

Assessment of the measurement uncertainty of the determination of the methane steam conversion catalyst activity in a 4-channel Tiomkin-type reactor

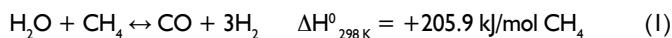
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Introduction

Steam reforming of natural gas is currently the most common process, starting the natural gas conversion to carbon monoxide and hydrogen, which are substrates for multiple syntheses of basic products vital for the economy. The process is conducted in gas heated tubular reactors filled with relevant catalyst.

The process of methane conversion with steam, represented by the equation (1), is one of the most common processes of chemical engineering.



An endothermic reaction, the equilibrium constant of which is temperature-specific (Tab. I) [1].

Table I

Data of thermodynamic reaction of methane conversion with steam acc. to [1]

Temp. °C	ΔH° , kJ/mol	ΔG° , kJ/mol	log(K)
725	224.6	-26.3	1,377
775	225.0	-38.9	1,938
825	225.3	-51.5	2,449
875	225.6	-64.1	2,916
925	225.7	-76.7	3,345
975	225.8	-89.3	3,739
1000	225.8	-95.6	3,925

According to the laws of thermodynamics, high temperature and low pressure are beneficial for the high reaction rate. In practice, process temperature reaches 850°C; pressure is 2.5 – 3.5 MPa due to the need to use reasonably sized instruments.

The reaction rate may also be described by the kinetic equation:

$$r = \frac{c_{\text{CH}_4 \text{ inlet}} - c_{\text{CH}_4 \text{ outlet}}}{m_{\text{cat}}} \cdot V = k \cdot p_{\text{CH}_4} \cdot \left(1 - \frac{p_{\text{CO}} \cdot p_{\text{H}_2}^3}{p_{\text{CH}_4} \cdot p_{\text{H}_2\text{O}} \cdot K_p} \right) \quad (2)$$

where:

r_{CH_4} – reaction rate of methane steam conversion

$c_{\text{CH}_4 \text{ inlet/outlet}}$ – methane concentration at the reactor inlet and outlet

m_{cat} – catalyst weight

k – reaction rate constant

p_{CH_4} , p_{CO} , p_{H_2} , $p_{\text{H}_2\text{O}}$ – pressure of components in the reaction mixture

K_p – equilibrium constant of methane conversion reaction.

The equation (2) is a version of equations postulated by Rostrup and Nielsen [1], used in INS, well describing the course of processes under industrial conditions (temperature in the reactor 700÷850°C, pressure 20÷35 bar). In order to ensure the necessary reaction rate, it is necessary to use suitable catalyst. The classic catalyst used in the steam reforming process is nickel catalyst applied on aluminium oxide, with admixtures, in the form of rings. Such catalysts (G-0117, G-0117-7H, G-0117-7H/C, G-0117K-7H/C, G-0217-7H/C) are manufactured by the New Chemical Syntheses Institute (INS Puławy) and commonly used in industrial plants in Poland and abroad.

The Institute has big research facilities required to maintain the high quality of production processes. One of the major tasks is to determine the activity of catalysts. As any other measurement, such determination is charged with uncertainty, the value of which is a critical component of the result. Pursuant to the principles, it can be determined [2÷6] using statistical procedures: (type A assessment method) – in case of a large number of repeated measurements; or type B method, consisting in using the knowledge of physical relations and accuracy of measuring instruments, e.g. based on the equation (2). If the determined value $W = W_{(x_1, x_2, \dots)}$ is the function of i variables, measured x_1, x_2, \dots , then the measurement uncertainty of the value W (so-called "composite uncertainty") may be estimated in the following way:

$$\Delta W = \sqrt{\sum_i \left(\frac{\partial W}{\partial x_i} \right)^2 \cdot u_{x_i}^2} \quad (3)$$

where

ΔW – composite standard uncertainty of determined value

u_{x_i} – standard uncertainty of determined value measured directly ($u_{x_i} = \text{limit uncertainty} / \sqrt{3}$)

$\partial W / \partial x_i$ – derivative partial function describing the relation between the determined value W and the value measured directly x_i .

Measurement of catalytic properties of catalysts in the reaction of steam reforming of methane

The New Chemical Syntheses Institute deals with i.a. measurements of methane conversion reaction rates, in the equipment working under the pressure 2.5 MPa (Fig. 1). The major component of such equipment is a 4-channel Tiomkin-type differential reactor, which is the specific case of a gradientless reactor [7], where the pressure of reactants in the reaction environment is the same as at the reactor outlet, which allows us to use their value in the kinetic equation (2) [8].

Methane mixed with surplus steam is fed to the reactor. Gases leaving the reactor condenses steam, and dry gas is used to determine the content of methane and carbon oxides by means of the gas chromatography method. The knowledge of water quantity fed to the reactor, the global volume of gas stream, methane concentration,

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carbon oxides in dry gas at the reactor outlet make it possible to calculate the pressure of components of the mixture reacting in the reactor, necessary for the calculation of the reaction rate constant, using the equation (2).

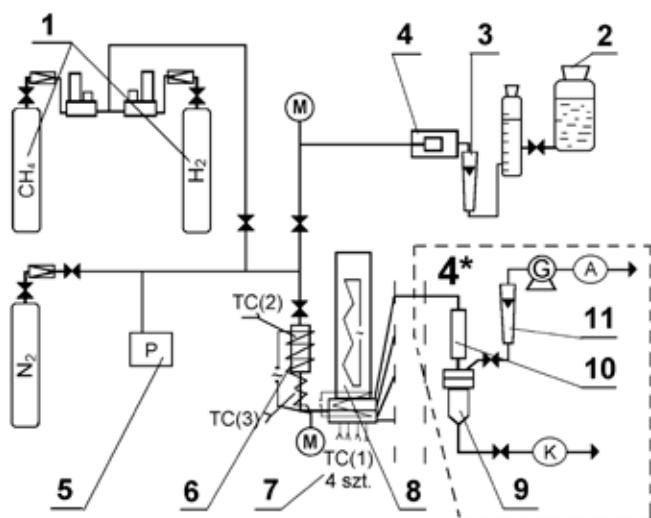


Fig. 1. Equipment measuring the activity of methane conversion catalysts in a 4-channel Tiomkin-type reactor at temperature up to 500°C, and pressure up to 2.5 MPa 1) gas cylinders; 2) water tank; 3) water flow meter; 4) water batching pump; 4*) measurement block; 5) pressure measurement and recording system; 6) steam generator; 7) thermocouples with temperature control and recording system; 8) 4-channel research reactor; 9) condensate traps; 10) water coolers; 11) post-reaction gas flow meters; TC – thermocouples; A – analysis; G – gas meter; K – condensate; M – manometer

Method for the estimation of the limit uncertainty value of the methane conversion reaction rate constant

In order to calculate the uncertainty value using the equation (3), it is necessary to have knowledge of uncertainties accompanying values directly measured in the experiment and their effect on the final result.

During the measurement process, the following values are measured:

1. $C_{\text{CH}_4 \text{ outlet}}$, CO, CO_2 – concentration of methane (at outlet), carbon monoxide and carbon dioxide, %. The knowledge of concentrations of: methane at outlet, and carbon oxides makes it possible to calculate quantities of reacted methane (carbon dioxide appears as a result of the side reaction of the conversion of some carbon monoxide with steam). After the precipitation of steam, gases discharged from each channel are subjected to chromatographic analysis (chromatograph SRI 310 fitted with methanizer and flame-ion detector FID). The limit uncertainty of determinations: CO – 0.08 %_{absol}, CH_4 – 0.4 %_{absol}, CO_2 – 0.2 %_{absol}
2. V – flow rate of reaction mixture (dry gas), dm^3/h , which is determined by the measuring time τ , s gas flow rate through burette vol. 25 cm^3 (bubble method) – typically ca. 18 s.

$$V_{[\text{dm}^3 \cdot \text{h}^{-1}]} = \frac{V_{\text{burette}} [\text{cm}^3]}{\tau [\text{s}]} \cdot \frac{0.001}{\frac{1}{1400}} = \frac{V_{\text{burette}} [\text{cm}^3]}{\tau [\text{s}]} \cdot 3.6 \quad (4)$$

Therefore, the limit uncertainty of volumetric flow rate shall be described using the following equation:

$$\Delta V = \left(\left| \frac{\partial V}{\partial V_b} \right| \Delta V_b + \left| \frac{\partial V}{\partial \tau} \right| \Delta \tau \right) 3.6 = \left(\frac{1}{\tau} \cdot \Delta V_b + \frac{V_b}{\tau^2} \cdot \Delta \tau \right) \cdot 3.6 \quad (5)$$

The value of reading uncertainty (ΔV_b) of the burette was adopted at 0.1 cm^3 (assuming that this is the accuracy of the eye catching the passing of the burette scale by the bubble membrane), and

uncertainty ($\Delta \tau$) of time measurement at 0.1 s. Therefore, the limit uncertainty of the volumetric flow rate measurement was estimated for time 18 s as follows:

$$\Delta V = [1/18 \cdot 0.1 + 25/(18)^2 \cdot 0.1] \cdot 3.6 = 0.0133, \text{ dm}^3/\text{h} \quad (5)$$

3. m_{cat} – catalyst weight, g; the limit uncertainty of measurement is 0.5 mg
4. t_0 – ambient temperature (for the calculation of volumetric flow rate), °C; with the limit uncertainty 0.5°C
5. p_a – atmospheric pressure (for the calculation of volumetric flow rate), mmHg; uncertainty of pressure reading from barometer is 0.5 mmHg
6. P_r – process pressure, MPa; reading uncertainty is 0.04 MPa (manometer range 4 MPa, accuracy class 1%)
7. t_r – temperature of catalyst bed in the reactor, °C; (thermocouple with meter EMT 100-K), instrument accuracy: $\pm 0.15\%$ range ± 1 digit, which with the range -100÷1200°C means the limit uncertainty 2.95°C (rounded to 3°C)
8. The jet of steam is also fed to the reactor, 400 g/h, measured as the volume of condensed water in the measuring cylinder with scale with steps every 5 cm^3 , time (ca. 1 hour) was measured using a stopper watch, and then obtained values were divided. The limit uncertainty adopted for the volume measurement is 2.5 cm^3 (weight = 2.5 g), and for the time measurement 1 s = 1/3600 h. Therefore, the steam jet measurement uncertainty can be determined using the equation described below:

$$\Delta s = \left| \frac{\partial s}{\partial V} \right| \Delta V + \left| \frac{\partial s}{\partial \tau} \right| \Delta \tau = \frac{1}{\tau} \Delta V + \frac{V}{\tau^2} \Delta \tau = 1 \cdot 2.5 + \frac{400}{1} \cdot \frac{1}{3600} \approx 2.5 \text{ g/h} \quad (6)$$

The composite uncertainty of the determination of the reaction rate constant can be calculated using the differential equation (3) related to the equation (2). In practice, however, such calculations are conducted in many stages, using MS EXCEL™. Therefore, partial derivatives in the equation (3) were calculated digitally by determining derivative values $\partial k / \partial x_i$ at the measuring point x_i acc. to the equation (7), where x_i are measured parameters and Δx_i are minor deviations in measured parameter, entered to the reaction rate constant calculation procedure:

$$\frac{\partial k}{\partial x_i} = \frac{k_{x_1, x_2, \dots, x_i + \Delta x_i} - k_{x_1, x_2, \dots, x_i - \Delta x_i}}{2 \Delta x_i} \quad (7)$$

Results

Pursuant to the equation (7), components of the limit uncertainty of the determination of the catalyst reaction rate constant k in the reaction of steam reforming of methane resulting from the measurement uncertainty of measured parameters were estimated. The results (following the conversion of limit uncertainties to standard uncertainties) are presented in Table 2, in lines marked with Δk . The penultimate column presents the absolute uncertainty of the composite constant k acc. to the equation (2); the last column presents the relative uncertainty.

Table 2 indicates that the uncertainty of the final result is mostly affected by the uncertainty of the measurement of carbon dioxide concentration (more than half of the total uncertainty) and – which is a little surprising – by the accuracy of the manometer indicating pressure in the reactor. The high limit uncertainty of the carbon monoxide concentration measurement as compared to the measured value ($\Delta C_{\text{CO}} = 0.08\%_{\text{absol}}$ versus $C_{\text{CO}} = 0.02$ and $0.1\%_{\text{absol}}$) does not affect the accuracy of the measurement to the extent to which the uncertainty of CO_2 concentration measurement does due to the fact that the above-mentioned values affect the result value in combination, and the effect of a much higher value of CO_2 is dominant.

Table 2

Example of the set of direct data from measurement of methane conversion catalyst activity (measurements I and 2), and components of standard uncertainties of the determination of the activity constant related to their measurement (Δk)

i=	1	2	3	4	5	6	7	8	9	10		
x (variable)	m, g	tr, °C	P, Mpa	H ₂ O g/h	Vgaz, dm ³ /h	composition of dry gas, %	CO	CH ₄	CO ₂	p atm mmHg	t amb °C	k Nm ³ CH ₄ /g h Mpa
measurement I	0.396	403	2.48	400	39.5	0.02	87.68	1.96	753	28	6.73	relative uncertainty
$\Delta k_{(xi)}$	8.5E-03		6.3E-02	1.4E-02	5.4E-04	9.7E-02	3.5E-03	2.4E-01	1.1E-03	2.7E-03	0.27	
measurement I	0.396	454	2.45	400	39.3	0.1	75.26	4.67	753	26	10.13	
$\Delta k_{(xi)}$	7.4E-03		9.5E-02	1.1E-02	1.4E-03	3.5E-02	1.0E-02	2.9E-01	2.7E-03	6.8E-03	0.31	3.0%

m – catalyst weight, tr – reaction temperature, P – reactor pressure, H₂O steam jet, V gas – the volume of gas mixture fed to the reactor, p atm – atmospheric pressure, t amb. – ambient temperature, k – reaction rate constant, $\Delta k_{(xi)}$ – standard uncertainty of the determination of the conversion rate constant resulting from the uncertainty of variable (i) measurement, $\Delta k_{(xi)} = |\partial k : \partial x_i| \times \Delta x_i / \sqrt{3}$, Δx_i – limit uncertainty of the variable (i) measurement

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Summary

Data presented in Table 2 indicate that measurements of methane conversion activity in INS are conducted with the relative standard uncertainty ca. 4–7%. The error related to the pressure measurement in the reactor appears to be surprisingly big. Replacing the 1% manometer class with a more accurate one may significantly improve the accuracy of measurements. The large share of the gas composition measurement uncertainty in the activity assessment uncertainty is not surprising, but the uncertainty of the measurement of carbon dioxide concentration in gas at the reactor outlet is dominant.

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