Introduction
Carbon monoxide conversion process described with equation (1) is one of the most widespread processes in the chemical technology

\[ \text{H}_2\text{O} + \text{CO} \leftrightarrow \text{CO}_2 + \text{H}_2 \quad \Delta H_{298K}^0 = -41.2 \text{ kJ/mol CO} \]  

(1)

This is an exothermal reaction with clearly temperature-dependent equilibrium constant \( K_{eq} \). For achieving high degree of conversion, low temperature is beneficial, but then reaction rate is low. Due to thermodynamic limitation, CO conversion process is conducted in two stages. In the first stage (high-temperature carbon monoxide conversion) the process is carried out at temp. 330–550°C in order to obtain higher reaction rates and lower CO content in the products down to approx. 2%. During the second stage (high-temperature carbon monoxide conversion) the process is conducted in lower temperature range (180–270°C). This allows lowering CO concentration to 0.1–0.2%. The stages use different catalysts: usually iron-chrome catalyst for high-temperature conversion and copper one for low-temperature conversion. Such catalysts, as well as other catalysts of processing line of natural gas to syngas are manufactured by Grupa Azoty S.A. and New Chemical Syntheses Institute (INS Pulawy). The Institute has a large research base necessary to maintain high production quality. One of the main tasks is determination of catalyst activity. As any other measurement, it is subject to some uncertainty whose value is an important part of the result. According to these rules, it can be determined \([1 – 5]\) using statistical procedures (assessment method type A), if there is sufficient number of measurement repetitions; or method type B, involving using knowledge of physical dependencies and measurement of instruments, e.g. using the equation (2). If the determined value \( W = W(x_1, x_2 \ldots) \) is a function of i measured variables \( x_1, x_2 \ldots \), then the uncertainty of quantity measurement \( W \) (so-called complex uncertainty) can be estimated in the following manner:

\[ \Delta W = \sqrt{\sum \left( \frac{\partial W}{\partial x_i} \right)^2 u_i^2} \]  

(2)

where:
- \( \Delta W \) – complex standard uncertainty of determined quantity,
- \( u_i \) – standard uncertainty of determination of directly measured quantity (boundary uncertainty /1,732),
- \( \partial W/\partial x_i \) – partial derivative of a function describing relation between the calculated quantity \( W \) and the directly measured quantity \( x_i \).

Measurement of catalytic properties of carbon monoxide conversion catalysts
New Chemical Syntheses Institute works on among others measurement of CO, carbon monoxide conversion reaction rate, which is conducted in the equipment under operational pressure of 2.5 MPa (Fig. 1). The main component of the equipment is four channel differential Tiomkin reactor (Fig. 2) allowing parallel analysis all of three catalyst samples (one channel left empty for reference). Gas leaving each channel, after steam condensation, are analysed in Hartmann analyzer to determine CO and CO\(_2\).

Fig. 1. Flow diagram of measurement equipment for measure of activity of carbon monoxide conversion catalysts
1 – gas dispensers; 2 – purification system; 3 – water metering pump; 4- steam generator; 5 – reactor; 6 – water cooler; 7 – condensate separator; 8 – gas meter; TC – thermocouples; A – analyzer.

Tiomkin reactor is a special case of gradientless reactor \([6]\) where reagent concentrations in the reaction environment is equal to their concentration at the reactor outlet, which allows using their value in the kinetic equation (3).
The equation is a variant of Bohlboro, Goodgidge and Quazi or Twigg equations [7] used in the FRI and describes well processes under industrial conditions (330–550°C – high-temperature conversion, 180–270°C – low-temperature conversion, 2.5–3.0 MPa).

\[
V = \frac{C_{\text{CO in}} - C_{\text{CO out}}}{m_{\text{cat}}} = \frac{v \cdot x_{\text{CO}} \cdot x_{\text{H}_2} \cdot x_{\text{H}_2O}}{K_{p} - \left(1 - f_{\text{H}_2O} \cdot x_{\text{CO}} \cdot x_{\text{H}_2} \cdot K_{p}\right) \cdot p^{1 + a + b + c}}
\]

where:
- \( r \) – reaction rate, \( \text{Ndm}^3\text{CO}/g_{\text{cat}} \times h \),
- \( C_{\text{CO in/outlet}} \) – CO concentration in reaction mixture (dry gas), at the inlet/outlet of the catalyst bed, \%vol,
- \( V \) – gas mixture flow rate (dry gas) through catalyst bed converted to NTP \( \text{Nm}^3/h \),
- \( m_{\text{cat}} \) – catalyst weight, g,
- \( k \) – CO reaction rate constant, \( \text{Ndm}^3\text{CO}/(g_{\text{cat}} \times h \times \text{bar}) \), \( d=0.65 \) for high-temperature conversion, \( d=0.4 \) for low-temperature conversion,
- \( X_{\text{CO}} \), \( X_{\text{CO}_2} \), \( X_{\text{H}_2} \), \( X_{\text{H}_2O} \) – mole fraction of reagents in reaction mixture (including steam),
- \( a, b, c \) – power series factor, where \( a = -0.3, b = -0.15, c = 0.1 \) for high-temperature conversion, while \( a = -0.3, b = -0.9, c = 0.6 \) for low-temperature conversion,
- \( K_{p} \) – conversion reaction equilibrium constant, dimensionless quantity,
- \( p_r \) – process pressure, bar.

A bit different set of data is directly measured, which allows calculation of activity coefficient in the equation (3).

### Methods for estimation of boundary uncertainty of reaction rate constant of carbon monoxide conversion

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

During the measurement, following quantities are measured:

1. \( C_{\text{CO in}} \) – carbon monoxide concentration in dried gas at the reactor inlet, \( C_{\text{CO out}} \) – as above at the reactor outlet, \( C_{\text{CO}_2} \) – carbon dioxide concentration. These concentrations were measured using Hartmann analyser. Instrument class 0.1%, range 0–25%, which gives measurement uncertainty of 0.025 percentage point.

2. \( V \) – reaction mixture flow, \( \text{dm}^3/h \), which is determined by time measurement, \( t, s \), gas flow through 25 ml burette (bubble method) — usually it is approx. 18 s.

Exemplary set of direct data from high temperature carbon monoxide conversion catalyst (measurement 1 - 3) and values of component standard uncertainties of determination of activity coefficient related to their measurement (\( \delta k \))

<table>
<thead>
<tr>
<th>Measurement of HTS catalyst activity of company A in 4-channel Tiomkin reactor</th>
<th>The composition of dry gas</th>
<th>Relative</th>
<th>complex</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>tr,</td>
<td>pr,</td>
<td>p atm,</td>
</tr>
<tr>
<td>measurement 1</td>
<td>°C</td>
<td>bar</td>
<td>mmHg</td>
</tr>
<tr>
<td>Δk</td>
<td>2,9E-02</td>
<td>1,2E-02</td>
<td>7,2E-04</td>
</tr>
<tr>
<td>measurement 2</td>
<td>348</td>
<td>24,9</td>
<td>745</td>
</tr>
<tr>
<td>Δk</td>
<td>1,29E-02</td>
<td>1,16E-02</td>
<td>4,26E-04</td>
</tr>
<tr>
<td>measurement 3</td>
<td>328</td>
<td>24,8</td>
<td>744</td>
</tr>
<tr>
<td>Δk</td>
<td>5,3E-03</td>
<td>1,2E-02</td>
<td>2,8E-04</td>
</tr>
</tbody>
</table>

\( \delta k \) – reaction rate constant, \( \delta V \) reaction rate, \( \delta V / \delta x \) reaction rate constant, \( \delta V / \delta p_r \) reaction rate constant, \( \delta V / \delta m_{\text{cat}} \) reaction rate constant, \( \delta V / \delta V \) reaction rate constant.
Results
Based on the equation (7), components of boundary uncertainty of determination of reaction rate constant \( k \) for catalysis in high temperature conversion of carbon monoxide resulting from the uncertainties of measured parameters were estimated. Results (after conversion of boundary uncertainties to standard ones) are presented in Table 1 in rows marked as \( \Delta k \). The last-but-one column presents absolute complex uncertainty of the constant \( k \) according to the equation (2); the last one – relative uncertainty.

Table 1 shows that highest contribution in final result uncertainty comes from the measurement of carbon monoxide and dioxide and – which may seem surprising – accuracy of manometer showing pressure in the reactor.

Analogously, uncertainty of determination of reaction rate constant \( k \) of catalyst in the low-temperature carbon monoxide conversion (Tab. 2).

Summary
Data presented in Table 1 and 2 show that measurements of activity of carbon monoxide conversion catalysts carried out at the INS have relative standard uncertainty approx. 3–7%. Error related to the measurement of doses water is not significant. Error related to the measurement of pressure in the reactor is surprisingly high. Replacing manometer of 1% class with more accurate can significantly improve measurement accuracy. It is not surprising that measurement of gas composition contributes highly to the uncertainty of activity. However, this contribution is much harder to lower them due to high equipment costs.

Literature