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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Abstract

Hydrogen production by sorption enhanced steam reforming (SESR) of bio-oil obtained from the fast pyrolysis of biomass was thermodynamically and experimentally studied by mixing two model compounds, 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 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.

Keywords: Acetic acid; Acetone; Bio-oil; Fluidized bed; Hydrogen; Sorption enhanced steam reforming (SESR)

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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 CO₂ 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 CO₂ 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 CO₂ sorbent, since it has previously been demonstrated to be an effective catalyst in the sorption enhanced water gas shift process [46] as well as in the sorption enhanced steam gasification of lignocellulosic biomass [47]. Moreover, this catalyst allows a continuous cycling operation, avoiding the need for a catalyst reduction step between the air-regeneration and reforming stages usually necessary to produce active catalyst. This is because Pd promotes the rapid production of H₂ and hence an early reduction of the metal oxide phases contained in the catalyst [48].

The steam reforming of pure bio-oil is very difficult due to the extensive formation of coke and catalyst deactivation. Therefore, to ensure the best operation conditions for hydrogen production, the catalytic steam reforming of bio-oil is performed using model compounds that represent its main constituents [49]. The oxygenated model compounds of the components present in the bio-oils produced by the fast pyrolysis of biomass selected for the present study are acetic acid (AcH), as oxygenated model compound of organic acids, and acetone (AcCO), as model compound of carbonyl-containing constituents (mainly aldehydes and ketones). Xie et al. [50] carried out a theoretical thermodynamic analysis of the steam reforming process with and without CO₂ sorbent for four typical model compounds of bio-oil (ethanol, acetic acid, acetone, and phenol), although blends of these compounds were not included in the study. Other studies on the SR process of model compounds of bio-oil include one or a few experiments performed after the addition of a CO₂ sorbent [51,52], carrying out a preliminary study of the variable (steam/C ratio). Finally, Yan et al. [53] and Xie et al. [54] carried out studies of the SESR process of the aqueous fraction of bio-oil produced from fast pyrolysis of rice hull and corn cob, respectively. Therefore, there are in the literature some useful contributions to the study of the SESR process through the use of model compounds of bio-oil, although the research is still very

scarce and no studies of the composition of the blends of model compounds of bio-oil has been carried out.

In this paper the behavior of blends of two model compounds commonly found in bio-oil has been investigated. In this way, it will be possible to evaluate at laboratory scale the optimum operating conditions in order to maximize H₂ yield, selectivity and purity, and to gather data of CH₄, CO and CO₂ concentrations in the effluent gas.

Therefore, the objective of the present study is to investigate the sorption enhanced steam reforming of blends of two oxygenated model compounds typically found in bio-oils, acetic acid and acetone, in a fluidized bed reactor. Pd/Ni-Co HT is used as reforming catalyst, while dolomite is used as CO₂ sorbent. The influence of the reaction temperature, steam/C feed molar ratio and feed space velocity on H₂ production is analyzed. A thermodynamic equilibrium analysis of the process is also performed so that the equilibrium values can be compared with the experimental results.

2. SESR process of bio-oil

The reactions involved in the conversion of acetic acid and acetone to hydrogen are shown in Eqs. (1) and (2), respectively, which are a combination of steam reforming and water gas shift (WGS) (Eq. (3)) reactions:

The reforming reaction is highly endothermic, while the shift reaction is moderately exothermic. Both the steam reforming and WGS reactions are reversible, i.e., they are equilibrium limited, and it is not possible to achieve the complete conversion of the model compound in a single reactor. The experimental yield of hydrogen is lower than the stoichiometric maximum value because two undesirable products, CO and CH₄, are also formed via the reverse of the WGS (Eq. (3)) and methanation (Eq. (4)) reactions. In addition, thermal decomposition of the organic compounds contained in the bio-oil may occur at the same time as the reforming reaction and lead to the formation of intermediates and carbonaceous deposits.

The principle behind SESR process is to shift the equilibrium of the reversible reforming and WGS reactions, based on Le Chatelier's principle, in order to enhance hydrogen production via the in situ removal of CO₂ from the reaction zone. In this way, a high hydrogen conversion can be obtained in a single step. CO₂ removal can be performed using high-temperature solid sorbents. If a CaO-based sorbent is used in the proposed SESR process, it is incorporated into the

catalyst bed in order to remove the CO₂ from the gaseous phase in situ, as shown in Eq. (5):

The CO₂ sorbent can capture CO₂ repeatedly via consecutive CaO-carbonation and CaCO₃-calcination cycles according to the reversible Eq. (5). Due to the equilibrium shift effect caused by the capture of CO₂, both the WGS reaction (Eq. (3)) and the CH₄ reforming reaction (the reverse of Eq. (4)) are promoted. The WGS reaction is directly promoted by the capture of CO₂. This provokes a decrease in the CO concentration in the gas phase, which will indirectly promote the CH₄ reforming reaction. Hence, the CO and CH₄ contents are significantly reduced, which in turn increases the hydrogen concentration in the product gas and allows almost complete conversion to be achieved.

The overall reactions for the sorption enhanced steam reforming (SESR) process of acetic acid and acetone are shown in Eqs. (6) and (7), respectively.

The complete conversion of acetic acid and acetone by SESR produces 4 and 8 mol of hydrogen, respectively, per mole of model compound.

In the present work, experiments were also conducted with three blends of acetic acid and acetone (3:1, 1:1 and 1:3 mol AcH/mol AcCO). The overall reactions for the SESR of the blends are shown in Eqs. (8), (9) and (10), respectively.

The complete conversion of the 3:1, 1:1 and 1:3 mol AcH/mol AcCO blends of acetic acid and acetone by SESR produces 5, 6 and 7 mol of hydrogen, respectively, per mole of blend.

During the SESR process the exothermic carbonation reaction supplies most of the heat required by the endothermic reforming reactions. Thus, the combination of the endothermic reforming reaction and exothermic CO₂ sorption balances the reactor's energy requirements and the whole reaction/sorption process can be performed at much lower temperatures than in the conventional SR process [32]. In this way, catalyst coking and sintering, as well as investment and operation costs, can be reduced. Nevertheless, it needs to be taken into account that more energy will be required to regenerate the sorbent in the energy-intensive calcination reaction.

2. Material and methods

2.1. Model compounds

The model compounds of bio-oil from the fast pyrolysis of biomass were acetic acid (AcH)

and acetone (AcCO). Glacial acetic acid (100% purity) and acetone (100% purity) were supplied by PANREAC. Aqueous solutions were prepared using steam/C molar ratios of 1.5-4.5 for acetic acid and 3.33-6.67 for acetone. Experiments were conducted with both model compounds separately, as well as with three blends of acetic acid and acetone (3:1, 1:1 and 1:3 mol AcH/mol AcCO).

2.2. *CO₂ sorbent*

Arctic dolomite was supplied by Franefoss Miljøkalk As, Norway. This has a purity of approximately 98.5 wt.% $\text{CaMg}(\text{CO}_3)_2$ and no sulfur according to X-ray fluorescence analysis. The dolomite was used as a precursor of CaO for the capture of CO_2 . Its initial maximum CO_2 capture capacity was estimated as being 0.46 g CO_2 /g sorbent. It was calcined in an air flow (200 mL min^{-1}) at 800 °C for 4 h prior to its storage.

2.3. *Catalyst preparation*

A 1%Pd/20%Ni-20%Co HT catalyst (Pd/Ni-Co HT) was prepared by means of the incipient wetness impregnation method using a 20%Ni-20%Co hydrotalcite-like material (Ni-Co HT) as precursor. The Ni-Co HT precursor was prepared by co-precipitation of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Mg}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. A stoichiometric ratio of cations was chosen so as to yield a material with a nominal composition of 20%Ni-20%Co. The precipitate obtained was filtered, washed, dried overnight and then calcined at 600 °C for 6 h. A detailed description of the precursor preparation procedure is reported elsewhere [55]. After calcination, the Ni-Co HT precursor was impregnated with a 1% (w/w) load of Pd. The Pd solution was prepared by dissolving PdCl_2 into two equivalents of HCl and diluting them in ethanol to the desired concentration. The sample was dried for 14 h at 100 °C and calcined in an air flow at 500 °C for 1 h in a muffle oven at a heating rate of 5 °C min^{-1} . A detailed description of the preparation procedure of the Pd/Ni-Co HT catalyst as well as its characterization is reported elsewhere [47,48]. The calcined catalyst was pelletized, ground and sieved to obtain a particle size of 106-212 μm .

2.4. *Experimental procedure*

A schematic flow diagram of the experimental setup used for the SESR experiments with the model compounds of bio-oil and their blends is shown elsewhere [56]. Briefly, it consists of an updraft bubbling fluidized bed quartz reactor (i.d. 27 mm), which in this work was loaded with a 12 g mixture of calcined dolomite (as CO_2 sorbent) and Pd/Ni-Co HT catalyst, at a sorbent-to-catalyst ratio of 5 g/g. The reactor is located inside a tubular electric furnace and the

reaction temperature is controlled by a K-type thermocouple inserted into the bed and connected to a temperature controller and data recorder. Gases are delivered by Bronkhorst[®] mass flow controllers. The liquid reactant mixture is fed in by means of a Gilson[®] high-performance liquid chromatography (HPLC) pump from the bottom of the reactor. The aqueous solution of the studied model compound is swept by a nitrogen flow, evaporated in an evaporator and then introduced updraft through the catalyst/sorbent bed as a fluidizing gas.

The SESR experiments were performed under atmospheric pressure and isothermally in the temperature range of 475-725 °C. Prior to each SESR experiment, the catalyst/sorbent mixture was subjected to a regeneration step at 800 °C in an air flow (200 NmL min⁻¹) until the CO₂ level fell to less than 0.1 vol.%. The regeneration temperature was selected taking into consideration the thermodynamic limitations of the decarbonation reaction and the kinetics of the decarbonation of dolomite. A regenerated catalyst/sorbent mixture was used for all of the SESR experiments in the present study. After regeneration, the reactor was purged with N₂ and cooled down to the desired experimental reaction temperature. Once the operating temperature was reached under a N₂ atmosphere, the liquid reactant mixture (steam/C = 1.5-6.67) was evaporated, blended with a 50 NmL min⁻¹ N₂ flow (used as internal standard) and then introduced updraft in the reactor at different space velocities (liquid flow rates of 5-20 g h⁻¹). During SESR experiments, the evolution of the gas effluent composition typically consists of three stages: pre-breakthrough, breakthrough and post-breakthrough. First, hydrogen production by the SESR process (pre-breakthrough) proceeds until the CO₂ sorbent (calcined dolomite) becomes saturated and loses its capacity for CO₂ removal (breakthrough). Afterwards, CO₂ capture by the sorbent is negligible (post-breakthrough) and a conventional steam reforming (SR) process occurs. In the present work, the data obtained during the pre-breakthrough stage were employed for the study of the SESR process, while data from the post-breakthrough stage were used to study the SR process.

The product gas was passed through a filter and cyclone to be cleaned of any solid particles that may have been elutriated from the bed. The excess steam, model compounds that did not react and all other condensable products and reactant vapors that may have formed were removed from the exiting gas by condensation in a thermoelectric cooling tank. The composition of the dried gas was determined by an on-line gas chromatograph Varian[®] CP-4900 Micro GC, equipped with a molecular sieve (Molsieve 5 Å) and HayeSep A columns, and with a thermal conductivity detector (TCD). Helium was used as the carrier gas. The species detected were H₂, CH₄, CO, CO₂ and N₂ (the N₂ was used as internal standard). The product distribution was calculated on the basis of nitrogen-free and dry composition of the gas effluent. The flow rates of the species generated during the experiment were calculated by means of a nitrogen balance,

since the amount of nitrogen fed in and the composition of the nitrogen evolved are known.

The H₂ yield was calculated from Eq. (11). It is defined as the ratio of the amount of H₂ in the actual effluent gas to the theoretical amount of hydrogen that could be obtained by complete reforming of the model compound (or blend) to CO₂ and H₂. In addition, H₂ selectivity, H₂ purity and the CH₄, CO, and CO₂ concentrations were calculated from Eq. (12)-(14), respectively.

$$\text{H}_2 \text{ yield (\%)} = 100 \cdot (F_{\text{H}_2} / N \cdot F_{\text{model compound/blend}}) \quad (11)$$

$$\text{H}_2 \text{ selectivity (\%)} = 100 \cdot [2 \cdot y_{\text{H}_2} / (2 \cdot y_{\text{H}_2} + 4 \cdot y_{\text{CH}_4})] \quad (12)$$

$$\text{H}_2 \text{ purity (vol.\%)} = 100 \cdot (y_{\text{H}_2} / \sum_i y_i) \quad (13)$$

$$\text{CH}_4/\text{CO}/\text{CO}_2 \text{ (vol.\%)} = 100 \cdot (y_{\text{CH}_4}/\text{CO}/\text{CO}_2 / \sum_i y_i) \quad (14)$$

where F_{H_2} is the molar flow rate of the H₂ produced (mol min⁻¹), N is the number of moles of H₂ theoretically produced per mol of model compound (4 for acetic acid and 8 for acetone) or per mol of blend (5, 6 and 7 for 3:1, 1:1 and 1:3 mol AcH/mol AcCO blends, respectively), $F_{\text{model compound/blend}}$ is the molar flow rate of the model compound or blend fed in (mol min⁻¹), and y_i is the molar content (N₂ free and on a dry basis) of each species i (H₂, CH₄, CO and CO₂). The weight hourly space velocity (WHSV) is defined as the ratio of the mass flow rate of the inlet model compound or blend to the mass of catalyst ($g_{\text{model compound/blend}} g_{\text{catalyst}}^{-1} \text{ h}^{-1}$).

2.5. Thermodynamic equilibrium calculations

Thermodynamic analysis of the SESR process was conducted under the reaction conditions used in the experimental study. The equilibrium composition was estimated by minimizing the Gibbs free energy of the system using Aspen Plus 7.2 software (Aspentech). The RGibbs reactor was specified as the reaction system and the Peng-Robinson thermodynamic package as the property method. The species produced in concentrations higher than 10⁻⁴ mol% were H₂, CO, CO₂, CH₄, H₂O, CaO and CaCO₃. C₂H₄, C₂H₆ and C (graphite as solid carbon) were also included in the product pool, but their concentrations in the equilibrium stream were negligible or not high enough to be considered as significant products, as pointed out in previous works [36]. The product mole fractions were calculated on a dry basis.

3. Results and discussion

3.1. Effect of the temperature on the SESR of AcH and AcCO

The effect of the temperature on the SESR of the individual model compounds of the bio-oil studied (AcH and AcCO) was evaluated at atmospheric pressure in the temperature range of 475-725 °C. The experimental steam/C molar ratio used was three times higher than the stoichiometric steam/C molar ratio of the each model compound, i.e., steam/C=3 for acetic acid and steam/C=5 for acetone. This corresponds to WHSV values of 0.8929 h⁻¹ for acetic acid and 0.4423 h⁻¹ for acetone.

3.1.1. SESR process

Fig. 1 shows the H₂ yield, H₂ selectivity, as well as H₂, CH₄, CO and CO₂ concentrations as a function of the temperature during the SESR of AcH and AcCO. The filled circles represent the experimental results for the SESR process, whereas the solid lines show the equilibrium values obtained from the thermodynamic analysis at equivalent conditions.

The results show that the temperature has a significant effect on the SESR process. As the reaction temperature increases, the H₂ yield (Fig. 1a) increases and reaches a maximum at 625 °C for AcH (92.44%) and at 575 °C for AcCO (95.90%). After that, the H₂ yield gradually decreases as the temperature increases. The H₂ selectivity (Fig. 1b) shows high values (>99.3%) at temperatures of 575-675 °C for AcH. For AcCO, it presents very high values (>99.7%) at the temperatures studied. The H₂ concentration (Fig. 1c) also increases with temperature and reaches a maximum value at 575 °C for AcH (99.29%) and at 525 °C in the case of AcCO (99.75%). After that, it decreases significantly as the temperature increases. The experimental H₂ selectivity values and H₂ concentrations follow the lines of the equilibrium quite closely between 525-725 °C. However, the experimentally obtained H₂ yield values are lower than those corresponding to the SESR equilibrium in the range of temperatures studied. On the other hand, the H₂ yield, H₂ selectivity and H₂ concentration show the lowest values at the temperature of 475 °C for both model compounds.

The CH₄ concentration (Fig. 1d) shows very high values at 475 °C for both model compounds (7.45% and 5.48% for AcH and AcCO, respectively). A high CH₄ concentration at low temperatures has previously been reported in sorption enhanced experiments with sorbitol [43] and glycerol [40] due to the fact that the steam methane reforming reaction is favored at high temperatures, which indicates that CH₄ is the main impurity found in the product gas at low temperature. The CH₄ concentration decreases as the temperature increases: from 1.75% to 0.15% between 525 °C and 675 °C in the case of the AcH, and from 0.14% to 0.02% between 525 °C and 725 °C in the case of the AcCO, following closely the lines of equilibrium. The

methanation reaction becomes thermodynamically unfavorable and steam methane reforming is kinetically enhanced as the temperature increases, which results in low CH_4 concentrations at higher temperatures. The lower CH_4 concentrations detected in the experiments at temperatures higher than 525 °C indicate the ability of the Pd/Co-Ni HT catalyst to suppress the methanation reaction and to successfully catalyze the methane steam reforming reaction during the SESR process. The suppression of the methanation reaction will be favored by the enhancement of the WGS reaction (by the CO_2 capture by the sorbent), since when the WGS is promoted and the CO concentration is then decreased, the methane reforming reaction will be indirectly promoted (reverse of Eq. 4). This will be a consequence of the integration of both phenomena, reaction and sorption, involved in the SESR process.

As in the case of the CH_4 content, the experimental CO concentration value (Fig. 1e) is situated above the equilibrium lines at the temperature of 475 °C for both model compounds (1.89% and 0.22% for AcH and AcCO, respectively). After that, the CO concentration increases from 0.04% to 2.81% as the temperature increases from 525 °C to 675 °C for AcH, and from 0.02% to 6.52% as the temperature increases from 525 °C to 725 °C for AcCO, reasonably close to the lines of the equilibrium. The CO_2 concentration (Fig. 1f) is also high (2.56%) at the temperature of 475 °C for AcH, while it increases from 0.11% to 6.10% as the temperature increases from 525 °C to 675 °C, again very close to the equilibrium lines.

In the case of AcCO, it increases from 0.06% to 17.61% as the temperature increases from 475 °C to 725 °C, close to the equilibrium lines. The favorable thermodynamics of the WGS reaction (exothermic) at low temperature explains the lower CO concentrations found at lower temperatures. Likewise, the favorable thermodynamics of the carbonation reaction (exothermic) at low temperature explains why the CO_2 concentration increases with increasing temperature since high temperatures inhibit the removal of CO_2 to some extent. A very weak CO_2 removal leads to a poor sorption enhancement of the process. Since CO_2 sorption implies an enhanced H_2 production because the equilibrium of both the steam reforming and WGS reactions are shifted to the product side, lower values of H_2 concentration and higher CO concentrations are detected at the higher temperature range studied. The poor results obtained when the SESR process is carried out at 475 °C could be due to the slow steam reforming and CO_2 capture rates. The kinetic limitations at such a low temperature, lead to a lower level of hydrogen production. It has been demonstrated that the SESR reaction, because of its very nature, is highly dependent on the rate of CO_2 removal by the sorbent [36,57].

Fig. 1. Effect of the reaction temperature on the H₂ yield (a), H₂ selectivity (b) and H₂ (c), CH₄ (d), CO (e) and CO₂ (f) concentrations during the SESR of AcH and AcCO. Reaction conditions: steam/C_{AcH}=3 mol/mol, WHSV_{AcH}=0.8929 h⁻¹, steam/C_{AcCO}= 5 mol/mol, WHSV_{AcCO}=0.4423 h⁻¹, sorbent/catalyst ratio=5 g/g, Pd/Ni-Co HT catalyst and dolomite as sorbent.

If the results for AcH and AcCO are compared (Fig. 1), it will be observed that slightly higher values for H₂ yield, H₂ selectivity and H₂ concentration, as well as slightly lower CO and CH₄ concentrations, were obtained in the SESR of AcCO than in the case of AcH at temperatures below 600 °C. These results suggest that the reactivity of AcCO is higher than that of AcH in SESR. The effect of the molecular identity of biomass-derived oxygenates on the activity under aqueous phase reforming has recently been reviewed and it has been concluded that the more reduced molecules (i.e. less OH groups) are easier to undergo C-C cleavage, although the effect of the molecule length could not be excluded [58]. The molecular structure dependence of the activity deduced from the results in the present work is in good agreement with the observed general trend.

Finally, in order to establish the optimum condition for the SESR of AcH and AcCO, it should be taken into account that the different trends observed for the H₂ yield and H₂ concentration values as the temperature increases suggests the need for a compromise between these parameters to select the best temperature for the SESR process. Thus, in the present study it can be concluded that a temperature of 575 °C is optimum for the SESR of acetic acid and acetone. High H₂ purity (99.3-99.4%) and high H₂ yields (90.2-95.9%), together with low concentrations of CH₄, CO and CO₂, can be achieved using steam/C ratios of 3 for AcH and 5 for AcCO, as well as WHSV values of 0.8929 h⁻¹ for AcH and 0.4423 h⁻¹ for AcCO.

3.1.2. SR process

Fig. 1 also shows the H₂ yield, H₂ selectivity, as well as H₂, CH₄, CO and CO₂ concentrations as a function of the temperature during the SR of the individual model compounds. The blank squares represent the experimental results of the SR process, whereas the dashed lines show the equilibrium values obtained from the thermodynamic analysis at equivalent conditions.

It can be observed that the H₂ yield (Fig. 1a), H₂ selectivity (Fig. 1b), H₂ concentration (Fig. 1c) and CO concentration (Fig. 1e) increase as the experimental temperature increases. This was to be expected since as a result of the endothermic character of the reforming reaction, higher temperatures favor the conversion of fuel resulting in a higher H₂ concentration. On the other hand, the CH₄ (Fig. 1d) and CO₂ concentrations (Fig. 1f) decrease with temperature. The exothermic character of the WGS reaction leads to higher concentrations of CO and lower concentrations of CO₂ at higher temperatures. This is due to the fact that the equilibrium of the reaction is shifted to the left, i.e., the reverse of WGS occurs resulting in the consumption of H₂ and the production of CO. The endothermic reforming reaction of CH₄ explains its lower concentration at higher temperatures.

Similar results to those of the SESR process were obtained by SR in relation to the thermodynamic equilibrium. Thus, the approach towards equilibrium between the temperatures of 525-675 °C is reasonably good in respect of H₂ selectivity and the H₂, CH₄, CO and CO₂ concentrations, whereas the experimental H₂ yield values are slightly lower than those of the SR equilibrium. In the case of the SR of AcH and AcCO at 475 °C, the values corresponding to H₂ yield, H₂ selectivity and the H₂ concentration are slightly higher than those obtained at the equilibrium. This could be due to the fact that CO₂ capture continues at a low degree during the SR process, because the CO₂ content is slightly lower than that of the equilibrium at this temperature. The activity dependence on the molecular structure is much clearer in the case of SR, where the produced hydrogen is higher from AcCO compared to from AcH at all the temperatures studied (Figure 1c).

3.2. Effect of the steam/C molar ratio on the SESR of AcH and AcCO

The effect of the steam/C molar ratio on the SESR of AcH and AcCO was evaluated at atmospheric pressure and at 575 °C. The steam/C molar ratios ranged from 1.5 to 4.5 for AcH and from 3.33 to 6.67 for AcCO. Thus, the space velocity of the compounds studied was varied (WHSV=0.6757-1.3158 h⁻¹ for AcH and WHSV=0.3327-0.6594 h⁻¹ for AcCO) to ensure the same total inlet liquid flow rate (5 g h⁻¹). Fig. 2 shows the H₂ yield, H₂ selectivity, as well as the H₂, CH₄, CO and CO₂ concentrations as a function of the steam/C molar ratio. The filled circles represent the experimental results of the SESR process, whereas the blank squares show the experimental results of SR. Likewise, the solid lines show the equilibrium values at equivalent conditions obtained from the thermodynamic analysis applied in the SESR process, while the dashed lines correspond to the SR process.

As expected for both SESR and SR processes, higher steam/C molar ratios increase the H₂ yield, H₂ selectivity and H₂ concentration, whereas they reduce the CH₄ and CO concentrations. The CO₂ concentration increases slightly with the steam/C molar ratio. Low steam/C ratios enhance methanation, while they decrease methane steam reforming and WGS reactions simultaneously [46]. Consequently the CH₄ concentration decreases as the steam/C molar ratio increases. The CH₄ content is an important factor for determining hydrogen selectivity during the SESR process. Moreover, with a low steam/C molar ratio, hydrogen purity is also strongly influenced by the methane content in the effluent gas.

Fig. 2. Effect of the steam/C molar ratio on the H₂ yield (a), H₂ selectivity (b) and H₂ (c), CH₄ (d), CO (e) and CO₂ (f) concentrations during the SESR of AcH and AcCO. Reaction conditions: 575 °C, WHSV_{AcH}=0.6757-1.3158 h⁻¹, WHSV_{AcCO}=0.3327-0.6594 h⁻¹, sorbent/catalyst ratio=5 g/g, Pd/Ni-Co HT catalyst and dolomite as sorbent.

Steam is often added beyond the stoichiometric limit in reforming processes to promote hydrogen productivity and to prevent coking. Carbon deposition, due to polymerization or thermal decomposition, occurs if the gas does not contain a sufficient amount of oxidizing component such as H_2O , resulting in blockage of the catalyst pores [42]. An excess of steam is known to be beneficial for the suppression of coking in steam reforming processes because it leads to the partial gasification of the carbon formed, enhancing the conversion of tars and intermediate compounds [12]. A high steam/C molar ratio is favorable from a thermodynamic point of view, but its value will be limited by the energy cost of the system due to the extra amount of steam generated [59]. Also high steam concentrations will undermine the energy efficiency of the process [42].

The results of the present work, indicate that in SESR catalyst activity is high at a minimum steam/C molar ratio of 3 for AcH and 5 for AcCO, since in these conditions the H_2 concentration shows a high value, together with acceptable H_2 yield values and low CH_4 and CO contents.

3.3. Effect of the weight hourly space velocity (WHSV) on the SESR of AcH and AcCO

The effect of the space velocity on the SESR of AcH and AcCO was evaluated under atmospheric pressure and at $575\text{ }^\circ\text{C}$. The WHSV ranges studied were $0.8929\text{--}2.6786\text{ h}^{-1}$ for AcH and $0.4423\text{--}1.7691\text{ h}^{-1}$ for AcCO. These values were experimentally obtained by changing the total inlet flow rate ($5\text{--}20\text{ g h}^{-1}$) while maintaining the steam/C molar ratio at 3 for AcH and 5 for AcCO. Fig. 3 shows the H_2 yield, H_2 selectivity, and the H_2 , CH_4 , CO and CO_2 concentrations as a function of the WHSV. The filled circles represent the experimental results of the SESR process, whereas the blank squares show the experimental results of SR. The solid and dashed lines represent the equilibrium values obtained under equivalent conditions from the thermodynamic analysis of the SESR and SR processes, respectively.

In general in the SESR process at atmospheric pressure, the H_2 selectivity and the H_2 , CH_4 , CO and CO_2 concentrations do not vary significantly in the space velocity range studied, although a slight decrease in the H_2 selectivity and H_2 concentration together with an increase in the CH_4 concentration, is observed at the highest space velocity used for AcH (2.6786 h^{-1}). However, the H_2 yield decreases significantly with the space velocity. The shorter contact time at higher WHSV values can be expected to cause a lower conversion of fuel. From the results, it can be seen that the H_2 yield is affected much more by WHSV than the H_2 selectivity and H_2 purity, which suggests that, together with a decrease in conversion, an increase in the formation of coke might have occurred at higher space velocities. A sharp decrease in H_2 yield as the space velocity increases was also detected in the SESR experiments with glycerol [41], indicating a

low reaction rate in the feedstock. Selection of an appropriate space velocity in the SESR process should ensure the largest possible supply of feedstock in order to maximize H₂ production and minimize the reactor size and the amount of catalyst required [60]. In the present work, acceptable H₂ yield values of 85.35% and 89.31% were obtained for AcH and AcCO, respectively, with relatively high WHVS values (1.7858 h⁻¹ for AcH and 1.7691 h⁻¹ for AcCO).

In SR, a slight decrease can be seen in the H₂ selectivity and H₂ concentrations, together with a slight increase in the CH₄ and CO₂ concentrations, as the space velocity increases (Fig. 3). However, the effect of the space velocity on the H₂ yield is much higher and so the decrease in H₂ yield as the WHVS increases is substantial. García-Lario et al. [60] have suggested that the catalyst may suffer from low activity at high space velocity values, and this decrease in catalytic activity would be reflected in both the pre-breakthrough and the post-breakthrough steps.

Fig. 3. Effect of the WHSV on the H₂ yield (a), H₂ selectivity (b) and H₂ (c), CH₄ (d), CO (e) and CO₂ (f) concentrations during the SESR of AcH and AcCO. Reaction conditions: 575 °C, steam/C_{AcH}=3 mol/mol, steam/C_{AcCO}= 5 mol/mol, sorbent/catalyst ratio=5 g/g, Pd/Ni-Co HT catalyst and dolomite as sorbent.

3.4. SESR of the blends of AcH and AcCO

To simulate the behavior of bio-oil during the SESR process, three mixtures of the two model compounds studied, acetic acid and acetone, were prepared containing 3:1, 1:1 and 1:3 mol AcH/mol AcCO. To refer to the blends, the labels 3AcH:1AcCO, 1AcH:1AcCO and 1AcH:3AcCO, respectively, were used. SESR experiments with the blends of model compounds were carried out at temperatures of 475-675 °C. The feed rate of the blend solutions was 5 g h⁻¹, and the experimental steam/C molar ratios were three times higher than the stoichiometric steam/C molar ratio of each individual blend, corresponding to steam/C molar ratio values in the range of 3.667-4.636 and WHSV values in the range of 0.5080-0.7152 h⁻¹.

Fig. 4 shows the H₂ yield, H₂ selectivity and H₂ concentration as a function of the temperature during the SESR of each of the blends studied. As can be seen, the effect of the temperature on the SESR of the blends of AcH and AcCO is similar to that of the individual model compounds.

In general, the blended samples reflect the behavior of the individual model compounds. As in the case of the individual compounds, the H₂ yield (Fig. 4a) of the blends increases with the reaction temperature until it reaches a maximum (at 625 °C), and then it decreases. The maximum H₂ yield values are 92.44% and 95.90% for AcH and AcCO, respectively. However, slightly lower values were obtained in the blends, i.e., 91.51% for 3AcH:1AcCO, 88.85% for 1AcH:1AcCO and 86.44% for 1AcH:3AcCO. In general, there is a slight decrease in H₂ yield as the proportion of AcCO in the blend increases. It seems to indicate that some interaction effect between the components of the blends occurred, which slightly hindered the conversion of the blend. In the case of H₂ selectivity (Fig. 4b), very high values (>99.5%) at temperatures between 575-675 °C were obtained for all three blends, as occurred with the individual compounds.

The H₂ concentration (Fig. 4c) of the blends reaches a maximum value at 525 °C and then decreases as the reaction temperature increases, as in the case of the individual compounds. The maximum values are 99.29% and 99.75% for AcH and AcCO, respectively, and similar to the maximum values obtained in the blends (99.60% for 3AcH:1AcCO, 99.77% for 1AcH:1AcCO and 99.78% for 1AcH:3AcCO).

Fig. 4. H₂ yield (a), H₂ selectivity (b) and H₂ concentration (c) during the SESR of blends of AcH and AcCO (3:1, 1:1 and 1:3 mol AcH/mol AcCO) at different temperatures. Reaction conditions: steam/C=3.667-4.636 mol/mol and WHSV=0.5080-0.7152 h⁻¹ (total inlet liquid flow rate=5 g h⁻¹), sorbent/catalyst ratio=5 g/g, Pd/Ni-Co HT catalyst and dolomite as sorbent.

Fig. 5 shows the CH₄, CO and CO₂ concentrations as a function of temperature during the SESR of the blends. As with the individual compounds, the CH₄ concentration is high at 475 °C in the blends, but it decreases sharply at higher temperatures. At 525 °C, low CH₄ concentrations (0.1-0.3%) are obtained for the blends, and they are lower than 0.1% at temperatures of 575-675 °C. This shows that the Pd/Co-Ni HT is an effective catalyst for suppressing the methanation reaction and/or for successfully catalyzing the methane steam reforming reaction during the SESR of blends of acetic acid and acetone. Also, as in the case of the individual model compounds, the CO and CO₂ concentrations increase as the temperature increases from 525 °C to 675 °C and their values are quite similar to those of the individual compounds in the temperature range studied. However, at very high temperatures (625-675 °C) a slight increase in the CO and CO₂ concentrations can be seen with the increase in the proportion of AcCO in the blend.

In summary, the results of the present work indicate that the blends of model compounds of bio-oil show similar results for the parameters studied than those of the individual compounds, acetic acid and acetone, except in the fact that lower H₂ yield values, and slightly higher concentrations of CO and CO₂ at the higher temperatures, are apparent in the blends compared to the individual compounds. Moreover, the H₂ yield decreases, while the CO and CO₂ concentrations increase slightly, as the proportion of AcCO in the blend increases.

As a basis for selecting the best conditions for the SESR of the blends, it should be borne in mind that the highest H₂ yield values (86.4-91.5%) were obtained at 625 °C for all three blends. Under these conditions, high values of H₂ selectivity were also obtained (99.9%), but the H₂ concentration was very low (96.1-97.4%). CO and CO₂ concentrations were also quite high (0.6-0.9% and 1.8-3.0%, respectively). The highest H₂ concentrations (99.6-99.8%) were obtained at 525 °C for all three blends whereas the H₂ yields decreased significantly (78.4-82.0%). Therefore, if the aim is to achieve a high H₂ concentration is aimed without excessively reducing the H₂ yield, the optimum temperature for the SESR of the blends of model bio-oil compounds is 575 °C, since at this temperature H₂ yields of 83.6-88.6%, together with H₂ concentrations of 99.2-99.3%, are obtained.

Fig. 5. CH_4 , CO and CO_2 concentrations during the SESR of AcH (a), 3AcH:1AcCO (b), 1AcH:1AcCO (c), 1AcH:3AcCO (d) and AcCO (e) at different temperatures. Reaction conditions: steam/C=3.667-4.636 mol/mol and WHSV=0.5080-0.7152 h^{-1} (total inlet liquid flow rate=5 g h^{-1}), sorbent/catalyst ratio=5 g/g, Pd/Ni-Co HT catalyst and dolomite as sorbent.

4. Conclusions

The operational parameters for the sorption enhanced steam reforming of acetic acid and acetone, two representative model compounds of bio-oil obtained from the fast pyrolysis of biomass, as well as their blends were studied in a fluidized bed reactor. The results show that acetic acid, acetone and their blends can be efficiently reformed to hydrogen over a Pd/Ni-Co HT catalyst and using dolomite as CO₂ sorbent in a SESR process. The H₂ yield and H₂ concentration increase with temperature up to a maximum value, and then they decrease. The H₂ selectivity values are very high in the temperature range of 525-675 °C. The CH₄ concentration decreases as the temperature increases, while the CO and CO₂ concentrations increase with temperature. In general, equilibrium for the SESR process was reached at temperatures in the 525-725 °C range. H₂ yield, H₂ selectivity and H₂ concentration all increase as the steam/C molar ratio increases, whilst they decrease when WHSV increases. The positive effect of increasing the steam/C ratio is ascribed to the enhanced steam reforming and WGS reactions, whereas the negative effect of increasing WHSV is the result of a lower fuel conversion due to a shorter contact time.

The SESR at 575 °C of the model compounds of bio-oil and their blends using Pd/Co-Ni HT as catalyst and calcined dolomite as CO₂ sorbent (sorbent/catalyst ratio of 5 g/g) under the conditions of the present study gives rise to H₂ purity values of 99.2-99.4% and H₂ selectivity values of 99.7-99.9%. The SESR of blends of model compounds of bio-oil show similar results for the parameters studied that those for the individual model compounds, acetic acid and acetone, except in that lower H₂ yield values are obtained from the SESR of the blends (83.3-88.6%) compared to the individual model compounds (90.2-95.9%). This effect is more marked as the proportion of AcCO in the blend increases.

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