Catalytic Gasification of Glycerol in Supercritical Water for Hydrogen Production

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1　Introduction

Glycerol is a polyalcohol with several commercial applications in food and cosmetics, but nowadays massive amounts of low-purity glycerol are being obtained as byproduct in the manufacture of fatty acids and biodiesel. The surplus amount generated from biodiesel is so large – more than 600 000 tonnes in Europe in 2006 [1] – that glycerol market price has decreased to less that 0.05 €/kg [2,3]. Due to its low purity, crude glycerol from biodiesel cannot be used in cosmetics or food unless a costly refining process is undertaken, but its wide availability and cheap price offer new opportunities for chemistry and energy [4]. Among those, the production of hydrogen by supercritical water processing of concentrated glycerol solutions is an option that is being studied nowadays.

Non-catalytic glycerol decomposition in SCW proceeds through a complex reaction mechanism that is summarized in two competing pathways, ionic and free-radical, whose predominance depends on water density and acidity [5, 6]. At low temperature and high pressure (i.e., high water density) a set of ionic reactions forms acetaldehyde, formaldehyde and acrolein as main products. At low water density a free-radical pathway leads to the preferential formation of allyl alcohol and methanol. Gases are typical products of the free-radical reactions, and their yield is favored by low water density. Complete gasification is achieved only above 700 °C, but hydrogen is not favored as the main product. Gasification efficiency is high with diluted glycerol solutions, but it decreases dramatically when the substrate concentration is above 20 wt%. This is because of the dominance of condensation reactions between glycerol decomposition products that lead to the formation of tarry materials and char [7,8].

Several heterogeneous catalysts have been studied to promote hydrogen yield and reduce the formation of tars and char [7]. Among those, Ruthenium-based catalysts have been shown to offer the best results for SCW gasification of biomass feedstocks [9,10], but still temperatures above 700°C are required to have a high selectivity towards hydrogen [11]. In fact, no catalyst capable of reaching complete conversion of glycerol and a hydrogen yield close to the stoichiometric value at a temperature below 550°C has been found yet, partially because of the formation of methane as competing final product.

In this work we focused on the SCW gasification of glycerol over a Ru/ZrO_2 catalyst in the low temperature range. Experiments at incomplete conversion of glycerol were performed and the reaction products were determined and quantified at increasing residence time. The influence of the catalyst on the pathways of glycerol conversion is discussed.

2   Experimental

A shell-type catalyst with an average content of 1% Ru, was prepared by incipient wetness impregnation following literature procedures [12-14]. The support (ZrO_2 with a particle diameter between 100 and 200 µm and a surface area of 0.1 m^2/g) was impregnated with the adequate amount of an aqueous solution of precursor ($RuCl_2$) and dried at 110°C for 24 h. Then the sample was crushed and oxidized at 500°C for 4 h, reduced with hydrogen at 400 °C for 5 h, cooled to room temperature under nitrogen and stored in caped vials until use. The catalyst was characterized by x-ray diffraction, surface area, SEM and ESEM. Activity of the catalyst was measured in a fixed-bed reactor with the catalyst (1 to 3 g) diluted with ZrO_2 particles (5 to 8 g) of the same size distribution to improve heat transfer and temperature homogeneity. Gaseous products were quantified by an on-line gas chromatograph (Agilent microGC 3000A), and condensable products by HPLC (Agilent 1100 series).
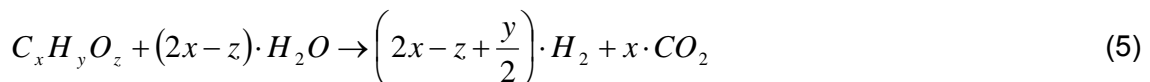
3   Results

Experiments were performed at 510 and 550°C using a glycerol feed concentration of 5% wt, and nominal residence times below 9s. The conversion of glycerol, X (equation 1), the yield of the identified reaction products, Y_j (equation 2), the carbon balance CB, (equation 3), and the hydrogen yield potential HYP, (equation 4) were calculated for each experiment. F_{Gly-0} and F_{Gly} are the molar flow rates of glycerol at the reactor inlet and outlet, respectively, F_j the molar flow rate of any specie at the reactor outlet, nC_j is the number of carbons in compound j, and $n_{H2,j}$ denotes the moles of hydrogen gas that would be formed if species j were completely converted into H_2 and CO_2 following the stoichiometric equation 5.

$$X[\%] = 100 \cdot \left(\frac{F_{Gly-0} - F_{Gly}}{F_{Gly-0}} \right) \tag{1}$$

$$Y_j \left[\frac{mol}{mol_{Glycerol}} \right] = \frac{F_j}{F_{Gly-0}} \tag{2}$$

$$CB[\%] = 100 \cdot \left(\frac{3 \cdot F_{Gly} + \sum_{j=1}^{m} n_{C_j} \cdot F_j}{3 \cdot F_{Gly-0}} \right) \tag{3}$$

$$HYP = \sum_{j=1}^{m} n_{H_2,j} \cdot F_j \tag{4}$$

$$C_x H_y O_z + (2x - z) \cdot H_2 O \rightarrow \left(2x - z + \frac{y}{2} \right) \cdot H_2 + x \cdot CO_2 \tag{5}$$

$$\tau[s] = \frac{V_R \cdot \phi \cdot \rho_{m,R}}{m_0} \tag{6}$$

The residence time of the reacting mixture inside the reactor, τ, was estimated with equation 6, assuming that the density of the reacting mixture approached that of pure water at the temperature and pressure of the experiment. This is a coarse approximation in our case since glycerol concentration was relatively high (5 wt% in the feed), and therefore density of the reaction mixture should be calculated accounting for the change of composition due to the conversion of glycerol and the formation of products. However, this calculation is not straightforward at supercritical conditions and we used this simplified procedure to have an approximate estimation of the residence time. In equation 6, V_R is the volume of the catalyst bed, φ is the void fraction of the bed, m_0 the mass flow rate of water and glycerol fed to the reactor, and $ρ_{m,R}$ is the density of pure water at the reactor conditions of P and T. The latter was calculated according to Wagner and Kruse [15].

Preliminary experiments were developed to assess the stability of the catalyst. Glycerol conversion and the composition of the gas products were monitored for extended periods to determine changes in the activity of the catalyst and product selectivity. In general the catalyst had an initial period in which significant changes in gas composition were observed, but its activity reached stable conditions after 4h of operation. Figure 1 shows glycerol conversion and gas composition for an extended experiment at 350 bar and 550°C. The first section corresponded to a residence time of around 7.5 s, in which complete glycerol conversion was achieved. After 1100 min of operation the feed flow was increased to reduce the residence time to 2.0 s, which resulted on an average conversion of 0.91 when the system did reach a new steady state. Again, around 4 h were required for stabilization. Therefore, all experiments were performed after the catalyst was stabilized for at least 5 h at the intended operation conditions.
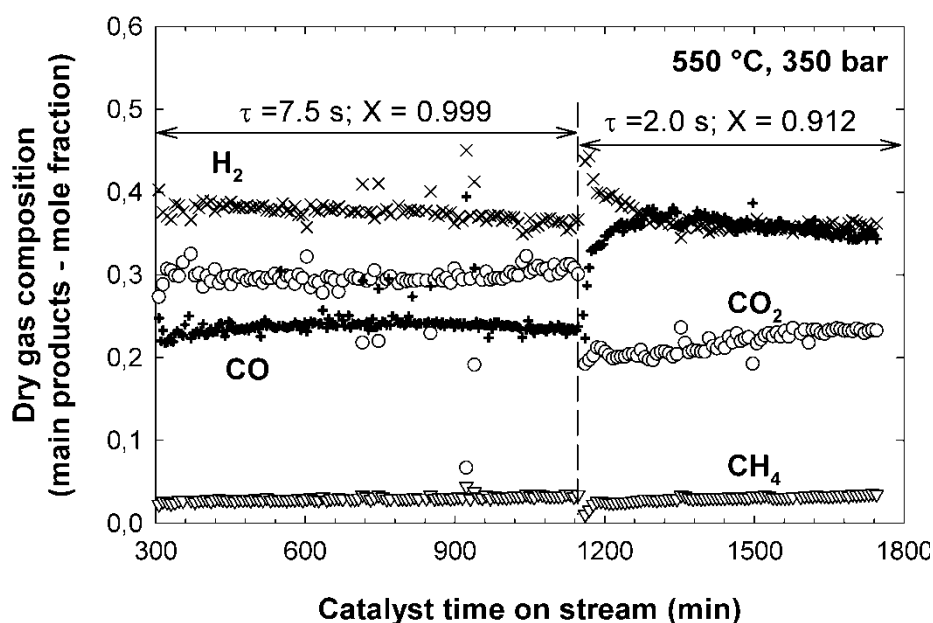

Figure 1:   Catalyst stability. Dry gas composition for an extended experiment at 550°C and 350 bar at two different residence times.

Figure 2 shows the conversion of glycerol at 510 °C and 350 bar, for non-catalyzed experiments using a bed of ZrO_2 particles and for experiments with the Ru/ZrO_2 catalyst. Conversion reached 22% at a residence time of 8.2 s in the non-catalyzed experiment, and it was increased to 98% at the same residence time. The overall pseudo-first rate constant for the non-catalytic gasification of glycerol was 0.034 s^{-1}, in agreement with the values reported in other studies [5], and 0.377 s^{-1} for the catalyzed reaction. Figure 2 also shows the effect of increasing reaction temperature to 550°C. Glycerol conversion was 99.9% at 7.5 s, with a reaction rate constant of 0.992 s^{-1}.

The yields of the main reaction product, which were expressed as mole of product formed per mole of glycerol fed to the reactor (equation 6), are reported in Figures 2 and 3. For the hydrothermal processing at 510°C the main condensable reaction products were acetaldehyde, hydroxyacetone and acetic acid, and gaseous products comprised hydrogen, carbon oxides and methane. Minor amounts of allyl alcohol, propionaldehyde and acrolein, and trace amounts of acrylic acid and ethylene were also detected. This wide variety of products reflects the complexity of the reaction mechanisms involved in the hydrothermal decomposition of glycerol, which can be summarized into the coexistence of competing ionic and free radical pathways [5].
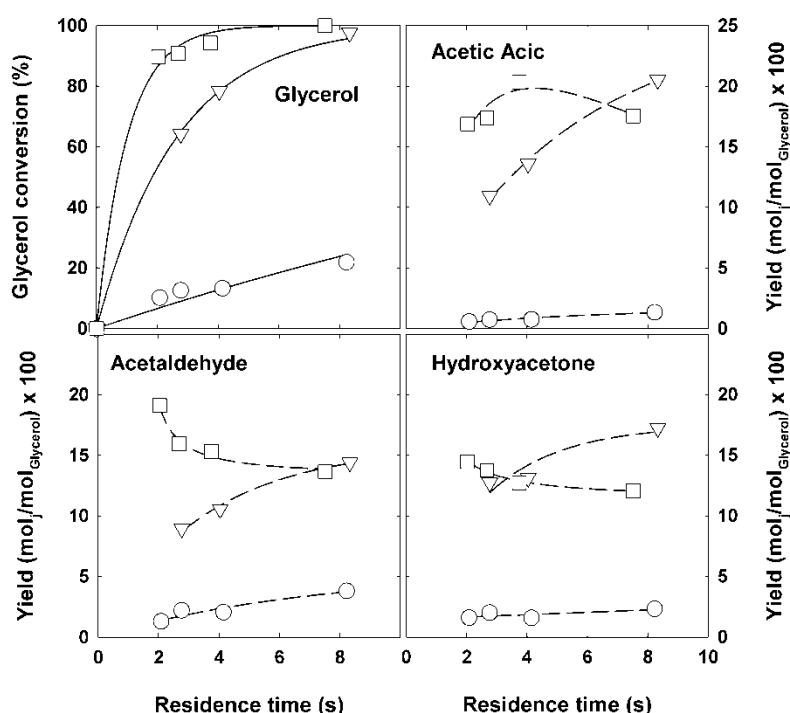

Figure 2: Glycerol conversion at 350 bar and main condensable products for the non-catalytic reaction at 510°C (○) and the catalyzed reaction at 510°C (▽) and 550°C (□).
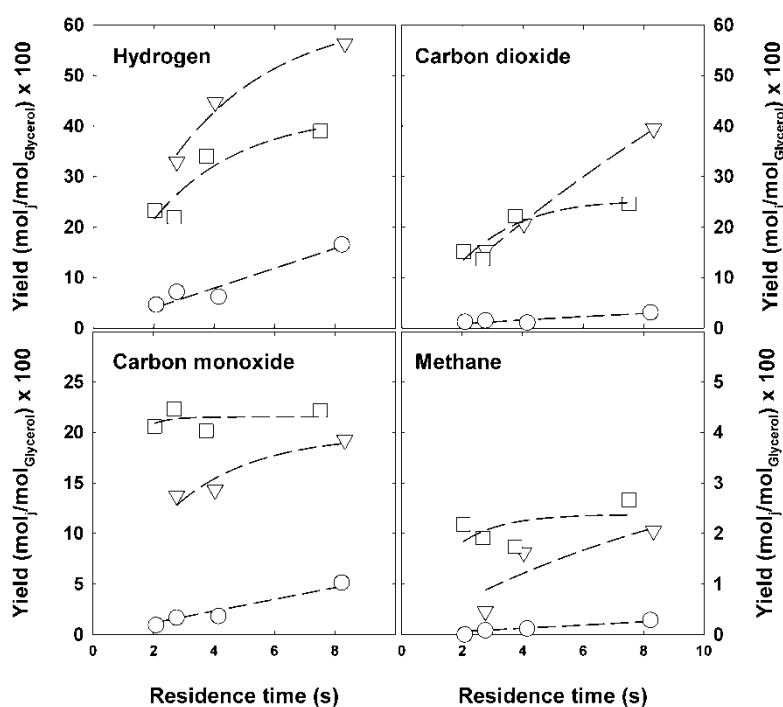
Figure 3: Main gaseous products for the non-catalytic reaction at 350 bar and 510°C (○) and the catalyzed reaction at 510°C (▽) and 550°C (□).

The ionic path dominates at high-water density – low temperature and high pressure – a situation in which the ion product of water is high enough to allow the existence of free protons and hydroxyl ions that may catalyze ionic reactions, and the static dielectric constant of water is high enough to stabilize ionic species and reaction intermediates. The free radical decomposition route dominates at low water density – high temperature and low pressure – where ionic chemistry is not favored due to the low dielectric constant of the media and low water ion product. Table I shows relevant properties for the conditions we have covered in our study, which were calculated according to Wagner and Kruse [33]. At 510°C and 350 bar the ion product of water is six orders of magnitude lower than for water at room temperature and the dielectric constant is close to that of steam, which indicates that the ionic route will play a minor role in our case and that the free-radical pathway should dominate.

The catalyst had a significant influence on the selectivity of the different reaction products. Acetic acid became the main condensable product instead of acetaldehyde. For instance, at 510°C and 8.5 s residence time – complete glycerol conversion – the yield of acetic acid grew from 0.015 mol/mol$_{Gly}$ in the non-catalyzed experiments to 0.25 mol/mol$_{Gly}$, while that of acetaldehyde only went from 0.045 to 0.15 mol/mol$_{Gly}$. The yield of hydroxyacetone grew from 0.025 to 0.18 mol/mol$_{Gly}$, also below the yield of acetic acid. Permanent gases – shown in Figure 3 – were the major products, and the yields of hydrogen, carbon oxides and methane all increased when the catalyst was used. The catalyst favored both C-C cleavage reactions that formed acetic acid and acetaldehyde, and dehydration reactions that formed C3 products, mainly hydroxyacetone. The catalyst also promoted reforming to form hydrogen, carbon oxides and methane (secondary products), although glycerol was preferentially converted into primary products (i.e. acetic acid, acetaldehyde and

hydroxyacetone), which were then converted into gases at a slower rate. This may be observed in the experiment at 550°C. A glycerol conversion above 95% was reached in 4 s, when a maximum in acetic acid yield was attained. Notably, the yields of acetaldehyde, hydroxyacetone, and other condensable primary products decreased with residence time in the entire interval covered by the experiment, showing that they were converted into secondary products. The yield of hydrogen was lower than at 510°C because more carbon monoxide and methane were formed, thus reducing hydrogen yield. However, gases were not the sole secondary products. Figure 4 shows the carbon balances for the non-catalyzed and catalyzed experiments. At 510°C the carbon balance closure in the non-catalyzed experiments was better than 90%, and it was between 70 and 85% at 550°C. The carbon unaccounted for was mostly attributed to formaldehyde and methanol – which were not properly recovered nor quantified in our experimental setup – since no carbon formation on the surface of the bed particles could be observed. On the contrary, the catalyzed experiments had carbon balance closures between 80 and 60%, decreasing continuously as the residence time was increased. Although the formation of methanol and formaldehyde represented a fraction of the carbon unaccounted for, the main reason for the poor carbon balance closure was the formation of carbon deposits on the bed. In fact carbon deposits were not observed on the particles of Ru/ZrO_2 catalyst but on the inert ZrO_2 particles that were used to dilute the catalyst bed, and eventually caused partial plugging of the bed and pressure build-up during extended experiments when temperature was below 510°C. This implies that carbon deposits evolved from the primary reaction products through condensation reactions in the aqueous phase that formed tar-like carbon precursors. The formation of tar at temperatures below 600°C has been reported for the hydrothermal gasification of glucose. In our case a proton-catalyzed ionic reaction pathway may be considered due to the relative high concentration of acetic acid and other acidic species. However, the low ion product (kW) and static dielectric constant (ε) of water at the reaction conditions we used – for instance, kW and ε were 1.67×10^{-20} $(mol/kg)^2$ and 1.984 at 510°C and 350 bar, respectively [33] – point to a more likely free-radical pathway as dominant.
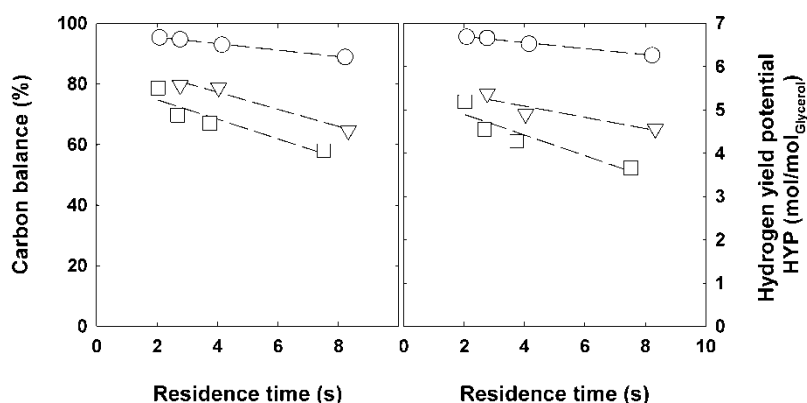

Figure 4:   **Carbon balance and hydrogen potential yields for glycerol conversion at 350 bar: 510°C non-catalyzed (○) and catalyzed at 510°C (▽) and 550°C (□).**

4   Conclusions

The hydrothermal and catalytic conversion of glycerol has been studied in supercritical water at 350 bar and intermediate temperatures (510 and 550°C), covering an interval of residence time that gave incomplete conversion of glycerol. The catalyst – 1% Ru on CaO-stabilized ZrO^2 – augmented the rate of glycerol conversion and favored carbon-carbon scission reactions to form acetic acid and acetaldehyde as the main primary products. The catalyst also converted the primary products into gases through reforming, although the rate of reforming was slower than that of the formation of primary products. When the catalyst was used, the higher concentration of acidic species in the fluid prompted the formation of tar-like adducts that lead to the deposition of carbon on the bed – particularly on the surface of the inert particles of ZrO_2 that were used to dilute the catalyst particles – and a poor carbon balance. In conclusion, although the Ru/ZrO_2 catalyst presented good stability and overall activity, its selectivity towards reforming reactions was not high enough in the intermediate temperature range we studied. From a practical standpoint, low temperature and pressure are desirable in the hydrothermal processing of biomass in supercritical water to reduce the requirements of construction materials and operation costs. Optimization of the properties of the catalyst to enhance the reforming activity at low temperature and the selectivity towards gas products, and the capacity for processing high concentrations of biomass, are key aspects that need to be solved for the implementation of technology of supercritical water gasification.

Acknowledgments

References

[1]   M. Pagliaro, M. Rossi, The Future of Glycerol. New Usages for a Versatile Raw Material, RSC Publishing, Cambridge, UK, 2008.

[2]   D.T. Johnson, K.A. Taconi. Environ. Prog. 26 (2007) 338-348.

[3]   Miller-Klein Associates, Impact of Biodiesel Production on the Glycerol Market (2006). http://www.hgca.com/document.aspx?fn=load&media_id=3605&publicationId=2363

[4]   M. Pagliaro, R. Ciriminna, H. Kimura, M. Rossi, C. Della Pina. Angew. Chem. Int. Ed. 46 (2007) 4434-4440.

[5]   W. Bühler, E. Dinjus, H.J. Ederer, A. Kruse, C. Mas. J. Supercrit. Fluid. 22 (2002) 37-53.

[6]   M.J. Antal, W.S.L. Mok, J.C. Roy, A.T. Raissi. J. Anal. Appl. Pyrol. 8 (1985) 291-303.

[7]   L. Kong, G. Li, B. Zhang, W. He, H. Wang. Energ. Source. Part A 30 (2008) 1166-1178.

[8]   X. Xu, Y. Matsumura, J. Stenberg, M.J. Antal Jr. Ind. Eng. Chem. Res. 35 (1996) 2522-2530.

[9]   M. Osada , T. Sato, M. Watanabe, T. Adshiri, K. Arai. Energ. Fuel. 18 (2004) 327-333.

[10]   X. Hao, L. Guo, X. Zhang, Y. Guan. Chem. Eng. J. 110 (2005) 57-65.

[11] A.J. Byrd, K.K. Pant, R.B. Gupta. Fuel 87(2008) 2956-2960.

[12] Y. Boucouvalas, Z. Zhang, X.E. Verykios. Catal. Lett. 40(1996) 189-195.

[13] D.C. Elliott, T.R. Hart, G.G. Neuenschwander. Ind. Eng. Chem. Res. 45(2006) 3776-3781.

[14] D. Li, N. Ichikuni, S. Shimazu, T. Uematsu. Appl. Catal. A-Gen. 180 (1999) 227-235.

[15] W. Wagner, A. Kruse, Properties of Water and Steam. Springer-Verlag, Berlin, 1998.