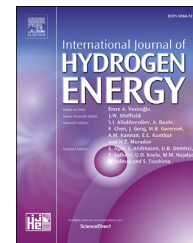


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Steam reforming of propionic acid: Thermodynamic analysis of a model compound for hydrogen production from bio-oil

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ARTICLE INFO

Article history:

Received 3 April 2017

Received in revised form

14 May 2017

Accepted 15 May 2017

Available online 8 June 2017

Keywords:

Propionic acid

Steam reforming

Thermodynamic equilibrium

Bio-oil

Model compound

Biohydrogen

ABSTRACT

The thermodynamic equilibrium of steam reforming of propionic acid (HPAc) as a bio-oil model compound was studied over a wide range of reaction conditions ($T = 500\text{--}900\text{ }^{\circ}\text{C}$, $P = 1\text{--}10\text{ bar}$ and $\text{H}_2\text{O}/\text{HPAc} = 0\text{--}4\text{ mol/mol}$) using non-stoichiometric equilibrium models. The effect of operating conditions on equilibrium conversion, product composition and coke formation was studied. The equilibrium calculations indicate nearly complete conversion of propionic acid under these conditions. Additionally, carbon and methane formation are unfavorable at high temperatures and high steam to carbon (S/C) ratios. The hydrogen yield versus S/C ratio passes a maximum, the value and position of which depends on temperature. The thermodynamic equilibrium results for HPAc fit favorably with experimental data for real bio-oil steam reforming under same reaction conditions.

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Introduction

Hydrogen is an important raw material in chemical industries and it is also a potential fuel for internal combustion engines and fuel cell applications. There is an increasing interest in the production of hydrogen from biorenewable sources (biohydrogen). Unlike conventional hydrogen, which is produced from fossil fuel feedstocks such as natural gas [1], biohydrogen is a “carbon-neutral” product [2].

Bio-oil (or pyrolysis oil) being produced by fast pyrolysis of abundant lignocellulosic biomass is a promising source of biofuels. However, its chemical composition (C/H/O mass

ratio of 0.54–0.58/0.055–0.07/0.35–0.40 [3]) makes it unsuitable for many fuel applications. The upgrading of bio-oil involves partial or total deoxygenation either by treatment with hydrogen to remove oxygen as H_2O and/or alternatively as carbon oxides. The commonly used catalytic upgrading techniques include decarboxylation, hydrodeoxygenation (HDO) and zeolite cracking [4–6]. However, rapid catalyst deactivation and poor yield is common to all of them.

Catalytic steam reforming (SR) is also an important technology for valorizing bio-oil to synthesis gas (mixture of hydrogen and carbon oxides). The resulting synthesis gas (or syngas) can be further processed for production of valuable hydrocarbons and oxygenates or biohydrogen. The hydrogen

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<http://dx.doi.org/10.1016/j.ijhydene.2017.05.108>

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from the SR can be used as a fuel or a reactant in either the hydrodeoxygenation of the bio-oil or in other chemical processes like hydrotreating or ammonia synthesis which uses H₂ or in the Fischer–Tropsch synthesis for production of synthetic crude, which uses syngas [7].

With the addition of water, bio-oil can be separated in two distinct fractions: a monomer-rich aqueous fraction (containing typically 20 wt% organics) and a hydrophobic fraction composed mainly of oligomers derived from lignin [8]. The steam reforming of the whole bio-oil and the aqueous phase has been tested over different catalysts under different operating conditions [7]. Catalyst deactivation problems are more serious with the whole bio-oil [9]. Despite the fact that the hydrogen yields obtained from the whole oil are higher than when only the aqueous fraction is processed, the economics of the whole bio-oil reforming is less favorable. On the other hand, the water-insoluble fraction can be used in high value applications producing phenolic resins and fuel additives [10].

Both promoted non-precious (Ni) and noble metal (Pd, Pt, and Rh) catalysts are active in steam reforming of bio-oils to hydrogen [11,12]. Catalytic steam reforming of bio-oil at 750–850 °C over a Ni-based catalyst is a two-step process that includes the shift reaction. The overall stoichiometry gives a maximum yield of 0.172 g H₂/g bio-oil (11.2% based on wood) [13,14].



The SR of oxygenates is, like the conventional SR, endothermic and therefore it is favored by high temperatures. Low pressures will also favor the SR as predicted by Le Châtelier's principle [7].

The mechanism of metal-catalyzed SR of oxygenated organic molecules is proposed to correspond to a similar bifunctional mechanism of the reforming of hydrocarbons [15]. Organic molecules dissociatively adsorb on metal (nickel) crystallite sites, while water molecules are adsorbed on the support (alumina) surface. Hydrogen is produced by the dehydrogenation of adsorbed organic molecules and by reaction of adsorbed organic fragments with hydroxyl groups, which migrate from the alumina support to the nickel crystallites/alumina interfaces. The second reaction also results in the formation of carbon oxides. Side reactions leading to the formation of carbon deposits on the catalyst surface occur along with the above chemical processes.

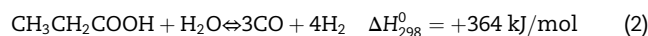
Simple oxygenated organic compounds such as methanol or acetic acid are more reactive than hydrocarbons and can be reformed at lower temperatures [16]. However, complex biomass-derived liquids that include large, thermally unstable molecules need higher temperatures and more steam to effectively gasify the carbonaceous deposits formed by thermal decomposition.

Deactivation of the catalyst due to coking is one of the major problems, and bio-oils have more deactivation problems than petroleum-derived feedstocks [17]. In order to mitigate the deactivation problem, several strategies were followed, e.g., modification of the catalyst, which is usually Ni-based, and optimization of the reaction conditions to suppress coke formation, development and application of quick and effective method for periodic restoration of the

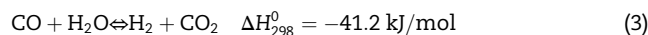
catalytic activity. The most promising approach uses a dual catalytic system, in which a cheap, so-called guard catalyst, e.g., calcined dolomite is applied in front of an active Ni-catalyst in order to protect the latter catalyst from extensive contact with tar and, thereby, reduce catalyst coking and maintain its high activity for a long period of time [18].

Because of the complex chemical composition of bio-oils, model compounds (e.g. ethanol, acetic acid, acetone, phenol and *m*-cresol) are commonly studied because of their well-defined chemical structure [19–21]. Research on the steam reforming of ethanol and acetic acid is now relatively mature, with high reactant conversions, hydrogen yields, and stability of the catalysts [21,22]. However, some bulky oxygenated compounds in bio-oil show inferior reforming behavior. Phenol cannot be completely converted even at a high steam-to-carbon ratio, while *m*-cresol and sugars not only show low reactivity over Ni catalysts, but also easily form coke [23]. To improve the steam reforming process, investigations on separating such compounds are needed.

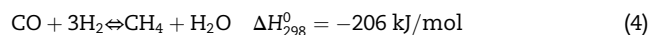
Propionic acid (HPAc) is a main constituent of bio-oils [24]. The carbon/hydrogen/oxygen mass ratio in propionic acid (0.49/0.08/0.48) is very similar to that of bio-oil. Therefore, the thermochemistry of HPAc steam reforming could be considered as a good representative model compound for bio-oil as a whole.



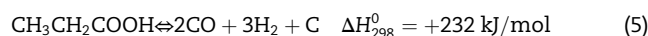
Over metal catalysts, a number of side reactions might occur including water gas shift (WGS):



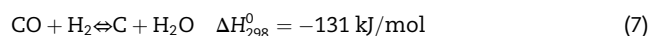
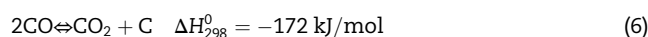
And methanation of carbon oxides:



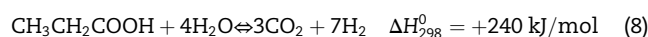
Thermal decomposition or cracking is another side reaction which is favored at the prevalent high reaction temperature, for example:



Coke formation may also occur via Boudouard reaction (Eq. (6)) or CO reduction (Eq. (7)):



When bio-oil is being considered as a carbon source for organic synthesis via syngas, Eq. (2) is the desirable reaction. When high hydrogen yield is of interest stoichiometry according to Eq. (8) is most desirable, which is a combination of Eqs. (2) and (3) and is equivalent to Eq. (1) for real bio-oil:



Consequently, the SR reaction of bio-oils is often described by Eq. (1) (and (8) for HPAc SR) although at high temperatures the WGS is shifted to the left and CO will also be present in significant amounts [7]. Unfortunately, reaction (2) is favored at high temperatures while the complementary reaction (3) is favored at low temperatures. Therefore, conversion of bio-oil

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