

Hydrogen Production via Reforming of the Aqueous Phase of Bio-Oil over Ni/Olivine Catalysts in a Spouted Bed Reactor

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Hydrogen produced from renewable energy sources can present significant environmental benefits as a means for clean power generation via fuel cells. The aqueous fraction of bio-oil can be used as a source for hydrogen production, if reformed in the presence of active catalytic materials. Recently, we introduced the concept of the spouted bed reactor for this particular process. The aim of the current work is to further investigate the suitability of the novel reactor. The effect of temperature, H₂O/C ratio, space velocity, and heat treatment of support was investigated in the presence of Ni/Olivine catalysts. Runs were conducted with ethylene glycol and acetic acid as representative model compounds of the aqueous phase of bio-oil. The organics converted fully toward gases with high selectivity in hydrogen, while the known problem of coking was notably avoided. Ethylene glycol reforming seems to proceed primarily via decomposition followed by reforming of secondary products. Hydrogen yield during acetic acid reforming is higher under equivalent conditions. Tests using the aqueous phase of bio-oil proved more complicated due to the serious thermal instability of the feed. A new injection-cooling system was developed in order to achieve efficient feeding of bio-oil.

1. Introduction

The extensive use of fossil fuels has led to severe pollution of the environment. At the same time, the concern for the depletion of oil reserves is wide, leading to a growing research interest for alternative energy sources. Hydrogen has emerged as the energy carrier of the future, being able to be used as a means for the production of electricity via fuel cells, as well as a clean transport fuel. Currently though, it is mainly produced from nonrenewable sources, namely natural gas and petroleum fractions,¹ leading to high CO₂-emissions and significantly contributing to the greenhouse effect. Environmental benefits can only be gained when hydrogen is derived from renewable energy sources, such as biomass.

Bio-oil, a product of biomass pyrolysis, can be separated with addition of water into a hydrophobic, lignin derived, fraction and an aqueous fraction containing mostly the carbohydrate-derived monomeric compounds at a ratio of ~20% organics/~80% water.² Steam reforming of the aqueous phase of bio-oil appears as a promising route for sustainable hydrogen production, while the lignin-derived fraction can be used to produce different chemicals and additives.³ Bio-oil, being a liquid, is a lot easier to transport and handle compared to bulky solid biomass. Consequently, the steps of pyrolysis and reforming can occur at different sites. Moreover, the high water content of the aqueous phase of bio-oil significantly reduces the use of additional water necessary for the steam reforming reaction. The coreforming of pyrolysis liquids with other biobased gases containing methane, such as biogas, could further increase hydrogen production in a biomass-based plant.⁴

The catalytic reforming of the water soluble fraction of biomass pyrolysis liquids was studied extensively in our previous publications. Employing a pilot scale fixed bed reactor,⁵

representative model compounds (acetone, ethylene glycol, and acetic acid) were reformed effectively in the presence of a commercial nickel-based catalyst. Hydrogen yields up to 90% were achieved with complete conversion of the organics. On the contrary, reforming of the aqueous phase of bio-oil resulted in a much lower hydrogen yield, around 60%, due to the high extent of coking. The major problem of coke deposition led Chornet and co-workers⁶ to suggest the use of a fluidized bed as more suitable for the reforming of bio-oil, while Mirodatos et al. proposed a sequential process alternating between cracking/reforming and combustion steps.⁷ A two-stage reactor concept was presented by vanRossum et al.,⁸ where a sand fluidized bed is followed by a fixed catalytic bed, in order to decouple the atomization/cracking of bio-oil and the catalytic conditioning of the produced gases.

Recently, we introduced and evaluated for the first time an alternative reactor configuration for the steam reforming of bio-oil, that of the spouted bed.⁹ The implementation of the reactor, modified by the use of an injection nozzle, was proven successful, resulting in efficient processing of ethylene glycol, selected as a model compound of bio-oil. Sand, olivine, and a Ni/olivine catalyst were tested, with coke formation drastically limited, regardless of the particles tested. The favorable hydrodynamics of the spouted bed and especially the continuous recirculation of the catalyst that leads to exposure of carbon to varying reaction atmospheres¹⁰ helped in minimizing coke deposition. Ni/olivine appeared to be a suitable catalytic system due to its high mechanical strength and anticoking characteristics.

In the current work, we continue the evaluation of the spouted bed reactor, presenting experimental results of reforming of ethylene glycol, acetic acid, and the aqueous phase of bio-oil. The effect of catalyst properties, temperature, steam to carbon ratio, and space velocity is investigated in the presence of Ni/olivine catalysts.

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2. Experimental Section

2.1. Catalysts Preparation, Pretreatment, and Characterization. Natural olivine, provided from Olivinites, Macedonia Greece, was used as the support for the nickel catalysts. Its composition corresponds to a mean formula $(\text{Mg}_{0.9}\text{Fe}_{0.1})_2\text{SiO}_4$, containing also small quantities of MgSiO_3 and Fe oxides.

The Ni/olivine catalysts were prepared by wet impregnation of olivine with a solution of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in deionized water so as to obtain a nickel content of 5 wt%. After water evaporation in a mild vacuum at 95 °C, the samples were dried overnight at 105 °C and then calcined under synthetic air. The preparation method was varied so as to obtain two different catalytic samples. Olivine, which had been calcined at 1100 °C for 4 h prior impregnation, was used as the carrier of the first catalyst (Ni/OI-1100). After impregnation, the calcination of the catalyst took place also at 1100 °C for 4 h. Natural olivine (not calcined) was used as the carrier of the second catalyst (Ni/OI-800), while after impregnation, the calcination of the sample was conducted at 800 °C for 4 h. In both cases, calcination took place with a heating rate equal to 5 °C/min. Prior testing catalytic particles were subjected to cold flow spouting to evaluate their resistance to attrition. As explained in more detail elsewhere,⁹ fines created during this process were, primarily, a loosely bound NiO shell. However, as was seen from SEM/EDS analysis, a thin layer of NiO (~10 μm) strongly linked to olivine remained afterward. The resulting stable particles after cold flow spouting are the ones actually loaded in the reactor during catalytic tests. Catalytic particles were sieved in order to get a particle size of 250–355 μm.

Carbon deposits on used samples were examined on a C,H elementary analyzer (LECO-800). The specific surface area was determined by the BET-method on a Tristar Micromeritics instrument on the basis of the N_2 physisorption capacity at -196 °C. XPS measurements were carried out in an ultra high vacuum system equipped with a SPECS LHS-10 hemispherical electron analyzer. The unmonochromatized Al K α (1486.6 eV) line was used in all XPS measurements. The binding energy of C1s (284.6 eV) was used as a reference.

2.2. Experimental Unit. The tests were performed in the SYNGAS pilot plant facility. More details on the experimental unit can be found elsewhere.^{5,9} The reactor made of stainless steel (Figure 1) comprises an inverted conical base followed by a cylindrical part (50 mm ID). Steam plus the gas feed is admitted to the reactor from the preheater region through a nozzle located at the cone apex. The mixture of steam and gases create a jet that entrains catalyst particles and forms a spout around the reactor centerline. A paraboloidal fountain of particles is formed in the freeboard above the bed surface when the jet momentum is high enough to maintain stable spouting. Entrained catalyst particles from the spout region are separated from the product gases in the fountain and fall back to the top of the annular catalyst bed. The organic feed reaches the reactor cooled from a separate line and is subsequently mixed in liquid form with the spouting jet just before the cone apex. Thus, the injected liquid organics come into immediate contact with the particle bed. Heat is supplied to the reactor by a two-zone furnace surrounding the catalyst bed. The furnace is controlled by thermocouples located outside the reactor while the temperature profile along the catalyst bed is monitored by thermocouples placed inside a thermowell.

2.3. Experimental Conditions and Procedures. The experiments were performed in the spouted bed reactor, using constant pressure (1 barg), while the operating parameters varied were

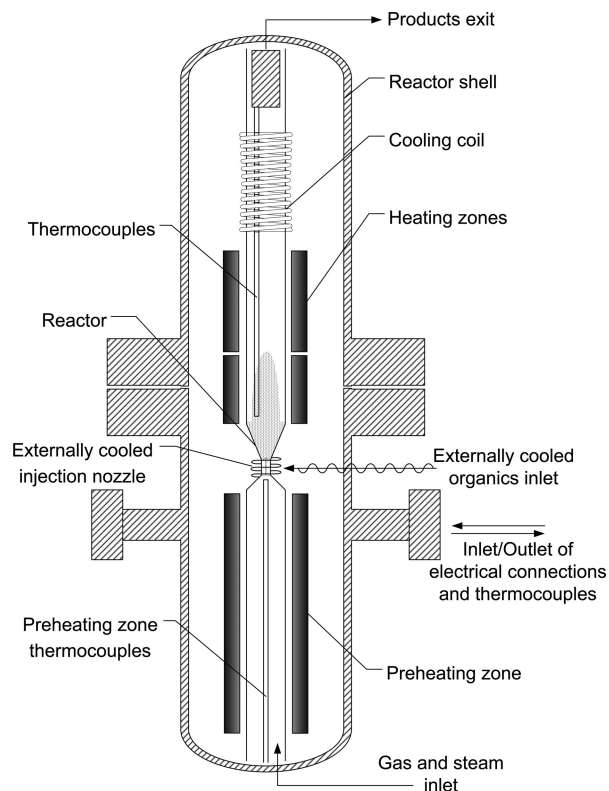


Figure 1. Schematic diagram of the spouted bed reactor

temperature, $\text{H}_2\text{O}/\text{C}$ ratio in the feed and space velocity. Ethylene glycol (99.7%, Prolabo) and acetic acid (99.9%, Carlo Erba) were selected as model compounds of the aqueous phase of bio-oil. For the experimental tests using the aqueous phase of bio-oil, a pine wood derived bio-oil, supplied from BTG, was used. The crude oil was separated by adding water at a mass ratio equal to 1.5:1 in order to extract the aqueous fraction. The final aqueous mixture, after filtration, contained 22.5 wt% organics ($\text{CH}_{1.94}\text{O}_{0.88}$), the rest being water, corresponding to a $\text{H}_2\text{O}/\text{C}$ equal to 5.37. An online gas chromatograph (HP 6890) is used for the analysis of gas products. Two columns (PoraplotQ and Molecular Sieve 5A) in series-bypass configuration and two detectors (thermal conductivity and flame ionization) are used for the analysis of gases. Liquid samples collected are analyzed offline in a Varian 3300 gas chromatograph using a FFAP capillary column and a flame ionization detector.

The results presented in the subsequent section are expressed in terms of the following parameters:

Carbon to gas (C-to-gas) conversion:

$$X_{\text{gas}} = \frac{\text{moles of carbon converted to gas products}}{\text{moles of carbon in the feed}} \times 100 \quad (1)$$

Hydrogen yield:

$$\text{H}_2 \text{ yield} = \frac{\text{moles of hydrogen obtained}}{n \times \text{moles of carbon fed}} \times 100 \quad (2)$$

Selectivity to hydrogen:

$$S_{\text{H}}(\text{H}_2) = \frac{\text{moles of hydrogen obtained}}{\text{moles of hydrogen contained in gas products}} \times 100 \quad (3)$$

Selectivity to x carbon containing gas product:

$$S_{\text{C}}(x) = \frac{\text{moles of carbon converted to } x \text{ compound}}{\text{moles of carbon converted to gas products}} \times 100 \quad (4)$$

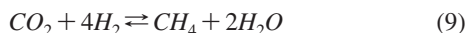
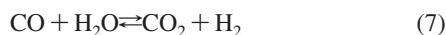
where $n = 2$ for acetic acid, 2.5 for ethylene glycol and 2.1 for the aqueous fraction of bio-oil. These values actually represent the maximum hydrogen yield in moles of hydrogen per mole of carbon input and are derived from the stoichiometric reforming reaction of the respective feed.^{5,6} Carbon balance closure in all tests was in the order of $100 \pm 5\%$.

3. Results and Discussion

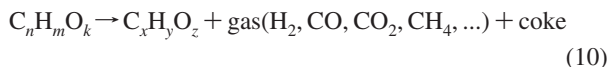
The aqueous fraction of bio-oil is a complex mixture of oxygenated compounds, which can be classified in the main categories of acids, alcohols, aldehydes, and ketones.¹¹ For ethylene glycol and acetic acid, the two model compounds under study, stoichiometric H_2 yield can be achieved via the following reactions:



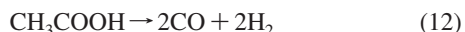
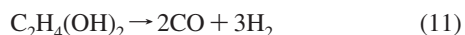
However, the yield of hydrogen is always lower than the stoichiometric maximum, because two undesirable products, CO and CH_4 , are also formed via the water gas shift (7) and methanation (8)–(9), reactions.



At the same time, an important factor in the performance of the process is the thermal decomposition of the organic compounds contained in the bio-oil. Coking not only leads to lower hydrogen yields, but also causes severe catalyst deactivation and reactor blockage. Many of the compounds contained in bio-oil are thermally unstable, so that steam reforming competes with thermal decomposition reactions:



Actually, for the model compounds studied in the current work, production of syngas can occur only via direct decomposition, as seen in the reactions below:



3.1. Ethylene Glycol Reforming. Ethylene glycol, the concentration of which in the aqueous fraction of bio-oil can reach up to 2%,¹² was selected as a representative compound of the entire alcohol group. The autothermal steam reforming of ethylene glycol was studied recently by Dauenhauer et al.,¹³ while reforming using the spouted bed reactor was first tested in our previous communication.⁹ The experimental results of ethylene glycol reforming over the Ni/OI-1100 and Ni/OI-800 catalysts are presented in Figures 2 and 3, respectively. Besides 650 °C for Ni/OI-1100 catalyst, where 98.5% of incoming carbon converted to gaseous products, in every other condition C-to-gas conversion was complete. This was also verified via GC analysis of the liquid products, which were found free of any organic compounds. Over the Ni/OI-1100 catalyst 3–4% of ethylene glycol converted to C_2H_6 , while the corresponding values for C_2H_4 were lower than 2%. Over the Ni/OI-800 catalyst the selectivities toward these compounds were lower than 1% for all temperatures. Worth commenting on is CH_4 selectivity. At 650 °C, 10% of ethylene glycol converted to CH_4 ,

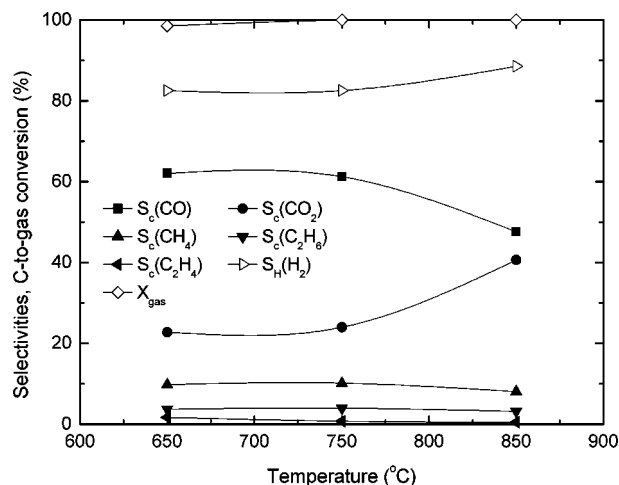


Figure 2. Ethylene glycol conversion to gas products and their selectivities versus temperature at $H_2O/C = 4.6$ and $W/F = 0.015 \text{ g}^*\text{min}/\text{cm}^3$, load: Ni/OI-1100.

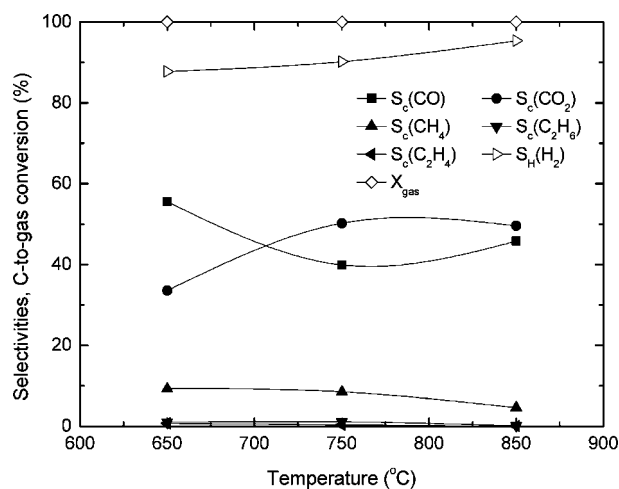


Figure 3. Ethylene glycol conversion to gas products and their selectivities versus temperature at $H_2O/C = 4.6$ and $W/F = 0.015 \text{ g}^*\text{min}/\text{cm}^3$, load: Ni/OI-800.

with this value lowering to 8% at 850 °C for Ni/OI-1100 and 5% for Ni/OI-800.

Comparing the results of the two catalysts, we can observe the increased activity of Ni/OI-800 over Ni/OI-1100. This is exhibited by the marginally higher conversion to gases, but mainly via the improved selectivities of the gas products. Besides a small percentage that was lost as CH_4 (and C_2H_x for Ni/OI-1100), ethylene glycol converted completely to CO_x and H_2 . Selectivity to H_2 over Ni/OI-1100 ranged from 82% to 89% depending on temperature, while over Ni/OI-800 this value spanned from 88% at 650 °C to 95% at 850 °C. The catalyst is active enough to reform compounds, such as CH_3CHO and C_2H_x , which were major thermal products in the noncatalytic runs.⁹ CH_4 is the only compound, produced via decomposition, that makes it to the gas products, implying that the concentration of active Ni sites in the catalysts and/or the residence time under our conditions is not high enough to totally reform it.

Thus, increasing W/F ratio will improve CH_4 conversion. The higher contact time provides equivalently more time for the thermal products to react catalytically toward H_2 and CO_x . This affects not only CH_4 , but also other compounds that decompose toward CH_4 . Figure 4 depicts experimental results of ethylene glycol reforming over Ni/OI-800 at increased catalyst loading ($W/F = 0.030 \text{ g}^*\text{min}/\text{cm}^3$ instead of $0.015 \text{ g}^*\text{min}/\text{cm}^3$) with all

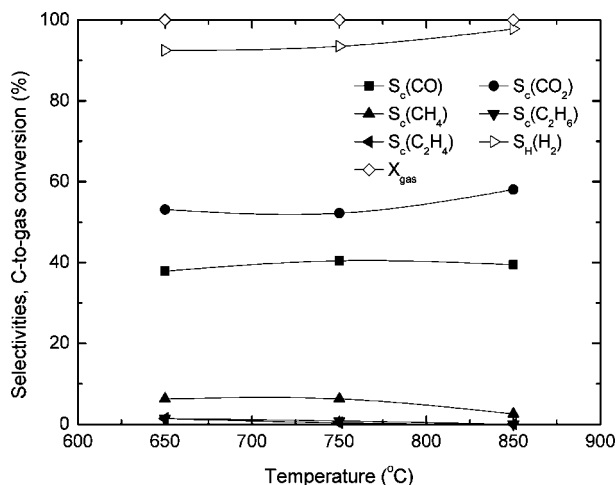


Figure 4. Ethylene glycol conversion to gas products and their selectivities versus temperature at $\text{H}_2\text{O}/\text{C} = 4.6$ and $W/F = 0.030 \text{ g}^*\text{min}/\text{cm}^3$, load: Ni/OI-800.

Table 1. H_2 Yield Achieved during Ethylene Glycol Reforming at $\text{H}_2\text{O}/\text{C} = 4.6$

T (°C)	Ni/OI-1100	Ni/OI-800	
		$W/F = 0.015 \text{ g}^*\text{min}/\text{cm}^3$	$W/F = 0.030 \text{ g}^*\text{min}/\text{cm}^3$
650	50.5	61.1	74.0
750	51.7	67.6	77.9
850	68.1	80.0	89.2

other conditions identical to Figure 3. As expected, conversion of ethylene glycol to gas products is complete. CH_4 is again the only hydrocarbon not fully converted to H_2 , but its selectivity is reduced when compared to the higher space velocity runs. At 650 °C, 6% of carbon input converted to CH_4 with this amount dropping to only 2.5% at 850 °C. The favorable reaction time benefited also the water gas shift reaction as can be seen from Figure 4. CO_2 selectivity was higher than that of CO in every condition, contrary to what can be observed in Figure 3. The promotion of the water gas shift reaction was especially evident at 650 °C. The combination of these two effects led to an increase in H_2 selectivity that ranged from 93% to 98% with increasing temperature.

In Table 1, we present the yield of hydrogen achieved under these sets of experiments. The significant effect of reaction temperature is evident in all cases studied. At the same time, the better performance of Ni/OI-800 can be clearly identified. Finally, it can be seen that the beneficial effect of increased contact time over Ni/OI-800 leads to an increase of, roughly, 10% in the production of hydrogen for each respective temperature. The highest hydrogen yield is observed at 850 °C at $W/F = 0.030 \text{ g}^*\text{min}/\text{cm}^3$, reaching almost 90% of the stoichiometric maximum.

The main parameters accountable for this difference in the activity of the two catalytic samples are discussed below. The calcination of olivine that took place prior to impregnation for the production of the Ni/OI-1100 catalyst led to a significant drop in the surface area of the carrier. As a result, a lower amount of nickel was able to enter the pores of the carrier. The above observations were verified via BET and XPS analyses, respectively.

The BET surface area results are summarized in Table 2. As can be seen, the surface areas of the catalytic samples after impregnation and calcination are lower than that of natural olivine, obviously due to the calcination and partial blocking of the carrier pores from nickel impregnation. Even so, the area

Table 2. BET surface area of catalytic samples during preparation stages

	olivine carrier	after impregnation and calcination	after cold flow spouting
Ni/OI-800	3.02 ^a	1.58	1.10
Ni/OI-1100	0.48 ^b	0.15	0.10

^a Natural. ^b Calcined at 1100 °C for 4 h.

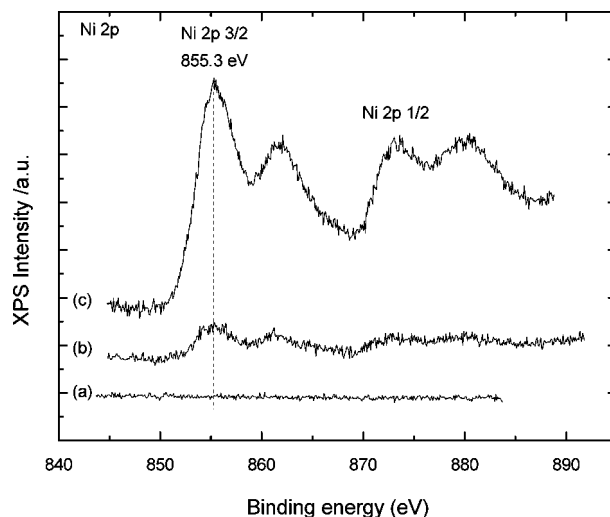


Figure 5. XP Ni 2p spectra of natural olivine (a), Ni/OI-1100 (b), and Ni/OI-800 (c) catalysts after cold flow spouting.

of Ni/OI-800 is significantly higher to that of Ni/OI-1100, since the calcination of the olivine carrier at 1100 °C leads to a substantial drop in surface area. The stable catalytic particles that were received after cold flow spouting presented an even lower surface area compared to the initial ones due to the removal of a loosely bound NiO layer in the form of fines created during this process. The above surface area values might seem very low compared to other catalysts, especially for the case of Ni/OI-1100, but are typical for this type of materials.^{14–17} In fact, their high mechanical strength can be partly attributed to this feature. At the same time, the lower catalytic activity of the Ni/OI-1100 catalyst can be clearly related to the lower surface area and consequently lower Ni dispersion.

Catalytic samples were analyzed via X-ray Photoelectron Spectroscopy after their subjection to cold flow spouting, as they were used for the experiments. Figure 5 presents spectra in the Ni 2p 3/2 peak area. The spectrum of natural olivine is also given for comparison. It is obvious that the carrier's surface prior impregnation does not contain any measurable amount of nickel. The appearance of a peak at binding energy equal to 855.3 eV at both catalytic samples indicates the existence of NiO.¹⁸ It is evident that the surface of Ni/OI-800 is enriched in Ni compared to Ni/OI-1100 explaining its increased catalytic activity. This can be more clearly seen from the Ni/(Mg + Fe + Si) surface atomic ratios that were calculated equal to 0.94 and 0.09 for the Ni/OI-800 and Ni/OI-1100 catalysts, respectively.

3.2. Acetic Acid Reforming. Acetic acid is the most frequently selected model compound of the aqueous phase of bio-oil.^{19–29} Its concentration can reach up to 12%, partly explaining the large number of publications focusing on it. The reforming of acetic acid was evaluated at experimental conditions identical to the ethylene glycol runs and the respective results are presented in Figures 6 and 7. In particular, the effect of temperature was tested at a $\text{H}_2\text{O}/\text{C} = 4.6$ using two different W/F ratios over the Ni/OI-800 catalyst. At both cases, conversion of acetic acid to gas products was complete with no organic

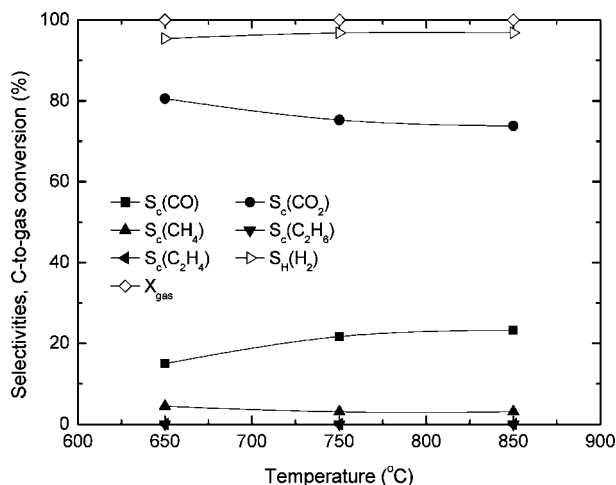


Figure 6. Acetic acid conversion to gas products and their selectivities versus temperature at $\text{H}_2\text{O}/\text{C} = 4.6$ and $W/F = 0.015 \text{ g}^*\text{min}/\text{cm}^3$, load: Ni/Ol-800.

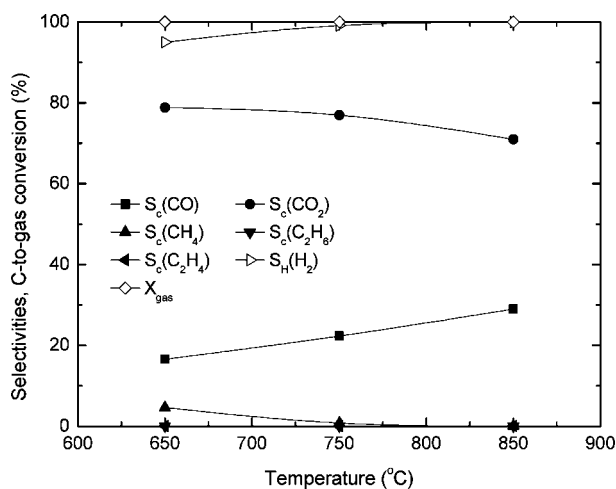


Figure 7. Acetic acid conversion to gas products and their selectivities versus temperature at $\text{H}_2\text{O}/\text{C} = 4.6$ and $W/F = 0.030 \text{ g}^*\text{min}/\text{cm}^3$, load: Ni/Ol-800.

compounds detected in liquid samples. H_2 and CO_x were again the only products detected, apart from a very small production of CH_4 , while selectivity in higher hydrocarbons was zero. However, examination of selectivities of gas products and comparison with that of ethylene glycol reforming reveals possible difference in the reaction pathway followed by the two compounds.

The runs with the lower W/F ratio are better suited for the comparison, since it is easier to observe the reaction network under shorter contact times. Even though the conversion over both organics is almost complete, the distribution of the products is not controlled from thermodynamics but from the kinetics of the reaction steps. Selectivity of CO_2 in the gas products is significantly higher than that of CO in all temperatures examined (Figure 6). On the contrary, in the case of ethylene glycol production of CO was notably more increased, especially at 650°C , as seen in Figure 3. The high production of CO_2 accompanied by the high selectivity in H_2 indicates the high participation of the acetic acid reforming reaction (6). The ratio of H_2/CO_2 in the product stream for all temperatures was close to 2 further indicating that the reforming reaction (6) is dominant. Previously, we discussed that most probably a primary decomposition of ethylene glycol takes place followed by reforming of secondary products. Given the fact that reactor,

catalyst and operating conditions used in the evaluation of the two compounds were identical, it can be inferred that acetic acid reforming is more feasible under all temperatures. Correspondingly, the participation of decomposition reactions appears lower. Additional evidence is given upon examination of CH_4 selectivity that ranged from 4.5% to 3% with increasing temperature (as opposed to 10% to 5% for the equivalent ethylene glycol runs). As has been discussed in literature,³⁰ methanation reactions are not favored thermodynamically at the temperature range studied in our work. The main CH_4 producing reaction is probably the following decomposition reaction of acetic acid:



further implying the small extent of thermal decomposition. The same is deduced from the absence of any higher hydrocarbons in the products. This is in agreement with the work of Basagiannis and Verykios,¹⁹ who studied the reaction network of acetic acid over Ni catalysts. It was found in that report that at temperatures above 600°C and at a $\text{H}_2\text{O}/\text{C} = 1.5$, the dominating reactions are acetic acid reforming (6) and the water gas shift reaction (7). Very high hydrogen selectivity, always above 95%, was subsequently achieved at all temperatures.

Increasing contact time led to further improvement with respect to hydrogen production and the composition of products (Figure 7). The high selectivity in CO_2 was retained in all temperatures, while more interestingly CH_4 selectivity was practically zero above 750°C . As was also observed during ethylene glycol reforming, the longer contact time leads to increased reforming of intermediate thermally produced compounds, explaining the complete reforming of CH_4 . Selectivity in hydrogen above 99% was thus measured at 750°C and higher. H_2 yield at these temperatures for both W/F ratios was higher than 90%, while even at 650°C it reached 85% of the stoichiometric maximum, significantly higher than what was achieved in ethylene glycol and a lot closer to the thermodynamically predicted.

In our previous communication,⁹ we noted that coke deposits during the ethylene glycol reforming runs were practically zero on account of two facts. The favorable hydrodynamic characteristics of the spouted bed reactor on one hand provide efficient and rapid mixing of reactants and catalytic particles. Coke generation and accumulation is thus suppressed, while internal steam gasification of carbonaceous deposits is facilitated. On the other hand, as has been reported in literature,¹⁴ the Ni/olivine system possesses noticeable anticoking characteristics further increasing carbon deposition resistance. Given the aforementioned lower participation of decomposition reactions in the case of acetic acid, it was no surprise to find that coke deposition on the catalyst bed was practically inexistent in all conditions studied.

Acetic acid proved easier to reform compared to ethylene glycol, so it was decided to study the effect of $\text{H}_2\text{O}/\text{C}$ ratio in the feed. Although stoichiometrically only a $\text{H}_2\text{O}/\text{C} = 1$ is needed for full conversion of acetic acid, in actual conditions higher ratios are always used to prevent coke formation and shift thermodynamic equilibrium to more favorable products. $\text{H}_2\text{O}/\text{C}$ ratio was varied from 0 to 4.6 at constant temperature equal to 750°C . The respective results are presented in Figure 8.

A significant influence on products selectivities can be easily observed. Decrease of $\text{H}_2\text{O}/\text{C}$ leads to increase of selectivities of CO and CH_4 , with a proportional decrease of CO_2 and H_2 selectivity. The observed change cannot only be attributed to

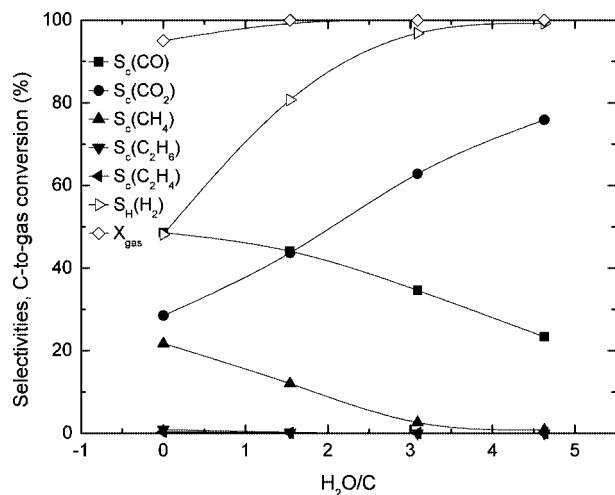


Figure 8. Acetic acid conversion to gas products and their selectivities versus H_2O/C at $T = 750\text{ }^{\circ}\text{C}$ and $W/F = 0.030\text{ g}\cdot\text{min}/\text{cm}^3$, load: Ni/OI-800.

the varying extent of WGS and reforming reactions. The results, and especially the high CH_4 selectivity, strongly indicate the increasing participation of decomposition reactions over reforming reactions. The direct decomposition of acetic acid toward CO and H_2 via reaction (12) results in a H_2/CO ratio equal to 1. In our experiments at $H_2O/C = 0$ this molar ratio approaches unity, evident of the domination of the reaction at that conditions. In addition, the high percentage of CH_4 can be explained by the high extent of decarboxylation reaction (13). The fact that at $H_2O/C = 0$ the concentration of CH_4 was very close to that of CO_2 supports even further this assumption. Of course, as mentioned above, the water gas shift reaction participates inevitably in every H_2O/C ratio examined at varying degree, enhancing final composition. By the addition of water even at low $H_2O/C = 1.5$, the domination of the reforming reactions is evident leading to high H_2 and CO_2 selectivity.

The conversion of acetic acid toward gas products remained, however, very high in all H_2O/C ratios. A small drop to 95% was only observed at $H_2O/C = 0$. In that case, besides acetone traces, acetic acid was the only organic compound detected in the liquid products. The presence of acetone is relatively expected, since it can easily be produced from acetic acid via the following ketonization reaction:^{31,32}



This reaction is catalyzed by a variety of metal oxides and hence the existence of acetone has been mentioned in various reports concerning acetic acid reforming.^{19,20,22,26}

The high conversion of acetic acid to gas products, even in the absence of steam, indicates that the catalyst presents activity in decomposition reactions. Naturally, thermal decomposition participates at some percentage. The conclusions of Davidian et al.,²² were similar when they studied the decomposition of acetic acid over various catalysts. Nickel was proved to be the most active metal achieving full conversion of acetic acid over $600\text{ }^{\circ}\text{C}$, on the contrary to various noble metals that required temperatures higher than $750\text{ }^{\circ}\text{C}$. The use of a fixed bed reactor in that report led to considerable coke deposition, which at $750\text{ }^{\circ}\text{C}$ was equal to $\sim 11\%$ of incoming carbon. In the present work, coke production was significantly lower due to the use of a fluidized bed reactor.

In any case, from current results we see that under the conditions applied, a $H_2O/C \geq 3$ and temperature equal or greater than $750\text{ }^{\circ}\text{C}$ are needed to successfully reform acetic

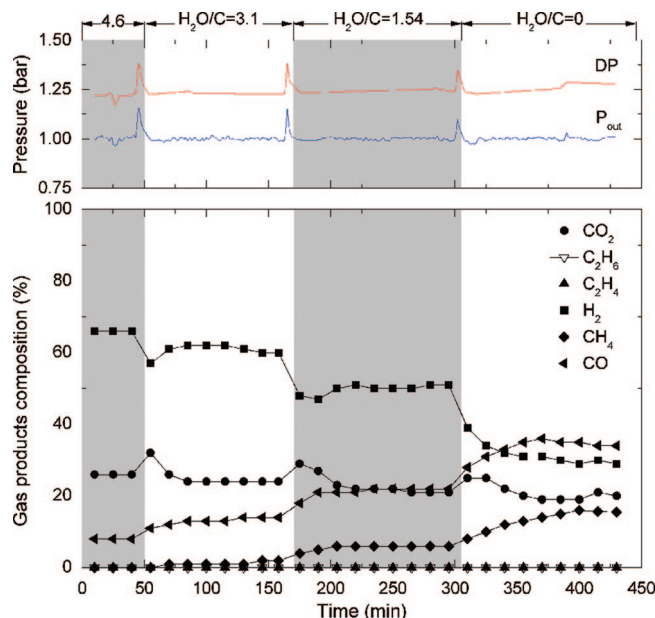


Figure 9. Change in molar concentration and pressure drop in reactor during acetic acid reforming at $T = 750\text{ }^{\circ}\text{C}$ and $W/F = 0.030\text{ g}\cdot\text{min}/\text{cm}^3$, load: Ni/OI-800.

Table 3. H_2 Yield Achieved during Acetic Acid Reforming at $T = 750\text{ }^{\circ}\text{C}$ and $W/F = 0.030\text{ g}\cdot\text{min}/\text{cm}^3$

H_2O/C	H_2 yield
0.00	18.4
1.54	49.4
3.10	78.6
4.60	93.3

acid and achieve high hydrogen selectivity, as is evident from Table 3. The effect of H_2O/C ratio is determinant on hydrogen production raising its yield from as low as 18% to higher than 93% of the stoichiometric maximum. However, it must be commented that for $H_2O/C = 0$ the calculation of hydrogen yield is more correct to be based on the decomposition reaction of acetic acid (12) and not on the reforming reaction (6), since the only hydrogen source is acetic acid. In that case, the yield of hydrogen is twice the value given in Table 3 and equal to 37%.

As mentioned above, the production of coke was very low during the study of the H_2O/C variation. The decrease in steam ratio leads to more favorable conditions for coke generation and, as we have seen during the discussion of results, the increasing participation of decomposition reactions is evident. Even so, the evolution of these experiments was smooth without any problems observed in the differential pressure of the reactor, as can be clearly seen in Figure 9, underlying the advantages of using a spouted bed reactor and a fluidized bed reactor in general over a classic fixed bed reactor.

3.3. Aqueous phase of Bio-Oil Reforming. Tests using the aqueous phase of bio-oil pointed the significant differences that exist compared to the simple monomeric model compounds. The thermal instability of the feed led to very frequent plugging of the injection nozzle, the internal diameter of which was 1.6 mm, even though the bio-oil feed line, as well as the premixing part of the nozzle, was externally cooled. Thus, a new system was developed specifically for the feeding of bio-oil. The main issue to be faced was the more efficient cooling of bio-oil, so as to prevent its decomposition prior to reaching the catalytic bed. The new system comprises various concentric tubes that are used for the feeding of gases, the injection of bio-oil and

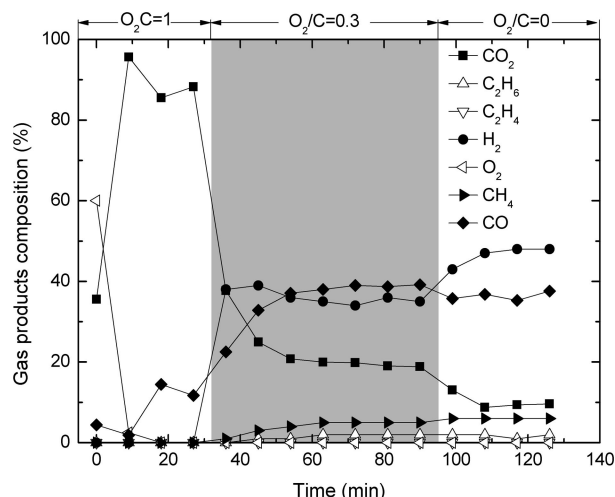


Figure 10. Change in molar concentration of gas products during bio-oil reforming at $T = 850\text{ }^{\circ}\text{C}$, load: Ni/OI-800.

the cooling of these lines. The outer pipes serve as a cooling jacket. The aqueous phase of bio-oil is fed via a needle that has been attached to the feed line and has been placed concentrically to the initial injection nozzle. This system was incorporated in the preheat zone of the reactor.

No additional water was used in these experiments due to the already high content of the aqueous phase. A high percentage of nitrogen dilution was necessary to properly inject the bio-oil. It was also decided to cofed oxygen for two reasons. First, the problem of efficient heat supply to the endothermic reforming reactions can be solved via this method, sacrificing part of the produced hydrogen. Second, the entrance of the reactor can be protected from coke generation. Carbon content at this section is at its highest value, while temperature is at its lowest value, due to the injection of the cold liquids. Thus, oxygen can remove coke and at the same time increase temperature, facilitating the initiation of reforming reactions.

In Figure 10, we present experimental results of reforming the aqueous phase of bio-oil using the spouted bed reactor over the Ni/OI-800 catalyst. At the beginning of the experiment air is fed in the reactor at a O_2/C ratio equal to 1, leading to full oxidation of the organic content, as evident by the high CO_2 content and the total consumption of O_2 . The observed change in the composition of gas products after the reduction of O_2 to 30% of incoming carbon indicates a gradual increase in the percentage of decomposition and/or reforming reactions over combustion reactions. The percentage of CO , CH_4 and H_2 increases, while a respective drop in CO_2 is observed. It is interesting to compare the results with equivalent ones over olivine (not presented here). Minor modifications to that experiment indicate a slightly higher promotion of reforming reactions due to the catalytic action. The percentage of H_2 in gas products rises from 27% for olivine to 37% for the catalyst. A simultaneous decrease in the percentage of CH_4 and C_2H_6 from 8.5 and 3% to 5 and 1.5% over the presence of olivine and catalyst, respectively, proves that the formation of the products proceeds via the same reaction pathways as in the case of the simple model compounds. Specifically, decomposition reactions unavoidably take place to some extent and subsequently it is possible, depending on the catalytic material used, for partial or full reforming of the decomposition products and the rest of the bio-oil to take place. The percentage of H_2 in the gas products further increases to 48% upon complete removal of O_2 from the inlet of the reactor. The simultaneous decrease of CO_2 concentration to 10% indicates either a low participation

Table 4. Results of Bio-Oil Aqueous Phase Reforming at $850\text{ }^{\circ}\text{C}$

	olivine ($\text{O}_2/\text{C} = 0.3$)	Ni/OI-800 ($\text{O}_2/\text{C} = 0.3$)	Ni/OI-800 ($\text{O}_2/\text{C} = 0$)
$\text{S}_\text{C}(\text{CO})$	43.5	57.2	65.1
$\text{S}_\text{C}(\text{CH}_4)$	10.9	7.1	10.7
$\text{S}_\text{C}(\text{CO}_2)$	37.6	31.5	18.2
$\text{S}_\text{C}(\text{C}_2\text{H}_6)$	7.6	4.2	6.0
$\text{S}_\text{C}(\text{C}_2\text{H}_4)$	0.4	0.0	0.0
$\text{S}_\text{H}(\text{H}_2)$	49.4	72.9	72.8
H_2 Yield	16.5	28.9	43.0
X_gas	100.0	100.0	100.0

of the WGS reaction or a low percentage of reforming reactions compared to the maximum possible. Obviously, combustion reactions were responsible for the high CO_2 percentage under the presence of air.

In Table 4, we present the selectivities of gas products for the cases studied, as well as the hydrogen yield and the carbon to gas conversion achieved. The influence of the parameters on the production of hydrogen is evident. The observed change in gas products composition leads to an increase in the yield of hydrogen from 16.5% over olivine and oxygen, to 29% over Ni/OI-800 and oxygen up to 43% over Ni/OI-800 and no oxygen. Hydrogen selectivity follows an equivalent trend, surpassing 70% over the catalyst. The “lost” hydrogen is bound in CH_4 and C_2H_6 , and in smaller percentage C_2H_4 . As commented, the high CO_2 selectivity in the presence of O_2 is attributed to partial oxidation of the organics, a fact that is emphasized by the low value observed during reforming conditions ($\sim 18\%$) and the respectively high CO selectivity (65%). It is obvious that at the present conditions the catalyst lacks in reforming activity.

The study in the fixed bed reactor⁵ had shown a much higher participation of reforming reactions, but at the same time, a much more intense production of coke. In the spouted bed reactor, the production of carbonaceous deposits was practically nonexistent. The concurrent feeding of oxygen, naturally, contributed to the low coke production. However, the role of the fluid dynamic characteristics of the bed is also very important. The fast and efficient mixing between hot particles and cold injected reactants, in conjunction with the continuous cyclic movement of the solids, significantly reduces the accumulation of coke deposits. At the same time, it facilitates their gasification. Carbon, formed in the lower regions of the bed, is transported along with the catalyst to higher bed parts, where various gasifying agents (H_2 , CO_2 , and H_2O) are at high concentrations.¹⁰ Unfortunately, as was made evident, the implementation of a spouted bed in bio-oil reforming imposes restrictions on the mechanical strength of catalytic materials that have an immediate impact on catalytic activity. The group of Dr Chornet at NREL,^{6,33} that has also studied the reforming of bio-oil in a catalytic fluidized bed reactor came to similar conclusions. The researchers developed reforming catalysts using attrition resistant $\alpha\text{-Al}_2\text{O}_3$ carriers supplied by CoorsTek. All of the research catalysts presented higher mechanical strength but lower activity when compared to various commercial reforming catalysts (designed for fixed bed use). Comparable problems in bio-oil gasification led vanRossum et al.⁸ in the introduction of a two stage reactor concept that consists of a sand fluidized bed and a catalytic fixed bed.

The current study revealed that successful reforming of the aqueous phase of bio-oil will significantly depend on efficient processing of all compounds contained in it. Even simple molecules, like ethylene glycol and acetic acid, present different behavior, meaning that a highly active catalyst will be necessary to handle all of the unstable oxygenates and the products of

their decomposition. Although the developed Ni/olivine catalyst is active under applied conditions, the development of more active catalytic materials will only benefit the process. As was discussed previously, a significant percentage of nickel loaded is removed via cold flow spouting prior actual catalytic testing. Interactions between the olivine carrier and Ni during calcination lead to the development of a loosely bound NiO layer and a much more strongly bound layer, well integrated in the olivine structure. The hydrodynamic characteristics of the spouted bed reactor make the development of such higher activity materials even more necessary. For a given combination of spouting gas, solid particles and reactor geometry, stable spouting is observed only over a specific range of gas velocities. Increasing gas velocity leads to transition from static to coherent spouting, bubbling, slugging or simply fluidization.³⁴ A high activity catalyst will provide more flexibility in space velocity choice, a parameter that cannot be chosen freely in spouted bed operation.

4. Conclusions

In this work, we report the experimental work carried out in a pilot scale spouted bed reactor for the reforming of ethylene glycol and acetic acid, used as model compounds of bio-oil, and the aqueous phase of a bio-oil. The implementation of the spouted bed reactor configuration, modified by the use of an injection nozzle, was proven successful, resulting in efficient processing of the organic model compounds. Coke formation, a major problem encountered in most reforming processes, was drastically limited owing to the favorable hydrodynamics of the spouted bed. Ethylene glycol reforming proceeds to a high extent primarily via decomposition followed by reforming of secondary products. Acetic acid reforming leads to higher hydrogen yields under equivalent conditions. At a temperature of 750 °C or higher and a $H_2O/C \geq 3$, the main reactions taking place are reforming and water gas shift, leading to high H_2 selectivity. The calcination temperature during preparation of the Ni/olivine catalysts significantly affects the surface area of the samples and consequently the dispersion of Ni and reforming activity. The suitability of the reactor was further investigated by conducting tests with the aqueous phase of a pine derived bio-oil resulting in full conversion to gases. Even though the Ni/Olivine catalyst presents the necessary mechanical strength for fluidized bed use, the low surface area does not allow the loading of high Ni amounts, thus leading to low reforming activity in the case of the aqueous phase of bio-oil.

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