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Analysis of experimental errors in catalytic tests for production of synthesis gas

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Abstract

The proper determination of experimental errors in catalytic processes may be very important because experimental errors can exert a major impact upon the analysis of experimental results. For this reason, the influence of temperature upon the experimental errors observed during the combined carbon dioxide reforming and partial oxidation of methane over Pt/γ-Al_2O_3 is studied here. It is shown that fluctuations of output stream compositions may decrease more than one order of magnitude as reactor temperature increases in the range from 600 to 1100 °C during catalytic tests. Additionally, it is shown that the covariance matrix of composition measurements is not diagonal, as usually assumed, and may change very significantly with the experimental conditions. Therefore, experimental errors should not be regarded as constant and covariance matrices should not be assumed to be diagonal a priori for kinetic model building and parameter estimation. It is also shown that the covariance matrix may contain significant amount of information about the reaction mechanism, which can be used for model building and interpretation of kinetic experiments. Particularly, it is shown that the actual experimental error may be much smaller than usually obtained when covariance terms are neglected and that fluctuation of catalyst activity may concentrate most of the experimental fluctuations observed experimentally.

Keywords: Experimental error; Covariance matrix; Catalyst; Catalytic process; Synthesis gas; Combined carbon dioxide reforming and partial oxidation of methane

1. Introduction

The study of experimental errors is of paramount importance if one is interested in analyzing the performance of chemical processes and in model building. As it is well known, the quality of the experimental data can only be specified when experimental errors are known and are properly characterized with the help of statistical methods [1]. In spite of that, the proper characterization of experimental errors and the analysis of the influence of errors upon process analysis and model building are seldomly performed. This is particularly true in the field of catalysis and catalytic processes. Even when errors are introduced into the analysis, additional simplifying assumptions are usually made a priori, without any experimental support. For instance, experimental errors are often assumed to follow the normal distribution, independent variables (those manipulated by the operator to perform the experiment) are usually assumed to be free of error, and

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Nomenclature

b_{ij}	sensitivity coefficient, defined in Eq. (5)
$\underline{B}$	sensitivity matrix, defined in Eq. (5)
F	objective function, defined in Eq. (3)
h_{ij}	sensitivity coefficient, defined in Eq. (2)
$\underline{H}$	Hessian matrix, defined in Eq. (2)
Me	input mass flow rate
Ms	output mass flow rate
NE	number of experiments
$\underline{V}_\chi$	covariance matrix of experimental errors
$\hat{\underline{V}}_\chi$	covariance matrix of model prediction errors, defined in Eq. (4)
$\underline{V}_\beta$	covariance matrix of parameter uncertainties, defined in Eq. (1)
z_{ij}^k	kth evaluation of variable i at condition j
$\bar{z}_{ij}$	average of the measurements of variable i at condition j

Greek symbols

β_i	model parameters
ζ	extent of reaction
ξ_j^{im}	covariance between variables i and m at reaction condition j, defined in Eq. (8)
ρ_j^{im}	correlation coefficient between variables i and m at reaction condition j, defined in Eq. (9)
σ_{ij}	standard deviation of variable i at reaction condition j
σ_{ij}^2	variance of variable i at reaction condition j, defined in Eq. (7)
$\underline{\chi}$	vector of model predictions
$\underline{\chi}^{\mathrm{e}}$	vector of experimental measurements

measurement errors are normally assumed to be independent and constant throughout the experimental region. The main problem, though, is that the statistical interpretations of the final results obtained depend strongly on the nature of the experimental errors. Therefore, the use of those simplifying assumptions may lead to doubtful (at best) statistical interpretation of the results obtained. This has been discussed in a recent letter published by Buzzi Ferraris [2].

In the particular field of catalysis, studies of catalytic processes are usually carried out with the help of mathematical models and parameter estimation procedures. These are powerful tools for investigation of kinetic mechanisms and discrimination of kinetic models [3]. These mathematical techniques also find widespread use for estimation of kinetic parameters, such as activation energies and equilibrium constants, and interpretation of kinetic mechanisms [3–7]. Besides, these techniques are also used to describe reactor operation conditions [8], to evaluate mass and heat transfer rate constants [9–11], to study catalyst deactivation [12] and to optimize catalytic processes [13,14]. In all these cases, the proper characterization of experimental errors is very important if one is interested in analyzing the significance of the results obtained. For instance, Bard [15] shows that the covariance matrix ($\underline{V}_\beta$), that describes the parameter uncertainties during parameter estimation procedures, may be described as

$$\underline{V}_\beta = \underline{H}^{-1} \tag{1}$$

where

$$\underline{H} = [h_{ij}], \quad h_{ij} = \frac{\partial^2 F}{\partial\beta_i\,\partial\beta_j} \tag{2}$$

where β_i ($i = 1, \ldots, \mathrm{NP}$) are the model parameters and F is the objective function used for parameter estimation, usually given in the form

$$F = (\underline{\chi} - \underline{\chi}^{\mathrm{e}})^{\mathrm{T}}(\underline{V}_\chi)^{-1}(\underline{\chi} - \underline{\chi}^{\mathrm{e}}) \tag{3}$$

where $\underline{\chi}$ is a vector of model predictions, $\underline{\chi}^{\mathrm{e}}$ the vector of experimental measurements and $\underline{V}_\chi$ is the covariance matrix of experimental errors. Therefore, parameter estimates and parameter (and model) significance depend on the quality of the experimental data, summarized in $\underline{V}_\chi$. Besides, it can also be shown that the covariance matrix of the model prediction errors ($\hat{\underline{V}}_\chi$) may be given by

$$\hat{\underline{V}}_\chi = \underline{B}\,\underline{V}\beta\,\underline{B}^{\mathrm{T}} \tag{4}$$

where

$$\underline{B} = [b_{ij}], \quad b_{ij} = \frac{\partial\chi_i}{\partial\beta_j} \tag{5}$$

so that the quality of the model predictions also depend on the experimental errors. Therefore, if experimental errors are not characterized properly, all posterior statistical interpretation may be meaningless.

The importance of the proper characterization of experimental errors was shown very clearly by Cerqueira et al. [16,17], who studied how conversion and coke formation in a fluid catalytic cracking (FCC) unit depended on reactor operation conditions for different catalysts. The performances of the different catalysts were evaluated with the help of kinetic and empirical models and it was verified that independent variables were not free of errors and that the measurements of different experimental variables might be subject to significant correlations. They concluded that the use of the simplifying assumptions would lead to erroneous conclusions about the performance of the catalysts and to inefficient model discrimination.

The main objective of this paper is to provide additional experimental evidences that experimental errors may present a much more complex pattern than usually assumed a priori in catalytic tests. It is shown here that experimental errors in catalytic processes may vary very significantly with the reaction conditions, so that assuming that the experimental errors are constant may lead to a gross oversimplification of the experimental problem. In the particular case analyzed (the combined carbon dioxide reforming and partial oxidation of methane over Pt/γ-Al_2O_3), it is shown that the experimental error depends on the reaction temperature strongly and may decrease more than one order of magnitude as the reactor temperature increases from 600 to 1000 °C. It is also shown that measurement correlations are significantly different from zero in this case, so that the covariance matrix is not diagonal. Besides, covariances depend on the experimental conditions, which means that the covariance matrix may not be regarded as constant. Finally, it is shown that the covariance matrix of experimental measurements may contain a significant amount of information about the reaction mechanism, which may also be used for model building and kinetic interpretation of experimental results.

2. Experimental

2.1. Reaction tests

The reaction studied was the combined carbon dioxide reforming and partial oxidation of methane, in order to produce synthesis gas with low H_2/CO ratios, near 1 [14,18–20]. The overall reaction may be presented as

$$2CH_4 + CO_2 + \tfrac{1}{2}O_2 \rightarrow 3CO + 4H_2 \qquad (6)$$

and results from the coupling of an endothermic and an exothermic reaction [21–23].

The reaction was performed in a micro-U-shaped tubular reactor, built of quartz with cross-section diameter of 6 mm. The catalyst bed was placed in an enlarged reactor section with 15 mm of diameter and height of 25 mm. Reactor temperature was measured and controlled with a K thermocouple linked to a digital controller/programmer (Therma). The inlet flowrates of the individual gas streams were controlled with mass flow meters (MKS Instruments). Gas compositions were analyzed with a gas chromatograph (Chrompack CP 9001), using a packed column (HAYESEP D) and a thermal conductivity detector. In order to avoid condensation of water along the output lines, the temperature of the lines that connect the reactor output to the chromatograph and the temperature of the injection valve of the chromatograph were controlled and kept constant at 120 and 150 °C, respectively. As blank tests performed without catalyst at reaction conditions did not indicate any significant modification of the composition of the feed stream, homogeneous gas phase reaction along the output lines can certainly be neglected. Reactor operating pressure was kept constant and equal to the atmospheric pressure in all experiments, as the outlet gas flow rate was measured in a vent line, open to the atmosphere [14].

A 1.12% Pt/γ-Al_2O_3 catalyst was used for reaction tests, with 196 m^2/g of specific area and a metal area of 100 m^2/g_{Pt}, prepared by dry impregnation of the support (γ-Al_2O_3, AL-3916P, Engelhard Corporation Catalyst) with an aqueous solution of $Pt(NH_3)_4Cl_2$ (Aldrich, 98% purity). The reactants used were natural gas (79% CH_4, 17% C_2H_6 and 4% C_3H_8), compressed and dried air (20% O_2, 79% N_2 and 1% Ar) and ultrapure CO_2 (99.99%). Reactor feed contained $O_2/CH_4 = 0.40$ gmol/gmol and $CO_2/CH_4 = 0.37$ gmol/gmol, while the feed flow rate was equal to 0.008 ml/min. Reactions were performed in a temperature range from 600 to 1100 °C, with 0.3600 g of catalyst. The interested reader is encouraged to refer to Larentis et al. [14] for additional details regarding the experimental apparatus and procedure.

In order to estimate the experimental errors, at least five reaction runs were performed for each particular reaction condition. As explained by Cerqueira et al. [17], the accuracy of the experimental variances increases very slowly with the number of experiments when the number of replicates is larger than 5. For this reason, the number of experimental replicates was kept constant and equal to 5 in the whole manuscript, unless stated otherwise. Experimental errors were then computed as

$$\sigma_{ij}^2 = \frac{\sum_{k=1}^{\mathrm{NE}} (z_{ij}^k - \bar{z}_{ij})^2}{\mathrm{NE} - 1} \tag{7}$$

$$\xi_j^{im} = \frac{\sum_{k=1}^{\mathrm{NE}} (z_{ij}^k - \bar{z}_{ij})(z_{mj}^k - \bar{z}_{mj})}{\mathrm{NE} - 1} \tag{8}$$

$$\rho_j^{im} = \frac{\xi_j^{im}}{\sigma_{ij}\sigma_{mj}} \tag{9}$$

where σ_{ij}^2 is the variance of variable i at reaction condition j, ξ_j^{im} the covariance between variables i and m at reaction condition j, ρ_j^{im} the correlation coefficient between variables i and m at reaction condition j, z_{ij}^k the kth evaluation of variable i at condition j and $\bar{z}_{ij}$ is the average of the measurements of variable i at condition j (z_{ij}^k are the elements of χ^{e} defined in Eq. (3)). Statistical significance of experimental variances and covariances were computed with the help of the software STATISTICA [24] with the assumption that fluctuations followed the normal distribution.

It is important to say that the catalyst bed was replaced by a new load of catalyst after every experiment, in order to avoid any undesirable effect caused by coke deposition. In spite of that, after finishing the experiments, reactor temperatures were always set to the initial temperature value in order to check for possible catalyst deactivation due to coke formation. As observed in all experiments, catalyst activity did not decrease when experiments were performed at temperatures equal to or lower than 1000 °C. However, significant catalyst deactivation could be observed when temperatures were equal to or higher than 1100 °C. Besides, stability catalyst tests performed at 900 °C showed that the catalyst activity remained constant for more than 36 h. As it does not take at least 10 h for one to perform the catalyst tests, it can be assured that coke deposition does not exert any significant influence upon the experimental results obtained at temperatures equal to or lower than 1000 °C.

2.2. Chromatographic tests

In order to evaluate the errors associated with the chromatographic analysis in the temperature range from 600 to 1100 °C, blank experiments were performed in the reaction setup without catalyst, which was replaced by the support γ-Al_2O_3. Three different feed compositions were used, in order to simulate conditions of low temperature and low conversion (19% CH_4, 29% H_2, 9% CO_2, 43% N_2), of intermediate temperature and intermediate conversion (6% CH_4, 35% H_2, 60% N_2) and of high temperature and high conversion (4% CH_4, 39% H_2, 2% CO_2, 55% N_2). This was made in order to simulate the compositions obtained at low, intermediate and high temperatures and to analyze whether chromatographic procedures might concentrate on a significant part of the experimental errors. As explained before, five replicates were performed for each feed condition. At these tests, reactor temperature was kept equal to the room temperature, while the temperatures of the output feed lines were controlled and kept constant as described previously.

3. Results and discussion

The results obtained for the combined carbon dioxide reforming and partial oxidation of methane over Pt/γ-Al_2O_3 are presented in Table 1. Detailed kinetic and thermodynamic analysis of the experimental data is presented elsewhere [14]. The standard deviations of output stream concentrations for all system components (CH_4, CO, H_2, CO_2, H_2O and N_2) and for each temperature in the range of 600–1100 °C are shown in Table 2. This table shows that for all reaction components the standard deviation tends to decrease as temperature increases. More interesting, this trend may be observed both for components whose concentrations decrease with temperature (as CH_4, CO_2, H_2O) and for components whose concentrations increase for higher temperature values (as H_2 and CO), and can be verified more easily in Fig. 1, for CH_4, CO_2 and H_2.

The observed pattern of experimental errors could be associated either to the chromatographic analysis

Table 1
Experimental results obtained (z_{ij}^{k})

T (°C)	Concentrations (g mol/m^3)						
	CH_4	O_2	CO	H_2	CO_2	H_2O	N_2
700	1.146	0.000	2.576	3.861	0.520	0.580	3.842
801	0.629	0.000	3.008	3.868	0.194	0.161	3.496
900	0.402	0.000	3.018	3.682	0.070	0.000	3.216
1001	0.377	0.000	2.799	3.378	0.060	0.000	2.958
600	2.042	0.000	1.771	3.247	1.087	1.405	4.407
700	1.277	0.000	2.432	3.654	0.581	0.762	3.817
801	0.815	0.000	2.726	3.805	0.301	0.318	3.401
850	0.690	0.000	2.768	3.650	0.235	0.259	3.259
900	0.597	0.000	2.720	3.672	0.200	0.071	3.121
1001	0.511	0.000	2.629	3.406	0.139	0.000	2.888
1100	0.364	0.000	2.609	3.172	0.041	0.000	2.650
600	1.918	0.000	1.882	3.395	0.975	1.451	4.337
700	1.175	0.000	2.557	3.820	0.453	0.748	3.772
801	0.608	0.000	3.163	4.006	0.093	0.000	3.476
850	0.484	0.000	3.153	3.879	0.031	0.000	3.305
900	0.425	0.000	3.078	3.700	0.000	0.000	3.185
1001	0.391	0.000	2.795	3.442	0.019	0.000	2.918
1100	0.332	0.000	2.608	3.218	0.000	0.000	2.717
600	2.182	0.000	1.496	3.106	1.291	1.374	4.509
700	1.146	0.000	2.452	3.732	0.462	1.116	3.616
800	0.520	0.000	3.128	4.095	0.091	0.126	3.397
850	0.412	0.000	3.147	3.992	0.034	0.000	3.266
900	0.359	0.000	3.037	3.853	0.022	0.000	3.118
1000	0.306	0.000	2.818	3.560	0.016	0.000	2.873
1100	0.262	0.000	2.623	3.323	0.000	0.000	2.667
600	1.694	0.000	1.806	3.455	1.029	1.609	4.366
700	0.880	0.000	2.596	4.021	0.402	0.852	3.774
800	0.377	0.000	3.104	4.230	0.070	0.089	3.486
850	0.285	0.000	3.070	4.149	0.022	0.000	3.325
900	0.240	0.000	2.965	4.015	0.000	0.000	3.169
1000	0.190	0.000	2.756	3.683	0.000	0.000	2.943
1100	0.173	0.000	2.559	3.405	0.000	0.000	2.739
600	1.777	0.000	1.668	3.364	1.060	1.692	4.399
700	0.927	0.000	2.520	4.049	0.406	0.826	3.796
800	0.437	0.000	3.049	4.238	0.077	0.000	3.555
850	0.328	0.000	2.976	4.196	0.023	0.000	3.328
900	0.285	0.000	2.907	3.989	0.000	0.000	3.208
1000	0.215	0.000	2.698	3.704	0.000	0.000	2.956
1100	0.187	0.000	2.525	3.429	0.000	0.000	2.734

CH_4 concentrations lump the methane, ethane and propane concentrations measured through chromatography.

Table 2
Standard deviations for data presented in Table 1 (σ_{ij}, calculated from Eq. (7))

T (°C)	Concentration standard deviation (g mol/m^3)						
	CH_4	O_2	CO	H_2	CO_2	H_2O	N_2
600	0.197	0.000	0.149	0.138	0.121	0.138	0.065
700	0.154	0.000	0.067	0.156	0.069	0.176	0.080
800	0.156	0.000	0.159	0.181	0.092	0.119	0.060
850	0.160	0.000	0.159	0.221	0.093	0.116	0.032
900	0.125	0.000	0.129	0.157	0.079	0.029	0.042
1000	0.120	0.000	0.073	0.142	0.054	0.000	0.036
1100	0.085	0.000	0.041	0.112	0.019	0.000	0.040

or to inherent reaction characteristics. In order to verify the importance of the errors committed during the chromatographic analysis, tests were carried out without presence of the catalyst, as described previously. These results are shown in Table 3 and in Fig. 1. It is clear that chromatographic errors are relatively unimportant for CH_4 and CO_2, although they probably play the major role for explanation of the variances of H_2. As it is well known, determination of H_2 by chromatographic techniques is subject to large fluctuations when helium is used as carrier gas, because both gases present similar conductivities on TCD [25].

Thus, it may be said that the error variation observed as temperature increases is mostly due to the reaction system itself, which may include packing of the catalyst bed, fluctuation of reaction temperature and

Table 3
Chromatographic analysis made without catalyst

Temperature	CH_4	H_2	CO_2	N_2
Concentrations (g mol/m^3)				
Low	7.779	11.843	3.661	17.609
Intermediate	2.591	14.187	0.000	24.114
High	1.543	16.138	0.871	22.341
Low	7.831	11.591	3.705	17.765
Intermediate	2.605	14.106	0.000	24.181
High	1.568	15.792	0.898	22.634
Low	7.809	11.694	3.693	17.696
Intermediate	2.604	14.206	0.000	24.082
High	1.554	15.822	0.894	22.621
Low	7.759	11.802	3.665	17.665
Intermediate	2.585	14.354	0.000	23.953
High	1.532	16.142	0.901	22.317
Low	7.785	11.630	3.853	17.623
Intermediate	2.620	14.136	0.000	24.136
High	1.555	15.873	0.891	22.573
Concentration standard deviation (g mol/m^3)				
Low	0.028	0.108	0.079	0.062
Intermediate	0.014	0.096	0.000	0.086
High	0.014	0.173	0.012	0.155

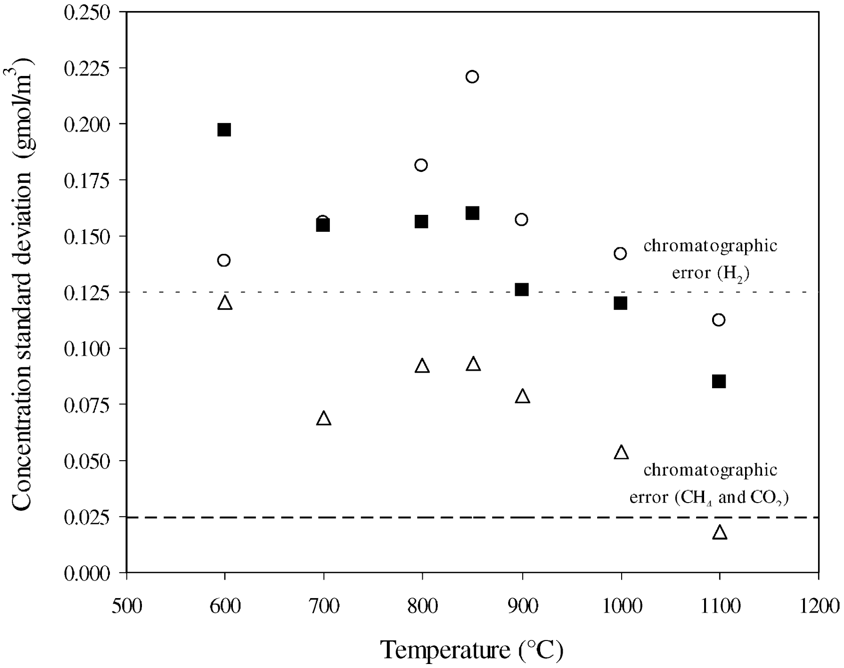

Fig. 1. Standard deviations as functions of temperature: (■) CH_4; (○) H_2; (△) CO_2.

feed compositions, etc. The experiments performed without the catalyst showed that the chromatographic analysis is not likely to be responsible for the decrease of the experimental errors observed with increasing temperatures. It is well known [3,19,26–30] that the syngas reaction network is very complex and involves many possible reactions. The reaction network includes steam reforming, carbon dioxide reforming, partial and total oxidation of methane, water–gas shift reaction, carbon formation (by *Boudouard* reaction and/or methane dehydrogenation) and carbon monoxide/carbon dioxide methanation. All these reactions can occur at temperatures above 600 °C. The observed trend is probably related to the evolution of this complex reaction network as temperature increases. For instance, it may be wondered that at the lowest temperatures, almost all of these reactions occur simultaneously. As some of these reaction steps are endothermic and others are exothermic, compositions may be very sensitive to small variations of the operation conditions, particularly the reaction temperature. At the highest temperatures, though the system becomes much more selective, in the sense that there is enough energy available to overcome intermediate activation energy barriers. Thus, the reaction system becomes controlled by a smaller number of reaction steps, leading to lower experimental fluctuations.

However, no matter what the actual sources of variation are, the fact is that data obtained at higher temperatures may be regarded as much more valuable for model building and parameter estimation then data obtained at lower temperatures. Assuming that traditional maximum-likelihood procedures are used for data analysis (see [15]), then the data can be weighed by the inverse of the variance of the experimental error observed. In this case, data obtained at the highest temperatures may be regarded to contain 4–40 times more information than data obtained at the lowest temperatures, when CH_4, CO_2 and CO are analyzed, because variances are 4–40 times smaller at the highest temperatures. This may certainly exert significant impact on model building and parameter estimation. However, this analysis is beyond the scope of this manuscript and the interested reader is encouraged to refer to Cerqueira et al. [16,17] for additional details.

Data presented in Tables 1 and 3 were also used to compute the covariance matrix of composition data at each particular reaction condition. The obtained correlation coefficients are presented in Tables 4 and 5. It is interesting to observe first in Table 5 that chromatographic measurements are not independent. This is because the area normalization procedure, used to provide gas compositions, propagates the errors through the whole set of components analyzed. In this case, the most important components are the ones with the highest concentrations: nitrogen and hydrogen. This explains why nitrogen and hydrogen correlations are not significant for low conversions and become significant for high conversions. The picture in Table 4 is completely different: correlations are much more important for methane and carbon dioxide, in spite of the much lower concentrations of these components. As observed previously, the observed pattern of experimental errors is not controlled by the chromatographic analysis, but by some inherent characteristics of the catalytic test.

Table 4 indicates very clearly that the covariance matrix of measurement fluctuations is not diagonal and is not constant in the experimental region. Cerqueira et al. [17] showed how important this fact might be for model building, parameter estimation and data analysis. Given the relatively small number of degrees of freedom used to compute correlations and as correlation significance changes for each particular experimental condition, one might wonder whether these numbers might be of any real physical significance. This question is answered in graphical forms in Figs. 2–7. It can be seen that correlation coefficients change smoothly and steadily as temperature increases in all cases analyzed, so that it can be guaranteed that the numbers presented in Table 4 were not obtained by chance and can be interpreted in physical terms.

Fig. 2 indicates that correlation coefficients between methane and hydrogen concentrations are always close to −1, indicating that methane and hydrogen always vary in opposite directions. This is easy to explain in terms of the global Eq. (6), because methane is a reactant and hydrogen is a product, as the main reaction steps are the partial oxidation and the CO_2 reforming of methane:

$$CH_4 + 0.5O_2 \rightleftharpoons CO + 2H_2 \qquad (10)$$

$$CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2 \qquad (11)$$

Table 4
Correlation coefficients of concentration measurements in Table 1 (ρ_j^{im}, calculated from Eq. (9))

	CH_4	CO	H_2	CO_2	H_2O	N_2
Temperature = 600 °C						
CH_4	1.00	−0.55	**−0.93**	0.74	**−0.89**	0.73
CO	−0.55	1.00	0.80	**−0.94**	0.18	**−0.96**
H_2	**−0.93**	0.80	1.00	**−0.91**	0.70	**−0.92**
CO_2	0.74	**−0.94**	**−0.91**	1.00	−0.48	**0.99**
H_2O	**−0.89**	0.18	0.70	−0.48	1.00	−0.43
N_2	0.73	**−0.96**	**−0.92**	0.99	−0.43	1.00
Temperature = 700 °C						
CH_4	1.00	−0.58	**−0.94**	**0.87**	−0.16	−0.01
CO	−0.58	1.00	0.72	−0.53	−0.49	0.40
H_2	**−0.94**	0.72	1.00	**−0.82**	−0.12	0.25
CO_2	**0.87**	−0.53	**−0.82**	1.00	−0.36	0.30
H_2O	−0.16	−0.49	−0.12	−0.36	1.00	**−0.93**
N_2	−0.01	0.40	0.25	0.30	**−0.93**	1.00
Temperature = 800 °C						
CH_4	1.00	−0.75	**−0.95**	**0.90**	0.73	−0.55
CO	−0.75	1.00	0.65	**−0.93**	**−0.86**	0.35
H_2	**−0.95**	0.65	1.00	**−0.89**	−0.73	0.50
CO_2	**0.90**	**−0.93**	**−0.89**	1.00	**0.90**	−0.46
H_2O	0.73	**−0.86**	−0.73	**0.90**	1.00	−0.68
N_2	−0.55	0.35	0.50	−0.46	−0.68	1.00
Temperature = 850 °C						
CH_4	1.00	−0.63	**−0.98**	**0.90**	**0.88**	−0.78
CO	−0.63	1.00	0.50	−0.87	**−0.89**	0.33
H_2	**−0.98**	0.50	1.00	−0.84	−0.82	0.80
CO_2	**0.90**	−0.87	−0.84	1.00	1.00	−0.69
H_2O	**0.88**	**−0.89**	−0.82	1.00	1.00	−0.65
N_2	−0.78	0.33	0.80	−0.69	−0.65	1.00
Temperature = 900 °C						
CH_4	1.00	−0.53	**−0.86**	**0.87**	**0.83**	−0.43
CO	−0.53	1.00	0.08	−0.80	**−0.89**	0.37
H_2	**−0.86**	0.08	1.00	−0.62	−0.46	0.11
CO_2	**0.87**	−0.80	−0.62	1.00	**0.94**	−0.45
H_2O	**0.83**	**−0.89**	−0.46	**0.94**	1.00	−0.56
N_2	−0.43	0.37	0.11	−0.45	−0.56	1.00
Temperature = 1000 °C						
CH_4	1.00	−0.31	**−0.90**	**0.88**	–	−0.48
CO	−0.31	1.00	−0.05	−0.60	–	0.06
H_2	**−0.90**	−0.05	1.00	−0.71	–	0.26
CO_2	**0.88**	−0.60	−0.71	1.00	–	−0.37
H_2O	–	–	–	–	1.00	–
N_2	−0.48	0.06	0.26	−0.37	–	1.00
Temperature = 1100 °C						
CH_4	1.00	0.77	**−0.99**	0.66	–	−0.72
CO	0.77	1.00	−0.78	0.32	–	−0.76
H_2	**−0.99**	−0.78	1.00	−0.68	–	0.69
CO_2	0.66	0.32	−0.68	1.00	–	−0.71
H_2O	–	–	–	–	1.00	–
N_2	−0.72	−0.76	0.69	−0.71	–	1.00

Numbers in bold are significant within the 95% confidence level.

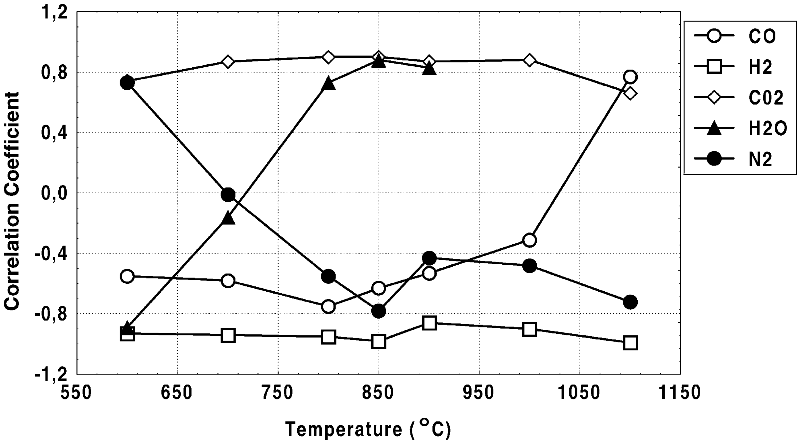

Fig. 2. Correlation coefficients for methane.

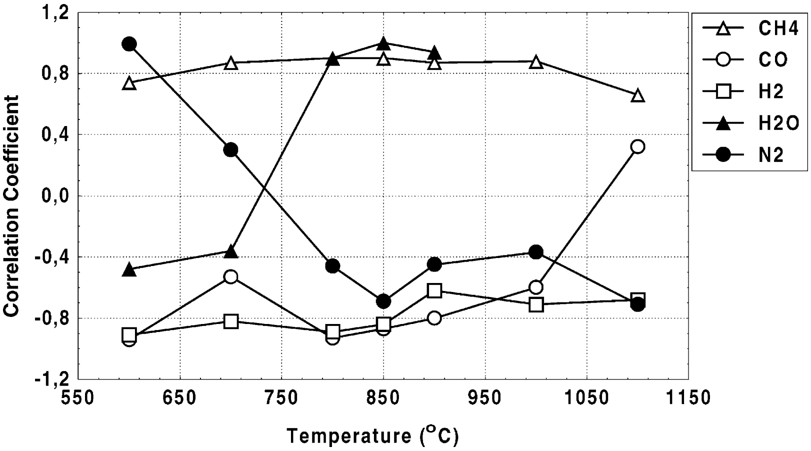

Fig. 3. Correlation coefficients for carbon dioxide.

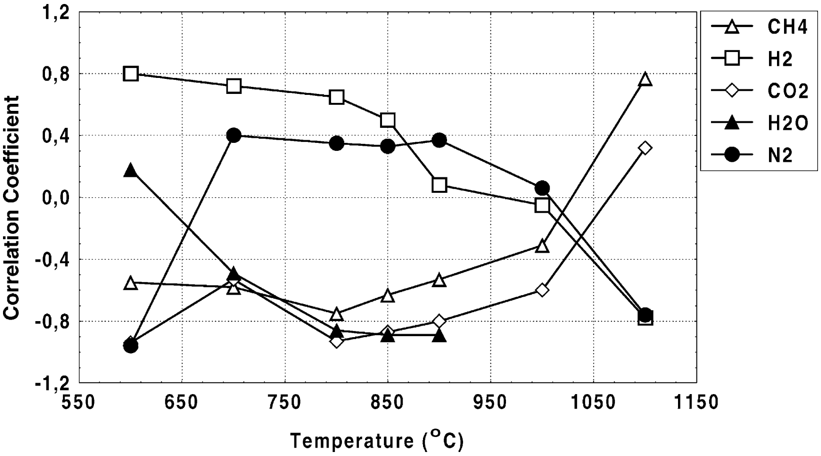

Fig. 4. Correlation coefficients for carbon monoxide.

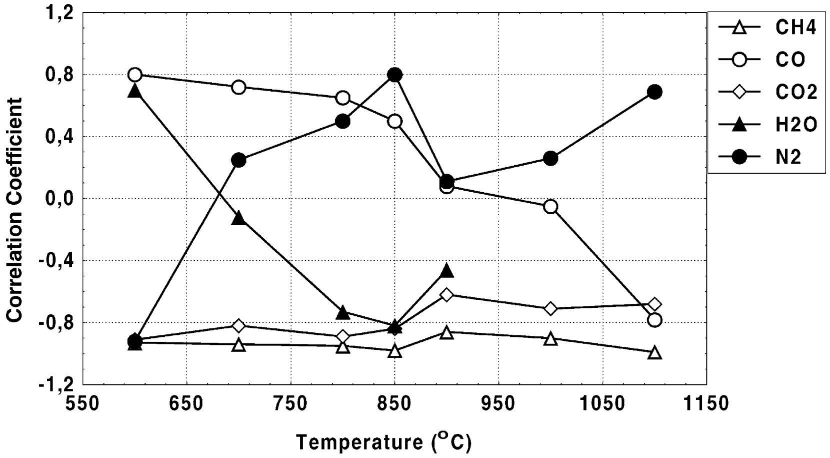

Fig. 5. Correlation coefficients for hydrogen.

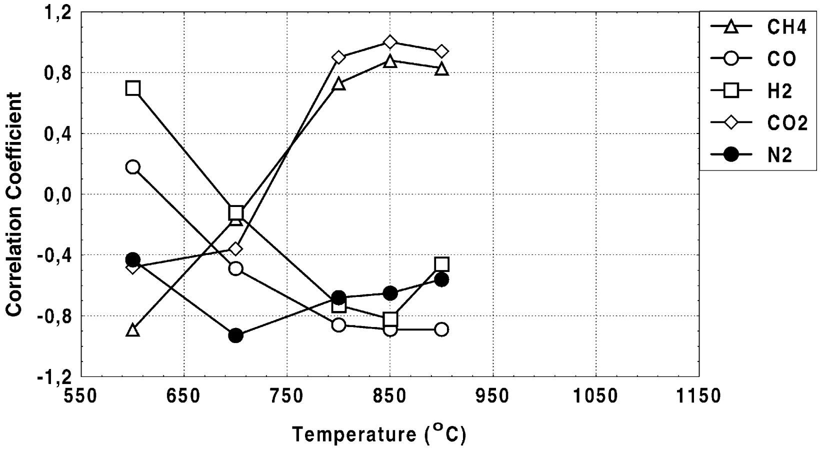

Fig. 6. Correlation coefficients for water.

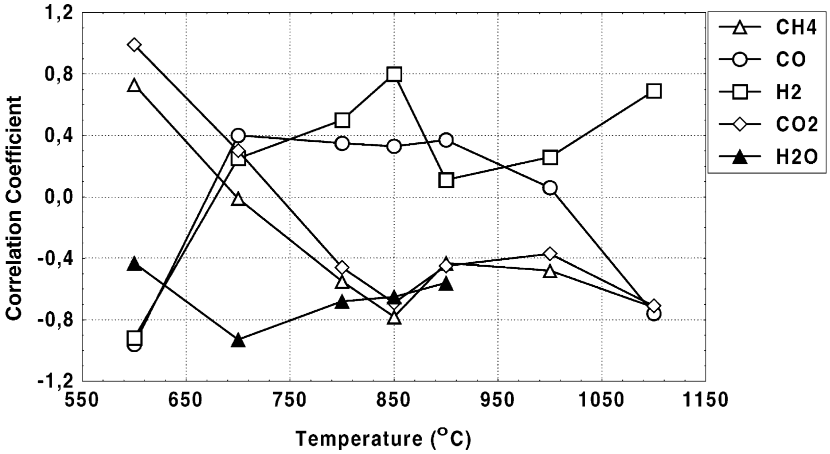

Fig. 7. Correlation coefficients for nitrogen.

Table 5
Correlation coefficients of concentration measurements in Table 3 (ρ_j^{im}, calculated from Eq. (9))

	CH_4	H_2	CO_2	N_2
Low conversion				
CH_4	1.00	−0.75	0.07	0.78
H_2	−0.75	1.00	−0.62	−0.61
CO_2	0.07	−0.62	1.00	−0.23
N_2	0.78	−0.61	−0.23	1.00
Intermediate conversion				
CH_4	1.00	−0.75	–	0.67
H_2	−0.75	1.00	–	**−0.99**
CO_2	–	–	–	–
N_2	0.67	**−0.99**	–	1.00
High conversion				
CH_4	1.00	**−0.91**	0.15	**0.91**
H_2	**−0.91**	1.00	−0.41	**−1.00**
CO_2	0.15	−0.41	1.00	0.36
N_2	**0.91**	**−1.00**	0.36	1.00

Numbers in bold are significant within the 95% confidence level.

Therefore, fluctuations are expected to occur at opposite directions if they have a common source. A similar line of thought may be used to explain why correlation coefficients between methane and carbon dioxide are always very close to 1, as Eqs. (6) and (11) indicate that these two chemical species are the main reactants. However, the behavior of the remaining correlation coefficients as temperature increases requires a deeper analysis. Regarding water, the correlation coefficient is initially very close to −1 and increases steadily, crossing the zero line around 700 °C. Initially, water is a major product of the reaction network, produced through the oxidation of methane as

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \qquad (12)$$

$$CH_4 + 1.5O_2 \rightarrow CO + 2H_2O \qquad (13)$$

This reaction is so fast that oxygen cannot be detected at the outlet stream, regardless of the reaction conditions. However, as temperature increases, the importance of the steam reforming step, given by

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \qquad (14)$$

is expected to increase, so that water becomes an important reactant. This may explain why correlation coefficients cross the zero line around 700 °C, which may be seen as the transition temperature for this particular reaction step. Regarding carbon monoxide, the correlation coefficient is initially negative and around −0.60, but grows slowly as temperature increases. When temperature reaches around 1000 °C, the correlation coefficient increases very fast to values that are close to 1. This may be explained initially in terms of Eqs. (10), (11), (13) and (14), as CO is a product of methane reforming and oxidation. However, as temperature increases above 1000 °C, significant amounts of coke are formed in the catalyst bed, as observed experimentally. The coke formation may be written as

$$2CO \rightleftharpoons C + CO_2 \qquad (15)$$

so that CO becomes a reactant of the reaction network. Therefore, as temperature increases, both methane and carbon monoxide may be subjected to fluctuations along the same direction. Regarding nitrogen, as it does not take part in any reaction, correlation coefficients reflect mostly measurement fluctuations and variations of the number of moles, caused by fluctuations of the reaction extent. For instance, as the methane concentration increases, conversion decreases. Therefore, if the correlation coefficient between methane and nitrogen is positive, it indicates that the increase of conversion causes the decrease of the nitrogen concentration, indicating the increase of the number of moles in the system. Eq. (6) indicates that the number of moles is expected to increase with conversion, which justifies the initially high positive correlation coefficients observed between methane and nitrogen. The steady reduction of the correlation coefficient as temperature increases may indicate the increase of the importance of other parallel reactions, such as the one presented in Eq. (15), and the increase of the importance of chromatographic correlations, as the methane concentration decreases steadily while the nitrogen concentration remains high (see Table 1).

When Fig. 3 is analyzed, one may observe that the same discussion presented before for methane remains valid for CO_2. This is not difficult to understand, as methane and carbon dioxide are the main reactants of the reaction network, as presented in Eq. (6). The correlation coefficients obtained for CO and shown in Fig. 4, however, present a somewhat different pattern. First, one should observe the fast variation of all correlation coefficients at higher temperatures, indicating the modification of the fluctuation patterns probably due to coke formation. Besides, the steady reduction of the correlation coefficient between H_2 and CO seems to indicate that a different source of variation appears for these two chemical species and becomes very important around 850 °C. A possible explanation is the increasing importance of the water–gas shift step, given by

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \quad (16)$$

as temperature increases. According to Eq. (16), hydrogen is a product, while CO is a reactant, leading to reduction of the correlation coefficient between the two main products of the reaction network.

Figs. 5–7 present the correlation coefficients for the other chemical species. Results presented can be interpreted as in the previous cases. For example, Fig. 5 shows that results obtained for hydrogen are similar to the ones obtained for carbon monoxide, because both of them are major products of the reaction network. Differences can be observed at higher temperatures, probably due to coke formation. It is interesting to observe that methane dehydrogenation may also lead to coke formation at high temperatures, as

$$CH_4 \rightleftharpoons C + 2H_2 \quad (17)$$

However, when coke formation is taken into consideration, in accordance with Eqs. (15) and (17), hydrogen is kept as a product of the reaction network, while carbon monoxide becomes a reactant. Fig. 6 presents the correlation coefficients for water, which can be explained in terms of the behavior of the oxidation and steam reforming reactions (Eqs. (12)–(14)) when temperature increases, as mentioned previously. Correlation coefficients for water are not shown at temperatures above 900 °C because water is not detected in the product stream at such conditions. Fig. 7 shows correlation coefficients for nitrogen. As already discussed, these correlation coefficients reflect mostly measurement fluctuations and variations of the number of moles, caused by fluctuations of the reaction extent.

The mechanistic interpretation of results presented in Table 4 and Figs. 2–7 is only possible if it is assumed that the observed fluctuations of outlet stream compositions are governed by a common source of error, such as the intrinsic fluctuation of catalyst activity. If fluctuations are governed by chromatographic errors, for instance, mechanistic interpretation of the covariance matrix does not make sense. It is important to notice that the mechanistic interpretation obtained here from the covariance matrices is consistent with the kinetic and thermodynamic results presented by Larentis et al. [14].

It is important to emphasize that the covariance matrix may be used to characterize the region where experimental fluctuations are expected to occur, as shown in Eq. (3) [1]. This region, which is normally called the confidence region, has an ellipsoidal shape whose axis may have different sizes (as a cigar) and do not necessarily coincide with the axis of coordinates of the particular measurement space analyzed. The eigenvectors of the covariance matrix may be interpreted as the directions of variable fluctuation (the axis of the ellipsis), while the eigenvalues indicate the relative importance of each individual fluctuation direction (the size of each individual axis). When the eigenvectors do not coincide with the axis of coordinates, then variable correlations cannot be neglected, as simultaneous variable fluctuations should be expected. When a small set of eigenvalues are much larger than the remaining ones, then fluctuations are expected to occur in a much smaller region of the measurement space, also indicating that certain sources of fluctuation are much more important than others.

In order to investigate whether fluctuations are indeed induced by a common source of error, the eigenvalues and eigenvectors of the covariance matrices obtained experimentally are computed at each particular experimental condition and ordered in a series of decreasing order of importance. This procedure is usually called principal component analysis (PCA) [31] and constitutes a usual tool of statistical analysis. PCA analysis has been performed here with the software STATISTICA [24] and the significant results (within the 95% confidence levels) are presented in Table 6.

The first important piece of information obtained from the PCA analysis is that the experimental covariance matrices have characteristic dimensions smaller than or equal to 3, although they are 6 × 6 matrices. This indicates that a smaller number of variables are responsible for most of the experimental variation observed. Additionally, the eigenvectors do not coincide with the axis of coordinates. This indicates that individual compositions are not allowed to fluctuate independently in the variable space, but along specific and common directions.

The second important piece of information is that the two directions concentrate on more than 80% of

Table 6
Principal directions of fluctuation, calculated using the PCA tools

	Temperature						
	700 °C		800 °C	900 °C		1000 °C	
	Factor 1	Factor 2	Factor 1	Factor 1	Factor 2	Factor 1	Factor 2
CH_4	**0.936778**	0.227175	**0.932022**	**0.927496**	0.347308	**0.978681**	−0.131465
CO	**−0.802922**	0.390904	**−0.874348**	**−0.775139**	0.504111	−0.429067	**−0.897524**
H_2	**−0.980168**	0.032180	**−0.904360**	−0.640498	**−0.763601**	**−0.833940**	0.428375
CO_2	**0.860441**	0.466245	**0.975837**	**0.971046**	0.003992	**0.947729**	0.240947
H_2O	0.097553	**−0.989425**	**0.927605**	**0.969639**	−0.201742	–	–
N_2	−0.182074	**0.944998**	−0.637789	−0.565840	0.404206	−0.529242	0.241004
Explained variance	0.544332	0.382470	0.778417	0.679105	0.193656	0.603131	0.224495

Numbers in bold are significant within the 95% confidence level.

the total experimental variance observed in all cases. Besides, in all cases the most important direction of fluctuation establishes a clear link among the main reactants (methane, CO_2 and water) and the main reaction products (CO and hydrogen). The second most important direction seems to indicate changes of the reaction mechanism. At lower temperatures, the relevant nitrogen loading (eigenvector component) may be an indication of the relative importance of chromatographic errors or of the volumetric reaction effects, as discussed previously. As temperature increases, these effects become less important due to the development of the water gas shift reaction (Eq. (16)) above 850 °C and of the coke formation (Eq. (15)) above 1000 °C. This may explain the significant changes of hydrogen and carbon monoxide loadings. Therefore, PCA analysis seems to confirm the hypothesis that the observed fluctuations respond to common sources of error and that the mechanistic interpretation of the covariance matrix is indeed possible. Thus, it is very likely that fluctuation of catalyst activity is the main source of fluctuation in the system analyzed.

Catalyst activity may change during catalyst tests for a number of reasons. First, temperature fluctuations within 5 °C are normal in this type of experiment due to limitations of the experimental apparatus, due to the high temperatures required for reaction tests and due to the high exotermicity of the overall chemical reaction. This may lead, for instance, to development of undetected hot spots in the catalyst bed. Second, it is impossible to reproduce flow conditions exactly from one experiment to the other, especially when the catalyst bed has to be replaced.

The results presented indicate that the analysis of the covariance matrix of experimental errors obtained through replication of experiments may be valuable for interpretation of reaction mechanisms. This fact has been completely neglected in the technical literature. In a certain sense, PCA and correlation analysis may provide a local interpretation of the kinetic mechanism, as results obtained depend on the small fluctuations that occur around a nominal set point. Therefore, the mechanistic interpretation of the covariance matrix of experimental data may be linked to a group of mathematical techniques used for analysis of complex reaction mechanisms called “sensitivity analysis” [32,33]. The sensitivity analysis consists in perturbing certain process variables and analyzing the effects upon certain process responses. If the magnitudes of the process perturbations are small, then one is able to observe the local effects of process inputs upon the process outputs. Both process inputs and process outputs, and process perturbations are defined and controlled by the analyst. In the particular case analyzed here, process perturbations are not known and not controlled because the experiments are supposed to be replicates. Therefore, the technique presented here is used to characterize the experimental errors; however, if the main error sources are not the measurement errors, as observed in the example analyzed, then local mechanistic interpretation of the covariance matrix of experimental errors becomes possible. As kinetic experiments are rather complex and involve a number of factors that cannot be completely controlled and can be more important than measurement errors, it is very likely that covariance matrices of experimental errors can provide valuable local mechanistic interpretation for a large number of complex kinetic systems.

It is also important to emphasize that the correlation and PCA analysis indicated that experimental fluctuations of output responses could not be described by independent normal distributions, as usually assumed during the analysis of the reaction data. This is because the main error sources may not be the measurement errors, but factors linked to the overall experimental procedure. As a consequence, the covariance matrix of the experimental errors may not be diagonal and the simple computation of variances of output responses may provide a very bad overestimation of the actual measurement errors. Given the results presented by Cerqueira et al. [16,17], one should make efforts to improve the characterization of experimental errors in catalytic experiments; otherwise, statistical analysis may indeed be a meaningless exercise.

In order to illustrate how important the computation of covariance matrices can be for proper kinetic modeling and correct interpretation of experimental results, a very simple problem is proposed below. Based on the results presented previously by Larentis et al. [14] and due to lack of space, detailed kinetic modeling is not pursued here. Instead of that, a simple data reconciliation procedure is proposed, by assuming a priori that the following kinetic mechanism is valid to describe the reaction network:

$$CH_4 + 0.5O_2 \rightleftharpoons CO + 2H_2 \tag{10}$$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \tag{12}$$

$$CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2 \tag{11}$$

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \tag{14}$$

Based on the discussion presented in the previous paragraphs, these reaction steps are assumed to be the most important ones for interpretation of the obtained experimental data. In this case, the model equations become

$$Me_1 - Ms_1 - \zeta_1 - \zeta_2 - \zeta_3 - \zeta_4 = 0 \tag{18}$$

$$Me_2 - Ms_2 - 0.5\zeta_1 - 2\zeta_2 = 0 \tag{19}$$

$$Me_3 - Ms_3 + \zeta_2 - \zeta_3 = 0 \tag{20}$$

$$Me_4 - Ms_4 + \zeta_1 + 2\zeta_2 + \zeta_4 = 0 \tag{21}$$

$$Me_5 - Ms_5 + 2\zeta_2 - \zeta_4 = 0 \tag{22}$$

$$Me_6 - Ms_6 + 2\zeta_1 + 2\zeta_3 + 3\zeta_4 = 0 \tag{23}$$

$$Me_7 - Ms_7 = 0 \tag{24}$$

where Me and Ms are input and output mass flow rates (mol/min, the subscripts 1, 2, 3, 4, 5, 6 and 7 stand for methane, oxygen, carbon dioxide, carbon monoxide, water, hydrogen and nitrogen, respectively) and ζ are the extents of reaction (the subscripts 1, 2, 3 and 4 stand for Eqs. (10), (12), (11) and (14), respectively). By providing a set of input and output mass flow rates it is possible to estimate the extents of reaction. In order to illustrate the procedure, the first set of experimental data obtained at 700 °C and shown in Table 1 is used for estimation of the reaction extents. Two different procedures were used: usual least squares estimation and maximum-likelihood estimation, using the full covariance matrices as described by Cerqueira et al. [16,17]. Results obtained are presented in Tables 7 and 8.

Table 7 shows that both final parameter estimates and model results are very different in both cases. Particularly, when the least squares estimator is used, the confidence regions for parameter estimates are too large, which means that none of them are significant. Besides, model predicts the existence of detectable amounts of oxygen in the output stream, which has never been confirmed experimentally. Finally, model results indicate that steam reforming of methane is the most important reaction in this case, which can be supported neither by independent available data [14] nor by thermodynamic analysis. When the maximum-likelihood is used, results obtained are much more consistent. First, parameter estimates are much more precise and all of them are significant; second, the main reactions observed are the partial oxidation and the CO_2 reforming of methane, as expected; third, no oxygen is predicted at the output stream. Table 8 also shows that the least squares estimator is unable to detect the fact that some model parameters are correlated very strongly. The existence of such strong correlations is relatively easy to understand if the experimental data and the model equations are compared to each other. For instance, as there is no oxygen at the output stream, Eq. (19) indicates that ζ_1 and ζ_2 should vary in opposite directions, as detected by the maximum-likelihood estimator. Also, in order to keep the water concentration at low levels, Eq. (22) indicates that ζ_2 and ζ_4 should

Table 7
Data reconciliation results

Variable	Least squares	Maximum-likelihood	Measured data
ζ_1 (mmol/min)	6.392 ± 9.526	9.403 ± 0.961	–
ζ_2 (mmol/min)	3.519 ± 6.180	3.159 ± 0.240	–
ζ_3 (mmol/min)	2.300 ± 13.506	5.195 ± 0.532	–
ζ_4 (mmol/min)	7.285 ± 10.640	2.232 ± 0.987	–
CH_4 (mol/m^3)	1.141	1.093	1.146
O_2 (mol/m^3)	0.077	0.000	0.000
CO (mol/m^3)	2.025	1.755	2.576
H_2 (mol/m^3)	3.835	3.508	3.861
CO_2 (mol/m^3)	1.108	0.790	0.520
H_2O (mol/m^3)	0.582	1.665	0.580
N_2 (mol/m^3)	3.00	3.00	3.842

Confidence intervals computed for 95% of confidence.

Table 8
Parameter correlations after data reconciliation results

	ζ_1	ζ_2	ζ_3	ζ_4
Least squares				
ζ_1	1.00	−0.51	−0.59	0.14
ζ_2	−0.51	1.00	0.16	0.29
ζ_3	−0.59	0.16	1.00	−0.24
ζ_4	0.14	0.29	−0.24	1.00
Maximum-likelihood				
ζ_1	1.00	−1.00	0.21	−1.00
ζ_2	−1.00	1.00	−0.21	1.00
ζ_3	0.21	−0.21	1.00	−0.24
ζ_4	−1.00	1.00	−0.24	1.00

vary along the same direction. Therefore, based on the model described by Eqs. (18)–(24) and on the error information contained by the full covariance matrix, the maximum-likelihood estimator indicates that the number of independent reaction steps is not larger than two, in accordance with the previously performed PCA analysis. It must be clear, though, that we do not intend to defend the proposed model here, but to stress that taking the full covariance matrix into consideration during the analysis of reaction data can be of fundamental importance.

4. Conclusions

The influence of the reaction temperature on the experimental error was studied in the combined process of carbon dioxide reforming and partial oxidation of methane. It was verified that the standard deviations of reactants and products concentrations tend to decrease for higher reaction temperatures and that this behavior is mostly due to the reaction procedure and not due to the chromatographic analysis. From a practical point of view, the results obtained show that the amount of information may increase 40 times as temperature increases from 600 to 1000 °C.

The analysis of the covariance matrix of experimental errors through correlation and PCA analysis showed that the experimental errors of the many process variables may be significantly correlated. Besides, it was shown that this matrix may provide valuable information about the local reaction mechanism of the reaction system when the measurement errors are not the main sources of fluctuation, as commonly observed in catalytic systems.

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