

# **Application of Methods of Optimization in the Calculation of Combined Chemical and Phase Equilibria for Processes with Synthesis Gas**

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The development of the internal combustion engines at the beginning of the XX century brought a rupture with the energy source used by the steam machines, the mineral coal. The use of modern engines generated a liquid fuel necessity for their functioning. New economical and institutional factors have brought back the interest in processes of synthetic fuel, a new technological trajectory. Availability of natural gas reserves, new requirements in environmental legislation, and the demand for flexibility in the transport of the natural gas have been the main factors for such renewed interest. The synthesis gas is a mixture of carbon monoxide and hydrogen produced from the reaction of water vapor or oxygen with hydrocarbons. The objective of the present work is to identify the more favorable operating conditions for such reactions, using techniques of global optimization in the calculation of combined chemical and phase equilibrium, for processes with synthesis gas. Two sets of processes were considered: the production of synthesis gas from methane, and the use of synthesis gas to produce synthetic fuels.

## **Introduction**

With the aid of appropriate catalysts, the synthesis gas can be converted into desired chemical products. For example, it can be converted into hydrocarbons of larger carbonic chain (in the range of gasoline or diesel) by the Fischer-Tropsch process. The conversion and yield depends on the catalyst used and the residence time in the reactor, but it is important to know if the operating conditions are thermodynamically favorable. In this work, a thermodynamic analysis is done to study the equilibrium composition, both to produce the gas synthesis, from methane, and its use in the Fischer-Tropsch process. The rate of reaction is not taken into consideration, but the equilibrium analysis includes restrictions in the mass balance to account for the catalysts influence, which speeds up some reactions and not others.

## **1. Thermodynamic Equilibrium**

The necessary conditions for the determination of the chemical equilibrium and phase equilibrium can be formulated through the following restrictions (Sandler, 1999):

$$T^\alpha = T^\beta = \dots = T^\pi \quad (1)$$

$$P^\alpha = P^\beta = \dots = P^\pi \quad (2)$$

$$\mu_i^\alpha = \mu_i^\beta = \dots = \mu_i^\pi \quad i = 1, \dots, N \quad (3)$$

$$\sum_{i=1}^N \nu_{ij} \cdot \mu_i^k = 0 \quad j = 1, \dots, M \quad k = \alpha, \dots, \pi \quad (4)$$

where  $\pi, \beta, \alpha$  are the phases of system and  $i$  represents the different chemical species present in the system. Usually one works with the condition of uniform and constant pressure and temperature, in such a way that the conditions (1) and (2) are automatically satisfied. Moreover, it is necessary that the mass balance of each species be respected, in accordance to the stoichiometry of the reactions involved. These conditions, although necessary, are not sufficient to guarantee stable equilibrium. A sufficient condition, at constant temperature ( $T$ ) and pressure ( $P$ ), is given by the Gibbs free energy that must be a minimum in relation to all possible modifications of the system, so that in the neighborhood of the equilibrium point the following restriction holds:

$$(dG)_{T,P} \leq 0 \quad (5)$$

The equilibrium calculation consists of the resolution of the necessary conditions, given by system of equations (3) and (4), which in general are nonlinear, followed by a stability analysis of the phases, which must obey the condition of minimum  $G$ , in order to verify if the number of phases initially considered was correct, or if there is a division of phases (unstable phase equilibrium).

The Gibbs free energy of the system obeys the following equation (Sandler, 1999):

$$dG = -S \cdot dT + V \cdot dP + \sum_{i=1}^N \sum_{k=1}^F \mu_i^k \cdot dn_i^k \quad (6)$$

where  $i$  represents the different chemical species and  $k$  represents the different phases in the system. Moreover, being an extensive variable, the Gibbs free energy also can be written:

$$G = \sum_{i=1}^N \sum_{k=1}^F n_i^k \cdot \mu_i^k \quad (7)$$

and thus must obey the Gibbs-Duhem equation (Sandler, 1999):

$$-S \cdot dT + V \cdot dP - \sum_{i=1}^N \sum_{k=1}^F n_i^k \cdot d\mu_i^k = 0 \quad (8)$$

The chemical potential  $\mu_i^k$  can be calculated using expressions as:

$$\mu_i^k = \mu_i^\circ + R \cdot T \cdot \ln \frac{f_i^k}{f_i^\circ} \quad (9)$$

where  $\mu_i^\circ$  is the chemical potential at some reference state, and the fugacity  $f_i^k$  must be calculated for each composition in each phase. Therefore, equation (7) can also be written as:

$$G = \sum_{i=1}^N \sum_{k=1}^F n_i^k \cdot \left[ \mu_i^\circ + R \cdot T \cdot \ln \frac{f_i^k}{f_i^\circ} \right] \quad (10)$$

However, simple expressions for the fugacity of each composition in the mixture are only available for some situations, such as ideal gases or ideal solutions, in such a way that for cases far from ideality the use of more complex expressions becomes necessary.

## 2. Formulation as a problem of minimization

The calculation of phase equilibrium, with or without chemical reactions, can also be formulated as a problem of global minimization of the Gibbs free energy of the system, at constant  $T$  and  $P$ , satisfying restrictions of non-negativity of the number of moles of each component in each phase, and restrictions of mass balances, given by the following nonlinear program model:

$$\min G = \sum_{i=1}^{NC} \sum_{k=1}^{NF} n_i^k \cdot \mu_i^k \quad (11)$$

$$\mu_i^k = \mu_i^\circ + R \cdot T \cdot \ln \frac{f_i^k}{f_i^\circ} \quad (12)$$

satisfying the restrictions:

(a) non-negativity of the number of moles:

$$n_i^k \geq 0, \quad i = 1, \dots, NC; \quad k = 1, \dots, NF \quad (13)$$

(b) conservation of moles of components or atoms:

- For phase equilibrium only:

$$\sum_{k=1}^{NF} n_i^k = n_i^0 \quad i = 1, \dots, NC \quad (14)$$

- For chemical and of phase equilibrium, using atom balance (non-stoichiometric):

$$\sum_{i=1}^{NC} a_{mi} \cdot \left( \sum_{k=1}^{NF} n_i^k \right) = \sum_{i=1}^{NC} a_{mi} \cdot n_i^0 \quad m = 1, \dots, NE \quad (15)$$

where  $n_i^0$  is the initial number of moles of component  $i$  in system, and  $a_{mi}$  is the number of atoms of element  $m$  in component  $i$ .

The direct global minimization of Equation (11), satisfying the restrictions of mass balances given by (14) or (15), and non-negativity of number of moles given by (13), will satisfy both the necessary and sufficient conditions for equilibrium. This global minimization can be done using techniques of nonlinear programming and analysis of convexity of the models to guarantee finding the global minimum.

In the nonlinear program model, the parameters are the temperature ( $T$ ), pressure ( $P$ ), the initial composition ( $n_i^0$ ), and all quantities that depend on them (such as physical properties), while the variables are the number of moles ( $n_i^k$ ), and all quantities that depend on them (molar fractions, fugacities).

In the formulation of the model, it is important that all potential phases and components that may form in the system must be included. The resolution of the model will automatically indicate whether a phase or component exists or not at equilibrium ( $n_i^k > 0$  if it exists, and  $n_i^k = 0$  otherwise).

### 3. Production of CO and H<sub>2</sub> from CH<sub>4</sub> and H<sub>2</sub>O

Methane can be found either as natural gas or produced from biological sources, so that it is a useful raw material in the production of synthesis gas. In the water reform of methane, temperatures are usually high, so that thermodynamics has a strong influence in the conversion. Considering an adequate residence time, the composition can be calculated by thermodynamic equilibrium. For steam reform of biomass, the nonlinear program formulation has shown good results in calculating the equilibrium composition (Rossi et al, 2009). In this work, it was considered a gas phase and a solid phase for the possibility of coke formation, even in the cases where only a gas phase exists. Coke formation is undesirable, so it is important to know the conditions that favor it. The chemical species considered in the system were: C, CO, CO<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>, and H<sub>2</sub>O.

The following definitions were used to calculate conversion and yield:

$$\text{Fractional Yield } H_2 = \frac{n_{H_2}^f - n_{H_2}^0}{(2 \cdot (n_{CH_4}^0 - n_{CH_4}^f)) + (n_{H_2O}^0 - n_{H_2O}^f)} \cdot 100\% \quad (16)$$

$$\text{Conversion } H_2O = \frac{n_{H_2O}^0 - n_{H_2O}^f}{n_{H_2O}^0} \cdot 100\% \quad (17)$$

The numerical results are presented in Table 01, for two different pressures and several temperatures. The initial molar ratio in all cases was 11 CH<sub>4</sub>: 2 H<sub>2</sub>O.

TABLE 01. Hydrogen and Carbon Monoxide Productions (%).

T(K)	Yield (1atm)		Conversion(1atm)		Yield (5atm)		Conversion(5atm)	
	H <sub>2</sub>	CO	H <sub>2</sub> O	CH <sub>4</sub>	H <sub>2</sub>	CO	H <sub>2</sub> O	CH <sub>4</sub>
400	100.000	0.000	0.121	0.666	99.609	0.000	0.012	0.064
500	100.000	0.025	0.739	4.066	99.988	0.015	0.390	2.145
600	100.000	0.936	2.165	11.964	99.996	0.488	1.153	6.355
700	99.999	9.620	3.627	27.296	100.000	6.792	2.134	12.603
800	99.999	17.903	2.620	66.056	99.996	9.912	1.262	40.145
900	99.998	39.681	3.759	85.844	99.957	15.021	1,193	65.999
1000	99.989	70.777	6.254	93.568	99.746	22.319	1.778	82.566
1100	99.949	98.981	8.791	96.782	99.232	29.541	2.515	91.212
1200	99.831	99.395	8.983	98.722	98.435	33.888	3.050	95.426
1300	99.449	98.320	9.035	99.358	97.294	34.223	3.300	97.503
1400	98.282	94.838	9.056	99.617	95.245	31.096	3.462	98.565

It can be observed from Table 01 that water conversion is very low for temperatures below 1100 K. Therefore, higher temperatures favor higher water conversion. The yields of hydrogen and carbon monoxide are higher for 1 atm than 5 atm, in all cases.

It can also be observed that the selectivity to CO is directly affected by both the conversion of methane and water. Due to the low water conversion, an excess of water

favors carbon monoxide production and avoids coke formation. No formation of coke was observed in the cases tested for the molar ratio of 1:1.

#### 4. Products from Synthesis Gas

The Fischer-Tropsch process uses synthesis gas to produce heavier hydrocarbons. The operating conditions are very different from the ones used in the production of synthesis gas. The pressures are higher and the temperatures are lower, so that the catalyst influence is much stronger. If the equilibrium calculation were done using only non-stoichiometric balances given by Equation (15), the result would not be the observed products found in practice, but only C, CO<sub>2</sub> and CH<sub>4</sub>. Therefore, stoichiometric balances were used, considering the formation of linear hydrocarbons and not considering the formation of coke and methane. This takes into account the catalysts influence, which favors molecules with larger carbon chain over methane and coke. The nonlinear program model formulation considered a gas phase and a liquid phase, with chemical species CO, CO<sub>2</sub>, H<sub>2</sub>O, H<sub>2</sub>, and all linear hydrocarbons from C<sub>2</sub>H<sub>6</sub> to C<sub>20</sub>H<sub>42</sub>.

We tested six pressures, with eleven temperatures, and five H<sub>2</sub>: CO feed molar ratios: 1:1, 2:1, 3:1, 1:2, and 1:3. The best results were obtained for 2 H<sub>2</sub>: 1 CO as feed molar ratio. In Table 02 it is presented the results of fractional yield of n-hexane, chosen as an example. Table 03 presents the results of hydrogen and carbon monoxide conversion.

TABLE 02. Fractional Yield of n-hexane (%).

<b>T (K)</b>	<b>1 (atm)</b>	<b>5 (atm)</b>	<b>10 (atm)</b>	<b>50 (atm)</b>	<b>100 (atm)</b>	<b>200 (atm)</b>
413.15	0.000	0.004	0.088	12.043	13.486	13.486
423.15	0.000	0.003	0.029	9.984	12.786	12.786
433.15	0.000	0.002	0.006	7.308	11.986	11.986
443.15	0.000	0.001	0.005	4.548	11.135	11.135
453.15	0.000	0.001	0.004	2.479	10.050	10.265
463.15	0.000	0.001	0.003	1.245	8.418	9.406
473.15	0.000	0.001	0.002	0.586	6.584	8.585
483.15	0.000	0.001	0.002	0.258	4.677	7.805
493.15	0.000	0.000	0.002	0.104	2.987	7.086
503.15	0.000	0.000	0.002	0.029	1.737	6.423
513.15	0.000	0.000	0.001	0.015	0.926	5.819

It can be observed from Table 03 that the conversions are high for all temperatures and pressures tested. However, heavier hydrocarbons were only observed when a liquid phase was formed in the system. From Table 02, it can be seen that the yield of n-hexane is small for low pressures, but high for higher pressures, due to the liquid phase.

#### 5. Conclusion

The synthesis gas can be produced by steam reform of methane. Depending on the operating conditions, it could be maximized just the production of hydrogen, or both hydrogen and carbon monoxide. Also, coke formation is not desirable. The equilibrium composition was calculated using a nonlinear program model, minimizing the Gibbs free energy subject to constraints in the number of moles. By testing several operating conditions, it was found that an excess of water is necessary to obtain high conversions and yields, without forming coke. The results are in agreement with results found in

literature. H<sub>2</sub> yield is high for all feed molar ratios, while CO yield was higher for a feed molar ratio of 1 CH<sub>4</sub>: 11 H<sub>2</sub>O.

TABLE 03. Conversion of Hydrogen and Carbon Monoxide (%).

T (K)	1 (atm)		5 (atm)		10 (atm)		50 (atm)		100 (atm)		200 (atm)	
	H <sub>2</sub>	CO	H <sub>2</sub>	CO	H <sub>2</sub>	CO	H <sub>2</sub>	CO	H <sub>2</sub>	CO	H <sub>2</sub>	CO
<b>413.15</b>	99.9	80.2	99.9	80.4	100	80.9	100	88.2	100	89.1	100	89.1
<b>423.15</b>	99.9	80.2	99.9	80.4	99.9	80.6	100	87.1	100	88.6	100	88.6
<b>433.15</b>	99.9	80.2	99.9	80.3	99.9	80.5	100	85.8	100	88.2	100	88.2
<b>443.15</b>	99.9	80.1	99.9	80.3	99.9	80.4	100	84.4	100	87.8	100	87.8
<b>453.15</b>	99.9	80.1	99.9	80.3	99.9	80.4	100	83.2	100	87.3	100	87.4
<b>463.15</b>	99.9	80.1	99.9	80.3	99.9	80.4	100	82.4	100	86.5	100	87.0
<b>473.15</b>	99.9	80.1	99.9	80.2	99.9	80.4	100	81.8	100	85.6	100	86.6
<b>483.15</b>	99.8	80.0	99.9	80.2	99.9	80.3	100	81.3	100	84.7	100	86.3
<b>493.15</b>	99.8	80.0	99.9	80.2	99.9	80.3	100	81.0	100	83.7	100	86.0
<b>503.15</b>	99.8	79.9	99.9	80.2	99.9	80.3	99.9	80.7	100	82.9	100	85.7
<b>513.15</b>	99.7	79.9	99.9	80.2	99.9	80.3	99.9	80.6	100	82.2	100	85.5

From the synthesis gas, a variety of products can be obtained, depending on the catalyst used. In this work, a Fischer-Tropsch catalyst was considered, which promotes the formation of linear hydrocarbons. In order to get results consistent with the ones found in practice, a stoichiometric moles balance was used to calculate the equilibrium concentration. Using an initial molar ratio of 2 H<sub>2</sub>: 1 CO, it was found that higher pressures favor higher yields of heavier hydrocarbons, when a liquid phase is formed, with temperatures in the range 413.15 K to 503.15 K.

It must be pointed out that all these results were based on thermodynamic analysis only, without considering rates of reaction. Nevertheless, it is important to know if the operating conditions are adequate in order to obtain high conversions and high yields.

## 6. References

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