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Catalytic upgrading of lignocellulosic biomass pyrolysis vapours: Effect of hydrothermal pre-treatment of biomass

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ABSTRACT

The main objective of the present work was the study of the effect of hydrothermal pretreatment of lignocellulosic biomass (beech wood) on the product yields and bio-oil composition produced from biomass flash pyrolysis as well as from the catalytic upgrading of the biomass pyrolysis vapours. The hydrothermal pretreatment of lignocellulosic biomass was performed at a severity factor (Ro) of 3.55 leading to ~35 wt.% loss of solids, mainly due to solubilization and removal of hemicellulose. The production of sugars (mainly levoglucosan) was significantly increased by the use of the hydrothermally pretreated biomass instead of the untreated biomass in the non-catalytic flash pyrolysis experiments. On the other hand, the concentration of carboxylic acids, ketones and phenols was decreased in the bio-oil derived from the pretreated biomass. The catalysts tested in the upgrading of the biomass pyrolysis vapours were the strongly acidic zeolites H-ZSM-5 and silicalite (with very low number of acid sites) and the mildly acidic mesoporous aluminosilicate Al-MCM-41. The effect of catalysts on product yields and composition of bio-oil in the upgrading of pyrolysis vapours, was similar for both the pretreated and untreated biomass. The use of zeolite H-ZSM-5 decreased the total liquid yield (bio-oil) via decreasing the organic phase of bio-oil and increasing its water content, accompanied by increase of gases and moderate formation of coke on the catalyst. The zeolite silicalite and the Al-MCM-41 induced similar effects with those of H-ZSM-5 but to a less extent, except of the significantly higher coke that was deposited on Al-MCM-41. With regard to the composition of the bio-oil, all the catalysts and mostly the strongly acidic H-ZSM-5 zeolite reduced the oxygen content of the organic fraction, mainly by decreasing the concentration of acids, ketones and phenols in the untreated biomass pyrolysis oil or the concentration of sugars in the pretreated biomass pyrolysis oil. Aromatics and polycyclic aromatic hydrocarbons (PAHs) were significantly increased by the use of all catalysts, for both types of biomass feed. A substantial increase in the concentration of phenols was observed in the upgraded bio-oil derived by the hydrothermally pretreated biomass, using the less acidic silicalite and Al-MCM-41 catalysts.

1. Introduction

Most of the energy consumed nowadays originates from non-renewable resources, such as coal, petroleum and natural gas. Global energy crisis (depleting deposits and consequent increasing prices of petroleum oil) combined with environmental problems associated with the use of coal and petroleum based fuels, strongly motivated our society to search for alternative, renewable energy sources and environment-friendly liquid fuels. In this respect, biomass is an abundant, low-cost renewable energy source, expected to play a substantial role in the future global energy balance [1–3]. Different types of lignocellulosic biomass can be utilized as source of energy/fuels, such as agricultural and forestry residues/waste (e.g. wheat straw, tree branches), industrial wood processing residues (e.g. sawdust), municipal solid waste (e.g. waste paper), and perennial or annual crops with high yield 1–4 ton/1000 m^2 year (e.g. eucalyptus, pseudoacacia, willow, miscanthus, switch grass, cellulosic sorghum, etc.).

Biomass flash pyrolysis (BFP) is one of the most promising thermochemical processes for the conversion of biomass mainly into liquid (bio-oil, up to ca. 75 wt.% based on biomass), as well as gaseous (CO, CO_2, H_2 and gaseous C_1–C_4 hydrocarbons) and solid (char) products [1,4,5]. The main characteristics of the BFP process are the very high heating rates (e.g. 500–1000 °C/s), the medium pyrolysis temperatures (e.g., 400–550 °C), short vapour contact time (e.g. less than 2–3 s) and fast vapour cooling rates (quenching). Biomass is usually pyrolyzed in the presence of inert solid heat

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carrier, like silica sand, in order to enhance heat transfer rates and to increase the available "hot" surface for thermal pyrolysis. All the above process characteristics aim at maximizing the production of liquids (bio-oil) compared to gases and char, via suppressing secondary reactions of the primary pyrolysis products. Bio-oil can be utilized as a source of commodity chemicals (e.g. phenols), can be used directly as a fuel (e.g. in boilers for steam/heat production) or can be further converted to fuels or fuel additives (e.g. in the gasoline or diesel pool). However, bio-oil usually presents several undesirable characteristics, such as high water and oxygen content, corrosiveness, instability under storage and transportation conditions, immiscibility with petroleum fuels, high acidity, high viscosity, and low calorific value [3,6,7]. All these become the primary obstacles for its direct application as a fuel in various types of engines or turbines. In the case where bio-oil is intended for the production of high quality transportation fuels or fuel additives, via processing or co-processing with petroleum fractions in typical refining processes such as Fluid Catalytic Cracking [8,9] or hydroprocessing [10,11], minimization of oxygenated compounds (e.g. acids, furans, ketones, etc.) and increase of hydrocarbons (aromatics, aliphatics, etc.) is required.

A way to alter and fine-tune the composition of bio-oil is the use of catalysts during pyrolysis, i.e. the catalytic pyrolysis of biomass [2,12]. The specific catalytic function of various catalysts can alter the product yields and selectivity, thus affecting the composition of bio-oil and its physical and chemical properties. In catalytic pyrolysis, solid acid catalysts such as zeolites are usually utilized, as in the case of pyrolysis (cracking) of large hydrocarbon fractions in petroleum refining [12,13]. In the cracking of hydrocarbons the main reaction routes involve C–C bond scission [14], while in the case of biomass pyrolysis the cleavage of C–OH bonds (dehydration) or C–CO(OH) bonds (decarbonylation or decarboxylation) becomes also important due to the carbohydrate and phenolic components of cellulose, hemicellulose and lignin from which the lignocellulosic biomass consists of. Thus, reactions such as dehydration, decarboxylation, decarbonylation, (de)alkylation, cracking, isomerization, cyclization, oligomerization and aromatization can take place on the acid sites of zeolites during biomass pyrolysis. Several types of zeolites, such as Y, ZSM-5, Mordenite and Beta, have been studied as catalysts for biomass pyrolysis or for upgrading of bio-oil [2,3,8,9,12,15–20]. The type of biomass and the reactor system/conditions play an important role on product yields; however, it is generally accepted that zeolitic catalysts increase the water content of bio-oil due to the enhanced dehydration reactions, reduce the concentration of oxygenated compounds in bio-oil via de-oxygenation reactions and in some cases reduce the yield of the organic phase of bio-oil in favor of hydrocarbon gases and coke. Zeolite ZSM-5 has been also shown to increase the aromatic species while decreasing the bio-oil molecular weight.

In an effort to better match the size of oligomers derived from the initial thermal degradation of the cellulose, hemicellulose and lignin macromolecules of biomass with the pore size of the catalysts, ordered mesoporous (alumino)silicates have started over the last years to be the subject of study for the catalytic pyrolysis of biomass. Some representative mesoporous materials that have been tested so far are MCM-41 [12,21–26], SBA-15 [23], MSU-F [26], and MSU-S [27]. Despite the relatively limited number of studies with mesoporous catalysts, some general trends have been already recognized. It was shown for example that the water in bio-oil increases, as it was observed with zeolites, while changes in total liquid yield (total amount of produced bio-oil) relevant to the yields of gases and char/coke depend on the type of mesoporous catalyst and biomass used. In some cases, increased concentration of phenols (a valuable raw chemical) in the bio-oil, has been observed [12,22], while a highly de-oxygenated bio-oil was produced by the use of the MSU-S mesoporous catalysts that have been synthesized by the use of zeolite seeds [27]. A direct comparison between representative zeolitic and mesoporous catalysts is given in our recent work [28].

The hydrothermal treatment of lignocellulosic biomass is one of the various pretreatment methods usually applied to improve the enzymatic saccharification of biomass in the second generation bio-ethanol process. This type of pretreatment induces the solubilization of a large fraction of hemicellulose, and part of lignin in the biomass. Removal of these chemical/physical barriers leads to the formation of an "open" structure, which in turn results to enhanced enzymatic hydrolysis of cellulose to fermentable glucose molecules [29]. The modified structure and chemical composition of the pretreated biomass could also have an effect on the pyrolysis products, if it was used as a feedstock in this process. This was shown for pine wood biomass that was pretreated with different acidic and alkaline solutions prior to testing as feedstock in biomass flash pyrolysis [30].

In the present work, we studied the flash pyrolysis (non-catalytic) and the catalytic upgrading of pyrolysis vapours of lignocellulosic biomass (beech wood) in its parent state or after being subjected to hydrothermal pretreatment. The obtained product yields and selectivity of various compounds in bio-oil are discussed with regard to the effect of hydrothermal pretreatment of biomass or the effect of catalyst's type (zeolitic or mesoporous).

2. Experimental

2.1. Catalytic materials

The catalytic materials used for the biomass pyrolysis experiments were the microporous zeolites ZSM-5 (Zeolyst CBV 5524G, Si/Al =25) and silicalite (Union Carbide), and an Al-MCM-41 mesoporous material (Si/Al = 30) synthesized in the laboratory [21]. Since the commercial ZSM-5 zeolite was provided in NH_4^+ form, it was previously calcined at 500 °C for 2 h to convert it to H^+ form.

2.2. Characterization of catalytic materials

The catalytic materials tested in this work were characterized by: (a) ICP-AES for the determination of the chemical composition (wt.% of Al and Na), using a Plasma 400 (PerkinElmer) spectrometer, equipped with Cetac6000AT+ ultrasonic nebulizer, (b) powder X-ray diffraction (XRD) for the verification of the crystalline zeolite MFI structure and of the aluminosilicate mesophase in Al-MCM-41, using a Rigaku Rotaflex 200B diffractometer equipped with Cu Kα X-ray radiation and a curved crystal graphite monochromator operating at 45 kV and 100 mA; counts were accumulated in the range of 5–75° 2θ (for zeolites) and 1–10° 2θ (for MCM-41) every 0.02° (2θ) with counting time 2 s per step, (c) N_2 adsorption/desorption experiments at −196 °C for the determination of surface area (the Dubinin–Radushkevich method was used for the microporous zeolites and the BET method for the mesoporous MCM-41), total pore volume (at $P/P_o = 0.99$) and pore size distribution (BJH method) of the samples which were previously outgassed at 150 °C or 430 °C (for MCM-41 or zeolite samples, respectively) for 16 h under 5×10^{-9} Torr vacuum, using an Automatic Volumetric Sorption Analyzer (Autosorb-1MP, Quantachrome), (d) temperature Programmed Desorption (TPD) of ammonia for the determination of the number of total acid sites, using a commercial TPD apparatus (Altamira AMI-1) and an on-line mass spectrometer (Baltzers, Omnistar); the desorbed NH_3 was quantitatively determined based on the $m/z = 15$ fragment, and e) FT-IR spectroscopy combined with *in situ* adsorption of pyridine for the determination of the Brönsted (band at 1545 cm^{-1} attributed to pyridinium ions) and Lewis