Thermodynamic analysis and reaction routes of steam reforming of bio-oil aqueous fraction

K.A. Resende [a], C.N. Ávila-Neto [a], R.C. Rabelo-Neto [b], F.B. Noronha [b], C.E. Hori [a, *]

[a] Federal University of Uberlândia, School of Chemical Engineering, Av. João Naves de Ávila, 2121, Bloco 1 K, 38408-144 Uberlândia, MG, Brazil
[b] National Institute of Technology, Division of Catalysis and Chemical Processes, Av. Venezuela, 82, Centro, 20081-312 Rio de Janeiro, RJ, Brazil

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ABSTRACT

Steam reforming of the bio-oil aqueous fraction is a potential process to produce hydrogen. Therefore, to perform a thermodynamic study of this process can be interesting to determine the most favorable operating conditions. The calculations were made using a model compound and an aqueous fraction of a specific bio-oil. The data were obtained at different temperatures and for different steam(S)/fuel(F)ratios. Thermodynamic data showed that the behavior of model compounds was very similar to the one observed for the aqueous fraction of bio-oil. Therefore, acetic acid was used as a model compound of the aqueous fraction of bio-oil in the experimental tests. Temperature-programmed acetic acid desorption, temperature programmed reaction and steam reforming reactions were conducted. The experimental results were correlated with data predicted by thermodynamic analyses. There was a good correlation between the experimental results and predicted by equilibrium calculations. It helped to clarify the possible reactions pathways that are present in the reform process studied. According to the results the steam reforming of acetic acid can follow two different routes: (i) acetic acid can be converted to acetone at intermediate temperatures or (ii) acetic acid is transformed into adsorbed acetate species (CH_3COO^*) followed by decomposition into acetyl species (CH_3CO^*).

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1. Introduction

Bio-oil is the liquid obtained from condensation of gases produced during fast pyrolysis of biomass. It is a mixture of different organic compounds such as carboxylic acids, ketones, aldehydes, sugars, alcohols, phenols, and more complex species [1]. Bio-oils can be separated into two fractions in the presence of water. The first fraction is not soluble in water and contains products derived from lignin. It has characteristics similar to those of diesel oil, which gives to this fraction a high economic value. The other fraction is water soluble, and it is composed of acids, ketones, aldehydes, etc. The aqueous fraction lacks specific applications, which makes it to be discarded in most cases. One possible application for the aqueous fraction of bio-oil is the production of hydrogen by catalytic steam reforming [2–5], which may also increase its economic value [6].

The general form of steam reforming of aqueous fractions of bio-oils (SRBO) is given by Eq. (1).

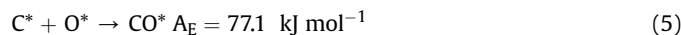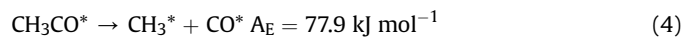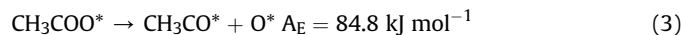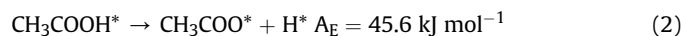$$C_nH_mO_k + (n + k)H_2O \rightarrow nCO + (n + m/2 + k)H_2 \quad (1)$$
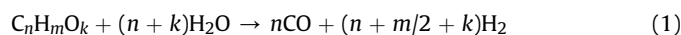
Due to the wide variety of substances found in aqueous fractions of bio-oils produced from different feedstocks, bio-oils are generally represented by model molecules. This strategy facilitates the conduction of catalytic tests and computational modeling. Since acetic acid is, in most cases, the most abundant compound in this mixture [7], it is usually reported as the model molecule of most aqueous fractions of bio-oils. However, other model molecules such as acetol [8], ethylene glycol [9], acetone [10], etc., are also employed.

Wang et al. [11] studied the steam reforming of acetic acid (SRAC) with Co-based catalysts and proposed the reaction pathway described by Eqs. (2)–(5) using theoretical (DFT, Density Functional Theory) calculations. According to the authors, the initial decomposition of acetic acid on the surface of Co-based catalysts may take two distinct routes. In the first route, acetic acid is adsorbed with abstraction of an H atom and converted into adsorbed acetate species (CH_3COO^*) (Eq. (2)). Once formed, acetate species is easily decomposed into acetyl species (CH_3CO^*) (Eq. (3)), which decomposes into CH_3^* and CO^* radicals (Eq. (4)). The radical CO^* is

* Corresponding author.
E-mail address: cehori@ufu.br (C.E. Hori).

oxidized or desorbed but the radical CH$_3$* may take two different pathways: (i) it is hydrogenated to CH$_4$ or (ii) it undergoes successive dehydrogenation and forms carbon (C*) [12,13]. The deposited carbon is than oxidized with O* atoms provided by water, cleaning the catalyst surface (Eq. (5)).

$$CH_3COOH^* \rightarrow CH_3COO^* + H^* \quad A_E = 45.6 \text{ kJ mol}^{-1} \quad (2)$$

$$CH_3COO^* \rightarrow CH_3CO^* + O^* \quad A_E = 84.8 \text{ kJ mol}^{-1} \quad (3)$$

$$CH_3CO^* \rightarrow CH_3^* + CO^* \quad A_E = 77.9 \text{ kJ mol}^{-1} \quad (4)$$

$$C^* + O^* \rightarrow CO^* \quad A_E = 77.1 \text{ kJ mol}^{-1} \quad (5)$$

Instead of being converted into acetyl species (Eq. (3)), the acetate species can be directly decomposed into CH$_3$* and CO$_2$* (Eq. (6)). This path was also proposed by Wang et al. [14], which employed commercial Ni-based catalysts. However, as this reaction has higher activation energy than Eq. (3), it is believed that it must occur to a smaller extent.

$$CH_3COO^* \rightarrow CH_3^* + CO_2^* \quad A_E = 194.8 \text{ kJ mol}^{-1} \quad (6)$$
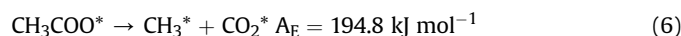
The second route proposed by Wang et al. [11] involves the conversion of acetic acid into adsorbed acetyl species (Eq. (7)). The route would then follow to Eqs. (4) and (5). However, this step requires higher activation energy than Eq. (2), which makes it unfeasible.

$$CH_3COOH^* \rightarrow CH_3CO^* + OH^* \quad A_E = 89.5 \text{ kJ mol}^{-1} \quad (7)$$
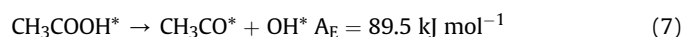
Ketonization is an alternative route in the conversion of acetic acid over polycrystalline oxide samples [15]. It is a bimolecular reaction in which two molecules of acetic acid are coupled to produce the symmetric ketone (in this case, acetone), also generating water and CO$_2$ as by products (Eq. (8)).

$$2CH_3COOH \rightarrow CH_3COCH_3 + CO_2 + H_2O \quad (8)$$
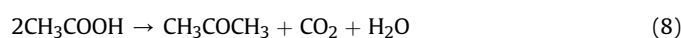
Different metals were studied in SRAC. Hu and Lu [16] investigated the activity, selectivity and stability of different transition metals, such as, Ni, Co, Fe and Cu. The catalysts were prepared by impregnating the metals on γ-Al$_2$O$_3$. In the conditions studied (steam/carbon = 7.5, $573 \leq T \leq 873$ K, space velocity = 8.3 h^{-1}, P = 1 atm), they observed the formation of H$_2$, CH$_4$, CO, CO$_2$, acetone, ketene and C* for all metals. In general, Ni and Co showed the highest catalytic activity, and the difference among the metal performances was attributed to the way that each metal cleaves the C—H and the C—C bonds of acetic acid.

Basagiannis and Verykios [17] also studied the performance of different metals: Pt, Pd, Rh and Ni supported on Al$_2$O$_3$. Their catalytic tests were carried out under the following operating conditions: steam/acetic acid molar ratio equals to 3, total flow of 290 mL min^{-1}, feed composition = 24% acetic acid and 72% H$_2$O diluted in He, from 1023 to 1223 K and 1 atm. Among all metals studied, the catalysts with Ni and Ru showed the highest activity and selectivity for hydrogen production. However, although the Ni-based catalysts have shown the smallest rate of carbon accumulation, the Ru-based catalysts were more stable.

As demonstrated above, both the rate of carbon accumulation and the selectivity to the species produced during reforming of acetic acid are dependent on the electronic properties of the metal particles. As in reforming of ethanol, which also has a C—C bond to be cleaved, the size and oxidation state of the metal particles, the type of reagent fed to the reactor and the temperature must also affect the reaction products [12,13]. Concerning the type of reagent, temperature and pressure, thermodynamic analysis may help to estimate the effect of these variables not only in the products of SRAC but also in SRBO, which is the goal of this work. It may for example predict the best operating conditions to obtain higher concentrations of hydrogen and smaller rates of carbon accumulation.

Thermodynamic analyses are usually made with model molecules, but few studies show a complete thermodynamic analysis of bio-oil or its aqueous fraction. Wang et al. [18] conducted a thermodynamic analyses of reforming of the aqueous fraction of bio-oils with software Aspen Plus using syringol, furfural and acetic acid as model molecules. The authors concluded that the water-gas shift (WGS) reaction, the reforming reactions of the compounds present in bio-oil and the steam to fuel ratio play important roles in the selectivity to H$_2$. Vagia and Lemonidou [10] also studied the thermodynamic behavior of SRBO. They used acetic acid, acetone and ethylene glycol as model molecules in a wide temperature range (400–1300 K) and various steam to fuel ratios (S/F = 1–9). The calculations were performed using software Aspen Plus11.1. The authors also evaluated the formation of ethane, ethylene, acetylene and other oxygenates, but the molar fractions of these compounds were negligible. In general, the profiles of the molar fractions were very similar for the three compounds studied (acetic acid, acetone and ethylene glycol). Xie et al. [19] evaluated the thermodynamic equilibrium of steam reforming of methanol, acetic acid and ethylene glycol. They observed that the best selectivity to hydrogen (15–25%) occurred around 660 K and at low pressures (1 atm).

In this work we analyzed the thermodynamics of steam reforming of the aqueous fraction of bio-oil and of two model compounds: acetic acid and acetol. The thermodynamic analyses were then related to experimental tests under conditions of steam reforming of acetic acid using a LaNiO$_3$ perovskite-type oxide catalyst. Both the experimental and thermodynamic results were used to verify if the mechanism proposed by Wang et al. [11] is consistent. Also, the best operational conditions to conduct steam reforming with acetic acid, acetol and with the aqueous fraction of bio-oil were demonstrated.

2. Methodology

2.1. Thermodynamic analysis

2.1.1. Formulation of the thermodynamic problem

The thermodynamic equilibrium of a closed system with specific temperature (T) and pressure (P) is achieved when the total Gibbs energy (G^t) reaches a minimum. For a single gas phase with specified T and P, the total Gibbs energy depends on the number of moles of the species involved. The goal is to find a set of number of moles that minimizes the total Gibbs energy submitted to restrictions imposed by the mass balance.

The equilibrium point may be calculated by two distinct methods: (i) Stoichiometric method and (ii) Non-stoichiometric method (Lagrange Multipliers). Both methods result in systems of non-linear algebraic equations. The first method is easier to apply for systems with few species (i.e., few independent reactions) but becomes not so trivial to solve when the number of species is large. The second method is independent of the reaction system and more straight forward to solve [20].

The Lagrange Multipliers method takes into account that although the number of moles of each species i (n_i) is not conserved in a closed system, the total number of element k (A_k) is constant (Eq. (9)). If Eq. (9) is multiplied by a factor λ_k (the Lagrange multiplier for element k), summed over k and added to the total Gibbs