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Dedicated to Professor Liviu Literat
On the occasion of his 85th birthday

THERMODYNAMIC STUDY AND KINETIC MODELING OF BIOETHANOL STEAM REFORMING

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ABSTRACT. Reforming of bioethanol, mainly produced from biomass fermentation, provides a promising method for hydrogen production from renewable resources. This paper describes the research work carried out on the themodynamic analysis and kinetic modeling of bioethanol steam reforming using Ni-Al_2O_3 10% at the temperature 350°C. The thermodynamic analysis which takes into account the main chemical species involved in the reactions was performed at more H_2O/EtOH molar ratio. Following the thermodynamic study has resulted that the maximum concentration of H_2 was obtained at the molar ratio of H_2O/EtOH 3:1 temperature of 550°C and 1 bar pressure. The experimental measurements were performed at laboratory scale and were done in isothermal conditions. The Langmuir-Hinshelwood-Hougen-Watson model was used in the kinetic modeling. The experiments for kinetic modeling was conducted under conditions 350°C, 3 bar and at molar ration water/ethanol 24:1 and was observed that. High concentrations of hydrogen were obtained when low inert gas flow was used.

Keywords: *Bioethanol, Steam reforming, Thermodynamic analysis, Hydrogen production, Kinetic modeling*

INTRODUCTION

Over the last 10 years have become a certainty that fossil fuel resources are limited and CO_2 emissions cause global warming and severe climate change. To reduce dependence on fossil fuels and reduce CO_2 emission a

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lot of research work focuses in seeking new or alternative renewable sources of fuel and energy. Hydrogen is considered to be a clean energy carrier that will play an important role in the future global economy [1]. The demand for hydrogen is increasing in recent times because of its wide applications in areas such as: chemicals, crude oil refining, heavy oil, oil sands, metallurgy and aerospace propulsion upgrading and as fuel for the proton exchange membrane (PEM) fuel cell [2]. Hydrogen production is particularly attractive and interesting for fuel cell applications, which are regarded as having the potential to provide a source of clean energy for cars as an alternative to current fossil gasoline and diesel [1]. Biomass is recommended as an alternative for the production of hydrogen, because it is an abundant and renewable resource that does not contribute to net increase of CO_2 in the atmosphere.

The SRE (Steam Reforming of Ethanol) process involves the reaction between ethanol and water over a metal catalyst capable of breaking the C−C bond in the ethanol to produce a mixture of H_2 and CO_2 [1]. The main reaction is highly endothermic, (ΔH^0_{298}=+173.3 kJ/mol) and occurs at relatively higher temperatures typically between 300 and 800°C. The literature proposes different chemical reactions to describe the SRE process. For this study the following reactions were chosen [1, 3-11]:

$CH_3CH_2OH_{(g)}+3H_2O_{(g)} \rightarrow 6H_{2(g)}+2CO_{2(g)}$ $\Delta H^0_{298}=+173.3$ kJ/mol (1)
$CH_3CH_2OH_{(g)}+H_2O_{(g)} \rightarrow 4H_{2(g)}+2CO_{(g)}$ $\Delta H^0_{298}=+255.5$ kJ/mol (2)
E_1: $CH_3CH_2OH_{(g)} \rightarrow H_{2(g)} + CO_{(g)} + CH_{4(g)}$ $\Delta H^0_{298}=+49.7$ kJ/mol (3)
E_2: $CH_3CH_2OH_{(g)} + H_2O_{(g)} \rightarrow CO_{2(g)} + CH_{4(g)} + 2H_{2(g)}$ $\Delta H^0_{298}=+8.7$ kJ/mol (4)
R_1: $CH_{4(g)} + 2\ H_2O_{(g)} \leftrightarrow CO_{2(g)} + 4\ H_{2(g)}$ $\Delta H^0_{298}=+206.2$ kJ/mol (5)
R_2: $CO_{(g)} + H_2O_{(g)} \leftrightarrow CO_{2(g)} + H_{2(g)}$ $\Delta H^0_{298}=-41.2$ kJ/mol (6)
$CO_{(g)} + 3\ H_{2(g)} \rightarrow CH_{4(g)} + H_2O_{(g)}$ $\Delta H^0_{298}=-206{,}2$ kJ/mol (7)
$CH_{4(g)} + H_2O_{(g)} \rightarrow CO_{(g)} + 3\ H_{2(g)}$ $\Delta H^0_{298}=+205.8$ kJ/mol (8)

Although the stoichiometric molar ratio of steam/ethanol (H_2O/EtOH) should be 3:1 according to reaction (1), alcohol obtained by fermentation of biomass contains approx. 9 [% wt.] ethanol and 88 [% wt.] water, the remainder being impurities such as lactic acid and glycerol, equivalent to a molar ratio $H_2O/EtOH \approx 24$, thus, using a large molar H_2O/EtOH is considered advantageous because it can eliminate the cost of ethanol distillation. However the excess water can promote the water gas shift (WGS) reaction to convert CO formed in the steam reforming reaction (2) and/or ethanol decomposition (3) [3].

Different kinetic models were proposed in literature to describe the SRE process. The Langmuir-Hinshelwood-Hougen-Watson (LHHW) model [12] was widely used and the main parameters of this model were determined based on experimental measurements.

Thermodynamic analysis

A thermodynamic analysis can be used to determine the favorable operating conditions in order to maximize the efficiency of the process. The most significant parameters influencing the process are: temperature *T*, pressure *p* and H_2O/EtOH molar ratio *r* [12]. In this work, for the thermodynamic analysis, it has been considered for these three parameters a data range as follows: temperature between 300-800^oC, pressure between 1 and 30 bar and the molar ratio of H_2O/EtOH in the domain 3-25. These values were chosen so to cover a significant area of the possible operating conditions of the process.

The reaction main products was considered $H_{2,}$ and CO_2. The following compounds were considered as potential reaction byproducts: CO, CH_4, CH_3CHO, C_2H_4 and other, their initial concentrations are equal to 0. Concentrations of the reaction mixture were recalculated for dry mixture.

Steam reforming of ethanol leads to: H_2, CO, CO_2 and CH_4. The formation of CH_4 is predominant at low temperature (300-400^oC) when the decomposition reaction is intensified, and at high temperature (650-800^oC) production of H_2 is enhanced. CH_4 is an unwanted byproduct that radically reduces the amount of H_2 produced. In order to perform the thermodynamic study reactions 1 to 8 were considered [4-11].

Kinetic modeling

There are few papers in the literature on kinetic studies of ethanol steam reforming, because the system complexity. Ethanol was used as the representative component for bioethanol because of its much higher concentration compared to other components that are present in the bioethanol mixture.

Some published kinetic studies used power law, Eley Rideal (ER), Langmuir Hinshelwood (LH) and Langmuir-Hinshelwood-Hougen-Watson (LHHW) as kinetic expressions [2, 12-14]. Empirical and mechanistic rate models were developed to fit the experimental data as follows. Firstly, an empirical, irreversible fixed feed molar ratio power law rate model was developed as shown by the following equation [2]:

$$r_A = k_0 \cdot e^{\left(-\frac{E_a}{R \cdot T}\right)} \cdot N_A^m \qquad (9)$$

Secondly, different mechanistic models were developed based on LHHW and ER mechanisms. Fundamentally, LHHW differs from the ER mechanism in that the former requires the adsorption of the two reactant species on the catalyst active site for any transformation to take place whereas the latter requires only one of the two reactants species to be adsorbed [2].

The criterion used in the selection of the kinetic model was the temperature range and the available kinetic data. Considering these aspects the LHHW kinetic model was selected and used in this work.

As it was established, the kinetic model consists only of 4 reactions: E_1, E_2, R_1 and R_2 - reactions (3-6) [12]. The reaction rates for these four reactions are [10-12, 15, 16]:

$$r_{E1} = \frac{k_{E1} \cdot y_E \cdot y_{CH4}^{-1} \cdot y_{H2}^{-\left(\frac{1}{2}\right)}}{DEN^2} \tag{10}$$

$$r_{E2} = \frac{k_{E2} \cdot y_E \cdot y_{CH4}^{-1} \cdot y_{H2}^{-1} \cdot y_{H2O}}{DEN^2} \tag{11}$$

$$r_{R1} = \frac{k_{R1} \cdot y_{CH4} \cdot y_{H2O}^{2} \cdot y_{H2}^{-\left(\frac{5}{2}\right)} \cdot (1-\beta_{R1})}{DEN^2} \tag{12}$$

$$r_{R2} = \frac{k_{R2} \cdot y_{CO2} \cdot y_{H2}^{\left(\frac{1}{2}\right)} \cdot (1-\beta_{R2})}{DEN^2} \tag{13}$$

where the *DEN* term of these expressions is defined as:

$$DEN = 1 + K_{Et} \cdot y_{Et} + K_{Etx} \cdot y_{Et} \cdot y_{H2}^{-(1/2)} + K_{Ac} \cdot y_{Et} \cdot y_{H2}^{-1} + K_{CHO} \cdot y_{Et} \cdot y_{CH4}^{-1} \cdot y_{H2}^{-(1/2)} + K_{CH3} \cdot y_{CH4} \cdot y_{H2}^{-(1/2)} + K_{CH2} \cdot y_{CH4} \cdot y_{H2}^{-1} + K_{CH} \cdot y_{CH4} \cdot y_{H2}^{-(3/2)} + K_{H2O} \cdot y_{H2O} + K_{OH} \cdot y_{H2O} \cdot y_{H2}^{-(1/2)} + K_{CH4} \cdot y_{CH4} + K_{CO} \cdot y_{CO} + K_{CO2} \cdot y_{CO2} + K_{H2} \cdot y_{H2}^{1/2} + K_{H2} \cdot y_{H2} \tag{14}$$

The kinetic model parameters considered are presented in Table 1.

Table 1. Kinetic model parameters [9, 11, 12, 15]

$k_{i(T)} = k_{i(898.15K)}\, e^{-(Ea,i/R)\,((1/T)-(1/898.15\text{ K}))}$ [mol/min mg] $K_{i(T)} = K_{i(898.15K)}\, e^{-(\Delta Hi/R)\,((1/T)-(1/898.15\text{ K}))}$ [dimensionless]		Ea_i, ΔH_i [kJ/mol]	
$k_{E1,(898.15K)}$	$1.13 \cdot 10^{-7}$	Ea_{E1}	122.9
$k_{E2,(898.15K)}$	$3.06 \cdot 10^{-7}$	Ea_{E2}	195.5
$k_{R1,(898.15K)}$	$2.48 \cdot 10^{-3}$	Ea_{R1}	174.0
$k_{R2,(898.15K)}$	$9.12 \cdot 10^{-4}$	Ea_{R2}	166.3
$K_{Et(898.15K)}$	$8.76 \cdot 10^{-27}$	ΔH_{Et}	–601.4
$K_{CHO(898.15K)}$	$2.10 \cdot 10^{-1}$	ΔH_{CHO}	–410.4
$K_{CH2(898.15K)}$	$1.93 \cdot 10^{-22}$	ΔH_{CH2}	–118.4
$K_{CH(898.15K)}$	$3.05 \cdot 10^{-1}$	ΔH_{CH}	–360.7
$K_{CH3(898.15K)}$	$1.93 \cdot 10^{-22}$	ΔH_{CH3}	–126.8
$K_{H2(898.15K)}$	$1.93 \cdot 10^{-22}$	ΔH_{H2O}	–83.1
$K_{OH(898.15K)}$	$1.93 \cdot 10^{-22}$	ΔH_{OH}	–145.5
$K_{CH4(898.15K)}$	$6.34 \cdot 10^{-18}$	ΔH_{CH4}	–86.1
$K_{CO(898.15K)}$	$1.93 \cdot 10^{-22}$	ΔH_{CO}	–83.1
$K_{H(898.15K)}$	$8.76 \cdot 10^{-27}$	ΔH_{H}	–247.4
$K_{CO2(898.15K)}$	$1.93 \cdot 10^{-22}$	ΔH_{CO2}	–83.4
$K_{H2(898.15K)}$	$1.93 \cdot 10^{-22}$	ΔH_{H2}	–931.2

RESULTS AND DISCUSSION

Thermodynamic analysis

The goal of the thermodynamic analysis is to determine the conditions favorable to maximize the concentration of H_2 and to reduce to as low as possible the concentration of unwanted byproducts as: CH_4, CO_2 and CO. The thermodynamic study was performed using CHEMCAD process simulator. The equilibrium composition was determined for all possible combinations of the following values of parameters T, p and r:

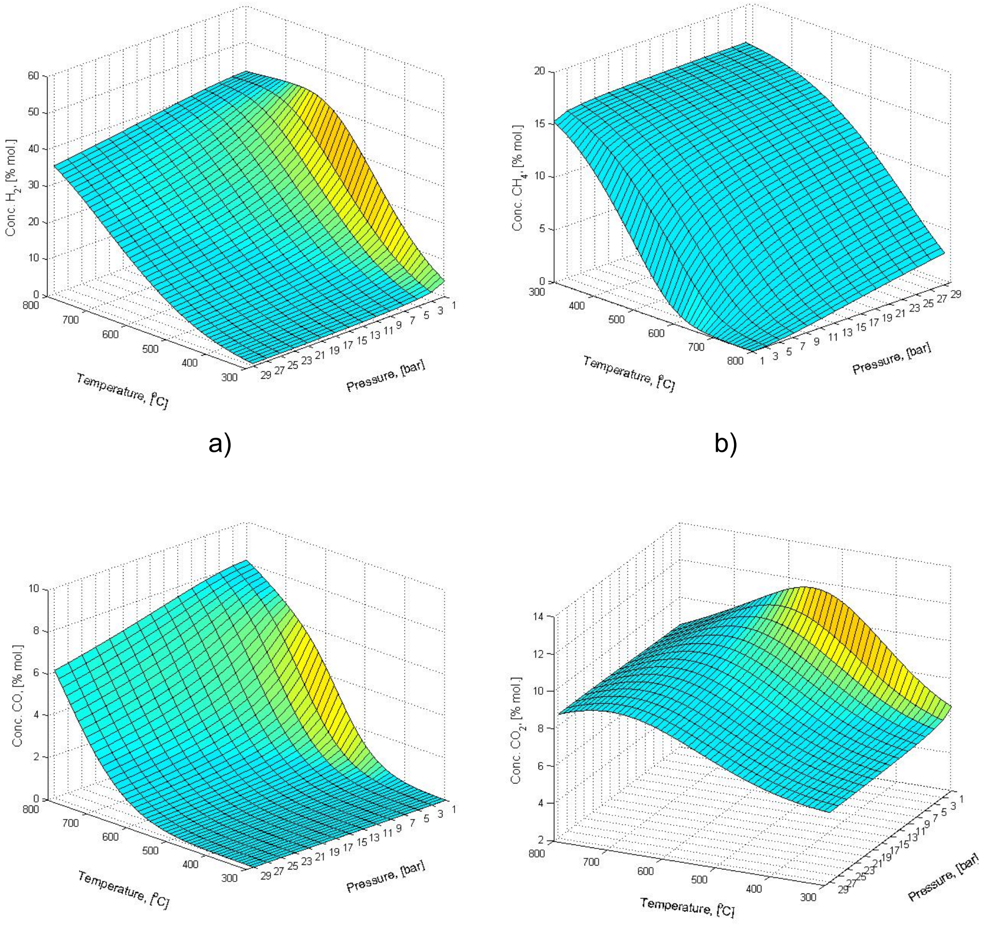
- T: 300, 350, 400, 450, 500, 550, 600, 650, 700, 750 and 800°C;
- p: 1, 5, 9, 13, 17, 21, 25 and 30 bar;
- r: 3, 5, 7, 9, 11, 13, 15, 17, 19, 21, 23 and 25.

The thermodynamic analysis results are presented bellow. The variation of H_2, CH_4, CO and CO_2 concentration with temperature and pressure at the molar ratio of water/bioethanol, 7:1 is presented in Figure 1.

Figure 1.a shows that the maximum concentration of H_2 is reached at 1 bar in the temperature range of 550-600°C. At lower temperatures H_2 concentration is reduced because is favored CH_4 production. The maximum hydrogen concentration that was obtained is 45%. As shown in the Figure 1.b the maximum concentration of CH_4 (16-17%) is achieved at temperatures of 300°C and a pressure of 30 bar. At low temperatures the methane steam reforming reaction is favored. The maximum concentration of CO is achieved at temperatures of 800 °C and 1 bar pressure (Figure 1.c). As shown in the Figure 1.d the maximum concentration of CO_2 (12%) is obtained in the temperature range of 550-600°C and pressure of 1 bar. The maximum concentration of CO is 8-8.5%. CO and CO_2 concentrations are strongly influenced by the WGS reaction.

Figure 2 presented variation of major components concentrations as a function of temperature and pressure variation, at molar ratio water/ bioethanol is 7:1.

As shown in Figure 2.a the increasing of temperature increase the concentration of H_2 from 3% to 68% and the concentration of CH_4 decreases from 71% to 5%. The variation of CO and CO_2 concentration is insignificant until the temperature 550°C, after that the concentration of CO increases from 0.5% to 12% and the concentration of CO_2 decreases from 25% to 17%. Figure 2.b shows that the variation of major components concentration with pressure is insignificant for CO and CO_2, H_2 and CH_4 is significant.

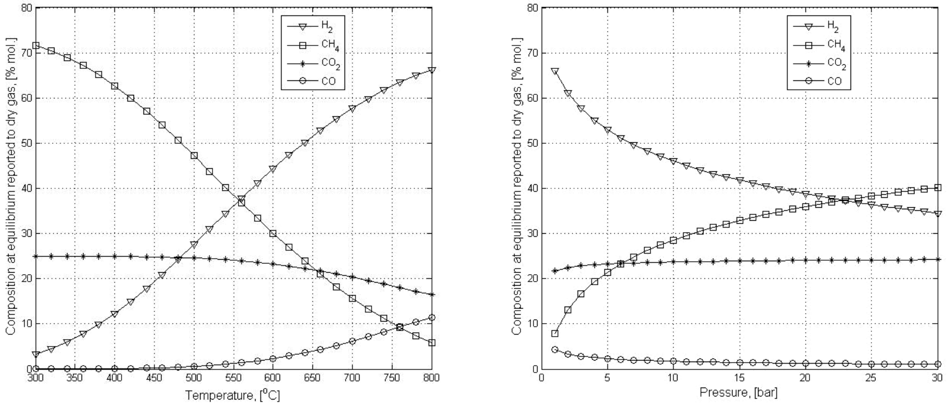


a) b)

c) d)

Figure 1. Variation of concentration of main products in the temperature and pressure at the molar ratio of water/bioethanol, 7:1.
a) H_2, b) CH_4, c) CO, d) CO_2.

Figure 3 represents the variation of major products concentration as a function of water/ethanol molar ratio at the temperature of 800 °C and 30 bar. It can be observed that at high values of the water/ethanol molar ratio the mixture contains almost only H_2 and CO_2, while at low molar ratio values we have a significant concentration in all components (CH_4; CO and CO_2 each one's concentration is over 12%).



a) b)

Figure 2. Variation of major components concentrations as a function of a) temperature at pressure 30 bar and b) pressure variation at 550 ^oC, at molar ratio water/bioethanol 7:1.

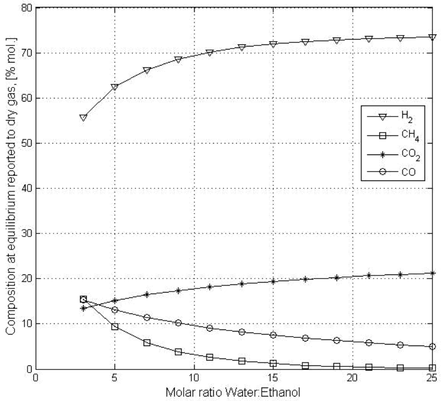


Figure 3. Variation of major products concentration as a function of molar ratio water/ethanol at the temperature of 800^{o}C and 30 bar.

Kinetic model adjustment based on experimental data

As it was previously specified, based on the literature, LHHW kinetic model was considered in this work, but the main constants of the model need to be recalculated in order to assure the fitness of the model with available experimental data.

The experiments for kinetic model adjustment were performed at INCDTIM Cluj-Napoca. The laboratory plant for steam reforming of ethanol is composed of three main parts:

1. The feed part which in turn consists of two components:
    a. the gaseous feeds (steam and carrier gas) is carried out by pressure regulators
    b. the liquid feed (water/ethanol mixture) is done by using HPLC Schimadzu pump
2. The reactions take place in a stainless steel tubular reactor equipped with a stainless steel pill that catalyst ordering. The reactor is placed in a thermostatic enclosure with a maximum achievable temperature of 350 ^oC. The quantity of catalyst (10%Ni-Al_2O_3 was used) to be introduced is 1 g which is mixed with the same quantity of support material (Al_2O_3). In order to carry out the reaction, for each experimental run the catalyst is pre-treated 3 hours at 350^{o}C in H_2.
3. Composition analysis part of the setup consists of two different chromatographs equipped with two detectors: one is TCD (thermal conductivity detector) and the other FID (flame ionization detector). The liquid products resulting from the reaction are analyzed by FID with a 5% Carbowax column 80/100 mesh length 1.5 m.

The experimental conditions are presented in Table 2.

Table 2. Main experimental parameters

Parameters	U.M.	Values
$F_{V,T}$	[mL/min]	10.1, 35.1, 133.1, 200.1, 300.1
$F_{V,dry}$	[mL/min]	0.1
W	[g]	1
T	[C]	350
Time	[h]	24
P	[bar]	3
D	[mm]	8
Dp	[µm]	88

Argon was used as carrier gas. Experiments were performed at five different Ar flows (10, 35, 133, 200, 300 mL/min) in order to have a set of space time ($\theta_V = W/F_{V,T}$) values, a parameter that influences the reaction rate.

The kinetic model presented in literature [2, 12] was adapted to describe our system (10%Ni-Al_2O_3 catalyst working on 350 ^{o}C) by recalculation of the four kinetic constants of reactions (3-6), parameters considered the most important from the mathematical model point of view.

The four kinetic parameters were recalculated by minimizing the objective function that describes the relative deviations between experimental and calculated concentration date on the set of 5 different experimental sets as follows:

$$fob = \sum_{i \to 6}^{Exp} \left[\left(\frac{y_{exp} - y_{calc}}{y_{calc}} \right)^2 \right]^{1} = \min \qquad (16)$$

The calculated values of the four kinetic model parameters are presented in Table 3.

Table 3. Global kinetic constants of SRE

Parameter	Calculated values
k_{E1sim}	$3.64 \cdot 10^{-5}$
k_{E2sim}	$1.44 \cdot 10^{-5}$
k_{R1sim}	$0.55 \cdot 10^{-3}$
k_{R2sim}	$4.33 \cdot 10^{-2}$

Using these recalculated values, the variations of the main components concentrations obtained from the adjusted kinetic model are presented in Figure 4.

The kinetic model was implemented in MATLAB.

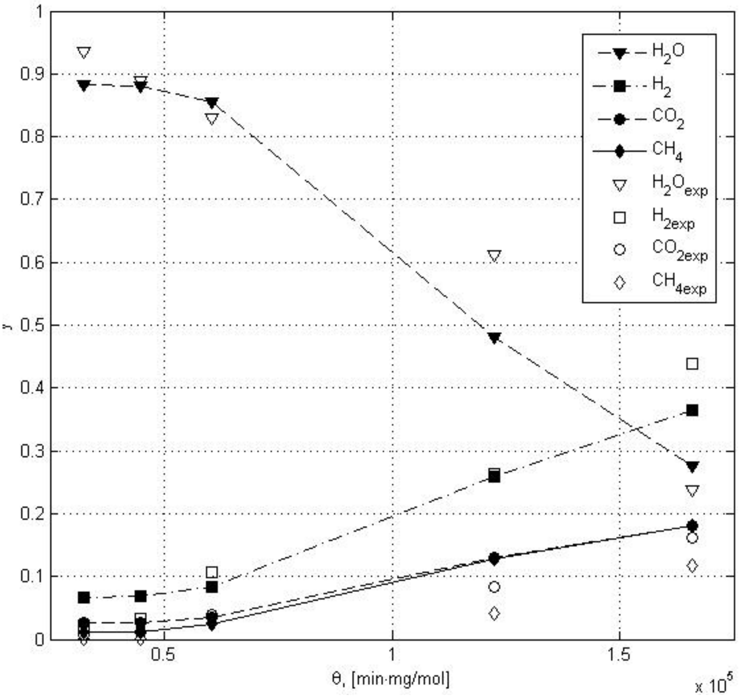


Figure 4. Measured and simulation data of steam reforming of bioethanol (with symbols are shown the experimental data and with lines and symbols the simulation results)

The results obtained by simulation compared with experimental data are presented in Table 4.

Table 4. Experimental and calculated values of components concentration

Comp.	Θ										$\overline{\varepsilon_2}$ %
	θ_1		θ_2		θ_3		θ_4		θ_5		
	Exp	Calc	Exp	Calc	Exp	Calc	Exp	Calc	Exp	Calc	
H_2	0.02	0.07	0.03	0.07	0.10	0.08	0.26	0.26	0.44	0.36	35.2
H_2O	0.94	0.88	0.89	0.88	0.83	0.86	0.61	0.48	0.24	0.27	9.9
CO_2	0.01	0.03	0.01	0.03	0.04	0.04	0.08	0.13	0.16	0.18	36.6
CH_4	$1 \cdot 10^{-3}$	0.01	$2 \cdot 10^{-3}$	0.01	0.04	0.02	0.04	0.13	0.12	0.18	74.5
$\overline{\varepsilon_1}$ %	58.7		51.2		32.1		33.7		19.4		

The average errors $\overline{\varepsilon_1}$ and $\overline{\varepsilon_2}$ were calculated with the equations:

$$\overline{\varepsilon_1} = \frac{1}{4} \sum_{comp} \left(\frac{y_{calc} - y_{exp}}{y_{calc}} \right) \cdot 100 \tag{17}$$

$$\overline{\varepsilon_2} = \frac{1}{5} \sum_{\Theta} \left(\frac{y_{calc} - y_{exp}}{y_{calc}} \right) \cdot 100 \tag{18}$$

As it can be observed, the fitness of the adjusted model is not very good; the overall average error is 39 %. This was due mainly to the lack of sufficient experimental data. It is also necessary to include in the adjustment of the kinetic model, other parameters besides the kinetic constants considered in this work.

CONCLUSIONS

This paper describes the research work done on the thermodynamic analysis of the process of bioethanol steam reforming. Also, for a kinetic model reported in the literature, the kinetic constants were recalculated to adjust the model to the experimental data obtained by using 10%Ni-Al_2O_3 catalyst in isothermal conditions at 350°C. The thermodynamic analysis takes into account the main chemical species involved in the reactions (reactants as well as products). Following the thermodynamic study has resulted that the maximum concentration of H_2 was obtained at the molar ratio of water/ethanol 3:1, temperature of 550°C and 1 bar pressure.

The adjustment of the LHHW kinetic model based on the experimental data obtained in a laboratory plant succeeds to determine the kinetic constants of the process but the fitness of the model was rather poor. In order to improve the kinetic model accuracy, new experiments need to be considered and more parameters of the model have to be included in the adjustment process.

NOTATIONS:

D	reactor diameter [mm]
Dp	particle diameter [μm]
Ea	activation energy [kJ/mol]
$F_{V, dry}$	total dry gas flow [mL/min]
$F_{V,T}$	total flow [mL/min]
H	enthalpy [kJ/mol]
k_i	kinetic coefficient of *i* reaction [mol/min mg]
K_j	adsorption constant of *j* species [-]
p	pressure [bar]
R	gas constant
r_i	reaction rate of *i* reaction [mol/min mg]
T	temperature [K]
W	catalyst mass [mg]
y_{et}	ethanol molar fraction [-]
y_{H2O}	water molar fraction [-]
y_j	molar fraction of the *j* species [-]
$y_{exp,i}$	molar fraction of the experimental values [-]
y_{calc}	molar fraction of the simulation values [-]
ΔH_i	reaction enthalpy of *i* reaction [kJ/mol]
ΔH_j	adsorption enthalpy of *j* species [kJ/mol]
θ_V	space time [min·mg/mL]
θ_i	space time for experiment *i* [min mg/mL]
$\bar{\varepsilon}_i$	average error [%]

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