Methanol steam reforming: A comparison of different kinetics in the simulation of a packed bed reactor

R. Tesser, M. Di Serio, E. Santacesaria *

Dipartimento di Chimica, Università degli Studi di Napoli Federico II, Complesso Universitario del Monte di Sant'Angelo, 80126 Napoli, Italy

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ABSTRACT

The kinetics of the steam reforming of methanol have been studied in experimental conditions similar to those used in industrial applications, i.e., by using a commercial catalyst in cylindrical pellets. The catalyst used is based on a mixture of Cu–Zn–Al oxides and is normally employed in industry for the low-temperature CO water gas shift reaction. Two kinetic laws have been tested on kinetic runs, performed in a CSTR gradientless Berty reactor and reported in our previous work, by comparing in particular the detrimental effect on the reaction rates of water and/or hydrogen, by comparing in this way the results reported by different authors on this subject. These kinetic laws, together with others reported in the literature, based on different reaction mechanisms, have then been tested for the simulation of runs performed in a tubular pilot-scale packed bed reactor, taking into account for both mass and heat balance along the reactor and inside the catalyst particles. Effectiveness factors were determined through both a rigorous calculation method and experimentally.

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1. Introduction

Methanol plays a fundamental role both as a building block for the production of many chemicals such as, for example, formaldehyde and acetic acid, and as a low-cost energy vector like MTBE, biodiesel and gasoline production, this last on H-ZSM5 based catalysts (MTG Mobil process [1]). Moreover, methanol has also been considered a hydrogen reservoir that allows us to overcome the problems related to hydrogen storage and transportation. The production of hydrogen, for example, as a combustible in fuel cell applications, can be readily carried out through methanol catalysed steam reforming. The most active and selective catalysts for this endothermic reaction have been found to be commercial CuO–ZnO–Al$_2$O$_3$ based catalysts, developed for the low-temperature CO gas shift reaction. This methanol application has undergone a renewed growth in interest and many works have recently been published on the subject exploring scientific aspects like kinetics and mechanisms [2–9] as well as technological ones with end-use applications [10–12]. Methanol steam reforming (MSR) can give good yields of hydrogen through the following reaction:

$$CH_3OH + H_2O \rightleftarrows CO_2 + 3H_2 \tag{1}$$

This reaction can be performed on different types of catalysts, but the most active and selective proved to be the catalysts developed for low-temperature CO conversion (gas shift reaction, GSR or WGSR) [13,14]:

$$CO + H_2O \rightleftarrows CO_2 + H_2 \tag{2}$$

These catalysts are mainly constituted by mixtures of CuO, ZnO and Al$_2$O$_3$ and have been extensively studied [2–14] in the methanol steam reforming reaction both in the low-temperature range (180–210 °C) and also at higher temperatures (200–300 °C).

Other selective catalysts used for hydrogen production through methanol steam reforming are based on Pd–Zn mixtures [18]. For these catalysts a reaction mechanism involving aldehydic and carboxylic intermediates has been suggested [19,20].

Various papers [15,16] have underlined the need for reliable data and kinetic models to design the reformer reactors to be employed together with the fuel cells. After our pioneering works on this topic [13,14], a lot of papers have been published in the literature with contradictory conclusions about the components affecting the reaction rate [16]. As a consequence, many different kinetic expressions have been proposed for experimental data correlation [2–5,16] as Lee et al. have recently reviewed [16]. These authors have found that also for very similar catalysts, different reaction rate expressions have been proposed, based on different reaction schemes and mechanisms. In particular, one of the most controversial aspect for the kinetics of this reaction focus on the reaction order of methanol, water, hydrogen and carbon dioxide, that must be introduced in the rate expressions and the models proposed range from the very sim-

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* Corresponding author.
 E-mail address: elio.santacesaria@unina.it (E. Santacesaria).

ple [12], to complex and comprehensive models [4,5] involving a very high number of adjustable parameters. Another fundamental aspect on which the discussion is still open, regards the reaction scheme, that is, the reaction sequence that brings to the hydrogen formation. Two different alternatives have been proposed that are: (1) methanol decomposition (MD) to CO and hydrogen firstly occurs, followed by the water gas shift reaction (WGS) to CO_2 and hydrogen, or (2) the direct methanol steam reforming (MSR) to CO_2 and hydrogen occurs before, again followed by the WGS reaction, but starting from the reverse side. The formation of CO in both cases would correspond to the equilibrium value foreseen by the WGS reaction but in the first case the amount of CO would be greater or at least equal to the equilibrium value, on the contrary, in the second case the CO amount would be always less than or equal to the equilibrium value. Lee et al. [16], measuring CO at the outlet of a packed bed reactor, in the range 160–260 °C, have found negligible amounts of this component at temperatures smaller than 200 °C and values smaller than the equilibrium value at higher temperatures. On the basis of these findings they concluded that the second reaction scheme is operative. However, it must pointed out that their catalyst contained $CuO/ZnO/Al_2O_3$ but also about 2% of MgO. On the contrary, Santacesaria and Carrà [13,14] in their early works on the same topic, by studying both the methanol decomposition and the methanol steam reforming on the catalyst (BASF K-3-10) containing $CuO/ZnO/Al_2O_3$, have found that methanol decomposition and steam reforming have comparable rates and the same activation energies. As it is well known that the WGS reaction, on the same catalyst, is very fast they concluded that the first reaction scheme is operative.

As the kinetics have been studied by Santacesaria and Carrà [13,14] in the range 160–200 °C the amounts of CO formed in those conditions were negligible, in agreement with Lee et al. [16]. At higher temperatures, Lee et al. [16] have clearly shown that CO formed in the experimental runs is always lower than the equilibrium value but according to us this cannot be considered a definitive argument for excluding the reaction scheme proposed by Santacesaria and Carrà [13,14]. The reaction scheme remains, therefore, still controversial. Other problem is the most reliable reaction mechanism, that is, the sequence of elementary steps of the slower reaction in the scheme. The mechanism clearly affects the kinetic law and as reported by Lee et al. [16] many different kinetic expressions have been proposed for this reaction. In this work we have considered more recently reported developments related to the methanol steam reforming reaction, revisiting our previously published data [13,14] to verify some experimental observations. These mainly regard the eventual hydrogen partial pressure detrimental effect. We also investigated the catalyst effectiveness factor which becomes a key aspect when the catalyst is employed in the form of commercial-size pellets (in the range 3–7 mm or more). In fact here, catalyst effectiveness strongly influences the performances of the reformer. A comparison was made between effectiveness factor values obtained respectively by experiments and calculations.

Moreover, further experimental data were collected in a pilot-scale packed bed tubular reactor, operated in non-isothermal and non-adiabatic conditions, using the same commercial pelletized catalyst on which extensive experimental work was conducted [14] in a CSTR (internal loop gradientless Berty reactor). A packed bed reactor model was developed for kinetics validation and scale-up purposes. This model takes into account kinetics and mass/heat transfer effects and good agreement was found between the experimental runs and model predictions using our proposed kinetic law. At last, the reactor model has also been used by introducing some kinetic expressions reported in the literature for a useful comparison. Comments on the obtained results and simulation will conclude the paper.

2. Experimental

Catalysts investigated in the preliminarily published screening work [13] are commercially available materials based on $CuO–ZnO–Al_2O_3$ mixtures and had the acronyms: BASF K-3-10, BASF S-5-10, ICI 52-1, Girdler-9 and Girdler-66-A. The runs performed in the differential micro-reactor, had been performed by using powdered catalysts (40–60 mesh) diluted with alundum in 1:2 ratio [13], while, in CSTR reactor, only BASF K-3-10 catalyst, has been used in the form of cylindrical pellets (5 mm diameter, 5 mm height), diluted with glass balls of the same equivalent diameter [14].

In this work, the experimental device consists of a stainless steel tubular pilot-scale reactor which scheme is reported in Fig. 1. The reactor contains a packed bed of catalyst cylindrical pellets (bed: length 12 cm, diameter 4 cm; pellets: height 0.5 cm, diameter 0.5 cm), jacketed with an outer tube of stainless steel. In the jacket of the reactor a thermal vector oil is circulated by means of a thermostat that provide for a thermal control of the system. The reactor is fed with a mixture of methanol and water in the desired molar ratio by means of two metering pumps; each liquid reactant is separately vaporised by electrical heater and then mixed before entering the reactor. At the outlet of the reactor a sampling valve allows a sample withdrawal to be sent to GC for analysis. Inlet reactor temperature explored are in the range of 125–325 °C and feed molar flow rates change between 1.621×10^{-6} and 2.341×10^{-6} kmol/s.

3. Results

3.1. Investigation on the kinetic law

As mentioned in Section 1, a preliminary catalytic screening in a differential micro-reactor had been performed on commercial catalysts promoting both low- and high-temperature operative conditions [13]. Low-temperature gas shift reaction catalysts have been found more active and selective. For these reasons a more detailed kinetic investigations had been performed on BASF K-3-10 [13].

At this purpose, by performing experimental runs obtained at fixed methanol partial pressure and varying water concentration, we had found (see Ref. [14]) that water has an inhibitory effect on the reaction rate and, at low conversion, a linear relation exists between the reciprocal of the reaction rate and the water/methanol
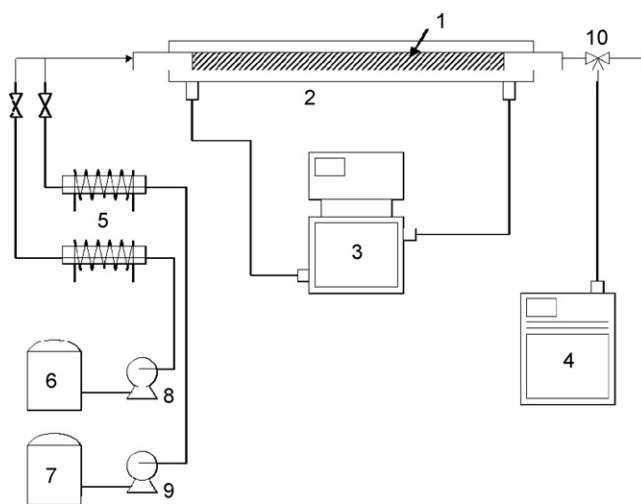

Fig. 1. Pilot reactor scheme. (1) Catalytic bed, (2) heating/cooling jacket, (3) circulation thermostat, (4) GC for analysis, (5) water and methanol vaporisers, (6) methanol reservoir, (7) water reservoir, (8) methanol feeding pump, (9) water feeding pump, and (10) sampling valve.
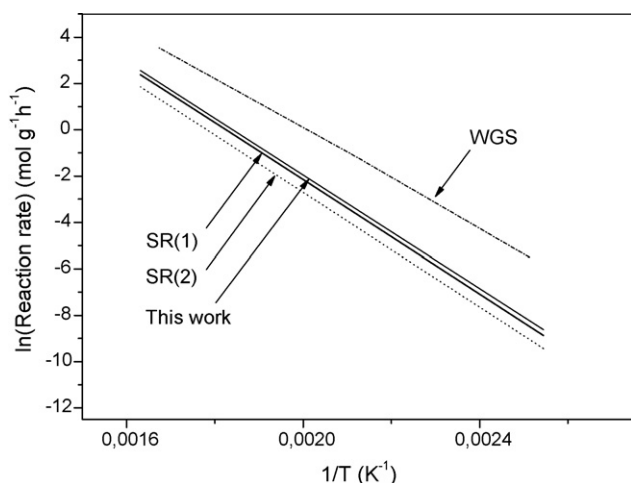
Fig. 2. Reaction rate for methanol steam reforming and water gas shift reaction. Comparison of water gas shift reaction (WGS [17]) and methanol stream reforming rate (SR) from various references: SR(1) – Ref. [14]; SR(2) – Ref. [16], this work. The reaction rate is calculated in correspondence of the following operative conditions: $P_{tot} = 5$ atm, water/methanol molar ratio = 1.8, temperature range 120–325 °C.

molar ratio in the feed as follows:

$$\frac{1}{r} = A + B\left(\frac{p_W}{p_M}\right) \tag{3}$$

This result had further been deepened and experimental runs in the absence of water with the aim of studying the methanol decomposition MD, confirmed that the reciprocal of the reaction rate of MD corresponds to the extrapolation of Eq. (3) to $p_W/p_M = 0$. Moreover, the MD reaction resulted faster than methanol steam reforming (MSR) [14] while the two reactions have about the same activation energy. Therefore, the high activity in MSR of the catalysts, normally employed in the WGS, suggest that the overall reaction of methanol steam reforming (1) occurs through the two following steps:

$$CH_3OH \rightarrow CO + 2H_2 \tag{4}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \tag{5}$$

In which, reaction (4) represents the rate-determining step [13,14] while the reaction (5), considering the catalyst characteristics, is very fast. A rough comparison between the relative reaction rates of (4) and (5) can be better appreciated in Fig. 2, where, the natural logarithm of both steam reforming and WGS reaction rates are plotted, as a function of the inverse of temperature obtaining straight lines. In this figure is put in evidence that, in the temperature range of interest, the reaction rate of WGS reaction [17] is about two order of magnitude higher than the ones related to methanol steam reforming. Moreover, the values of the reaction rates related to steam reforming, taken from various literature [14,16] and determined in the present work, are of the same order of magnitude.

In our previous work [14], a Langmuir–Hinshelwood–Hougen–Watson (LHHW) type model has been developed for taking into account for water adsorption on catalyst surface in competition with methanol. The experimental evidence that water has an inhibitory effect on the reaction rate, has been interpreted by an expression, for the intrinsic rate, of the following form:

$$r = \frac{k_M b_M p_M}{1 + b_M p_M + b_W p_W} \tag{6}$$

The intervention of the internal diffusion resistance, as occurs in the runs performed in CSTR reactor with catalyst pellets, can then

Table 1
Kinetic parameters.

Parameter	Units	Model 1	Model 2
K_M^0	mol h^{-1} g$_{cat}^{-1}$	3.063×10^{10}	6.142×10^9
ΔE	cal/mol	25799	24331
b_M^0	atm^{-1}	2.365×10^{-2}	2.122×10^{-1}
ΔH_M	cal/mol	−8211	−7906
b_W^0	atm^{-1}	1.605×10^{-1}	1.845×10^{-2}
ΔH_W	cal/mol	−4639	−4334
$b_{H_2}^0$	atm^{-1}	–	4.531×10^{-5}
ΔH_{H_2}	cal/mol	–	−7509
Mean % error on methanol conversion	%	10.95	11.03

be accounted by the introduction of the effectiveness factor η:

$$r = \frac{\eta k_M b_M p_M}{1 + b_M p_M + b_W p_W} \quad (\text{model 1}) \tag{7}$$

If also the hydrogen partial pressure is considered as detrimental with respect to the reaction rate, as suggested in the literature [4,5,16], Eq. (7) would be modified for taking into account also for hydrogen competition, resulting in the following alternative LHHW model:

$$r = \frac{\eta k_M b_M p_M}{1 + b_M p_M + b_W p_W + b_H p_H} \quad (\text{model 2}) \tag{8}$$

In the kinetic expressions (7) and (8) the kinetic constant and the adsorption parameters are considered function of the temperature according to the usual relations:

$$k_M = k_M^0 \exp\left(-\frac{\Delta E}{RT}\right), \qquad b_i = b_i^0 \exp\left(-\frac{\Delta H_i}{RT}\right), \quad i = M, W, H \tag{9}$$

Both the kinetic models represented by Eqs. (7) and (8) have been fitted by non-linear regression to the entire set of experimental CSTR data [14] (133 values) by minimising the sum of absolute differences between experimental and calculated methanol conversion. The resulting kinetic parameters are listed in Table 1 and the related parity plots are reported in Fig. 3a and b with the indication of the error range −10/+10%. As it can be seen, an increasing in the number of adjustable parameters from 6 (model 1) to 8 (model 2) does not corresponds to a significant improvement of the fitting, being the average percent error on methanol conversion quite similar in the two cases. Lee et al. [16] have found, on the contrary, the experimental evidence that water does not affects the reaction rate while hydrogen has a remarkable effect on the conversion lowering the reaction rate. However, these authors have explored a temperature range that is higher than the one investigated by us [14] that is 160–200 °C. Their experimental runs are extended up to 260–280 °C and is mainly in the central range of their data, 230–260 °C, that hydrogen inhibitory effect is more evident. This observation can be presumably explained by considering that, at low temperature, water adsorption is the predominant effect in competition with methanol while, at higher temperature, this effect vanishes in comparison with a more remarkable one represented by hydrogen adsorption.

As a further investigation we have considered an empirical power law rate equation of the form:

$$r = k p_M^a p_W^b p_{CO_2}^c p_{H_2}^d \tag{10}$$

For which the reaction orders, a, b, c and d, have been fitted to ours experimental data in various combinations, as reported in Table 2. The obtained results show that various combinations of the reaction order are equivalent in terms of fitting performances, giving place to almost the same mean error in the description of experimental data. Moreover, the values of pre-exponential factor and activation energy are similar and cannot be used as a criterion for
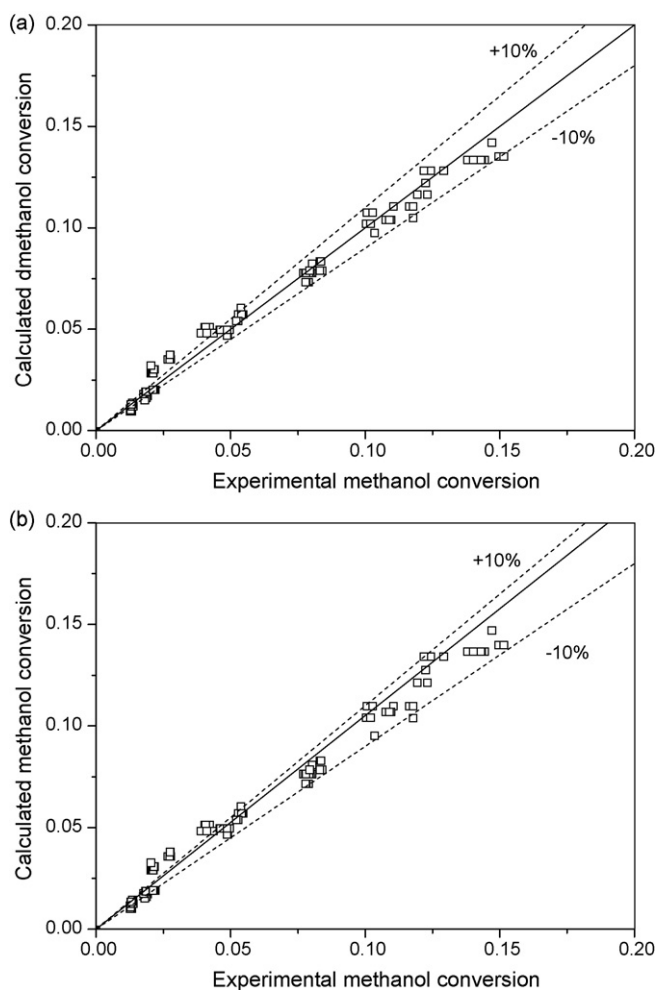
Fig. 3. Parity plot for methanol conversion. (a) Kinetic model in which adsorptions of both methanol and water are taken into account. (b) Adsorption of methanol water and hydrogen.

discriminating between models that resulted comparable, in terms of performances, with LHHW models 1 and 2 (Eqs. (7) and (8)).

As a conclusion, the parameter estimation by non-linear regression cannot be considered, in many cases, the unique useful tool that allows a discrimination between different kinetic models, particularly when many parameters are involved in the model. A sequential experiments programming, for investigating separately the various effects on the reaction rate, should be more suitable for this scope and the influence of parameters correlation should be attenuated. At this purpose, more difficult is to discriminate between different reaction mechanisms on the catalyst surface on the basis of kinetic laws experimentally found. Other information are needed,

in this case, as for the example of methanol decomposition as rate-determining step.

3.2. Effectiveness factor

The catalyst effectiveness factor is usually introduced for taking into account for particles internal diffusion limitations and is particularly important when large particle sizes are used or when temperature is increased in order to have an high reaction rate. Experimental investigations reported in the literature are usually conducted on finely powdered catalyst so that internal diffusion does not represents a limitation and the collected data are referred as intrinsic reaction rate. Very few works, on the contrary, are reported in which catalyst pellets of commercial size are used, in methanol steam reforming reaction, with internal diffusion strongly affecting the reaction rate also considering the highly exothermic character of the reactive system. Lee et al. [16] have used catalyst particle size in the range of 0.3–0.435 mm and they evaluate effectiveness factor above 0.95 for a temperature up to 200 °C. Above this temperature, their effectiveness factors drop down to values of about 0.6–0.8, depending on composition, and considering the size of the pellets used by us, we can expect, for our catalyst, values of this parameter well below these values.

In our previous work [21] we have described a rigorous approach for the calculation of the effectiveness factor in the presence of a generic reaction network characterised by and arbitrary kinetic expression. This approach is constituted by the solution of material and energy balance equations governing the simultaneous reaction and diffusion in a catalytic particle:

$$D_{\text{eff } i} \left[\frac{\partial^2 C_i}{\partial r_p^2} + \frac{2}{r_p} \frac{\partial C_i}{\partial r_p} \right] = \rho_p \sum_{j=1}^{N_R} \nu_{i,j} r_j,$$

$$K_{\text{eff}} \left[\frac{\partial^2 T}{\partial r_p^2} + \frac{2}{r_p} \frac{\partial T}{\partial r_p} \right] = \rho_p \sum_{j=1}^{N_R} (-\Delta H_j) r_j \quad (11)$$

The numerical solution of the system (11) allows the evaluation of temperature and concentration profiles inside the pellet from which the effectiveness factor can be calculated by means of the relation:

$$\eta = \frac{\int_0^{r_p} 4\pi x^2 r(C_i, T) \, dx}{(4/3)\pi r_p^3 r(C_i^S, T^S)} \quad (12)$$

For the evaluation of the effectiveness factor we have used effective diffusivity values, referred to methanol, reported in our previous work [14], that is 0.0016 cm² s⁻¹. For this calculation the following parameters have been employed: molecular diffusivity 0.2260 cm² s⁻¹; tortuosity factor 2.5; catalyst porosity 0.23.

In Fig. 4 a comparison is reported of the catalyst effectiveness factor evaluated in an approximated way and with a rigorous approach by solving particle equations (11). The experimental val-

Table 2
Comparison of power law models.

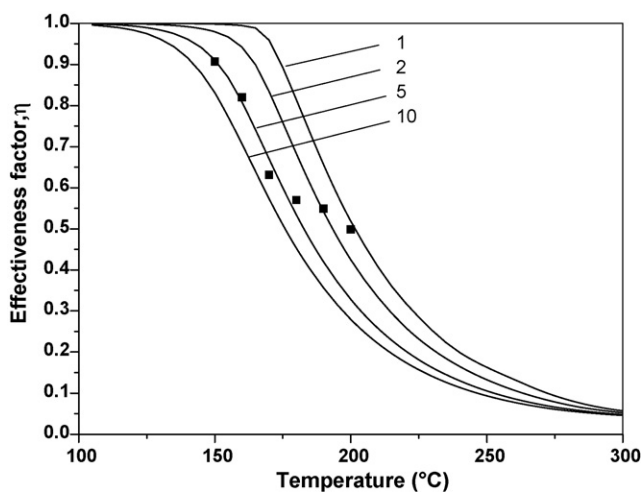|	Model 1	Model 2	Model 3	Model 4	Model 5
$r = k p_M^a p_W^b p_{CO_2}^c p_{H_2}^d$ (mol/(g h))					
CH₃OH (a)	0.351	0.389	0.310	0.235	0.402
H₂O (b)	0	−0.151	0	0.216	−0.468
CO₂ (c)	0.134	0	0	0	0.578
H₂ (d)	0	0	0.195	0.436	−0.793
k_0 (mol/(g h))	6.587×10^8	5.609×10^9	1.533×10^8	2.948×10^6	2.673×10^{11}
E_A (cal/mol)	21667	24163	20345	19028	27874
Mean % error	12.1	12.0	12.1	12.6	11.9

$k = k_0 \exp(-\Delta E_A/RT)$.

Fig. 4. Comparison of catalyst effectiveness factor. Dots are experimental values of effectiveness factor for BASF-K3-10 catalyst evaluated as reaction rates ratio of the CSTR reactor [13] and the tubular differential micro-reactor [14]. Continuous lines represent the calculated effectiveness factor [21] at the reactor inlet conditions for different molar ratio water/methanol.

Fig. 5. Run R1 – axial reactor profiles of temperature and composition. Kinetic model 1 and parameters of the present work.

ues of the catalyst effectiveness factor have been evaluated as the ratio between the reaction rate respectively measured with a Berty-type CSTR reactor filled with catalyst pellets [14] and the assumed intrinsic rate measured in a PFR micro-reactor operated with powdered catalyst [13]. The effectiveness factors, numerically obtained by solving the coupled equations (11), are reported as a function of the temperature and the composition at the surface of the catalytic pellets. The continuous curves reported in Fig. 4 are referred to a gas mixture at the reactor inlet conditions in which only methanol and water are present, in different molar ratios, at the catalyst surface. As it can be seen from this comparison, a rigorous approach in the calculation of the effectiveness factor is in a satisfactory agreement with the experimental values. On the basis of this observation we have made an assumption, in the correlation of experimental data for kinetic parameter evaluation, of using an effectiveness factor that is constant with composition and that is a function only of the temperature [14] (0.81 at 160 °C, 0.66 at 180 °C and 0.53 at 200 °C).

3.3. Pilot-scale tubular reactor

A set of experimental runs has been performed in a tubular packed bed pilot-scale reactor with the scope of verifying the kinetic and mass transfer parameters obtained in the previous steps of investigation. The performed runs are summarised in the Table 3 where are reported feed rates and compositions, inlet temperatures and outlet methanol conversions.

The generalised monodimensional model adopted for packed bed reactor has been extensively described in [21] and consists in
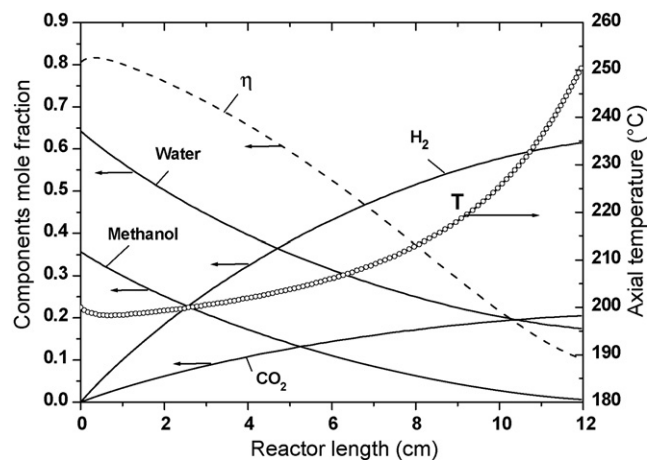
a set of ordinary differential mass and heat balance equations to be integrated along the reactor axis. In this model radial profiles (temperature and composition) have been neglected and only axial profiles of the variables of interest can be calculated. However, the differential mass balance for each component, in a system in which occur N_R chemical reactions, is the following:

$$\frac{dF_i}{dz} = \rho_B \frac{\pi D^2}{4} \sum_{j=1}^{N_R} \nu_{i,j} R_j, \quad i = 1, \dots, N_C \tag{13}$$

while, the heat balance equation can be written as:

$$\left(\sum_{i=1}^{N_C} F_i Cp_i \right) \frac{dT}{dz} = \rho_B \frac{\pi D^2}{4} \sum_{j=1}^{N_R} (-\Delta H_j) R_j + \pi D U (T_H - T) \tag{14}$$

In the derivation of the above equation, an assumption of constant temperature of the oil in the jacket has been introduced. This assumption is justified by the high circulation flow rate adopted in the thermostat.

In the presence of mass transfer limitation phenomena, like in the present case, chemical reaction and diffusion cannot be treated separately and a rigorous approach involves the calculation of the catalyst effectiveness factor at each step of the integration of the relations (13) and (14) along the reactor axis. The evaluation of the catalyst effectiveness factor has been performed by solving material and energy balance on the individual pellet represented by the coupled partial differential equations (11).

In Table 3, column a, the outlet methanol conversions, calculated with the described procedure and using the kinetic parameters of Table 1 (model 1), are reported in comparison with the experimental values. As it can be seen a good agreement is obtained between

Table 3
Experimental runs performed in tubular pilot reactor.

Run	T_{inlet} (°C)	Total feed ($\times 10^{-6}$ kmol/s)	Experimental methanol conversion (%)	Calculated methanol conversion (%)		
				a	b[a]	c
R1	200	2.341	97	98	86–90	100
R2	125	1.621	52	53	41–45	97
R3	325	2.341	99	99	89–92	100

Other conditions: water/methanol molar ratio = 1.8; heating fluid temperature = 400 °C; pressure = 5 atm; ΔH_R = −13 900 cal/mol; catalyst bulk density = 1.115 g/cm³; overall heat transfer coefficient = 0.018 kJ/(m² s K). (a) Kinetics of the present work (catalyst BASF K-3-10), (b) kinetics of Lee et al. [16] (catalyst Synetix 33-5), (c) kinetics of Jiang et al. [8] (catalyst BASF S3-85).

[a] The lower values have been obtained by using the kinetics of Ref. [16] unchanged. The highest values of conversion are calculated by using a scale factor of 1.7 for the kinetic constant that corresponds to the ratio of the specific surface area (112 m²/g of our catalyst with respect to 66 m²/g of catalyst from Ref. [16]).
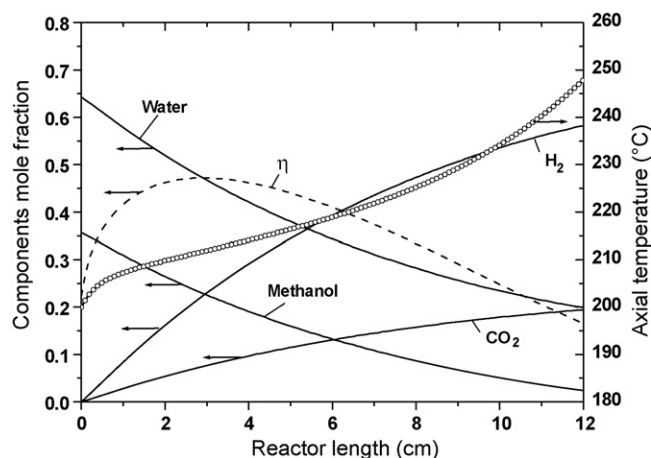
Fig. 6. Run R1 – axial reactor profiles of temperature and composition. Kinetics of Lee et al. [16].

experiments and model simulations. As a further comparison, also two kinetic expressions and parameters, taken from the literature, have been introduced in the reactor model and the corresponding results are reported also in Table 3 column b and c. For the case b, the kinetic expression and parameters of Lee et al. [16] have been used, first by considering no modifications on the original kinetics and in second approach simply by adjusting the kinetic constant by a factor of 1.7 that corresponds to the difference in the specific surface area between the catalyst used by the authors and the one used in the present work. A reasonably good agreement was obtained, particularly if an area ratio is used as a rough correction factor instead of more specific catalyst characteristics such as copper surface, also by considering that the two catalytic systems were different both for composition and textural properties and a detailed correlation between catalytic properties and performances results impractical.

In Fig. 5, the temperature and concentration profiles along the reactor are reported for the run R1 of Table 3, as an example. As it can be seen, methanol is almost completely reacted along the catalytic bed and the hydrogen is correspondingly produced. The temperature profile is affected by the endothermic character of the reaction and by the heat transfer between the reactor and the heating device. The increase in temperature, due to the heating device is evident mainly in the final part of the reactor when the reaction rate decreases (the reaction is endothermic) and the heat transfer effect prevails, while, in the initial part of the reactor, near the inlet, the heat consumed by reaction is almost balanced by the heat transferred from surrounding. In the same figure also the profile of the effectiveness factor is reported.

In Fig. 6 reactor profiles are reported for a simulation related to the kinetics of Lee et al. [16] (case b of Table 3 with adjusted constant). As it can be appreciated in this plot, very similar reactor behaviour is obtained, both for what concerns the composition profiles and for the thermal aspects, despite the use of a different kinetic law. In this figure the profile of the effectiveness factor is also reported.

4. Conclusions

A critical revision of our previously published data, on methanol steam reforming kinetic in a CSTR gradientless Berty reactor, has been carried out for investigating more recently observed effects on the reaction rates such the hydrogen inhibitory role in the adsorption. For our experimental data this effect cannot be considered as markedly present, in the low-temperature range explored, while the inhibitory effect of water on the reaction rate seems confirmed.

Moreover, the previously collected data have been considered in a general approach to kinetic and mass transfer modelling that includes the following steps: (i) catalysts screening; (ii) determination of the intrinsic kinetic law in a differential micro-reactor; (iii) confirmation of the kinetic law in an isothermal CSTR gradientless Berty reactor; (iv) evaluation of the internal diffusion resistance in commercial pelletized catalysts and (v) simulation of a pilot-size tubular reactor. The kinetic model and related parameters have been successfully applied to the description of integral data collected on the pilot-size tubular reactor. The other tested kinetic laws show worst agreement with the experimental data, although the performances are comparable despite the differences in the kinetic expression. This could be an explanation of the disagreement on both reaction scheme and mechanism appeared in the literature. However, as the amount of CO formed is a fundamental aspect for the use of the produced hydrogen in fuel cells the kinetics and mechanism of CO formation must be further deepened.

5. List of symbols

a, b, c, d	exponents in power-law model
A	constant in Eq. (3)
B	constant in Eq. (3)
b_M	methanol adsorption constant
b_W	water adsorption constant
b_H	hydrogen adsorption constant
C_i	concentration of component i
C_i^S	concentration of component i at the particle surface
C_{pi}	specific heat for component i
D	reactor diameter
$D_{eff i}$	effective diffusivity of component i
F_i	feed molar flow rate
K_{eff}	effective thermal conductivity
k_M, k	kinetic constants
N_C	number of components
N_R	number of reactions
p_W	water partial pressure
p_M	methanol partial pressure
P	total pressure
r	reaction rate
r_j	intrinsic reaction rate
R_j	actual reaction rate
r_p	particle radial coordinate
r_p	particle radial coordinate
T	temperature
T^S	temperature at the particle surface
T_i	temperature of heating fluid
U	overall heat transfer coefficient
$v_{i,j}$	stoichiometric coefficient of component i in the reaction j
z	axial coordinate
ρ_p	catalytic particle density
ρ_B	bed bulk density
η	catalyst effectiveness factor
ΔE	activation energy
ΔH	heat of reaction
ΔH_M	methanol heat of adsorption
ΔH_W	water heat of adsorption
ΔH_H	hydrogen heat of adsorption

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