

Estimation of RWGS kinetic parameters for methanol production

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The hydrogenation process of Natural Gas (NG) with high CO₂ content can potentially be employed for a novel process of methanol production that avoids CO₂ extraction and emission, at the same time yielding high CO₂ conversion to methanol. However, the required hydrogenation reactor has not yet been designed in detail because kinetic information of the Reverse Water Gas Shift (RWGS) reaction, which is indispensable for its simulation, is unavailable. In this paper, the kinetics of the RWGS reaction over a Pd-Ce/ α -Al₂O₃ catalyst is analyzed for mixtures of CO₂-CH₄-H₂. The reaction rate expression is experimentally obtained using an isothermal fixed-bed reactor at 600 °C and 1.62 bar. The experimental results demonstrated the absence of the dry reforming reaction and a negligible activity for methanation. The mass balance equation for a pseudo-homogeneous one-dimension reactor model was solved firstly assuming a power-law (PL) model and then, a Langmuir-Hinshelwood-Hougen-Watson (LH-HW) approach in order to obtain the kinetic parameters. By pre-processing the data set with an evolutionary algorithm before applying the Levenberg-Marquardt method, satisfactory results were obtained. The achieved rate equations will be useful to carry out improvements in the simulation and economic analysis of the process of interest.

1. Introduction

Over the past decade a subject of considerable research interest has been the production of methanol or other valuable chemicals from CO₂ hydrogenation, with the main objective of reducing emissions. Methanol is an important primary raw material for the energy and chemical industries, due to its wide range of applications. For methanol production, the generation of synthesis gas (syngas) is required, which is a mixture that essentially contains H₂, CO and CO₂ in appropriate proportions. Syngas generation is usually achieved through the well-known steam reforming (SR) process applied to NG. This process operates at high temperature (850 °C - 900°C) and the reaction is endothermic. Hence, its high energy consumption gives rise to significant CO₂ emissions. In the last decade studies have been intensified on different processes that use CO₂ as raw material, Although the main difficulties of the related technologies have already been removed, practical implementations are limited by the high costs of pure hydrogen. As an alternative, a process based on the direct use of natural gas (NG) with a high CO₂ content as raw material has been proposed (Cañete et al., 2014). It was demonstrated that an option, which is valid from the technical and economic point of view, is using NG with high CO₂ content as raw material. By means of the combined reforming (CR) process, i.e. making simultaneous use of the SR and dry reforming reactions, it is possible to generate syngas at lower cost and energy consumption. In Argentina there are numerous NG deposits with high CO₂ content, justifying their eventual use to produce methanol.

However, when the CO₂ content is higher than 30 %, it is necessary to reduce the CO₂ concentration to maintain the above mentioned advantages. This could be accomplished by partial hydrogenation of the feed mixture prior to syngas generation via CR (Cañete et al, 2017). Therefore, a suitable catalyst is necessary to carry out the reverse water gas shift (RWGS) reaction and the correspondent kinetic equation becomes indispensable for

proper reactor design and process simulation. In Cañete et al. (2017) a kinetic equation that had been derived for a standard water gas shift (WGS) reaction catalyst (Joo, 1999) was employed. Hence, it was unsuitable for high temperature operation. With a view to confirming or modifying the economic conclusions of the mentioned process, an equation derived for an appropriate catalyst is required.

Since kinetic expressions for the RWGS reaction in CH₄ presence are lacking, the kinetic study of a low-loaded Pd-Ce/ α -Al₂O₃ catalyst has been carried out. The experimental work and the methodology applied to obtain the corresponding kinetic parameters are summarized below.

2. Kinetic Modelling

2.1 Background

In the 1950s, presumably due to the advent of computers in chemical engineering, kinetic modeling in heterogeneous catalysis had a great impulse and various techniques for the determination and analysis of the parameters were studied. In Mezaki and Kittrell (1967) kinetic models and classical construction methods are described, warning that, in many cases, the conclusions had to be extracted from small sets of unclear kinetic data. Therefore, they emphasized the importance of the adequate experimental design to avoid ambiguous conclusions. They recommended an efficient experimental strategy that involves making a continuous iteration between the computational modeling and the experimentation inside the laboratory. In turn, Seinfeld (1970) suggested using non-linear estimates to find kinetic parameters from experimental reactor data and he discussed theoretically about the accuracy of estimates in Ordinary Differential Equations (ODEs), stating that it is necessary to compute the corresponding sensitivity coefficient.

The effect of temperature on rate equations should be taken into account. Xu and Froment (1989) reported kinetic equations for the design, simulation and optimization of an industrial reformer that are still used. They studied the reforming, methanation and RWGS reactions by making distinctions for different temperature ranges. At low temperatures (300-400 °C), the kinetic parameters of the RWGS and methanation reactions were obtained, whereas the determination of SR kinetic parameters was performed at higher temperatures (400-575 °C). Assuming different elementary stages, a large number of kinetic models were derived for these reactions by the well-known Langmuir-Hinshelwood-Hougen-Watson (L-H-H-W) method. Finally, the parametric adjustment was made by using experimental data that had been attained at all temperatures.

Later, Hou and Hughes (2001) studied the SR reaction on Ni/ α -Al₂O₃, also separating the main reaction of RWGS into different temperature intervals. The experimental results of CH₄ and CO₂ conversions as a function of W/F were correlated by polynomials, and the corresponding reaction speeds were obtained by derivation. Six kinetic models were proposed by using different elementary stages, the approach being similar to Xu and Froment's (1989). The optimal kinetic parameters were obtained by applying the least-squares method to the difference between the experimental reaction speeds and those estimated by the model. According to the authors, the detected discrepancies with Xu & Froment's modelling had arisen due to the characteristics of the catalyst.

2.2 Reactions

When NG with high CO₂ content is combined with H₂, the RWGS reaction (Eq. 1) takes place. Other reactions, such as dry reforming and methanation, may also occur, but they are absent on the selected PdCe/ α -Al₂O₃ catalyst.



In this analysis a homogeneous one-dimensional model for an isothermal fixed-bed reactor was adopted. Eq. 2 is the corresponding mass balance equation for the *i*-th component in the reaction, where X_i is the conversion of the *i*-th component, r_i is its reaction rate in gmol/ h g_{cat}, F_i^0 is the initial molar flowrate of the feed and W is the catalyst mass expressed in g.

$$\frac{dX_i}{d(W/F_i^0)} = r_i \quad (2)$$

As to the rate equation for RWGS, r_{RWGS} , the following main approaches were applied: power-law (PL) and Langmuir-Hinshelwood-Hougen-Watson (LH-HW). PL (Eq. 3) is the simplest model that can give an overview of the reaction process. Equations based on the LH-HW theory make assumptions on the sequence of elementary steps that are involved, based on either known or assumed mechanisms. In this work, the LH-HW equation (Eq. 4 and Eq. 5) was derived using information from a very recent study (Nelson and Szanyi, 2020). The authors demonstrated that the RWGS reaction on Pd/ Al₂O₃ takes place on Pd atoms located on the metal-

support interface (Pd), with the participation of OH groups on the support surface to form intermediate carboxyl species (COHPd). The rate determining step for the reaction was assumed to be the interaction between a CO₂ molecule on Pd atoms and OH groups. It is also important to remark that the mentioned study was based on RWGS study at lower temperature (≤ 300 °C). Using a similar sequence of elementary steps, but taking into account the reversible character of the RWGS reaction a LH-HW type equation for the prepared catalyst (Eq.4) has been derived.

In Eq.4, K_1 is a constant that combine the equilibrium adsorption of H₂ on Pd and also to the formation of OH groups on Ce. In contrast, K'_0 is a constant that combines the equilibrium of the carboxylate decomposition step and the equilibrium adsorption of H₂. In the formulation of both Eq.3 and Eq.4, the equilibrium constant for the RWGS reaction at 600 °C is $K_{RWGS}=0.37$ and the partial pressure of CO, p_{CO} , is squared because there were equal concentrations of CO and H₂O in the experiments due to the absence of other reactions.

$$r_{RWGS} = k_f p_{CO_2}^\alpha p_{H_2}^\varepsilon p_{CO}^\gamma \left[1 - \frac{1}{K_{RWGS}} p_{CO_2}^{-1} p_{H_2}^{-1} p_{CO}^2 \right] \quad (3)$$

$$r_{RWGS} = k_f \left(p_{CO_2} p_{H_2} - \frac{p_{CO}^2}{K_{RWGS}} \right) / den \quad (4)$$

$$den = (1 + K_1 p_{H_2})(1 + K_{CO_2} p_{CO_2} + K'_0 p_{CO}^2) \quad (5)$$

3. Methodology

3.1 Experimental approach

The experimental work was carried out at 600°C and 1.6 bar with CO₂-CH₄-H₂-Ar mixtures on a Pd (0.08 %) Ce (3.84 %) / α -Al₂O₃ catalyst. Pd (≈ 1 %) - Ce catalysts supported on α -Al₂O₃ were used earlier (Costilla, 2012) for the dry reforming reaction above 600 °C. It was demonstrated that the presence of Ce (0.3 % - 2.5 %) avoided C deposition, while enhancing the RWGS reaction. Further studies indicated that the Pd amount could be reduced to very low levels (< 0.1 %) to suppress the dry reforming reaction. For the present study, the sample was prepared by depositing Ce firstly using Ce(NH₄)₂(NO₃)₆ as precursor, followed by Pd addition with a benzene solution of Pd(C₅H₇O₂)₂ (1.5 cm³/g). In CH₄ presence, the dry reforming reaction was not observed and a high CO₂ conversion for the RWGS was maintained. In addition, the methanation reaction leads to negligible levels of CH₄ formation.

A significant advantage of this catalyst is the absence of deactivation processes. For this Pd-Ce catalyst no carbonaceous deposits are present, in contrast with a commercial Ni catalyst, where C formation cannot be avoided in the absence of H₂O (Genovese et al, 2020).

For a set of 52 runs, Pd-Ce/ α -Al₂O₃ catalyst masses in the range of 10-100 mg were used. Catalyst particles of approximately 0.3 mm were employed. Eight feed compositions and the catalyst loads that had been selected are shown in Figure 1, with total flow rates in the range 99-127 cm³/min. It should be remarked that the CH₄ concentration was held constant, while the H₂ and CO₂ contents were varied.

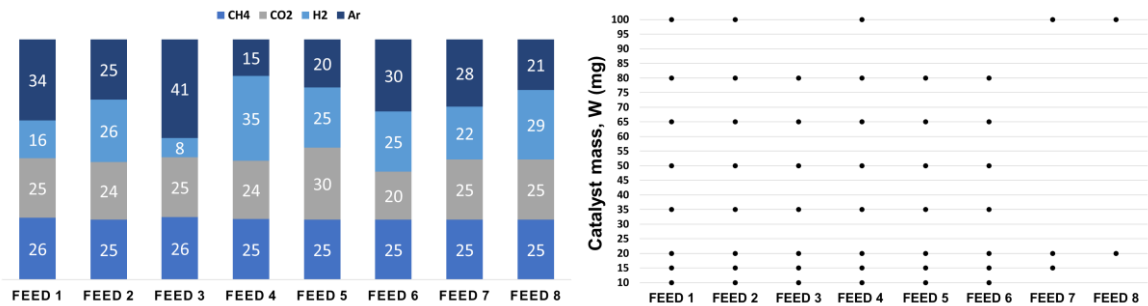


Figure 1. Volumetric composition of each feed and catalyst loads for the experimental tests.

Experimental data were obtained in a reactor formed by a quartz tube of 1 m long and 5 mm in diameter located inside a Lindberg-Blue M electric furnace, which has 3 independent heating zones. The dead volume in the tube reactor was minimized by using quartz rods to avoid the homogeneous reaction. The reactor was fed by CH₄, H₂, CO₂ and Ar gas cylinders regulated by a controller and their respective mass flow meters. The furnace output was fed to a water trap, which was a fixed bed of silica gel and a molecular sieve. Then, it was analyzed in a

Perkin Elmer Autosystem gas chromatograph that operated with a thermal conductivity detector (TCD). The temperature of the catalyst bed (600 °C) was determined with a K-type thermocouple and the pressure, with a low pressure manometer (1.6 bar). Before each run, the fresh catalyst was reduced with a hydrogen stream for half an hour at 500 °C. Then, it was heated in pure Ar up to 600 °C. After the flow rate had been switched to the feed mixture, the system was monitored for 2 or 3 h to ensure that the composition of reactants and products corresponded to the steady state.

3.2 Numerical approach

Two kinetic equations were proposed to model the RWGS reaction on a Pd-Ce/ α -Al₂O₃ catalyst. The kinetic parameters for a PL and an LH-HW model were obtained from experimental data obtained at 600 °C and constant pressure.

The experimental information was employed to fit the kinetic parameters by using the well-known Levenberg-Marquardt method (Moré, 1977), which is a robust technique that has widely been applied to least-squares problems. Prior to the optimization, a pre-processing task had to be performed since the behavior of the Levenberg-Marquardt (LM) method was unsatisfactory since it was rather slow and strongly dependent on the initialization. Apparently, it was being trapped in a local minimum.

To overcome this problem, an evolutionary algorithm (EA) was employed to split the data in order to find a well-posed subset. For regression tasks involving small kinetics datasets, pre-processing the data with optimized bias values that are close to the global optimal solution helps to bypass the traps of the local optimal solution. In real problems the bias can be substantial. The generalization error can be broken down into bias and variance. This decomposition poses a dilemma among them, known as "the bias-variance dilemma", this one being a well-known phenomenon in machine learning (Hastie et al., 2017). The origin of this dilemma arises from the attempts to simultaneously minimize these two different sources of error. The ideal state is to achieve a dataset that simultaneously exhibits the lowest bias together with the lowest variance values. Taking into account this approach, the experimental data were classified by means of an EA whose fitness function was related to the Mahalanobis distance model (Cuadras, 2019). This preprocessing helped to search for the optimum because the LM performance improved significantly. Since the extracted data were still adequate experimental data, they were employed for validation purposes.

4. Results and discussion

Fifty-two experiments were carried out, which allowed to obtain CO₂ conversions in the range of 10-35 %, while CH₄ formation was kept below 2 %. The conversion was in the 10-15% range for a few runs, but differential conditions were not assumed to process the data. The absence of intraparticle mass transfer and heat resistance was verified by applying the Weisz criterion (Schulz et al., 2005). In order to verify the absence of interphase CO₂ concentration gradient, the procedure described by Froment et al. (2010) was employed. The highest initial reaction rate, which corresponds to 36% H₂ concentration, was adopted for these calculations. For intraparticle and interphase transport the mentioned criteria were fully satisfied. Regarding the presence of interphase temperature gradients, the criterion proposed by Mears was applied (Mears, 1971). In this case the results cast some doubts about the absence of temperature differences, mainly at the reactor entrance where the rates were higher.

The mass balance equation for the pseudo-homogeneous one-dimensional reactor model was solved firstly employing the PL equation and then, the LH-HW model, in order to obtain the kinetic parameters reported on Table 1.

Table 1. Kinetic parameters for both PL and LH-HW equations.

Approach	Kinetic parameters			
PL	K	α	ξ	γ
PL	0.0768±0.00001	0.9438±0.00004	0.7982±0.00009	-1.2348±0.00002
LH-HW	K _f	K ₁	K _{CO₂}	K' ₀
LH-HW	26.8317±0.0002	1.1394±0.00001	0.7244±0.00002	1085±0,004

Satisfactory agreement between experimental and model predicted data was obtained. The estimated errors in the kinetic parameters correspond to the upper and lower levels of the 95 % confidence intervals. To assess the standard deviation the data of 60 (PL) and 40 (LH-HW) executions were used. Figure 2 shows a parity plot that exhibits the good correlation of predicted and experimental conversions for the PL equation.

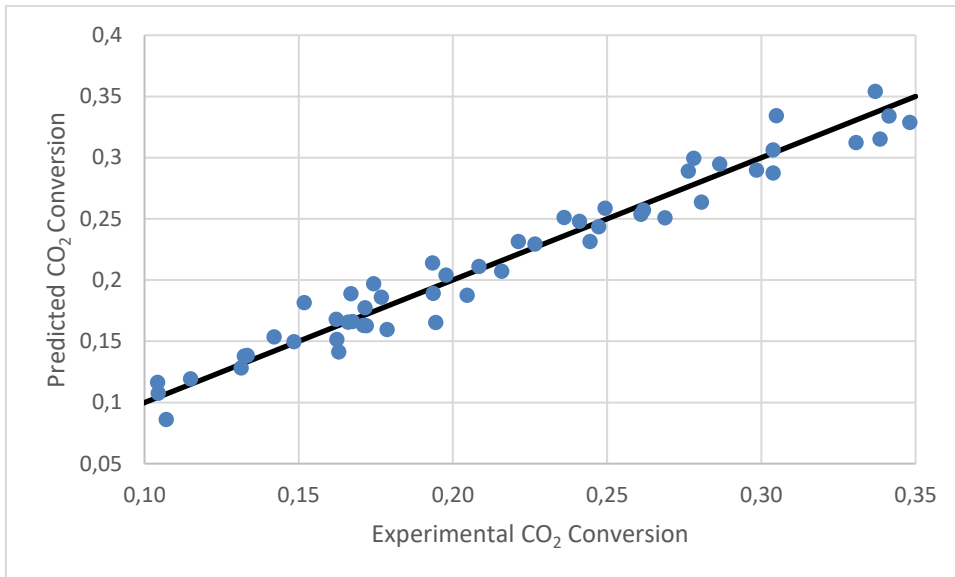


Figure 2. Parity plot for PL kinetics

Experimental datasets in chemical engineering are commonly limited in size. Despite the small datasets, both models achieved high accuracy, as can be noticed in the confidence intervals. The canonic LM optimizer was very effective for the PL model, but it proved to be slow, erratic and strongly dependent on the initialization for the LH-HW problem. Numerical problems of sensitivity and inefficiency arose in the first attempt. The convergence behavior was erratic, depending on the initial parameters. A key aspect that had to be considered was the judicious choice of initial estimates. In this work, a simplified regression model was chosen to find a proper initialization. First of all, a logarithmic rearrangement was applied to the reaction rate equation. Then, Mac Laurin series were used to avoid loss of significance. In the first place, parameter fitting was carried out for the linearized rate equation only, without solving the differential equations. Once the initial values had been obtained, the parameters were fit using the complete model.

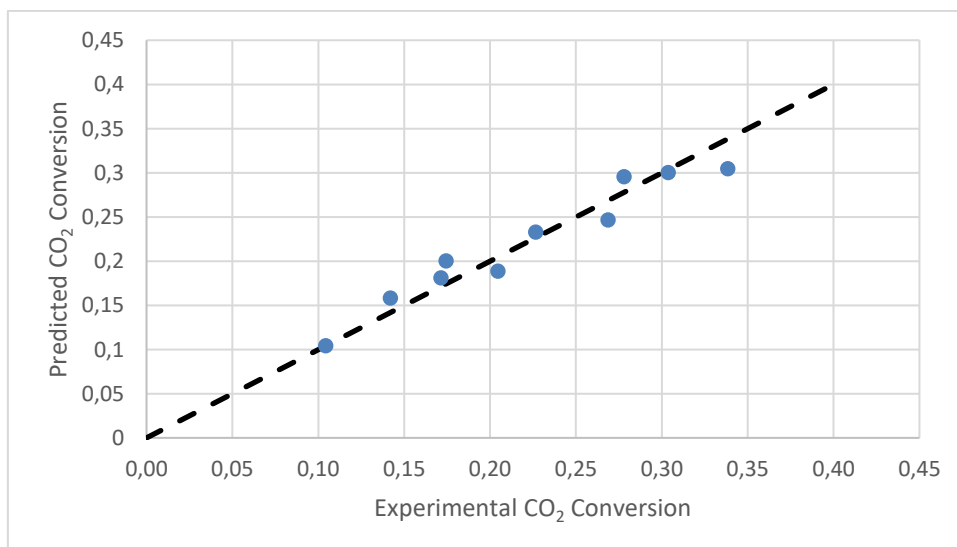


Figure 3. Validation of the LH-HW model for the 80-20 % split.

Nevertheless, the anomalous LM performance was avoided by resorting to data splitting. It was necessary to make the fitting problem easier by choosing the best data subset from a statistical viewpoint. The dataset was split in 80-20 % with an evolutionary algorithm that could individualize the 80 % data points with the lowest bias and variance within the experimental dataset. LM behaviour improved significantly yielding the parameters shown on Table 1 when 10 unsuitable data points had been extracted. These data were exclusively employed

for validation purposes. Figure 3 shows good agreement between the experimental CO₂ conversion and the one predicted by means of the LH-HW approach.

Finally, it is important to point out that the rates of CO₂ hydrogenation were measured in an ample range: 0.04-0.41 gmol/h gcat. It was also verified that rates calculated through either the PL approach (Eq. 3) or the LH-HW model (Eq. 4) were close because the difference was about 1-10 % for most runs.

5. Conclusions

The kinetics of the RWGS reaction over a Pd-Ce/ α -Al₂O₃ catalyst was analyzed for mixtures of CO₂-CH₄-H₂. The use of a catalyst with a very low Pd loading reduced CH₄ formation and led to a more competitive catalyst than the Ni-based ones. The derived kinetic equations for the RWGS reaction are adequate to design the hydrogenation reactor of a methanol production process modified to accept NG with a feedstock of high CO₂ content (50-60 %).

Despite small datasets, the fitting approach proposed here allowed an LM optimizer to successfully predict kinetic parameters for both PL and LH-HW rate expressions. Satisfactory agreement between experimental and model data was attained. Before applying traditional robust optimizers, such as LM, pre-processing the available data to choose the most suitable subset from a statistical viewpoint can be a reasonable choice for regression tasks in small data sets. In this work, the classification was carried out by assessing the interaction between bias and variance. This evolutionary approach contributed towards accuracy since it was useful to select a judicious set of experimental data, which was as noiseless as possible, that served to speed up convergence of the optimization. In this way, parameters that exhibited remarkably small trust intervals could be found.

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