

Industrial-Scale Hydrogen Production Plant Modelling

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Abstract : Considering the process characteristics, hydrogen production via steam methane reforming is a vital part of oil refinery not just in terms of materials, but of energy integration as well. This work extends the mathematical model describing hydrogen production by ATE (Approach to Equilibrium) parameters implemented within the chemical reactors' models. Equations for ATE parameter prediction, i.e. mass flow of process feed (natural gas) and reaction temperature, were formulated. Verification of the whole model as well as of its parameters was performed using process data from a real hydrogen plant. The extended mathematical model is suitable for the evaluation of the influence of increased hydrogen content in natural gas on plant's material and energy efficiency, as renewable hydrogen injection and co-transport in natural gas pipelines in future is proposed by the European Union as a means of decreasing carbon dioxide emissions.

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1 Introduction

Nowadays, 63% of global demand for hydrogen [1] is used in chemical and petrochemical industry, where ammonia production is the largest consumer, followed by methanol production [2]. Moreover, hydrogen demand for ammonia and methanol production is expected to increase due to economic and population growth [3]. Refineries represent the second largest consumer of hydrogen with 30% market share [3] using hydrogen for hydro-processing of crude oil and petroleum products, which involves removal of impurities (sulphur, nitrogen...), as well as the production of lighter and more valuable fuels and materials [4].

Hydrogen production can be achieved in several ways: from fossil fuels, water electrolysis, biomass-based or biological production [5]. Natural gas steam reforming constitutes 48% of world's hydrogen production [5]. As it produces significant amounts of carbon emissions, there is a need to look for more environmentally friendly ways of production such as gasification of waste fuels [5,6] or usage of bioethanol instead of methane [7]. Another approach is focused on

enhancing the efficiency of natural gas steam reforming and carbon dioxide capture [8-10].

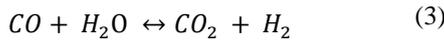
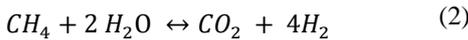
Within the plan of the European Union (EU) to cut down carbon emissions, enrichment of natural gas with hydrogen produced by water electrolysis, using electrical energy from renewable sources, has been considered [11]. One of the goals set in this plan is to reach 10% hydrogen content in the natural gas pipelines until 2030 [12], as this can be achieved without the need for significant investments to existing infrastructure. Thus the increased interest in the influence of hydrogen presence on flame characteristics [13], leakage of hydrogen in pipelines [14], their embrittlement [15], etc.. However, the impact of hydrogen presence in natural gas on hydrogen production by natural gas steam reforming remains unexplored.

The aim of this work is to extend the existing mathematical model of hydrogen production, based on material and energetic balances, by calculation of chemical equilibrium in chemical reactors [16] to evaluate the impact of hydrogen content in natural gas on hydrogen production efficiency of steam reforming. The Approach to Equilibrium (ATE) was chosen as a suitable way to assess real operation of chemical reactors, i.e. the deviation of the real composition of

outflow reaction mixture from its equilibrium composition. This approximation adjusts the calculation of system temperature on which the value of equilibrium constant is dependent. This simplification allows summing up the influence of various catalyst-, material- and process-related aspects on equilibrium, hence the composition of reaction mixture, by a single parameter value. Approaching the chemical equilibrium in the chemical reactor is dependent on factors such as reaction time and temperature, which were subjected to closer examination.

2 Mathematical model

Steam reforming chemistry is based on chemical equations (1), (2) and (3). Hydrogen yield depends on reaction temperature, pressure, ratio of steam and hydrocarbons in the reaction mixture, and ratio of hydrocarbons and hydrogen in the reaction mixture.



Design of the examined hydrogen plant is outlined in Figure 1. To preheated natural gas, high-pressure superheated steam is added in the mass ratio of approximately 1:3.5. This mixture is then preheated again and passed through pipes of a reforming reactor filled with Ni-containing catalyst. Temperature in this reactor is above 800°C, which favours reactions (1) and (2). Reaction mixture leaving the reforming reactor is cooled down in a steam generator to below 400°C and continues to a high-temperature shift (HTS) reactor filled with Fe-based catalyst, selective towards reaction (3) only. Under these conditions, carbon monoxide is transformed (shifted) to carbon dioxide and hydrogen. At the outlet of the HTS reactor, another steam generator is located followed by a series of heat exchangers, so the reaction mixture cools down to 40°C, as required for the Pressure Swing Adsorption (PSA) process. In PSA, pure hydrogen (over 99.9 % vol.) is separated from the reaction mixture, while the offgas from this process is burned in the reformer furnace as the main fuel, together with natural gas as the supplementary fuel.

Mathematical model of the plant is based on the solution of material and energy balances. As chemical equilibrium constants of reactions (1), (2) and (3) serve as a base for the reactors' material balances, equilibrium composition was calculated from equations (4) and (5) while equilibrium constants were calculated from equations of polynomial interpolation curves. Polynomial coefficients were evaluated from equations (6) and (7) using temperature dependent heat capacity,

formation enthalpies and entropies, in the temperature interval of (700 - 900) °C. The obtained coefficients of polynomial equation (8) are shown in Table 1.

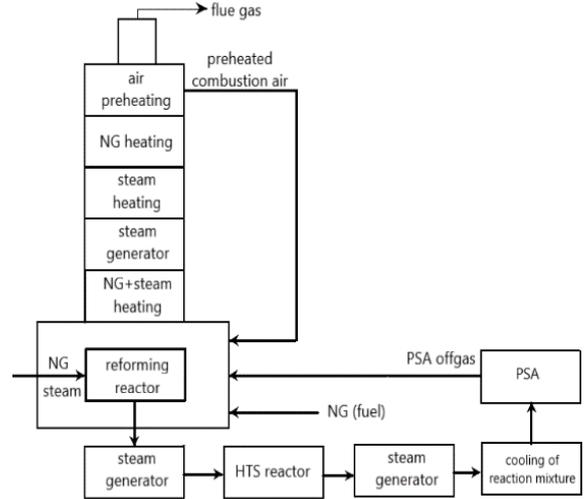


Figure 1 Scheme of steam methane reforming (SMR) hydrogen plant. HTS = high-temperature shift, NG = natural gas

$$K_a = \left(\frac{p}{p^\theta}\right)^{\Delta_v} \left(\frac{1}{\sum \dot{n}_i}\right)^{\Delta_v} \prod_{i=1}^I (\dot{n}_i)^{v_i} \quad (4)$$

$$\dot{n}_i = \dot{n}_{0,i} + \sum_{j=1}^J v_{ji} \dot{\xi}_j \quad (5)$$

$$\Delta_r G = \Delta_r H - T \Delta_r S \quad (6)$$

$$\Delta_r G = RT \ln K_a \quad (7)$$

$$K_a = a(T - 273,15)^5 + b(T - 273,15)^4 + c(T - 273,15)^3 + d(T - 273,15)^2 + e(T - 273,15) + f \quad (8)$$

Higher hydrocarbons (C2+) present in natural gas were assumed to react quantitatively in the reforming reactor during reaction mixture heating, in accordance with their preferred reactions. Selection of the preferred reaction was based on the value of the corresponding equilibrium constant. Equilibrium constants were compared at 500°C, as this was the design temperature of the reaction mixture entering the reforming reactor. Reactions of higher hydrocarbons with the highest value of equilibrium constant are summarised in Table 2.

Steam production was also calculated. As it results from Figure 1, steam production takes place in convective section of the furnace of the reforming reactor and in steam generators placed before and after the HTS reactor. Heat flux was obtained using design temperatures, calculated composition of reaction

mixture and heat capacity in the form of polynomial coefficients. Enthalpy of water steam was taken from the h-s diagram.

Table 1 Coefficients of polynomial equation (8) describing equilibrium constant dependence on temperature for chemical reactions (1), (2) and (3)

	a (10 ⁻¹²)	b (10 ⁻⁹)	c (10 ⁻⁶)	d (10 ⁻³)	e	f
(1)	1.62	-5.18	6.61	-4.21	1.33	167
(2)	0.79	-2.47	3.10	-1.94	6.07	75.5
(3)	0.00	6.41	-0.14	1.13	-4.18	595

Table 2 Preferable reactions of higher hydrocarbons – stoichiometric coefficients of reactants and products

v	H ₂ O	CO	CO ₂	H ₂	CH ₄
C ₂ H ₆	-2	0	1	3	1
C ₃ H ₈	-3	2	1	7	0
C ₄ H ₁₀	-2	0	1	1	3
C ₅ H ₁₂	-2	0	1	0	4

3 Approach to Equilibrium

To assess the influence of uneven heat and mass transfer, uneven velocity profiles and mixing intensity, distribution of catalyst, etc., parameter Approach to Equilibrium (ATE) was employed. It was assumed that the above factors can be summed up by the change of equilibrium composition of the reaction mixture. As the deviation from chemical equilibrium is mainly determined by the reaction temperature, ATE value was added to the measured reaction temperature. Equilibrium constant for reactions (1) to (3) was calculated with the help of modified polynomial interpolation curves equations as shown in equation (9).

$$K_a = a(T - 273.15 - ATE)^5 + b(T - 273.15 - ATE)^4 + c(T - 273.15 - ATE)^3 + d(T - 273.15 - ATE)^2 + e(T - 273.15 - ATE) + f \quad (9)$$

The value of this parameter was first calculated from design data. Considering the design feed and comparing the calculated and designed composition of the reaction

mixture leaving the reforming reactor, ATE values for reactions (1) and (2) were calculated to obtain results as close to the design data as possible. Similarly, ATE value for reaction (3) was calculated by comparing calculated and design composition of the reaction mixture leaving the HTS reactor. The obtained composition of dry reaction mixture is provided in Table 3. These values are related to the ATE values given in Table 4. Difference of calculated and designed water steam production was below 1%.

The initial ATE values, valid for design conditions, were adjusted in accordance with the real reaction temperature in the chemical reactor and real mass flow of processed natural gas, equation (10), to achieve higher difference from the equilibrium composition due to reduced reaction rate as a result of lower reaction temperature. Similarly, higher mass flow of reaction mixture means shorter reaction time, thus higher difference from equilibrium composition can be expected.

Table 3 Comparison of design and calculated composition of dry reaction mixture HTS = High-temperature shift

Mole %	Outlet/reforming reactor		Outlet/HTS reactor	
	design data	calc. data	design data	calc. data
H ₂	71.57	71.51	71.57	71.51
CO	12.39	12.45	12.39	12.45
CO ₂	8.54	8.56	8.54	8.56
N ₂	0.23	0.23	0.23	0.23
CH ₄	7.27	7.26	7.27	7.26

Table 4 Calculated approach to equilibrium (ATE) values for design data

ATE(1)	13.8
ATE(2)	16.8
ATE(3)	1.7

$$ATE = ATE_0 \frac{\dot{m}_{NG} T_0}{\dot{m}_{NG,0} T} \quad (10)$$

4 Results and Discussion

Hydrogen production plant operation data comprising nine months of operation were used for model verification. The data included mass flow of natural gas, steam mass flow, mass flow of recirculated hydrogen used for natural gas desulphurisation, combustion air mass flow and temperatures of reaction mixture leaving the reforming reactor and the high temperature shift reactor. Average composition of natural gas during the considered period was adopted [17]. Data measured during plant outage, as well as data measured during co-processing of refinery off-gases for hydrogen production were discarded.

Rates of reactions (1) and (2) were calculated by iteration, so the composition complied with equation (4), where equilibrium constant was obtained by equation (9). As the initial value for the iteration, ATE value adjusted by equation (10) was used. Calculated methane content of the reaction mixture leaving the reforming reactor was compared with the measured one and ATE parameter values for reactions (1) and (2) were iterated to minimise the difference between calculated and measured methane content.

Similarly, calculated carbon monoxide content of the reaction mixture leaving the high temperature shift reactor was compared with the measured one and ATE value of reaction (3) was iterated to minimise the difference.

This approach provided three ATE values daily for the data set; these values were further examined to determine their dependence on reaction temperature and natural gas mass flow, resulting in equation (11). ATE for reaction (1) is presented as an example.

$$ATE = a + b \dot{m}_{NG} + c T_R \quad (11)$$

Figure 2 provides the course of average daily temperatures measured in the reforming reactor and corresponding ATE values of reaction (1) for 145 days, followed by the outage of the steam reforming plant.

Equation (11) was used to predict ATE values. For this application, parameters of equation (11) were iterated to obtain predicted ATE values with the lowest sum of the squares of the deviations from calculated ATE values.

Comparison of calculated and predicted values of the ATE parameter of reaction (1) is shown in Figure 3.

As it can be seen in Figure 3, prediction of ATE values based on the values of natural gas mass flow and reaction temperature provides ATE values sufficiently close to the calculated ones. However, mass flow of natural gas and reaction temperature are not the only factors affecting the composition of the reaction mixture at the reactor outlet. Catalyst aging was also considered,

but this approach was later dismissed due to the lack of relevant data on the catalyst age.

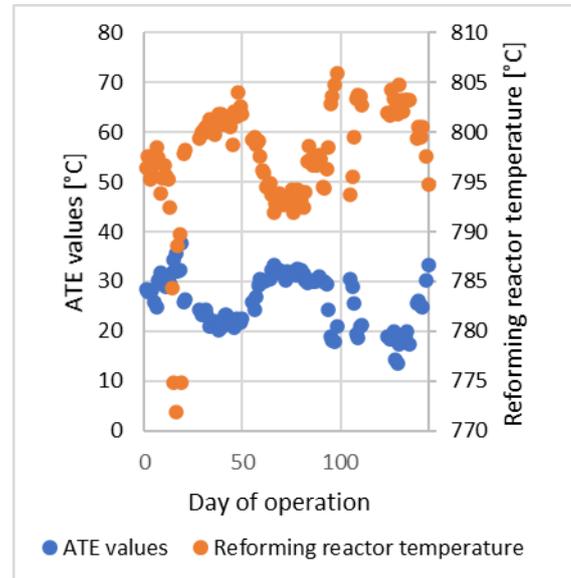


Figure 2 Average daily values of reaction temperature and calculated approach to equilibrium (ATE) value during plant operation

This approach was applied for each ATE parameter and the values of this parameter in equation (11) for reactions (1) and (2) are summarised in Table 5.

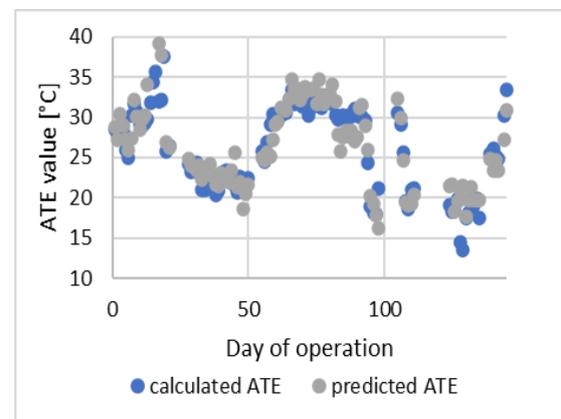


Figure 3 Comparison of calculated and predicted ATE values for reaction (1)

Table 5 Parameters of equation (11) for reactions (1) and (2)

	a [K]	b [10^{-3} K.h/kg]	c [-]
ATE of reaction (1)	1102.81	0.38	-1.35
ATE of reaction (2)	0.00	-1.81	0.05

To evaluate the dependence of reaction (3) on reaction temperature inside the reforming reactor (as this temperature determines the composition of the reaction mixture at the inlet of the HTS reactor), its ATE value was obtained using equation (12), parameters of this equation are provided in Table 6.

$$ATE = a + b \dot{m}_{NG} + c T_R + d T_{HTS} \quad (12)$$

Table 6 Parameters of equation (12)

a [K]	b [10^{-12} K.h/kg]	c [-]	d [-]
0.00	8.75	0.17	0.40

Equations (11) and (12) were included in the mathematical model and methane content of the reaction mixture at the outlet of the reforming reactor and carbon monoxide content at the outlet of the HTS reactor were determined.

Figure 4 shows the comparison of measured and calculated methane content of dry reaction mixture at the outlet of the reforming reactor. Calculated data were obtained using the original equation (6) and equation (11), for ATE parameters prediction.

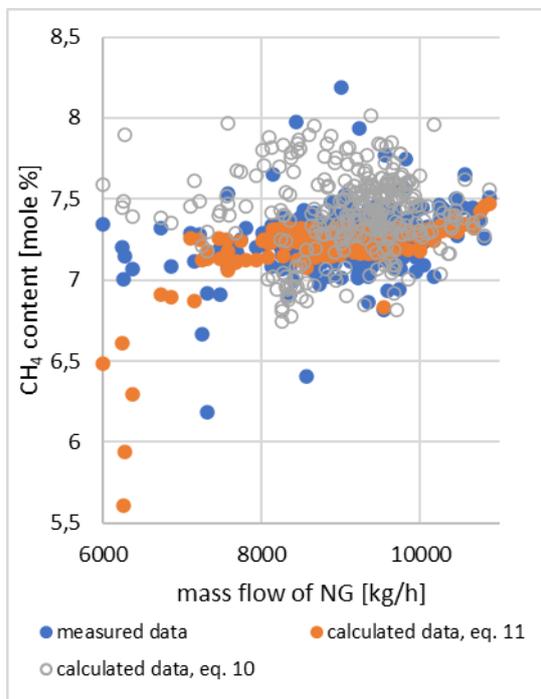


Figure 4 Comparison of measured and calculated methane content of dry reaction mixture at the outlet of the reforming reactor

As it can be seen in Figure 4, equation (11) results in smaller differences between measured and calculated data than equation (6). Despite the mismatch of some experimental data, it can be assumed that equation (11)

is capable of reliable prediction of ATE values used for the determination of the reaction mixture composition. Its use is limited to values of natural gas mass flow for hydrogen production in the range of 8 to 10 tons per hour. Mass flow below 8 tons per hour occurs only seldom. Thus, their impact on the overall accuracy of the model is negligible.

Similar comparison was performed to demonstrate applicability of equation (12) for the prediction of ATE value of reaction (3). Comparison of measured and calculated carbon monoxide content of dry reaction mixture at the outlet of the HTS reactor is shown in Figure 5.

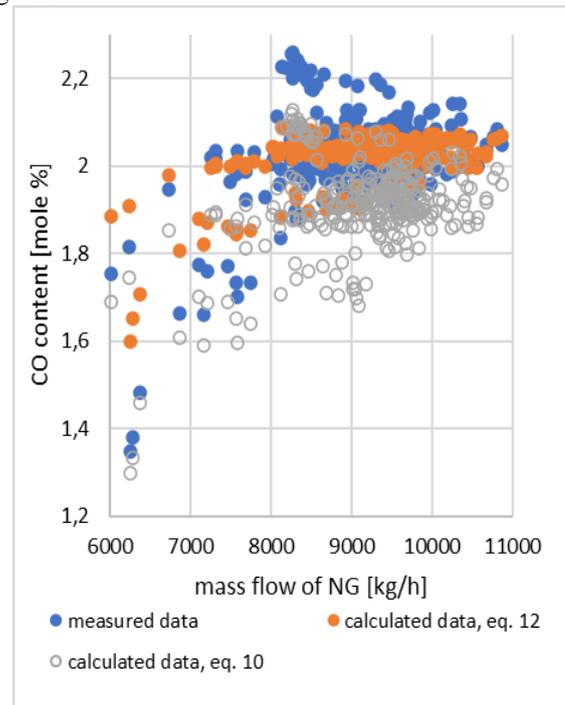
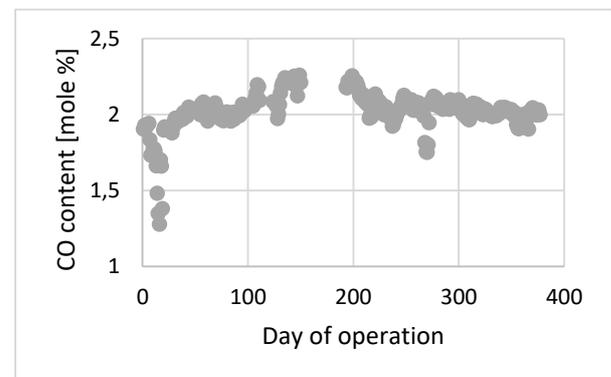


Figure 5 Comparison of measured and calculated carbon monoxide content of dry reaction mixture at the outlet of the HTS reactor

Figure 6 Measured carbon monoxide content at the outlet of the HTS reactor



Following the results shown in Figure 5, it is obvious that equation (12) accurately describes the composition of the reaction mixture at the outlet of the HTS reactor.

Figure 6 shows values of measured carbon monoxide content at the outlet of the HTS reactor. Similarly as in Figure 4, not all measured data were closely followed by the calculated ones. Inaccuracy is eminent for carbon monoxide content above 2.2 mole %, appearing shortly before the outage and a few days after the unit's repeated start of operation (Figure 6). As such high carbon monoxide content seldom occurs, sufficient model accuracy can be declared.

5 Conclusions

The aim of this work was to extend the existing mathematical model of industrial-scale hydrogen production plant by equations able to predict ATE parameters. The use of predicted ATE values in the plant model yielded outlet data in compliance with the measured ones. As these data are fundamental for reliable estimation of reaction mixture composition at the outlet of chemical reactors used for hydrogen production, they are also vital for the modelling of the whole process. On the other hand, this model is not suitable for the description of process behaviour before or after the plant outage. The presented mathematical model is applicable for the prediction of steady state process changes resulting from the higher hydrogen content in natural gas. Non-negligible differences of model results and measured data are visible shortly before and after the plant outage and can be attributed to unsteady state operation. Further model extension will be pursued in our future work.

Nomenclature

a, b, c, d, e, f : Coefficients of model equations
 ATE : Approach to equilibrium
 i : i -th component
 I : Number of elements in the system
 j : j -th chemical reaction
 J : Number of chemical reactions in the system
 K_a : Chemical equilibrium constant
 \dot{m} : Mass flow ($kg \cdot s^{-1}$)
 \dot{n} : Molar flow ($kg \cdot s^{-1}$)
 p : Pressure (Pa)
 R : Universal gas constant
 T : Temperature (K)
 ν : Stoichiometric coefficient
 ξ : Reaction rate ($mol \cdot s^{-1}$)
 $\Delta_r G$: Gibbs reaction energy (J)
 $\Delta_r H$: Reaction enthalpy (J)
 $\Delta_r S$: Reaction entropy ($J \cdot K^{-1}$)

Indices:

RM : Reaction mixture
 NG : Natural gas
 HTS : High Temperature Shift (reactor)
 0 : Initial (state, value)

θ : Standard (thermodynamic state)

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