

1- Abdel-Aal, H.K., Shalabi, M.A., Al-Harbi, D.K., Hakeem, T. Simulation of Direct Production of Synthesis Gas from Sour Natural Gas by Noncatalytic Partial Oxidation (NCPO): Thermodynamics and Stoichiometry, Ind. Eng. Chem. Res. , Vol. 38, pp. 1069, 1999.

2- Khoshnoodi, M., Lim, Y. S. Simulation of Partial Oxidation of Natural Gas to Synthesis Gas using ASPEN PLUS, Fuel Processing Tecnology, Vol. 50, pp. 275, 1997.

3- Karim, G.A., Zhou, G. The Uncatalyzed Partial Oxidation of Methane for Production of Hydrogen with Circulation. Journal of EnergyRersources Technology. , Vol. 115, pp. 307, 1993.

4- Abdel-Aal H.K., Shalabi, M.A. Noncatalytic Partial Oxidation of Sour Natural Gas versus Catalytic Steam Reforming of Sweet Natural Gas. Ind. Eng. Chem. Res., Vol. 35, pp. 1785, 1996.

5- Sloane, T. Ignition and Flame Propagation Modeling within Improved Methane Oxidation Mechanism. Combustion Science and Technology. , Vol. 63, pp. 287, 1989.

6- JANAF Thermo chemical Tables. 3rd. Ed. The Dow Chemical Company, Michigan, 1985.

7- Mungen, R., Kratzer, M. B. Partial Combustion of Methane with Oxygen. Ind. Eng. Chem, Vol. 43, pp.2782, 1951.

8- Karim, G.A., Hanafi, A.S. An Analytical Examination of the Partial Oxidation of Rich Mixture of Methane and Oxygen. Journal of Energy Resources Technology. , Vol. 114, pp. 152, 1992.

9- Kakabadze, V.SH. Experimental Investigation of the High Temperature Conversion of Natural Gas in a Reactor with Swirling Jets. Int. J. of Hydrogen Energy, Vol. 11, pp. 513, 1986.

10- Christensen, T.S., Primdahl, I.I. Improve Syngas Production Using Auto thermal Reforming. Hydrocarbon Processing. March 1994.

11- Smith, J.M., Van Ness, H.C. Introduction to Chemical Engineering Thermodynamics. 3rd. ed. Chapter 15, McGraw-Hill Pub. Co. New York, 1987.

12- Din Mohammad, M.; Sadegh Zadeh Ahari, J. Determination of Suitable Concentrations of H2O and CO2 in the feed of Syngas Production. Int. J. of Eng. Iran.