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Kinetic model considering catalyst deactivation for the steam reforming of bio-oil over Ni/La_2O_3-αAl_2O_3

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ABSTRACT

Kinetics of the steam reforming (SR) of bio-oil over a Ni/La_2O_3-αAl_2O_3 catalyst is investigated in a two-step reaction system, which consists of a first thermal unit for pyrolytic lignin separation, followed by on-line reforming in a fluidized bed reactor where the catalyst is located. The kinetic data were obtained under the following operating conditions: 550–700 °C; steam-to-carbon ratio in the feed (S/C), 1.5–6.0; space–time, of up to 0.38 $g_{catalyst}h/g_{BO}$; time on stream, up to 5 h. Experiments in the absence of catalyst were also carried out with a view to quantifying the contribution of thermal routes of bio-oil decomposition. A kinetic scheme with six reaction steps is assumed for the process, and contribution of thermal and catalytic routes are considered in the kinetic equations. The reaction steps are: i) SR of bio-oil ($C_{3.9}H_{6.1}O_{3.0}$); ii) water–gas-shift (WGS) reaction; iii) bio-oil decomposition (thermal/catalytic) into ($CO + CH_4 + H_2$); iv) bio-oil decomposition (thermal/catalytic) into (CO_2 + hydrocarbons + H_2); v) methane SR and vi) hydrocarbons SR. The kinetic model also considers the catalyst deactivation by means of a deactivation equation, which is dependent on the partial pressure of bio-oil oxygenates. The complete kinetic model proposed is suitable for predicting the evolution with time on stream of the concentration of products (H_2, CO_2, CO, CH_4, hydrocarbons), un-reacted bio-oil and water in the reaction medium for the whole range of operating conditions studied.

1. Introduction

Hydrogen has a great strategic interest as clean fuel because of its high combustion efficiency and energy intensity (127 kJ g^{-1}). The increasing demand of H_2 is also promoted by its interest as a reactant in hydroprocessing units in refineries and in agrochemistry (e.g., ammonia production). Although it is currently produced by steam reforming (SR) of methane, the SR of oxygenates derived from biomass has attracted wide attention with a view to reducing the exploitation of fossil resources and reducing the CO_2 emissions [1,2]. In this regard, the bio-oil SR is a process with great prospects for H_2 production on a large scale [3–5].

The bio-oil is a complex mixture of oxygenates with high water content (20–30 wt%), which is obtained by fast pyrolysis of lignocellulosic biomass with a yield of up to 70–80 wt%. The pyrolysis can be carried out in small-scale units that are geographically delocalized and by using simple technologies of low environmental impact [6–8]. The valorization of bio-oil by steam reforming avoids the costly separation of water, which is required in other alternatives for valorizing bio-oil to produce fuels. However, the catalytic valorization of raw bio-oil is hampered by the high content of phenolic compounds (30–40 wt %) which come from the lignin contained in biomass. These compounds repolymerize in the reactor (as pyrolytic lignin), thus causing the rapid deactivation of the catalyst [9].

The good performance of a two-step reaction system for attenuating the catalyst deactivation was previously verified in the SR of raw bio-oil [10]. The pyrolytic lignin is deposited in the first step (at 500 °C, without catalyst) and the remaining volatile oxygenates are reformed on-line in the second step (fluidized bed catalytic reactor). The H_2 yield obtained from the raw bio-oil in this reaction system is higher than that attained by other strategies aimed at separating the pyrolytic lignin (e.g., removal of organic fraction from bio-oil by water addition [11], and thermal aging of raw bio-oil [12]). The two-step reaction system enables the separate collection of pyrolytic lignin, which has a composition similar to those of commercial lignins produced in the paper industry [9,13]. Furthermore, this is a system of continuous operation, which is suitable for the scaling up of the process.

Moreover, the good behavior of Ni/La_2O_3-αAl_2O_3 catalyst was previously assessed by using the two-step reaction strategy [14–16], and the range of operating conditions suitable for attaining high yield

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Nomenclature

a	activity
BO	oxygenates in bio-oil
d	deactivation order
dV	differential element of volume
E_d, E_j	activation energy of the kinetic constant of deactivation and of the reaction step *j*, respectively, kJ mol^{-1}
F, F_i	total molar flow rate and flow rate of each *i* compound, respectively, mol h^{-1}
$F_{(1-\alpha)}$, $F_{(A-B)}$	critical value of the Fischer test and critical value of improvement of model *B* with respect to model *A*, respectively
K_{dW}	constant that quantifies the attenuation of deactivation by adsorption of water
K_{SRM}, K_{WGS}	equilibrium constants for methane steam reforming and WGS reactions, respectively
k_j, k_j^*	kinetic constant of each *j* step at T temperature and at the reference temperature (600 °C), mol $(g_{cat}{\cdot}h)^{-1}{\cdot}atm^{-n}$
k_{DB1}^t, k_{DB2}^t	kinetic constants of the steps corresponding to thermal routes
k_d	deactivation constant, $atm^{-2}\,h^{-1}$
n	exponent of the partial pressure of bio-oil oxygenates in the kinetic equation of deactivation
n_c, n_e, n_p,, n_t	number of compounds in the reaction medium, experimental conditions, kinetic parameters to be estimated, and number of time-on-stream values for which experimental data are taken, respectively
OF, OF_d	objective function to be minimized for the calculation of the kinetic parameters with the results at zero time on stream and with the deactivation results, defined in Eqs. (1) and (29), respectively
p_i	partial pressure of compound *i*, atm
R	universal gas constant, kJ $mol^{-1}\,K^{-1}$
r_i, r_{i0}	formation rate of *i* compound, at *t* time and at zero time on stream, respectively, mol $(g_{cat}{\cdot}h)^{-1}$
r_j, r_{j0}	reaction rate for each step *j* of the kinetic scheme, at *t* time and at zero time on stream, respectively, mol $(g_{cat}{\cdot}h)^{-1}$
r_j^c, r_{j0}^c	catalytic contribution to the reaction rate for each step *j* of the reaction scheme, at *t* time and at zero time on stream, respectively, mol $(g_{cat}{\cdot}h)^{-1}$
r_j^t	thermal contribution to the reaction rate for each step *j* of the kinetic scheme, mol $(g_{cat}{\cdot}h)^{-1}$
SSE	sum of square errors
T, T^*	temperature and reference temperature, respectively, K
t	time on stream, h
w_i	weight factor for each *i* compound of the kinetic scheme
x_{cal}, x_{exp}	calculated and experimental molar fraction (on a wet basis), respectively
x_i	molar fraction on a wet basis of *i* compound
$x_{i,k}^*$, $x_{i,k}$	value of molar fraction (on a wet basis) of each *i* compound at the experimental condition *k*, and the corresponding value calculated by the kinetic model, respectively
$\overline{x}_{i,k,t}^*$, $x_{i,k,t}$	value of molar fraction (on a wet basis) of each *i* compound at the experimental condition *k* and at *t* time on stream and the corresponding value calculated by the kinetic model, respectively

Greek symbols

α_W	parameter in the kinetic equation of thermal routes of decomposition/cracking
ν	degrees of freedom
$(\upsilon_i)_j$	stoichiometric coefficient of compound *i* in the reaction step *j* of the kinetic scheme
σ_A^2, σ_B^2	variance of model A and model B, respectively
ρ_b	catalyst weight per unit volume of the reactor (also considering the zone at the reaction temperature but without catalytic bed)
τ, τ_z	space–time and space–time for a longitudinal position z in the reactor, respectively, $g_{catalyst}$ h $(g_{BO})^{-1}$
ΔH_{WGS}	apparent reaction enthalpy for WGS reaction, kJ·mol^{-1}

and selectivity of H_2, and good catalyst stability was established [17]. However, although the catalyst deactivation by coke deposition is attenuated, this is still significant and should be considered for designing the reactor. This paper aims to progress towards the large-scale implantation of the two-step reaction system by establishing an original kinetic model for the SR of bio-oil, which considers the deactivation of the catalyst. The vast majority of the studies reported in the literature on the kinetic modeling of the SR of oxygenates have been carried out mainly with pure compounds (e.g., methanol [18–22], DME [23,24], ethanol [25–35], glycerol [36–39]), with different catalysts and reactors and using either empirical kinetic equations (potential models) or mechanistic equations. The latter take into account the reactants and products adsorption on the catalyst active sites with models of Langmuir-Hinshelwood-Hougen-Watson (LHHW) or Eley Rideal (ER).

The large differences between the kinetic results reported in the literature are explained by the fact that these are obtained under different reaction conditions and using a wide range of catalysts. Focusing on the kinetic models reported for the steam reforming of ethanol (SRE), Akande et al. [25] established a potential equation of 0.46 order for ethanol and of 0 order for water, based on the kinetic data obtained with Ni/Al_2O_3 catalyst in the 320–520 °C range. Mathure et al. [26] used $Ni/MgO\text{-}Al_2O_3$ catalyst in the 400–600 °C range for the SRE and they established values of 0.71 and 2.72, for ethanol and water, respectively, with these orders being 0.91 and 0 for Patel et al. [28], with $Ni/CeO_2/ZrO_2$ catalyst and 600–700 °C range. Wu et al. [29] improved the fitting of the potential kinetic model for the SRE by applying a LHHW type model (with 9 elemental reaction steps) to the results obtained with Ni/Al_2O_3 catalyst in the 200–600 °C range. They reported similar value of activation energy (31.8 kJ/mol) as that obtained with the potential model. Bakhtiari et al. [40] compared different kinetic models for fitting the SR of an oxygenated mixture (composed of ethanol, propanol, butanol, lactic acid, ethylene glycol and glycerol) carried out over $Ni/Ce_{0.5}Zr_{0.33}Gd_{0.166}O_2$ catalyst in a fixed bed reactor, at 550–600 °C and vapor/oxygenates molar ratio between 2 and 6. The best fitting of the experimental results was obtained with a mechanistic model that assumes the adsorption of oxygenates on the catalyst active sites as the controlling step of the reaction rate.

It is worth pointing out that afore-mentioned papers do not study the SR of a real bio-oil (complex mixture of oxygenates) and that formation of by-products by thermal decomposition is not considered, even though it is appreciable in the absence of catalyst [17]. Deactivation by coke deposition, whose extent depends on the oxygenates nature and reaction conditions [17,41] is neither considered. With a view to filling these gaps, the contribution of thermal decomposition routes of bio-oil oxygenates to the catalyzed reaction steps (steam reforming, WGS) and the influence of catalyst deactivation has been quantified in this paper. In order to achieve these objectives, calculation of the kinetic model has been carried out in two stages. Firstly, the zero-time kinetics has been established (considering both the contribution of thermal and catalytic routes in bio-oil conversion). In the second stage, a kinetic equation for the catalyst deactivation by coke deposition has been included.