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Paper-ID 36311
Paper title From lab- to pilot-scale: Scale-up and optimization of pyrolysis bio-oil upgrading via ketonization
Presentation format Poster
Date of submission 28.01.2017 05:21 Uhr
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Content

Fast pyrolysis is a low-cost thermochemical process that can convert lignocellulosic biomass to a liquid bio-oil fuel with high yields. Small acid compounds that represent up to 10% of bio-oil bring not only corrosion problems, but also reduce the bio-oil stability. Conversion of these acids to larger molecules with simultaneous oxygen removal via ketonization represents a promising process concept for bio-oil upgrading. In this work, we present the ketonization of bio-oil vapors directly after production in thermal fast pyrolysis, in a second reactor, closely-coupled to the fluidized bed pyrolyzer, using commercial ZrO₂ as ketonization catalyst. Due to the complex nature of the process and the complicated bio-oil composition, we followed a step-wise approach to scale-up and optimize the process both in terms of reactor and feed. Initial experiments were performed on a lab-scale fixed bed reactor unit using acetic acid as feedstock. ZrO₂ demonstrated appreciable ketonization activity, with selectivity to acetone close to the theoretical maximum. Experiments were then conducted with progressively more complex feeds, starting from diluted acetic acid (5 and 10 wt%) and finally testing of the aqueous phase of a real thermal bio-oil. Reactivity was similar, with conversion ranging between ~75-80%. The catalytic performance was then assessed in the upgrading of real bio-oil vapors with lignocellulose as feed, in a bench-scale fixed bed reactor pyrolysis unit loaded with a dual catalytic bed comprising of silica sand and the ketonization catalyst. Compared with a reference thermal test, the presence of ZrO₂ induced a decrease in the bio-oil yield and the concentration of acids in the product and an increase in the production of water and CO₂, indicative of decarboxylation reactions. Finally, pilot-scale tests were performed in a continuous fast pyrolysis fluidized bed reactor unit coupled to second fluidized bed upgrading reactor. The first reactor was filled with inert sand and was operated at 500°C, while the second reactor contained the ZrO₂ sample. Experiments were performed with lignocellulosic biomass at different temperatures for the ketonization reactor (400-450°C) and at different catalyst/biomass ratio (0.15-0.75). Both the increase of temperature and catalyst/biomass ratio progressively led to lower bio-oil yield and higher CO₂ production, achieving however significant deoxygenation of the bio-oil (~30% reduction of the bio-oil oxygen content). Moreover, the results of the pilot-scale tests were comparable to those obtained in the bench-scale fixed bed reactor unit, indicative of the scalability of the process. Overall, the results of this work clearly indicate that the concept of vapor phase ketonization for the upgrading of bio-oil is scalable and can be successfully applied in the real process.

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Paper-ID 42616

Paper title Production of High-Grade Carbonaceous Materials from Degradative Solvent Extraction of Biomass at 350°C Using 1-Methylnaphthalene and Petroleum Based Solvent

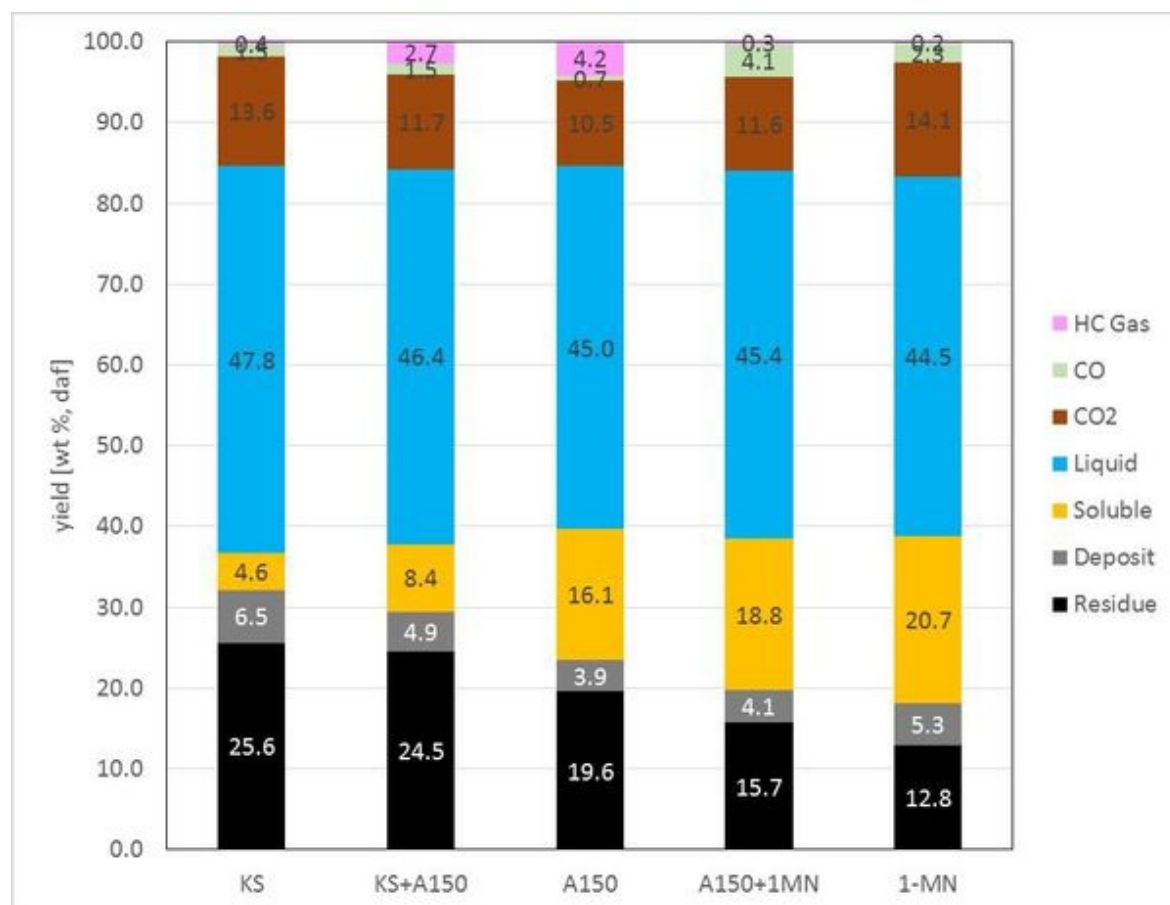
Presentation format Oral presentation

Date of submission 30.01.2017 08:19 Uhr

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Content

Rice straw was subjected to a degradative solvent extraction method that treats rice straw in a non-hydrogen donor at around 350 °C. This method can upgrade biomass by removing the oxygen functional groups in the form of CO₂ and H₂O, and also extract the low-molecular weight compound. Rice straw was separated into the residue which cannot be extracted by solvent at 350 °C (termed Residue), the fraction which can be extracted at 350 °C but precipitates from solvent at room temperature (Deposit), and the fraction which is solvent soluble even at room temperature (Soluble). In this study, 1-Methylnaphthalene (1-MN), two petroleum based solvents (Kerosene (KS) and A150), and their mixed solvent were used as solvents. Figure 1 shows the weight basis yield (wt%, d.a.f.) from extraction of rice straw by using different solvents. It was found that the yields of Soluble fraction were 4.6, 16.1 and 20.7% when using KS, A150 and 1-MN as solvent, respectively. The elemental compositions of Soluble fraction were C = 80.8 – 84.7 wt%, H = 7.1 – 8.8 wt%, and O = 7.1 – 10.3 wt%. Most of the ash was concentrated in the Residues, whereas the Solubles were most completely free from ash. The Solubles melted completely below 90 °C, and 60 – 70% of the Solubles were devolatilized below 400 °C. Detailed characterization of the Soluble fractions showed potential utilization of the fractions as precursors of carbon materials.



Paper-ID 52716

Paper title Selective valorisation of lignocellulose to fuels or aromatic platform chemicals: a self-sufficient depolymerisation–gasification–hydrodeoxygenation pathway catalyzed by Ni₂P/SiO₂

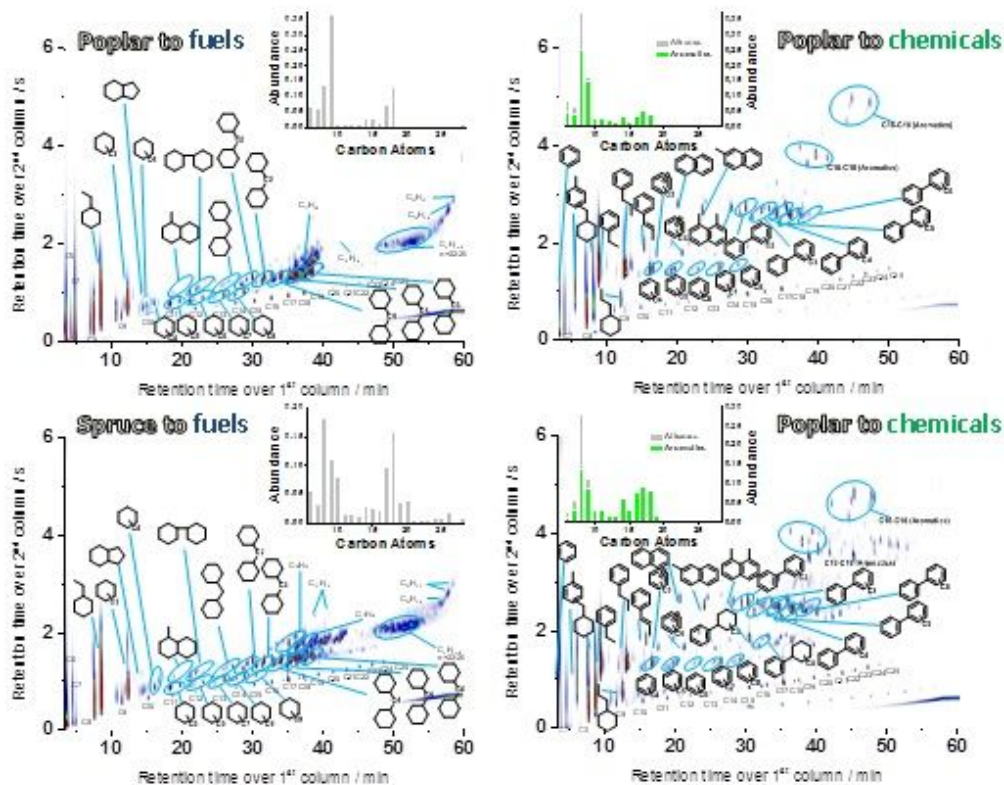
Presentation format Poster

Date of submission 30.01.2017 17:03 Uhr

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Content

The deconstruction and downstream upgrading of lignocellulosic biomass into fuels and value-added chemicals has the potential to partially reduce the dependence on diminishing and non-renewable petrochemical resources. The desired products – either aliphatic fuels or aromatic platform chemicals – can be individually obtained in high selectivity by simple adjustment of the reaction parameters (foremost pressure of H₂ and temperature), employing an identical Ni₂P/SiO₂ catalyst and setup. Adopting this new strategy, valuable hydrocarbon fuels or aromatic platform chemicals of $\geq C_6$ are directly obtained. (Figure 1)



Paper-ID 46931
Paper title Stability investigations of low and high Mw fractions from lignin HTL derived bio-oil
Presentation format Oral presentation
Date of submission 30.01.2017 13:29 Uhr
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Content

Retaining information about the stability properties of hydrothermal liquefaction (HTL) lignin bio-oils is of utter importance, today studies have been performed on biomass pyrolysis derived bio-oils. However, biomass pyrolysis bio-oils have been shown to have rather low thermal and chemical stability, due to: high water (20–30 %), oxygen (45–60 %) and acid (pH 2.0–4.0) contents. In this study, the stability of HTL bio-oil from lignin depolymerized by subcritical water conditions (350°C, 25 MPa) have been investigated. An accelerated aging at 50 °C and 80 °C for 1h to 1 week/month have been performed on both raw HTL bio-oil and fractions of this bio-oil (light oil and heavy oil). A multi-level analysis approach have been used i.e. GC-MS, elemental analysis, water content, GPC and 2D ¹H, ¹³C-HSQC NMR (18.8 T) to retain chemical structural information of changes of both high and low Mw structures in the bio-oil during aging. (Lyckeskog et al. 2016; Lyckeskog et al. 2017) Generally minor changes of the bio-oil yield and composition was detected, however, polymerization/condensation to higher Mw structures (called “THF insoluble” in this study) occurred and found to increase by time and temperature. By aging raw HTL bio-oil at 80 °C for one week in presence of “THF insolubles” gave a minor decrease of light oil yield (2.4%, low Mw fraction). However, when the separated light oil fraction (low Mw fraction) was aged at the same conditions (80 °C, 1 week) undetectable changes in yield (100% to 99.5%) was found. However, a slight disproportion of the phenolic monomers was detected and anisole/alkyl-anisole and xanthene structures was found to be reactive components in the low Mw fraction. This indicate that aromatic methoxyl groups as well as phenolic structures with bridging methylene groups (Ar-CH₂-Ar) are involved in the aging mechanisms of the light oil. The high Mw fraction (heavy oil) aged at 80 °C for 1 week showed slightly higher reactivity than the light oil with and without “THF insolubles” and the yield for the heavy oil decreased with 2.2% (with catalyst) and 3.1%, respectively. The high Mw insoluble fractions formed from light oil and heavy oil was further analysed by 2D NMR. It was seen that the formed “insolubles” had distinct different structures which point to their different origin structures (i.e. small phenolics vs. macromolecule structure). Accelerated aging studies of HTL bio-oil revealed a remarkable high stability with or without “insolubles” and this is very promising for future development for conversion of lignin by hydrothermal liquefaction with subcritical water.

Lyckeskog, H.N., Mattsson, C., Olausson, L., Andersson, S.-I., Vamling, L., Theliander, H. (2016) Thermal stability of low and high Mw fractions of bio-oil derived from lignin conversion in subcritical water. *Biomass Conversion and Biorefinery*:1-14; (2017) Accelerated aging of bio-oil derived from lignin conversion in subcritical water. *Tappi J.*

Paper-ID 43596
Paper title Steam reforming of the producer gas obtained from the gasification of beech wood: scale up from laboratory benches to full-size demonstrator
Presentation format Oral presentation
Date of submission 30.01.2017 10:08 Uhr
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Content

This paper compiles the extensive collaborative work performed within the European FASTCARD project for the development of improved catalysts for steam reforming (SR) of producer gas from biomass gasification. The objective is the development of SR catalysts more resistant to deactivation by sulfur and tars. With this purpose, combined lab-scale testing with selected contaminant tar and sulfur molecules and concomitant pilot scale testing has led to insight in the total reforming of producer gas. During lab-scale tests with target contaminants, sulfur was seen to cause more severe deactivation than tar molecules. PGM-based catalysts were found to perform better than Ni-based catalysts. Stable near-complete tar conversion was demonstrated for 100 hours operation with the selected PGM-mesoporous catalyst under real gasification conditions. To avoid deactivation of precious steam reforming catalyst during reforming of producer gas, upstream gas pre-treatment configurations are currently under development.

Paper-ID 54026

Paper title Synergetic effects in the catalytic co-pyrolysis of lignocellulose/plastic mixtures for upgrading the bio-oil properties

Presentation format Oral presentation

Date of submission 30.01.2017 17:40 Uhr

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Content

Catalytic fast co-pyrolysis of lignocellulosic biomass with waste plastics allows increasing the bio-oil yields with enhanced properties (higher H/C ratios and lower oxygen concentration) for the production of bio-fuels [1]. This effect is due to the role of the plastic feedstock as hydrogen donor during the pyrolysis reactions. In addition, the use of plastic wastes as a co-reactant would be an interesting way for the valorization of this type of residues.

The present work focuses on studying the effect of varying the lignocellulose/plastic mass ratio (0-1) as well as the catalyst/feedstock ratio ($X \text{ g} / 4 \text{ g feedstock}$), using a nanocrystalline H-ZSM-5 zeolite as catalyst, Eucalyptus (EU) as lignocellulosic biomass and low-density polyethylene (LDPE) as plastic. The pyrolysis reactor was a downdraft stainless steel fixed-bed with two separated zones, pyrolysis and catalytic. Reactions were performed at atmospheric pressure and temperatures of 550°C and 500°C for the pyrolysis and catalytic zones, respectively.

Firstly, the optimal EU/LDPE ratio was selected by thermogravimetric analyses in nitrogen flow in order to minimize the char formation since it causes the highest penalty in the bio-oil energy yield. The best performance was achieved with a mixture consisting of 40 wt. % LDPE and 60 wt.% EU. A minimum amount of 1.6 g catalyst/4 g feedstock was needed to get a homogeneous and monophasic bio-oil. Fig. 1 shows the bio-oil* (bio-oil in water free basis) oxygen concentration versus its energy yield, corresponding to reactions at different catalyst/feedstock ratios. A decrease in the bio-oil* energy yield was observed when increasing the proportion of catalyst, which was associated to a higher production of gases and coke. However, the bio-oil oxygen concentration was significantly reduced. Comparing with the catalytic pyrolysis of 100 % Eucalyptus, a strong improvement in both bio-oil* oxygen content and energy yield was attained when LDPE was co-fed, whereas the selectivity towards aromatic hydrocarbons was strongly increased. These results denote the existence of a very positive synergetic effect between lignocellulose and LDPE plastic when co-processed through catalytic pyrolysis.

[1] Y.Xue, S. Zhou, R.C. Brown, A. Kelkar, X. Bai, Fuel 156 (2015) 40–46

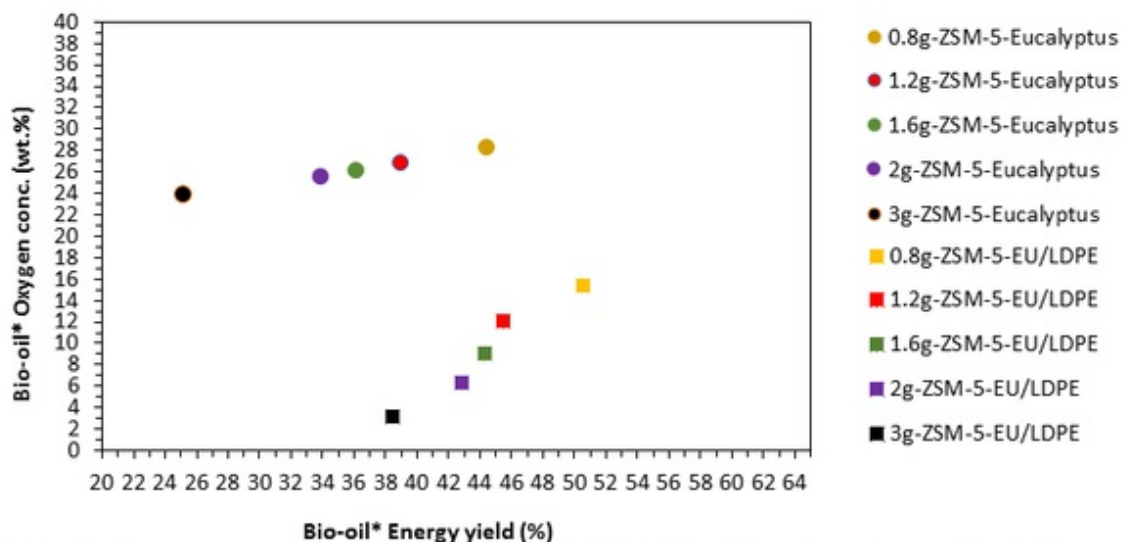


Figure 1. Oxygen concentration versus energy yield of Bio-oil* obtained by catalytic fast-pyrolysis of both Eucalyptus and Eucalyptus/LDPE feedstocks using different H-ZSM-5 catalyst loadings ($X \text{ g} / 4 \text{ g feedstock}$).