

A comparative study of two various empirical methodologies for deriving kinetics of methane/steam reforming reaction

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Abstract. Despite methane/steam reforming is the conventional method for hydrogen production, there are widespread disagreements between formulations of the process kinetic derived in the literature. In the present research, the mathematical baseline of the classical calculation methodologies of the reaction kinetic are presented and compared. They include methodologies based on: I) the assumed constant partial pressure of steam and methane and II) the minimization of the summed relative standard deviation of the calculated reaction constant. Their results are compared with generalized least squares approach. The calculation methodologies are correlated with the planned experimental measurement set. This paper aims for the clarification of the observed differences and pointing the most suitable methodology for the decreasing the overall uncertainty of the model.

1. Introduction

Internal reforming of hydrocarbon fuel is the one of advanced attractions for Solid Oxide Fuel Cells (SOFCs), appreciating its inherent characteristic of electrochemistry, in general known as fuel flexibility. The precise modelling of methane-fuelled SOFC systems requires knowledge about the kinetic of the fuel reforming process. The kinetic of the methane/steam reforming has been widely studied in the literature for industrial nickel-based catalytic reactors. Nickel (especially in the form of Ni/YSZ cermet) is also one of the most conventional materials used in the production of SOFC anodes. However, when the reforming dedicated for both of those applications is considered, significant differences has to be addressed. The kinetic expressions found in the literature are divergent among themselves, and moreover only a limited number of researches was conducted for the methane/steam reforming on SOFC dedicated materials.

The mathematical forms of expression describing the highly non-linear kinetics of the reforming process are not consistent. One of the most common description methodology is power law expressions derived from data fitting [1–7], nonetheless the empirical parameters found in the literature are divergent among themselves. For instance, Table 1 shows one of the empirical parameters, the so-called reaction orders in respect to the partial pressures of methane (reaction order *a*) and steam (reaction order *b*) found in the literature [2–11]. All of the studies presented in Table 1.3 were focused on the Nickel based catalysts. Noticeable differences can be found, although, the



empirical parameters, the reaction order coefficients a and b , should be independent from the specific property of the investigated sample, as far as the same type of catalyst is used [2]. Moreover, uncertainties of the obtained result, which may have influenced the derived reaction kinetics, were not substantially discussed in the published investigations. The observed divergences may be partially connected with the experimental and numerical methodology applied for derivation of the empirical parameters. In the scope of this study, two different approaches to derive reaction kinetic, commonly applied in the literature, will be compared. As the method to improve the reliability of the classical modelling method, the Generalized Least Square Algorithm will be proposed.

Table 1 Comparison of the reaction orders a and b for Ni/YSZ cermet [2–11]

Reference	a	b	Reference	a	b
Lee et al. (1990) [7]	1	-1.25	Wei and Iglesia (2004) [12]	1	0
Achenbach (1994) [13]	1	0	Timmermann et al. (2006) [4]	1.19	0
Odegard et al. (1995) [3]	1.2	0	King et al. (2008) [10]	1	0
Ahmed and Foger (2000) [6]	0.85	-0.35	Mogensen (2011) [11]	0.7	0
Yakabe et al. (2001) [5]	1.3	-1.2	Iwai et al (2012) [2]	0.82	0.14

2. Methane/steam reforming reaction process

2.1. General formulation of kinetic equation

Methane/steam reforming is the conventional method for hydrogen production. The chemical reactions governing the process are following [3]:

Methane/steam reforming (MSR) reaction: $\text{CH}_4 + \text{H}_2\text{O} \rightarrow 3\text{H}_2 + \text{CO}$ (1)

Water-gas-shift (WGS) reaction: $\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{H}_2 + \text{CO}_2$ (2)

The overall process is highly endothermic and a substantial supply of thermal energy is required to maintain the reaction temperature. The WGS reaction is considerably faster than the MSR reaction and can be assumed to be in equilibrium at the reforming temperature [7,8,14], so the overall rate of the process is determined by the MSR reaction kinetic. In the present study, the primarily assumed form of the equation describing the methane/steam reforming reaction kinetic is derived by the power law expression with respect to the partial pressures of methane and steam. This approach provides the general derivation without additional assumptions and simplifications [15] and is superior to the modelling concept of first order reaction with respect to methane.

The reaction rate of the reforming reaction can be presented in the form of the following equations:

$$r = k(p_{\text{CH}_4})^a (p_{\text{H}_2\text{O}})^b \quad (3)$$

$$k = A \exp(-E/RT) \quad (4)$$

where r is the reaction rate [$\text{mol s}^{-1} \text{ g}^{-1}$], k is the reaction constant, p_{CH_4} and $p_{\text{H}_2\text{O}}$ are the partial pressures of CH_4 and H_2O [Pa], a and b are the reaction order coefficients [-], A is the pre-exponential factor [$\text{mol g}^{-1} \text{ s}^{-1} \text{ Pa}^{-(a+b)}$], E is the activation energy [J mol^{-1}], R is the universal gas constant ($R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) and T is the temperature [K].

The first step for determining the methane/steam reforming reaction kinetics proposes is an algorithm to estimate the values of reaction constant for various different sets of methane and water flow rates, respectively for determining reaction orders a and b . The reaction orders depend on the reaction mechanism and can be determined experimentally. Two approaches are proposed to evaluate reaction orders in the methane/steam reforming process: standard and modified.

2.2. Standard method for determining the reaction order coefficients a and b

In the standard approach for the estimation of the empirical parameters of reaction order coefficients a and b , their values are calculated separately and laborious experimental measurements, divided for two independent data sets, have to be conducted. The experiment is based on the assumption, that constant

partial pressure is preserved for one of the species: steam or methane. The determination of the coefficient a is done on the basis of measurements conducted with the constant partial pressure of steam and the varying partial pressure of methane. Those conditions are achieved by the manipulation of the flow rates of methane and nitrogen and maintaining the constant flow of water.

It can be noticed that the reforming reaction constant k depends only on the temperature of reaction as it is described in the formula (3). Because the partial pressure of steam is assumed to be constant, the new modified parameter k' can be defined:

$$k' = k(p_{\text{H}_2\text{O}})^b \quad (5)$$

It can be noticed that the value of this parameter depends only on the reaction temperature $k' = f(T)$ and is constant at a certain level of temperature. Therefore, the reaction rate equation can be rewritten as:

$$r = k'(p_{\text{CH}_4})^a \quad (6)$$

After the transformation, the following linear equation can be obtained:

$$\ln(r) = a \ln(p_{\text{CH}_4}) + \ln(k') \quad (7)$$

It is denoted that $\ln(k')$ is a constant value in the case of a constant temperature. Hence, on the basis of the Eq. (7) and the linear approximation of the experimental results presented in a logarithmic graph, the parameter a can be found. The method of finding coefficient b is analogical. The algorithm of the standard approach used to determine reaction orders is presented in Fig. 1.

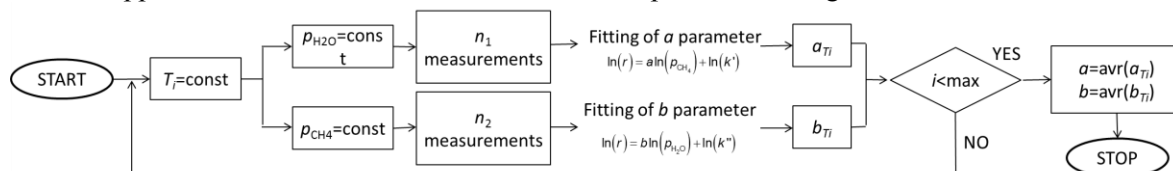


Figure 1. Algorithm of the standard approach to evaluate reaction orders a and b

2.3. Modified method for determining the reaction orders a and b

The modified approach for the calculation of the reaction order coefficients a and b is based on the combined experimental-numerical methodology proposed by Odegard [3] and modified by Brus et al. [16]. The modified method significantly decreases the number of necessary experimental measurements and provides the higher independency and reliability improved by the reduced experimental errors. As it does not impose the assumption of constant partial pressures of any of the species, the approach is more general. The experiment is conducted in various temperatures, however, the parameter a and b are considered to be calculated simultaneously on the basis of the same experimental measurements. The modified approach is based on the observation, that the reaction constant is independent of the assumed Steam-to-Carbon (SC) and Nitrogen-to-Carbon (NC) ratios in the constant temperature.

To find the values of empirical parameters, different combinations of the coefficients a and b in the preliminary assumed intervals are tested and used to calculate the reaction constants. The values of the reaction constant were compared with the experimental results from the conditions, at which widely dispersed SC and NC ratios were applied. For each computation conducted for different temperature experimental conditions, the possible coefficients a and b , at which the results shows the smallest standard deviation found on the reaction constant k , were selected. The relative standard deviation on the reaction constant RSD_k is expressed as follows:

$$RSD_k = \sqrt{\sum_{i=1}^n (k_i - k_{ave})^2} / n \cdot k_{ave} \quad (8)$$

where, n and k_{ave} stand for the number of measurements and the average of the reaction constant k at each temperature condition, respectively. In this stage, the reaction constant k was derived by the following equation from the experimental data [17]:

$$k_i = k_i(a, b) = \frac{F_{\text{CH}_4}}{w_{\text{cat}}} \int_0^x \frac{(1 + SC + NC + 2x)^{a+b}}{(1-x)^a (SC-x-y)^b P^{a+b}} dx \quad (9)$$

The modified algorithm is presented in Fig. 2. In this study, the range of tested parameters a and b was chosen in accordance with published data [3,10,16] as the intervals $<0; 1.5>$ and $<-0.5; 0.5>$, respectively for reaction orders a and b .

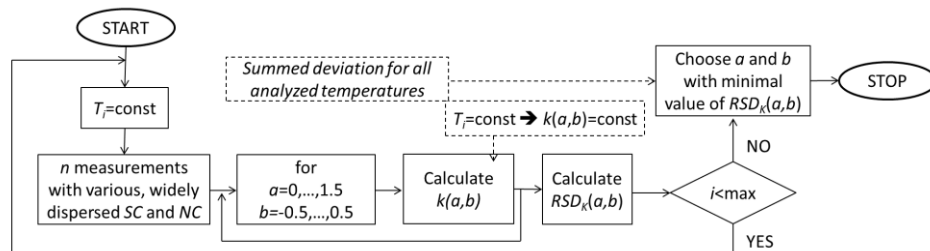


Figure 2.
Algorithm of the modified approach to evaluate reaction orders a and b

2.4. Calculation of activation energy E and pre-exponential factor A

In order to develop a full kinetic model of the methane/steam reforming process, the approximation of the activation energy and Arrhenius pre-exponential factor is necessary. The applied method is derived from the formula for temperature dependence of the reaction rates proposed by Arrhenius and the empirical values are found by fitting of the Arrhenius plot.

3. Experimental procedure

The schema of the experimental setup is provided in the Fig 3. The experiment was performed with high purity methane supplied from a gas cylinder via the mass flow controller. Steam was supplied by the evaporation of pure water fed by a pump. Additionally, nitrogen was supplied to the reactor to maintain the reforming conversion rate at a low level, by changing the partial pressures of the components. The gas mixture of CH_4 , N_2 and H_2O was supplied to the stainless steel reformer. The fine powder catalyst (Ni/YSZ , 60:40%vol.) was dispersed to be a homogeneous distribution over the quartz wool-made bed located in the middle of the reactor. The catalyst was covered with additional layer of quartz wool and Al_2O_3 balls used to prevent a cooling effect of the entering fluid. A reformer tube was placed in the electrical furnace which temperature was controlled by four thermocouples located before and after reaction zone, inside the reaction zone and on its surface as indicated in the Fig 3. The exhaust gas was analysed by the gas chromatograph (GC390B by GL Sciences) by Thermal Conductivity Detector (TCD) and Flame Ionization Detector (FID). Before conducting the measurements, the catalyst was treated at the evaluated temperature of 600 °C with a mixture flow of nitrogen and hydrogen due to the necessity for reduction process of NiO .

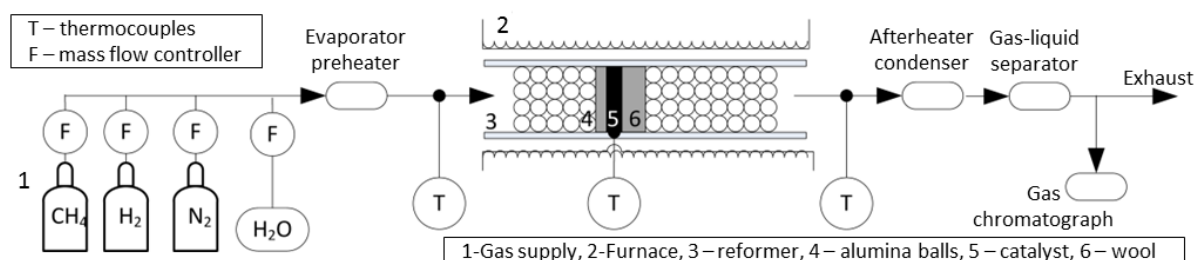


Fig. 3. Schema of the experimental set-up

The measurements were carried out with different conditions based on the various temperatures (in the range of 500-750 °C), SC ratio and NC ratio. SC and NC were manipulated to satisfy the constant total molar flow rate $F_{\text{total}}^i = 1.43 \times 10^{-2} \text{ mol min}^{-1}$, in order to keep the Gas Space Hourly Velocity

(GSHV) constant. The experimental conditions are divided into three different measurements series (see Fig. 4). In Series 1, experimental conditions with the constant molar flow rate of methane and varied SC ratio in the range of 2.5-5.5 were provided. In Series 2, experimental conditions with the constant molar flow rate of steam were defined, however the SC ratio in the range of 2.5-5.5 was changed while the flow rate of methane is varied. Finally, in Series 3, consistent of measurements with widespread distribution of experimental conditions for the molar flow rates of water and methane (the SC ratio is in the range of 2.5-6). Different measurement series are defined to specify the requirements for the calculation methodologies proposed to derive the kinetic of the methane/steam reforming: Series 1 and Series 2 for standard methodology and Series 3 for modified methodology.

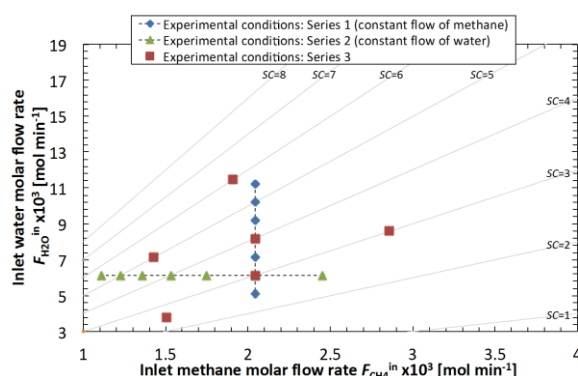


Figure 4 Distribution of experimental conditions for various experimental series

4. Results and discussion

4.1. Comparison of classical methodologies for deriving reaction kinetics

The results of the carried-out measurements in the standard and modified conditions are presented in Fig. 5 in the form of the methane conversion rate over the investigated conditions. The three main types of numerical analyses were conducted: I) the standard methodology calculated with the experimental data obtained for standard experimental conditions (Series 1 and 2), II) the modified calculation method with the modified experimental data (Series 3) and, additionally, III) the standard experimental data were applied to the calculation procedure of the modified methodology.

The exemplary results of the calculations case I) in temperature of 500 °C and the case II) are presented in Fig. 6A and B. The case I) approximation of parameters is $a=0.35$ and $b=0.20$ for all temperatures averaged (Fig. 6A). In the case II) the approximation is $a=0.38$ and $b=0.21$ (Fig. 6B). It can be noticed, that the modified method provides the more general approach; in the standard method it has to be assumed, that the partial pressure of one of the components is constant. The reason of the observed differences between results and superiority of modified method can be explained by

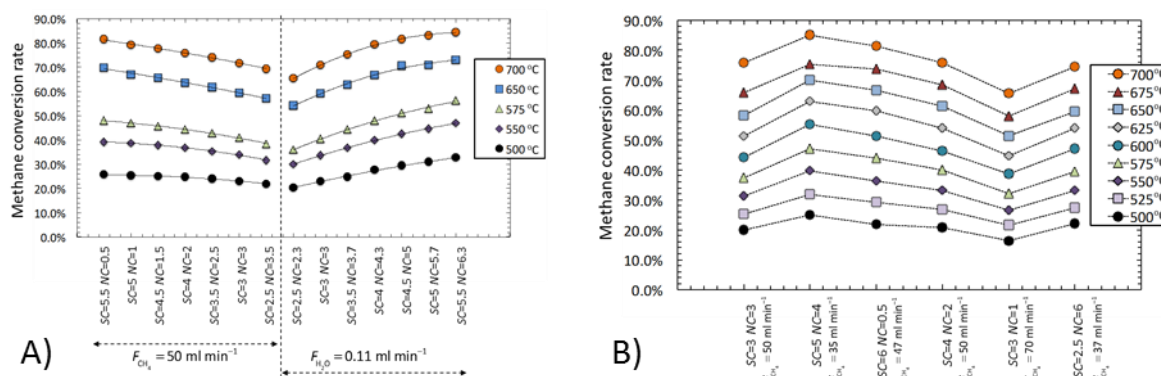


Figure 5 Experimental results of the methane conversion rate at A) the constant flow rates of methane and of water (standard approach), B) various flow rates of methane and water (modified approach)

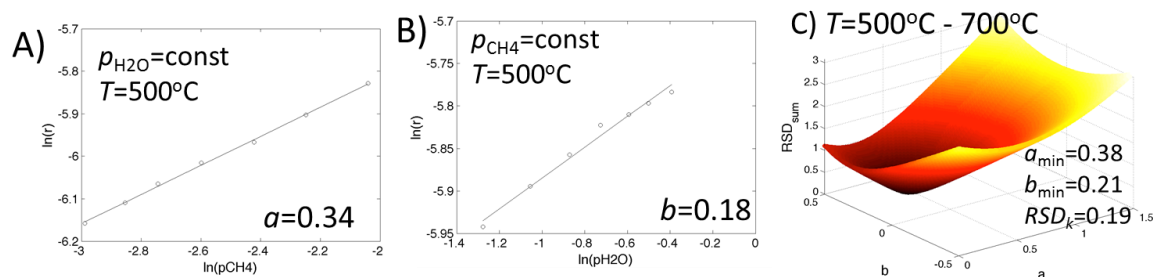


Figure 6 Results of standard method at the constant flow rates A) of water (Series 2), B) methane (Series 1) and C) results of modified method with modified experimental condition (Series 3)

application of the third calculation case. difference in the calculation is visible, especially in a higher reaction temperature compared to the data obtained with the standard method. The value estimated at a temperature of 700 °C from the merged data is $a=59$ [-] and $b=0.31$ [-], while for separated data the values decreased to $a=46$ [-] and $b=0.17$ [-], which is consisted with the results of standard method. The characteristic feature observed in Fig. 7 for the separated experimental conditions is lack of one significant extreme point, minimizing the value of the relative standard deviation calculated for the reaction constants. In all of the previous cases and the studies found in the literature, for the analysis of the reaction orders by the modified method, the isolines of the constant value of the relative standard deviation calculated for reaction constant k creates the concentric ellipsoids. In Figs. 7B, 7C, 7E and 7F, the minimum isoline is not degenerated to the point, but has a linear shape, parallel to the b axis in Figs. 7B and 7E and to axis a in Figs. 7C and 7F. This shape is resulted from the assumed experimental condition. In the case of experiments with the constant flow rate of water (in Figs. 7B and 7E), the influence of methane flow rate is only investigated. Therefore, we can estimate its effect on the reaction rate, which is expressed in the form of reaction order coefficient for the parameter a . The effect of the water flow rate, predominantly determining the partial pressure of steam, is neglected, so that the trustful value of parameter b cannot be estimated from this data series. The analogical situation is observed for the constant molar flow rate of methane with the varied flow rate of water (in Figs. 7C and 7F), which gives a correct estimation only for the influence of the flow rate of water (to predominantly the partial pressure of steam) expressed in parameter b . The comparison presented in Fig. 7 explains the uncorrected results obtained for the analysis with merged Series 1 and Series 2. The value of reaction order coefficients a and b scoring the minimum value of RSD_k , in the case of merged data (in Fig. 7A), can be found in the intersection of the isoline of minimal RSD_k for separated measurements in Series 1 (in Fig. 7B) and Series 2 (in Fig. 7C). At the temperature of 500°C, the results obtained by the merging-data approach (determining $a=0.39$ [-] and $b=0.21$ [-]) and the separately treating-data approach (determining $a=0.39$ [-] and $b=0.19$ [-]) are convergent. On the other hand, at the temperature of 700 °C, the differences between two approaches are clear. It is caused by the deviation in the final partial pressures, which are difficult to be defined as constant, even though the initial flow rates were the same. The high conversion rate changes the results significantly in each measuring conditions, therefore interferes with the expected results. This effect is also observed in the constant RSD_k isolines, which are not parallel to the axis in Figs. 7E and 7F.

The results provided by the modified method with experimentation of Series 3 are the most trustful estimation, as there is no assumption of the constant partial pressure of one of the substrates and experimental data are widely distributed. The values calculated by this method were taken as final estimation of the reaction orders a and b . The Arrhenius plot was used to estimate activation energy and pre-exponential factor. The final form of the reaction rate equation is:

$$r = w_{\text{cat}} \cdot 11.6 \cdot \exp(-48105/RT) (p_{\text{CH}_4})^{0.38} (p_{\text{H}_2\text{O}})^{0.21} \quad (10)$$

Reaction rate equation was used in order to simulate the gas composition at the reactor outlet from the defined initial conditions of a system with the methane/steam reforming process, which results are presented in Fig 8. Good agreement between experimental and numerical results is observed for the

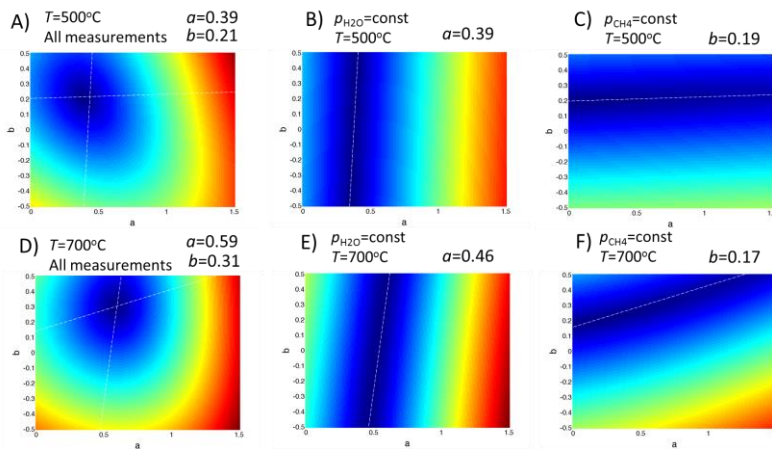


Figure 7 The influence of the unstable partial pressure of methane for the approximation of reaction orders at a temperature of 500 °C (in A-C) and 700 °C (in D-F)

lower conversion rates in the range of 20-60%. As it was presented in Fig. 5 these conversion rates are reached in the experiments conducted below 650°C. With an increasing temperature, the conversion rate increases and the divergence between numerical and experimental methane conversion rates becomes more significant. The high conversion rates indicate that the reforming process was carried out at the condition close to the equilibrium state. Generally, the experimental conversion rate should be kept at a low level in order to estimate kinetic changes in the reaction rate.

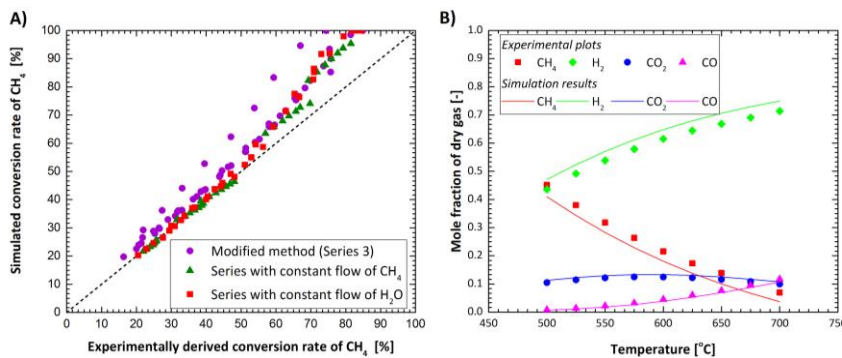


Figure 8 A) Comparison of conversion rates obtained experimentally and calculated by simulation B) Comparison of experimental and numerical molar fraction of species (in condition of $F_{CH_4} = 50 \text{ ml min}^{-1}$, $SC=3$, $NC=3$)

4.2. Application of Generalized Least Squares Algorithm

The method for further improvement of the quality of estimation reaction rate of methane/steam reforming process is applying complex method of Generalized Least Squares (GLS) in details described in [17–19]. To provide example of proper modelling of kinetic equation, the non-sintered catalyst was applied, which exhibits lower catalytic activity (the conversion rate below 35%). The experimental condition was the same as previously (Series 3). Firstly, the initial approximation by modified method was applied:

$$r_{\text{ini}} = w_{\text{cat}} \cdot 1.554 \cdot 10^{-3} \exp(-117 \cdot 10^3 / RT) (p_{CH_4})^{0.97} (p_{H_2O})^{-0.08} \quad (11)$$

The formula was further improved by the GLS algorithm:

$$r_{\text{corr}} = w_{\text{cat}} \cdot 1.354 \cdot 10^{-3} \exp(-123 \cdot 10^3 / RT) (p_{CH_4})^{0.89} (p_{H_2O})^{0.05} \quad (12)$$

The comparison of the first approximation and improved reaction kinetic is presented in the Fig. 9 for the simulation of the outlet gas composition and the quality of modelling of conversion rate.

By the application of the GLS algorithm, the mass and energy balances as well as the physical constraints describing the measurement system are closed and the model is coherent. The application of the GLS method results in an improvement in the quality of the obtained solution by decreasing the uncertainties of the model. The proposed GLS method not only allows for obtaining the most probable values of the estimated parameters but also makes possible the *a posteriori* evaluation of the errors of

the directly measured variables and unknown parameters. The GLS method is useful in securing higher accuracy of measured data and decreasing the value of the residuum of the constraint equations.

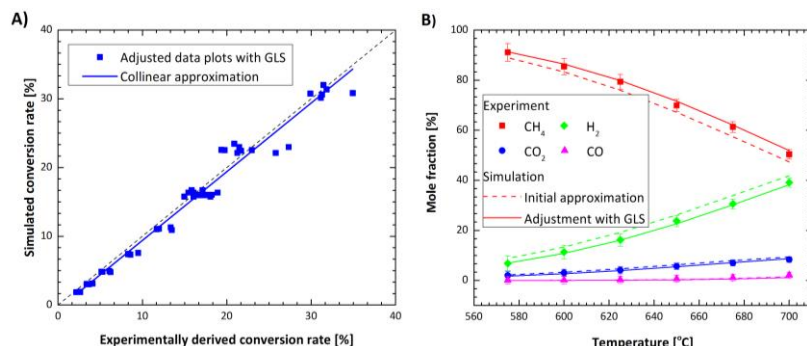


Figure 9 A) Correlation plot of the measured against the calculated conversion rates, after the GLS method applied
B) Comparison of experimental and numerical molar fraction of species (in condition of $F_{CH_4}^i=50 \text{ ml min}^{-1}$, $SC=3$, $NC=3$) for modified method and GLS algorithm

5. Conclusions

Widespread disagreements between kinetic of the reforming proceeded on the typical industrial catalysts in spite of the extensive research in the field and lack of suitable kinetic on real SOFC anode materials, induce the necessity for reliable data dedicated to SOFC design. In the scope of this research, the classical approaches adopted for estimating the reaction kinetics of methane/steam reforming processes were analysed and compared with Generalized Least Squares Algorithm. The standard and modified methods popularly adopted in the literature were compared. An improvement in the modified method for the simultaneous calculation was proposed: the appropriate reaction order was selected in terms of giving the smallest sum of the relative standard deviation found in the reaction constant for all of the temperatures simultaneously. The influence of the experimental data set for every calculated algorithm was discussed. The divergences observed in literature can be related to the applied calculation method. It is postulated that GLS algorithm can result in the significant improvement in the security of numerical modelling of the non-equilibrium chemical reactions.

6. Acknowledgements

The present study was financially supported by the Polish National Science Centre (grant no. 2015/17/N/ST8/01185).

7. References

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