Investigation of CO_2 and H_2O Addition to Natural Gas for Production of Synthesis Gas

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Abstract
General modeling and optimization of syngas production via noncatalytic autothermal partial oxidation of methane are carried out using our developed scientific software which was based on the minimization of total Gibbs energy. In this work, a novel application of the direct search and Newton-Raphson methods was introduced to apply to 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 less than 1.5% and the non-endothermic conversion area of reaction prevail, 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]

Keywords: *Syngas, Simulation, Optimization*

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 compositions in carbonylation, hydroformylation, and hydrogenation in petrochemical plants as well as for iron ore reduction in the steel industry. Starting in 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 feedstocks 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 of industrial syngas

Product / Process	Volume Ratio in Syngas (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

## Syngas from Natural Gas

There are several commercial methods for

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conversion of natural gas to synthesis gas. The different technologies used in various applications are:

- Steam Methane Reforming (SMR)
- Steam Methane and Oxygen Reforming (SMR /O_2)
- 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
- Gas Heated Reforming (GHR)

International companies including Texaco, Shell, Lurgi, Topsøe, Foster Wheeler, Kellogg and Midrex have commercialized 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:

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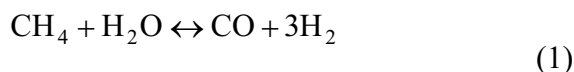
Today, the promising method for syngas production is partial oxidation of methane with pure oxygen:

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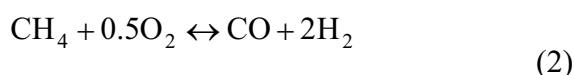
In this non-catalytic partial oxidation (NCPO), desulfurized natural gas is preheated, mixed thoroughly with oxygen and then ignited. Because the reaction is exothermic, a considerable amount of steam or electrical power may be generated while cooling the reactor. With no catalyst, the peak reaction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

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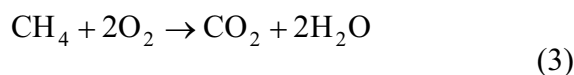
Simulation of Syngas Production

Recently, a number of studies have been reported on the simulation of noncatalytic partial oxidation of methane and natural gas with various compositions [1-5]. 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 ASPEN PLUS [2].

In the present work, an advanced software was developed, to simulate autothermal partial oxidation of natural gas combined with CO_2 and H_2O reforming of methane. To accelerate the calculation, a modified Newton-Raphson method accompanied by direct search was employed. This is a very complicated problem and has no reported analytical 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 grows 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 thorough 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 ana-lysis 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 of 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 [7-10], concluding satisfactory agreement.

Theory
The total Gibbs energy of a single-phase mixture is expressed as [11]:

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

n_i's are the numbers of moles of chemical species and N is the number of components in the product. For specified T and P the set of n_i's is determined by minimizing G^t, while meeting 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 the kth element, a_{ik} is the number of atoms of the kth element present in each molecule of chemical species i, and ε 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 slight mathematical manipulation on equations 4 and 5, the final set of equations is derived as follows:

$$\Delta G_{f_i}^{o} + RT \ln(y_i \hat{\phi}_i P) + \sum \lambda_k a_{ik} = 0 \qquad (6)$$

$$(i = 1, 2, 3, ..., N)$$

$\Delta G_{f_i}^{o}$ is the Gibbs energy for each product component at the reaction temperature. All of $\hat{\phi}_i$'s are set to unity. All of n_i's and λ_k's will be found by solving the set of equations 5 and 6 at specified T, P and A_k, simul-taneously [11].

In the present work, the feed of reaction is assumed to be a mixture of CH_4, O_2, H_2O and CO_2 with variable concentration. By applying the "direct search" and "Newton-Raphson" methods 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 flowchart depicted 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 as initial guess for all runs and it took 0.05 second to complete each run.

Results and Discussion
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
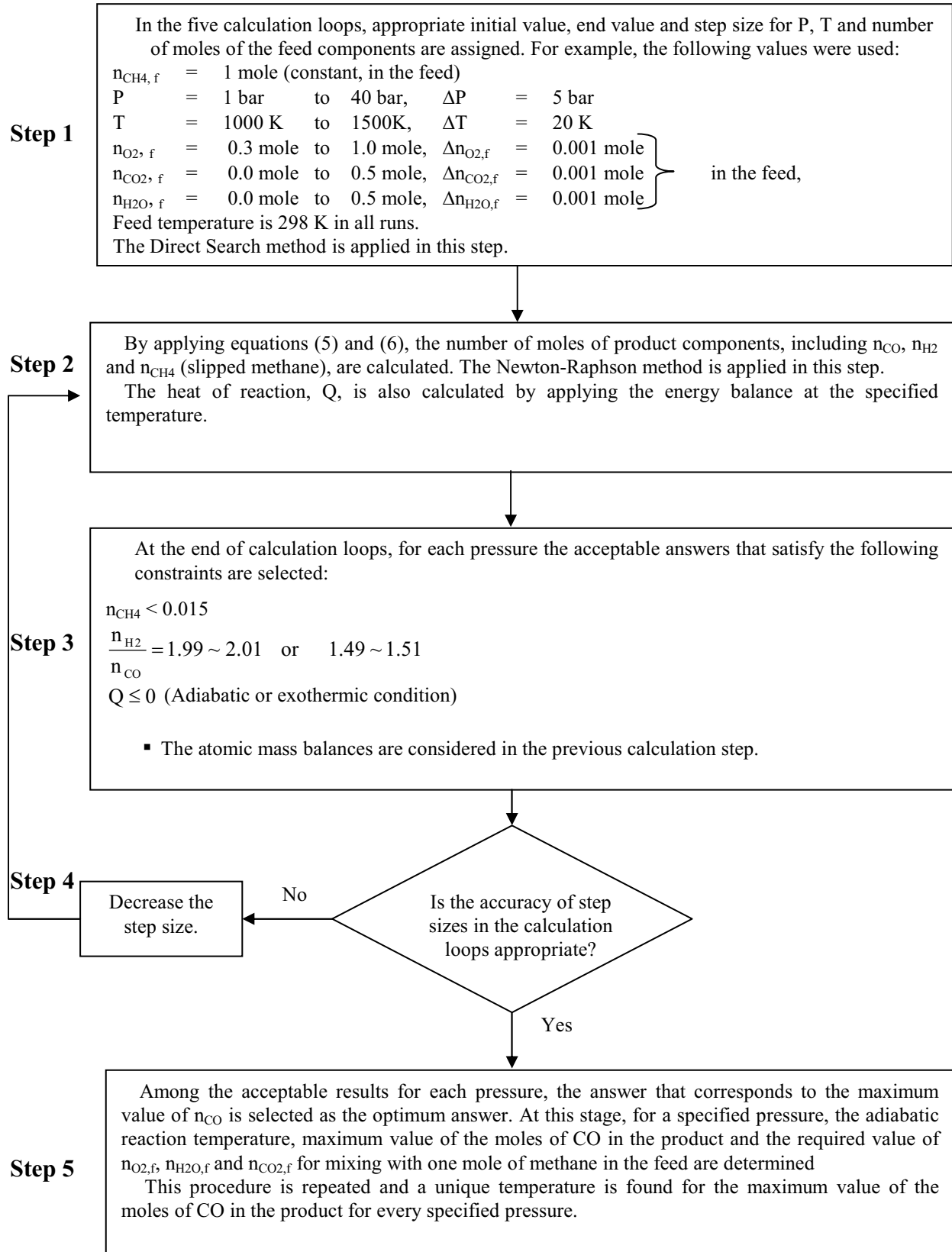
Step 1

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, the following values were used:

$n_{CH4, f}$ = 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 in all runs.
The 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. The 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)

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

Step 4 | Decrease the step size. | ← No — Is the accuracy of step sizes in the calculation loops appropriate?

Yes

Step 5

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.

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:
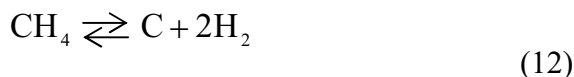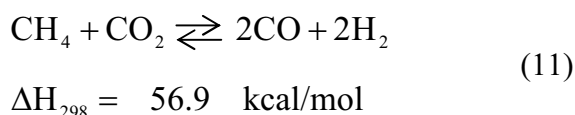
$$CH_4 + nO_2 \rightarrow CO_2 + H_2O$$
$$+ CO + H_2 + O_2 + CH_4 \tag{10}$$
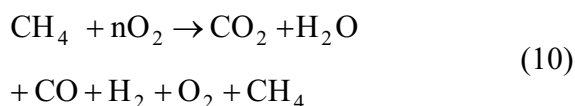
The number of moles of oxygen provided to the number of moles of CH_4 in the feed is defined as the molar equivalence ratio, n.
Another comparison is carried out with the simulation results already obtained by one of the authors using ASPEN PLUS [2]. The operational data from SGP reactor in the Shell 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 of pure oxygen and 57 kg per hour of hydrogen are fed to the reactor at 1390 °C and 46 bar producing 32787 kg per hour of synthesis gas. Equilibrium concentrations of 29 species in the syngas stream are compared in Table 2.
Slight differences between the two simulation results are due to the accuracy of the Gibbs energy values taken from different sources. Although the material balance is satisfied in both simulators, a lower value is calculated for the total Gibbs energy in the present work indicating a more accurate result.
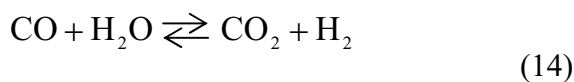
Acceptable Mole Ranges of O₂, CO₂ and H₂O in the Feed
Reaction (2) is an ideal description of the partial oxidation process. Some other relevant reactions are
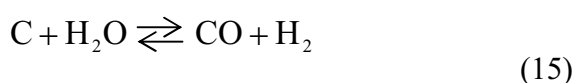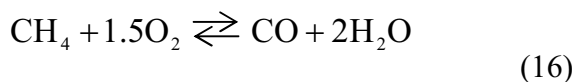
$$CH_4 + CO_2 \rightleftarrows 2CO + 2H_2$$
$$\Delta H_{298} = 56.9 \quad kcal/mol \tag{11}$$

$$CH_4 \rightleftarrows C + 2H_2$$
$$\Delta H_{298} = 17.89 \tag{12}$$

$$CO_2 + C \rightleftarrows 2CO$$
$$\Delta H_{298} = 41.2 \tag{13}$$

$$CO + H_2O \rightleftarrows CO_2 + H_2$$
$$\Delta H_{298} = -9.7 \tag{14}$$

$$C + H_2O \rightleftarrows CO + H_2$$
$$\Delta H_{298} = 31.4 \tag{15}$$

$$CH_4 + 1.5O_2 \rightleftarrows CO + 2H_2O$$
$$\Delta H_{298} = -123.6 \tag{16}$$

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, the 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 and 40 bar). In all outputs the following assumptions were made: the amount of CH_4 in the feed is constant and equal to one mole, the ratio of H_2 to CO is equal to 2, the reaction is auto thermal (exothermic or adiabatic conversion), and the maximum methane slip (mole fraction of CH_4 in the syngas) is 0.015.
In Figures 3 to 6 the pressure and temperature for the partial oxidation process combined with the reforming reactions are chosen and set and the corresponding acceptable number of moles of O_2, CO_2 and H_2O that can be

Table 2. Comparison between the outputs of the developed software and Ref. [2]

Species	Elements				Gibbs Energy from JANAF	Moles in the Product	
	C	O	H	N		This Work	ASPEN PLUS
O_2	0	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
N_2	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

mixed with one mole of CH_4 in the feed are read. For example, the temperature is assumed at 1100 K and the 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 a suitable syngas with the specification of $H_2/CO=2$, a methane slip less than 1.5% and the reaction to take place at the autothermal 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 the product is 0.936 moles (Figure 6).

Optimization of CO Yield

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

For example, the maximum moles of CO in the syngas at the pressure of 5 bar, is produced only in 1270 K (Figure 6), which 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 of methane. General constraints are an H_2/CO of 2, $y_{CH4}<0.015$ in the product, and feed temperature at 298 K.

Simulation Results for Industrial Applications

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

Figure 11 shows the optimum operation for syngas reaction at conditions $H_2/CO=2$ and

$H_2/CO=1.5$. Figure 10 shows the maximum mole values of CO in the product versus the reactor pressure. This figure shows that as pressure increases, the yield of CO initially decreases rapidly and as pressure goes beyond 10 bars, with a lower slope.

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

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, autothermal conversion and methane slip in the product stream. Optimization, design specification and sensitivity analysis tools are incorporated into the simulator. The results may be reported as different tables or graphical presentations. The simulator is especially helpful in studying monetizing CO_2 surplus in the petrochemical and steel industries [12].
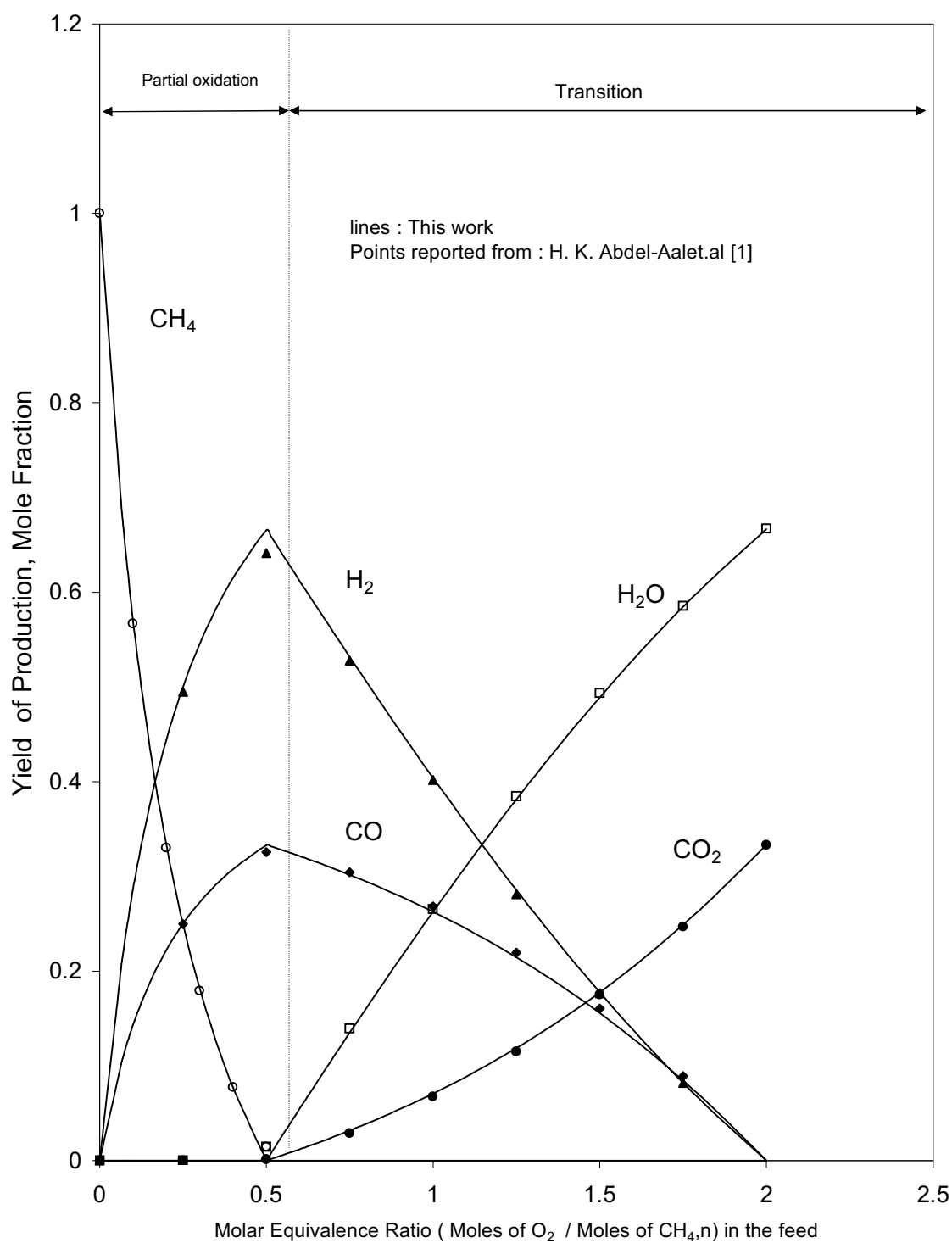
Figure 2. Concentration of some important species in partial oxidation of methane at 1477 K and 1 bar
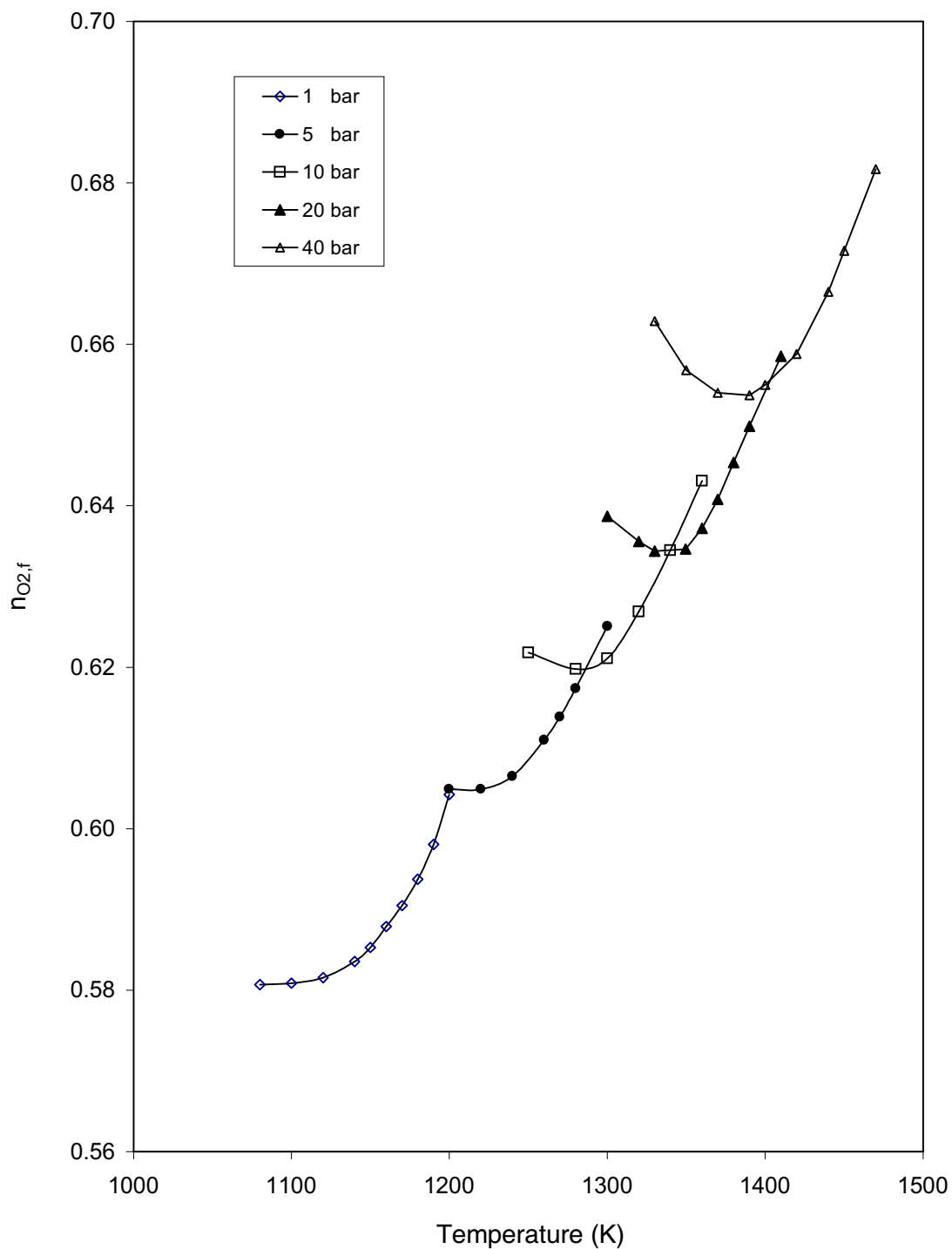
Figure 3. Acceptable moles of O_2 addition to the feed per mole of methane as a function of reaction temperature for $H_2/CO=2$
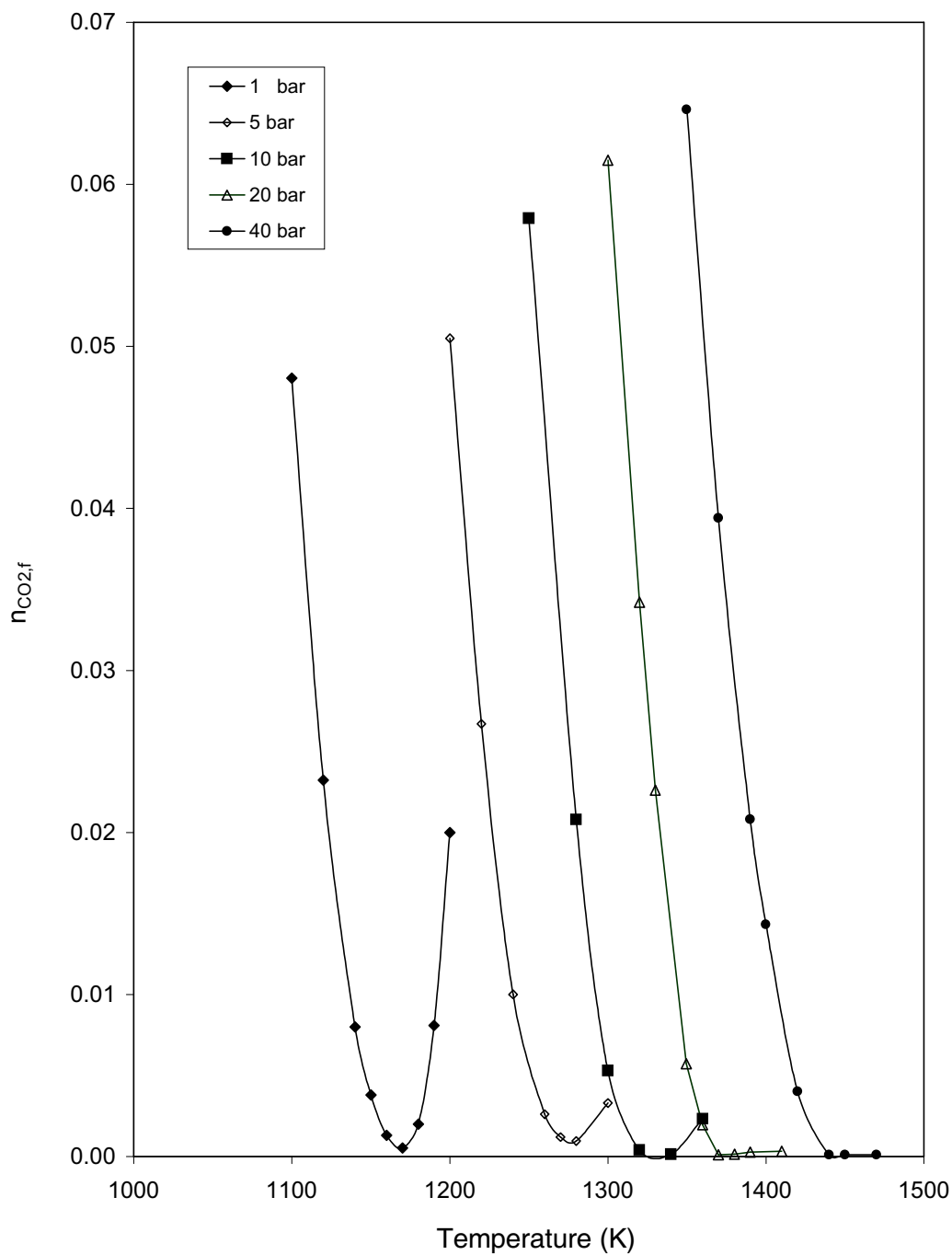
Figure 4. Acceptable moles of CO_2 addition to the feed per one mole of methane as a function of reaction temperature for $H_2/CO=2$
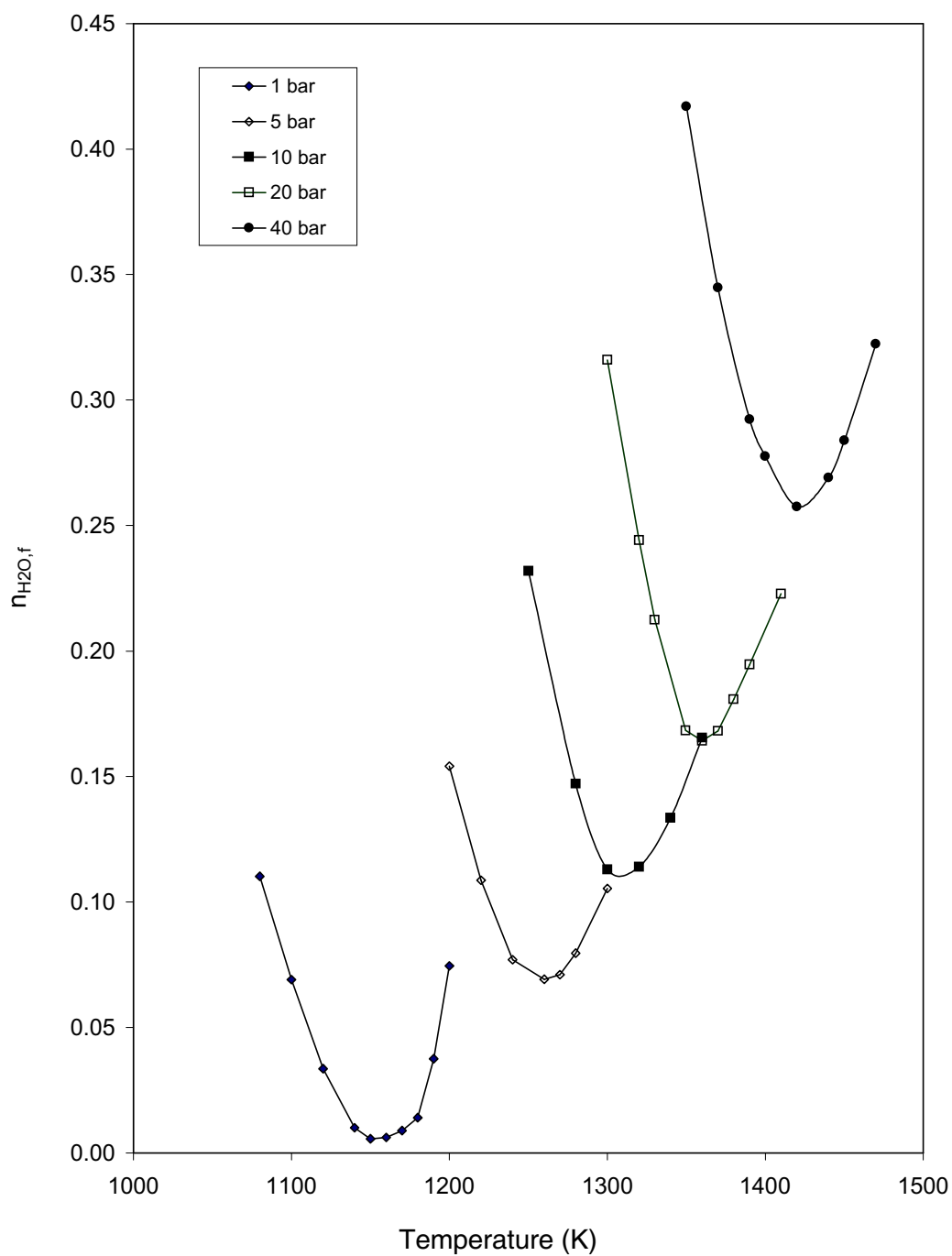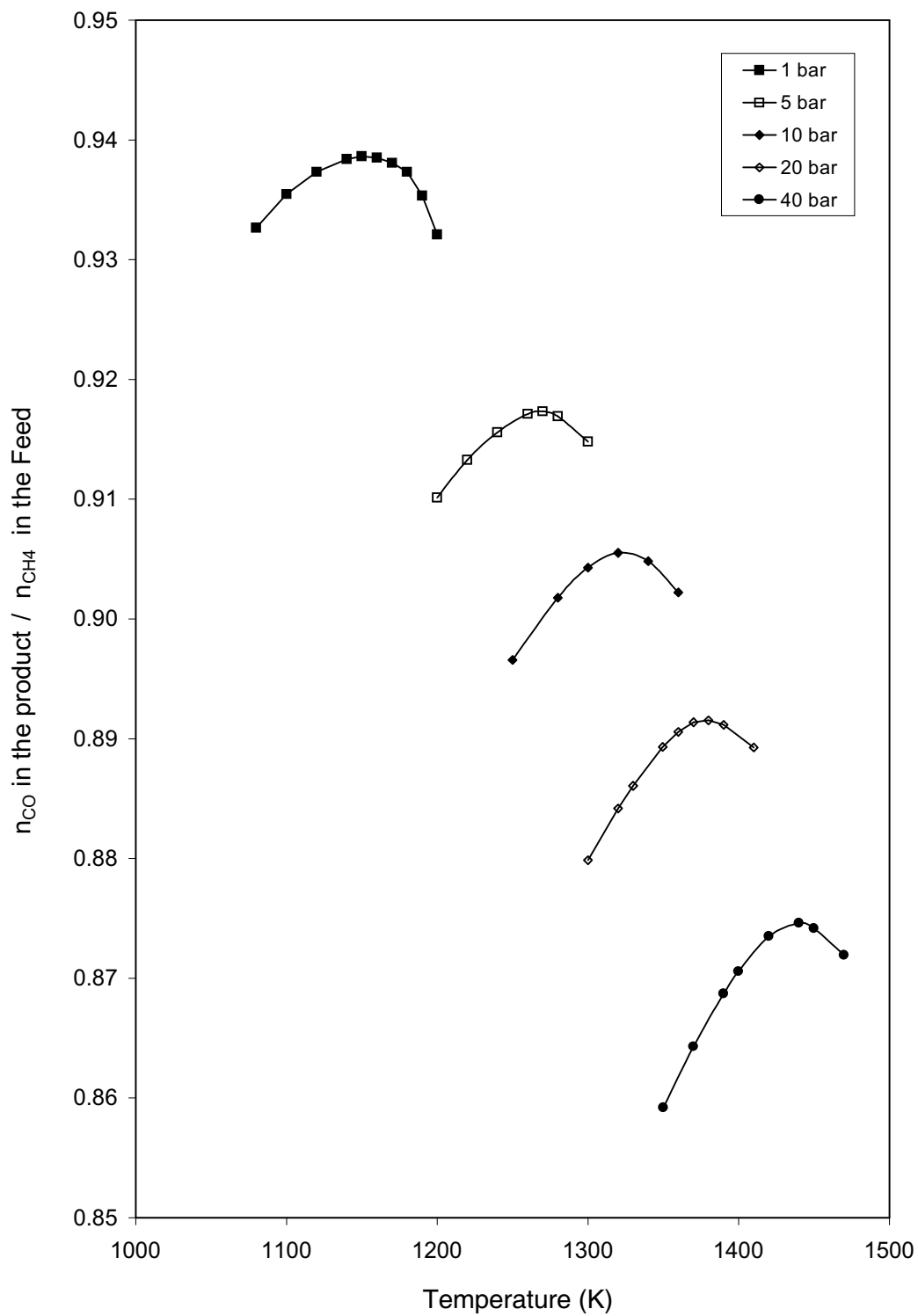
Figure 5. Acceptable moles of H_2O addition to the feed per one mole of methane as a function of reaction temperature for $H_2/CO=2$

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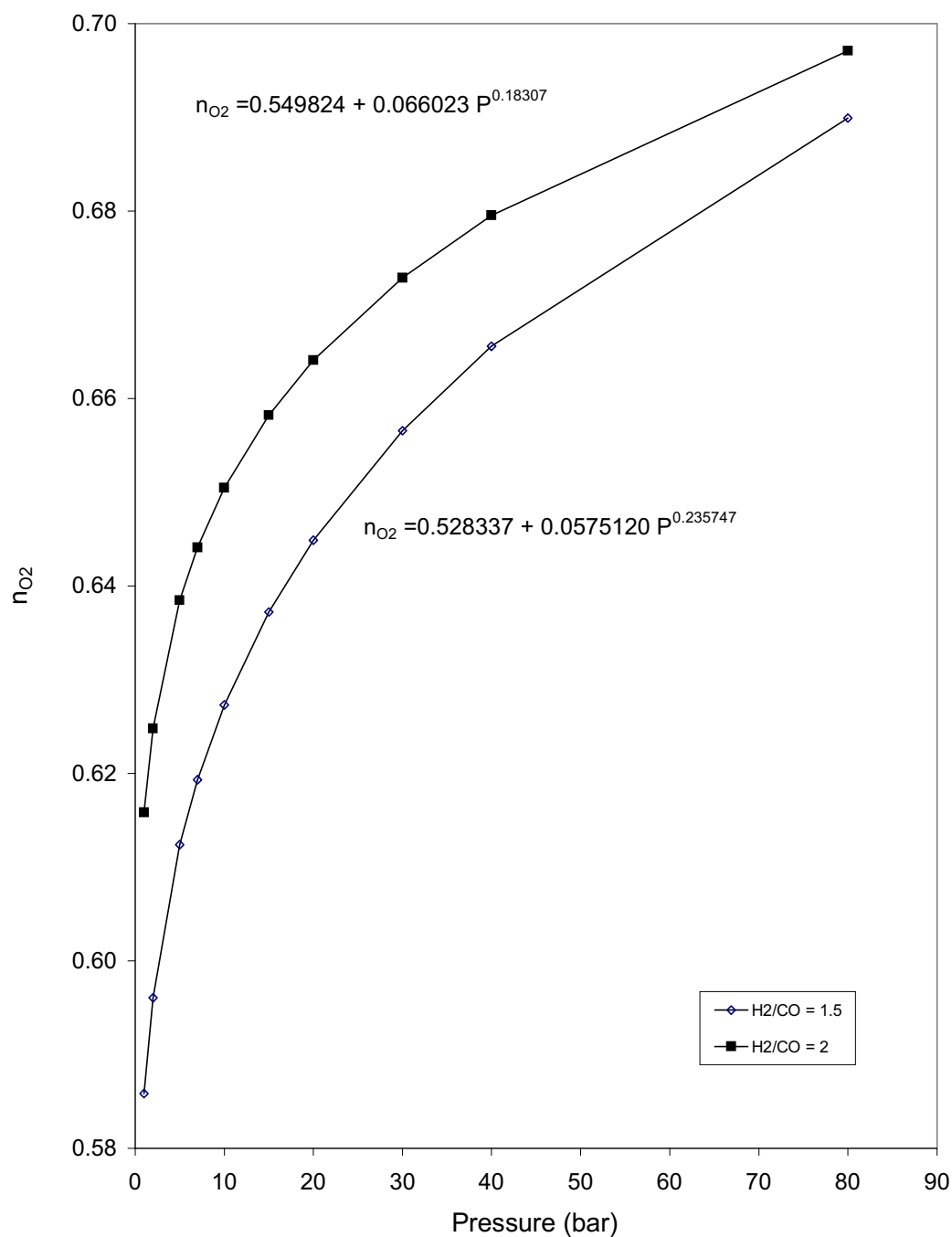
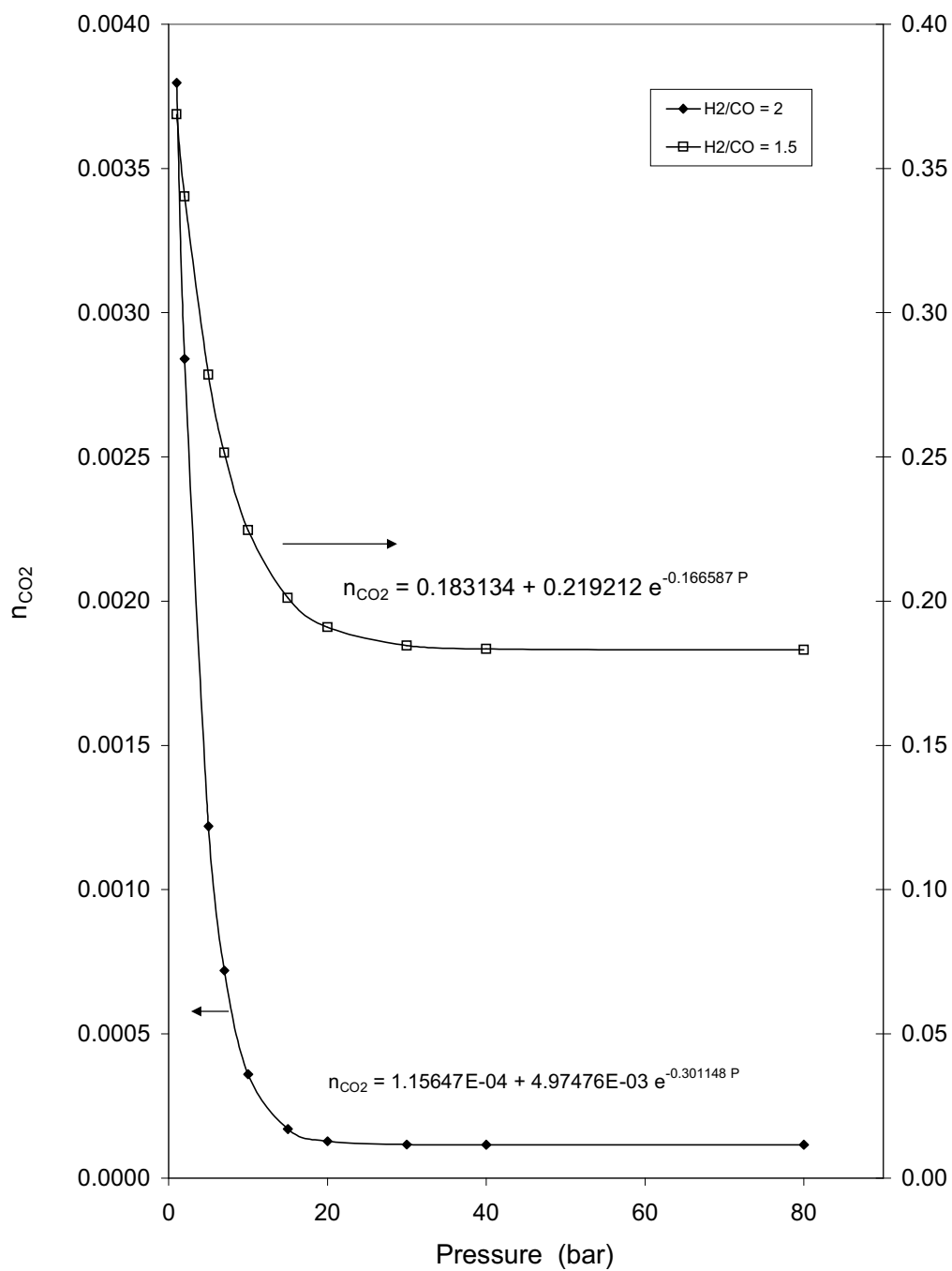**Figure 7.** Optimum mole addition of O_2 to the feed per mole of CH_4

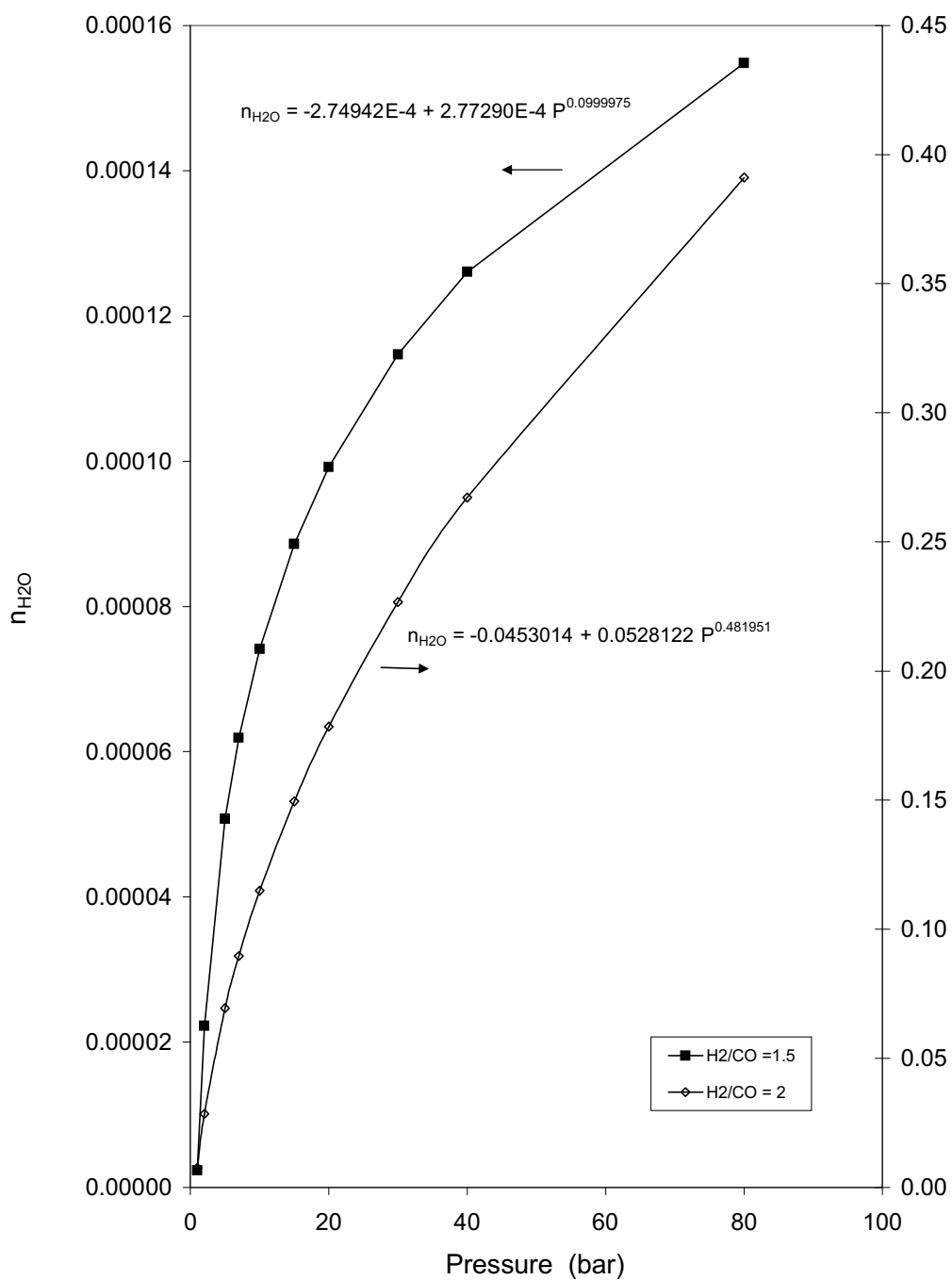**Figure 8.** Optimum mole addition of CO_2 to the feed per mole of CH_4

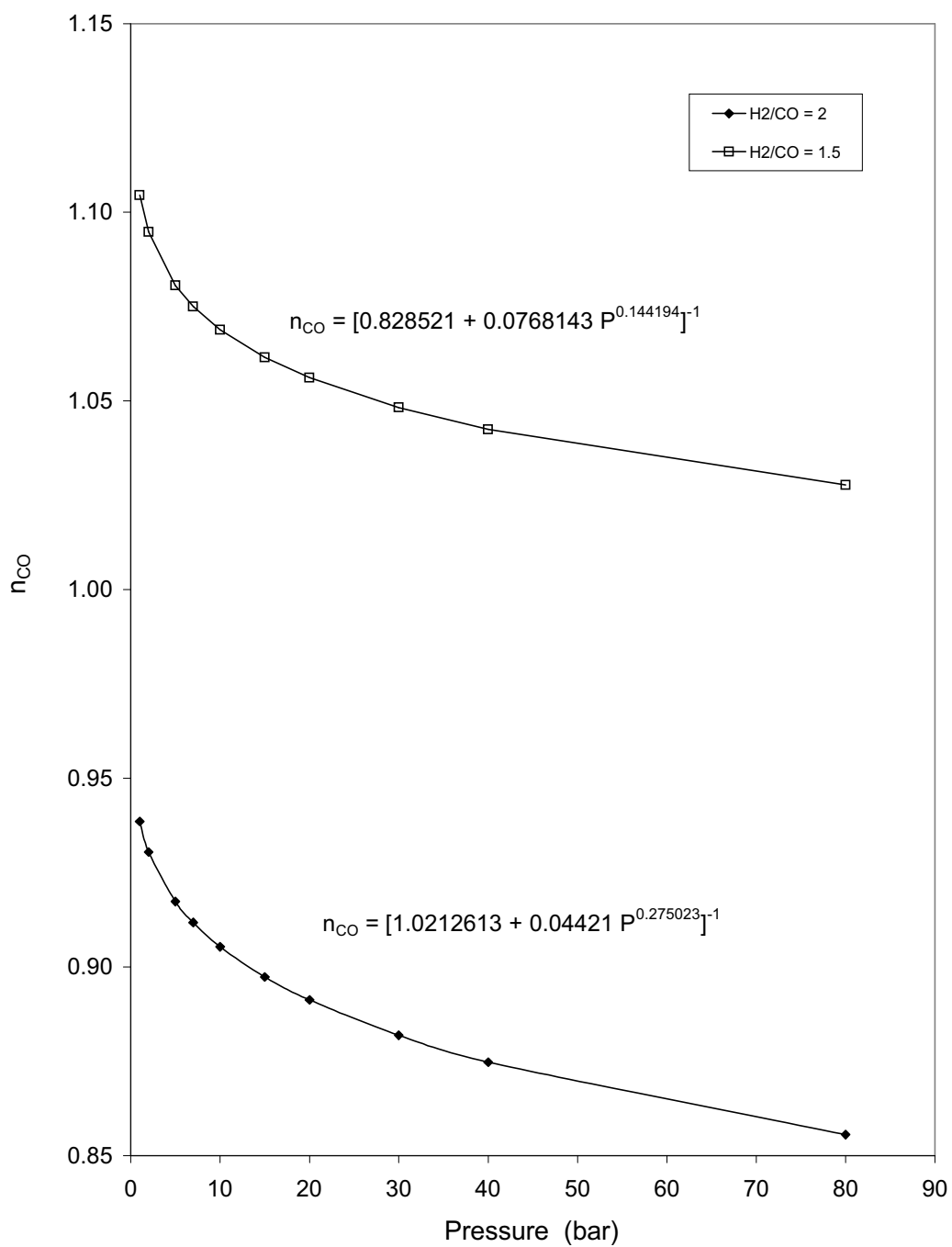**Figure 9.** Optimum mole addition of H_2O to the feed per mole of CH_4

Figure 10. Optimum yield of CO

Temperature (K)

1600

1500

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

1400

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

1300

1200

1100

H2/CO=2
H2/CO = 1.5

1000

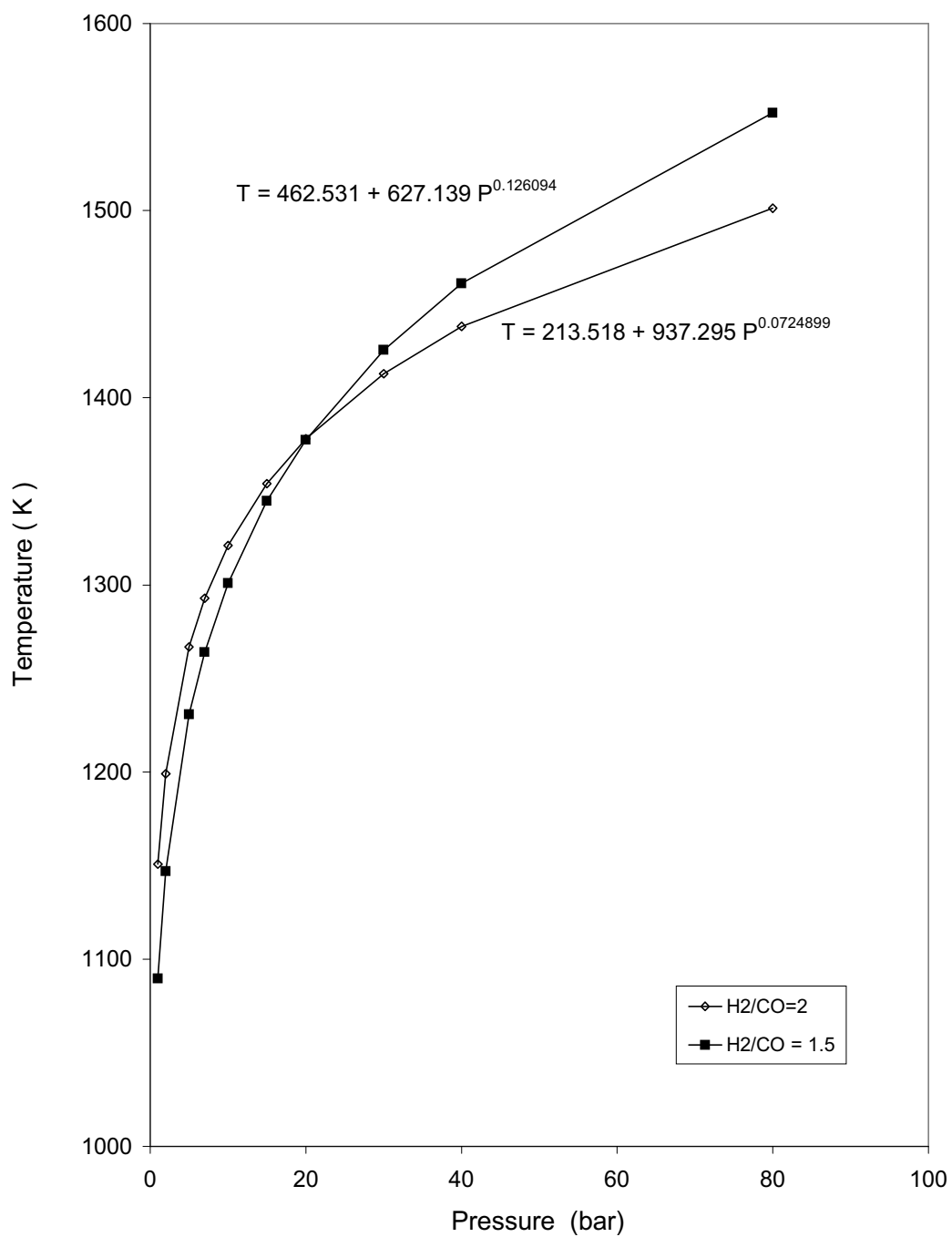0   20   40   60   80   100

Pressure (bar)

Figure 11. Optimum operating conditions for maximization of CO

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