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Evaluation of an Inconel-625 Reactor and its Wall Effects on Ethanol Reforming in Supercritical Water

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ABSTRACT: Continuous ethanol reforming in supercritical water was investigated in an Inconel-625 reactor without catalyst addition. Experiments were carried out for different operating conditions: temperatures from 450 to 600 °C, pressures from 225 to 300 bar, ethanol concentrations from 2.5 to 10% wt, and feed flow rates from 0.88 to 2.88 g/min. Higher temperatures increased the conversion and the hydrogen production, but above 575 °C the experiments failed due to excessive tar formation, which plugged the reactor and/or the back pressure regulator. The pressure effect in the range considered here was insignificant. Ethanol dehydrogenation to acetaldehyde was the main reaction pathway, followed by acetaldehyde decomposition to CH_4 and CO. The catalytic effects of the reactor's wall were studied by varying the reactor's surface-to-volume ratio (S/V) by inserting Inconel wires. The results confirmed the significant catalytic effects of Inconel 625, especially above 525 °C, and also demonstrated that at 550 °C and for an S/V ratio of 3.1 1/mm, conversion up to 96% was achieved without carbon deposition problems. Finally, a kinetic study for the ethanol dehydrogenation was carried out. This kinetic study revealed that ethanol dehydrogenation occurs mostly through wall-catalyzed reactions and that the homogeneous reaction is negligible in the reactor system considered here. Finally, an Arrhenius expression for the rate constant of the wall-catalyzed ethanol dehydrogenation reaction is proposed.

1. INTRODUCTION

Ethanol reforming is attracting considerable attention since it has been identified as a promising source of hydrogen from renewable sources.[1,2] Raw ethanol produced from fermentation can reach a concentration of up to 15% (by volume), which makes this raw ethanol/water mixture suitable for ethanol steam reforming. Research on ethanol steam reforming at atmospheric pressure is an active field of research. Hydrogen storage is another important issue and, until now, compressed hydrogen remains the most common storage method. However, this storage method suffers from high compression energy penalty when hydrogen is produced at atmospheric or low pressure. Production of hydrogen at high pressure can significantly reduce compression energy penalty. Since ethanol/water mixtures are incompressible fluids, pressurization of such feed mixtures is not energy intensive. In the present work, it is proposed to carry out ethanol steam reforming at high pressure (above 23 MPa). Since ethanol reforming requires temperatures above 400 °C, the reaction conditions are those of supercritical water (SCW), whose critical pressure and temperature are 22.1 MPa and 374 °C, respectively. A benefit for reactions in supercritical water is also the absence of multiple phases, thus eliminating mass transport limitations.[3]

There are a number of papers describing the gasification of various feedstocks for hydrogen production in supercritical water, some of them addressing the effects of the reactor's wall. For example, Antal's group (Yu et al.[4]) conducted gasification of glucose in SCW in tubular reactors made of Inconel-625 and Hastelloy-C276. Using an Inconel reactor, the formation of hydrogen, carbon dioxide, carbon monoxide, and methane at 600 °C, 34.5 MPa, and 30 s residence time was achieved with nearly no tar or char product detected in the product stream. They found that the conversion and yield were highly dependent on the material used for the reactor and on the initial glucose concentration. Complete gasification was achieved with low glucose concentration. Also the Inconel reactor yielded higher selectivity toward hydrogen because of the enhancement of the water−gas shift reaction, producing a gas rich in hydrogen and carbon dioxide; whereas the Hastelloy reactor produced more carbon monoxide. Therdthianwong et al.[5] investigated ethanol reforming in supercritical water without catalyst in an Inconel-625 reactor. Ethanol conversion of only 24% was obtained at 500 °C, 25 MPa, and water/ethanol ratio of 20. Van Bennekom et al.[6] studied glycerol reforming in supercritical water in an Incoloy-825 reactor. They found that the conversion increased when increasing temperature and residence time but the conversion was nearly independent of the feed concentration. Gadhe et al.[7] carried out methanol supercritical water reforming in a tubular Inconel-600 reactor at 700 °C, 276 bar. Low residence time and high feed methanol concentration favored conversion. Boukis et al.[8] studied methanol steam reforming in SCW for hydrogen production using a reactor made of Inconel-625 in the temperature range 400−600 °C, at a pressure of 25 MPa, and initial concentrations ranging from 5 to 64 wt %. Methanol conversions up to 99.9% without adding a catalyst resulted in a hydrogen rich gas with small amounts of CO, CO_2, and methane. Depending on the operating conditions, gas products containing up to 75 vol % hydrogen (the theoretical

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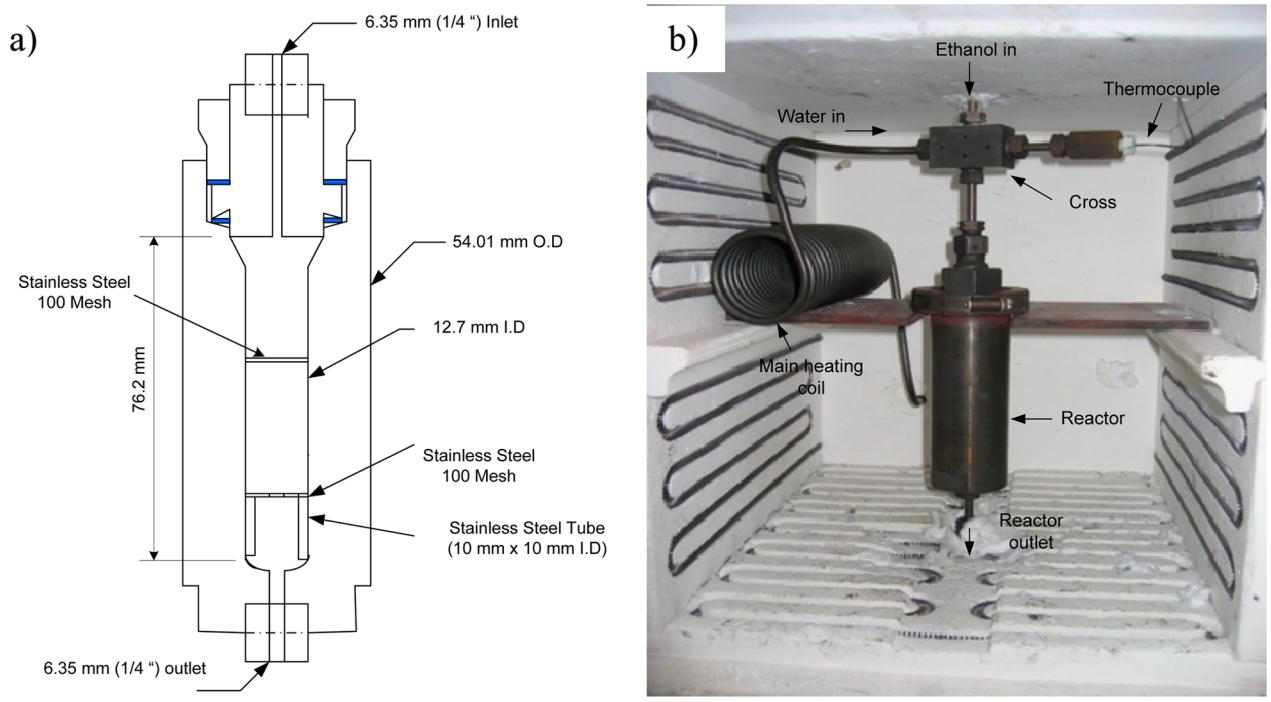

Figure 1. (a) Schematic of the reactor and (b) picture of the reactor assembly located inside the furnace.

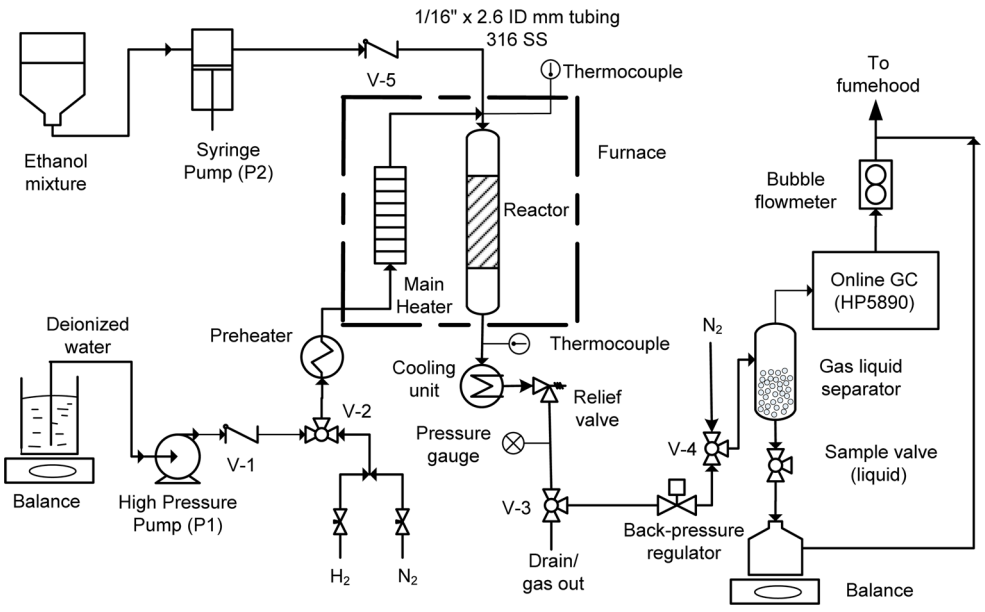

Figure 2. Supercritical water ethanol reforming experimental setup.

equilibrium limit) was achieved for residence times less than 1 min. Even though no catalysts were used, they recognized the significant impact on the conversion of the catalytic activity of the reactor's wall made of Inconel 625. Pretreatment of the inner reactor with hydrogen peroxide (strong oxidizing agent) enhanced the reaction activity toward hydrogen production. Wall effects are well recognized by researchers working on reactions in supercritical water. As mentioned earlier, Yu et al.[4] noticed significant differences depending on the type of reactor used. Croiset et al.[9] studied the surface effects on the decomposition of hydrogen peroxide in supercritical water by varying the surface-to-volume ratio of the reactor. Arita et al.[10] investigated the hydrolysis of ethanol in supercritical water using a flame-sealed quartz tube as a reactor in order to minimize any catalytic reactions at the reactor's surface.

The present paper presents an evaluation of the reactor's activity for continuous ethanol reforming in SCW. The effects of varying temperature, pressure, ethanol feed concentration, residence time, reactor surface-to-volume ratio, and reactor pretreatment were studied.

2. EXPERIMENTAL METHOD

The reactor is a 9.65 cm^3 Kuentzel reactor made of Inconel 625, and supplied by Autoclave Engineers. A schematic and a photograph of the reactor are presented in Figure 1. It was necessary to use specialty alloys to accommodate the extreme

operating conditions. Originally, to avoid reactions on the reactor's wall, the reactor was designed to insert a quartz tube, but it was found that the quartz partly dissolved after several trials in SCW, forming small particulates that accumulated at the back pressure regulator (BPR). Therefore, the reactor was used "as is", but the effect of the reactor's wall was examined in more detail, as described later in this paper. In order to protect the back pressure regulator, a 100 mesh stainless steel screen was placed at the bottom of the reactor to prevent/limit transfer of small particles, which may form during the reaction.

Figure 2 presents the diagram of the experimental setup. Deionized water was delivered to a preheater at a set flow rate between 1 and 3 g/min by a high-pressure pump. The deionized water feed was placed on a balance in order to monitor and confirm the actual mass flow rate. The temperature of the preheater was set at 200 °C. The water feed was then further heated to the desired reaction temperature in a 1/4 in. × 0.083 in. coil, 16-ft long, made of Hastelloy tube prior to entering the reactor. The main heater and the reactor were both located in a furnace (Figure 1b). An ethanol/water mixture, with composition of 75 wt % ethanol, was injected through a 1/16 in. 316 SS tubing with 0.26 mm i.d. by a high-precision syringe pump, model 260D ISCO. The ethanol mixture then mixed with the water from the main preheater in a cross (made of Hastelloy) above the reactor. The reactant fluid flew downward through the reactor. The cross was connected to the reactor using 5 cm of Hastelloy 1/4 in. o.d. × 0.083 in. i.d. tubing. Since a thermocouple could not be inserted directly into the reactor, a 1/16 in. type J thermocouple was placed at the cross where ethanol and water mixed. This arrangement for the ethanol feed was designed for rapid heat-up of the ethanol, thus limiting ethanol decomposition prior to entering the reactor. The purpose of the thermocouple placed inside the cross was to ensure minimum temperature drop when injecting the ethanol feed. This feed system is significantly different from that described in a relatively recent paper published by our group,[3] where ethanol was preheated in a coil similar to the one indicated here as "main heater". It was realized that preheating ethanol in such a coil led to significant ethanol decomposition before reaching the reactor.

The product stream exiting the reactor and the furnace was cooled to 10 °C through a heat exchanger before entering the back pressure regulator (BPR) where the pressure was decreased from the reaction pressure (typically 25 MPa) to atmospheric pressure. A flow of 8 mL/min of nitrogen was supplied at the BPR outlet as an internal standard for the online gas analysis. The condensable species were separated from the gaseous species in a gas liquid separator. The gaseous product stream exits the separator at its top and was directed either to a gas chromatography (GC) or to a soap bubble flow meter for composition and flow rate analysis, respectively. The liquid collected at the bottom of the separator and was periodically sampled for further analysis. The liquid flow rate was monitored using a balance and by recording the weights on a computer while the GC was performing its analysis. Gases and liquids were analyzed separately using two gas chromatographs (GC-1(TCD) and GC-2(FID)) model HP5890 series II, which were equipped with either a thermal conductivity detector (TCD) or a flame ionization detector (FID). The GC-1, equipped with a 60/80 mesh Carboxen 1000 (Supelco Inc.), was used to analyze the gas product. The liquid sample mixed with 1-propanol as internal standard was analyzed using GC-2 by a capillary column of 30 m × 0.53 mm i.d. DB-Wax with helium as a carrier gas.

The volume and the total surface area of the reactor are 9685 mm^3 and 3050 mm^2, respectively. Therefore, the surface-to-volume ratio of the reactor is 0.31 1/mm. The Hastelloy tubing connected to the reactor, through which ethanol was fed, has a length of 5.1 cm and a volume of 0.1 cm^3. The small volume of this Hastelloy tube led to small residence times within this tube (for example, at 500 °C, 250 bar, and 1.88 g/min, the residence time is only 0.3 s). Because the residence time in the Inconel reactor for similar conditions is 29 s (2 orders of magnitude greater), we consider that the wall effects of the Hastelloy tubing were negligible. It will be shown later in the kinetic study that this is not exactly true and that a small fraction of ethanol does react prior to entering the reactor. Experiments with different reactor surface-to-volume ratios were carried out by inserting a desired length of Inconel-625 wire.

The activity of the reactor was evaluated based on ethanol conversion and product selectivity, which are defined according to eqs 1 and 2, respectively.

Ethanol conversion, X_{EtoH}

$$X_{EtoH} = \frac{F_{EtOH,in} - F_{EtOH,out}}{F_{EtOH,in}} \tag{1}$$

where, $F_{EtOH,in}$ and $F_{EtOH,out}$ are the feed and outlet molar flow rates of ethanol (mol/min), respectively.

Product selectivity of species i

$$S_i(\%) = \frac{F_i}{\sum_{i=n} F_i} \times 100 \tag{2}$$

where, F_i is the molar gas flow rate of product i and $\Sigma_{i=n}F_i$ is the total molar flow rate of the products. More than half of the experiments were repeated two or three times to address the reproducibility of the results. The carbon balance errors reported are within ±10%. To estimate the error among a set of experiment data, a 95% confidence interval was used to calculate the level of error.

3. RESULTS AND DISCUSSION

The reactor was made of Inconel 625, which contains a large amount of nickel, as indicated by its composition (weight basis): 61.15% Ni, 0.02% C, 0.09% Mn, 0.11% Si, 0.05% P, 0.001% S, 21.41% Cr, 0.03% Co, 8.85% Mo, 3.56% (Nb + Ta), 0.32% Ti, 0.26% Al, 4.15% Fe, 3.55% Nb, and 0.007% Ta. Nickel is the most common active metal used for ethanol steam reforming at atmospheric pressure. Other components such as Fe, Mo, and Cr are also known to be catalytically active. In this work, the experiments were performed for pressures between 22.5 and 28 MPa, and temperatures between 450 and 600 °C. The ethanol concentration was varied between 2.5 and 10% wt, and the total ethanol/water flow rate ranged from 0.88 to 2.88 g/min. For each experiment, at least five data points were collected every 40 min.

3.1. Effects of Temperature and Residence Time. The minimum reaction temperature was 450 °C, as below this temperature very low activity was observed. The reactor system was designed for a maximum allowable temperature of 650 °C (at 25 MPa). However, at 600 °C, the experiments failed because of plugging, highlighting the importance of decomposition/cracking reactions at higher temperatures. Therefore, the highest temperature reported here is 575 °C. The results

regarding the effects of temperature and feed flow rate on ethanol conversion are presented in Figure 3. At 575 °C it was

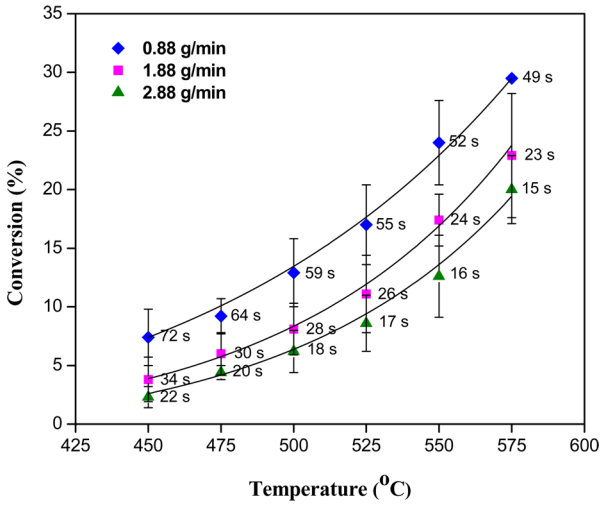

Figure 3. Effects of temperature and feed flow rate on ethanol conversion at 25 MPa and 5 wt % ethanol (corresponding residence time—in seconds—shown at the data points).

not possible to collect more than 1 or 3 data points for feed flow rates of 0.88 and 1.88 g/min, respectively, because of reactor plugging. The pressure was monitored at the water feed pump and at the back pressure regulator (BPR). The pressure at the BPR was set constant, usually at 25 MPa. The water feed pump pressure was allowed to increase up to a maximum of 35 MPa, although it should, in principle, remain close to the BPR pressure. In some experiments (such as those at 575 and 600 °C), the pump pressure increased, suggesting plugging of the reactor system where tar or coke deposited on the filter screen at the bottom of the reactor. This was actually observed through visual inspection of the screen at the end of the experiments carried out at high temperatures. Therefore, the range of temperature that was considered was constrained to 450−550 °C.

The residence time is defined as the ratio of the fluid flow rate at reaction conditions to the reactor volume. To calculate the volumetric flow rate in the reactor at reaction conditions, the density of the fluid was assumed to be similar to that of pure water since the feed liquid mixture contained more than 90 wt % water. The water density in the temperature range 450−550 °C at 25 MPa decreases linearly from 0.1091 to 0.0786 g/cm^3. The calculated residence time are shown in Figure 3 for all data points. The results indicate that temperature and flow rate (hence residence time) affect noticeably the conversion. At 500 °C, ethanol conversion is comparable to that observed by Therdthianwong et al.[5] (at 500 °C and 250 bar), Hsiao[11] (at 500 °C and 250 bar), and Schanzenbacher et al.[12] (496 °C and 246 bar). In the present work, at 500 °C and for 5 wt % ethanol feed concentration, the ethanol conversion is 6.2% (±1.8%) for a residence time of 18 s and 12.9% (±2.9%) for a residence time of 58 s. Schanzenbacher et al.[12] observed an ethanol conversion of about 7.4% for 6 s residence time and 16.5% for 16 s with an initial concentration of ethanol of 1 mmol/L (0.0046 wt.%). The higher conversion in Schanzenbacher's experiments may be attributed to the considerably lower ethanol feed concentration. Therdthianwong et al.[5] reported a much higher conversion, close to 40%. This high conversion was due to the ethanol feeding system, where the total water/ethanol feed mixture was preheated in a long Hastelloy coil. Not only did this result in a higher residence time for the reaction to occur, but also, the surface-to-volume ratio of the Hastelloy tube was much higher than that of the reactor, thus favoring surface reactions on the wall.

The selectivity for each detected species at various temperatures and flow rates are shown in Figure 4. The main reaction products detected were hydrogen, methane, CO, CO_2, C_2H_4, and C_2H_6 in the gas phase, and acetaldehyde in the liquid phase. These main products were also reported by Arita et al.[10] and by Hsiao.[11] In the temperature range considered here, the two most important products were acetaldehyde and hydrogen, suggesting that the main reaction is ethanol dehydrogenation (eq 3). At the lower temperatures of 450 and 475 °C, the selectivity of acetaldehyde and hydrogen remained constant over time at approximately 50% (±5%) and 40% (±5%), respectively. It is also seen that up to 525 °C, the selectivity of the major products did not change when varying the feed flow rates from 0.88 to 2.88 g/min. The results show that the selectivity of acetaldehyde is greater than that of hydrogen for temperature below 525 °C; whereas, it is the opposite for temperature above 525 °C. Considering the uncertainty in hydrogen selectivity (shown by the error bar), the hydrogen selectivity remained more or less constant at around 40% for the whole temperature and flow rate ranges considered here. One exception is at 575 °C with 2.88 g/min (15 s residence time) where hydrogen selectivity was closer to 50%, but then decreased to around 40% for 1.88 g/min (23 s residence time). The acetaldehyde selectivity remained close to 50% for temperatures between 450 and 475/500 °C but decreased as the temperature increased above 475/500 °C. At 525 °C, the acetaldehyde selectivity was around 40% (similar to that of H_2); at 550 °C it was around 30/35%, and at 575 °C it was around 25/30%. The decrease in acetaldehyde selectivity was accompanied by an increase in both CO and CH_4 selectivities (around 10% at 550 and 575 °C). At 550 and 575 °C, one can notice that the selectivity of CO or CH_4 was slightly lower for 2.88 g/min than for 1.88 g/min, suggesting that CO and CH_4 were produced via secondary reactions, typically acetaldehyde decomposition (eq 4), which was not complete at lower residence time. The selectivity of the other species (CO_2, C_2H_4, C_2H_6) remained below 5%, even at higher temperatures.

As the temperature increases up to 550 °C, Figure 4 shows that the C_2H_4 selectivity increases but decreases above 550 °C. The experiments at 575 °C and feed flow rate of 0.88 g/min (49 s residence time) and 1.88 g/min (23 s residence time) were characterized by plugging of the reactor. As mentioned previously, at 575 °C we could collect only one data point for 0.88 g/min and three data points for 1.88 g/min. Note that we were able to collect six data points (normal procedure in those experiments) without problems at 2.88 g/min and 575 °C (shortest residence time of 15 s). The plugging of the reactor at 575 °C and low feed flow rates, combined with the increase in C_2H_4 selectivity when the temperature increases up to 550 °C, and the abrupt decrease in C_2H_4 selectivity at 575 °C, points to coking from the polymerization of ethylene and subsequent plugging of the reactor, as suggested by Dybkjaer:[13]

Polymerization of ethylene

$$C_2H_4 \rightarrow \text{olefins} \rightarrow \text{polymers} \rightarrow \text{coke}$$

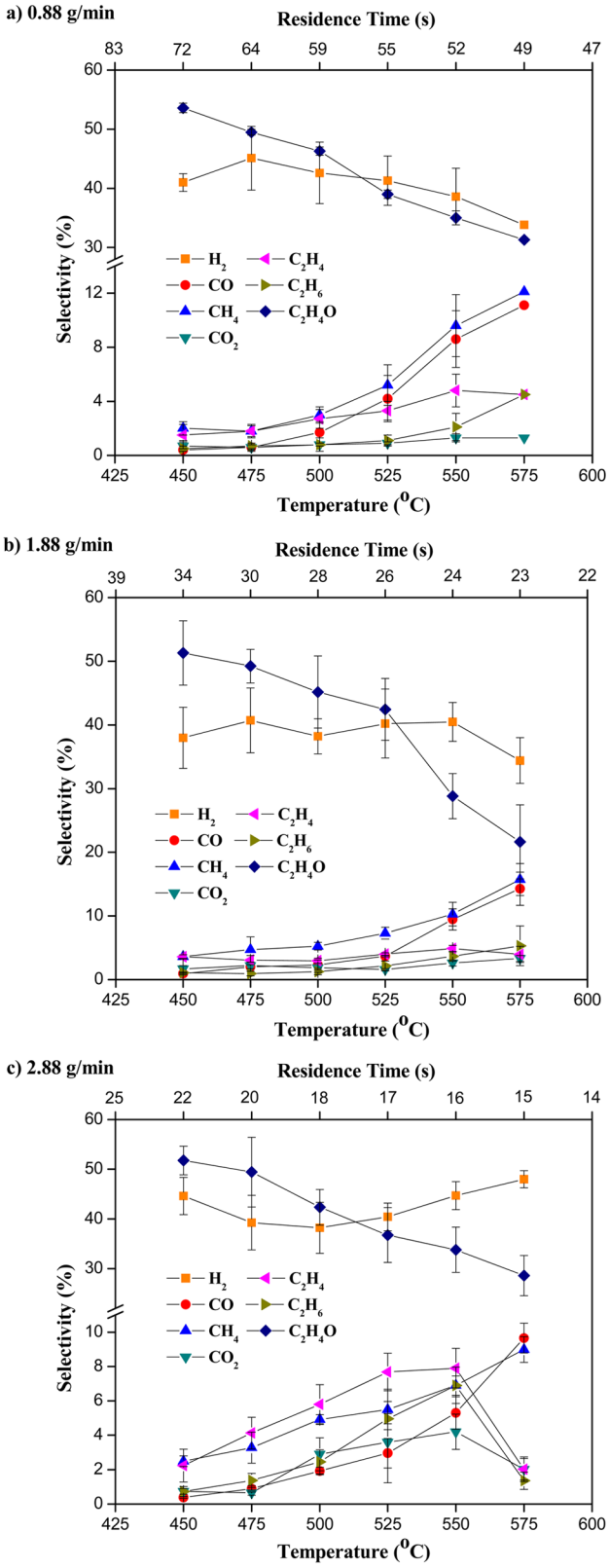

Figure 4. Product selectivity as a function of temperature and flow rate (i.e., residence time) (a) 0.88, (b) 1.88, and (c) 2.88 g/min. (pressure of 25 MPa, feed 5 wt % ethanol).

The results in Figure 4 indicate that ethanol is consumed primarily via dehydrogenation, yielding acetaldehyde and hydrogen (eq 3), followed by acetaldehyde decomposition to form methane and CO (eq 4). The production of hydrogen, acetaldehyde, and other species can be explained by the mechanism proposed by Arita et al.[10] who conducted ethanol hydrolysis in SCW in a batch reactor. The initial step for ethanol reforming is the dehydrogenation of ethanol to form acetaldehyde and hydrogen:

$$C_2H_5OH \rightarrow C_2H_4O + H_2 \quad (3)$$

Acetaldehyde is then decomposed to methane and CO (eq 4):

$$C_2H_4O \rightarrow CH_4 + CO \quad (4)$$

Ethanol can also decompose via dehydration yielding ethylene and water (eq 5):

$$C_2H_5OH \rightarrow C_2H_4 + H_2O \quad (5)$$

Subsequently, this reaction can be followed by hydrogenation of ethylene to produce ethane (eq 6):

$$C_2H_4 + H_2 \rightarrow C_2H_6 \quad (6)$$

CO_2 is likely formed via the water-gas-shift reaction (eq 7):

$$CO + H_2 \rightarrow CO_2 + H_2O \quad (7)$$

3.2. Effects of Ethanol Concentration. Figure 5 illustrates the effect of ethanol concentration (2.5, 5.0, 7.5, and 10 wt %)

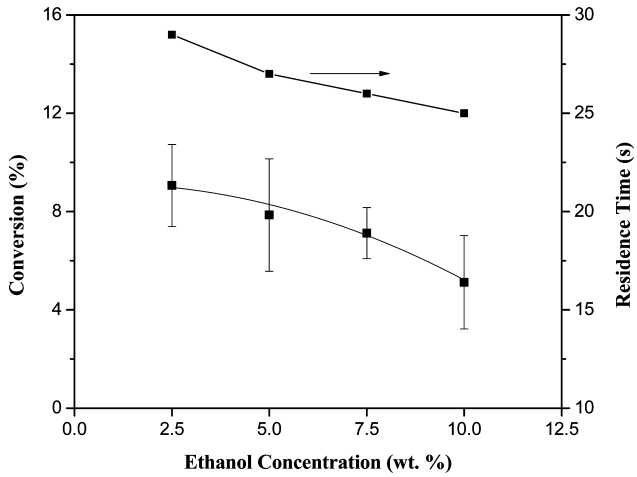

Figure 5. Ethanol conversion and residence time as a function of ethanol concentration for the empty reactor at 500 °C, 25 MPa bar, and 1.88 g/min.

at 500 °C, 250 bar, and 1.70 g/min water. It is important to note that with our current feedwater pump (Thar pump P50) it was not possible to vary the ethanol concentration while keeping a constant residence time. Indeed, the flow rate for the Thar pump could be adjusted only in increments of 1 g/min. Here, the feedwater flow rate was kept constant at 1.70 g/min, and the water/ethanol mixture at the ISCO pump was changed to obtain the desired ethanol concentration.

Figure 5 shows that ethanol conversion decreased as the ethanol concentration increased; but at the same time, the residence time also decreased. It is expected that conversion decreases at shorter residence time. Therefore, it was initially difficult to conclude whether the change in conversion is due mostly to ethanol concentration, residence time, or a combination or both. We have then plotted in Figure 6 the data shown Figure 5 in terms of conversion vs residence time and compared them with data obtained at constant ethanol concentration. The slope of the effect of residence time at

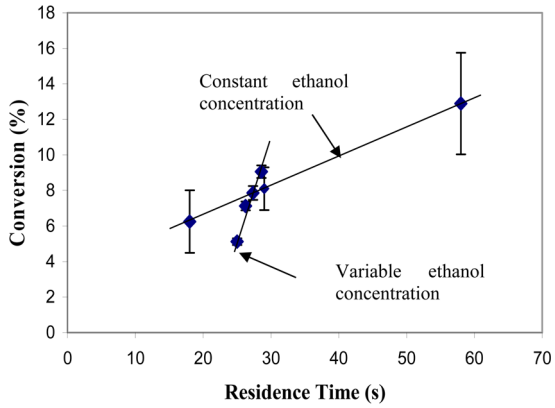

Figure 6. Ethanol conversion vs residence time (500 °C, 25 MPa).

constant ethanol concentration was considerably lower than that at different ethanol concentrations. Therefore, it was concluded that the effect seen in Figure 5 was mostly due to ethanol concentration. The decrease in ethanol conversion at higher ethanol concentration may be due to the saturation of ethanol on the active sites on the reactor's wall. This effect has been suggested by Taylor et al.[14] who conducted methanol reforming in SCW in a tubular reactor made of Inconel 625. The increase in ethanol concentration from 2.5 to 10% wt did not change the hydrogen selectivity, which remained around 40%, as shown in Figure 7. The selectivity of other gas reaction

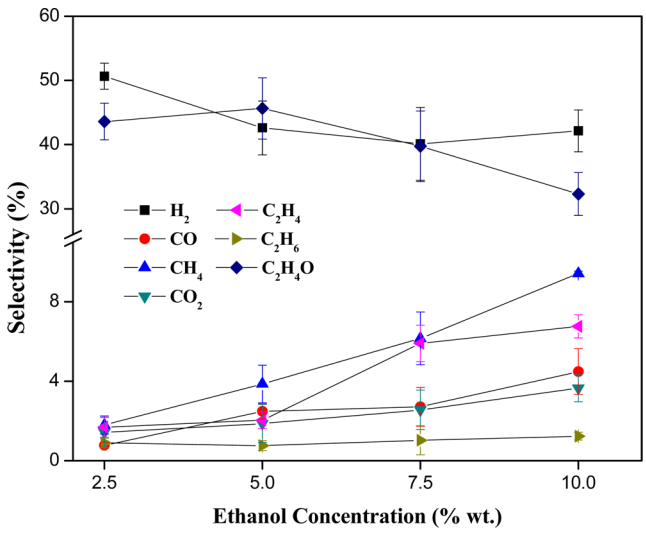

Figure 7. Distribution of reaction gas product as a function of ethanol concentration for a tubular reactor at 500 °C, 250 bar, and 1.88 g/min feed.

products such as CO, CH_4, CO_2, and C_2H_4, C_2H_6 increased when increasing ethanol concentration, suggesting that increasing the ethanol concentration favors the decomposition of acetaldehyde, hydrogenation of C_2H_4 toward C_2H_6, and water–gas shift reaction of CO toward CO_2.

3.3. Reactor Wall Surface Effects. In order to evaluate the catalytic effects of the reactor wall, experiments at different values of S/V ratio were carried out. As described earlier, the S/V ratio of the empty reactor was 0.31 1/mm. To obtain higher ratio of S/V, different lengths of a 0.25 mm o.d. Inconel wire were placed in the reactor. These wires were rolled into a spring shape in order to be easily inserted in the reactor. By introducing 14.1 and 29 m of this wire, it was possible to increase the ratio of S/V to 1.55 1/mm (5-fold increase) and 3.1 1/mm (10-fold increase), respectively. This method increased the surface of reactor significantly, while the void fraction of the reactor just decreased slightly from 1 (empty reactor) to 0.93 at S/V of 1.55 1/mm and to 0.85 at S/V of 3.1 1/mm. The experiments were carried out at a constant pressure of 25 MPa bar and in the temperature range 500–575 °C. The results are shown in Figure 8. At 500 °C, the effect of the S/V

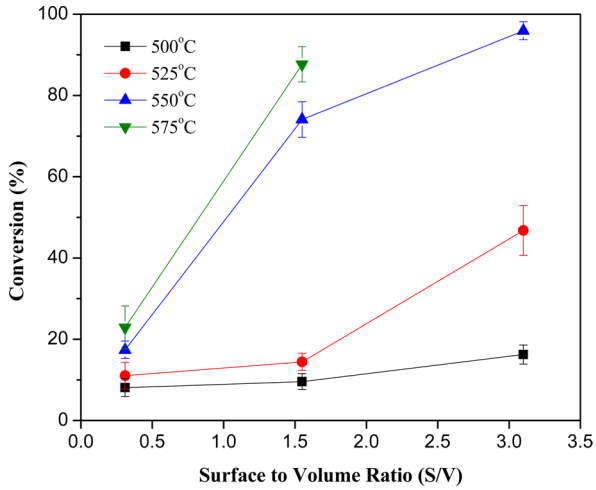

Figure 8. Influence of the S/V ratio on ethanol conversion at different temperatures (500–575 °C; 250 bar; 5 wt % ethanol; 1.88 g/min).

ratio was moderately important, as the conversion increased by 8 percentage points (from ~8% to ~16%) when increasing the S/V ratio 10-fold. At 525 °C, ethanol conversion increased slightly from ~11% to ~15% when increasing 5-fold the S/V ratio, but shows a rapid increase to 46.8% when further increasing the S/V ratio 10-fold. At 550 and 575 °C, the ethanol conversion increased significantly with the S/V ratio: a 5-fold increase in S/V led to about a 4-fold increase in ethanol conversion. At 550 °C and an S/V ratio of 3.1 1/mm, the conversion reached 96%. The data were not available at 575 °C for the S/V ratio of 3.1 1/mm because of reactor plugging at the screen and BPR. This study highlights the high catalytic activity of the Inconel-625 material on ethanol conversion in SCW, particularly important at temperatures of 550 °C and above. However, as the temperature increases, so does the occurrence of carbon formation that may block the reactor and/or cause malfunction of the BPR.

3.4. Effect of Wall Pretreatment with Hydrogen. Since the reactor's wall is catalytically active, the next phase was to investigate whether this wall activity could be enhanced by reducing the reactor's wall with hydrogen prior to the reforming step. To do so, a 20%/80% hydrogen/nitrogen mixture was flowed at a flow rate of 20 mL/min for 2 h at the same temperature as the desired reforming temperature. Prior to hydrogen pretreatment, the reactor was treated in supercritical water and air to remove any possible char or tar deposited on the reactor's wall or on the 316 SS screen. The goal of this H_2 treatment was to reduce some metal oxides that cover the wall to metallic form (in particular reducing nickel oxide to metallic nickel). Figure 9 shows the ethanol conversion versus time-on-stream for cases with and without H_2 pretreatment (or prereduction). Without pretreatment, the ethanol conversion remained quite constant during the 200 min of the

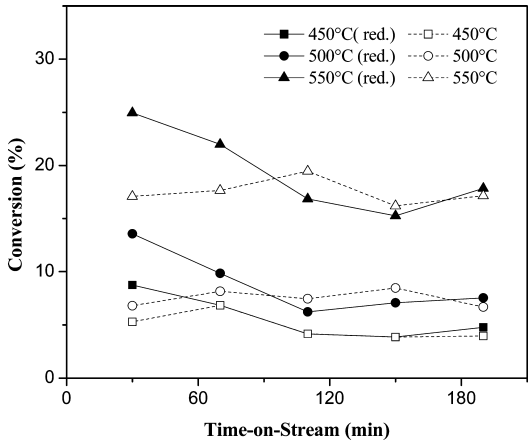

Figure 9. Comparison between ethanol conversion with and without H_2 pretreatment as a function of time-on-stream (min). Closed symbols (also indicated as "red") are for experiments with H_2 pretreatment. Open symbols are for experiments without H_2 pretreatment of the reactor.

experiments (~17% at 550 °C, ~8% at 500 °C, and ~4−5% at 450 °C). With pretreatment, the conversion of the first sample (30 min after ethanol injection) was higher than without pretreatment. For longer time-on-stream, the conversion dropped and became similar to that obtained without pretreatment. Ethanol conversions at all three temperatures were about the same for the empty reactor with and without pretreatment with H_2 after ~90 min. This result indicates that SCW likely reoxidizes the wall's surface. Here, the presence of a small amount of hydrogen formed from ethanol reforming does not seem to be sufficient to maintain the metallic state of nickel on the wall's surface.

3.5. Effects of Pressure. At a constant temperature of 500 °C, increasing the pressure from 22.5 to 28.0 MPa increased the water density from 0.078 to 0.105 g/cm^3. The effect of increasing the pressure from 225 to 280 bar on ethanol conversion and SCW density is presented in Figure 10. There are no significant differences of the mean and the variance using a Turkey and Levene test in a statistical analysis of one way ANOVA method. Also, no significant differences in terms of reaction product yields were observed (results not shown).

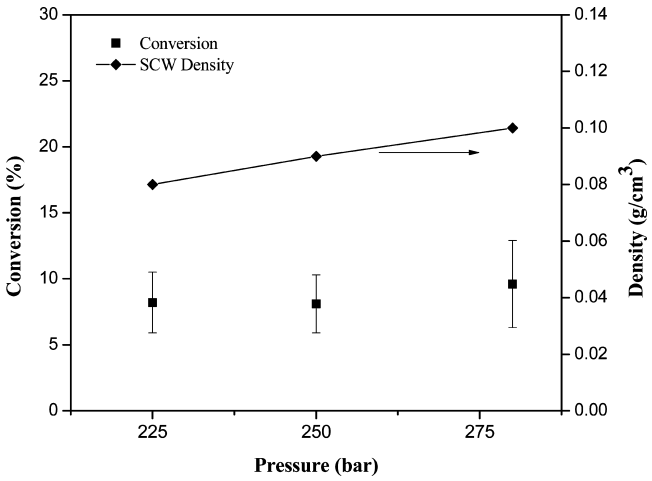

Figure 10. Effect of pressure on ethanol conversion at 500 °C, 1.88 g/min, and 5% wt ethanol.

This denotes that in the pressure range studied here, the corresponding change in water density did not affect the conversion.

3.6. Ethanol Dehydrogenation Kinetics. Since the first step in ethanol reforming in SCW is ethanol dehydrogenation into acetaldehyde and hydrogen, it is reasonable to expect that the reaction kinetics for the disappearance of ethanol should follow first-order kinetics:

$$\frac{d[C_2H_5OH]}{dt} = -k_g[C_2H_5OH] \tag{8}$$

where k_g (1/s) is a global reaction constant and t (s) is the residence time. Equation 8 can be written, in terms of ethanol conversion, as

$$\ln(1 - X) = -k_g t \tag{9}$$

Using the data presented in Figure 3, the plot of $\ln(1 - X)$ as a function of residence time, t, is shown in Figure 11.

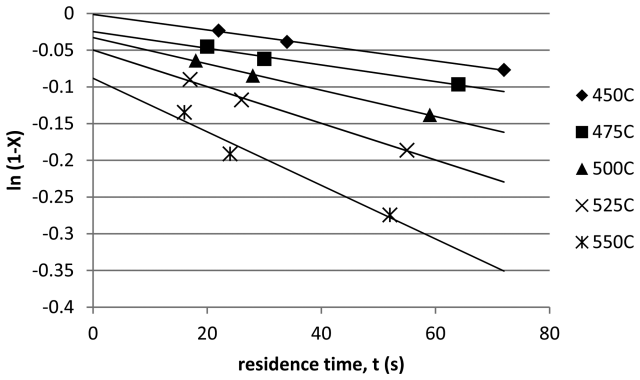

Figure 11. Variation of $\ln(1 - X)$ as a function of residence time. P = 25 MPa.

Figure 11 indicates that the assumption of first-order kinetics is valid since the data follow a linear trend. Although at 450 °C, the line intercepts the x-axis at a value of almost zero, it is observed that, as the temperature increased, so did the absolute value of the intercept. This means that a certain amount of ethanol dehydrogenated prior to entering the reactor (i.e., in the small Hastelloy tube connected to the reactor through which ethanol is fed). Keeping the definition of X as ethanol conversion at the exit of the reactor (based on the feed ethanol concentration), and defining X_1 as the ethanol conversion prior to entering the reactor, the relationship between X and X_1 is given as

$$\ln(1 - X) = -k_g t + \ln(1 - X_1) \tag{10}$$

Therefore, the intercept in Figure 11 is used to determine the ethanol conversion prior to entering the reactor (X_1), and the slope is used to determine the global reaction constant (k_g). Results for k_g and X_1, as functions of temperature, are given in Table 1. This table indicates that, prior to the reactor, ethanol conversion varied between 0.13% at 450 °C and 8.45% at 550 °C.

The values of k_g were plotted in an Arrehnius plot in the range 475−550 °C to determine the values of the activation energy and pre-exponential factors:

$$k_g = 410\exp[-(80\ \text{kJ/mol})/RT]\ (1/\text{s}) \tag{11}$$

Table 1. Values of the Global Rate Constant (k_g) and Conversion Prior to Entering the Reactor (X_1) at Temperatures between 450 and 550 °C

T (°C)	450	475	500	525	550
k_g (1/s)	0.0011	0.0011	0.0018	0.0025	0.0036
X_1	0.0013	0.0245	0.0324	0.0486	0.0845

We have shown that the wall effects are significant, especially at temperatures above 525 °C (see Figure 8). The value of k_g reported in eq 11, therefore, includes both the homogeneous and wall-catalyzed dehydrogenation reactions. Similar to the work of Croiset et al.,[9] we assume that the wall-catalyzed reaction varies linearly with the S/V ratio. The global reaction constant is thus written as

$$k_g = k_h + k_w\left(\frac{S}{V}\right) \tag{12}$$

where k_h (1/s) and k_w (mm/s) are the homogeneous and wall-catalyzed rate constants, respectively.

Using the data presented in Figure 8, for temperatures between 500 and 550 °C, values of k_g were calculated (using eq 10) at different (S/V) ratios. Note that the change in void fraction was taken into account when determining the residence times for the configurations where Inconel wires were inserted in the reactor. Figure 12 represents the change in k_g as a function of S/V for temperatures between 500 and 550 °C.

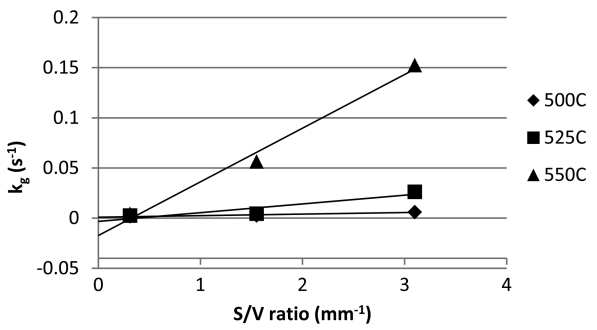

Figure 12. Variation of the global rate constant, k_g, as a function of the S/V ratio.

As per eq 12, the intercept in Figure 12 represents k_h. From this figure, we can see that at 525 and 550 °C the intercepts are negative, which is not possible, as k_h has to be positive. The intercepts are also quite close to zero, and their values are highly dependent on the experimental errors. Low values for k_h are also supported by the work of Arita et al.,[10] who found, using flame-sealed quartz reactors, a rate constant for ethanol dehydrogenation in the order of 10^{-5} 1/s at 500 °C. Therefore, to determine k_w, we assumed that the homogeneous decomposition of ethanol is negligible compared to the wall-catalyzed reaction in our system. The values of k_w were then calculated through fitting the data in Figure 12 using a linear relationship with intercept at the origin. The following values for k_w were determined: 0.0019, 0.0074, and 0.0464 (mm/s) at 500, 525, and 550 °C, respectively. An Arrhenius expression of k_w in the temperature range 500−550 °C was then calculated as

$$k_w = 1.1 \times 10^{20}\exp[-(337\ \text{kJ/mol})/RT]\ (\text{mm/s}) \tag{13}$$

At 500 °C, in the empty reactor not loaded with wires (i.e., lowest S/V), the value of $k_w(S/V)$ is equal to 6×10^{-4} 1/s, which is about 1 order of magnitude greater than the homogeneous rate constant reported by Arita et al.[10] It is thus concluded that, in our system, ethanol dehydrogenation indeed occurs mostly through wall-catalyzed reactions and that the assumption of neglecting the homogeneous reaction is valid.

4. CONCLUSIONS

Ethanol reforming in the absence of a catalyst has been carried out in supercritical water using an Inconel-625 reactor. The effects of temperature, flow rate, concentration, and pressure have been studied, and the results are summarized as follows:

Not surprisingly, ethanol reforming strongly depends on temperature, where conversion increases with increasing temperature. Temperatures below 450 °C are too low to yield any meaningful conversion.

At temperatures of 575 °C and above, plugging of the reactor and/or BPR occurs, especially at low feed flow rates (i.e., at higher residence times). Reactor plugging occurs due to deposition on the screen of particles formed during the reaction. A practical temperature range for ethanol reforming in SCW is thus 450−550 °C.

The selectivity results have shown that the production of hydrogen originates mostly from ethanol dehydrogenation, producing H_2 and acetaldehyde. The subsequent decomposition of acetaldehyde is believed to be the main route of CO and CH_4 formation. The low CO_2 selectivity indicates that the water−gas shift reaction is not significant in this reactor configuration. The dehydration step is also significant here, especially at the higher temperatures (above 550 °C), as evidenced by the presence of C_2H_4 and by the formation of tar (ethylene is a known precursor for coke formation).

Pretreatment of the reactor with hydrogen was found to have a beneficial effect on ethanol conversion only during the first few minutes of the reaction. After less than 2 h, the conversion dropped to levels similar to those obtained in a reactor without H_2 pretreatment. Such pretreatment is therefore not needed.

The effect of pressure, at least in the range 22−28 MPa, is insignificant.

This study also confirmed the catalytic effect of the Inconel-625 reactor's wall on ethanol reforming. The effects of the reactor's wall were studied through varying the surfaced-to-volume (S/V) ratio by adding a known amount of Inconel wire. A kinetic study of the ethanol dehydrogenation reaction demonstrated that it follows first-order kinetics and that, in our reactor, the reaction occurs almost exclusively through wall-catalyzed reactions, the homogeneous dehydrogenation of ethanol being negligible. An Arrhenius expression for the rate constant of the reactor's wall-catalyzed dehydrogenation reaction has been proposed.

Our results suggest that the best conditions, in terms of high conversion and stability, to carry out ethanol reforming in supercritical water are: temperature of 550 °C, pressure of 25 MPA, and high S/V ratio (e.g., 3.1 1/mm). Under such conditions (which correspond to a residence time of about 20 s), it was possible to achieve conversions up to 96% without carbon deposition problems.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Ni, M.; Leung, D. Y. C.; Leung, M. K. H. A review on reforming bio-ethanol for hydrogen production. *Int. J. Hydrog. Energy* **2007**, *32*, 3238.

(2) Mattos, L. V.; Jacobs, G.; Davis, B. H.; Noronha, F. B. Production of hydrogen from ethanol: Review of reaction mechanism and catalyst deactivation. *Chem. Rev.* **2012**, *112*, 4094.

(3) Savage, P. E.; Gopalan, S.; Mizan, T. I.; Martino, C. J.; Brock, E. E. Reactions at supercritical conditions: applications and fundamentals. *AIChE J.* **1995**, *41*, 1723.

(4) Yu, D.; Aihara, M.; Antal, M. J. Hydrogen production by steam reforming glucose in supercritical water. *Energy Fuels* **1993**, *7*, 574.

(5) Therdthianwong, S.; Srisiriwat, N.; Therdthianwong, A.; Croiset, E. Hydrogen production from bioethanol reforming in supercritical water. *J. Supercrit. Fluids* **2011**, *57*, 58.

(6) Van Bennekom, J. G.; Venderbosch, R. H.; Assink, D.; Heeres, H. J. Reforming of methanol and glycerol in supercritical water. *J. Supercrit. Fluids* **2011**, *58*, 99.

(7) Gadhe, J. B.; Gupta, R. B. Hydrogen production by methanol reforming in supercritical water: Suppression of methane formation. *Ind. Eng. Chem. Res.* **2005**, *44*, 4577.

(8) Boukis, N.; Diem, V.; Habicht, W.; Dinjus, E. Methanol reforming in supercritical water. *Ind. Eng. Chem. Res.* **2003**, *42*, 728.

(9) Croiset, E.; Rice, S. F.; Hanush, R. G. Hydrogen Peroxide Decomposition in Supercritical Water. *AIChE J.* **1997**, *43*, 2343.

(10) Arita, T.; Nakahara, K.; Nagami, K.; Kajimoto, O. Hydrogen generation from ethanol in supercritical water without catalyst. *Tetrahedron Lett.* **2003**, *44*, 1083.

(11) Hsiao, W. W.-W. *Hydrogen Production from Ethanol by Supercritical Water Partial Oxidation*; University of Waterloo: Waterloo, 2003.

(12) Schanzenbächer, J.; Taylor, J. D.; Tester, J. W. Ethanol oxidation and hydrolysis rates in supercritical water. *J. Supercrit. Fluids* **2002**, *22*, 139.

(13) Dybkjaer, I. Tubular reforming and autothermal reforming of natural gas - an overview of available processes. *Fuel Process. Technol.* **1995**, *42*, 85.

(14) Taylor, J. D.; Herdman, C. M.; Wu, B. C.; Wally, K.; Rice, S. F. Hydrogen production in a compact supercritical water reformer. *Int. J. Hydrog. Energy* **2003**, *28*, 1171.