

Comparative study of two theoretical models of methane and ethane steam reforming process

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Abstract. From the chemical point of view the reforming process of heavy hydrocarbons such as Associated Petroleum Gas (APG) is very complex. One of the main issue is a set of undesired chemical reactions that causes deposition of solid carbon and consequently block catalytic property of a reactor. The experimental investigation is crucial to design APG reforming reactors. However, the experiment needs to be preceded by careful thermodynamical analysis to design safe operation conditions. In case of small number of reactants and reactions such as in case of steam reforming of pure methane, the problem can be solved by treating each equilibrium reaction constant as an element of the system of non-linear equations. The system of equations can be solved by Newton-Raphson method. However in case of large number of reactants and reaction, such as in case of APG reforming this method is inefficient. A large number of strongly non-linear equations leads often to converge problem. In this paper the authors suggest to use different approach called Parametric Equation Method. In this method a system of non-linear equations is replaced by a set of single non-linear equations solved separately. The methods were used to simulate steam reforming of methane-ethane rich fuel. The results of computations from both methods were juxtaposed and comparative study were conducted. Finally safe operation conditions for steam reforming of methane-ethane fuel were calculated and presented.

1. Introduction

Associated Petroleum Gas (APG) is a form of natural gas that contains hydrocarbons heavier than methane. Typically its contains 50-70% of methane (CH_4), 5-10% of ethane (C_2H_6), 5-15% propane (C_3H_8), 1-10% butane (C_4H_{10}), 1-10% of carbon dioxide (CO_2) and 1-10% of nitrogen (N_2). According to the report elaborated under the auspices of the European Bank for Reconstruction and Development, 20 billion cubic meters per year of associated gas is simply flared in main APG producing countries such as Russia, Kazakhstan, Turkmenistan and Azerbaijan [1]. For the targeted countries flaring remains at 24-30% of total APG production. The number is even grated in the scale of the entire World where 150 billion cubic metres of associated gas is flared. This gives an economical lost of approximately 30.6 billion dollars. The cost do not include environmental impacts which might be significant since flaring is responsible for 400 million tons in CO_2 emissions. This makes APG flaring significant producer of greenhouse gases and make it responsible for about 2% of total global CO_2 emission. Breakthrough in the high temperature fuel cell technology can put this wasted gas to more productive use. Fuel cells might help to use associated gas at the spot to provide electricity for the refinery and to obey the necessity to send gas via pipelines. High temperature fuel cells such as Solid Oxide Fuel Cells



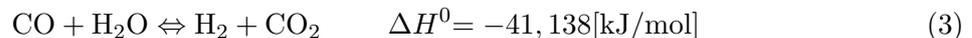
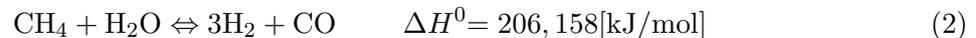
(SOFC) can oxidise as a fuel not only hydrogen but also carbon monoxide [2,3]. The mixture of hydrogen and carbon monoxide can be obtained from wide range of hydrocarbons based fuels via methane steam reforming. Reforming process of APG can be schematically represented as follows:



It was previously reported that ethane can be successfully reformer with steam [4,5]. It was also shown that heavy hydrocarbons such as ethane, propane and butane can be adopted as a fuel for SOFC application [6,7]. One of the main problems during reforming process of hydrocarbons is carbon formation. A number of studies on carbon deposition during reforming processes have been carried out by different research groups. Carbon deposition during steam reforming [8], methanol reforming [9], dry reforming [10,11] or reforming of biogas [12] were studied in the past. However, there has been little research on carbon formation during the reforming of associated gas. The reason might be connected in large number of reactions involved in the process that results in strongly non-linear problem. The authors aim to fill a gap presented in literature review and provide a thermodynamic analysis of associated gas reforming process. An alternative model approach called Parametric Equation Formalism is introduced. To allow the comparison of the proposed approach with conventional method the model APG used in this study is assumed to be a mixture of methane and ethane.

2. Thermodynamic model

A typical methane reforming process carried out with steam can be described by the following reactions [13-17]:



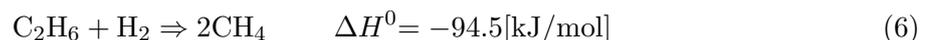
When the fuel mixture contains ethane, it reacts with steam according to the following reaction:



The reaction (4) is strongly endothermic and never occurs in the direction of reactants [14]. In considered range of temperatures reaction (4) is accompanied by the following reaction:



It can be assumed that in the presents of hydrogen, reactions (4) and (5) can be substituted by a summary reaction [6,7]:



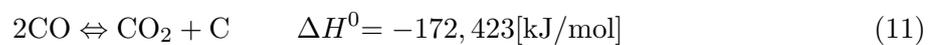
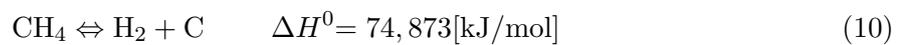
Chemical equilibrium of reactions (2), (3) and (6) is represented by the equilibrium constants of each reaction, which is a function of temperature:

$$K_{st} = \frac{p_{CO}p_{H_2}^3}{p_{CH_4}p_{H_2O}} = \frac{x_{CO}x_{H_2}^3}{x_{CH_4}x_{H_2O}}P^2 = \exp\left(-\frac{\Delta G_{st}^0}{RT}\right) \quad (7)$$

$$K_{sh} = \frac{p_{CO_2}p_{H_2}}{p_{CO}p_{H_2O}} = \frac{x_{CO_2}x_{H_2}}{x_{CO}x_{H_2O}} = \exp\left(-\frac{\Delta G_{sh}^0}{RT}\right) \quad (8)$$

$$K_{\text{et}} = \frac{p_{\text{CH}_4}^2}{p_{\text{C}_2\text{H}_6} p_{\text{H}_2}} = \frac{x_{\text{CH}_4}^2}{x_{\text{C}_2\text{H}_6} x_{\text{H}_2}} = \exp\left(-\frac{\Delta G_{\text{et}}^0}{RT}\right) \quad (9)$$

where ΔG_{st}^0 , ΔG_{sh}^0 , and ΔG_{et}^0 are the changes in the standard Gibbs free energy of, respectively, the methane/steam reforming (reaction (2)), shift reaction (3) and methanation (6) [J mol^{-1}], R is the universal gas constant $8.314482 [\text{J mol}^{-1} \text{K}^{-1}]$, and T [K] is the reaction temperature. However, thermodynamically favorable carbon deposition should be considered in an analysis aside from methane/steam reforming, shift reaction and methanation (the reactions (2), (3), and (6)). The equilibrium gas mixture consists of CH_4 , H_2O , CO , CO_2 , and H_2 , which at a particular temperature and total pressure reach thermodynamic equilibrium. Carbon formation can therefore occur as the effect of the following reactions [18]:



The chemical equilibrium of reactions (10) and (11) is represented by the equilibrium constants of each reaction and is equal to the ratio between the partial pressures of the reactants and the products:

$$K_{\text{m}} = \frac{p_{\text{H}_2}^2 a_{\text{m}}}{p_{\text{CH}_4}} = \exp\left(-\frac{\Delta G_{\text{m}}^0}{RT}\right) \quad (12)$$

$$K_{\text{c}} = \frac{p_{\text{CO}_2} a_{\text{c}}}{p_{\text{CO}}^2} = \exp\left(-\frac{\Delta G_{\text{c}}^0}{RT}\right) \quad (13)$$

The co-existence of (CO/CO_2) and (H_2/CH_4) in the gas product of reactions (2), (3) and (6) suggests the course of reactions (10) and (11) with carbon deposition. With assumption that activities of pure substances (carbon (a_{m}) and (a_{c})) is equal one, the parameter α can be defined to determine the possibility of carbon formation [8,9,11,12]:

$$\alpha_{\text{m}} = \frac{p_{\text{CH}_4} K_{\text{m}}}{p_{\text{H}_2}^2} \quad (14)$$

$$\alpha_{\text{c}} = \frac{p_{\text{CO}}^2 K_{\text{c}}}{p_{\text{CO}_2}} \quad (15)$$

When the parameter $\alpha > 1$, the system is not in equilibrium, reactions (10) and (11) are shifted to the right side, and carbon is formed. When the parameter $\alpha = 1$, the reactions are in a state of equilibrium, and when $\alpha < 1$, carbon formation is thermodynamically impossible. The parameters α_{m} and α_{c} limited to the range 0 to 1 will directly describe the carbon chemical activity where $\alpha_{\text{m}} = \alpha_{\text{c}} = 1$ responds to carbon in the solid form.

3. A Numerical Jacobian Approach

The outlet composition per 1 mole of methane can be calculated from the stoichiometry of reactions (2), (3) and (6). The molar flow rate of each chemical component participating in the fuel reforming process in the reformer can be expressed by assuming x as the conversion rate of methane/steam reforming reaction, y as the rate of CO consumed by the steam shifting reaction and z as the conversion rate of C_2H_6 through methanation (see Table 1). Thus the partial pressures of each chemical species caused by the methane/steam reforming reaction, shift reaction and methanation are calculated as follows:

$$p_{\text{CH}_4} = \frac{1-x+2u}{1+SC+2x+EC}P, p_{\text{H}_2\text{O}} = \frac{SC-x-y}{1+SC+2x+EC}P \quad (16)$$

$$p_{\text{H}_2} = \frac{3x+y-u}{1+SC+2x+EC}P, p_{\text{CO}} = \frac{x-y}{1+SC+2x+EC}P \quad (17)$$

$$p_{\text{CO}_2} = \frac{y}{1+SC+2x+EC}P, p_{\text{C}_2\text{H}_6} = \frac{EC-u}{1+SC+2x+EC}P \quad (18)$$

Table 1: Molar change of gas composition in the reactor (A Numerical Jacobian Approach).

i	Inlet [mol]	Steam ref.	Shift reac.	Ethane hydr.	Outlet [mol]
CH ₄	1	- x	0	$2z$	$1-x+2z$
H ₂ O	SC	- x	- y	0	$SC-x-y$
H ₂	0	$3x$	y	- z	$3x+y-z$
CO	0	x	- y	0	$x-y$
CO ₂	0	0	y	0	ycr
C ₂ H ₆	EC	0	0	- z	$EC-z$
Total	$1+SC+EC$	$2x$	0	0	$1+SC+2x+EC$

The equilibrium gas composition can be calculated by solving the following system of equations:

$$\begin{cases} (p_{\text{CO}} \times p_{\text{H}_2}^3)/(p_{\text{CH}_4} \times p_{\text{H}_2\text{O}}) = \exp(-\Delta G_{\text{st}}^0/(RT)) \\ (p_{\text{CO}_2} \times p_{\text{H}_2})/(p_{\text{CO}} \times p_{\text{H}_2\text{O}}) = \exp(-\Delta G_{\text{sh}}^0/(RT)) \\ (p_{\text{CH}_4}^2)/(p_{\text{C}_2\text{H}_6} \times p_{\text{H}_2}) = \exp(-\Delta G_{\text{et}}^0/(RT)) \end{cases} \quad (19)$$

To solve the system of nonlinear equations (19) the Newton method was used, in each iteration the system of linear equations was solved using the current Jacobian matrix J as it is presented below:

$$\underbrace{\begin{pmatrix} f_1(x,y,z) \\ f_2(x,y,z) \\ f_3(x,y,z) \end{pmatrix}}_{f(\mathbf{X})} = \underbrace{\begin{pmatrix} x \\ y \\ z \end{pmatrix}}_{\mathbf{X}} \underbrace{\begin{pmatrix} \frac{\partial f_1(x,y,z)}{\partial x} & \frac{\partial f_1(x,y,z)}{\partial y} & \frac{\partial f_1(x,y,z)}{\partial z} \\ \frac{\partial f_2(x,y,z)}{\partial x} & \frac{\partial f_2(x,y,z)}{\partial y} & \frac{\partial f_2(x,y,z)}{\partial z} \\ \frac{\partial f_3(x,y,z)}{\partial x} & \frac{\partial f_3(x,y,z)}{\partial y} & \frac{\partial f_3(x,y,z)}{\partial z} \end{pmatrix}}_{\mathbf{J}} \quad (20)$$

in each iteration the solution is approximated by the following formula:

$$\mathbf{X}_{\text{new}} = \mathbf{X}_{\text{old}} - \mathbf{J}^{-1}f(\mathbf{X}_{\text{old}}) \quad (21)$$

where the subscript "new" indicate value at new iteration and "old" at previous iteration. Iterative procedure is continued until converge of the results is obtained. This procedure was implemented into an in-house program written in MATLAB (The Math Works, Inc.).

4. Parametric equations approach

The formalism was first introduced by Ptak and Sukiennik [19] and significantly developed later [8,11,20,21]. The following are the basic assumptions of parametric equation formalism used in calculations. For the s -dimensional space (where s -number of reagents), any chemical reaction can be described by the equation:

$$\sum_{i=1}^s k_i B_i = 0 \quad (22)$$

where: B_i is reactant i , k_i is stoichiometric coefficient of reactant i .

For products, positive values for the stoichiometric coefficients are assumed, for substrates negative, and for reagents not taking part in a chemical reactions the stoichiometric coefficients are assumed to be zero. For isothermal-isobaric conditions, the composition of reaction gas phase change along the straight line. The transition of reactants from the initial state to the equilibrium state can be recognised as the vector parallel to the straight line. The parametric equation of a straight line can be written as:

$$x_i = x_i^0 + \tau \cos \theta_i \quad (23)$$

where x_i and x_i^0 are equilibrium and inlet molar fraction of gas component i , θ_i is direction angle. Direction cosine of a line can be expressed as follows:

$$\cos \theta_i = \frac{k_i - x_i^0 \sum_{i=1}^s k_i}{\sqrt{\sum_{i=1}^s \left(k_i - x_i^0 \sum_{i=1}^s k_i \right)^2}} \quad (24)$$

Consequently the gas composition can be calculated as it is presented in Table 2.

Table 2: Change of molar fraction of gas component in the reactor (Characteristic Equation Approach).

i	Steam reforming	Shift reaction	Ethane hydrocracking
CH ₄	$x_{\text{CH}_4}^0 + (-0.5 - x_{\text{CH}_4}^0)\tau$	$x_{\text{CH}_4}^0$	$x_{\text{CH}_4}^0 + \frac{2\tau}{\sqrt{6}}$
H ₂ O	$x_{\text{H}_2\text{O}}^0 + (-0.5 - x_{\text{H}_2\text{O}}^0)\tau$	$x_{\text{H}_2\text{O}}^0 - 0.5\tau$	$x_{\text{H}_2\text{O}}^0$
H ₂	$x_{\text{H}_2}^0 + (1.5 - x_{\text{H}_2}^0)\tau$	$x_{\text{H}_2}^0 + 0.5\tau$	$x_{\text{H}_2}^0 - \frac{\tau}{\sqrt{6}}$
CO	$x_{\text{CO}}^0 + (0.5 - x_{\text{CO}}^0)\tau$	$x_{\text{CO}}^0 - 0.5\tau$	x_{CO}^0
CO ₂	$x_{\text{CO}_2}^0 - x_{\text{CO}_2}^0\tau$	$x_{\text{CO}_2}^0 + 0.5\tau$	$x_{\text{CO}_2}^0$
C ₂ H ₆	$x_{\text{C}_2\text{H}_6}^0 - x_{\text{C}_2\text{H}_6}^0\tau$	$x_{\text{C}_2\text{H}_6}^0$	$x_{\text{C}_2\text{H}_6}^0 - \frac{\tau}{\sqrt{6}}$

The characteristic parameter τ can be calculated by implementing equilibrium molar fraction of gas components listed in Table 2 in to the equilibrium constant equations (Eqs 7-9)

$$K_{\text{st}} = \frac{[x_{\text{CO}}^0 + (0.5 - x_{\text{CO}}^0)\tau] [x_{\text{H}_2}^0 + (1.5 - x_{\text{H}_2}^0)\tau]^3}{[x_{\text{CH}_4}^0 + (-0.5 - x_{\text{CH}_4}^0)\tau] [x_{\text{H}_2\text{O}}^0 + (-0.5 - x_{\text{H}_2\text{O}}^0)\tau]} = \exp\left(-\frac{\Delta G_{\text{st}}^0}{RT}\right) \quad (25)$$

$$K_{\text{sh}} = \frac{[x_{\text{CO}_2}^0 + 0.5\tau] [x_{\text{H}_2}^0 + 0.5\tau]}{[x_{\text{CH}_4}^0] [x_{\text{H}_2\text{O}}^0 - 0.5\tau]} = \exp\left(-\frac{\Delta G_{\text{sh}}^0}{RT}\right) \quad (26)$$

$$K_{\text{et}} = \frac{\left[x_{\text{CH}_4}^0 + \frac{\tau}{\sqrt{6}}\right]^2}{\left[x_{\text{C}_2\text{H}_6}^0 - \frac{\tau}{\sqrt{6}}\right] \left[x_{\text{H}_2}^0 - \frac{\tau}{\sqrt{6}}\right]} = \exp\left(-\frac{\Delta G_{\text{et}}^0}{RT}\right) \quad (27)$$

This procedure was solved using an in-house program written in MATLAB (The Math Works, Inc.). The procedure was iteratively repeated until each equilibrium constant is satisfied.

5. Results and discussion

A numerical model can be a useful tool in the design process of SOFC reformers and optimisation of the entire steam reforming process. In the numerical models presented in this paper, the equilibrium gas composition can be predicted based on the initial conditions and the reaction temperature. Our study includes the effect of inlet conditions, and the reaction temperature on the boundary of carbon formation. In particularly the addition of steam and ethane.

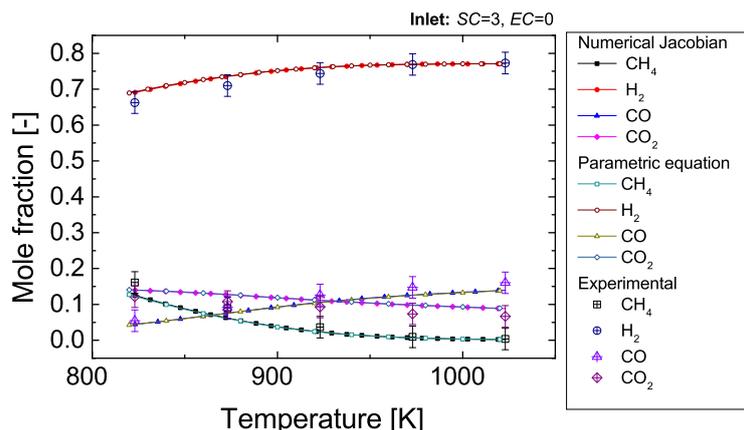


Figure 1: Experimental data versus model approaches [12].

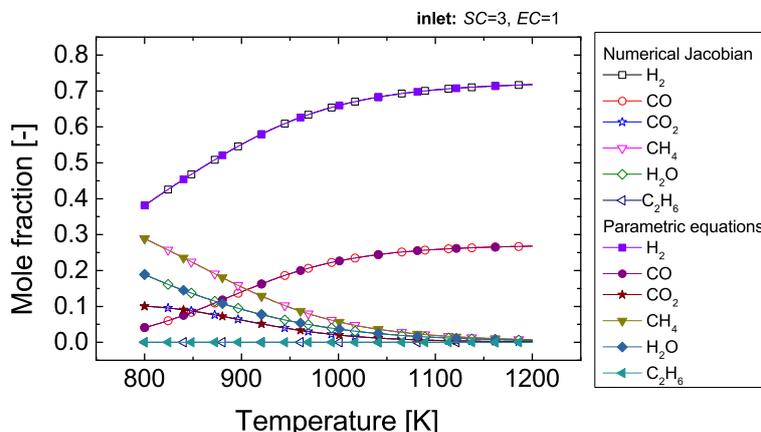


Figure 2: Comparison of calculated molar fractions of equilibrium gas components during steam reforming of methane-ethane mixture. Numerical Jacobian method versus parametric (characteristic) equation method.

Priori to conduct numerical analysis, both of proposed models were juxtaposed with experimental data available in the literature [12]. Please mind that experimental data presented in Fig. 1 comes from gas chromatography and steam is excluded. The experimental measurements were compared with the theoretical calculations of the equilibrium state and good agreement has been found (see Fig. 1). Therefore the developed numerical models was used to numerically analyse the methane/ethane/steam reforming process to address the problem of carbon formation.

Figure 2 presents the theoretical calculations of the equilibrium state for two different model approaches in case of ethane addition in the fuel. As can be seen in Fig. 2 models present excellent agreement between each others. Therefore it can be assumed that Parametric Equation Approach can successfully replace Numerical Jacobian Approach in case of fully developed model of APG reforming process.

To select the carbon deposition regime, the initial values of SC and T were varied and the corresponding values of the parameter α calculated (Equations (14) and (15)). The results of the numerical computation are presented in Figure 3. The data indicates that carbon formation can be minimised by increasing the SC ratio or by increasing the temperature of the process. Figure 3 shows a negative correlation between addition of ethane and carbon deposition in the process.

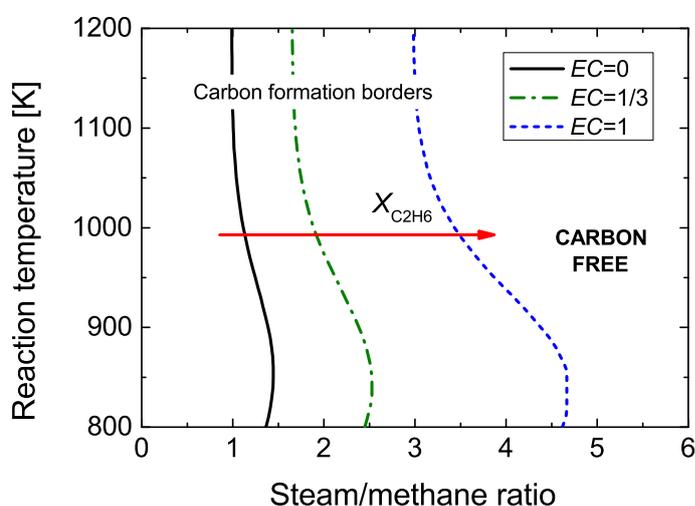


Figure 3: Carbon deposition regime and its dependency on temperature and initial fuel composition.

6. Conclusion

The paper demonstrated two different approaches to steam reforming of model APG gas. The proposed novel approach helps to simplify computation procedure by substituting non-linear system of equation by iteratively solved set of single non-linear equations. The proposed model were used to conduct thermodynamical analysis of carbon formation process of APG steam reforming. The results indicate that steam reforming of APG is an interesting option for high temperature solid oxide fuel cell applications. It was demonstrated that for small addition of ethane ($EC=1/3$), the reaction can be conducted safely outside the carbon deposition regime with reasonable small steam addition $SC \approx 2.5$. Increasing reaction temperature up to 1000 [K] can allow reduction of steam-to-methane ration even below 2.0. However, for ethane-to-methane ratio 1 required amount of steam increases up to 4.5. SC as high as 4.5 is difficult and disqualify fuel for SOFC application.

Acknowledgments

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