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Thermodynamic comparison between bio-oil and ethanol steam reforming

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ABSTRACT

The thermodynamic analysis of the steam reforming (under catalytic steam reforming conditions) of a simulated bio-oil (composed of model compounds of components in a real bio-oil) and of ethanol is performed by minimization of Gibb's free energy method with Pro II-SimSci® 8.3 software, and their results are compared. At the equilibrium conditions both oxygenated feeds are completely converted, with H₂, CO₂, CO and CH₄ being the only significant gaseous products. Coke formation is observed below 700 °C for low steam/carbon (S/C) molar ratios (below the stoichiometric value). H₂ yield, which is very similar for both reforming processes (with small differences only for S/C < 2), increases with S/C ratio and goes through a maximum with temperature, being higher than 90% for S/C > 5 and in the 540–640 °C range. Above 600–650 °C (depending on the S/C molar ratio), the energy requirement for steam reforming of ethanol is slightly higher than for bio-oil steam reforming. These results evidence the viability of the joint valorisation of bio-oil and bio-ethanol by means of steam reforming.

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Introduction

Nowadays nearly 90% of the hydrogen is obtained by steam reforming of natural gas or naphtha, but the need to reduce CO₂ emissions has promoted H₂ production from renewable raw materials, such as biomass [1]. These new alternatives for obtaining hydrogen are interesting due to its use as a clean fuel and because it is one of the most important supply in petrochemical, agrochemical, metallurgic, and medicines industries.

Hydrogen can be obtained from biomass directly (gasification, high temperature pyrolysis, catalytic pyrolysis and biological processes) and by routes for obtaining oxygenated hydrocarbons followed by a catalytic reforming process [2]. Bio-ethanol (obtained by biomass fermentation) and bio-oil (a complex mixture of more than 300 oxygenates compounds obtained by flash pyrolysis of biomass), are considered promising biomass derived intermediates for obtaining H₂ by steam reforming [3]. Ethanol is probably the most studied oxygenate for obtaining hydrogen by means of catalytic reforming processes, because it is easy to store, handle and

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less toxic than other oxygenates [4,5]. Among ethanol reforming processes, the catalytic ethanol steam reforming (ESR) has received a preferential attention, since it allows a direct valorisation of bio-ethanol (~86% H₂O), thus avoiding the cost of its dehydration for use as a fuel [5–9]. Bio-oil is currently receiving increasing attention as a raw material for hydrogen production since it can be obtained in a delocalized way and subsequently transported to a large-scale and centralized catalytic reforming unit especially designed for this purpose [10–13]. Similarly, bio-oil has a great amount of water (~30–40%), which means that steam reforming is also a suitable strategy for bio-oil valorisation. The joint valorisation of a bio-oil/ethanol mixture by steam reforming over a Ni based catalyst has also been recently studied [14], which is considered an interesting route for the development of the bio-refinery concept.

ESR is an endothermic process, whose global reaction has the following stoichiometry:

Nevertheless, the reaction mechanism is complex and is comprised of numerous individual stages and secondary reactions, such as those in Eqs 2–12, which produce intermediate compounds and sub products, thus reducing H₂ yield and causing catalyst deactivation by coke deposition [4,9].

The steam reforming of oxygenates in bio-oil (BSR) (whose overall chemical formula is C_nH_mO_k) takes place through the formation of CO + H₂,

followed by the water gas shift (WGS) reaction, Eq. (7), with the overall reaction being as follows:

As a result, the maximum stoichiometric hydrogen yield by bio-oil steam reforming is $(2n + m/2 - k)$ mol_{H₂}/mol_{oxygenate},

although the H₂ yield is lower than this maximum depending on the operating conditions, mostly because of the equilibrium of the WGS reaction, Eq. (7), and other secondary reactions such as methanation, Eq. (8), methane steam reforming, Eq. (9), and coke formation by Boudouard reaction, Eq. (10), by cracking of oxygenates in bio-oil, Eq. (15), and by cracking reactions of hydrocarbons, Eq. (16).

In order to identify the most favourable operating conditions that maximize H₂ yield in both ESR and BSR, the thermodynamic study of both processes is an important tool. The thermodynamics of ESR has been widely studied [15–21], as well as of other ethanol reforming process such as partial-oxidation, oxidative steam reforming and autothermal reforming [20–23]. Nevertheless, there is more scarce information concerning the thermodynamics of bio-oil reforming processes, due to the complex nature of this feed. This last topic has been previously approached in literature with bio-oil selected oxygenated compounds, such as acetic acid [24–27], acetone [24,25], hydroxyacetone (acetol) [28,29], ethylene glycol [24–26], isopropyl alcohol, lactic acid and phenol [30], as well as with a mixture of three model oxygenates (acetic acid, ethylene glycol and acetone) [24,25]. Although the same reaction products are obtained in the thermodynamic equilibrium of the steam reforming of different oxygenated compounds (H₂, CO, CO₂, CH₄ and coke), the results in the literature show that the maximum H₂ yield and the operating conditions corresponding to that maximum depend on the nature and composition of the oxygenated feed. Thus, according to Aktas et al. [30], the temperature/steam-to-fuel ratio combinations that favoured desired syngas features (such as molar H₂/CO ratio around 2 with minimal presence of CO₂ and CH₄) were (1200 K, 4), (1200 K, 5) and (1000 K, 9) for steam reforming of isopropyl alcohol, lactic acid and phenol, respectively. Similarly, the thermodynamic study of sorption enhanced steam reforming of alcohols performed by Lima da Silva and Müller [31] reports that, in order to maximize H₂ formation with minimum CO content, the optimum steam-to-fuel ratio increases as the number of carbon atoms in the alcohol is increased (being 4:1, 6:1, 9:1 and 12:1 for methanol, ethanol, glycerol and n-butanol, respectively).

The afore mentioned thermodynamic studies are the basis for choosing the reforming conditions maximizing the production of H₂ and minimizing the formation of by-products (CO and CH₄), which are the precursors for coke formation, and therefore responsible for catalyst deactivation. In this work, a thermodynamic analysis of the steam reforming of a simulated crude bio-oil is performed with the aim of determining the operating conditions (temperature and S/C molar ratio) allowing the maximum H₂ yield and minimum yield of by-products (CO, CH₄) and coke. This simulated bio-oil is composed of model compounds representative of the main families of components in bio-oil (acids, esters, ketones, aldehydes, ethers, alcohols, phenols). Moreover, the results corresponding to ethanol steam reforming are also presented in order to compare the operating conditions required for

obtaining high hydrogen yields from these two biomass derived oxygenated feeds, with the objective of assessing the viability of the joint reforming of both oxygenated feeds. Furthermore, in view of the interest of this joint feed, the thermodynamics has been studied for the reforming of 50 wt% ethanol/bio-oil mixture.

Methodology

Bio-oil composition

The model compounds selected as representative of each family of components in the bio-oil are the following: cyclohexanone and hydroxyacetone (ketones), acetic acid and levulinic acid (acids), vanillin (aldehydes), propylenglycol and heptanol (alcohols), methoxyphenol (phenols), trioxane (ethers) and ethyl propionate (esters). The amount of each component in the simulated bio-oil was based on the composition of a real raw bio-oil obtained by fast pyrolysis of pine sawdust (at 480 °C in a spouted bed reactor) and subsequently subjected to a thermal treatment at 500 °C, in which the controlled separation of some bio-oil components took place [32]. This treatment consists on the controlled deposition of pyrolytic lignin, which is formed by polymerization of part of the phenolic compounds in the raw bio-oil, i.e., those produced by the pyrolysis of lignin in biomass [13]. The formula of the simulated bio-oil (calculated from the detailed composition of the bio-oil determined by means of Gas Chromatography–Mass Spectroscopy, GC–MS) is $C_{4.86}H_{8.26}O_{1.92}$ and its molecular weight is 97.3 g/mol [32]. Table 1 shows the composition (weight percent) of the family of components in the thermally treated bio-oil (left) and of simulated bio-oil (right).

Taking into account its composition, the stoichiometry of the steam reforming for the simulated bio-oil is as follows:

Calculation procedure

The calculations of the equilibrium compositions were performed by minimization of the Gibbs free energy method and considering the non-stoichiometric approach, which do not

require the definition of the simultaneous reaction steps involved in each process.

The total Gibbs free energy of the system can be expressed [31]:

$$\frac{G}{RT} = \left(\sum_{i=1}^N n_i \left[\frac{G_i^0}{RT} + \ln(y_i P) \right] \right)_{\text{gas}} + \frac{1}{RT} \left(\sum_{i=1}^N n_i G_i^0 \right)_{\text{condensed}} \quad (18)$$

where G and G_i^0 are the Gibbs free energies of the system and of i product at their standard states; R , T and P are the universal gas constant, temperature and pressure, respectively; y_i is the mole fraction of i product; N is the total number of products, and; n_i is the number of moles of i product.

The number of moles of the different components in the equilibrium, n_i , are those that minimize the Eq. (18), while fulfilling the elemental mass balance:

$$\sum_{i=1}^N n_i \alpha_{ik} = b_k \quad k = 1, \dots, M \quad (19)$$

where b_k is the total number of atoms of each k atomic species (C, H, or O) in the system; α_{ik} is the number of atoms of k atomic species (C, H or O) contained in each molecule of i product, and; M is the total number of atomic species (C, H or O).

Different calculation programs have been used in literature for minimizing Gibbs free energy [15,17,20,21,31,33,34]. In order to minimize the objective function given by Eq. (18), with the restrictions given by Eq. (19), the Pro II-SimSci[®] 8.3 software (Invensys SimSci) was used in this work. The program includes the option of a Gibbs reactor and an extensive thermodynamic database, with a great number of components of state equations. Soave-Redlich-Kwong state equation was considered for the calculations [33,34].

The reaction products specified for the calculation in the software were H_2 , CO , CO_2 , CH_4 and coke (defined as graphitic carbon). Other simulations at low temperature have also been carried out by including other reaction products apart from the previous ones, such as ethylene, acetaldehyde and acetone. The results of these simulations (not shown) evidence that all hydrocarbon products (except CH_4) are absent in the reaction product stream, because they are intermediate products in the reaction scheme, whose absence in the equilibrium conditions has also been experimentally proven both in ESR [8,9] and in BSR [13,14]. Ethanol and bio-oil conversion is full in all cases and the sole products in the reaction medium under thermodynamic equilibrium conditions are H_2 , CO , CO_2 , CH_4 and coke.

Fig. 1 shows the scheme of the simulated process, which includes: a mixer for the oxygenated feed and water (M1), an evaporator for heating the mixture (E1), and the reforming reactor (R1).

The simulation conditions for both ethanol and simulated bio-oil were: atmospheric pressure, 300–1000 °C (which is a suitable temperature range for attaining rapidly the thermodynamic equilibrium in the catalytic steam reforming process of these oxygenated feeds) and steam/carbon ratio (S/C) between 1 and 16. Taking into account the composition of ethanol and simulated bio-oil, and the stoichiometry of the steam reforming reactions for both feeds, Eqs. (1) and (17), the stoichiometric S/C ratio for the ESR and BSR are 1.5 and 1.61

Table 1 – Composition (wt%) of the thermally treated real bio-oil (left) [32] and simulated bio-oil (right).

Family of real compounds		Model compounds	
Ketones	26.7	Cyclohexanone	8.4
Carboxylic acids	17.4	Hydroxy acetone	18.3
		Acetic acid	10.9
Aldehydes	16.2	Levulinic acid	6.5
		Vanillin	16.2
Alcohols	19.1	Propylene glycol	7.1
		Heptanol	12.0
Phenols	11.4	Methoxyphenol	11.4
Ethers	3.8	Trioxane	3.8
Esters	5.4	Ethyl propionate	5.4

Fig. 1 – Scheme of the global process considered for the simulation of ESR and BSR.

respectively, and the stoichiometric potential for H_2 production from ethanol and bio-oil are $6 \text{ mol}_{H_2}/\text{mol}_{\text{ethanol}}$ and $11.49 \text{ mol}_{H_2}/\text{mol}_{\text{bio-oil}}$ (or $3 \text{ mol}_{H_2}/\text{mol}_C$ and $2.5 \text{ mol}_{H_2}/\text{mol}_C$, for ESR and BSR, respectively).

The following is obtained from the simulation: i) the molar flow of H_2 in the thermodynamic equilibrium, by molar flow unit of the oxygenated feed; ii) the molar flow of carbon-containing by-products, and; iii) the reaction enthalpy under standard conditions (ΔH_r°), which is used for the calculation of the energy requirement.

The H_2 yield is calculated by Eq. (20) as a fraction of the maximum allowed by stoichiometry according to Eqs. (1) and (17) and assuming total conversion, and the yield of each carbon-containing by-product is quantified by Eq. (21), based on the total C fed into the reactor.

$$Y_{H_2} = \frac{\text{molar flow of } H_2}{(2n + \frac{m}{2} - k) \times \text{molar flow of oxygenates feed}} \quad (20)$$

$$Y_i = \frac{\text{molar flow of } i \text{ (CO, CO}_2, \text{CH}_4, \text{ coke)}}{\text{molar flow of C in the feed}} \quad (21)$$

Results and discussion

In order to validate the method for Gibbs free energy minimization used in this work, the results calculated in this work for H_2 molar flow in the ESR equilibrium (by molar flow unit of ethanol in the feed) have been compared with other results in literature at 800, 1000 and 1100 K and with different steam/ethanol (S/E) molar ratios. The results are shown in Table 2. The great similarity between the results of this work and those obtained by other authors proves the validity of the

Table 2 – Comparison of the molar flow of H_2 in the equilibrium in ESR reaction, referred to the molar flow of ethanol in the feed, calculated in this work with other results in literature.

T (K)	800				1000				1100			
S/E	1	3	6	9	3	6	9	3	6	9		
Sun et al. [20]	1.5	2.5	3.8	4.2	4.5	5.1	5.4	4.6	4.9	5.1		
Lima da Silva et al. [18]	1.2	2.2	3.2	4.2	4.5	4.9	5.3	4.5	4.8	5.1		
this work	1.4	2.2	3.4	4.2	4.5	5	5.3	4.5	4.9	5.1		

calculation procedure. The small differences are attributable to the different methods used for minimizing Gibbs free energy.

Equilibrium composition of the gaseous products

The evolution with temperature and steam to carbon molar ratio (S/C) of the yields of products for ESR and BSR processes are shown in the Figs. 2 and 3. Fig. 2 corresponds to H_2 yield, and Fig. 3 corresponds to gaseous carbon by-products.

The H_2 yield (Fig. 2) increases noticeably with temperature until a maximum is reached (in the 500–800 °C range, depending on the S/C ratio), and decreases slightly for higher temperatures. For both processes, the maximum H_2 yield is reached at a lower temperature as the S/C ratio is increased. The comparison of the results for both processes shows that for $S/C < 2$ the hydrogen yield is slightly lower for BSR than for ESR, whereas for higher S/C ratios the H_2 yield tends to similar values for both steam reforming processes. This result is consistent with those of Lima Da Silva and Müller [31], who

Fig. 2 – Evolution of hydrogen yield with temperature, for different S/C ratios in BSR (continuous line) and ESR (dashed line).

reported no significant differences in the H₂ yield obtained by steam reforming of different oxygenates (ethanol, methanol, glycerol and n-butanol).

The yields of gaseous carbon by-products are shown in Fig. 3. For both processes, CO₂ yield (Fig. 3a), increases noticeably with temperature in the 300–600 °C range for all S/C ratios, which evidences that the reforming reactions, Eqs. (1) and (17), are favoured in this temperature range, and that WGS reaction is thermodynamically favoured below 500 °C, which justifies the absence of CO below this temperature (Fig. 3b). CO₂ yield decreases above 600 °C, and an increase in CO yield is observed (Fig. 3b), almost in parallel to the decrease in CO₂ yield for high S/C ratios. This result is a consequence that the exothermic WGS reaction is clearly disfavoured above 600 °C. Furthermore, as temperature is increased Boudouard reaction, Eq. (10), is disfavoured, which contributes to decreasing the yield of CO₂ and enhancing the formation of CO.

On the other hand, it should be noted that there is a lower yield of CO₂ and higher yield of CO in ESR than in BSR. The higher yield of CO₂ in BSR should be attributed to the significance of decarboxylation of oxygenates in the bio-oil (reaction included in Eq. (15), in which several reactions for the decomposition of oxygenates in the bio-oil are outlined). Likewise, the higher yield of CO and CH₄ in ESR should be attributed to the significance of reactions that are irreversible under the conditions studied, as are the decomposition of acetaldehyde, Eq. (5) and ethanol, Eq. (6), to form CO and CH₄.

CH₄ yield (Fig. 3c) is very high at low temperature (below 400 °C), decreases sharply as temperature is increased, especially for high S/C ratios, and is null above 800 °C for all S/C ratios. This result evidences that, for both reforming processes, CH₄ formation through methanation reaction of CO, Eq. (8), is notably favoured at low temperature (below 500 °C), especially for low S/C ratios, which contributes, together with the WGS reaction, to the absence of CO in the reaction medium below 400 °C. As temperature and S/C ratio are increased, CH₄ reforming rate also increases, Eq. (10). Furthermore, the methanation reaction is thermodynamically disfavoured by the increase in temperature above 500 °C, which explains the sharp decrease in CH₄ yield with temperature and contributes to the sharp increase in CO yield observed in Fig. 3b for low S/C ratios. It is observed that in the BSR process a lower amount of CH₄ is predicted by thermodynamics than in ESR process, especially for S/C ratio lower than 1.61 (stoichiometric S/C ratio for BSR). This result is explained by the significance of CH₄ formation under these conditions by decomposition of acetaldehyde (Eq. (5)) and ethanol (Eq. (6)).

Regarding the effect of S/C ratio on product yields, it is observed that the yields of H₂ and CO₂ increase noticeably with S/C ratio, CO yield decreases, whereas CH₄ yield goes through a maximum for temperatures below 500 °C. These results evidences that high steam content in the reaction medium favours the reforming and WGS reactions.

Fig. 3 – Evolution of carbon by-products yield with temperature, for different S/C ratios in BSR (continuous line) and ESR (dashed line). CO₂ yield (graph a), CO yield (graph b) and CH₄ yield (graph c).

Fig. 4 – Evolution with S/C ratio of the maximum H₂ yield and the temperature required for attaining this maximum (a), and the by-product distribution (b), for BSR (continuous lines) and ESR (dashed lines).

Fig. 4 shows the maximum H₂ yield and the temperature at which that maximum is attained in the steam reforming of both oxygenated feeds for different S/C ratios in the feed (Fig. 4a), and the gaseous carbon-containing product yields for these conditions (Fig. 4b). For both processes, the maximum H₂ yield increases continuously with S/C ratio, this increase being very noticeable up to S/C = 5 (at which H₂ yield reaches 90% for both ESR and BSR) and subsequently it is attenuated. The maximum H₂ yield obtained from both feeds is very similar, and only small differences are observed for S/C ratio < 2. The temperature required for attaining the maximum H₂ yield decreases exponentially with S/C ratio for S/C < 6 and almost linearly for higher S/C ratios, from 620 °C for S/C = 6 to 530 °C for S/C = 16 in BSR. The temperatures required for attaining the maximum H₂ yield for each S/C ratio are slightly higher (around 10–20 °C) for ESR.

Fig. 4b shows that, for the operating conditions corresponding to the maximum H₂ yield, CO₂ yield evolves with S/C ratio in parallel to H₂ yield, whereas CO yield shows the

opposite behaviour, with a slightly lower CO yield being obtained in BSR than in ESR. CH₄ formation is almost insignificant for the operating conditions corresponding to the maximum H₂ yields, especially for S/C > 6, due to the efficient CH₄ reforming under these conditions.

Coke predictions

The coke formation was analysed because it is the main cause of catalyst deactivation in the reforming processes [8,9,13,14], and consequently conditions the industrial implementation of the process. In the simulations, the coke was considered as graphite type. Coke yields, calculated according to the Eq. (21), are plotted in Fig. 5 for BSR (continuous line) and ESR (dashed line). For both processes, coke deposition is only predicted for S/C ratio < 2 and temperatures below 700 °C, and the coke yield predicted is noticeably higher for BSR than for ESR. For both processes, there is a sharp decrease in coke yield with the increase in temperature and S/C ratio, which evidences the noticeable promotion of coke gasification reactions (reverse Eq. (10) and Eq. (12)) with the increase in both operating variables. Consequently, it is predicted that coke deposition is avoided for the operating conditions that maximize H₂ yield.

Nevertheless, it should be mentioned that these coke predictions are not coherent with experimental results obtained for BSR over a Ni-based catalyst [13,14] or ESR over Ni and Co based catalysts [8], that show a high coke deposition of coke below 600 °C for S/C > 6, especially for ESR. This result shows that the use of the thermodynamic properties of graphite for representing coke deposition in reforming processes is not complete. A previous study of Diaz Alvarado and Gracia approached this problem by assuming 3 different carbon representations, (graphite, nanotubes and amorphous carbon) for describing the equilibrium composition for ESR [19]. The

Fig. 5 – Evolution of coke yield with temperature, for different S/C ratios in BSR (continuous line) and ESR (dashed line).

results of these authors predicted that carbon deposits are formed for S/E ratio below 4 and, in this zone, the presence of graphite dominated below 400 °C, whereas above 400 °C the formation of multi-wall carbon nanotubes prevailed. Nevertheless, their prediction for amorphous carbon (which was absent in equilibrium conditions) did not match with some experimental results in real systems, which showed amorphous carbon deposits. From the aforementioned results, it is evident that the description of coke deposition corresponding to thermodynamic equilibrium is a very complex task, because of the heterogeneous structure of the coke deposited in the reforming process [8,35]. Quantification of coke yield may be improved by assuming different carbon representations whose thermodynamic properties are not available in conventional thermodynamic databases. Accordingly, it is interesting to step further in the characterization of the coke because its composition will presumably have considerable incidence on the reactivity of reverse Boudouard (Eq. (10)) and gasification (Eq. (12)) reactions. It has been experimentally proven that these coke gasification reactions are significant above 600 °C in the steam reforming of ethanol [36], bio-oil [37] and isooctane [38].

Energy requirements

In order to determine the overall energy requirement of BSR and ESR processes, it was assumed that the global process consist of 3 steps [20]: i) the reactants (water and the oxygenated feed) are mixed and heated up to the reforming temperature; ii) the reforming reaction takes place in the isothermal Gibb's reactor and the thermodynamic equilibrium is reached, iii) the reaction products are cooled down to the reference temperature. Consequently, the global energy balance includes the energy required for the heating, reforming and cooling steps:

$$Q_{\text{total}} = Q_{\text{heating}} + Q_{\text{reforming}} + Q_{\text{cooling}} \quad (22)$$

Assuming that both the feed and the reactor output stream are at standard conditions and that there is no heat loss the following is fulfilled:

$$Q_{\text{total}} = -\Delta H_r^0 = \sum n_p \Delta H_{c,p}^0 - \sum n_r \Delta H_{c,r}^0 \quad (23)$$

where ΔH_r^0 is the standard reaction enthalpy (the result provided by the simulation), and ΔH_c^0 is the combustion enthalpy of products (p) and reactants (r).

For convenience, as proposed by Sun et al. [20], the total energy of the system has been expressed by a non-dimensional parameter ($Q_{\text{total}}/\Delta H_{c,r}^0$), where $\Delta H_{c,r}^0$ is the combustion heat of the oxygenated feed, which is -1235 kJ/mol for ethanol and -2620 kJ/mol for the simulated bio-oil (this last value has been calculated considering the contribution of each component in the mixture). Thus, values of $Q_{\text{total}}/\Delta H_{c,r}^0 > 0$ correspond to an endothermic global system, whereas the system is considered exothermic for values lower than zero.

Fig. 6 shows the non-dimensional total heat as a function of S/C ratio and temperature for BSR (continuous line) and ESR (dashed line). The global process of steam reforming for both

feeds is exothermic at low temperatures and for low S/C ratios, which is explained because methanation and WGS reactions are promoted under these conditions. For high reforming temperatures (above 550 °C) both processes are clearly endothermic for any S/C ratio. Therefore as temperature and the S/C ratio increases (that is, for the conditions that favour high H_2 yield), the energy required for the steam reforming of both feeds increases. Both processes are nearly thermoneutral ($Q_{\text{total}}/\Delta H_{c,r}^0 = 0$) at 530 °C for S/C = 1, and at lower temperatures as S/C ratio is increased. Unfortunately, taking into account the results of Fig. 2, it is observed that a thermoneutral steam reforming process produces low H_2 yields (between 20 and 30%) for both oxygenated feeds. Below 600–650 °C (decreasing temperature as S/C molar ratio increases, Fig. 6) both reforming processes have almost the same energy requirements. However, for higher temperatures the global energy requirements for ESR are slightly higher than those for BSR.

Equilibrium composition for the steam reforming of a ethanol/bio-oil mixture

Given the interest of the joint reforming of ethanol and bio-oil [14], a study has been carried out on the reforming of 50 wt% ethanol/bio-oil mixture ((E + B)SR). The simulations have been carried out for low S/C ratios, for which the greatest differences have been obtained in the reaction medium composition for ESR and BSR processes (Fig. 3). Table 3 shows the yields for the gaseous products and coke in the steam reforming of 50 wt% ethanol/bio-oil mixture, as well as the values corresponding to ESR and BSR processes. The results in Table 3 show a composition of the reaction products half-way between those corresponding to the steam reforming of ethanol and bio-oil, although slightly closer to the later than the former.

Conclusions

The H_2 yield corresponding to the thermodynamic equilibrium in the steam reforming of bio-oil and of ethanol is very

Fig. 6 – Non-dimensional energy requirements ($Q_{\text{total}}/\Delta H_{c,r}^0$), for BSR (continuous line) and ESR (dashed line) under different operating conditions.

Table 3 – Comparison of the yield of reaction products and coke yield at the equilibrium in the steam reforming of ethanol (ESR), bio-oil (BSR) and a mixture of ethanol/bio-oil (50 wt%) ((E + B)SR) for a S/C molar ratio of 1 and different temperatures.

Component	T (°C)	ESR	(E + B)SR	BSR
H ₂	300	0.03	0.02	0.02
	500	0.24	0.22	0.21
	700	0.64	0.60	0.58
	900	0.71	0.66	0.64
	1000	0.70	0.66	0.63
CO ₂	300	0.21	0.23	0.24
	500	0.32	0.35	0.35
	700	0.22	0.22	0.21
	900	0.12	0.12	0.12
	1000	0.10	0.10	0.10
CO	300	0.00	0.00	0.00
	500	0.06	0.06	0.06
	700	0.69	0.70	0.70
	900	0.88	0.88	0.88
	1000	0.90	0.90	0.90
CH ₄	300	0.67	0.51	0.44
	500	0.48	0.40	0.35
	700	0.10	0.09	0.08
	900	0.00	0.00	0.00
	1000	0.00	0.00	0.00
Coke	300	0.13	0.26	0.32
	500	0.15	0.19	0.24
	700	0.00	0.00	0.00
	900	0.00	0.00	0.00
	1000	0.00	0.00	0.00

similar, and there are small differences in the equilibrium yields predicted for carbon-containing products, with slightly lower yields of CO and CH₄ and higher yields of CO₂ for bio-oil steam reforming compared with ethanol steam reforming. The differences in products yields predicted for both reforming processes are notably attenuated for high S/C ratios. Assuming graphitic carbon, it is predicted that coke formation is higher for BSR than for ESR, and it can be avoided above 700 °C or for S/C ratios higher than 2. Nevertheless, it must be pointed out that the assumption of graphitic carbon is not a complete representation for coke deposition in both reforming processes, because the predicted coke formation is noticeable lower than the experimental values.

The operating conditions (temperature and S/C ratio) needed for maximum H₂ yield are similar both in ESR and in BSR. H₂ yield notably increases with S/C ratio and goes through a maximum with temperature, and the temperature required for attaining the maximum H₂ yield, which decreases with the S/C ratio in the feed, is only slightly higher (around 10–20 °C) for ESR than for BSR. Under the conditions that maximize H₂ yield, the CH₄ formation is almost negligible and coke deposition is avoided. For both reforming processes, S/C = 8 and reforming temperature around 600 °C are appropriate values for attaining high H₂ yield (~0.94) with relatively low values of CO yield (~0.14) and negligibly formation of CH₄ and coke.

The global energy requirements, expressed in a non-dimensional way, are almost the same for both reforming processes at low temperatures. For temperatures above 600–650 °C (depending on the S/C molar ratio) the energy

requirement for steam reforming of ethanol is slightly higher than for bio-oil steam reforming, which should be taken into account for the estimation of the energy requirements at industrial scale.

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Nomenclature

b_k	total number of atoms of each k atomic specie (C, H, or O) in the system
BSR	bio-oil steam reforming
ESR	ethanol steam reforming
G, G_i^0	Gibbs free energy of the system and of i product at its standard state
M, N	total number of atomic species (C, H and O), in Eq. (19), and total number of products, in Eq. (18), respectively
n, m, k	number of C, H and O atoms, respectively, in the oxygenated feed
n_i	number of moles of i product
P	pressure
Q_{total}	global energy requirement
T	temperature
R	universal gas constant
S/C	steam-to-carbon molar ratio
y_i	mole fraction of i product
Y_{H_2}, Y_i	yield of hydrogen and of i carbon-containing product (H ₂ , CO, CO ₂ , CH ₄ , coke)

Greek symbols

α_{ik}	number of atoms of k atomic species (C, H or O) contained in each molecule of i product
$\Delta H_{c,p}^0, \Delta H_{c,r}^0$	combustion enthalpy of products and reactants (oxygenates), respectively
ΔH_r^0	standard reaction enthalpy

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