Kinetic model considering catalyst deactivation for the steam reforming of bio-oil over Ni/La$_2$O$_3$-αAl$_2$O$_3$

Ana G. Gayubo$^a$, Beatriz Valle$^{a,b,*}$, Borja Aramburu$^a$, Carolina Montero$^b$, Javier Bilbao$^a$

$^a$ Department of Chemical Engineering, University of the Basque Country, Bilbao, Spain
$^b$ Faculty of Chemical Engineering, Central University of Ecuador, Quito, Ecuador

**Abstract**

Kinetics of the steam reforming (SR) of bio-oil over a Ni/La$_2$O$_3$-αAl$_2$O$_3$ 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$_\text{cat}\cdot\text{h}/\text{g}_{\text{bio-oil}}$; 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 hydropyrolysis 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$_2$O$_3$-αAl$_2$O$_3$ catalyst was previously assessed by using the two-step reaction strategy [14–16], and the range of operating conditions suitable for attaining high yield...
and selectivity of H2, 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 over Ni/Ce0.5Zr0.33Gd0.166O2 catalyst in a fixed bed reactor, respectively.

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 methane steam reforming and WGS reactions, respectively.

**Greek symbols**

- \( \alpha_w \): parameter in the kinetic equation of thermal routes of decomposition/cracking
- \( \nu \): degrees of freedom
- \( \sigma_i^2 \), \( \sigma_i^2 \): stoichiometric coefficient of compound i in the reaction step j of the kinetic scheme
- \( \sigma_i^2 \), \( \sigma_i^2 \): variance of model A and model B, respectively
- \( \rho_b \): catalyst weight per unit volume of the reactor (also considering the zone at the reaction temperature but without catalytic bed)
- \( \tau, \tau_x \): space–time and space–time for a longitudinal position z in the reactor, respectively
- \( \Delta H_{WGS} \): apparent reaction enthalpy for WGS reaction, kJ mol\(^{-1}\)

and at zero time on stream, respectively, mol (gcat·h)\(^{-1}\)

**Nomenclature**

- a: activity
- BO: oxygenates in bio-oil
- d: deactivation order
- dV: differential element of volume
- \( E_{d1}, E_{d2} \): 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\(^{-1}\)
- \( F_{(A-B)}, F_{(A-B)} \): 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
- \( k_1, k_1^j \): kinetic constant of each j step at T temperature and at the reference temperature (600 °C), mol (gcat·h)\(^{-1}\) atm\(^{-n}\)
- \( k_{(DBI)}, k_{(DI)} \): 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
- \( n_1, n_2, n_3 \), \( n_1 \): 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
- \( OF, OF_{C} \): 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 (gcat·h)\(^{-1}\)
- \( r_{j1}, r_{j0} \): reaction rate for each step j of the kinetic scheme, at t time and at zero time on stream, respectively, mol (gcat·h)\(^{-1}\)
- \( r_j \): thermal contribution to the reaction rate for each step j of the kinetic scheme, mol (gcat·h)\(^{-1}\)
- \( \sigma_{A1}, \sigma_{B1} \): critical value of the Fischer test and critical value of improvement of model B with respect to model A, respectively
- \( T, T_r \): temperature and reference temperature, respectively
- \( w_i \): weight factor for each i compound of the kinetic scheme calculated and experimental molar fraction (on a wet basis), respectively
- \( x_i, x_{i,k} \): molar fraction on the kinetic results reported in the literature.

**Results and Discussion**

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/Al2O3 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/Ce0.5Zr0.33Gd0.166O2 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.
2. Experimental

2.1. Reaction equipment and operating conditions

The kinetic data were obtained in a two-step reaction system previously described in detail [15], which was designed by modifying an automated reaction equipment (Microactivity Reference of PID Eng & Tech, Madrid, Spain) and has the following main characteristics:

i) The first unit, for the thermal treatment of raw bio-oil, is a U-shaped steel tube of 15.9 mm of internal diameter. This unit is kept at 500 °C, which is suitable for both maximizing re-polymerization of phenolic compounds (more difficult to reform) and allowing a high concentration of oxygenates liable to reforming in the second step. The controlled deposition of pyrolytic lignin in this step minimizes operating problems, with a loss of bio-oil oxygenates in the reaction medium of only 4.7 wt%, and attenuates catalyst deactivation in the subsequent reforming step [42].

ii) Steam reforming of the thermally treated bio-oil (i.e., the volatile stream leaving the thermal step) is carried out over the Ni/La2O3–αAl2O3 catalyst in a fluidized bed reactor of 22 mm of internal diameter and 116 mm length. This reactor is suitable for ensuring bed isothermality and also for the scaling up. The gas flow-rate in the fluidized bed is 9–10 times the minimum fluidization velocity, which was established in a previous fluid-dynamics study [43]. The catalyst (particle size of 150–250 μm) is mixed with inert solid (SiC, particle size 37 μm) (inert/catalyst mass ratio > 4/1) so that the height of catalytic bed is the same in all the experiments (about twice the reactor internal diameter) in order to assure a correct fluidization regime. The absence of internal and external diffusional limitations has been proven by applying the Weisz-Prater and Mears criteria. Montero et al. [46] studied in detail the absence of these limitations in the SR of ethanol over the same catalyst and under similar ranges of operating conditions as in this work.

The reaction equipment is connected online to gas micro-chromatograph (Micro-GC Agilent 3000) for the analysis of reaction products. The micro-chromatograph is provided with four analytical modules with TCD detectors and the following columns: molecular sieve (MS-5), Porapak Q (PPQ), Alumina, and Stabilwax.

The operating conditions were: 550–700 °C; space-time (referred to the oxygenates in bio-oil, BO) up to 0.38 gcat/m3·h; steam-to-carbon molar ratio (S/C), 1.5–6; time on stream, up to 5 h. Blank experiments without catalyst (i.e., only with SiC inert solid in the bed) were also carried out with the aim of quantifying the contribution of thermal routes to bio-oil conversion.

2.2. Bio-oil

The bio-oil was obtained by fast pyrolysis of pine sawdust at 480 °C in a semi-industrial plant with a biomass feeding capacity of 25 kg/h, located in Ikerlan-IK4 technology centre (Alava, Spain) [47]. The elemental composition of this bio-oil was analyzed using a Leco CHN-932 analyzer and ultra-microbalance Sartorious M2P, and the water content (48 wt%) was determined by Karl Fischer titration (KF Titrino Plus 870). Bio-oil contents of carbon (C), hydrogen (H), and oxygen (O) are 48.1%, 6.0% and 45.9%, respectively.

Considering the composition of raw bio-oil (C4.0H6.0O2.9) and the amount (1.7 wt%) and composition (C7.1H2.8O0.7) of the pyrolytic lignin deposited in the thermal treatment unit, the bio-oil entering the catalytic reforming reactor has a composition of C3.9H6.1O3.0.

2.3. Catalyst

The Ni/La2O3–αAl2O3 catalyst was prepared by the incipient wetness impregnation technique. The La2O3–αAl2O3 support was obtained by impregnation of α-Al2O3 with an aqueous solution of La(NO3)3·6H2O (Alfa Aesar, 99%) under vacuum at 70 °C. The La-modified support was dried at 100 °C for 24 h and calcined at 900 °C for 3 h. Subsequently, Ni was added by impregnation with Ni(NO3)2·6H2O and the solid was calcined at 550 °C for 3 h and it was sieved (150–250 μm). Before each reforming reaction, the catalytic bed was reduced in situ for 2 h at 700 °C by using H2/He flow (5% v/v of H2). These synthesis conditions were previously determined as suitable for obtaining a high H2 yield, and stable behavior of Ni/La2O3–αAl2O3 catalyst in the SR reaction of a raw bio-oil/bio-ethanol mixture [16].

3. Results and discussion

3.1. Methodology of data analysis for zero time on stream

3.1.1. Calculation of kinetic parameters

The kinetic parameters of best fit for each proposed model were determined according to the methodology previously developed for other catalytic processes with complex reaction schemes [48–51]. The main calculation steps for the kinetic modeling of these processes were explained by Toch et al. [50]. The kinetic parameters have been calculated by fitting the experimental results to those calculated by integrating the mass conservation equations of each compound of the kinetic scheme using multivariable non-linear regression. The optimization of the fitting has been carried out by minimizing an error objective function (OF) defined as:

\[
OF = \frac{1}{2} \sum_{k=1}^{n_c} w_i \sum_{i=1}^{n_k} (x_{i,k} - x_{i,k})^2
\]

where: \(x_{i,k}\) is the experimental value of concentration (molar fraction) of each \(i\) compound in the kinetic scheme for each \(k\) experimental condition (temperature, space-time, and S/C molar ratio); \(x_{i,k}\) is the corresponding value calculated by integrating the mass balance; \(n_i\) is the number of compounds in the kinetic scheme; \(n_c\) is the total number of experimental conditions. The weight factor for each \(i\) compound of the kinetic scheme, \(w_i\), is inversely proportional to its average composition in the range of operating conditions studied [48,52]:

\[
w_i = \frac{1}{\sum_{k=1}^{n_c} x_{i,k}}
\]

The molar fraction of each compound at each experimental condition, \(x_{i,k}\), has been obtained by solving the mass balances applied to a differential element of volume of the catalytic bed (dv). For this purpose, plug flow for the gas, no radial concentration gradients and iso-thermal regime along the catalytic bed was assumed. Accordingly, the mass conservation equation for each \(i\) compound of the kinetic scheme, considering the variation in the total molar flow (F) along the reactor, at zero time on stream, is as follows:

\[
\frac{dF_i}{dV} = \frac{d(Fx_i)}{dV} = \frac{dx_i}{dV} + x_i \frac{dF}{dV} = r_0 \left( \text{mol of } i \text{ time-volume} \right)
\]

Thus, the evolution with the longitudinal position in the reactor of the molar fraction of each \(i\) compound is:

\[
\frac{dx_i}{dV} = \frac{r_0 \cdot x_i}{F} \frac{dF}{dV}
\]

The formation rate for each \(i\) compound at zero time on stream is calculated considering the different steps of the reaction scheme in which it is involved:

\[
r_0 = \sum_1^n (v_i)F_i
\]
where \((n_b)\) is the stoichiometric coefficient for the \(i\) compound in the reaction step \(j\) and \(r_{j0}\) is the reaction rate at zero time on stream for each step \(j\). In order to minimize the correlation between the pre-exponential factor and the activation energy, the kinetic constants for each \(j\) reaction have been reparameterized [52–54], Eq. (6):

\[
k_j = k_j^0 \exp \left[ \frac{E_j}{R} \left( \frac{1}{T} - \frac{1}{T^*} \right) \right]
\]

(6)

Thus, the parameters to be optimized are the kinetic constants \(k_j^0\) at a reference temperature \((T^* = 600 ^\circ C)\) and their corresponding activation energies \((E_j)\).

The concentration of compounds in the reaction rate expressions is defined as partial pressure, \(p_i\), taking into account all the compounds in the reaction medium.

### 3.1.2. Calculation program

A Matlab program has been developed for integrating the kinetic equations and for the non-linear multiple regressions aimed at calculating the kinetic parameters (Fig. 1). The main program acquires the kinetic data from an external file (SBR_data.txt), it assigns initial values for the parameters to be optimized, and calls the subroutines for the non-linear regression according to a three-step protocol: i) search for the optimum by means of a self-developed function (aju_mul) based on the Levenberg-Marquardt method [54,55], which allows a fast but gross approach to the optimal values of the parameters; ii) detailed search for the optimum by the fminsearch function of Matlab, with the starting point being the optimum previously calculated with the aju_mul function; iii) a new optimum search by the aju_mul function (starting from the optimum calculated by fminsearch) with the aim of determining the confidence intervals of the kinetic parameters.

In addition, the fun_error subroutine calculates the objective function, Eq. (1), and the fun_int function calculates the composition of each \(i\) compound for each experimental condition \(j\) by integrating the mass conservation equations, Eq. (4), with the Matlab ode15s function. The fun_deriv subroutine defines the system of mass conservation equations to be integrated, which is different for each kinetic model proposed.

Significance test aimed at discerning the kinetic model that best describes the SRB process was carried out on the basis of the analysis of variance (comparative significance tests). This analysis is conventionally conducted by means of the F-test for the residuals of different models. Thereby, when comparing two different models, the improvement achieved with model \(B\) with respect to model \(A\) is significant if the following condition is fulfilled:

\[
F_{A-B} = \frac{\alpha^2}{\sigma^2} = \frac{\text{SSE}_A/\nu_a}{\text{SSE}_B/\nu_b} > F_{1-\alpha}(\nu_a,\nu_b)
\]

(7)

where \(\alpha^2\) is the variance of residuals (with \(\alpha^2 > \sigma^2\)), SSE is the residual sum of squares (or the sum of squares due to error), and \(\nu\) is the degrees of freedom. These terms are calculated with the following expressions:

\[
\text{SSE} = \sum_{i=1}^{n_c} \sum_{k=1}^{n_p} (x_{ik}^*-x_{ik})^2
\]

(8)

\[
\nu = n_c \cdot n_p - n_p
\]

(9)

where \(n_p\) is the number of kinetic parameters. In Eq. (7) the critical value of the Fischer distribution function, \(F_{1-\alpha}(\nu_a,\nu_b)\), is a function of the degrees of freedom for the compared variances (\(\nu_a,\nu_b\)) and of the percentage of confidence sought for the comparison, 100(1-\(\alpha\)). This value is calculated using the function fminv(1-\(\alpha\),\(\nu_a,\nu_b\)) of Matlab.

### 3.2. Kinetic modeling for zero time on stream

#### 3.2.1. Reaction scheme

Significant bio-oil conversion was previously observed when operating in the absence of catalyst under the reaction conditions used in this paper, especially at 700 °C. This fact is caused by decomposition/cracking reactions that undergo the bio-oil compounds through thermal routes. These reactions lead to significant formation of CO and CH4, and to a lesser extent of CO2, light hydrocarbons and H2 [17]. Consequently, the following reactions have been considered: i) decomposition reactions of bio-oil oxygenates through different pathways which consider the formation of H2 and by-products (CO, CO2, CH4, light hydrocarbons); ii) WGS reaction; iii) reforming reactions of bio-oil oxygenates (SRB), methane (SRM), and hydrocarbons (SRHC). The WGS and SRM are reversible reactions in the temperature range studied in this paper [56], whereas the steam reforming reactions of bio-oil (SRB) and hydrocarbons (SRHC), and also the bio-oil decomposition reactions are irreversible.

Given that bio-oil is a complex mixture of oxygenated compounds, it has been considered as a lump of C3.9H6.1O3.0 molecular formula. The C2-C4 light hydrocarbons (mostly C2- and C4-) have been grouped into a lump (HCS) of C2.5H5 average molecular formula. The rest of the reaction medium products (i.e., H2, CO, CO2, CH4, and H2O) have been considered as individual compounds. The reaction rate of each step \(j\) of the reaction scheme at zero time on stream, \(r_{j0}\), for established conditions of temperature, space-time and S/C molar ratio, is quantified by considering the contribution of the reaction rates of the catalytic routes, \(r_j\) (which depends on the catalyst amount), and of thermal routes, \(r_j^t\) (not dependent on the catalyst amount), according to the expression:

\[
r_{j0} = r_{j0} + r_j^t
\]

(10)

where the terms \(r_{j0}\) and \(r_j^t\) are expressed per volume unit of the reactor, and \(r_{j0}\) is expressed per weight unit of the catalyst. The parameter \(r_{j0}\) is the catalyst weight per volume unit of the reactor. Firstly, the expressions for \(r_{j0}\) and \(r_j^t\) rates were posed assuming elementary reactions and subsequently, different modifications were incorporated with the aim of improving the quality of the fitting to the experimental results. Some of these modifications were the fitting of the reaction order for each compound, and the inclusion in the equations of terms that quantify the adsorption of compounds.

Consideration of both summands in Eq. (10) is an additional challenge in the development of a suitable methodology for kinetic modeling of catalytic processes (explained in Section 3.1.1). In order to address this issue, a two-phase study has been conducted: i) elucidating the steps of the reaction scheme for which thermal routes contribution to the reaction rate is significant, and establishing a kinetic model for quantifying the kinetics of these routes, based on the results obtained without catalyst; ii) establishing a kinetic model that considers the contribution of both catalytic routes and thermal routes (if these are significant) for quantifying the reaction rate of each step, according to
3.2.2. Contribution of the thermal routes

In order to quantify the products distribution obtained by thermal pathways, kinetic models of different complexity have been considered (Table S1 of Supporting Information). The quality of the fitting to the experimental results obtained without catalyst (Table S2 of Supporting Information) reveals that the simplest model (T1 Model, Table S1) is the one that best quantifies the thermal effect in the bio-oil SR. This model only considers the contribution of two decomposition reactions of bio-oil, denoted as DB1 and DB2:

- **DB1:** $C_3H_8 + O_3 \rightarrow 0.9CH_4 + 3CO + 12.5H_2$ (11)
- **DB2:** $C_3H_8 + O_3 \rightarrow 0.96C_2H_5 + 1.5CO_2 + 0.65H_2$ (12)

Consideration of WGS, SRB and SRM reactions (T4-T6 Models, Table S1) does not improve the fitting of the experimental results, which suggests that the extent of these reactions is not significantly affected by thermal routes. DB1 and DB2 reactions explain adequately the formation of $H_2$ and byproducts (CH₄, H₂C, CO and CO₂) in the absence of catalyst. Consequently, these are the decomposition reactions considered in the reaction scheme proposed for the SR of bio-oil (Table 1), along with reforming reactions of bio-oil (SRB), $CH_4$ (SRM) and $C_2H_5H_2$ hydrocarbons (SRHC), and the WGS reaction.

Furthermore, after testing different empirical equations, the best fitting to the experimental results of bio-oil thermal decomposition has been obtained assuming the following kinetic equation for reactions of Eqs. (11) and (12):

$$r_{DB} = \frac{k_{DB} p_{BO} \gamma_{BO}}{p_W^{\alpha_W}}$$  

where $p_{BO}$ and $p_W$ are the partial pressure of oxygenates in bio-oil and water, respectively, and $k_{DB}$ and $\alpha_W$ are kinetic parameters. It is worth noting the attenuating role of water in the rate of bio-oil thermal decomposition routes. In addition, the rate is proportional to the concentration of oxygenates in bio-oil, so it depends on the rate of the catalytic routes.

Fig. 2 shows an example of the fitting quality of the kinetic model that uses kinetic equations Eq. (13). This figure compares the experimental results of the reaction medium composition obtained at 700 °C and different S/C ratios in the feed with those calculated with the model.

### 3.2.3. Kinetic model of the catalytic steam reforming

In order to quantify the extent of the reactions involved in the reaction scheme (Table 1), expressions for the rate of catalytic pathways (term $r_f$ in Eq. (10)) assuming elementary reactions were firstly used. Moreover, the values previously calculated of thermodynamic equilibrium constants for SRM and WGS reactions were considered [56]. Although a good fitting was attained between the experimental and calculated values (OF = 0.158, SSE = 0.113), some modifications of the kinetic equations were studied with the aim of improving this fitting. The main modifications were: i) setting an adjustable reaction order for the terms of partial pressure in irreversible reactions; ii) including a term (in the denominator) for quantifying the water adsorption in order to consider its attenuating effect on the reaction rate; iii) calculating the equilibrium constants of reversible reactions (SRM and WGS) as adjustable parameters that follow an exponential relation with temperature, either increasing or decreasing according to its endothermic (SRM) or exothermic (WGS) nature, respectively; iv) considering the mechanistic equation (Eley-Rideal mechanism) proposed by Bakhtiar et al. [40] for the SRB reaction.

Taking into account these modifications, the kinetic parameters were calculated by fitting the experimental results according to the methodology described in Section 3.1.1. The results can be summarized as follows:

1. The catalytic contribution to the extent of SRB, DB1, DB2 and SRM reactions of the kinetic scheme (Table 1) is better quantified by kinetic equations with expressions corresponding to elementary reactions.
2. The equation of best fit for the SRHC reaction is a potential expression of first order for the lump of hydrocarbons and of 0.5 order for water.
3. The fitting is significantly improved by setting the WGS equilibrium constant as an adjustable parameter exponentially dependent on the operating temperature instead of using the equilibrium constant predicted by thermodynamics [56].

Consequently, the following kinetic equations have been established for the reactions in Table 1:

$$r_{SRB} = \rho_{kr} k_{SRB} p_{BO}^{\alpha_W}$$  

where $\rho_{kr}$ is the concentration of oxygenates in the bio-oil and $k_{SRB}$ is the kinetic parameter of the SRB reaction.
As observed, both thermal and catalytic routes contribute to the reaction rate of bio-oil decomposition, according to Eqs. (16) and (17) that follow the general expression of Eq. (10). In the rest of kinetic equations, the reaction rate is only consequence of the catalyst activity.

The relationship between the term $\alpha_W$ with temperature is:

$$\alpha_W = \alpha_W^\text{exp} \left[ -\frac{E_W}{R} \left( \frac{1}{T} - \frac{1}{T^*} \right) \right]$$

The equilibrium constant for WGS reaction follows the expression:

$$K_{\text{WGS}} = K_{\text{WGS}}^\text{exp} + \frac{\Delta H_{\text{WGS}}}{R} \left( \frac{1}{T} - \frac{1}{T^*} \right)$$

whereas the equilibrium constant for SRM reaction is calculated with the expression predicted by thermodynamics [56].

---

**Fig. 3.** Parity plots between the experimental ($x_{\text{exp}}$) and predicted values ($x_{\text{cal}}$) of the molar fractions of bio-oil oxygenates and reaction products at zero time on stream, in the SR of bio-oil over Ni/La$_2$O$_3$-αAl$_2$O$_3$ catalyst.
The kinetic parameters of best fit in Eqs. (14)-(21), i.e., the kinetic constants at the reference temperature of 600 °C and activation energies are summarized in Table 2, along with their corresponding confidence intervals at 95%. The value of the objective function (OF, Eq. (1)) and the index of the fitting quality (residual sum of squares SSE, Eq. (8)) are also shown. Fig. 3 shows the goodness of fitting (parity plots) between the experimental values of molar fraction of bio-oil oxygenates (Fig. 3a) and reaction products (Fig. 3b-f) and those calculated with the kinetic model. As shown in Table 2, the kinetic constants at the reference temperature \( k_j^* \) of the reforming reactions follow the trend: \( k_{SRB} > k_{SRHC} > k_{SRM} \). This result reveals that the reaction rate of bio-oil SR is higher than the SR of hydrocarbons, with this reaction being slower as lower is the molecular weight. The activation energies show an opposite trend. Focusing on the kinetic constants that quantify the contribution of thermal \( k_{DB1}^t, k_{DB2}^t \) and catalytic routes \( k_{DB1}, k_{DB2} \) in bio-oil decomposition, it should be noted that the value corresponding to the catalytic route of DB1 reaction is much higher than that of the thermal route \( k_{DB1}^t \), while the activation energy is lower \( (E_{DB1} < E_{DB1}^t) \). In contrast, both the kinetic constant and the activation energy corresponding to thermal contribution \( k_{DB1}^t, E_{DB1}^t \) are lower than those corresponding to the catalytic contribution \( k_{DB2}, E_{DB2} \) in the DB2 decomposition reaction. Furthermore, the kinetic constants of thermal decomposition \( k_{DB1}^t \) and \( k_{DB2} \) corresponding to DB1 and DB2 reactions, respectively, have similar values at 600 °C, whereas the
The activation energy of DB1 is higher. As for the catalytic routes, by comparing the values of \( k_{DB1} \) and \( k_{DB2} \) at 600 °C it can be inferred that the catalyst has a much greater contribution to bio-oil decomposition through the DB1 reaction (\( k_{DB1} >> k_{DB2} \)), although the contribution of both reactions become more similar as the temperature is raised (given that \( E_{DB2} > E_{DB1} \)). It should be noted that the value obtained in this work for the activation energy of the steam reforming reaction (84.19 kJ/mol) is slightly lower than those reported by Bakhtiari et al. [40] in the SR of a mixture of oxygenates by considering both a power-law kinetic model (99 kJ/mol) and a mechanistic equation (Eley-Rideal mechanism) (103 kJ/mol). This difference in the activation energy results may be attributed to the fact a real bio-oil was used in this paper, and that decomposition kinetics of bio-oil oxygenates and the kinetics of catalyst deactivation are quantified separately.

The suitability of this kinetic model to describe the evolution with space-time of the molar fraction of reaction products (a-e) and bio-oil oxygenates (f) with Ni/La₂O₃-\( \alpha \)Al₂O₃ catalyst, at 700 °C and different S/C ratios in the feed.
evolution with space-time of minor products concentration (CO, CH₄ and HCs lump). It should be noted that given the complexity of the reaction scheme, these compounds have different trend depending on the reaction temperature (increasing, decreasing or passing through a maximum).

It is worth noting that a low concentration of by-products (CH₄, HCs, CO) has a great impact on the quality of the product stream, which will require additional purification steps. Therefore, the thermal routes of bio-oil decomposition should be considered in the kinetic model in order to quantify these by-products concentrations.

### 3.3. Consideration of deactivation in the kinetic model

It is worth noting that when catalyst deactivation is remarkable, the kinetic model should be complemented with deactivation kinetics in order to correctly simulate the reactor. This section explains the calculation of the deactivation kinetics which would complement the zero-time kinetic model established above, which allows predicting the evolution with time on stream of products distribution.

#### 3.3.1. Kinetic equation of deactivation

It was assumed that all the catalytic reactions of the kinetic scheme are equally affected by the decrease in catalyst activity (i.e., non-selective deactivation model). The activity is defined as:

\[
a = \frac{r_j^fi}{r_j^0}\tag{23}
\]

where \( r_j^fi \) and \( r_j^0 \) are the contributions to the reaction rate at \( t \) time on stream and zero time on stream, respectively, of the catalytic routes of each step \( j \) of the reaction scheme.

Therefore, the reaction rate at \( t \) time on stream of each step \( j \) of the kinetic scheme is the sum of the contribution of the catalytic (subjected to deactivation) and thermal routes.

\[
r_j = \rho_j r_j^fi + a + r_j^0
\]

In order to establish the deactivation kinetics, different equations have been proposed (Table 3), which are particular expressions of the general equation:

\[
-\frac{da}{dt} = \psi(T,p) \cdot a^d
\]

#### Table 3

<table>
<thead>
<tr>
<th>Model</th>
<th>Deactivation equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>MD1</td>
<td>(-\frac{da}{dt} = k_P a^d)</td>
</tr>
<tr>
<td>MD2</td>
<td>(-\frac{da}{dt} = k_P a^d)</td>
</tr>
<tr>
<td>MD3</td>
<td>(-\frac{da}{dt} = \frac{k_P a^d}{1 + k_P a^d})</td>
</tr>
</tbody>
</table>

where \( d \) is the deactivation order and \( \psi(T,p) \) is a function dependent on the temperature and composition of the reaction medium, which can be established from empirical basis or considering the deactivation mechanism. In equations of Table 3, the deactivation rate depends on the partial pressure of bio-oil oxygenates (\( P_{BO} \)), since it was previously verified that these compounds are the main precursors of coke deposition [17, 41]. Different expressions of Eq. (25) were successfully used in previous papers for quantifying the catalyst deactivation by coke deposition in reactions with complex reaction schemes, such as methanol or ethanol conversion into hydrocarbons [51–53, 57].

#### 3.3.2. Analysis methodology of deactivation kinetic data

Discrimination of equations and calculation of the best-fit kinetic parameters was carried out by multiple nonlinear regressions, following a methodology similar to that described for the calculation of zero-time kinetics (Section 3.1) except for two differences explained below.

Firstly, a new term \( \text{err}_{0,ik} \) (error at zero time on stream) is included in the objective function to be minimized, so that the lack of fit of the zero-time kinetics do not interfere in the fitting of the deactivation kinetics:

\[
OF_i = \sum_{i=1}^{n_i} \sum_{k=1}^{n_k} \frac{1}{w_i} \left( X_{i,k} - X_{i,k}^* - \text{err}_{0,ik} \right)^2
\]

where \( n_i \) is the number of time-on-stream values for which the composition of the reaction medium has been determined (for each experimental condition \( k \)); \( \text{err}_{0,ik} \) is the difference between the experimental and calculated value of the concentration of each compound \( i \) for each experimental condition \( k \), at zero time on stream.

The second difference with respect to the methodology explained in Section 3.1 is the calculation of the evolution with time on stream of the concentration of each compound, for each experimental condition \( k \).
This calculation requires solving jointly the mass conservation equation, Eq. (4), and the kinetic equation of deactivation, Eq. (25). Besides, the reaction rate at time-on-stream, $r_i$, is used instead of the rate at zero time-on-stream, $r_{i0}$ in Eq. (4). It should be noted that this methodology allows for considering the “past history” of the catalyst at each position of the reactor, which is essential when deactivation depends on the reaction medium composition.

The afore-mentioned calculation differences are taken into account in the Matlab program developed for determining the best-fit kinetic parameters. This program solves the kinetic equation of deactivation together with the mass balances of all the compounds of the reaction scheme. In addition, the integration of partial differential equations should account for 2 independent variables (space-time and time on stream) so that more calculation time is required. The integration method is based on Gauss-Legendre quadrature and allows calculating the dependent variables (composition and activity) at all the positions of the two-dimensional grid defined using both independent variables. This method enables a faster solution than the conventional pdepe method for solving partial differential equations.

Furthermore, given that the catalyst activity is homogeneous in all the positions of the fluidized bed reactor at a given value of time-on-stream (i.e., perfect mixing regime for the catalyst) the integration method has been adapted. Thus, the activity for a given value of space-time $\tau_z$ (corresponding to the longitudinal position $z$ of the grid in which this independent variable is discretized) is calculated by the following expression:

$$a_{\tau_z} = \frac{\int_{0}^{\tau_z} a_{z} \, dz}{\tau_z}$$

(30)
Therefore, the activity is calculated as the average value of the activities at all bed positions for a given value of time on stream. This average activity is used to calculate the reaction rate of each step \( j \) of the reaction scheme, Eq. (24), and it is also used as the initial value for calculating the activity in the next time-on-stream set in the integration grid of this independent variable.

The constants in Eqs. (26)-(28) have been reparameterized by an expression similar to Eq. (6) (Section 3.1.1) for calculating the kinetic parameters (i.e., kinetic constants at a reference temperature of 600 °C and their corresponding activation energies).

In order to assess the improvement achieved with an equation compared with a simpler one, an analysis of variances has been carried out from the kinetic parameters calculated by using the different kinetic equations of deactivation (Table 3). The results of the fitting quality (shown in Table S3 of Supporting Information) reveal that Eq. (27) fits well the experimental results, and that the fitting with respect to Eq. (26) is significantly improved when using an exponent \( n \) with a value different from 1.0 for the partial pressure of bio-oil oxygenates. The optimal values of this exponent and that corresponding to the activity were \( n = 2.05 \) and \( d = 2.59 \), respectively. However, the inclusion of a new term in the denominator for considering the possible attenuation of deactivation by the water adsorbed on the active sites (Eq. (28)) does not involve a significant improvement. Consequently, the best-fit kinetic equation of deactivation is:

\[
\frac{da}{dt} = k_{d,BO}a^{2.5}
\]  

(31)

where the deactivation kinetic constant (with 95% confidence intervals) is related with reaction temperature by the following:

\[
k_d = (7.64 \pm 0.12) \times 10^2 \exp \left(- \frac{13.89 \pm 0.77}{R} \left(1 - \frac{1}{873} \right) \right)
\]  

(32)
3.3.3. Fitting of the kinetic model considering deactivation

The goodness of fitting of the complete kinetic model, which considers the kinetic equations of the thermal and catalytic routes, Eqs. (14)-(21), and the deactivation kinetics, Eq. (31), is shown in the parity plots for the experimental and calculated values of the molar fractions of reactants (Fig. 6) and products (Fig. 7). These results correspond to the whole range of operating conditions studied (temperature, space-time, S/C ratio) and different values of time-on-stream. A good fitting quality is observed, particularly for the major compounds of the reaction medium (H2 and water).

The suitability of the kinetic equation proposed for quantifying the catalyst deactivation can be appreciated in Figs. 8–10, where the evolution with time on stream of the molar fraction of some compounds of the reaction scheme (H2, CO and non-reacted bio-oil oxygenates) is shown. These results correspond to reaction conditions taken as an example. Figs. S1–S3 of the Supporting Information show the fitting between the experimental and calculated values of the molar fractions of other products (CO2, CH4, HCs) for the same conditions.

As shown, the proposed equation adequately predicts the influence of reaction temperature (Fig. 8), space-time (Fig. 9) and S/C molar ratio (Fig. 10) on the catalyst deactivation. The importance of considering the thermal pathways of bio-oil conversion in the kinetic model is noteworthy to adequately predict the results when the catalyst is highly deactivated, since in these conditions the yields and distribution of products are mainly a consequence of thermal routes.

The complete kinetic model proposed can be used in optimization studies. Based on the results obtained in this work, suitable conditions for obtaining a high yield and selectivity of H2 (higher than 90% and 65%, respectively) with a moderate deactivation can be established: temperature above 650 °C, space-time higher than 0.38 gcat/gBO and S/C molar ratio of around 3.5 (to avoid an excessive energy cost in water vaporization).

In this paper, the kinetic model proposed is based on experiments carried out in a two-step reaction system, with pyrolytic lignin separation in the first step and catalytic reforming in the second one (fluidized bed reactor). Therefore, application of this model for simulation, optimization and the scaling up of this reaction system is clearly interesting. A worthwhile application is the simulation of a fluidized bed reactor with catalyst circulation, aimed at maintaining constant H2 production. The catalyst would be regenerated by coke combustion in another fluidized bed reactor.

4. Conclusions

An original kinetic model for bio-oil steam reforming that quantifies the formation of all the reaction products (H2, CO, CO2, CH4 and C2–C3 hydrocarbons) and considers catalyst deactivation has been established. This model takes into account the thermal and catalytic pathways for bio-oil conversion, and is based on a kinetic scheme with 6 individual reactions: steam reforming of bio-oil, WGS reaction, two decomposition reactions of bio-oil (thermal/catalytic), and steam reforming reactions of CH4 and hydrocarbons. The kinetic equations for catalytic reactions of bio-oil reforming, bio-oil decomposition and CH4 reforming correspond to elemental reactions, whereas the kinetics of hydrocarbons reforming is a potential expression of first order for the hydrocarbons lump and of 0.5 order for water. The kinetic equation of deactivation considers the bio-oil oxygenates as the main coke precursors (with a potential expression of second order) and has a deactivation order of 2.5.

The kinetic model is valid to quantify the distribution of all the products obtained over Ni/La2O3-xAl2O3 catalyst in a wide range of operating conditions (550–700 °C and S/C ratio in the 1.5–6 range, time on stream up to 5 h). Consideration of the thermal routes of bio-oil decomposition allows a reliable quantification of by-products concentration (CO, CH4 and hydrocarbons), whose presence is relevant to evaluate the quality of the product stream. In addition, these thermal routes become more significant as the catalyst deactivation progresses.

Acknowledgements

This work was carried out with the financial support from the Ministry of Economy and Competitiveness of the Spanish Government (Project CTQ2012-35263 (MINECO/FEDER, UE) and CTQ2015-68883-R (MINECO/FEDER, UE)), the Basque Government (Project IT748-13) and the University of the Basque Country (UFI 11/39 pre-doctoral grant of B. Aramburu). Carolina Montero thanks the National Secretariat for Higher Education, Science, Technology and Innovation of Ecuador-SENESCYT for her Ph.D. grant (20110560).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cej.2017.09.063.
References


