Supercritical water reforming of model compounds of bio-oil aqueous phase: Acetic acid, acetol, butanol and glucose

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HIGHLIGHTS

- Supercritical water reforming of acetic acid, acetol, 1-butanol and glucose was studied.
- Acetic acid, acetol, 1-butanol and glucose are four model compounds of the bio-oil aqueous phase.
- Experimental investigation was performed in a tubular reactor without using a catalyst.
- A systematic thermodynamic analysis was also carried out by Aspen and Matlab.
- Experimental results match well simulation values if an equilibrium approach temperature is used.

ARTICLE INFO

ABSTRACT

An experimental study of the supercritical water reforming of model compounds (acetic acid, acetol, 1-butanol and glucose) of the aqueous phase of bio-oil was performed in a tubular reactor without using a catalyst, aimed at maximizing hydrogen yield. In addition, a systematic thermodynamic analysis was carried out using two thermodynamic approaches by simulation in AspenPlus™ (non-stoichiometric approach) and modelling in Matlab™ (stoichiometric approach), selecting first the thermodynamic method that describes the supercritical state more suitably. The effect of the main operating parameters (temperature, organic feed concentration and residence time) on the process performance was investigated thermodynamically and experimentally for each feedstock. Experimental and theoretical results were compared with each other, arising that experimental gas yields were far from equilibrium. However, a better agreement was achieved using an equilibrium approach temperature ranged from 125 to 225 °C.

1. Introduction

Bio-oil derived from biomass fast pyrolysis can be stored and transported, and used for fuel, chemicals or as an energy carrier. Bio-oil contains varying quantities of water ranging from 15 to 50 wt.%, depending on the feed material, how it was produced and subsequently collected [1].

Bio-oil can be separated into oil phase and aqueous phase by adding water. The water-rich phase of the bio-oil, containing mostly carbohydrate-derived compounds, consists of 20% organics and 80% water [2–6].

Oil phase contains a valuable material that can be used to generate different chemicals and additives, while the aqueous fraction is less valuable and its valorization has been sought during the last years. Due to the relative low content of the organic compounds, the cost of extraction technique is too high; as an alternative, hydrogen production via catalytic reforming has been mostly explored [3,4,7–9]. Bio-oil aqueous phase reforming is complex because it may content many oxygenated compounds [10], mainly alcohols, ketones, aldehydes, and carboxylic acids [11]. Most of studies have focused on performance of some model compounds using different catalysts, trying to found the most suitable for H₂ production.

The paper reported by Oasmaa and Meier [12] may be used as a reference guide of the compounds identified in the chemical characterization of biomass pyrolysis liquids [13]. Those researchers determined that acetic acid and acetol are major constituents of the carboxylic acids and ketonic fraction of biomass pyrolysis liquids. Likewise, they observed that 1-butanol is also present within the alcohol fraction of bio-oil. Thus, acetic acid [2,14–19], acetol (or hydroxyacetone) [13,20], and 1-butanol [13,21] have

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been utilized as representative of the oxygenates in the aqueous fraction of bio-oil.

On the other hand, glucose, as a model compound of biomass clearly representative of cellulose [22], was the fourth feedstock selected in the studied process. Although glucose is not common in aqueous phase of bio-oil, it is similar to levoglucosan (1,6-anhydro-β-D-glucopyranose), which is a main product from the fast pyrolysis of cellulose and it is also present in the aqueous phase of bio-oil. However, the difficulty to find levoglucosan, and its high price, lead us to substitute it by glucose. Moreover, levoglucosan may be produced with a high yield by the dehydration of glucose in high temperature water and pressure [23], which justifies the use of glucose in the present study. As below explained, progressive dehydration of organics is considered a main decomposition route of organics into smaller molecules. Unlike the other model compounds selected, more studies have been carried out on thermochemical conversion of glucose using supercritical water [24–28]. However, the aim of this study is not focused on glucose, but a set of model compounds (characteristic of bio-oil aqueous phase) separately before mixing all of them.

As aforementioned, although the catalytic steam reforming has been the most studied conversion process to valorize energetically the bio-oil aqueous phase, supercritical water reforming (SCWR) is an emergent technology that has attracted much attention in the last five years [29–31], which has not been fully investigated. In previous works, we have experimentally verified that it is possible to perform SCWR of glycerol without adding a catalyst at high temperatures (about 800 °C) and long residence times (35–160 s) [32]. Likewise, a Ni-based catalyst makes it possible to reduce the reforming temperature needed when no catalyst is used (from 800 °C to 600 °C), achieving a high-yield of hydrogen (close to equilibrium), and requiring less energy [33].

Therefore, this study is aimed at investigating the supercritical water reforming of the model compounds selected at different values of temperature, feed concentration and residence time, at 240 bar. The paper is divided into a thermodynamic analysis and an experimental study carried out without adding a catalyst. The former is performed using both non-stoichiometric (by AspenPlus) and stoichiometric (modelling in Matlab) approaches. Simulation and experimental results are compared with each other, and good match is obtained assuming a suitable equilibrium approach temperature. The main novelty of this study is that, to our knowledge, no other work considers a comprehensive study of the SCWR of the four model compounds selected as representative of aqueous phase of bio-oil. This research will continue by testing different mixtures of those compounds, focusing in the process performance as well as interactions among them, which will be further compared with modelling results.

The paper contents includes two methodological sections, which involves theoretical and experimental aspects. In the former, the simulation of supercritical state is investigated and two thermodynamic approaches are described. In the latter, the plant where the tests were carried out and the analytical methods used for analyzing the samples drawn are described. The other relevant section involves the results obtained from simulation and experimentation, which are compared and discussed, with especial attention to an explanation of the SCWR of each model compound studied.

2. Theoretical

2.1. Simulation of supercritical state

The predictive Soave–Redlich–Kwong (PSRK), which is an extension of the SRK equation of state that uses the generalized

Mathias–Copeman α-function and the mixing rule of Holderbaum–Gmehling, was determined as the most appropriate thermodynamic method to describe the supercritical state, when studying the supercritical water reforming of glycerol [34]. However, with the aim of revisiting and updating this issue, several methods were checked again through different physical properties and thermodynamic state variables (or functions).

In this work, enthalpy and entropy, as well as the specific heat, density and viscosity were selected to compare five thermodynamic methods applied to water, acetic acid, acetol, 1-butanol and glucose. The investigated methods were based on Equations of State (EoS), since methods based on activity coefficients cannot represent the changes that occur in the critical region in continuous form due to the different manner that they treat each phase in a phase equilibrium with supercritical fluids. Apart from the PSRK EoS, the methods assessed were: (1) SR-Polar based on modification of SRK EoS proposed by Schwarzentruber–Renon; (2) SRK-BM that uses the SRK EoS with the mixing rule of Boston and Mathias; (3) the PR-MHV2 based on the Peng–Robinson EoS with the second mixing rule of Huron and Vidal modified, and (4) PR-BM that uses the Peng–Robinson EoS with the mixing rule of Boston and Mathias.

All the methods showed good fit to supercritical curves, although the best two ones were the PSRK and the SR-Polar, showing minima deviations in properties and thermodynamic functions between liquid and vapor state. As in case of glycerol, water showed major deviations than organic compounds for all the EoS, but PSRK describes better its supercritical state, as previously described in detail [34]. However, SR-Polar exhibited minima deviations for the model compounds, so it is an interesting method to be further studied in supercritical reforming.

Table 1 shows the deviations in enthalpy and entropy of the four model compounds with all the methods. More tables and figures depicting the dependence on temperature are not shown due to the high number of compounds, properties, functions and thermodynamic methods tested. Additionally, at a pressure of 240 bar, the selected model compounds exhibited a very good fit, with minor deviations in case of glucose, especially regarding enthalpy and entropy. Deviations among the curves would diminish as the pressure increases improving the fits, but higher pressures are not necessary in practice.

2.2. Thermodynamic analysis

Thermodynamic studies are very important because they provide information on conditions that are advantageous for hydrogen production. In this study, a thermodynamic analysis of reforming of the aqueous phase fraction of bio-oils with software AspenPlus using acetic acid, acetol (or hydroxyacetone), 1-butanol and glucose as model molecules is conducted. Likewise, a sensitivity analysis is performed to know the effect of the main operating parameters on hydrogen yield, both at equilibrium and using an equilibrium approach temperature in the reforming reactor. The non-stoichiometric approach used in Aspen is independent of the reaction system and straightforward to solve than the stoichiometric method, which is implemented in Matlab.

2.2.1. Process simulation by ASPEN

The thermodynamic equilibrium of an isolated system, with specific temperature and pressure, is achieved when the total Gibbs energy is minimum. The method of minimizing the Gibbs free energy is a non-stoichiometric approach, where no reactions must be defined and an initial estimation of the equilibrium is not required. This is very useful, especially when the reaction temperature and pressure are specified, because there are many reactions involved. Other researchers have previously used this