H₂ production by sorption enhanced steam reforming of biomass-derived bio-oil in a fluidized bed reactor: an assessment of the effect of operation variables using response surface methodology

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Abstract

High-purity H₂ was produced by the sorption enhanced steam reforming (SESR) of acetic acid, a model compound of bio-oil obtained from the fast pyrolysis of biomass, in a fluidized bed reactor. A Pd/Ni-Co hydrotalcite-like material (HT) and dolomite were used as reforming catalyst and CO₂ sorbent, respectively. The hydrogen yield and purity were optimized by response surface methodology (RSM) and the combined effect of the reaction temperature (T), steam-to-carbon molar ratio in the feed (steam/C) and weight hourly space velocity (WHSV) upon the sorption enhanced steam reforming process was analyzed. T was studied between 475 and 675 °C, steam/C ratio between 1.5 and 4.5 mol/mol and WHSV between 0.893 and 2.679 h⁻¹. H₂ yield, H₂ selectivity and H₂

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purity, as well as the CH₄, CO and CO₂ concentrations in the effluent gas, were assessed. The operating temperature proved to be the variable that had the greatest effect on the response variables studied, followed by the WHSV and the steam/C ratio. The results show that the H₂ yield, H₂ selectivity and H₂ purity increased, while the CH₄, CO and CO₂ concentrations decreased, concurrently with the temperature up to around 575-625 °C. Higher values of the steam/C ratio and lower WHSV values favored the H₂ yield, H₂ selectivity and H₂ purity, and reduced the CH₄ concentration. It was found that the SESR of acetic acid at atmospheric pressure and 560 °C, with a steam/C ratio of 4.50 and a WHSV of 0.893 h⁻¹ gave the highest H₂ yield of 92.00%, with H₂ purity of 99.53% and H₂ selectivity of 99.92%, while the CH₄, CO and CO₂ concentrations remained low throughout (0.04%, 0.06% and 0.4%, respectively). The results also suggested that a slow CO₂ capture rate led to a poor level of hydrogen production when the SESR process was carried out at low temperatures, although this can be improved by increasing the sorbent/catalyst ratio in the fluidized bed.

Keywords: hydrogen production; sorption enhanced steam reforming (SESR); Pd/Ni-Co catalyst; bio-oil; response surface methodology; fluidized bed

1. Introduction

1.1. SESR process

Hydrogen is considered to be one of the most promising clean energy carriers for the near future. The demand for H₂ is expected to increase exponentially, both for conventional industrial uses and for clean energy generation, particularly in fuel cell applications [1]. However, hydrogen is still mainly produced from fossil fuels, either by

means of the steam methane reforming (SMR) of natural gas or via the partial oxidation of heavy oil fractions, which produces hydrogen with CO_2 as a by-product. Various strategies for the reduction and sequestration of CO_2 are under study, among which the sorption enhanced steam reforming (SESR) process is attracting a great deal of attention since it combines both hydrogen production and CO_2 separation. In the SESR process, carbon dioxide is captured by an in situ sorbent, which shifts the reversible reforming and water gas shift (WGS) reactions to the product side beyond their conventional thermodynamic limits, giving rise to a higher hydrogen production. The captured CO_2 is converted to a solid carbonate if a CaO -based sorbent is used. This sorbent can be regenerated using temperature or pressure swing desorption to release a relatively pure CO_2 stream that can be appropriate for sequestration. The SESR process can be carried out at much lower reaction temperatures than the conventional reforming processes, and in this way catalyst coking and sintering, as well as investment and operation costs, can be reduced. In addition, the heat released by the exothermic carbonation reaction will supply most of the heat required by the endothermic reforming reactions. Nevertheless, more energy will still be required to regenerate the sorbent in the energy-intensive calcination reaction.

The full environmental benefits of using hydrogen as an energy carrier can only be achieved if the hydrogen is produced from renewable sources, such as biomass [2]. Biomass is the best route for accelerating the introduction of green hydrogen as a major fuel in the future, since it does not contribute to a net increase in atmospheric CO_2 . The coupling of biomass conversion technologies with CO_2 capture and storage technologies offers the possibility of achieving an effective reduction of the amount of CO_2 in the atmosphere [3].

H₂ can be produced from biomass using different routes with intermediate oxygenate production steps, which can be subsequently reformed. Flash pyrolysis is presented as an attractive method to produce pyrolysis oil (bio-oil) from different types of biomass, which can later be subjected to catalytic reforming to obtain hydrogen. Bio-oil is a complex mixture of a large number of compounds, including acids, aldehydes, alcohols, ketones, phenols and sugars. The aqueous carbohydrate-derived fraction of the bio-oil can be steam reformed for hydrogen production. Acetic acid is one of the most representative constituents of the water soluble fraction of bio-oils and it is frequently chosen as a model compound of bio-oil produced from the fast pyrolysis of biomass. A number of studies on hydrogen production by the conventional steam reforming of acetic acid as a model compound of bio-oil have been reported in the literature, using both fixed bed [4-8] and fluidized bed reactors [9]. Fluidized bed reactors are commonly used in processes where catalysts need to be continuously regenerated, since they have a higher solids handling capabilities and they also facilitate heat and mass transfer, temperature uniformity, low pressure drop and higher catalyst effectiveness factors [10]. Florin and Harris [11] suggested that fluidized bed reactors could be suitable for hydrogen production from biomass coupled with carbon dioxide capture processes. However, the sorption enhanced concept in such reactors has so far received scarce attention in the literature.

The overall reaction for the conversion of acetic acid to hydrogen can be expressed in the form of Eq. (1), which is a combination of steam reforming and water gas shift, Eq. (2), reactions:

The reforming reaction is highly endothermic, while the shift reaction is moderately exothermic. Both reactions are equilibrium limited, and it is impossible to achieve the complete conversion of the acetic acid and CO in a single reactor under normal reaction conditions. Hence, CO and also CH₄ can be expected to be generated in large quantities due to thermodynamic equilibrium limitations and the complex reaction pathways, such as thermal decomposition and/or methanation, which could also lead to the formation of intermediates and coke.

In sorption enhanced H₂ production, a solid CO₂ sorbent, such as CaO, is incorporated into the catalyst bed. In this way, CO₂ can be removed in situ from the gas phase as it is formed, as illustrated in Eq. (3).

Due to the equilibrium shift effect, the decrease in CO₂ promotes the water gas shift reaction, Eq. (2), and in turn the CH₄ reforming reaction, Eq. (4).

As a result, the CO and CH₄ contents are significantly reduced, which increases the hydrogen concentration in the product gas and allows almost complete conversion to be achieved. The overall reaction for the sorption enhanced steam reforming (SESR) process of acetic acid is shown in Eq. (5).

Typical operating temperatures in SESR processes are between 400 and 650 °C. It requires the use of very active and stable reforming catalysts. The main functions required for the catalyst are a high activity and selectivity towards H₂ and CO formation, through the cleavage of C-C and C-H bonds, and a high catalytic activity in the high-temperature WGS reaction. Our previous studies have shown that a Ni-Co

catalyst derived from a hydrotalcite-like material (HT), used with dolomite as CO₂ sorbent, is very effective in enhancing hydrogen production and purity in the SESR process with biomass-derived compounds, such as syngas [12], glycerol [13, 14], ethanol [15] and glucose [16]. Moreover, an improved Pd/Ni-Co HT catalyst, which does not require a reduction step after air-regeneration of the sorbent in the cyclical SESR process, has recently been developed in our research group and successfully employed to produce a high H₂ yield of great purity from biomass-derived compounds [17]. It was then chosen for use in the present study. Besides the development of the catalyst, the process operating conditions will also influence the effectiveness of the catalyst in the sorption enhanced steam reforming of biomass. Although the SESR process has been shown to enhance hydrogen production, the operation variables still need to be thoroughly assessed taking into account the characteristics of different biomass-derived compounds to ensure optimum results. Response surface methodology (RSM) appears as a useful optimization method for attaining this objective.

1.2. Response surface methodology

RSM is a multivariate statistical technique that is used to optimize processes. Its objective is to simultaneously optimize the levels of all the variables involved in order to ensure optimal process performance [18]. This methodology involves the design of experiments and multiple regression analysis as tools to assess the combined effects of two or more independent variables on the dependent variables under study [19]. An important advantage of RSM is the possibility to detect interaction effects between independent variables upon the response within the range studied to obtain a better knowledge of the process. The technique is based on fitting a polynomial equation to

the experimental data in order to explain the behavior of a given set of data. This will generate mathematical equations that will allow a more detailed description of the studied process. Recently, several studies have been published on the application of RSM in order to optimize H₂ production by means of thermochemical processes, such as pyrolysis and gasification/reforming, exemplifying the potential of this methodology. Fermoso et al. [20] assessed the combined effect of the temperature and the oxygen and steam concentrations on the high-pressure coal gasification in a fixed bed reactor for H₂-rich gas production. Fan et al. [21] used RSM to find the optimum values of four process variables (carbon dioxide to methane ratio, gas hourly space velocity, oxygen concentration in the feed and reaction temperature) to maximize hydrogen production from the carbon dioxide reforming of methane over a Ni-Co/MgO-ZrO₂ catalyst. Monyanon et al. [22] used RSM to optimize the methanol steam reforming process over Au/CuO-CeO₂ catalysts, studying the temperature, steam to methanol ratio, liquid feed rate and catalyst weight to He flow rate ratio. Mante et al. [23] investigated the influence of temperature, weight hourly space velocity (WHSV) and vapor residence time on the catalytic pyrolysis of hybrid poplar wood in a bubbling fluidized bed reactor. This technique could therefore be satisfactorily applied to the study of the SESR process, although it has not to our knowledge been reported in the literature.

Therefore, the aim of the present study is to investigate, using the response surface methodology, the effect of the operating temperature, steam/C ratio and WHSV on H₂ production by means of the sorption enhanced steam reforming of acetic acid over a Pd/Ni-Co HT catalyst using CaO as sorbent material in a bench-scale fluidized bed reactor. The objectives of this study can be summarized as being: (i) to assess the combined effects of the temperature (475-675 °C), steam/C molar ratio (1.5-4.5) and

WHSV (0.893-2.679 h⁻¹) upon H₂ yield, H₂ selectivity and H₂ purity, and upon the CH₄, CO and CO₂ concentrations in the effluent gas, and (ii) to determine the optimum values of the operating variables for optimizing the response variables within the experimental region under study. A thermodynamic equilibrium analysis of the process was carried out in order to determine the theoretical feasibility of the process in the selected reaction conditions and to compare the equilibrium values obtained with the experimental results.

2. Experimental

2.1. Feedstock

Acetic acid was selected as an oxygenated model compound of organic acids present in the aqueous phase of bio-oils produced by the fast pyrolysis of biomass. Glacial acetic acid was supplied by PANREAC (100% purity). Aqueous solutions of acetic acid were prepared using water-to-acetic acid molar ratios between 3 and 9 (steam/C molar ratios of 1.5-4.5).

2.2. CO₂ sorbent

Arctic dolomite, used as a precursor of CaO for the capture of CO₂, was supplied by Franfoss Miljøkalk As, Norway. This has a purity of approximately 98.5 wt.% CaMg(CO₃)₂ and no sulfur according to X-ray fluorescence analysis. The dolomite sample was calcined in an air flow (200 mL min⁻¹) at 770 °C for 4 h prior to its application as CO₂ sorbent. The initial maximum CO₂ capture capacity was estimated as being 0.46 g CO₂/g sorbent.

2.3. Catalyst preparation

The 1%Pd/20%Ni-20%Co HT catalyst (Pd/Ni-Co HT) used in the present work was prepared by 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 40 wt.% total metal load of Ni and Co, resulting in a material with 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 has been reported elsewhere [24]. 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 then 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. The calcined catalyst was pelletized, ground and sieved to the desired particle size (250-500 µm). A detailed description of the Pd/Ni-Co HT catalyst preparation procedure has been reported elsewhere [17].

2.4. Experimental procedure

Fig. 1 shows a schematic flow diagram of the experimental setup used for the SESR experiments with acetic acid. It consists of an updraft bubbling fluidized bed quartz reactor (i.d. 27 mm), which was loaded with a 12 g mixture of calcined dolomite (as CO₂ sorbent) and Pd/Ni-Co HT catalyst, at a sorbent-to-catalyst ratio of 5 g/g. The SESR experiments were carried out at atmospheric pressure and isothermally at

temperatures between 475 and 675 °C. The gases were delivered by Bronkhorst[®] mass flow controllers. Prior to each SESR experiment, the catalyst/sorbent mixture was subjected to a regeneration step at 770 °C in an air flow (200 NmL min⁻¹) until the CO₂ level fell to less than 0.1 vol.%. The temperature of 770 °C was selected from preliminary experiments, taking into consideration the thermodynamic limitations of the decarbonation reaction and the kinetics of the decarbonation of dolomite [15]. A regenerated catalyst/sorbent mixture was used in all the SESR experiments in the present study. After regeneration, the reactor was purged with N₂ and cooled down to the desired experimental reaction temperature. The reaction temperature was controlled by a type K thermocouple which was inserted into the catalyst/sorbent bed and connected to a temperature controller and data recorder. Once the operating temperature was reached under N₂ atmosphere, the liquid reactant mixture (steam/C = 1.5-4.5) was swept by a 20 NmL min⁻¹ N₂ flow (used as internal standard), evaporated in an evaporator and then introduced updraft through the catalyst/sorbent bed at different space velocities (liquid flow rates of 5.0-15.452 g h⁻¹). The aqueous solution of acetic acid was fed in by means of a Gilson[®] high-performance liquid chromatography (HPLC) pump from the bottom of the reactor.

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 of acetic acid (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 is assumed to occur. In the present work, the data obtained during the pre-breakthrough stage were used for the

study of the SESR process.

The product gas was cleaned of solid particles that may have been elutriated from the bed by means of a cyclone. The excess steam, acetic acid that did not react and all other liquids that may have formed were separated from the exiting gas by condensation in a thermoelectric cooling tank. The composition of the dried gas was analyzed using an on-line dual channel Varian[®] CP-4900 Micro GC, equipped with both 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, and CO₂. The product distribution was calculated on the basis of the 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, H₂ selectivity, H₂ purity and CH₄, CO, and CO₂ concentrations were calculated from Eq. (6)-(9), respectively:

$$\text{H}_2 \text{ yield (\%)} = 100 \cdot (F_{\text{H}_2} / 4 \cdot F_{\text{acetic acid}}) \quad (6)$$

$$\text{H}_2 \text{ selectivity (\%)} = 100 \cdot [2 \cdot y_{\text{H}_2} / (2 \cdot y_{\text{H}_2} + 4 \cdot y_{\text{CH}_4})] \quad (7)$$

$$\text{H}_2 \text{ purity (vol.\%)} = 100 \cdot (y_{\text{H}_2} / \sum_i y_i) \quad (8)$$

$$\text{CH}_4/\text{CO}/\text{CO}_2 \text{ (vol.\%)} = 100 \cdot (y_{\text{CH}_4}/\text{CO}/\text{CO}_2 / \sum_i y_i) \quad (9)$$

where F_{H_2} is the molar flow rate of the H₂ produced (mol min⁻¹), $F_{\text{acetic acid}}$ is the molar flow rate of the acetic acid 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 acetic acid to the mass of catalyst ($g_{\text{acetic acid}} g_{\text{catalyst}}^{-1} \text{ h}^{-1}$).

2.5. Response surface methodology

Independent variables or factors are experimental variables that can be changed irrespectively of each other. In the present work, the factors studied were temperature (T), steam-to-carbon molar ratio in the feed (steam/C) and weight hourly space velocity (WHSV). The levels of these variables are the values at which the experiments are going to be carried out according to the experimental design. In this case, the three independent variables were investigated at five levels. T was studied between 475 and 675 °C, steam/C between 1.5 and 4.5 mol/mol and WHSV between 0.893 and 2.679 h⁻¹. The responses or dependent variables are those that are measured during the experiments. The response variables were H₂ yield, H₂ selectivity and H₂ purity, as well as the CH₄, CO and CO₂ concentrations.

The experimental design employed in this study was the central composite design (CCD). This was used to define the experiments needed to be carried out in the experimental region under study, i.e., the set of different combinations of the levels of the independent variables that were applied experimentally to obtain the values of the response variables. Table 1 shows the experiments performed according to the CCD. This design consists of the following parts: (1) a full factorial design; (2) a star design in which experimental points are at a certain distance, α , from the center and (3) a replicated center point. The α -value depends on the number of variables, k , and can be calculated by setting $\alpha = 2^{k/4}$, so that for three variables, the α -value is 1.682. The CCD is a better alternative to the full factorial three-level design since it requires a smaller number of experiments while providing comparable results [25]. In the present study, the CCD design involved 20 experiments, including eight factorial points (a 2³ full factorial design), six axial points and six replicates of the centre of the design. The

experiments were conducted in random order. To apply the RSM, the levels of the independent variables were coded in order to be able to compare variables with different units or of different orders of magnitude. In this way, they will all affect the response evenly, making the units of the parameters irrelevant. Codification of the levels of the variables consisted in transforming each real value into coordinates inside a scale with dimensionless values, which are proportional to their location in the experimental space. Table 1 shows the coded (in parentheses) and the decoded values of the independent variables (T, steam/C and WHSV), together with the experimental values obtained for the response variables (H₂ yield, H₂ selectivity, H₂ purity, CH₄, CO and CO₂).

The mathematical-statistical treatment of the experimental data consisted in fitting a polynomial function to the set of data collected from CCD. In this work, for the three independent variables, x_1 (T), x_2 (steam/C) and x_3 (WHSV), the following second-order polynomial equation was applied:

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \beta_{33} x_3^2 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{23} x_2 x_3 + \beta_{123} x_1 x_2 x_3 + \varepsilon \quad (10)$$

where y is the response variable; β_0 is the intercept term; β_1 , β_2 and β_3 are the coefficients of the linear terms; β_{11} , β_{22} and β_{33} are the coefficients of the quadratic terms; β_{12} , β_{13} , β_{23} and β_{123} are the coefficients of the interaction terms and ε is the residual associated with the experiments. Multiple regression analysis was used to fit Eq. (10) to the experimental data by means of the least squares method, which makes it possible to determine the β coefficients that generate the lowest possible residual. The equation obtained describes the behavior of a response variable in the experimental region as a function of the independent variables. In order to evaluate the fit of the quadratic model to the experimental data, tests for the significance of the regression

model and each individual coefficient term were performed. The statistical evaluation of the models was performed by analysis of variance (ANOVA) using SPSS Statistics 19.0 software. The p -value parameter is related to the comparison of the explained and residual variances in data and it is used to establish whether a model or parameter is significant, i.e. $p\text{-value} < 0.05$ for a confidence level of 95%. A significant p -value indicates that a regression model is suitable for describing the observed data. The accuracy of the fitted polynomial model is expressed by the coefficient of determination R^2 , which represents the proportion of variability for a set of data that is explained by a statistical model. However, R^2 increases as the number of variables included in the model increases. It would therefore be more appropriate to use $\text{Adj-}R^2$, which penalizes the statistic R^2 as extra variables are included in the model. In fact, $\text{Adj-}R^2$ decreases if unnecessary terms are added. Finally, the global quadratic model is modified by eliminating the non-significant terms to obtain the best model for each of the response variables.

To visualize the combined effect of two factors on the response, the model obtained can be three-dimensionally represented as a surface (response surface plot) and the best operation conditions inside the experimental region under study can be found by visual inspection. The two-dimensional display of the surface plot generates a contour plot, where the lines of a constant response are drawn on the plane of two independent variables. In this study, response surface and contour plots were generated using SigmaPlot 12.5 software. In this way, the optimum values for each independent variable that produce the best response in the experimental region under study were obtained.

2.6. Thermodynamic equilibrium calculations

Thermodynamic analysis of the SESR process was conducted taking into account the reaction conditions used in the experimental study. The equilibrium composition was estimated by minimizing the Gibbs free energy, since this non-stoichiometric approach offers greater flexibility when tackling complex problems where the reaction pathways are unclear [11]. Aspen Plus 7.2 software (Aspentech) was used for the calculations. The RGibbs reactor was specified as the reaction system. The Peng-Robinson property method was used to predict the thermodynamic behavior of the system. According to the results obtained for the prediction of the equilibrium under sorption enhanced conditions, the species produced in concentrations higher than 10^{-4} mol% were H_2 , CO, CO_2 , CH_4 , H_2O , CaO and $CaCO_3$. C_2H_4 , C_2H_6 and C (graphite as solid carbon) were also included in the product pool, but their concentrations in the equilibrium stream were null or not high enough to be considered as significant products, as pointed out in previous works [15]. The product mole fractions were calculated on a dry basis.

3. Results and discussion

3.1. Effect of T , steam/C and WHSV on the SESR process

The experimental values obtained for the response variables are shown in Table 1. Eq. (10) was fitted to the experimental data by multiple regression analysis and the fit of the model was evaluated by means of ANOVA tests which showed the terms of the model that were statistically significant for a confidence level of 95% (p -value<0.05), and those that were not statistically significant were eliminated from the models. The results of the fit of the reduced model to the experimental data by multiple regression analysis and the results of the evaluation of the fit of the model by ANOVA, together with the R^2 values, are shown in Tables 2 and 3. It can be observed that the final models obtained

were statistically significant for a confidence level of 95% (p -value <0.05) for all the response variables studied. The coded coefficient values for the reduced models were further decoded in order to obtain the polynomial models for the response variables as a function of the real independent variables, which are shown in Table 4. This allowed the response surface to be represented in real terms. Florin and Harris [11] suggest that the thermodynamic equilibrium should be considered the upper limit for representing the extent to which a fuel is converted, since deviations from chemical equilibrium are to be expected in experimental results. This is because chemical kinetics and heat and mass effects restrict the extent to which certain species participate in the chemical equilibrium in the reactor. Hence, as will be explained below, the response surface plots provided by the RSM analysis were adjusted taking into account the equilibrium values in order to fulfill the premise that the equilibrium represents the maximum boundary for H₂ yield, H₂ selectivity and H₂ purity (or the minimum boundary for the CH₄, CO and CO₂ concentrations) depending on the experimental conditions. Thus, the response surfaces directly obtained from the polynomial equations shown in Table 4 were constrained in those parts of the experimental region where the predicted values were higher (or lower depending on each case) than the equilibrium ones since the polynomial equation does not take into account the maximum limit by itself.

The results show that all the independent variables studied (T, steam/C and WHSV) have a significant influence on H₂ yield, H₂ selectivity, H₂ purity (Table 2) and CH₄ content (Table 3). Only T has a significant effect on CO and CO₂ content, whereas steam/C and WHSV have a non-significant influence on them (Table 3). Furthermore, an interaction effect between T and steam/C, and between T and WHSV, influenced the H₂ selectivity, H₂ purity and the CH₄ content variables, since the interaction terms in the

models, x_1x_2 and x_1x_3 , were statistically significant for a confidence level of 95% (p -value <0.05). On the other hand, H_2 yield, H_2 selectivity and H_2 purity depend directly on T and steam/ C and inversely on the WHSV, according to whether their coded coefficients (Table 2) have a positive or negative sign, unlike CH_4 (Table 3). Likewise, CO depends inversely on T , whereas CO_2 depends directly on T (Table 3).

Figs. 2-7 show the response surface and contour plots for all the variables studied. As explained above, the response surfaces obtained by RSM for each response variable were constrained by the equilibrium surface plot, given that the equilibrium values represent a maximum boundary for H_2 yield, H_2 selectivity and H_2 purity (and a minimum boundary for CH_4 , CO and CO_2 concentrations) depending on the different conditions used in the experimental runs. Figs. 2-7 therefore show the response surfaces corrected according to the equilibrium values. The results of the thermodynamic analysis of the SESR of acetic acid, i.e., the equilibrium values, for the studied conditions are also included (in gray) in Figs. 2-7 in order to be able to compare the experimental results with the corresponding equilibrium values, as well as to detect where deviations from the chemical equilibrium occur among the experimental data.

The response surface and contour plots for H_2 yield, H_2 selectivity and H_2 purity are shown in Figs. 2, 3 and 4, respectively. The letters (a-c) represent the response variable as a function of T and steam/ C , whereas the letters (d-f) represent the response variable as a function of T and WHSV. In general, it can be seen that the H_2 yield, H_2 selectivity and H_2 purity increase as T and steam/ C increase, whilst they decrease when WHSV increases. The positive effect of increasing the steam/ C ratio can be ascribed to enhanced steam reforming and WGS reactions. On the other hand, the negative effect of increasing WHSV is the result of a lower biomass conversion due to the shorter contact

time. The curvature in the response surface and the contour plot isolines indicates that the effect of T on these variables varies over the experimental range studied. Thus, increases in H₂ yield (Fig. 2) and H₂ selectivity (Fig. 3) are observed when temperature increases from 475 °C to approximately 600-625 °C, but after that the response variable values hardly change or decrease slightly. For H₂ purity (Fig. 4), a similar behavior is apparent, but its value increases with temperature up to approximately 575 °C, after which H₂ purity decreases significantly until it reaches 675 °C.

The coefficient values of the polynomial models in Tables 2 and 3 are coded coefficients since the values of the independent variables from which they were derived were also coded. The use of coded coefficients makes it possible to compare the relative influence of the different factors on the response variables. The absolute values of the coded coefficients show that T has the most significant influence on H₂ yield, H₂ selectivity and H₂ purity, followed by WHSV and steam/C (Table 2) and that an increase in the T value will have a greater effect on the response than a similar increase (in coded scale) in WHSV or steam/C within the experimental region studied.

On the other hand, in the case of the H₂ yield (Fig. 2), since no interaction effects between any of the three independent variables were detected, the positive effect of steam/C and the negative effect of WHSV are constant over the entire temperature interval studied. In fact, the H₂ yield is greatly affected by WHSV and an increase in space velocity causes a significant decrease in the H₂ yield, since it causes not only a decrease in the conversion, but also an increase in the formation of coke. In the case of the H₂ selectivity and H₂ purity (Figs. 3 and 4, respectively), since interaction effects between T and steam/C, as well as between T and WHSV, were detected, the influence of steam/C and WHSV on the response differs over the temperature interval. Thus,

when temperature is higher than approximately 600-625 °C, neither steam/C nor WHSV have a significant effect on the response variable. However, at lower temperatures, a positive effect of the steam/C ratio and a negative effect of the WHSV on the response are apparent. Therefore, at low temperatures, higher values of steam/C and lower values of WHSV are needed to obtain higher H₂ selectivity and H₂ purity values, whereas at high temperatures, the influence of these variables is very low or non significant.

Furthermore, Fig. 2 shows that the equilibrium values for H₂ yield are reached at temperatures between approximately 600-650 °C with low values of WHSV at the steam/C values studied. In the case of H₂ selectivity and H₂ purity (Figs. 3 and 4, respectively), the equilibrium values are reached at temperatures between approximately 575-625 °C with low or moderate values of WHSV at the steam/C values studied. When WHSV is higher than approximately 2.00, equilibrium is also reached at very high temperatures and very low steam/C values.

Fig. 5 shows the response surface and contour plots for CO₂ concentration as a function of T and steam/C (Fig. 5a) and as a function of T and WHSV (Figs. 5b, 5c and 5d). WHSV does not have a significant influence on CO₂ concentration, whereas an increase in steam/C significantly increases the CO₂ content at high temperatures. Carbonation is an exothermic and mole-reducing reaction, so the equilibrium CO₂ concentration increases concurrently with increasing temperature and decreasing CO₂ pressure due to an increase in the steam-to-carbon ratio, as can be seen in Fig. 5. The experimental CO₂ concentration decreases slightly as the temperature increases from 475 °C to 523 °C, after which its value again increases as the temperature increases up to 675 °C. In the low temperature range (475 °C-523 °C), the experimental CO₂ contents are higher than the equilibrium values, which may be the result of a lower carbonation rate at low

temperatures. The increase in CO_2 content with increasing temperature ($>523\text{ }^\circ\text{C}$) is mainly caused by the reaction equilibrium limit of the exothermic carbonation. Carbonation achieved equilibrium at temperatures between $523\text{--}575\text{ }^\circ\text{C}$ at all the steam/C values studied. When the temperature is higher than $575\text{ }^\circ\text{C}$, equilibrium is only reached at a high steam/C value of 4.5 (Fig. 5d) and carbonation is not very far from the equilibrium at a moderate steam/C ratio of 3.0 (Fig. 5c). However, a higher deviation between the experimental CO_2 contents and the equilibrium values is found at high temperatures ($>575\text{ }^\circ\text{C}$) at a low steam/C value of 1.5 (Fig. 5b), which is most likely the result of a low reaction rate in the generation of CO_2 . This results in a lower CO_2 partial pressure and in turn a lower carbonation rate.

Fig. 6 shows the response surface and contour plots for CH_4 concentration as a function of T and steam/C (Figs. 6a, 6b and 6c) and as a function of T and WHSV (Figs. 6d, 6e and 6f). As in the case of the previously studied variables, T has the greatest influence on this response variable, followed by WHSV and steam/C within the experimental region studied (Table 3). The effect of T on this variable varies along the range studied since interaction effects between T and steam/C, as well as between T and WHSV, occur (Table 3). Thus, the CH_4 concentration decreases noticeably as the temperature increases from $475\text{ }^\circ\text{C}$ to approximately $600\text{ }^\circ\text{C}$, but after that the response variable values hardly change or increase only slightly when the WHSV is very low. With increasing temperature, the methanation reaction becomes thermodynamically unfavorable and steam methane reforming is kinetically enhanced, resulting in very low CH_4 concentrations, which indicates that the Pd/Co-Ni HT catalyst has successfully catalyzed the methane steam reforming reaction. In the low temperature range, the CH_4 concentration decreases as steam/C increases or WHSV decreases, since steam methane

reforming is favored. The equilibrium of the methanation and steam methane reforming reactions is reached at temperatures between approximately 575-625 °C at low or moderate values of WHSV and at any steam/C value.

Fig. 7 shows the response surface and contour plots for the CO concentration as a function of T and steam/C (Fig. 7a) and as a function of T and WHSV (Figs. 7b, 7c and 7d). It can be seen that WHSV does not have a significant influence on the CO concentration. Steam/C only affects the CO content at very high temperatures, where an extremely low steam/C value significantly increases the CO concentration. The effect of T on the CO concentration is significant and varies over the experimental range studied. Thus, the CO content decreases as the temperature increases from 475 °C to 560 °C, whereas from 560 °C to 675 °C the CO concentration increases. The equilibrium CO content increases concurrently with increasing temperature, as might be expected due to the exothermicity of the WGS reaction. The equilibrium values for CO content are reached at temperatures higher than 560 °C, but not when the temperature is higher than 650 °C and the steam/C value is very high. The large deviation between the experimental CO concentration surface and the equilibrium values at low temperatures can be attributed to the lower carbonation reaction (Fig. 5), as well as lower reforming reactions that generate CO and hence a lower WGS reaction.

In summary, the results show that the carbonation reaction is crucial for hydrogen production in the SESR process, as it determines the effect of sorption enhancement. At high temperatures, the reaction rate of carbonation, steam reforming of acetic acid, methanation, steam methane reforming and water gas shift reactions is fast enough to make all the reactions approach equilibrium. However, hydrogen production in terms of selectivity and purity is not thermodynamically favorable due to the fact that the

exothermic carbonation reaction of CaO is thermodynamically unfavorable at high temperatures. At lower temperatures, hydrogen production is kinetically limited due to the low reaction rates of the reactions mentioned above. Therefore, there exists an optimal temperature for hydrogen production under different conditions such as steam/C ratio and WHSV. It follows that both the activity of the catalyst and reactivity of the CaO in the sorbents play a very significant role in the low temperature range. The hydrogen yield surfaces shown in Fig. 2a-c can therefore be considered as good activity indicators along with temperature, where lower space velocity values push activity to lower temperatures. It also means that more active catalysts and sorbents can lead to higher hydrogen yields and hydrogen purity values in the SESR process.

3.2. Optimum conditions to achieve maximum hydrogen production

The optimum response variable values and the conditions under which they are obtained within the experimental region under study are shown in Table 4, both for the experimental results and equilibrium calculations. According to the thermodynamic analysis, the optimal temperature would be 475 °C for maximizing H₂ purity (99.93%), but 675 °C for optimizing H₂ selectivity (99.95%). The H₂ yield would be maximized (99.82%) at 505 °C. The optimal steam/C value for these variables would be 4.50. Moreover, the minimum theoretical CH₄ concentration (0.024%) would be obtained at 675 °C and steam/C = 4.50, whereas the optimal temperature for minimizing the CO and CO₂ concentrations (0.002% and 0.010% respectively) would be 475 °C. However, the minimum value for the CO concentration would be obtained at steam/C = 4.20-4.50, while the minimal value for the CO₂ content would be obtained at steam/C = 1.5. The fact that different operating conditions are required to optimize each of the response

variables suggests that a trade-off solution has to be found in order to establish the best performance parameters for the SESR process.

The optimum experimental values and conditions (Table 4) indicate that the maximum value of H_2 purity that can be experimentally obtained within the region under study was 99.83%. This value was obtained at 523 °C, for a steam/C ratio of 4.50 and a WHSV of 0.893 h^{-1} . Under such conditions, the H_2 yield and H_2 selectivity values obtained were 75.34% and 99.38% respectively. However, their maximum values were obtained at higher temperatures (99.67% at 590 °C for the H_2 yield and 99.93% at 583-613 °C for the H_2 selectivity). However, the H_2 selectivity obtained between 530-590 °C, steam/C = 4.50 and WHSV = 0.893 h^{-1} was higher than 99.92%, i.e., in fact almost its maximum value, while the H_2 yield values obtained between 530-590 °C ranged between 79.05 and 99.67%. Since H_2 selectivity is almost unaffected by the temperature in the range under consideration, in order to choose the best conditions for carrying out the SESR of acetic acid in the experimental device used in this study, a temperature value that maximizes H_2 purity but without excessively lowering the H_2 yield is required. This means that a compromise must be found between H_2 purity and H_2 yield, since H_2 purity is favored by lower temperatures while higher values of H_2 yield are obtained at higher temperatures. The best conditions can be deduced from Fig. 8, which shows the area (in gray) where, simultaneously, H_2 purity is higher than 99.5%, H_2 selectivity is higher than 99.5% and H_2 yield is higher than 90%. On the other hand, the CH_4 and CO_2 concentrations obtained at 530-590 °C, steam/C = 4.50 and WHSV = 0.893 h^{-1} range between 0.036-0.041% and 0.144-0.896% respectively. The minimum CO concentration (0.062%) was obtained at 560 °C, with a steam/C ratio of 4.50 and a WHSV of 0.893 h^{-1} . In summary, the results of the present study indicate

that the optimum values for carrying out the SESR process of acetic acid can be established as 560 °C, a steam/C ratio of 4.50 and a WHSV of 0.893 h⁻¹. Under such conditions, the results achieved would be: a H₂ purity of 99.53%, a H₂ yield of 92.00%, a H₂ selectivity of 99.92%, with CH₄, CO and CO₂ contents of 0.039%, 0.062% and 0.372%, respectively.

3.3. An approach for improving the SESR process at low temperatures

As can be seen in Figs. 2-4, the H₂ yield, H₂ selectivity and H₂ purity values at 475 °C for all the conditions studied are very low (19-43%, 54-91% and 71-93% respectively) and very far from the equilibrium, whereas the CH₄, CO and CO₂ contents are quite high at 475 °C (Figs. 5-7). A high CH₄ concentration at low temperatures has been reported previously in sorption enhanced experiments with sorbitol [16] and glycerol [13] due to the fact that steam methane reforming reaction, Eq. (4), is favored at high temperatures. He et al. [15] found large deviations between the experimental H₂ content and the corresponding equilibrium value at low temperatures (500-525 °C) in their experiments on the SESR of ethanol, which they attributed to high concentrations of CH₄, the main impurity found in the product gas. However, CO and CO₂ concentrations can be expected to be small at low temperatures, since low temperature favors the exothermic water-gas shift, Eq. (2), and CO₂-capture, Eq. (3), reactions. As mentioned above, in the present work excessively high CO and CO₂ concentrations were found in the low temperature range (Figs. 6 and 7).

Wang et al. [26] simulated the sorption enhanced steam methane reforming process in a fluidized bed reactor and showed that methane conversion and hydrogen production depend heavily on sorbent capacity and the rate of CO₂ removal by the sorbent. As has

been highlighted by He et al. [15], because of its very nature, the SESR reaction is highly dependent on CO₂ removal. It is well known that the reaction between CaO and CO₂ is typified by an initial rapid-reaction phase, which is chemical-reaction controlled, followed by a slower reaction phase which is limited by diffusion resistance through the product layer of CaCO₃ formed on the free CaO surface [27]. However, the low capture rate in the latter regime has a limited effect on the enhancement of H₂ production. Many expressions have been reported in the literature to describe the carbonation kinetics of CaO-based sorbents. According to Sun et al. [28], the rate equation for CO₂ adsorption by a CaO sorbent, Eq. (2), can be expressed by:

$$R_a = dX/[dt (1-X)] = 56 k_s(1-X)(p_{CO_2}-p_{CO_2,eq})^n S \quad (11)$$

This equation shows that the reaction rate of CO₂ adsorption in the initial carbonation phase depends on the partial pressure of CO₂, p_{CO_2} , and the specific surface area of the sorbent, S . Thus, a slow carbonation reaction might occur if there is an insufficient amount of sorbent, since the residence time of the CO₂ in the sorbents would also be lower. Furthermore, if the CO₂ production rate is low, the partial pressure of CO₂ in the gas phase will also be low, and hence the reaction rate. Ochoa-Fernandez et al. [29] highlighted the importance of improving the kinetics of the acceptor at low CO₂ concentrations in order to increase the productivity and achieve greater efficiency in processes like sorption enhanced steam reforming for hydrogen production. Fernández et al. [30] concluded that slow-reacting CO₂ sorbents prevent the maximum hydrogen purity determined by the equilibrium for being achieved at elevated space velocities and that higher residence times are therefore needed. They highlighted that the limiting aspect of the sorption enhanced reforming process was found to be basically carbonation kinetics, since it is the difference between the partial CO₂ pressure and the

equilibrium pressure, $p_{\text{CO}_2}-p_{\text{CO}_2,\text{eq}}$, at a given temperature that represents the driving force behind the carbonation reaction.

In the present work, it seems that mass transfer and/or reaction kinetics were not fast enough for equilibrium to be reached at the operating conditions of run number 10, i.e. 475 °C, steam/C = 3.00 and WHSV = 1.786 h⁻¹ (Table 1), which was carried out using a bed mass of 12 g with a sorbent/catalyst ratio of 5 g/g. An additional SESR experiment was performed under the same conditions but using a higher sorbent/catalyst ratio value, the results of which are shown in Table 5. These results indicate that when a higher proportion of sorbent is used in the bed, i.e., a sorbent/catalyst ratio of 11, the H₂ yield, H₂ selectivity and H₂ purity values are considerably increased, whereas the CO and CO₂ contents in the product gas are decreased. The high concentration of CO found in the product gas when a sorbent/catalyst ratio value of 5 g/g was used suggests that the CO₂ capture rate may have been the rate-limiting step of the process. If the CO₂ capture is low, the shift of the water gas shift reaction to the product side will be lower and the CO content, and even the CO₂ concentration, in the effluent gas will be higher. This could be due to the fact that capture rates at low temperatures are presumably slower because of kinetic limitations. Chen et al. [31] in their numerical study of hydrogen production via sorption enhanced steam methane reforming in a fluidized bed reactor pointed out that the temperatures generally used in the literature for investigating sorption enhanced steam methane reforming processes were all over 500 °C because of the slow CO₂ capture kinetics below this temperature. Using a simulation approach, these authors proved that sorbents with slow kinetics can only serve as CO₂ acceptor, but cannot effectively enhance the steam reforming process. They concluded that good kinetics is

critical for determining whether a sorbent is suitable for use in fluidized bed reactors in SESR processes or not.

However, the rate of CO₂ removal from the gas phase can be increased by employing a larger amount of sorbent, as occurred in the present study when a sorbent/catalyst ratio of 11 was used, which led to an increase in H₂ yield, H₂ selectivity and H₂ purity values while the CO and CO₂ concentrations were considerably reduced (Table 5). At the same time a high CH₄ content was obtained due to the low temperature used, resulting in low H₂ yield, H₂ selectivity and H₂ purity values, which are far from the equilibrium. Therefore, although an increase in the sorbent load was found to improve H₂ production, future research works will need to study the effect that the activity of both the catalyst and the sorbent have on the SESR process at low temperatures in fluidized bed reactors to guarantee a high yield of high-purity H₂.

4. Conclusions

The results of the present work indicate that the SESR of bio-oils is a promising technology for the production of high-purity hydrogen from biomass in high yields. Acetic acid was selected as a model compound representative of organic acids contained in bio-oils obtained from the fast pyrolysis of biomass. Response surface methodology was successfully applied to evaluate the combined effect of the reforming temperature, steam-to-carbon molar ratio in the feed and weight hourly space velocity upon the H₂ yield, H₂ selectivity, H₂ purity, and on the CH₄, CO and CO₂ concentrations in the effluent gas from the SESR of acetic acid in a bench-scale fluidized bed reactor. The variable that had the greatest influence on all the response variables studied was the reaction temperature, followed by WHSV and steam/C ratio, except in the case of the

CO and CO₂ concentrations, where WHSV did not have a significant effect. It was observed that as the temperature increased, the H₂ yield, H₂ selectivity and H₂ purity increased up to around 575-625 °C whereas the CH₄, CO and CO₂ concentrations decreased. An increase in the steam/C ratio and a decrease in the WHSV led to an increase in the H₂ yield, H₂ selectivity and H₂ purity, but a decrease in the CH₄ concentration. Significant interaction effects were observed between T and steam/C and between T and WHSV upon H₂ purity, H₂ selectivity and the CH₄ concentration, indicating that at high temperature values the effect of steam/C and WHSV on these variables is non-significant. The SESR of acetic acid at 560 °C, a steam/C ratio of 4.50 and a WHSV of 0.893 h⁻¹ 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 gave rise to a H₂ purity of 99.53%, a H₂ yield of 92.00%, and a H₂ selectivity of 99.92% with low CH₄, CO and CO₂ concentrations. In general, equilibrium for the sorption enhanced steam reforming of acetic acid was reached at 550-650 °C and atmospheric pressure for a steam/C ratio in the range of 1.50-4.50 and a WHSV below 2 h⁻¹. The results suggest that a restriction in the effective CO₂ capture at low temperatures may have been due to slow reaction kinetics. Although the SESR results at low temperatures can be improved by increasing the amount of sorbent in the fluidized bed, further studies on the influence of the sorbent/catalyst ratio and the activity of both catalyst and sorbent on the SESR process need to be carried out.

In the present work, a preliminary screening of the sorption enhanced steam reforming of acetic acid under fluidized bed conditions has been successfully conducted with the aid of a statistical analysis technique. The findings of this study have led to a better understanding of the influence of different operating conditions (T, steam/C ratio and

WHSV) and their interactions on the characteristics of the effluent gas obtained from the enhanced reforming process. Furthermore, this study has highlighted the importance of other operating variables in the SESR process conducted in a fluidized bed reactor, such as the sorbent/catalyst ratio and the activity of both the catalyst and the sorbent, suggesting the need for further research works where these factors can be studied.

Acknowledgements

The financial support from the Research Council of Norway (RCN) is gratefully acknowledged. The authors thank Franefoss Miljøkalk A/S (Norway) for supplying Arctic dolomite. M.V. Gil acknowledges funding from the CSIC JAE-Doc program, Spain, co-financed by the European Social Fund, and support from the Research Council of Norway through the Yggdrasil program.

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Figure captions

Fig. 1. Schematic flow diagram of the experimental setup used for the SESR experiments with acetic acid.

Fig. 2. Response surface and contour plots for H_2 yield: (a, b, c) as a function of temperature, T , and steam-to-carbon molar ratio, steam/C; and (d, e, f) as a function of temperature, T , and weight hourly space velocity, WHSV.

Fig. 3. Response surface and contour plots for H_2 selectivity: (a, b, c) as a function of temperature, T , and steam-to-carbon molar ratio, steam/C; and (d, e, f) as a function of temperature, T , and weight hourly space velocity, WHSV.

Fig. 4. Response surface and contour plots for H_2 purity: (a, b, c) as a function of temperature, T , and steam-to-carbon molar ratio, steam/C; and (d, e, f) as a function of temperature, T , and weight hourly space velocity, WHSV.

Fig. 5. Response surface and contour plots for CO_2 concentration: (a) as a function of temperature, T , and steam-to-carbon molar ratio, steam/C; and (b, c, d) as a function of temperature, T , and weight hourly space velocity, WHSV.

Fig. 6. Response surface and contour plots for CH_4 concentration: (a, b, c) as a function of temperature, T , and steam-to-carbon molar ratio, steam/C; and (d, e, f) as a function of temperature, T , and weight hourly space velocity, WHSV.

Fig. 7. Response surface and contour plots for CO concentration: (a) as a function of temperature, T , and steam-to-carbon molar ratio, steam/C; and (b, c, d) as a function of temperature, T , and weight hourly space velocity, WHSV.

Fig. 8. Contour plots for H_2 yield, H_2 selectivity and H_2 purity: (a) as a function of temperature, T , and steam-to-carbon molar ratio, steam/C; and (b) as a function of temperature, T , and weight hourly space velocity, WHSV.

Table 1. Independent variables and experimental values of the response variables for the central composite design (CCD)

Run	Independent variables			Response variables					
	T (°C)	steam/C (mol/mol)	WHSV (h ⁻¹)	H ₂ yield (%)	H ₂ selectivity (%)	H ₂ purity (vol.%)	CH ₄ (vol.%)	CO (vol.%)	CO ₂ (vol.%)
1	516 (-1)	2.11 (-1)	1.255 (-1)	62.50	90.22	94.72	5.11	0.06	0.11
2	634 (+1)	2.11 (-1)	1.255 (-1)	92.48	98.77	96.53	0.51	1.27	1.70
3	516 (-1)	3.89 (+1)	1.255 (-1)	74.17	95.05	97.28	2.49	0.05	0.18
4	634 (+1)	3.89 (+1)	1.255 (-1)	94.71	99.75	96.55	0.17	0.64	2.65
5	516 (-1)	2.11 (-1)	2.317 (+1)	51.86	77.74	87.35	12.47	0.06	0.12
6	634 (+1)	2.11 (-1)	2.317 (+1)	86.37	98.56	96.25	0.43	1.13	2.19
7	516 (-1)	3.89 (+1)	2.317 (+1)	64.28	86.40	92.29	7.26	0.10	0.35
8	634 (+1)	3.89 (+1)	2.317 (+1)	88.33	99.80	96.42	0.08	0.69	2.80
9 ^a	575 (0)	3.00 (0)	1.786 (0)	85.35	98.82	98.94	0.55	0.11	0.40
10	475 (-1.682)	3.00 (0)	1.786 (0)	22.48	73.26	81.44	10.83	6.86	0.87
11	675 (+1.682)	3.00 (0)	1.786 (0)	89.70	99.40	91.09	0.15	1.19	7.57
12	575 (0)	1.50 (-1.682)	1.786 (0)	79.81	95.98	97.07	2.23	0.22	0.48
13	575 (0)	4.50 (+1.682)	1.786 (0)	83.88	99.42	99.12	0.23	0.10	0.55
14	575 (0)	3.00 (0)	0.893 (-1.682)	90.18	99.69	99.29	0.15	0.11	0.45
15	575 (0)	3.00 (0)	2.679 (+1.682)	72.44	89.89	94.12	5.30	0.11	0.47

^aCenter point mean of six replicates

T: temperature; steam/C: steam-to-carbon molar ratio; WHSV: weight hourly space velocity

Table 2. Results of the multiple regression analysis and ANOVA for the fit of the polynomial model to the experimental data for H₂ yield, H₂ selectivity and H₂ purity after the elimination of all non-significant terms

	H ₂ yield (%)				H ₂ selectivity (%)				H ₂ purity (vol.%)			
	Coded coefficient	Sum of squares	DF	p-value	Coded coefficient	Sum of squares	DF	p-value	Coded coefficient	Sum of squares	DF	p-value
Model		5269.274	4	0.000		1018.282	7	0.000		392.356	7	0.000
Intersection	84.634	87599.027	1	0.000	98.541	81018.999	1	0.000	98.881	81578.578	1	0.000
x_1	16.264	3613.053	1	0.000	6.448	567.931	1	0.000	2.221	67.402	1	0.000
x_2	2.572	90.335	1	0.057	1.574	33.832	1	0.000	0.815	9.083	1	0.011
x_3	-4.602	289.291	1	0.002	-2.766	104.468	1	0.000	-1.572	33.737	1	0.000
x_1^2	-9.325	1276.595	1	0.000	-3.954	227.679	1	0.000	-4.204	257.342	1	0.000
x_3^2					-1.317	25.272	1	0.001	-0.514	3.844	1	0.052
x_1x_2					-1.409	15.877	1	0.006	-0.914	6.680	1	0.023
x_1x_3					2.621	54.968	1	0.000	1.494	17.850	1	0.001
Residual		319.568	15			16.792	12			11.890	12	
Corrected total		5588.842	19			1035.074	19			404.247	19	
R^2	0.943				0.984				0.971			
Adj- R^2	0.928				0.974				0.953			

x_1 : T; x_2 : steam/C; x_3 : WHSV; DF: Degrees of freedom

Table 3. Results of the multiple regression analysis and ANOVA for the fit of the polynomial model to the experimental data for CH₄, CO and CO₂ concentrations after the elimination of all non-significant terms

	CH ₄ (vol.%)				CO (vol.%)				CO ₂ (vol.%)			
	Coded coefficient	Sum of squares	DF	p-value	Coded coefficient	Sum of squares	DF	p-value	Coded coefficient	Sum of squares	DF	p-value
Model		323.037	7	0.000		33.927	2	0.001		51.773	2	0.000
Intersection	0.704	4.130	1	0.016	-0.231	0.653	1	0.054	0.291	1.036	1	0.051
x_1	-3.629	179.880	1	0.000	-0.607	5.033	1	0.009	1.453	28.847	1	0.000
x_2	-0.874	10.427	1	0.001								
x_3	1.511	31.167	1	0.000								
x_1^2	2.235	72.712	1	0.000	1.403	28.894	1	0.001	1.250	22.926	1	0.000
x_3^2	0.687	6.862		0.003								
x_1x_2	0.899	6.462		0.004								
x_1x_3	-1.539	18.942		0.000								
Residual		6.240	12			28.105	17			4.743	17	
Corrected total		329.277	19			62.032	19			56.516	19	
R^2	0.981				0.604				0.916			
Adj- R^2	0.970				0.560				0.906			

x_1 : T; x_2 : steam/C; x_3 : WHSV; DF: Degrees of freedom

Table 4. Optimum values and polynomial models for the response variables as a function of the real operation variables (T is the temperature in °C; steam/C is the steam-to-carbon molar ratio in the feed in mol/mol; and WHSV is the weight hourly space velocity in h⁻¹)

Response	2 nd order polynomial equation from RSM	Optimum experimental value (optimum conditions) after equilibrium correction	Optimum equilibrium value (optimum conditions)
H ₂ yield (%)	$-938.1224 + 3.3076 T + 2.8838 \text{ steam/C} - 8.6697 \text{ WHSV} - 0.0026 T^2$	99.67% (590 °C, steam/C=4.50, WHSV=0.893 h ⁻¹)	99.82% (505 °C, steam/C=4.50)
H ₂ selectivity (%)	$-305.1601 + 1.3264 T + 17.0427 \text{ steam/C} - 36.2663 \text{ WHSV} - 0.0011 T^2 - 4.6754 (\text{WHSV})^2 - 0.0266 (T) (\text{steam/C}) + 0.0831 (T) (\text{WHSV})$	99.93% (583-613 °C, steam/C=4.50, WHSV=0.893 h ⁻¹) (583-650 °C, steam/C=4.50, WHSV=1.786 h ⁻¹) (627-650 °C, steam/C=4.35, WHSV=1.786 h ⁻¹)	99.85% (675 °C, steam/C=4.50)
H ₂ purity (vol.%)	$-300.2502 + 1.3724 T + 10.8240 \text{ steam/C} - 23.6621 \text{ WHSV} - 0.0012 T^2 - 1.8235 (\text{WHSV})^2 - 0.0172 (T) (\text{steam/C}) + 0.0473 (T) (\text{WHSV})$	99.83% (523 °C, steam/C=4.50, WHSV=0.893 h ⁻¹)	99.93% (475 °C, steam/C=4.50)
CH ₄ (vol.%)	$-229.6355 - 0.7519 T - 10.7267 \text{ steam/C} + 22.1783 \text{ WHSV} + 0.0006 T^2 + 2.4362 (\text{WHSV})^2 + 0.0170 (T) (\text{steam/C}) - 0.0488 (T) (\text{WHSV})$	0.0297% (645 °C, steam/C=4.50, WHSV=1.786 h ⁻¹)	0.0244% (675 °C, steam/C=4.50)
CO (vol.%)	$136.8715 - 0.4667 T + 0.0004 T^2$	0.0622% (560 °C, steam/C=4.50, WHSV=0.893 h ⁻¹)	0.0019% (475 °C, steam/C=4.20-4.50)
CO ₂ (vol.%)	$103.1317 - 0.3822 T + 0.0004 T^2$	0.0547% (523 °C, steam/C=1.50, WHSV=0.893 h ⁻¹)	0.0099% (475 °C, steam/C=1.50)

Table 5. Effect of the sorbent/catalyst ratio on the product gas composition (N₂ free and dry basis) during the SESR of acetic acid. Reaction conditions: 475 °C, 1 atm, steam/C = 3 mol/mol, WHSV = 1.786 h⁻¹, 1%Pd/20%Ni-20%Co HT catalyst, calcined dolomite as sorbent, bed mass = 12 g.

sorbent/catalyst ratio (g/g)	catalyst/sorbent ratio (g/g)	H ₂ yield (%)	H ₂ selectivity (%)	H ₂ purity (vol.%)	CH ₄ (vol.%)	CO (vol.%)	CO ₂ (vol.%)
5	0.20	22.48	73.26	81.44	10.83	6.86	0.87
11	0.09	58.18	80.82	89.30	10.60	0.02	0.09

Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.

Fig. 5.

Fig. 6.

Fig. 7.

Fig. 8.