

Effect of operating conditions on the sorption enhanced steam reforming of blends of acetic acid and acetone as bio-oil model compounds



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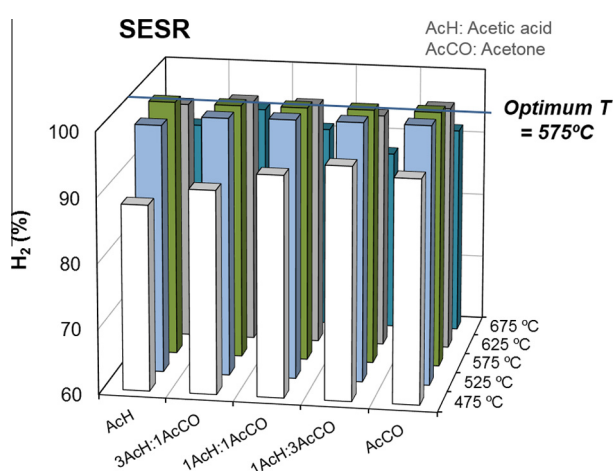
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HIGHLIGHTS

- SESR of blends of acetic acid and acetone as bio-oil model compounds was studied.
- Temperature, steam/C ratio and space velocity were experimentally evaluated.
- An optimum temperature of 575 °C at atmospheric pressure produced 99.2–99.4% of H₂.
- Similar H₂ purities were obtained from the SESR of individual compounds and blends.
- Lower H₂ yields were obtained by the SESR of blends compared to individual compounds.

GRAPHICAL ABSTRACT



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ABSTRACT

Hydrogen production by sorption enhanced steam reforming (SESR) of bio-oil model compounds was thermodynamically and experimentally studied by mixing acetic acid (AcH) and acetone (AcCO), in a fluidized bed reactor. In the SESR process the catalytic reforming reaction and CO₂ removal by sorption were carried out simultaneously in a single reactor. The SESR of the model compounds and their blends was performed under atmospheric pressure over a Pd/Ni–Co hydrotalcite-like material (HT) catalyst using dolomite as CO₂ sorbent. The effects of the reaction temperature (475–725 °C), steam/C molar ratio and weight hourly space velocity (WHSV) were studied. For the SESR of acetic acid, acetone and their blends it was observed that the H₂ yield and H₂ concentration increase as the temperature increases, reaching a maximum value, and then they decrease with the temperature. It was also found that the CH₄ concentration decreases as the temperature increases, while the CO and CO₂ concentrations increase with the rise in temperature. High steam/C molar ratio values and low WHSV values favor the H₂ yield and H₂ concentration, while they lead to a decrease in the CH₄ concentration. Hydrogen purities as high as 99.2–99.4% with small amounts of methane, CO and CO₂ were obtained for the SESR of the model compounds of bio-oil and their blends at a temperature of 575 °C at atmospheric pressure. The effect of temperature on the SESR of the blends of model compounds of bio-oil is similar to that of the individual model compounds studied, except in the fact that lower H₂ yield values are obtained by the SESR of

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the blends (83.3–88.6%) compared to the individual model compounds (90.2–95.9%), a decrease which becomes more noticeable as the proportion of acetone in the blend is increased.

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1. Introduction

Hydrogen is generally recognized as a clean transportation fuel and energy carrier and it will undoubtedly play an important role in the future global economy. Moreover, hydrogen is an important raw material in the chemical and petroleum industries, since large quantities are used in ammonia synthesizing facilities for urea (fertilizer production), in the refining of crude oil for use in the transportation sector and in methanol production facilities [1]. Most hydrogen is currently produced from fossil fuels, either by means of the steam methane reforming (SMR) of natural gas and other light hydrocarbons or the partial oxidation of heavy oil fractions. One of the main environmental concerns of the world is nowadays the global warming phenomenon that mainly results from fossil fuels burning. This issue along with the depletion of natural fossil fuel reserves and the dependency of human life to energy explain the importance of green energy sources development with the advantages of low emission of pollutants [2]. Thus, there is great interest in the development of technologies for producing hydrogen based on the exploitation of renewable energy sources, such as biomass, since these forms of energy are considered carbon neutral [3].

One of the most promising methods for using biomass to produce H_2 is via different routes with intermediate oxygenates production steps that are subsequently reformed. Thus, the fast pyrolysis of biomass is a method that produces bio-oil [4,5], which has a higher energy density and is easier to handle and transport than raw biomass. Bio-oil is a complex mixture of low and high molecular weight oxygenated compounds, such as carboxylic acids, alcohols, aldehydes, ketones and anhydrosugars derived from the carbohydrate fraction of biomass (cellulose and hemicellulose), as well as phenolics and cyclic oxygenates derived from lignin [6]. This means that the bio-oil can be separated into a carbohydrate-derived solution and a lignin-derived fraction. The latter can be used for producing phenolic resins or fuel-blending components, while the aqueous carbohydrate-derived fraction of the bio-oil can be catalytically steam reformed for hydrogen production.

A number of studies on the production of hydrogen via the steam reforming (SR) of model compounds of bio-oil have been reported in the literature [7–15]. During the experiments on the SR of different components of bio-oil in fixed bed reactors, it has been reported that the formation of carbonaceous deposits in the upper layer of the catalyst bed and in the reactor freeboard considerably reduced the reforming time, requiring more frequent catalyst regeneration [9,12]. Fluidized bed reactors are commonly used in processes where catalysts need to be continuously regenerated, since they have a higher solids handling capability, a wide feedstock adaptability and permit a uniform mixture of gas and solids. They also provide a better heat and mass transfer, greater temperature uniformity, apart from a low pressure drop and greater catalyst effectiveness factors [16]. Such reactors would be appropriate for processing thermally unstable complex liquids obtained from lignocellulosic biomass because of their tendency to decompose thermally and form carbon deposits, since in fluidized bed reactors the feedstock is in closer contact with the catalyst particles and carbon deposits on catalyst particles can be gasified more easily.

Ni-based catalysts are commonly used in steam reforming processes of hydrocarbons and, although they have high activity and

selectivity to hydrogen, they do not offer sufficient resistance to the deactivation caused by coke deposition on nickel particles. The main problem with the steam reforming of bio-oil concerns the formation of carbonaceous deposits, i.e., coke formation [17,18]. Although noble metal-based catalysts are more expensive than the traditional Ni-based ones, they may be of interest for certain applications where activity per unit volume is important, as in the case of the reforming of bio-oil. Furthermore, it has been demonstrated that the presence of noble metal catalysts reduces selectivity to CH_4 and increases the proportion of CO and H_2 in steam reforming processes [7].

The major process for hydrogen production currently used is steam methane reforming (SMR) of natural gas. It involves multiple steps (reformer, high- and low-temperature shift reactors, PSA unit) and severe operation conditions (800–900 °C, 15–30 bar). In recent years the concept of combining reaction and separation stages has received increased attention, since it simplifies the chemical processes involved, conserves energy and can improve the product quality and yield [19]. Therefore, some studies on novel systems for low-cost hydrogen production have been carried out, such as the sorption-enhanced steam reforming [20–23] and the chemical looping reforming [24–26]. The sorption enhanced steam reforming (SESR) process for hydrogen production is an emerging alternative technology to SMR based on the integration of the reforming reaction (H_2 production) and selective separation (CO_2 sorption) in a single unit operation. In this process, the reactor contains the catalyst required for the reforming process together with a CO_2 sorbent for the in situ removal of carbon dioxide from the gaseous phase. Thus, the steam reforming, WGS and CO_2 capture reactions are conducted simultaneously in one single reactor under moderate temperature and pressure conditions. Since the CO_2 is removed in situ by the sorbent as soon as it is formed, H_2 production is favored due to the displacement of the reforming and WGS reaction equilibriums towards higher hydrogen production. CO_2 can be removed in situ from the reaction environment using high temperature solid sorbents. Natural CaO-based sorbents, such as limestone and dolomite, are the most commonly used materials for CO_2 capture in SESR processes. These materials usually suffer from a decay in their CO_2 capture capacity after several cycles of carbonation/regeneration [27], but they are widely used due to their wide availability and very low cost. They are able to react with CO_2 at low CO_2 partial pressures at moderate temperatures and have fast kinetics and good adsorption capacities. If a CaO-based sorbent is used, the captured CO_2 is converted to a solid carbonate. This sorbent can then be regenerated using temperature or pressure swing desorption to release a relatively pure stream of CO_2 suitable for use or sequestration.

The SESR process has been widely studied in the literature using methane [16,28–35] and it has been shown to improve hydrogen production compared to conventional SR. Moreover, some studies have also been published on the SESR of biomass-derived compounds, such as ethanol [36–38], glycerol [39–42], glucose and sorbitol [43], waste cooking oil [44] and pine sawdust [45].

In the present work, the SESR process is proposed as a method to obtain highly pure hydrogen from bio-oil produced from the fast pyrolysis of biomass. A Pd/Ni-Co catalyst derived from a hydrotalcite-like material (HT) is employed in the process, together with dolomite as CO_2 sorbent, since it has previously been demonstrated to be an effective catalyst in the sorption enhanced

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