

STEAM REFORMING OF UPGRADED BIO-OIL AQUEOUS PHASE FRACTION FROM SUNFLOWER SEED HULLS: THERMODYNAMIC ANALYSIS

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Abstract— This work focuses on the study of hydrogen production process departing from waste lignocellulosic biomass. The bio-oil was first obtained by non-catalytic fast pyrolysis of sunflower seed hulls. Subsequently, it was upgraded to reduce the concentration of higher molecular weight compounds by water addition and mixing. A 1/1 bio-oil: water ratio was selected here. Later, a thermodynamic analysis based on free energy minimization was profited to study the steam reforming process of the upgraded bio-oil sample. The influence of the operation temperature on the reforming was analyzed. The highest hydrogen yields were obtained at ~740°C. A comparison with acetic acid used as model compound of the bio-oil is included. Results show that acetic acid is not a good approximation of a real aqueous phase of upgraded bio oil fraction. The study concludes with an analysis on the energetic efficiency, showing that its maximum is presented at lower temperatures than the maximum yield, due to the thermal requirements of preheating.

Keywords— Hydrogen, Thermodynamic analysis, Bio-oil, Steam reforming.

I. INTRODUCTION

In a global context characterized by population increase and the fast growing in per capita consumption in emergent countries, a wide variety of alternatives to satisfy the high demand of energy have been proposed. Hydrogen, apart from being a fundamental raw material in metallurgical, chemical and petrochemical industries, is a promising energy carrier for the future. The main sources of H₂ nowadays are not renewable, fossil fuels as CH₄, which is reacted in large-scale facilities with steam and/or air by different reforming process. By these means, syngas (H₂ + CO) is formed and further purified if required. In the actual context of increasing energy requirements and environmental concerns, biofuels have been pointed as promissory alternatives as non-fossil raw material sources. Although extensive knowledge about first generation biofuels is currently available (Naik *et al.*, 2010), the development of other options is needed. Among them, second generation biofuels, which include lignocellulosic biomass as raw material, result of interest. This type of biomass is generally obtained from agro-industrial, agricultural activities, forest waste products, and

even from ad hoc crops (Naik *et al.*, 2010). As a renewable energy source, biomass is cost-effective, presents an almost neutral CO₂ balance and generates remarkably low SO₂ and NO_x emissions (Chen *et al.*, 2011).

Bio-oil is the liquid fraction obtained from capturing the condensable gases exiting the pyrolysis unit. Storage and transportation of bio-oil are simpler than those of a gas (pyrolytic or by gasification of biomass) or raw biomass. As a disadvantage, it presents a polar character, and it is corrosive and viscous (Naik *et al.*, 2010). Bio-oil can be obtained by fast pyrolysis of sunflower seed hulls (SSH) as a complex mixture of different organic compounds such as acids of low molecular weight, ketones, aldehydes, furans, alcohols, phenols, aromatics, other acids of high molecular weight, esters and sugars (Casoni *et al.*, 2015), and subsequently fed to a steam reforming reactor to achieve a stream rich in hydrogen. The bio-oil used to feed catalytic steam reforming processes has a strong tendency to form carbonaceous depositions leading to the deactivation of the catalysts (Takanabe *et al.*, 2006). Numerous alternatives have been proposed in literature to mitigate this problem (Xiu and Shahbazi, 2012). Among others, the addition of water to the bio-oil in order to separate the light compounds (aqueous phase) from tar (oily phase) is profited (Scholze and Meier, 2001). The hydrophobic phase contains the products derived from lignin, while the aqueous phase mainly contains the species derived from holocellulose: acids, ketones, aldehydes, etc. (Yan *et al.*, 2010). Normally, the aqueous fraction does not have specific applications; its reforming to produce streams rich in hydrogen can increment its economic value (Resende *et al.*, 2015). After obtained and conveniently upgraded, the bio-oil can be converted into different products; the study of the transformation of aqueous phase of upgraded bio-oil fraction into syn-gas or hydrogen by steam reforming (SR) is the main aim of this work.

Several works reporting steam reforming of real bio-oil from pyrolysis biomass or its aqueous phase can be found (Remiro *et al.*, 2014; Valle *et al.*, 2013; Wu *et al.*, 2008). Because of the complexity of real bio-oil, model compounds or synthetic bio-oil are normally used to study the steam reforming of bio-oil (Wang *et al.*, 1997). Acetic acid has been widely studied as model compound, since it is reported as the most abundant compound in bio-oil mixtures (Esteves Nogueira *et al.*, 2014; Galdá-

mez *et al.*, 2005); acetol, acetone, phenol, among others, have been used as well (González-Gil *et al.*, 2015; Trane-Restrup *et al.*, 2015; Xu *et al.*, 2013).

Regarding thermodynamic studies of reforming of model compounds, the following works can be mentioned using acetic acid, methanol, ethylene glycol, acetone, ethanol, n-butanol, acetol, glycerol, phenol, syringol, furfural, isopropyl alcohol or lactic acid (Aktaş *et al.*, 2009; Goicoechea *et al.*, 2015; Lima Da Silva and Müller, 2011; Resende *et al.*, 2015; Vagia and Lemonidou, 2007; Xie *et al.*, 2014). Contrasting this number of papers, remarkably less references considering model mixtures with the main compounds of bio-oil are found (Montero *et al.*, 2015; Resende *et al.*, 2015).

Resende *et al.* (2015) conducted an interesting thermodynamic analysis of steam reforming of model compound and synthetic aqueous fraction of bio-oil. This aqueous phase was based on the average composition of the aqueous fraction obtained from pyrolysis of various feedstocks. Similarly, Domine *et al.* (2008) calculated the thermodynamic equilibrium composition for bio-oil steam reforming, assuming a simplified bio-oil mixture with seventeen oxygenated of the main bio-oil components and water, to match the ratio C:H:O revealed by the elemental analysis of their real bio-oil sample. The research of Montero *et al.* (2015) involves a thermodynamic study of steam reforming of a synthetic bio-oil composed of model species from real bio-oil components.

Thermodynamic analyses of steam reforming of real bio-oils from different raw sources is remarkably scarce. Even further, to our best knowledge, literature studies focusing the steam reforming of bio-oils derived from pyrolysis of sunflower seed hulls have not been published.

This contribution presents a thermodynamic study of steam reforming of the aqueous phases of real bio-oils from fast pyrolysis of SSH. The influence of the operative variables on the distribution of products from SR was analyzed through a Gibbs free energy minimization strategy. Additionally, the amount of deposited carbon as predicted by thermodynamics is estimated in the different operative conditions.

II. METHODS

A. Fast pyrolysis of sunflower seed hulls and bio-oil upgrading

Sunflower seed hulls were profited as biomass to feed the pyrolysis reactor. This lignocellulosic material presented a moisture content of 6% (OHAUS MB45). Before pyrolysis, the hulls were milled to particles in the range of 250 μm (HORIBA LA-950).

The pyrolytic reaction was performed in a vertical glass reactor implemented into an electric furnace previously heated at 430 °C. Nitrogen was employed as carrier gas, fed from the top of the reactor at 200 mL/min. The vapors downstream the reactor were condensed in an ice/water bath. The experimental conditions were selected to maximize the yield of liquid. A detailed description of pyrolysis process and bio-oil characterization is

given elsewhere (Casoni *et al.*, 2015).

The upgrading of the obtained bio-oil was carried out by mixing this liquid with water at a bio-oil/water mass ratio following a previous report in literature: 1/1 w/w (Rasendra *et al.*, 2011). To these ends, bio-oil was added dropwise to water previously cooled at 0 °C in a water/ice bath. The mixture was maintained under continuous stirring for 15 min in order to precipitate a paste-like phase (Park *et al.*, 2016) composed mainly by methoxy-phenols. On the other side, the aqueous phase retains the low-weight species, with acetic acid appearing as the major component. Through this approach, the upgraded bio-oil presented a much simpler composition than the original bio-oil.

The chemical compositions of the original and upgraded bio-oils were quantified using a GC-MS Perkin Elmer CLARUS 500 chromatograph, equipped with an Elite-5 MS column (60 m, 0.25 mm ID and 0.25 μm df). The method comprised an initial temperature of 65 °C held for 5 min followed by a ramp of 30 °C/min up to 280 °C held for 0.83 min. Towards the identification of chromatographic peaks, the NIST MS library was profited (global matches higher than 800).. The water content of the original bio-oil amounted 11% w/w (Karl-Fischer).

B. Free energy minimization as a tool for computing chemical equilibrium

The equilibrium composition of the reaction mixture was calculated by minimization of Gibb's free energy (Elliott and Lira, 2012). Carbon deposition is a strong restriction in reforming processes leading to deactivation of the reforming catalysts. Then, the inclusion of the prediction of solid carbon formation in the analysis acquires an outstanding relevance. This work considers the carbon modeled as graphite. Graphite presents a null Gibbs energy and a vapor pressure low enough as to be neglected it from the energy minimization. However, graphite cannot be omitted in the atomic balance of carbon.

Several studies regarding bio-oil steam reforming (BSR) (Aktaş *et al.*, 2009; Lima Da Silva and Müller, 2011; Montero *et al.*, 2015) have proved that at high enough residence times the gaseous mixture exiting the reactor is composed by H₂, H₂O, CO, CO₂, and CH₄, with negligible amounts of C₂₊ species, even at low temperature. As mentioned, the prediction of appearance of carbonaceous depositions was also considered.

C. Energetic evaluation

The reaction performance at equilibrium is evaluated through the yields (η_i) of the different products:

$$\eta_i = \frac{n_i}{n_{BO}^0} \quad (1)$$

where n_i corresponds to the molar quantities of each of the i species present in the output mixture, including the moles of solid carbon generated. n_{BO}^0 represents the molar quantity of the bio-oil fed to the reactor. The overall energy requirement of the process of bio-oil steam reforming is evaluated here through the thermal efficiency (φ), according to:

$$\varphi = \frac{n_{H_2}}{Q_T} \quad (2)$$

where Q_T amounts the reaction heat plus the heat required to preheat and evaporate the reactive mixture from 25 °C up to the reaction temperature:

$$Q_T = \sum_{\text{products}} (n_i \cdot H_i)_T - \sum_{\text{reactives}} (n_i \cdot H_i)_{298K} \quad (3)$$

where H_i is the molar enthalpy of each species at the correspondent temperature.

III. RESULTS

Table 1 shows the chemical composition in dry basis of the original and upgraded bio-oils (OR-BO and UP-BO, respectively). The original bio-oil presented a typical lignocellulosic composition, i.e., a relatively high concentration of acids, furans and methoxy-phenols, with average molecular formula $C_{4.55}H_{6.65}O_{1.92}$. It is worth mentioning that methoxy-phenols turn these liquids unstable upon storage due to repolymerization reactions. As seen from Table 1, these heavy compounds have been depleted when analyzing the aqueous phase from the upgrading. In this way, a more stable liquid is achieved. Moreover, the acetic acid fraction rises from 39% w/w of the original bio-oil to 45% w/w for the upgraded sample. The average molecular formula for the UP-BO is $C_{3.30}H_{5.28}O_{1.92}$.

A. Steam reforming of upgraded samples and model compounds

Figure 1 shows the equilibrium yields of the products for the steam reforming of the upgraded bio-oil as a function of the reaction temperature. The calculations were performed at a pressure of 1.2 bar. A steam-to-carbon ratio (STC) of 1.59 resulted for the UP-BO sample, slightly above the stoichiometric value of 1.42, considering the carbon amount present in the mixture.

The equilibrium mixture from steam reforming of UP-BO points that at the lowest temperatures under study (i.e., 300 C < T < 350 C), the upgraded bio-oil is decomposed in an almost equimolar mixture of CO_2 and CH_4 , possibly through a decarboxylation reaction of acetic acid, which, as mentioned, constituted the major compound of the UP-BO.

The evaluation and quantification of carbonaceous depositions are of interest since the phenomena represents one of the main restrictions for the steam reforming process implementation. From the thermodynamics approach, an operation temperature lower than 480 °C for the UP-BO (STC 1.59) ensures carbonaceous formations and must be avoided. Furthermore, the high η_{CH_4} leads to a very low η_{H_2} in this temperature range.

As temperature increases (up to approximately 550 °C), both steam reforming and cracking of the oxygenated compounds of bio-oil take place, leading to a decrease in CH_4 yield and an increase in H_2 and CO_2 yields. Above 550 °C, CH_4 reforming continues and some of the formed H_2 and CO_2 are consumed by the reverse water gas shift reaction. Around T = 740 °C, the H_2 yield attains

a maximum, matching with methane total depletion. The highest hydrogen yield reaches at 740 C a value of 5.23, which represents a 71.5% of the theoretical stoichiometric value of 7.32. Finally, at temperatures higher than 740 C the remaining reaction is the reverse WGS, yielding an unwanted consume of H_2 .

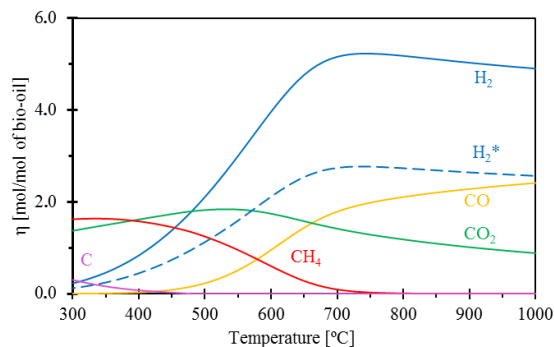


Figure 1: Yields of products in the BSR of the UP-BO as a function of the temperature, and its comparison with acetic acid (*).

Table 1. Chemical composition of original (OR-BO) and upgraded (UP-BO) bio-oils from SSH pyrolysis.

Compound name	OR-BO	UP-BO
formic acid	0.63	—
acetic acid	38.99	45.2
methyl acetate	2.77	2.54
propionic acid	0.42	3.21
2-methylpropan-1-ol	1.41	2.06
3-hydroxybutanone	4.99	7.59
2,3-butanodione	2.16	3.17
furfural	8.5	10.36
2-furanmethanol	2.3	2.84
2-cyclopenten-1-one,2-methyl-	1.16	—
2(5H)furanone	2.32	2.05
2-cyclopenten-1-one	3.04	3.33
phenol	1.12	—
4-heptanone	1.84	—
2-ethyl-2-cyclopentenone-1-one	2.93	3
2-methoxy-phenol	6.61	7.86
2-hepten-4-ol	2.98	1.84
phenol,2-methoxy-4-methyl	2.44	2.48
levoglucosan	0.6	—
1,2-benzenediol,3-methoxy	0.41	—
phenol,5-ethyl-2-methoxy	1.2	—
3-isopropylcatechol	2.92	2.47
2,6-dimethoxy-phenol	1.72	—
eugenol	0.34	—
isovanillin	0.99	—
isoeugenol	1.48	—
guaiacylacetone	1.26	—
phenol, 3-tert-butyl-4-methoxy-	1.06	—
4-hexyl-guaiacol	0.66	—
acetovanillone	0.73	—

Concerning the carbon formation, its presence is thermodynamically predicted at low temperature as consequence of both the Boudouard reaction and the thermal decomposition of bio-oil. However, operation at temperatures above 480 C assures negligible amounts of carbon depositions.

As already mentioned, acetic acid is usually selected as model compound to represent the complex bio-oil mixture since it is the major species. Therefore, for comparative purposes the H₂ yield from acetic acid SR has been incorporated into Fig. 1. The calculations were performed by using in the same operating conditions as selected for the steam reforming of bio-oil, i.e. pressure of 1.2 bar and 12% water excess. Under these conditions, the STC ratio for the acetic acid is 1.12, slightly above the stoichiometric value of 1.0. The distribution of products, not shown in Fig. 1, responds to the values found in literature as expected (Goicoechea *et al.*, 2015; Vagia and Lemonidou, 2007). The hydrogen yield for acetic acid SR shows a similar tendency to the already discussed corresponding to the UP-BO sample. However, the values are clearly inferior for the whole temperature range under study. In fact, the maximum yield for acetic acid is verified at the same temperature (740 °C) but the value achieved ($\eta_{H_2}=2.77$, 69.3% of the stoichiometric value of 4.0) is considerably lower than the maximum yield for UP-BO ($\eta_{H_2}=5.23$). As seen, although acetic acid is the major compound of the upgraded sample, the species of higher molecular weight should not be neglected for SR processes.

Aiming to extend the analysis of the steam reforming performance of the upgraded sample, different levels of water addition post-upgrading have been studied (i.e., UP-BO + additional water). Figure 2 presents contours of hydrogen yield at different STC ratios as influenced by the reaction yield at temperature. As expected, a positive influence of increasing the STC ratio on the hydrogen yield is observed. In line with the discussion of Fig. 1, for a fixed STC, as the temperature rises, so does the yield to hydrogen, until reaching a maximum. The set of maxima is plotted with a discontinuous line in Fig. 2. Reforming reactions prevail in the region to the left of the dotted line while operating points located to the right imply hydrogen losses due to the reverse WGS reaction.

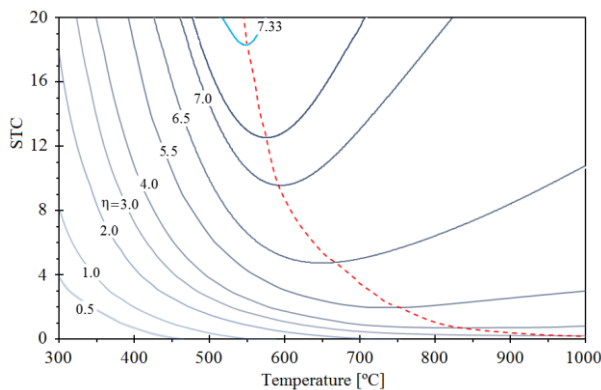


Figure 2: Hydrogen yield for the SR of the UP-BO, as a function of temperature and STC.

B. Thermal efficiency

The thermal efficiency (φ) and H₂ yield (η_{H_2}) from the steam reforming of the UP-BO at different temperatures are presented in Fig. 3. As shown, the thermal efficiency grows with temperature up to a maximum of $\varphi = 6.85$ mol/MJ, observed at T = 660°C. Since the main heat requirement is associated to the evaporation and preheating of the mixture, the augment of the efficiency attached to the increase in hydrogen yield seems reasonable. However, the condition of maximum H₂ yield occurs at a higher temperature (T=740°C with $\eta_{H_2}=5.23$). In fact, at T > 660°C, η_{H_2} remains almost constant while the heat requirement naturally associated to the evaporation and preheating increase. Therefore, thermal efficiency drops with the thermal level. This effect is even more pronounced after the maximum H₂ yield occurs (i.e., T > 740°C).

Considering that the energy requirement is strongly influenced by the water content in the UP-BO, the analysis has been extended for the steam reforming of the sample with a modified STC ratio (via extra water addition or water subtraction once the sample has been achieved by upgrading of the original bio-oil). Figure 4 shows contour lines of thermal efficiency as a function of the reforming temperature and the modified STC ratio.

Although an increase in the water content in the feed (i.e., increasing STC ratios) leads to higher yields of hydrogen (see Fig. 2), even higher amounts of energy for evaporation and preheating are required. Consequently, the efficiency decreases with STC for the whole range of temperatures under study.

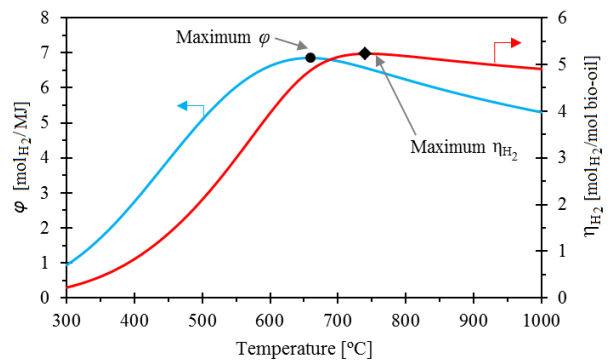


Figure 3: Thermal efficiency (φ) and hydrogen yield (η_{H_2}), as a function of temperature. STC = 1.59.

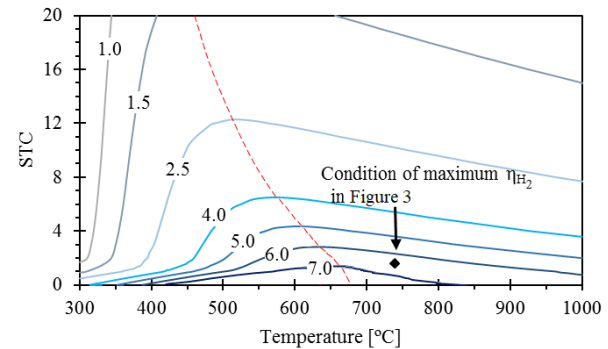


Figure 4: Contours of thermal efficiency, φ , [mol/MJ], as influenced by temperature and STC.

The analysis of the influence of the temperature on φ can be separated in two zones, which are limited by the dashed line in Figure 4 representing the locus of maximum thermal efficiencies. On the region located to the left of the dashed line, the augment in the thermal efficiency with temperature is governed by the increase in the hydrogen yield. To the right of the dashed line, both the drop in the hydrogen yield (as seen in Fig. 2) and the higher energy requirements to preheat the reactive mixture lead to a drop in φ . As already mentioned, the maxima of φ and η_{H_2} are not overlapped, appearing the correspondent to φ at lower temperatures than η_{H_2} for a given condition of STC ratio (The maximum η_{H_2} of Fig. 3 is reported in Fig. 4 to exemplify this behavior).

IV. CONCLUSIONS

This paper presents a study of the hydrogen production by steam reforming of bio-oil fractions from fast pyrolysis of sunflowers seed hulls. A thermodynamic analysis was performed on steam reforming of upgraded bio-oil aqueous fractions obtained by water addition to the original bio-oil sample.

A Gibbs free energy minimization strategy was profited here towards studying the influence of the operating variables on the performance of the steam reforming of the upgraded bio-oil sample (i.e., temperature and steam-to-carbon (STC) ratio). Overall, the steam reforming of the upgraded bio-oil showed a good performance producing high hydrogen yields. Operation temperature lower than 480 °C ensures carbonaceous depositions and must be avoided.

We also studied here the steam reforming of acetic acid as model compound of bio-oil (which is a common practice through the literature). It was concluded that, although similar behavior trends were observed, it provides a poor quantitative representation of the upgraded bio-oil sample in terms of hydrogen yield.

The steam reforming presented a gap in temperatures between the maximums of thermal efficiency and hydrogen yield. Then, the optimum temperature for steam reforming of the prepared bio-oil sample is in the range 660°C < T < 740°C. Post-upgrading water addition leads to a hydrogen yield increase, but, however, higher energy requirements cause a decrease in thermal efficiency.

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