

Hydrogen Production via Steam Reforming of the Aqueous Phase of Bio-Oil in a Fixed Bed Reactor

Panagiotis N. Kechagiopoulos,^{*,†} Spyros S. Voutetakis,[‡] Angeliki A. Lemonidou,[†] and Iacovos A. Vasalos^{†,‡}

Department of Chemical Engineering, Aristotle University of Thessaloniki, P.O. Box 1517, University City, Thessaloniki 54124, Greece, and Chemical Process Engineering Research Institute, Centre for Research and Technology Hellas, P.O. Box 361, GR 57001, Thessaloniki, Greece

Received February 24, 2006. Revised Manuscript Received June 1, 2006

Hydrogen produced from renewable energy sources is of great interest as an alternative to fossil fuels and as a means for power generation via fuel cells. The aqueous fraction of bio-oil can be effectively reformed to hydrogen-rich streams in the presence of active catalytic materials. In this paper, we present the experimental work carried out in a fixed bed reactor for the reforming of bio-oil. The performance of the reactor was studied at various conditions and compared to the values theoretically predicted by thermodynamic equilibrium. The effect of reaction temperature, steam-to-carbon ratio in the feed, and space velocity was investigated in the presence of a commercial nickel catalyst. Runs were conducted with acetic acid, acetone, and ethylene glycol, representative model compounds of bio-oil, and the aqueous phase of a real bio-oil derived from beech wood. The results of the selected model compounds show that all can be effectively reformed with hydrogen yields up to 90% at reaction temperatures higher than 600 °C and steam-to-carbon ratios higher than 3. The reforming of the aqueous fraction of bio-oil proved to be more difficult, with the hydrogen yield fluctuating at about 60%. The most serious problem encountered in these experiments is coking. The formation of carbonaceous deposits in the upper part of the catalyst zone limits the reforming time and necessitates frequent regeneration of the catalyst.

Introduction

The continuously increasing pressure on the pollution of the environment from the use of conventional fuels, in conjunction with the concern for the depletion of oil reserves, has made it necessary to intensify the search for alternative energy sources. Hydrogen is emerging as the energy carrier of the future, because it can be used as a clean transport fuel as well as a means for the production of electricity via fuel cells. It is thus appearing as an attractive selection for sustainable development. Nowadays, hydrogen is mainly produced from nonrenewable sources. The main hydrogen production processes are steam reforming of natural gas and naphtha and the partial oxidation of heavy oil fractions.^{1–6} The production of hydrogen via any of these conventional processes is accompanied by high CO₂ emissions, which are known to significantly contribute to the greenhouse effect. Steam reforming of methane, which is well-established, is providing the best economics for large-scale production but produces large amounts of CO₂ as a product of the reformer and as flue gas of the reformer burner.

Hydrogen can present environmental benefits only when derived from renewable energy sources. Biomass, a sustainable energy source, does not contribute to net CO₂ emissions if integrated over a long-term growth cycle. However, up to now, the biomass utilization processes such as gasification and pyrolysis have not been mature enough for commercialization.

Steam reforming of pyrolysis oil (bio-oil) is one of the promising routes of hydrogen production from renewable sources. Bio-oil is typically produced via the process of biomass pyrolysis. New developments in the fast pyrolysis techniques make possible the yields of around 75 wt % of anhydrous biomass.^{7–9} Though the composition of the bio-oil is very complex and depends on the types of biomass and the pyrolysis conditions, its main components belong to the following groups: acids, aldehydes, alcohols, ketones, phenols, sugars, and furans.^{10,11} Phenolics are derived from lignin, whereas the rest are mainly products of cellulose and hemicellulose.¹² The thermal depolymerization of cellulose and hemicellulose can yield, depending on the pyrolysis conditions, mainly monomeric

* To whom correspondence should be addressed. Phone: 30-2310-498318. Fax: 30-2310-498380. E-mail: kechagio@cperi.certh.gr.

[†] Aristotle University of Thessaloniki.

[‡] Chemical Process Engineering Research Institute.

(1) Rostrup-Nielsen, J. R.; Sehested, J.; Norskov, J. K. Hydrogen and Synthesis Gas by Steam and CO₂ Reforming. In *Advances in Catalysis*; Gates, B. C., Knözinger, H., Eds.; Academic Press: 2002; Vol. 47, p 65.

(2) Meyer, S.; Hsing, C. *Int. J. Hydrogen Energy* **1989**, *14*, 797–820.

(3) Faur Ghenciu, A. *Curr. Opin. Solid State Mater. Sci.* **2002**, *6*, 389–399.

(4) Brown, F. L. *Int. J. Hydrogen Energy* **2001**, *26*, 381–397.

(5) Seo, Y. S.; Shirley, A.; Kolaczowski, S. T. *J. Power Sources* **2002**, *108*, 213–225.

(6) Avci, A. K.; Ilse Onsan, Z.; Trimm, D. L. *Appl. Catal., A* **2001**, *216*, 243–256.

(7) Dielbold, J.; Scahill, J. W. In *Pyrolysis Oils From Biomass: Producing, Analyzing And Upgrading*; American Chemical Society: Washington, DC, 1988; p 31.

(8) Radlein, D.; Piskorz, J.; Scott, D. S. *J. Anal. Appl. Pyrolysis* **1991**, *19*, 41–63.

(9) Bridgewater, A. V.; Peacocke, G. V. C. *Renewable Sustainable Energy Rev.* **2000**, *4*, 1–73.

(10) Scott, D. S.; Piskorz, J.; Radlein, D. *Ind. Eng. Chem. Process Des. Dev.* **1985**, *24*, 581–588.

(11) Samolada, M. C.; Vasalos, I. A. In *Advances in Thermochemical Biomass Conversion*; Blackie Academic & Professional: Dordrecht, The Netherlands, 1993.

(12) Czernik, S.; Wang, D.; Montane, D.; Chornet, E. In *Developments in Thermochemical Biomass Conversion*; Blackie Academic & Professional: London, 1997; p 672–686.

volatile compounds. On the contrary, lignin depolymerization leads primarily to the production of oligomers. With the addition of water, it is possible to separate the pyrolysis oil into a hydrophobic lignin-derived fraction and an aqueous fraction (~50% bio-oil) containing mostly the carbohydrate-derived monomeric compounds at an approximate organics/water ratio of 20/80.^{12,13}

Pyrolytic lignin is a valuable material that can be used to produce different chemicals and additives,^{15–17} whereas the aqueous fraction can be steam reformed for hydrogen production. This integrated approach presents certain advantages compared to other hydrogen production processes from biomass, such as biomass gasification combined with water-gas shift. Bio-oil, being a liquid, has higher energy density and is easier to transport compared to solid biomass. This means that biomass pyrolysis and bio-oil reforming can occur at different sites. For example, the biomass pyrolysis plant could be situated near the place of agriculture cultivation, whereas the hydrogen production plant could be at the site of power generation or near the existing infrastructure for hydrogen use. Moreover, the fact that the aqueous phase of bio-oil contains ~80% water significantly reduces the need to use additional water for the steam-reforming reaction. A further increase in the hydrogen production in a biomass-based plant can be derived from co-reforming of pyrolysis liquids with other bio-based gases containing methane, e.g., landfill gas or anaerobic digester gas (biogas).¹⁸

Steam reforming of bio-oil or a bio-oil/biogas mixture is characterized with all the difficulties typical for most hydrocarbon reforming processes: high operating temperatures, formation of carbonaceous deposits, heat supply to the endothermic reaction, rather high CO and CO₂ content, etc. Additionally, problems originating from its extremely heterogeneous composition, including different components requiring different catalyst and operating conditions and pronounced thermal decomposition of various oxygenates leading to coke formation and catalyst deactivation, have to be faced.

The catalytic reforming of biomass pyrolysis-derived liquids has attracted some research interest recently, mainly by the Chornet group.^{19–24} The available publications in the literature so far could be categorized into those that focus on the reforming

of model compounds, predominantly acetic acid,^{19–21,25,26} and those that also use real bio-oil or its aqueous phase.^{22–24,27} For temperatures higher than 650 °C and a H₂O/C ratio higher than 5, conversion of acetic acid was complete. The most important problems encountered were severe catalyst deactivation and the reactor plugging because of coke deposition. In the case of the reforming of real bio-oil, these problems were even more serious and restricted the reaction time substantially. It was concluded by Chornet and co-workers²³ that a fluidized bed would be more suitable for the reforming of bio-oil, a suggestion also followed by Galdamez et al.²⁵ Until now, though, the work in this field was conducted in microreactors or bench scale setups. Results obtained with pilot plant units could be more reliably compared with established processes such as methane reforming. The viability of the proposed process largely depends on long-term stability at conditions close to current state of the art. Such assessments can be made only using pilot scale setups. It was thus decided to conduct pilot scale fixed bed reactor experiments to provide a solid comparison with conventional reforming processes, as well as with the already published lab scale findings.

We report here the results of the reforming of bio-oil model compounds and the aqueous fraction of a bio-oil derived from beech wood in a pilot plant unit employing reaction conditions similar to those industrially used in methane reforming with special emphasis on stability at these conditions.

SYNGAS Pilot Plant Unit

A schematic diagram of the SYNGAS pilot plant facility is presented in Figure 1. The unit is fully automated and can support a fixed-bed or a spouted-bed reactor under conditions covering both low- and high-pressure operation and temperatures up to 1050 °C.^{28,29} A description of the unit is given below.

Liquid and Gas Delivery. Two high-precision, computer-controlled syringe pumps deliver distilled water and the organic feed to the preheater at the system pressure. The two liquid streams are mixed before entering the preheater, whereas there is also the option of bypassing the preheater. The gas feed comprises two streams that are admitted to the reactor by separate lines.

Product Stream. The reactor effluent is cooled in a single-pass tube heat exchanger and subsequently fed to the gas–liquid separator equipped with a level control valve. The liquid product is collected in a vessel residing on top of a computer-interfaced electronic balance. A valve after the gas–liquid separator allows for the collection of liquid samples, which are analyzed offline in a Varian 3300 gas chromatograph using a FFAP capillary column and a flame ionization detector. The total gas flow out is recorded by means of a wet test meter with a digital interface. Part of the gas outlet is delivered to an online gas chromatograph (HP 6890) for analysis. Three columns (Porapak N, Molecular Sieve 5A, and Rt-Qplot) in series-bypass configuration and two detectors (thermal conductivity and flame ionization) were used for the analysis of gases. The pressure of the unit is adjusted by a pressure control valve manipulated by the process computer.

(13) Piskorz, J.; Scott, D. S.; Radlein, D. In *Pyrolysis Oils from Biomass: Producing, Analyzing and Upgrading*; American Chemical Society: Washington, D.C., 1988; p 167.

(14) Reference removed in proof.

(15) Samolada, M. C.; Patiaka, D. T.; Grigoriadou, E.; Vasalos, I. A. *The Direct Catalytic Methylation of the Phenolic Fraction of Biomass Flash Pyrolysis Liquids for the Production of Gasoline Blending Components*; Pergamon: Oxford, U.K., 1994; Vol. 3, p 1881.

(16) Kelley, S. S.; Wang, X. M.; Myers, M. D.; Johnson, D. K.; Scabill, J. W. In *Developments in Thermocatalytic Biomass Conversion*; Blackie Academic & Professional: London, 1997; p 557.

(17) Shabtai, J.; Zmierzak, W.; Chornet, E. In *Making a Business from Biomass in Energy, Environment, Chemicals, Fibers and Materials*, 3rd Biomass Conference of the Americas, Montreal, QB, Aug 25–28, 1997; Overend, R. P., Chornet, E., Eds.; Pergamon Press: Montreal, QB, 1997; pp 1037–1040.

(18) Iordanidis, A. A.; Kechagiopoulos, P. N.; Voutetakis, S. S.; Lemonidou, A. A.; Vasalos, I. A. *Int. J. Hydrogen Energy* **2006**, *31*, 1058–1065.

(19) Wang, D.; Montane, D.; Chornet, E. *Appl. Catal. A* **1996**, *143*, 245–270.

(20) Wang, D.; Czernik, S.; Montane, D.; Mann, M.; Chornet, E. *Ind. Eng. Chem. Res.* **1997**, *36*, 1507–1518.

(21) Marquovich, M.; Czernik, S.; Chornet, E.; Montane, D. *Energy Fuels* **1999**, *13*, 1160–1166.

(22) Garcia, L.; French, R.; Czernik, S.; Chornet, E. *Appl. Catal. A* **2000**, *201*, 225–239.

(23) Czernik, S.; French, R.; Feik, C.; Chornet, E. *Ind. Eng. Chem. Res.* **2002**, *41*, 4209–4215.

(24) Wang, D.; Czernik, S.; Chornet, E. *Energy Fuels* **1998**, *12*, 19–24.

(25) Galdamez, J. R.; Garcia, L.; Bilbao, R. *Energy Fuels* **2005**, *19*, 1133–1142.

(26) Takanabe, K.; Aika, K.; Seshan, K.; Lefferts, L. *J. Catal.* **2004**, *227*, 101–108.

(27) Rioche, C.; Kulkarni, S.; Meunier, M.; Breen, J.; Burch, R. *Appl. Catal. B* **2005**, *61*, 130–139.

(28) Voutetakis, S. S.; Tjatzopoulos, G. J.; Vasalos, I. A.; Olsbye, U. *Stud. Surf. Sci. Catal.* **1998**, *119*, 807–812.

(29) Marnasidou, K. G.; Voutetakis, S. S.; Tjatzopoulos, G. J.; Vasalos, I. A. *Chem. Eng. Sci.* **1999**, *54*, 3691.

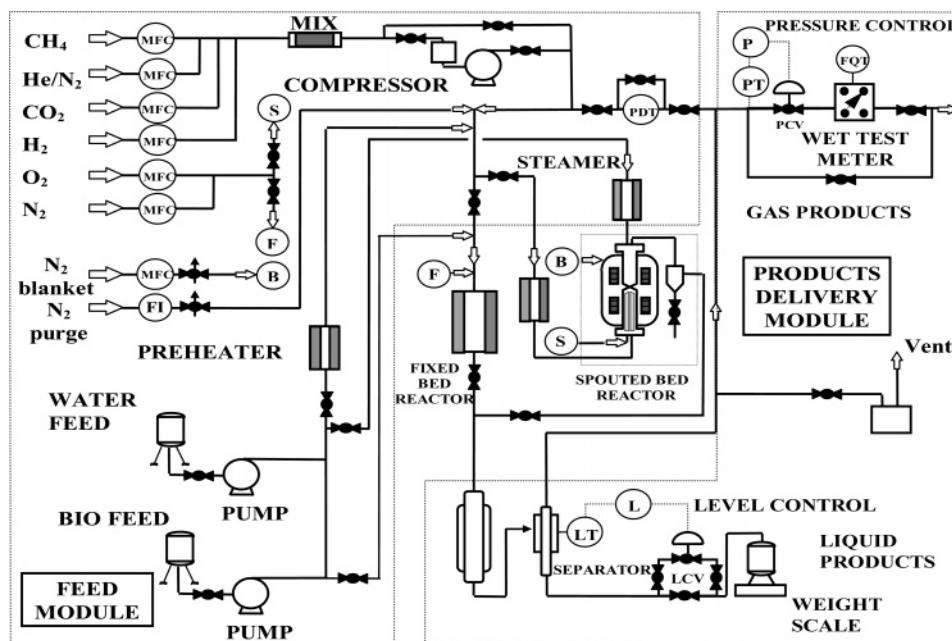


Figure 1. Simplified flowchart of the SYNGAS pilot plant unit used for the bio-oil reforming study.

Table 1. Characteristics of the Commercial Catalyst C11-NK Supplied by Süd-Chemie

NiO (wt %)	25
K ₂ O (wt %)	8.5
carrier	CaAl ₂ O ₄
ρ (kg/m ³)	1000.0

Reactor. The fixed bed reactor is made of high-temperature stainless steel. The internal surface of the reactor is covered with a special alumina-based layer to minimize the catalytic effect of the metal. A thermowell is inserted through its base union axially in order to monitor the temperature profile of the catalytic bed. The reactor has a total length of 71.2 cm and an internal diameter of 12.52 mm, whereas the outside diameter of the thermowell is 3.18 mm. Reduction of the internal volume can be achieved by inserting a tube as a deadman at the base of the reactor. The reactor is heated electrically by a three-zone furnace. The temperature of each zone is controlled independently.

Unit Automation. The process control of the unit is based on an industrial computer-control system, which is coordinated by FIX/MMI software. The system collects the values of the inputs and drives the output signals while maintaining a detailed digital time record of all signals. The state of the unit is displayed online on a PC screen in the form of a simplified process flow sheet. The control system drives the gas flow rates, relieves the process lines, and controls all temperatures. Software and hardware shutdown actions are implemented into alarming procedures.

Experimental Section

Catalyst. The catalyst used for the reforming in the framework of this study was an industrial Ni-based catalyst supplied by Süd-Chemie (C11-NK) used in naphtha reforming. Catalyst particles were crushed and sieved in order to get a particle size of 180–500 μ m. All samples were reduced in situ before testing in a hydrogen flow at 750 °C for 1 h. Selected characteristics of the catalyst are given in Table 1.

Testing Conditions. The experiments were performed in the fixed bed reactor, using constant weight of catalyst and pressure (1 barg); the operating parameters varied were the temperature, H₂O/C ratio in the feed, and the flow of the reactants. Three model

Table 2. Bio-oil Steam Reforming Experimental Conditions

	ethylene glycol	acetone	mixture	bio-oil
<i>T</i> (°C)	600–700	600–750	650–750	600–900
H ₂ O/C	2–6	3–6	3–6	8.2
<i>G</i> _{C1HSV} (h ^{−1})	1500	1500	1500	300–600

compounds were chosen for investigation: acetic acid (99.7%, Panreac), acetone (99.5%, J. T. Baker), and ethylene glycol (99.7%, Prolabo). Experiments were conducted with acetone and ethylene glycol separately, as well as with an equimolar mixture of the three compounds. The aqueous fraction of a bio-oil derived from catalytic pyrolysis of beech wood was also tested. The range of experimental conditions used in this set of experiments is summarized in Table 2. The gas hourly space velocity *G*_{C1HSV} presented in the table is defined as the volume of gas C₁-equivalent species in the feed at standard temperature and pressure per unit volume of catalyst per hour.

Reactor Loading. The catalyst particles were mixed with silicon carbide of 400 μ m average size, so as to have a 1:1 volumetric dilution in the catalytic bed. Quartz wool was placed at both ends of the bed to hold the catalyst in the tube. In the model compound reforming experiments, the catalytic bed was positioned accordingly to the second zone of the furnace. The pre- and postcatalyst part of the reactor was filled with inert SiC. Quartz wool was used to support the loading material. In the bio-oil aqueous fraction reforming experiments, the bed was positioned in the first zone of the furnace. The metallic rod was inserted at the post-catalyst volume of the reactor, to reduce the pressure drop inside the reactor.

Coke Measurements. Thermogravimetric analysis–differential scanning calorimetry (TGA–DSC) (SDT 2960, TA Instruments) was conducted to examine carbon deposits on samples of used catalyst using an air flow and a heating rate of 10 °C/min from room temperature to 1000 °C. The same samples were also examined in a C, H elementary analyzer (LECO-800). Finally, in situ combustion of carbonaceous deposits at a minimum temperature of 700 °C was used as a catalyst regeneration procedure, as well as a means for the calculation of coke deposited on the catalyst. Carbon oxides released during combustion were measured with online GC and integrated through time to give the amount of coke.

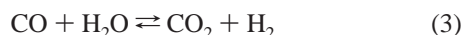
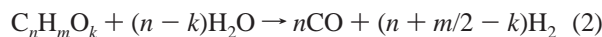
Results and Discussion

The aqueous fraction of bio-oil is a complex mixture of oxygenated compounds, which can be classified into the main

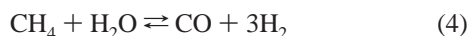
categories of acids, alcohols, aldehydes, and ketones.²¹ For an oxygenated compound with a chemical formula $C_nH_mO_k$, the stoichiometric steam reforming reaction



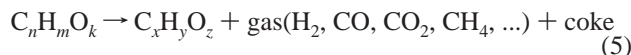
yields $2 + m/2n - k/n$ moles of hydrogen per mole of carbon input. This reaction is actually the sum of the steam reforming (reaction 2) and the water-gas shift (reaction 3)



For acetic acid, acetone, and ethylene glycol, the three model compounds under study, the stoichiometric H_2 yield per mole of carbon input is 2, 2.67, and 2.50, respectively. Methane reforming, as can be seen from reaction 4 when combined with reaction 3, has a hydrogen yield equal to 4, providing the highest yield compared to all feedstocks.



In actual conditions, though, the yield of hydrogen is lower than the stoichiometric maximum, because two undesirable products, CO and CH_4 , are also formed via the water gas shift (reaction 3) and methanation (reverse of reaction 4) reactions and/or thermal decomposition reactions. Thermal decomposition of the organic compounds contained in the bio-oil is an important factor in the performance of the process. Coking not only leads to lower hydrogen yields but also causes severe catalyst deactivation and reactor blockage. Many of these compounds, especially anhydrosugars,³⁰ are thermally unstable at the temperatures required for steam reforming, so that steam reforming reaction 1 competes with thermal decomposition reactions



Thermodynamic equilibrium calculations using the commercial simulation package PRO/II by SimSci showed that the representative bio-oil compounds are fully reformed even at very low temperatures (Figure 2). The steam-to-carbon ratio, temperature, and pressure are very important parameters affecting hydrogen formation. Higher H_2O/C ratios favor the hydrogen yield, whereas a lower hydrogen yield is observed with increasing pressure. Temperature generally leads to a maximum in hydrogen yield between 600 and 750 °C. The hydrogen yield, depending on the conditions chosen, can reach as high as 90% of the stoichiometric maximum. The addition of a WGS reactor after the reforming reactor, to convert CO via reaction 3, can push the hydrogen yield to almost 100%, with only minor amounts of hydrogen lost to CH_4 .

Ethylene Glycol Reforming. Ethylene glycol was chosen in our study as a model compound for the alcohols contained in the aqueous phase of bio-oil. The C11-NK catalyst, which has been used with positive performance in the reforming of bio-oil by Czernik et al.²³ as well as for the reforming of "trap grease"³¹ and plastics,^{32,33} was very active in reforming ethylene

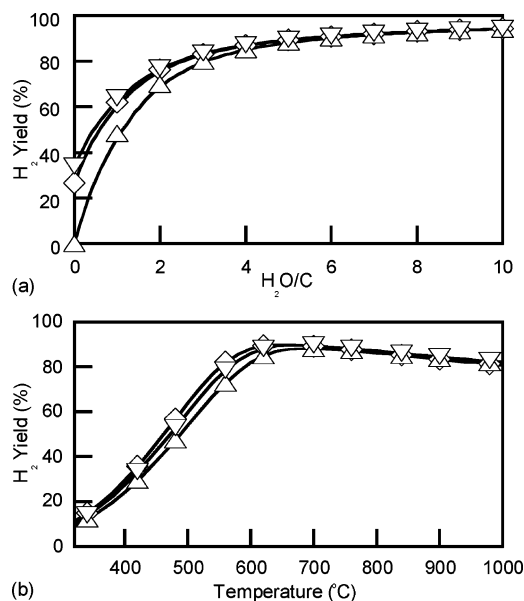


Figure 2. Equilibrium H_2 yield for the model compounds vs (a) H_2O/C ratio at $T = 700$ °C and (b) temperature at $H_2O/C = 5$ (▽, ethylene glycol; ◇, acetic acid; △, acetone).

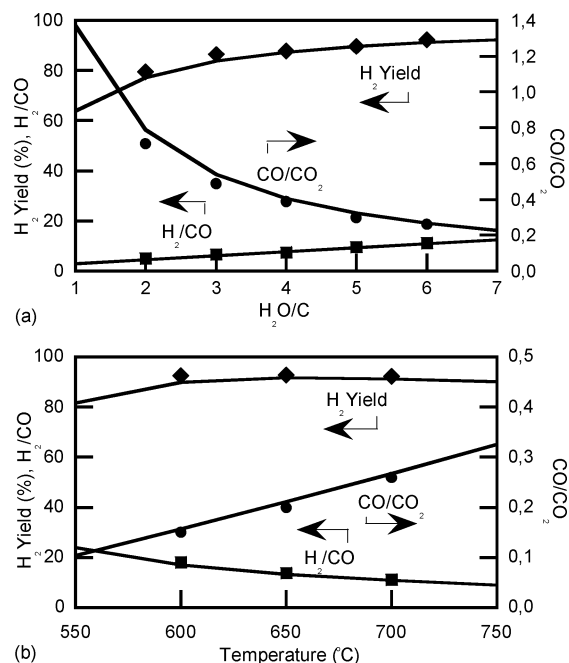


Figure 3. H_2 yield and gas product composition for steam reforming of ethylene glycol at (a) $T = 700$ °C and (b) $H_2O/C = 6$, $G_{C11HSV} = 1500$ h⁻¹ (lines represent equilibrium).

glycol, with complete conversion attained for all the conditions studied. The main advantage of the catalyst compared to other commercial Ni catalysts is its high K content, which is known to suppress coke formation by increasing its gasification.^{34,35} The only products detected were H_2 , CO, CO_2 , and CH_4 . The hydrogen yield produced from ethylene glycol reforming is presented as a function of the steam-to-carbon ratio and temperature in panels a and b, respectively, of Figure 3. The equilibrium values for the equivalent conditions are also presented as lines for comparison. As expected, higher H_2O/C ratios favor hydrogen and carbon dioxide production. On the

(30) Antal, M. J. *Advances in Solar Energy*; Solar Energy Society: New York, 1982; p 61.

(31) Czernik, S.; French, R.; Magrini-Bair, K.; Chornet, E. *Energy Fuels* **2004**, *18*, 1738–1743.

(32) Tsuji, T.; Okajima, S.; Sasaki, A.; Masuda, T. *J. Chem. Eng. Jpn.* **2005**, *38*, 859–864.

(33) Czernik, S.; French, R. J. *Energy Fuels* **2006**, *20*, 754–758.

(34) Rostrup-Nielsen, J. R. *Catalysis, Science and Technology*; Springer: Berlin, 1984.

(35) Twigg, M. V. *Catalyst Handbook*, 2nd ed.; Wolfe: London, 1989.

contrary, an increase in temperature reduces the production of carbon dioxide, because the equilibrium of the water-gas shift reaction is shifted to the left. The approach to equilibrium for all of the conditions studied is very good with hydrogen yield always well above 80%. At the most favorable reaction conditions, at 700 °C and a H_2O/C ratio of 6, the production of hydrogen approached 93% of the amount stoichiometrically possible. Small amounts of methane were also produced. Methane selectivity, expressed as the percentage of the methane carbon atoms contained in the gas product stream to the total carbon atoms in the gas product stream, dropped from 3.1 to 0.7% with an increase in the H_2O/C ratio from 2 to 6 at 700 °C, whereas a decrease in the temperature to 600 °C raised the value back to 3%. Mass balance closure for hydrogen and oxygen was on the order of $100 \pm 3\%$, whereas for carbon, it fluctuated around $97 \pm 3\%$, which is evidence that a small amount of carbon is lost in coke deposits.

The coking tendency of the oxygenated compound is highly dependent on the operating variables. Experiments were terminated because of reactor blockage for H_2O/C ratios less than 3 after approximately 7 h. Temperature-variation experiments proceeded more smoothly. Coke formation was noticeably smaller even for the lowest temperatures because of the high H_2O/C ratio (6) that was used. An excess of steam is known to be beneficial to the suppression of coking, because it leads to partial gasification of the carbon formed.³⁴ We managed to sustain a continuous run, even at a temperature of 600 °C, for more than 12 h.

Analysis of the liquid samples showed that ethylene glycol conversion was complete in the entire range of the experimental conditions used. Carbon deposits were removed after every experiment with air via in situ combustion. The activity of the catalyst was fully regained after this regeneration process.

Model Compound Mixture Reforming. To better simulate the features of bio-oil, we prepared an equimolar mixture of three oxygen-containing model compounds. Acids were represented by acetic acid and alcohols by ethylene glycol, whereas acetone was chosen to model the carbonyl-containing compounds (ketones and aldehydes). The results obtained for variable H_2O/C ratios and reaction temperatures are depicted in panels a and b, respectively, of Figure 4. Equilibrium product composition was attained under all the conditions used. The effect of the operating variables on the composition of the products is similar to what we observed in the ethylene glycol experiments. An increase in the H_2O/C ratio results in a reduction of carbon monoxide, whereas the opposite effect is observed in the case of a temperature increase. A hydrogen yield as high as 90% is attained with the catalyst being able to completely convert the organic compounds, effectively catalyzing the reforming and water-gas shift reactions. Methane production averaged at the same levels as in the case of ethylene glycol. At a temperature of 750 °C and a H_2O/C ratio of 6, conversion of the organics to methane was minimal, with a methane selectivity of less than 0.1%. Steady runs in every experimental condition lasted for more than 4 h. However, it was observed that coke formation was higher compared to ethylene glycol for the same conditions. Significant amounts of coke were deposited in the first zone of the reactor. As previously mentioned, the catalytic bed was positioned accordingly to the second zone of the furnace, with the part corresponding to the first zone filled with inert SiC. The temperature settings of the two zones were kept the same, in an attempt to have a more uniform temperature profile in the bed. This led, however, to thermal decomposition of the organics prior to

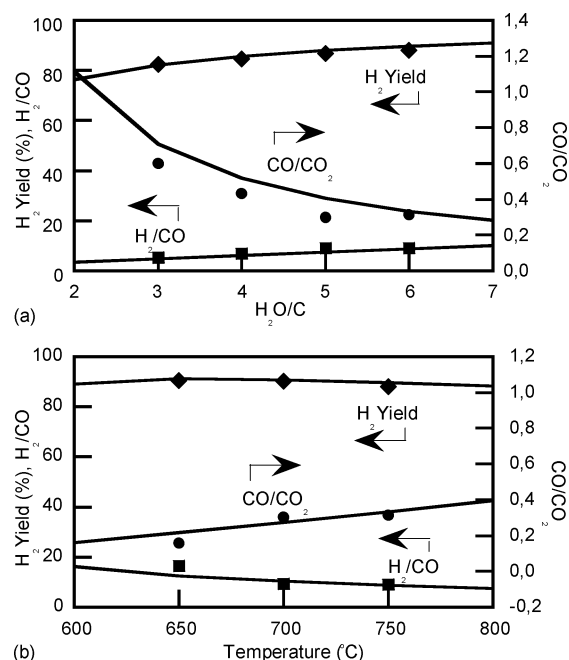


Figure 4. H_2 yield and gas product composition for steam reforming of the model compound mixture at (a) $T = 750$ °C and (b) $H_2O/C = 6$, $G_{CHSV} = 1500$ h^{-1} (lines represent equilibrium).

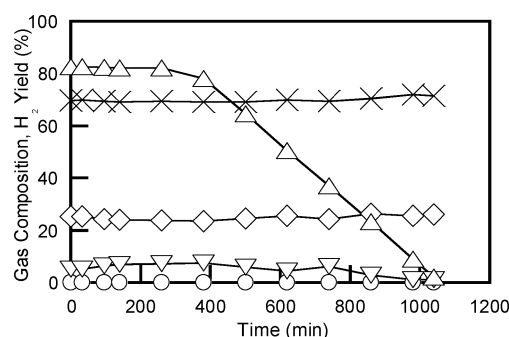


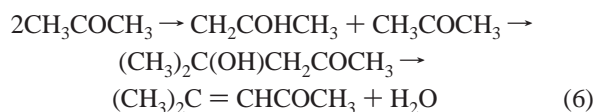
Figure 5. Time-dependent concentration profiles (% mole fraction) and H_2 yield (% stoichiometric) during reforming of the three-component mixture at 750 °C and $H_2O/C = 6$ (Δ , H_2 yield; \times , H_2 ; \diamond , CO_2 ; ∇ , CO ; \circ , CH_4).

entering the bed. By decreasing the temperature of this zone to 550 °C, we drastically reduced coke formation in this part of the reactor. Nonetheless, it was still evident in the catalytic bed.

The above indicate that the reforming of oxygenated compounds competes with thermal decomposition reactions that take place in the gas phase and cannot be totally avoided. On the other hand, cracking reactions on the acidic sites on the support of the catalyst also lead to coke deposits.²⁴ Coke formed via these pathways builds up in the reactor, leading to plugging and deactivation of the catalyst. This affects the long term activity of the catalyst, as can be clearly seen in Figure 5 where we present the time dependent profiles of gas composition and H_2 yield for the reforming of the model compound mixture. The reaction proceeds smoothly for the first 4 h of operation. The H_2 yield is higher than 80% of the stoichiometric possible with the composition of the gas products closely following thermodynamic equilibrium. A gradual drop in the yield of hydrogen is observed after 4 h time on stream (TOS) because of gradual deactivation of the catalyst. After 17 h on stream, the activity of the catalyst is completely lost. Sintering can be ruled out as the cause of deactivation, because catalyst activity was fully restorable after removal of the coke deposits and reduction of the catalyst. Thermogravimetric analysis of these

deposits showed that a temperature higher than 600 °C was necessary for the burning of coke. C, H elementary analysis did not detect any measurable amount of hydrogen. Both of these results suggest that the carbon formed is of graphitic type. Interestingly, the composition of the gaseous products remains invariable throughout the whole experiment, even though the carbon-to-gas conversion decreases.

Acetone Reforming. Coke formation during reforming of the three-component mixture was noticeably increased compared to the ethylene glycol experiments. It has been shown by Markevich et al. that in the temperature ranges covered in this study ($T > 650$ °C), acetic acid reforming proceeds without substantial coke deposits.²¹ On the other hand, acetone is known to undergo aldol condensation reactions at low temperatures under catalytic conditions, forming products such as mesityl oxide.³⁶



This reaction could take place at the lower temperatures that exist at the upper part of the catalytic bed. Ketene is another possible byproduct formed via the decomposition of acetone



Both compounds (ketene and mesityl oxide) can undergo oligomerization,^{19,26} forming deposits on the catalyst and leading to deactivation. In the recent work of Takanabe et al.,³⁷ it was suggested that the deactivation observed during acetic acid reforming at 600 °C was mainly due to the formation of acetone. It was proposed by the authors that the observed coke deposits were mainly due to the condensation of this intermediate product that led to mesityl oxide and isobutene. Thus, acetone being more susceptible for coke formation could be the reason for the higher carbon formation observed in the three-component mixture experiments compared to ethylene glycol. This was validated in a separate set of experiments with acetone as the oxygenated feedstock (panels a and b of Figure 6). At the same experimental conditions, acetone showed increased formation of coke deposits, as evident from the rising differential pressure drop in the reactor during the experiment. As can be seen from the graphs, the approach to equilibrium is good for temperatures higher than 650 °C and $\text{H}_2\text{O}/\text{C}$ ratios higher than 4. Coke formation restricted the time on stream operation to 2 h, under which steady conditions could be attained. Plugging of the reactor necessitated the frequent regeneration of the catalyst via burning of coke. Further analysis of the deposited coke by TG and C, H analyses showed that coke is burned at 550 °C and that the molar ratio of C/H is approximately 30. Again, the high C/H ratio indirectly shows that the carbon formed is of graphitic type. Nonetheless, the conversion of acetone was complete in the entire spectrum of conditions covered under steady operation.

Bio-Oil Aqueous Phase Reforming. Bio-oil produced from the catalytic pyrolysis of beech wood in the framework of the BIOCAT EU research program (ENK6-CT2001-00049) was separated by adding water at a 2/1 mass ratio in order to extract the aqueous fraction. The final aqueous mixture contained 16 wt % organics ($\text{CH}_{2.48}\text{O}_{0.94}$), the rest being water, corresponding to a $\text{H}_2\text{O}/\text{C}$ of 8.2. The steam-reforming experiments of bio-oil

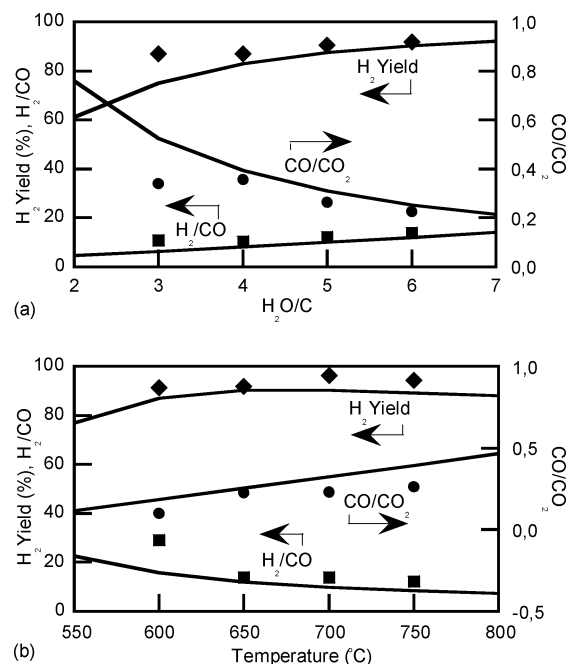


Figure 6. H_2 yield and gas product composition for steam reforming of acetone at (a) $T = 650$ °C and (b) $\text{H}_2\text{O}/\text{C} = 6$, $G_{\text{CHSV}} = 1500$ h^{-1} (lines represent equilibrium).

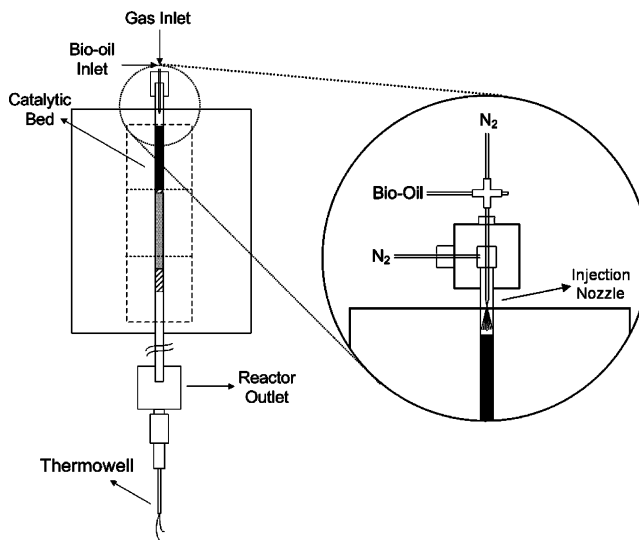


Figure 7. Schematic diagram of the reactor showing the injection system used for the reforming of bio-oil.

model compounds showed that coke formation would probably be an important problem in the reforming of bio-oil. Bio-oils at temperatures higher than 90 °C decompose thermally, forming large amounts of carbonaceous solids.³⁸ To avoid a high extent of thermal decomposition, we installed an injection system in the fixed bed reactor in order to feed the bio-oil at environmental temperature. A high percentage of N₂ dilution was used as an injection agent so as to achieve good atomization of the liquids and fast contact with the catalyst. The schematic diagram of the reactor is illustrated in Figure 7. Nitrogen and the aqueous fraction of the bio-oil are mixed just before their entrance in the reactor, using a proprietary configuration consisting of two nozzles. The mixture is then sprayed via a final nozzle on the

(36) Reichle, W. T. *J. Catal.* **1980**, *63*, 295–306.

(37) Takanabe, K.; Aika, K.-i.; Seshan, K.; Lefferts, L. *Chem. Eng. J.* **2006**, *120*, 133–137.

(38) Dielbold, J. *A Review of the Chemical and Physical Mechanisms of the Storage Stability of Fast Pyrolysis Bio-Oils*; Thermalchemie, Inc.: Lakewood, CO, 1999; p 56.

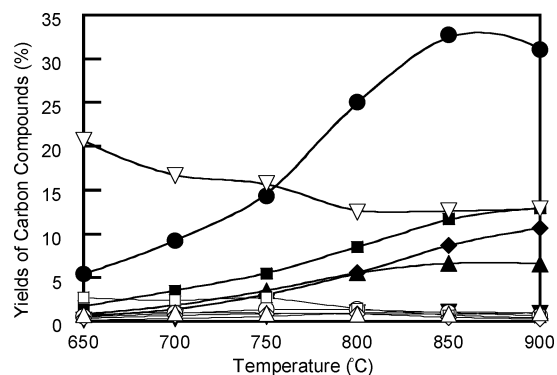


Figure 8. Yields of products on the basis of incoming carbon during noncatalytic reforming of bio-oil (●, CO; ■, CO₂; ◆, CH₄; ▲, C₂H₆; ▼, C₂H₄; ○, C₃; ◇, C₄; □, C₅; △, C₆; ▽, coke) (lines are only visual aids).

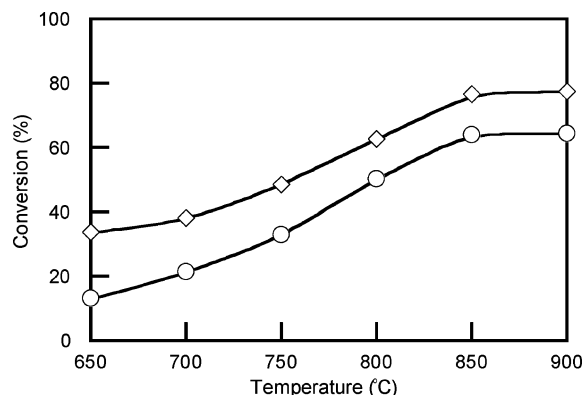


Figure 9. Carbon to gas (○) and total conversion (◇) during noncatalytic reforming of bio-oil (lines are only visual aids).

catalytic bed. A supplemental N₂ side stream helped significantly in keeping the tip of the injection nozzle clean from local carbon depositions.

Noncatalytic Runs. The first series of experiments with bio-oil as a feedstock were conducted in the absence of catalyst in order to investigate the extent of decomposition in the gaseous phase. The thermal decomposition of the bio-oil was investigated at various temperatures at a constant G_{C1}HSV of 500 h⁻¹ and pressure of 1 barg. The tubular reactor was filled with silicon carbide (average size of 400 μm). Carbon deposits in the reactor were removed via oxidation after every experimental condition in order to calculate the carbon percentage converted to coke. The yields on the basis of the carbon contained in the feed for the various carbon-containing compounds in the gas product of the noncatalytic experiments are presented in Figure 8. Figure 9 presents total conversion and carbon-to-gas conversion as a function of reaction temperature. The main products formed were CO, CO₂, CH₄, and C₂H₆. The yields of these products, as can also be seen from the carbon-to-gas conversion, increased with temperature. The conversion of the organics contained in the bio-oil to gaseous products was as low as 12% for 650 °C and increased up to 60% for temperatures higher than 850 °C (Figure 9). The difference between the upper and lower lines represents the amount of solid carbon formed from the decomposition. Coke formation was suppressed partially by the increase in temperature. More than 20% of the incoming carbon was deposited in the catalytic bed as coke at 650 °C, with this number lowering to 12% above 800 °C. Conclusively, the total conversion of the bio-oil spanned from 35 to 80% with increasing temperature. Minor products, such as C₃ to C₆ isomers, were also observed in the gas products at yields less than 1%. Increased yields of C₅ isomers were observed at

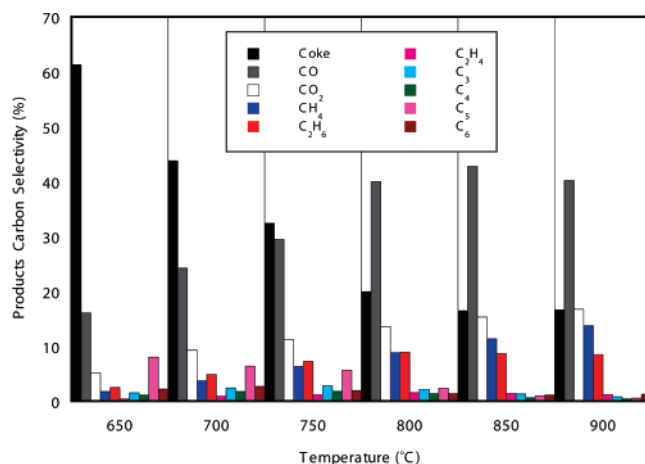


Figure 10. Carbon selectivities of products on the basis of converted carbon during noncatalytic reforming of bio-oil.

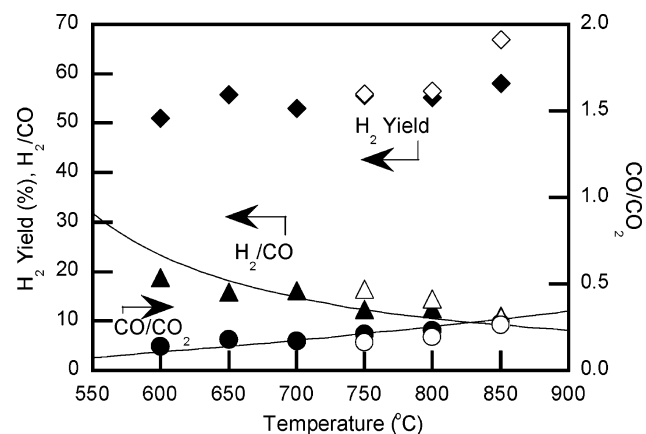


Figure 11. Catalytic reforming of bio-oil: effect of reaction temperature on H₂ yield and gas products composition, G_{C1}HSV = 300 h⁻¹ (filled symbols) and 600 h⁻¹ (open symbols) (lines represent equilibrium).

temperatures lower than 750 °C. Hydrogen was also detected in very small concentrations outside the integration limits of our gas chromatograph.

The variation in the selectivities of the carbon-containing products appears to be very interesting, as illustrated in Figure 10. More than 60% of the converted carbon is deposited as coke in the bed at 650 °C. With increasing temperature, the selectivity of the main gaseous products rises. Carbon oxides, CH₄, and C₂H₆ are the only products, and coke selectivity drops to 15%.

Catalytic Runs. The catalytic tests with bio-oil were performed in the presence of the same catalyst (C11-NK) provided by Süd-Chemie. Because the H₂O/C ratio of the aqueous phase of the bio-oil was already 8.2, it was decided to conduct these experiments without any further addition of external water. The effect of the reaction temperature and G_{C1}HSV of the reactants was evaluated.

To be able to compare the experimental results with the thermodynamic equilibrium, we conducted thermodynamic calculations using a mixture of model compounds. The mixture consisted of the following compounds: acetic acid, acetone, acetaldehyde, ethylene glycol, formic acid, methanol, formaldehyde, and ethanol. The molecular composition of this mixture was properly adjusted to simulate the composition of the aqueous fraction of bio-oil used in these experiments. The experimental results are presented in Figure 11. The yield of hydrogen did not surpass 60% in all of the conditions studied. The highest values were observed at the higher temperatures,

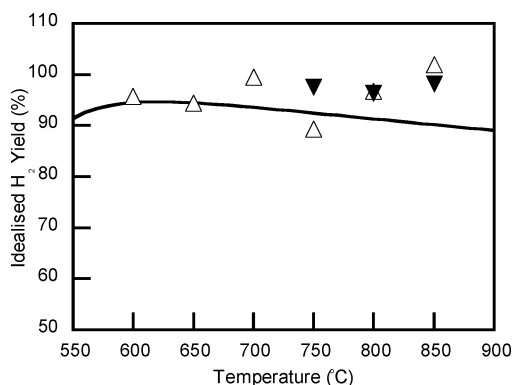


Figure 12. Idealized H_2 yield assuming that incoming carbon moles equal those in the gas product stream, $G_{C1}HSV = 300 \text{ h}^{-1}$ (filled symbols) and 600 h^{-1} (open symbols) (line represents equilibrium).

whereas the flow of the organics did not seem to have a notable influence. According to thermodynamic calculations, the hydrogen yield for these conditions is almost 90%. This deviation can be ascribed to the increased coke formation in the catalytic bed. The formation of carbonaceous deposits was intense under all experimental conditions covered and amounted to around 30 wt % of the incoming carbon. TG analysis of spent catalyst samples showed that coke was burned easier than in the case of model compounds, since a temperature of 450°C was adequate. C, H analysis further indicated the different nature of these carbonaceous deposits. The analysis revealed a C/H molar ratio equal to ~ 3 , suggesting that the structure of coke is more aromatic compared to that of the model compounds, where the results indicated a graphitic nature.

The majority of the experiments lasted for 4 h, followed by regeneration of the catalytic bed. It is worth noting, as can be seen from H_2/CO and CO/CO_2 ratios presented in Figure 11, that the composition of the gaseous products follows the thermodynamically predicted composition well, implying that the reactions of steam reforming and water–gas shift are at equilibrium. This can also be proved by calculating an idealized hydrogen yield by assuming that the incoming carbon moles are equal to the sum of those contained in the gaseous products (Figure 12). It is clear from this diagram that if coking was not existent, the hydrogen yield would be very close to the theoretically predicted value from equilibrium. The possibility that part of the produced hydrogen is due to thermal decomposition reactions (reaction 5) cannot be ruled out; however, on the basis of the experimental results of the noncatalytic runs, it is safe to consider this amount to be very small.

The role of the catalyst in the process is evident if the catalytic results are compared with the equivalent noncatalytic ones. Analysis of the liquid samples collected for every experimental condition did not show any detectable amount of any organic compound, proving that the conversion of bio-oil was complete. On the contrary, as we saw previously, even at 900°C , conversion of bio-oil because of thermal decomposition did not surpass 80%, whereas at 650°C , it was as low as 35%. Carbon oxides and hydrogen were the main gaseous products in the catalytic runs, with only small amounts of methane being observed at a volumetric percentage that did not surpass 1% of the total product for all of the temperatures studied. Additionally, we observed very small production of ethane and ethylene, whose concentrations spanned from 0.1 to 0.5% with increasing temperature. Unlike what we observed during the thermal runs, traces of C_3 , C_4 , and C_5 isomers were detected only at the gas chromatograph for reaction temperatures lower than 650°C . So it is clear that the catalyst is able to reform the majority of

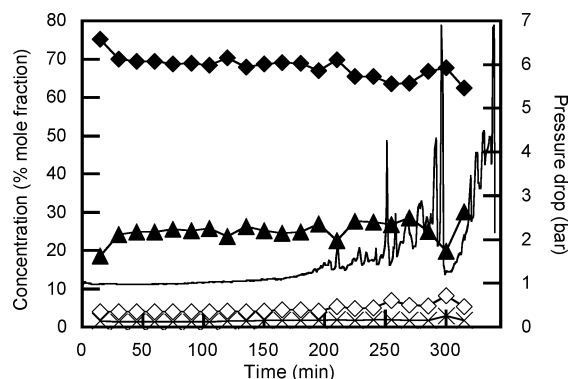


Figure 13. Product composition (% mole fraction) and pressure drop (dP) in the reactor during bio-oil reforming at 700°C (\blacklozenge , H_2 ; \blacktriangle , CO_2 ; \diamond , CO ; \times , CH_4 ; straight line, dP).

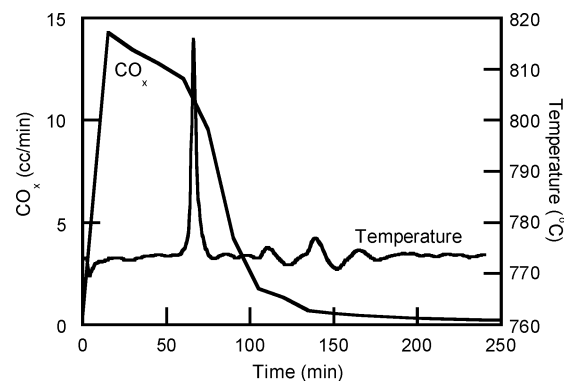


Figure 14. CO_x formed during oxidation of coke deposits after bio-oil reforming at 700°C and temperature as measured at the middle of the catalytic bed.

oxygenates contained in the aqueous phase of bio-oil, along with any other hydrocarbons that the thermal decomposition of bio-oil produces, even at the lowest temperatures studied.

Present results clearly show that the most serious problem encountered in bio-oil reforming using fixed bed reactors is coking. Carbon species arise from the thermal decomposition of oxygenates that takes place in the gas phase and from catalytic reactions. The formation of carbonaceous deposits limits the reforming time and often necessitates regeneration of the catalyst, which afterward regains its initial activity. In a typical experiment (Figure 13), composition of the gas products remains constant following thermodynamic equilibrium very well, whereas the differential pressure drop in the reactor increases steadily, leading to termination of the experiment because of reactor blockage.

As previously stated, coke removal is performed by treating the catalyst bed in an air flow. The amount of coke in the catalytic bed can be calculated from the sum of carbon oxides formed during this process (Figure 14). When integrated, the area under the CO_x curve equals the amount of carbon removed from the reactor. In Figure 14, we also plot the temperature as measured from a thermocouple positioned in the middle of the catalytic bed. It can be seen that the temperature rise, as measured at this point by the exothermic oxidation reaction, occurs later compared to the production of the main volume of carbon oxides. The results suggest that the largest amount of coke deposits is in the upper part of the catalytic bed.

The limitations of the fixed bed reactor in processing complex bio-oils are evident from the current study. The performance of the reactor during simple monomeric model compound reforming is adequate. The conversion of the organics to hydrogen is equilibrium-limited with insignificant deviations due

to low coke deposits. With proper design modifications, the stability and long-term efficiency of the reactor could be further improved. On the contrary, the complexity of bio-oils discourages the use of a fixed bed configuration. Even if the aqueous fraction is used, carbonaceous depositions cannot be totally avoided. Oligomers contained in bio-oil cannot be totally removed by the extraction of the aqueous phase. The extreme diversity of bio-oils whose composition and properties largely depend on the biomass feed and pyrolysis conditions increases this perplexity even more. These oligomers cannot be revolatilized without the formation of carbonaceous material. Therefore, reforming bio-oils require process conditions that allow for a good and immediate contact of the organic molecules with the catalyst, minimizing carbon formation. The use of a fluid bed reactor in a well-mixed regime equipped with a proper injecting system that allows for direct atomization and contact with the catalyst particles is necessary. Such a system will limit the extent of homogeneous thermal decomposition and will facilitate the sequential internal gasification of catalytically formed coke with steam and CO_2 . Consequently, a fluid bed reactor should extend the duration of the reforming activity and possibly eliminate the need for catalyst regeneration. However, the application of the fluid bed reactor imposes the use of suitable fluidizable catalysts that exhibit both high activity and mechanical strength at the conditions of the steam-reforming process. Work is in progress to develop attrition-resistant active catalytic materials to be tested in the spouted bed reactor of the pilot plant unit.

Conclusions

Biomass can be efficiently used for hydrogen production. Representative model compounds of bio-oil (acetone, ethylene glycol, and acetic acid) were reformed effectively in a fixed bed in the presence of a commercial nickel-based catalyst using a G_{C1HSV} equal to 1500 h^{-1} . Hydrogen yields up to 90% have been achieved at reaction temperatures higher than 600°C and steam-to-carbon ratios higher than 3. Conversion of the model compounds was complete. Out of the three model compounds, acetone showed a higher tendency in the production of coke, which the results suggest to be of graphitic nature. Reforming of the aqueous phase of bio-oil produced via the catalytic pyrolysis of beech wood resulted in a much lower hydrogen yield around 60% because of the high extent of coking. Contrary to the case of model compounds, coke produced during the aqueous phase of bio-oil seems to possess a polyaromatic structure. The severe coking caused from thermal decomposition of the unstable oxygenates and via catalytic reactions imposes the use of fluid bed reactors in processing the aqueous fraction of the bio-oil. By combining a proper reactor design with catalytic materials that minimize the catalytically produced coke, bio-oil has the potential to become an important hydrogen production method with significant environmental benefits.

Acknowledgment. The authors acknowledge Süd-Chemie for providing the catalyst samples. Financial support was provided by EPEAEK (Grant Pythagoras I) and PENED03.

EF060083Q