

Sustainable hydrogen production via reforming of bio-oil model compounds using a novel spouted bed reactor

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Abstract

Hydrogen produced from renewable energy sources can present significant environmental benefits as an alternative to fossil fuels or 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 the particular process. In this paper we continue with the presentation of experimental results employing the novel spouted bed reactor. Aim of the current work is to further investigate the suitability of the reactor in the process. The effect of reaction temperature, steam to carbon ratio in the feed and space velocity was investigated in the presence of a Ni/Olivine catalyst. Runs were conducted with ethylene glycol and acetic acid as representative model compounds of the aqueous phase of bio-oil. Efficient processing of the model compounds was achieved using a specially designed injection nozzle in the entrance of the reactor, in combination with the particular hydrodynamic characteristics of the spouted bed. The organics converted fully towards gases with high selectivity in H₂. Additionally, the known problem of coking was notably avoided. The developed Ni/Olivine catalyst appears to be a suitable catalytic material for the process presenting activity in reforming, anti-coking characteristics and high mechanical strength.

Keywords: hydrogen, bio-oil, reforming, spouted bed reactor, Ni/Olivine catalyst

1. Introduction

Severe pollution of the environment due to the use of conventional fuels, in combination with the concern for the depletion of oil reserves, has led to an intensification of research 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 non-renewable sources, namely natural gas and petroleum fractions (Rostrup-Nielsen, et al., 2002), 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 (~50% of bio-oil) containing mostly the carbohydrate-derived monomeric compounds at a ratio of ~20% organics/~80% water (Czernik, et al., 1997, Piskorz, et al., 1988). Steam reforming of bio-oil appears as a promising route for sustainable hydrogen production.

Pyrolytic lignin is a valuable material, which can be used to produce different chemicals and additives (Kelley, et al., 1997, Samolada, et al., 1994), whereas the aqueous fraction can be steam reformed for hydrogen production. 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 fact that the aqueous phase of bio-oil contains ~80% of water reduces significantly the use of additional water necessary for the steam reforming reaction. The co-reforming of pyrolysis liquids with other bio-based gases containing methane, e.g. landfill gas or anaerobic digester gas (biogas) (Iordanidis, et al., 2006) could further increase hydrogen production in a biomass-based plant.

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 (Kechagiopoulos, et al., 2006) 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-workers (Czernik, et al., 2002) 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 (Davidian, et al., 2007, Iojoiu, et al., 2007). A two-stage reactor concept was presented in another report, 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 (vanRossum, et al., 2007).

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 reactor (Kechagiopoulos, et al., 2007). The implementation of the reactor, modified by the use of a specially designed injection nozzle, was proven successful, resulting in efficient processing of ethylene glycol, used as a model compound of bio-oil. Sand, Olivine and a Ni/Olivine catalyst were tested, with coke formation drastically limited, regardless the particles tested. The favorable hydrodynamics of the spouted bed and especially the rapid and effective mixing between the hot solid particles and the cold injected reactants seemed beneficial in minimizing coke generation. Ni/Olivine appeared to be a suitable catalytic system due to its high mechanical strength and anti-

coking characteristics. Use of the catalyst resulted in the highest hydrogen yield of 80% at 850°C and H₂O/C ratio equal to 4.6. Ni/Olivine performance was attributed to strong nickel-olivine interactions developed during calcination.

However, the suitability of the reactor for the successful reforming of bio-oil must be further investigated by conducting tests in a wide range of operating conditions and model compounds of bio-oil concluding with actual bio-oil. In the current work we continue the evaluation of the spouted bed reactor, presenting further experimental results of reforming of ethylene glycol and acetic acid.

2. Experimental

2.1. Catalyst Preparation and Pretreatment

Natural olivine, provided from Olivinites Macedonia Greece, was used as the support for the nickel catalyst. Its composition corresponds to a mean formula (Mg_{0.9}Fe_{0.1})₂SiO₄, containing also small quantities of MgSiO₃ and iron oxides.

The Ni/Olivine catalyst was prepared by wet impregnation of natural olivine with a solution of Ni(NO₃)₂•6H₂O in de-ionized water so as to obtain a nickel content of 5wt%. After water evaporation in a mild vacuum at 95°C, the samples were dried overnight at 105°C and then calcined under air for 4h at 800°C. Prior testing, catalytic particles were subjected to cold flow spouting to evaluate their resistance to attrition. As explained in more detail elsewhere (Kechagiopoulos, et al., 2007), fines created were, primarily, a loosely bound NiO shell. However, as was seen from SEM/EDS analysis, a thin layer of NiO (~10µm) strongly linked to olivine remained afterwards. 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 250µm – 355µm. Carbon deposits on used samples were examined on a C, H elementary analyzer (LECO-800).

2.2. Experimental Unit

A schematic diagram of the SYNGAS pilot plant facility is presented in Fig. 1. The process control of the fully automated unit is based on an industrial computer control system, which is coordinated by the FIX/MMI software. The reactor made of stainless steel (Fig. 2) 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

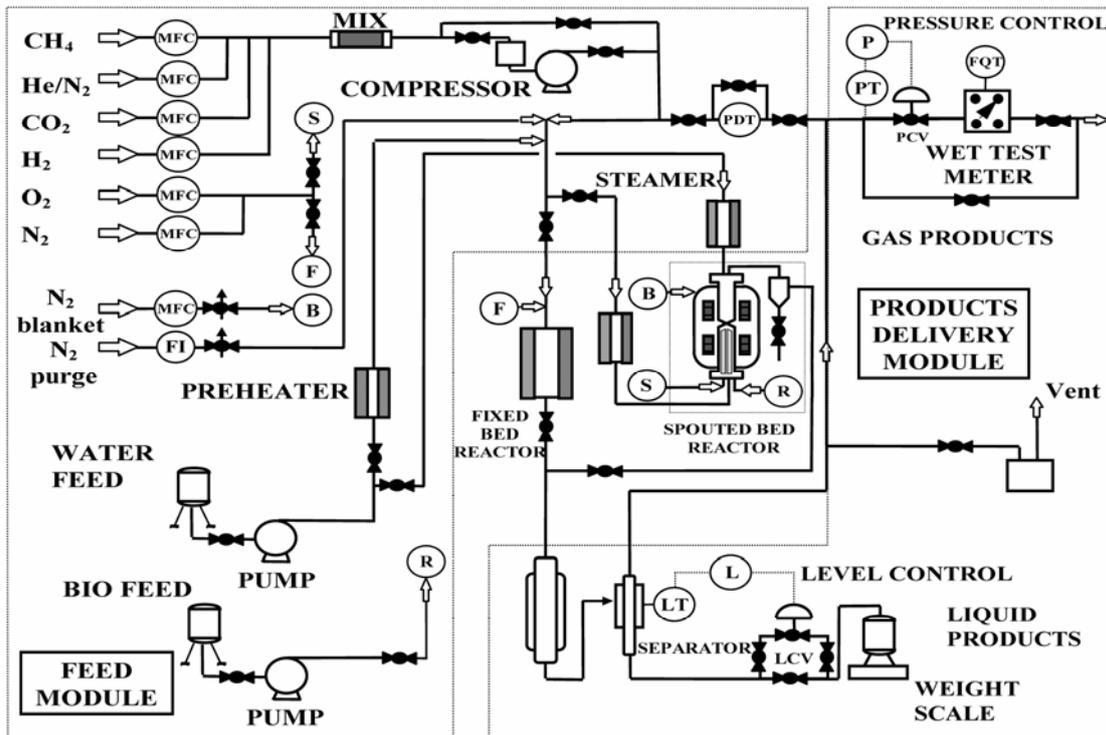


Fig. 1. Simplified flowchart of the SYNGAS pilot plant unit used for the bio-oil reforming study.

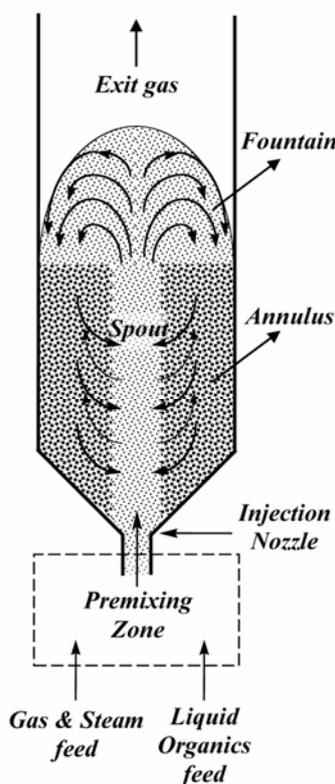


Fig. 2. Schematic diagram of the spouted bed reactor

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 temperature, H_2O/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. The range of experimental conditions used in these sets of experiments is summarized in Table 1. 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.

Table 1. Summary of bio-oil model compounds reforming experimental conditions over Ni/Olivine

| | Ethylene glycol | Acetic acid |
|------------------------------------|-----------------|---------------|
| T (°C) | 650 – 850 | 650 – 850 |
| H ₂ O/C | 4.6 | 0 – 4.6 |
| N ₂ Dilution (% vol.) * | 50 | 95 – 50 |
| Feed flow rate (slpm) | 9 | 9 |
| W/F (g*min/cm ³) | 0.0155 – 0.03 | 0.0155 – 0.03 |

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

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

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

Hydrogen yield:

$$H_2 \text{ Yield} = \frac{\text{moles of hydrogen obtained}}{n \times \text{moles of carbon fed}} \times 100 \quad (2)$$

Selectivity of hydrogen:

$$S_H(H_2) = \frac{\text{moles of hydrogen obtained}}{\text{moles of hydrogen contained in gas products}} \times 100 \quad (3)$$

Selectivity of x carbon containing gas product:

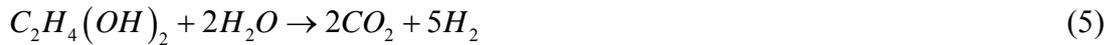
$$S_C(x) = \frac{\text{moles of carbon converted to x compound}}{\text{moles of carbon converted to gas products}} \times 100 \quad (4)$$

where n=2 for acetic acid and 2.5 for ethylene glycol. Carbon balance closure in all tests was in the order of 100±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 (Marquevich, et al., 1999). For ethylene glycol and acetic acid, the two model compounds under study, stoichiometric H₂ yield per mole of carbon input is 2.5 and 2 respectively, as indicated by the following reactions:

* N₂ dilution was varied accordingly to the H₂O/C ratio, so as to maintain a total flow of 9 slpm in the inlet stream for all experiments.



On the other hand, production of syngas can occur only via direct decomposition, as seen in the reactions below:



However, the yield of hydrogen is always lower than the stoichiometric maximum, because two undesirable products, CO and CH₄, are also formed via the water gas shift (9) and methanation (10), 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:



3.1. Ethylene Glycol Reforming

Ethylene glycol, whose concentration in the aqueous fraction of bio-oil can reach up to 2% (Dielbold, 1999), 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. (2006), while reforming using the spouted bed reactor over the Ni/Olivine catalyst was first tested in our previous communication (Kechagiopoulos, et al., 2007). In Fig. 3a we summarize the experimental results obtained in that work, where we can see that in the entire range of temperatures studied, the conversion of ethylene glycol to gaseous products was complete. H₂ and CO_x were the major gaseous products. Selectivity towards C₂H₄ and C₂H₆ was almost zero with only a small percentage of carbon input lost in CH₄. Thus high hydrogen selectivity was achieved averaging at 90-95% depending on temperature. Although results obtained were not enough to claim about the reaction network, thermal reactions and catalytic reforming reactions appear to take place simultaneously and in a way antagonize. Part of ethylene glycol decomposes thermally, while the rest is reformed with steam towards H₂ and CO_x. The catalyst was active enough to reform compounds, such as CH₃CHO, C₂H₄ and C₂H₆, which were the major thermal

products during non-catalytic runs. CH₄ was the only compound, produced via decomposition reactions that made it to the gas products, implying that the concentration of active Ni sites in the catalyst and/or the residence time under our conditions was not high enough to totally reform it.

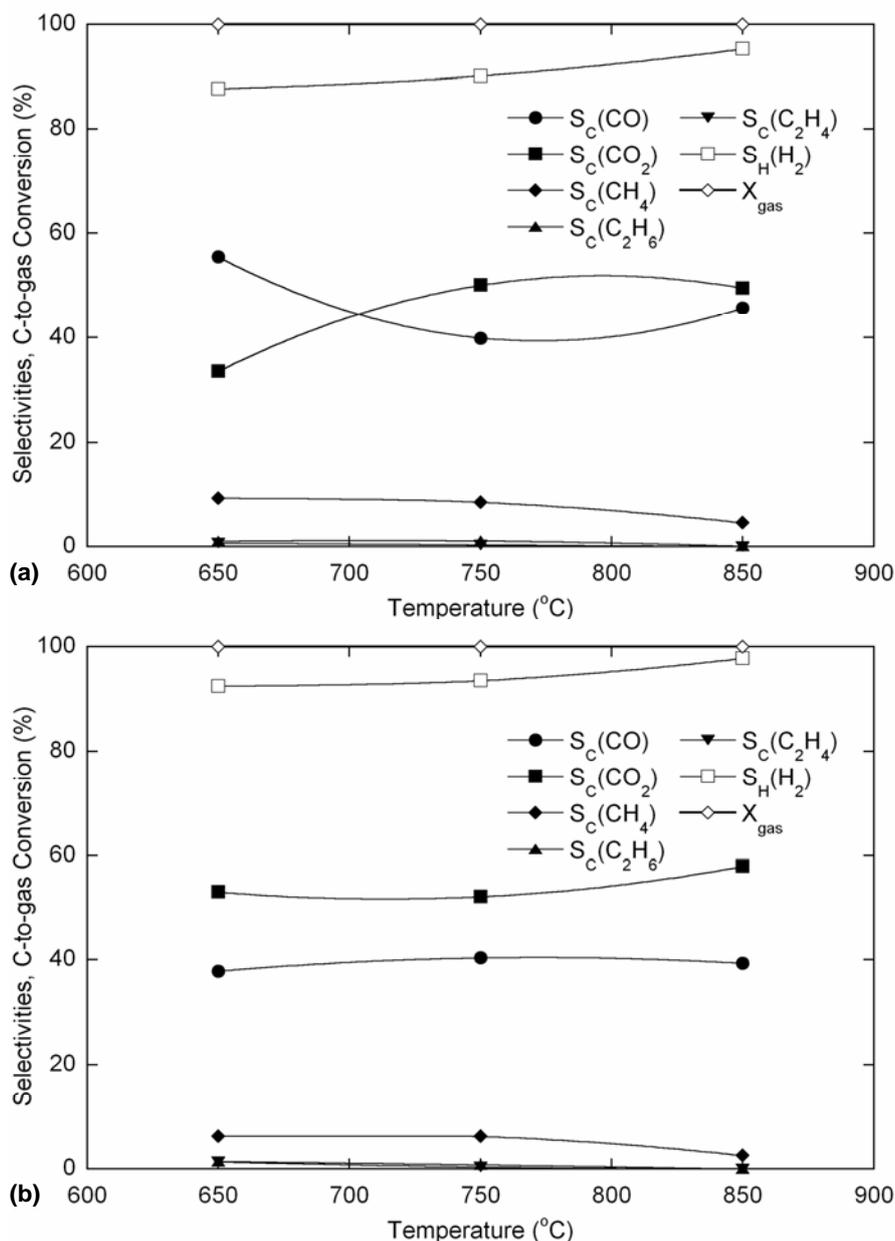


Fig. 3. Ethylene glycol conversion to gas products and their selectivities versus temperature at H₂O/C=4.6 and (a) W/F=0.0155g*min/cm³, (b) W/F=0.03g*min/cm³

Thus, increasing W/F ratio would logically improve conversion of CH₄. The higher contact time provides equivalently more time for the thermal products to react catalytically towards H₂ and carbon oxides. This affects not only CH₄, but also other compounds whose decomposition leads to CH₄. Fig. 3b depicts experimental results of ethylene glycol reforming at increased catalyst loading (W/F=0.03g*min/cm³

instead of $0.0155\text{g}\cdot\text{min}/\text{cm}^3$) with all other conditions identical to Fig. 3a. As expected, conversion of ethylene glycol to gas products is complete, with samples of liquid products free of any organic compounds. CH_4 is again the only hydrocarbon that is 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 favourable reaction time benefited also the water gas shift reaction as can be seen from Fig. 3b. CO_2 selectivity was higher than that of CO in every condition, contrary to what can be observed in Fig. 3a. The promotion of the water gas shift reaction was especially evident at 650°C . The combination of these two effects led to an equivalent increase in H_2 selectivity that ranged from 93% to 98% with increasing temperature.

In Table 2 we present the yield of hydrogen achieved under these two sets of experiments. The beneficial effect of increased contact time is evident in all temperatures. An increase of, roughly, 10% is brought about in production of hydrogen for each respective temperature. The highest hydrogen yield is observed at 850°C using 270g of catalyst, reaching almost 90% of the stoichiometric maximum.

Table 2. H_2 Yield achieved during ethylene glycol reforming at $\text{H}_2\text{O}/\text{C}=4.6$

| Temperature ($^\circ\text{C}$) | $\text{W}/\text{F}=0.0155\text{g}\cdot\text{min}/\text{cm}^3$ | $\text{W}/\text{F}=0.03\text{g}\cdot\text{min}/\text{cm}^3$ |
|----------------------------------|---------------------------------------------------------------|-------------------------------------------------------------|
| 650 | 61,06 | 73,97 |
| 750 | 67,60 | 77,94 |
| 850 | 80,02 | 89,22 |

3.2. Acetic Acid Reforming

The concentration of acetic acid in the aqueous phase of bio-oil can reach up to 12%, so it has been chosen as a model compound for the process of bio-oil reforming by numerous reports in literature (Basagiannis and Verykios, 2006, Galdamez, et al., 2005, Marquevich, et al., 1999, Takanahe, et al., 2006, Takanahe, et al., 2006, Wang, et al., 1997, Wang, et al., 1996). The reforming of acetic acid was evaluated at experimental conditions identical to the ethylene glycol runs and the respective results are presented in Figs. 4a and 4b. 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. At both cases, conversion of acetic acid to gas products was complete with no organic 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 completely zero. However, examination of selectivities of gas products and comparison with the equivalent 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. Selectivity of CO_2 in the gas products is significantly higher than that of CO in all temperatures examined (Fig. 4a). On the contrary, in the case of ethylene glycol production of CO

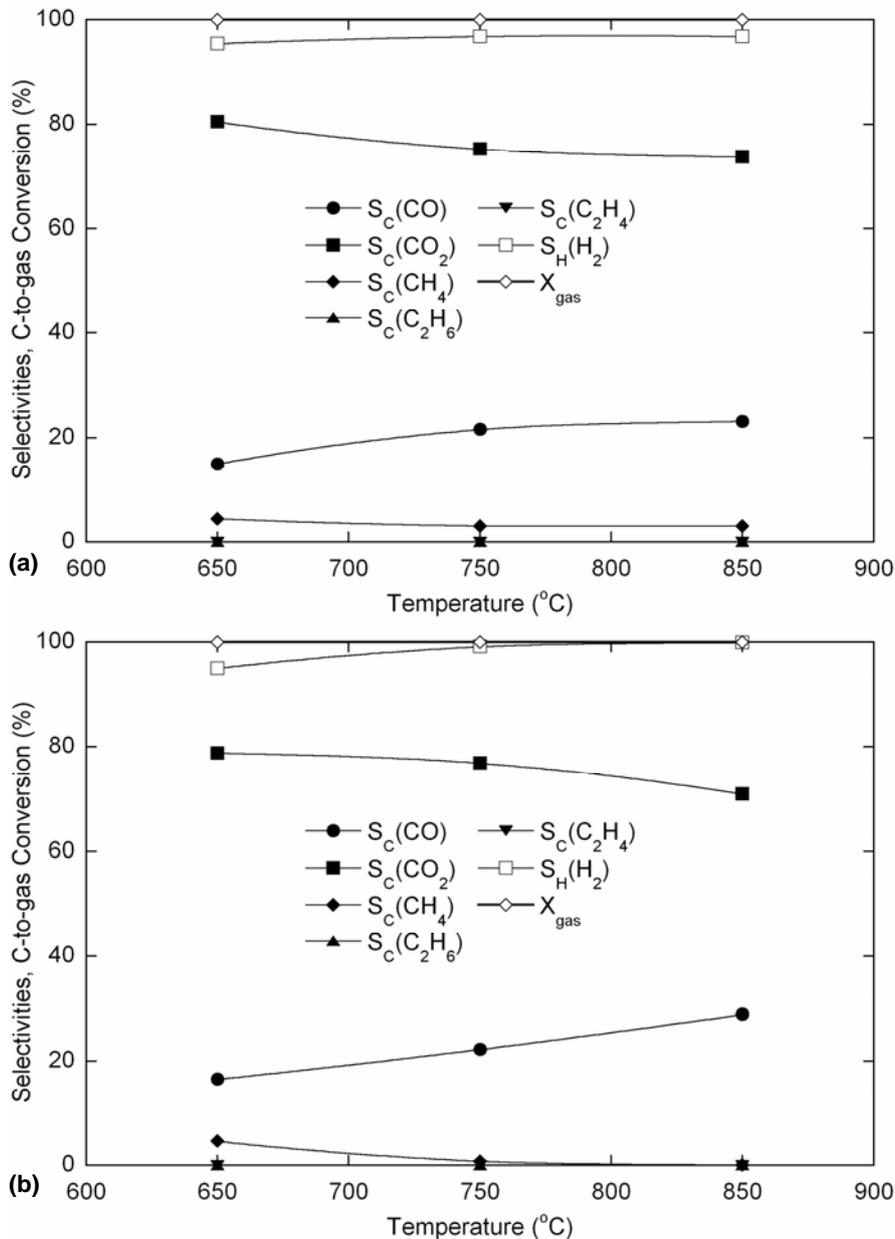


Fig. 4. Acetic acid conversion to gas products and their selectivities versus temperature at $H_2O/C=4.6$ and (a) $W/F=0.0155 \text{ g}\cdot\text{min}/\text{cm}^3$, (b) $W/F=0.03 \text{ g}\cdot\text{min}/\text{cm}^3$

was notably more increased, especially at 650°C , as seen in Fig. 3a. 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 concentration 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 has to take place followed by reforming of secondary products. Acetic acid reforming appears more feasible at all temperatures leading to a lower participation of decomposition reactions. Additional evidence is given upon examination of CH_4 selectivity that ranged from

4.5% to 3% with increasing temperature (as opposed to 10%-5% for the equivalent ethylene glycol runs). As has been discussed in literature (Wheeler, et al., 2004), methanation reactions are not favored thermodynamically at the temperature range studied in our work. The main CH₄ producing reaction must probably be the following decomposition reaction of acetic acid:



further implying the small extent of thermal decomposition. This is in agreement with the work of Basagiannis and Verykios (2006), 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 H₂O/C=3, the dominating reactions are acetic acid reforming (6) and the water gas shift reaction (9). Very high hydrogen selectivity, always above 95%, was subsequently achieved for all temperatures.

Increasing contact time led to further improvement in respect of hydrogen production (Fig. 4b). The high selectivity in production of CO₂ was retained in all temperatures, while more interestingly CH₄ selectivity was practically zero above 750°C and only 4% at 650°C. As was also observed during ethylene glycol reforming, the longer contact time leads to increased reforming of thermal decomposition products, explaining the complete reforming of CH₄. Selectivity in hydrogen above 99% was thus measured at 750°C and above. H₂ yield above 750°C 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.

In our previous communication (Kechagiopoulos, et al., 2007) 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 (Swierczynski, et al., 2006), the Ni/Olivine system possesses noticeable anti-coking characteristics further increasing carbon deposition resistance. Given the afore mentioned 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 H₂O/C ratio in the feed. Although stoichiometrically only a H₂O/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. H₂O/C ratio was varied from 0 to 4.6 at constant temperature equal to 750°C. The respective results are presented in Fig. 5.

A significant influence on products selectivities can be easily observed. Decrease of H₂O/C leads to increase of selectivities of CO and CH₄, with a proportional decrease of CO₂ and H₂ selectivity. The results strongly indicate the increasing participation of decomposition reactions. The direct decomposition of acetic acid towards CO and H₂ via reaction (8) results in a H₂/CO ratio equal to 1, as was the case in our experiments

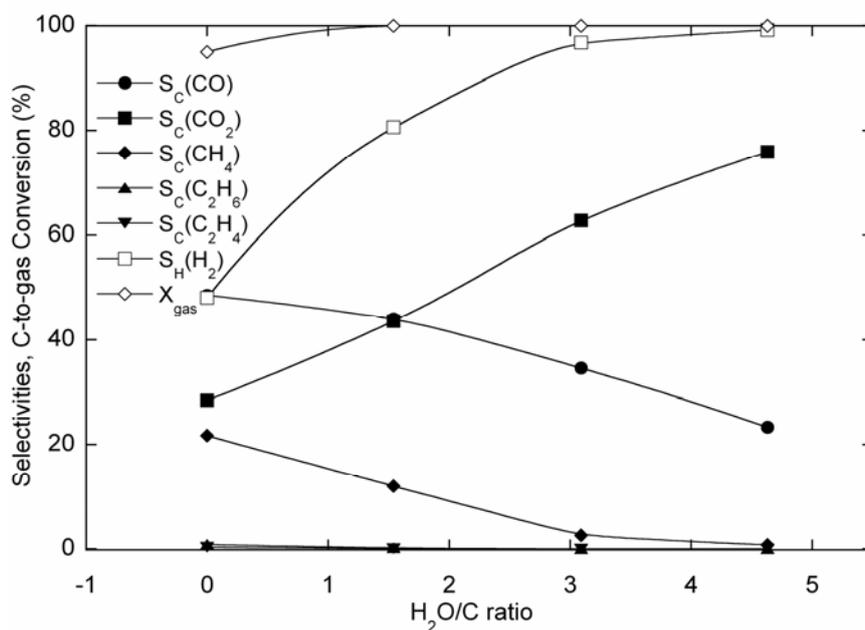


Fig. 5. Acetic acid conversion to gas products and their selectivities versus H₂O/C at T=750°C and W/F=0.03g*min/cm³

for H₂O/C=0, evident of the domination of the reaction at that conditions. On the other hand, the high percentage of CH₄ at lower H₂O/C ratios can be explained by the high extent of reaction (13). The fact that at H₂O/C=0 the concentration of CH₄ was very close to that of CO₂ supports even further this assumption. Of course, the water gas shift reaction participates inevitably in every H₂O/C examined at varying degree, enhancing final composition. From current results we see that at our conditions a H₂O/C ≥ 3 and temperature equal or greater than 750°C are needed to successfully reform acetic acid and achieve high hydrogen selectivity. This is better illustrated by looking at hydrogen yield values achieved depending on H₂O/C ratio, as seen on Table 3. The effect of H₂O/C ratio is determinant on hydrogen production raising its yield from as low as 18% to higher than 93% of the stoichiometric maximum.

Table 3. H₂ Yield achieved during acetic acid reforming at T=750°C and W/F=0.03g*min/cm³

| H ₂ O/C | H ₂ Yield |
|--------------------|----------------------|
| 0 | 18,40 |
| 1.54 | 49,43 |
| 3.1 | 78,64 |
| 4.6 | 93.25 |

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

decomposition. Although, the developed Ni/Olivine catalyst is active in our conditions, the development of higher activity 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. Work is still in progress in increasing the percentage of the strongly bound Ni and understanding the mechanisms that lead to its formation. 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 (Mathur and Epstein, 1974). A high activity catalyst will provide more flexibility in space velocity choice, a parameter that cannot be chosen freely in spouted bed operation. Testing of actual aqueous phase of bio-oil will follow over the Ni/Olivine catalyst, as well as new catalytic materials developed.

4. Conclusions

In this paper we reported the experimental work carried out in a spouted bed reactor for the reforming of ethylene glycol and acetic acid, used as model compounds of bio-oil. The implementation of the spouted bed reactor configuration, modified by the use of a specially designed injection nozzle, was proven successful, resulting in efficient processing of the organics. 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 in high extent primarily via decomposition followed by reforming of secondary products. A highly active catalyst would result in full conversion of ethylene glycol and any thermal products to H₂ and CO_x. Acetic acid reforming, on the other hand, proceeds more smoothly. At a temperature of 750°C or higher and a H₂O/C ≥ 3 the main reactions taking place are reforming and water gas shift, leading to high H₂ selectivity. Ni/Olivine performance, attributed to strong nickel-olivine interactions during calcination, is high under our conditions. However, further work on increasing the amount of strongly bound nickel to the olivine surface is in progress. The suitability of the reactor will be further investigated by conducting tests with actual bio-oil.

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