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

S. Stephanidis [a,b], C. Nitsos [c], K. Kalogiannis [a], E.F. Iliopoulou [a], A.A. Lappas [a], K.S. Triantafyllidis [c,*]

[a] Chemical Process Engineering Research Institute, CERTH, P.O. Box 60361, Thermi, 570 01 Thessaloniki, Greece
[b] Department of Mechanical Engineering, University of Western Macedonia, 50100 Kozani, Greece
[c] Department of Chemistry, Aristotle University of Thessaloniki, 541 24 Thessaloniki, Greece

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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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[*] Corresponding author. Tel.: +30 2310 997730; fax: +30 2310 997730.
E-mail addresses: ktrianta@chem.auth.gr, ktrianta@cperi.certh.gr (K.S. Triantafyllidis).

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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 $K\alpha$ 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

Table 1
Properties of untreated and hydrothermally pretreated biomass feedstock (Lignocel HBS 150–500, beech wood).

	Untreated Lignocel	Hydrothermally pretreated lignocel
Ash/solid residue (wt.%)	0.83	0.21
C (wt.%)	45.69	48.64
H (wt.%)	6.52	6.34
N (wt.%)	0.16	0.14
O (determined by difference)	47.32	44.67
Moisture (wt.%)[a]	7.50	3.50

[a] Determined by drying at 105 °C for 6 h.

(band at 1450 cm^{-1} attributed to pyridine coordinated to Lewis acid sites) type acid sites of the catalysts, using a Nicolet 5700 FTIR spectrometer (resolution 4 cm^{-1}) and the OMNIC software; data processing was carried out via the GRAMS software and the quantitative determination of acid sites was performed by adopting the molar extinction coefficients provided by Selli and Forni [31].

2.3. Biomass feedstock properties and hydrothermal pretreatment

A commercial lignocellulosic biomass (Lignocel HBS 150–500) originating from beech wood was used in the current study. The biomass feedstock was tested in the fast pyrolysis experiments either as received or after hydrothermal pretreatment. The hydrothermal pretreatment of the lignocellulosic biomass was carried out in a laboratory scale Parr Reactor (Model 4563) with a total volume of 600 ml. The biomass solid sample was stirred with distilled H_2O at a liquid to solids ratio (LSR) of 15 and heated to 190 °C with a rate of 7 °C/min. The slurry was kept at that temperature for 8 min, leading to a severity factor (log Ro) of 3.55 for the hydrothermal pretreatment process. The severity factor (log Ro) is an expression of the combined effect of time and temperature of the hydrothermall pretreatment. It is defined by the equation $Ro = t^*\exp[(T-100)/14.75]$ where t is the time of the hydrothermal pretreatment in minutes and T is the temperature of the pretreatment in °C [29]. The autogeneous pressure at these experimental conditions was 180 psi. The stirring rate of the slurry in the reactor was 150 rpm. The liquid products were analyzed by gas chromatography (GC, Hewlett Packard 5890II) using an flame ionization detector (FID) and a DB-wax (30 m × 0.53 mm ID × 1 μm) column, for the determination of carboxylic acids, carbonyl and phenolic compounds. The content of sugars was determined by high pressure liquid chromatography (HPLC, Shimadzu) using a Refractive Index (RI) detector (RID-6A) and a SP0810 Sugar Column (Shodex) with H_2O as the mobile phase. The solids were separated with vacuum filtration, washed with distilled H_2O, dried at ambient conditions and tested as feedstock in the fast pyrolysis experiments. The properties of both the untreated and the hydrothermally pretreated biomass are shown in Table 1. The ash content of biomass samples was determined by a method similar to ASTM E1755-01 and was determined as the solid residue after dry oxidation of biomass in air at 575 °C for 12 h. The moisture of the samples was determined by drying at 105 °C for 6 h. C, H and N content was determined by elemental analysis using a LECO-800 CHN analyzer.

2.4. Biomass flash pyrolysis (non-catalytic) and catalytic upgrading experiments

All biomass flash pyrolysis experiments were performed on a bench-scale fixed bed tubular reactor (ID 1.4 cm, height 36 cm), made of stainless steel 316 and heated by a 3-zone furnace. The solid biomass was introduced by a specially designed piston system to the central hot zone of the reactor, where it was vaporized at 500 °C. The biomass vapours were then directly transferred with the aid of N_2 (flow rate 100 cc/min) through a fixed bed of inert solid heat carrier. The temperature of the solid was 500 °C and the time of purging with N_2 was 15 min. An additional purging with N_2 (50 cc/min) was performed for another 10 min during cooling of the reactor. The inert solid used was silica sand with particle size of 90–180 μm. A typical residence time of the vapour phase in the silica sand bed was <0.1 s. For the catalytic experiments, the inert silica sand was replaced with the various catalysts under study. This type of experiments can be referred to as *in situ* catalytic upgrading of biomass pyrolysis vapours and are of the “ex-bed” type (i.e. there was no mixing of solid biomass with the solid catalyst). A detailed description of the experimental unit can be found in our previous communication [27].

The amount of biomass used in all experiments was 1.5 g and the amount of silica sand (in non-catalytic experiments) or of catalyst (in catalytic upgrading experiments) was 0.7 g. The liquid products (bio-oil) were collected and quantitatively determined using a pre-weighted glass receiver in a liquid bath (−17 °C). The water content of the bio-oil was determined by the Karl-Fischer method (ASTM E203-08). The water/aqueous phase usually present in the bio-oil was separated from the organic phase using an organic solvent (dichloromethane). The organic phase of the bio-oil was analyzed by GC–MS using an Agilent 7890A/5975C gas chromatograph–mass spectrometer system (Electron energy 70 eV; Emission 300 V; Helium flow rate: 0.7 cc/min; Column: HP-5MS (30 m × 0.25 mm ID × 0.25 μm)). Internal libraries were used for the identification of the compounds found in the bio-oil and their categorization into main functional groups. The semi-quantitative analysis of the organic phase of bio-oil was based on the relative intensity (area) of each individual compound peak, compared to the sum of intensities of all the peaks in the GC–MS chromatogram. The gaseous products were collected and measured by the water displacement method. The gaseous products were analyzed in a HP 5890 Series II gas chromatograph, equipped with four columns (Precolumn: OV-101; Columns: Porapak N, Molecular Sieve 5A and Rt-Qplot (30 m × 0.53 mm ID) and two detectors (TCD and FID). The total amount of solid products (char and coke on catalyst) was determined by direct weighting while the coke on catalyst was determined by C/H elemental analysis and regeneration (calcination) experiments of the used catalysts.

3. Results and discussion

3.1. Physicochemical characteristics of zeolitic and mesoporous catalysts

The most important physicochemical properties of the zeolitic (ZSM-5 and silicalite) and mesoporous (Al-MCM-41) catalytic materials used in the catalytic upgrading of biomass flash pyrolysis vapours are presented in Table 2. ZSM-5 was selected as a typical crystalline zeolitic catalyst comprising a 2-D channel like pore system with perpendicularly intersecting channels. The diameter of the channels is about 0.51 nm × 0.55 nm and 0.53 nm × 0.56 nm while the size of the free space at the intersection is about 0.9 nm [32]. The H^+-exchanged ZSM-5 possesses mainly Brönsted acid sites (bridging hydroxyls connected to framework aluminum atoms) of high acidic strength. However, during the calcination process at about 550–600 °C, initially for removing the organic template and then for transforming the NH_4^+-exchanged form into the H^+-form, the zeolitic framework is dexydroxylated leading to the formation of positively charged tri-coordinated Si atoms as well as extra-framework octahedrally coordinated aluminum oxy-hydroxy species that can act as Lewis acid sites [33]. The presence of Lewis acid sites in the H-ZSM-5 zeolite is verified by the results of the Py-FT-IR measurements which are shown in Table 2. The

Table 2
Chemical composition, porosity and acidity characteristics of zeolitic and mesoporous (alumino)silicate catalytic materials for upgrading of biomass flash pyrolysis vapours.

Catalyst	Chemical composition (ICP-AES)	Porosity characteristics (N_2 porosimetry)			Acidic properties		
	Si/Al atomic ratio	Surface area[a] (m^2/g)	Pore size[b] (nm)	Pore volume[c] (cm^3/g)	Total acid sites (TPD-NH_3) (mmoles NH_3/g)	Brönsted acid sites (mmoles pyridine/g)	Lewis acid sites (mmoles pyridine/g)
Silicalite	>1000	410 (382)	~0.55	0.23	0.07	0.06	0.07
ZSM-5	25	480 (424)	~0.55	0.54	0.61	0.43	0.21
Al-MCM-41	30	860 (694)	2.69	1.12	0.28	0.08	0.24

[a] The values in parentheses correspond to the surface area of the catalysts after reaction and regeneration by burning the deposited coke (see Section 2).
[b] The mesopore size of Al-MCM-41 was determined by BJH method from nitrogen adsorption data; the micropore size of silicalite and ZSM-5 was taken from Ref. [32].
[c] At $P/P_o = 0.99$.

amount of adsorbed pyridine on the Brönsted and Lewis acid sites was calculated based on the intensities of the IR bands at 1545 cm^{-1} and 1450 cm^{-1}, respectively, using the molar extinction coefficients proposed by Selli and Forni [31]. However, if the coefficients proposed by Emeis [34] were used, the number of both types of acids sites would be significantly different/lower; the Brönsted acid sites would be divided by a factor of 2.3 and the Lewis acid sites divided by a factor of 3.5. In that latter case, however, the total amount of acid sites would be significantly different/lower compared to that determined by TPD-NH_3 (data also shown in Table 2). By combining all the above experimental evidence, and considering that most of the aluminum in the H-ZSM-5 sample is in tetrahedral coordination in the zeolitic framework (^{27}Al MAS NMR data, not shown), it can be suggested that the coefficients suggested by Selli and Forni provide a number of Brönsted acid sites (by Py-FT-IR) which is comparable with that provided by TPD-NH_3 and in accordance with the chemical composition data (Al content), considering that most of the Al atoms is in tetrahedral framework sites.

Silicalite, which is the aluminum-free isostructural to ZSM-5 zeolite, was also tested as catalyst for the catalytic upgrading of biomass pyrolysis vapours, in order to elucidate the effect of acidity and exclude the effect of porous structure. However, as it can be seen in Table 2, silicalite exhibits also some acidity due to aluminum impurities usually found in the synthesis mixtures of this zeolite. It has been previously shown by ^{27}Al MAS NMR studies that these Al traces can be in tetrahedral sites in the zeolitic framework [35], thus providing a very low number of strong Brönsted acid sites, such as those found in H-ZSM-5 [36]. The Al-MCM-41 was selected as being representative of ordered mesoporous amorphous aluminosilicates with high surface area and relatively small mesopores (~3 nm). This sample possesses Brönsted and mainly Lewis acid sites, as it can be seen in Table 2, with weak/medium acidity strength compared to that of crystalline zeolites [37].

The three above catalysts were tested in the catalytic upgrading of the biomass pyrolysis vapours and were subsequently regenerated by calcination at 550 °C in air, in order to burn the deposited carbon (see Section 3.3). This regeneration procedure had a relatively small effect on their surface area, which was reduced by up to 10% for the two zeolites and 20% for the Al-MCM-41 catalyst, as can be seen from the respective results in Table 2.

3.2. *Non-catalytic flash pyrolysis of untreated and hydrothermally pretreated biomass*

The hydrothermal pretreatment of the lignocellulosic biomass (beech wood) under the experimental conditions applied, led mainly to the hydrolysis and dissolution of the hemicellulosic fraction of biomass. Acetic acid was formed *in situ* via degradation of the acetylated sugars present in hemicellulose and induced a mild acid hydrolysis of biomass. The pH of the suspension of untreated biomass in water was ~5 (equal to the pH of deionized water) while that of the yellow liquid product derived from the hydrothermal treatment of biomass was ~3.6. The GC analysis of the liquid products revealed the presence of acetic acid (1 mg/ml), furfural (0.15 mg/ml), hydroxymethylfurfural (0.55 mg/ml) and trace amounts of lignin monomeric molecules (e.g. syringyl and guaiacyl alcohol). The HPLC analysis of the liquid product showed the presence of xylose (7.50 mg/ml), cellobiose (0.20 mg/ml), galactose (0.12 mg/ml) and arabinose (0.21 mg/ml). The formation of furfural and hydroxymethylfurfural is attributed to the dehydration of pentose (xylose) and hexose (glucose) sugars, respectively. The solid product, which accounted for the ~65 wt.% of the initial solid biomass, had a relatively darker brown colour compared to that of the untreated biomass, due to the repolymerization of dissolved lignin on the surface of the hydrothermally treated biomass. From the data presented in Table 1, it can be seen that the ash content of biomass is reduced due to removal of metals (as verified by ICP-AES analysis, not shown), such as calcium (Ca), magnesium (Mg), potassium (K) and sodium (Na) that were present in small amounts (less than 0.2 mg/kg biomass, each) in the untreated biomass. Furthermore, the C/H and C/O ratio was similar for the untreated and hydrothermally treated biomass. However, as it is shown below, the non-catalytic flash pyrolysis of the above two types of biomass leads to substantially different composition of the produced bio-oil.

The product yields (based on biomass) and the composition of gases and bio-oil (representative compounds in the organic phase) in the non-catalytic flash pyrolysis of the untreated and hydrothermally pretreated lignocellulosic biomass (beech wood) are shown in Table 3. The pretreated biomass leads to higher yields of total liquid products/bio-oil by about 8 wt.% compared to the untreated biomass, while the gases and char decrease by ca. 3.5–4.5 wt.%. Interestingly, the water content of bio-oil is decreased (by 5 wt.%) and the content of organic phase is increased (by 13 wt.%). The reason however for the noticeable increase of the organics in the bio-oil produced from the hydrothermally pretreated biomass is solely the very high production of 1,6-Anhydro-.beta.-D-glucopyranose (levoglucosan), as can be seen from the composition of the organic phase in Table 3. Levoglucosan is the primary product in cellulose pyrolysis and can be formed directly from cellulose or indirectly through the intermediate formation of 1,2- or 1,4-anhydro-.alpha.-D-glucopyranose compounds [38]. In order to assess the applicability of the previously proposed mechanism in our experimental setup and conditions, we conducted flash pyrolysis of pure cellulose (results not shown for brevity) and we found that the resulting organic phase of the bio-oil consisted mainly of sugars (1,6-Anhydro-.beta.-D-glucopyranose, 1,4:3,6-Dianhydro-.alpha.-D-glucopyranose, polysaccharides), and ketones and aldehydes in less amounts as secondary dehydration/decomposition products, in accordance with other works [38,39]. It is thus obvious that the high amount of levoglucosan measured in the organic phase of the bio-oil derived from the hydrothermally pretreated biomass is related with the higher portion of cellulose in this hemicellulose-free biomass derivative (see discussion above). However, the significant difference in the concentration of levoglucosan in the organic phase of the two bio-oils cannot be attributed only to the differences in the composition

Table 3
Product yields and bio-oil composition (representative compounds) from non-catalytic flash pyrolysis of lignocellulosic biomass (untreated and hydrothermally pretreated).

Product/compound	Lignocel + silica sand	Hydrothermally pretreated lignocel + silica sand
Pyrolysis products		
Bio-oil (total liquids, wt.% on biomass)	60.23	68.28
Water (in bio-oil, wt.% on biomass)	21.40	16.51
Organics (in bio-oil, wt.% on biomass)	38.84	51.77
Oxygen (of organics, wt.% on bio-oil)	38.40	41.18
Gases (wt.% on biomass)	16.72	13.23
Char (wt.% on biomass)	23.01	18.49
Total gases (wt.% on biomass)	16.72	13.23
CO	6.04	6.19
CO_2	9.22	5.43
Other gases (H_2, C_1–C_6, C_2=, C_3=)	1.45	1.61
Composition of organic phase of bio-oil (wt.% on organics)		
Total aromatics	2.44	0.49
Phenanthrene, 9,10-dihydro-	0.29	0.00
2,2′-Dimethylbiphenyl	0.18	0.00
Diphenylmethane	0.18	0.14
Benzene, 1,1′-propylidenebis-	0.37	0.33
Total aliphatics	0.21	0.08
Undecane, 4-methyl-	0.15	0.00
Tetracyclo[7.3.1.0(2,7).1(7,11)]tetradecane	0.09	0.00
Total phenols	36.26	19.67
Phenol	0.50	0.16
Phenol, 2-methoxy-	1.28	0.68
1,2-Benzenediol	2.00	0.62
1,2-Benzenediol, 3-methoxy-	2.19	2.06
1,2-Benzenediol, 4-methyl-	1.51	0.23
2-Methoxy-4-vinylphenol	1.02	1.17
Phenol, 2,6-dimethoxy-	4.03	1.79
Phenol, 3,4-dimethoxy-	0.94	0.45
Phenol, 2-methoxy-4-(1-propenyl)-	4.77	0.00
1,4-Benzenediol, 2-(1,1-dimethylethyl)-	0.67	0.00
Phenol, 2,6-dimethoxy-4-(2-propenyl)-	4.60	3.36
Ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)-	1.16	0.83
Phenol, 2-methoxy-4-methyl-	1.07	1.26
Total Furans	0.79	0.30
2-Furanmethanol	0.66	0.26
Total acids	17.02	5.52
Acetic acid	14.34	3.85
3,5-Dimethoxy-4-hydroxyphenylacetic acid	1.21	0.13
n-Hexadecanoic acid	0.10	0.00
Total esters	3.75	3.01
Propanoic acid, 2-oxo-, ethyl ester	2.34	1.71
Butanoic acid, 2-hydroxy-, ethyl ester	0.28	0.16
Formic acid, 1-methylpropyl ester	0.15	0.00
2,4-Hexadienedioic acid, 3-methyl-4-propyl-, dimethyl ester	0.19	0.34
Total alcohols	0.33	0.37
2-Pentanol, 3-methyl-	0.09	0.00
Isopropyl alcohol	0.11	0.00
2-Cyclohexen-1-ol	0.00	0.33
Total ethers	1.45	1.61
Benzene, 1-ethyl-4-methoxy-	0.50	0.00
Benzene, 1-methoxy-4-(1-methyl-2-propenyl)-	0.12	0.00
Benzene, 1,2,3-trimethoxy-5-methyl	1.04	0.00
Benzaldehyde, 3,4-dimethoxy-, methylmonoacetal	0.37	0.00
1,2,3-Trimethoxybenzene	0.00	1.28
Total aldehydes	1.27	3.40
2-Furancarboxaldehyde, 5-methyl-	0.71	0.77
2,5-Furandicarboxaldehyde	0.00	0.76
2-Furancarboxaldehyde, 5-(hydroxymethyl)-	0.00	1.76
Total ketones	12.98	5.60
2-Propanone, 1-hydroxy-	3.00	0.69
2-Cyclopenten-1-one, 2-hydroxy-	2.36	0.55
1,2-Cyclopentanedione, 3-methyl-	1.77	0.45
Total polycyclic aromatic hydrocarbons (PAHs)	0.00	0.00
Total sugars	0.93	40.47
1,4:3,6-Dianhydro-.alpha.-D-glucopyranose	0.37	0.69
D-Allose	0.52	0.00
1,6-Anhydro-.beta.-D-glucopyranose(levoglucosan)	0.00	39.45
Total nitrogen compounds	5.95	2.55
Total unidentified	16.49	17.07

of the two biomass samples, since in this case the concentration of levoglucosan in the untreated biomass oil should have been as high as 20–25 wt.% on total organics (assuming for example that the rest 65 wt.% solids left after the hydrothermal treatment are split to about 45 wt.% cellulose and 20 wt.% lignin). It may be possible that the “open structure” of the treated biomass allows for faster removal of the initially formed levoglucosan in the pyrolysis vapour product stream, before it is converted to secondary products such as carbon monoxide/dioxide, water, aldehydes, ketones, furans, as well as water-soluble polysaccharides [38,39]. The formation of the secondary products could be enhanced by the presence of higher amount of ash (Table 1; traces of metals that can act as catalyst for the formation of the above products) in the untreated biomass, as well as by the char formed during pyrolysis of hemicellulose which is “surrounding” the cellulose fraction in the parent lignocellulosic biomass. A more systematic experimental approach is however required to better elucidate the observed significant difference in the production of sugars from the parent lignocellulosic biomass and the hydrothermally pretreated derivative.

Despite the high content of levoglucosan in the pretreated biomass pyrolysis oil, the oxygen content of its organic phase was only 3 wt.% (based on total organics) higher compared to that of the untreated biomass oil (41 versus 38 wt.%; Table 3). This is due to the lower concentration of carboxylic acids, ketones and phenols in the organic phase of the former bio-oil (Table 3). However, the differences in the contents of these compounds in the organic phase of the two bio-oils shown in Table 3 are not so high if the “dilution” effect of the high amount of levoglucosan in the pretreated biomass oil is considered. Nevertheless, the decrease of acids, which consists mainly of acetic acid, could be correlated with the removal of hemicellulose during the hydrothermal pretreament, since acetic acid is one of the major products of flash pyrolysis of hemicellulose [40]. The absence of hemicellulose from the pretreated biomass induced also the decrease of ketones since we have observed that these are also formed in relatively high amounts during pyrolysis of hemicellulose (results not shown). The decrease of phenols can be attributed to a partial dissolution of lignin during the hydrothermal pretreament of biomass. The rest of the groups in the organic phase of bio-oil (i.e., aliphatics, aromatics, furans, esters, ethers and alcohols) which are in lower concentrations, are not affected significantly by the pretreatment of biomass, except of aldehydes which show a small increase with that feed.

As far as the composition of gaseous products is concerned, there were no significant differences amongst the two types of biomass feedstock, except of the observed lower yield of CO_2 with the hydrothermally pretreated biomass, which could be related to the higher oxygen content of organics (Table 4) and the higher concentration of sugars in the liquid product (Table 3).

Table 4
Product yields (wt.% on biomass) in non-catalytic flash pyrolysis of lignocellulosic biomass (untreated and hydrothermally pretreated) and in the catalytic upgrading of the biomass pyrolysis vapours.

Catalyst	Total liquids (Bio-oil)	Organics (in bio-oil)	Water (in bio-oil)	Gases	Char/Coke on catalyst[a]	Oxygen[b]
Feedstock: untreated lignocellulosic biomass						
Non-catalytic (silica sand)	60.23	38.84	21.40	16.72	23.01/–	38.40
Silicalite	47.58	17.79	30.80	26.70	25.72/2.71	23.14
ZSM-5	43.95	9.98	33.97	30.08	25.88/2.87	14.21
Al-MCM-41	45.34	15.28	30.06	24.07	30.66/7.65	23.07
Feedstock: hydrothermally pretreated lignocellulosic biomass						
Non-catalytic (silica sand)	68.28	51.77	16.51	13.23	18.49/–	41.18
Silicalite	52.94	26.12	28.82	25.05	22.01/3.52	28.74
ZSM-5	45.88	15.76	30.12	31.25	22.87/4.83	25.94
Al-MCM-41	44.82	15.74	29.08	25.97	28.87/10.38	27.51

[a] The wt.% coke based on catalyst weight was 6.4%, 6.7% and 20.6% for silicalite, H-ZSM-5 and Al-MCM-41.
[b] wt.% on organics in bio-oil.

3.3. *Catalytic upgrading of flash pyrolysis vapours of untreated and hydrothermally pretreated biomass*

The product yields (wt.% on biomass) from the catalytic upgrading of the flash pyrolysis vapours of lignocellulosic biomass (untreated and hydrothermally pretreated) are presented in Table 4 (the yields of the non-catalytic pyrolysis are also included for comparison). As far as the untreated biomass is concerned, the effect of the strongly acidic zeolite H-ZSM-5 was similar to that observed in other studies with different lignocellulosic biomass feedstocks [3,12,16,18,19]. The yield of bio-oil (total liquid products) was decreased substantially compared to the non-catalytic pyrolysis due to the decrease of the organics and despite the significant increase of water. Gases were also increased markedly and the carbonaceous residue was increased due to increased coke deposited on the catalyst. It is interesting to note however, that the oxygen content of the organic phase of the bio-oil was reduced significantly, due to the enhanced removal of organic oxygenates from the bio-oil, as is discussed below. All the above changes by the presence of H-ZSM-5 are due to its strong acidity, mainly of Brönsted type. The increased water fraction is due to enhanced dehydration reactions, the decrease of organics and the increase of hydrocarbon gases (as is shown below) due to cracking reactions, and the increase of coke due to aromatization and polymerization reactions, that can all take place on H-ZSM-5. The effect of zeolite silicalite on product yields followed the same trend as that of H-ZSM-5, but the changes were not so intense. However, based on the difference in the number of strong acid sites (silicalite contains very few aluminum atoms) of the two zeolites, one would not expect such a pronounced effect of silicalite on product yields. The mesoporous aluminosilicate Al-MCM-41, which contain appreciable number of acid sites (both Brönsted and Lewis) of relatively mild/medium acidity strength, induced similar changes with those of silicalite, except that the coke deposited on the catalyst was significantly higher, even compared to that produced by H-ZSM-5. Similar results have been obtained previously with mesoporous Al-MCM-41 [21], depending however on the type of the feedstock biomass used and the type of MCM-41 tested (i.e. Si/Al ratio) [22]. The effect of strong zeolitic acidity compared to the mild acidity of Al-MCM-41 can also be identified by the increased production of ethylene and propylene with the two zeolitic catalysts (Table 5), due to enhanced cracking reactions that can take place on the surface of these two zeolites. Another noticeable effect in the composition of gases is the increase of CO and decrease of CO_2 concentration, with all the three catalysts tested.

In the case of the hydrothermally pretreated biomass, the three above acidic catalysts induce similar effects compared to those when the untreated biomass was used as feedstock (Table 4). This was expected since the remaining components of the pretreated biomass, which consists mainly of the cellulosic and lignin fractions of the parent biomass, are of the same type (carbohydrates and phenolics) with those of the untreated biomass. The only difference would be that the ratio of phenolics over carbohydrates increases in the former feedstock since the carbohydrates of hemicellulose have been removed during the hydrothermal treatment. The decrease of the total liquids (bio-oil) yield with the three catalytic materials is higher compared to that with the untreated biomass; however, this is attributed to the conversion over the acidic catalysts of the very high amounts of sugars (as is discussed above) that are present in the non-catalytic pyrolysis oil/vapours of the hydrothermally pretreated biomass. As a result the organics in bio-oil are significantly reduced by the use of all the catalysts while the increase of water in bio-oil and of gaseous products is higher with the pretreated biomass. Coke formation is similar with both biomass feeds while similar substantial decrease of the oxygen content of organics is observed in both cases with all the catalysts. However, when comparing the product yields between the catalytic upgrading experiments of the untreated and pretreated biomass pyrolysis vapours, it can be clearly seen that the use of all the three acidic catalysts with the hydrothermally pretreated biomass leads to higher

Table 5
Composition of gases (wt.% on total gases) produced by non-catalytic flash pyrolysis of lignocellulosic biomass (untreated and hydrothermally pretreated) and by catalytic upgrading of the biomass pyrolysis vapours.

Catalyst	H_2	CO	CO_2	CH_4	C_2H_4	C_3H_6	C_2–C_6 alkanes
Feedstock: untreated lignocellulosic biomass							
Non-catalytic (silica sand)	0.33	36.15	55.17	5.63	1.24	0.92	1.37
Silicalite	0.22	42.17	42.57	3.56	3.40	3.63	4.58
ZSM-5	0.15	46.01	38.68	3.26	5.38	3.78	2.78
Al-MCM-41	0.23	40.89	45.42	5.49	1.70	2.36	3.98
Feedstock: hydrothermally pretreated lignocellulosic biomass							
Non-catalytic (silica sand)	0.41	46.77	41.02	7.14	1.58	1.16	1.70
Silicalite	0.15	54.68	30.17	4.91	4.37	3.28	2.31
ZSM-5	0.19	59.49	24.24	4.34	5.83	3.53	2.32
Al-MCM-41	0.25	53.44	29.46	6.93	2.11	2.44	5.31

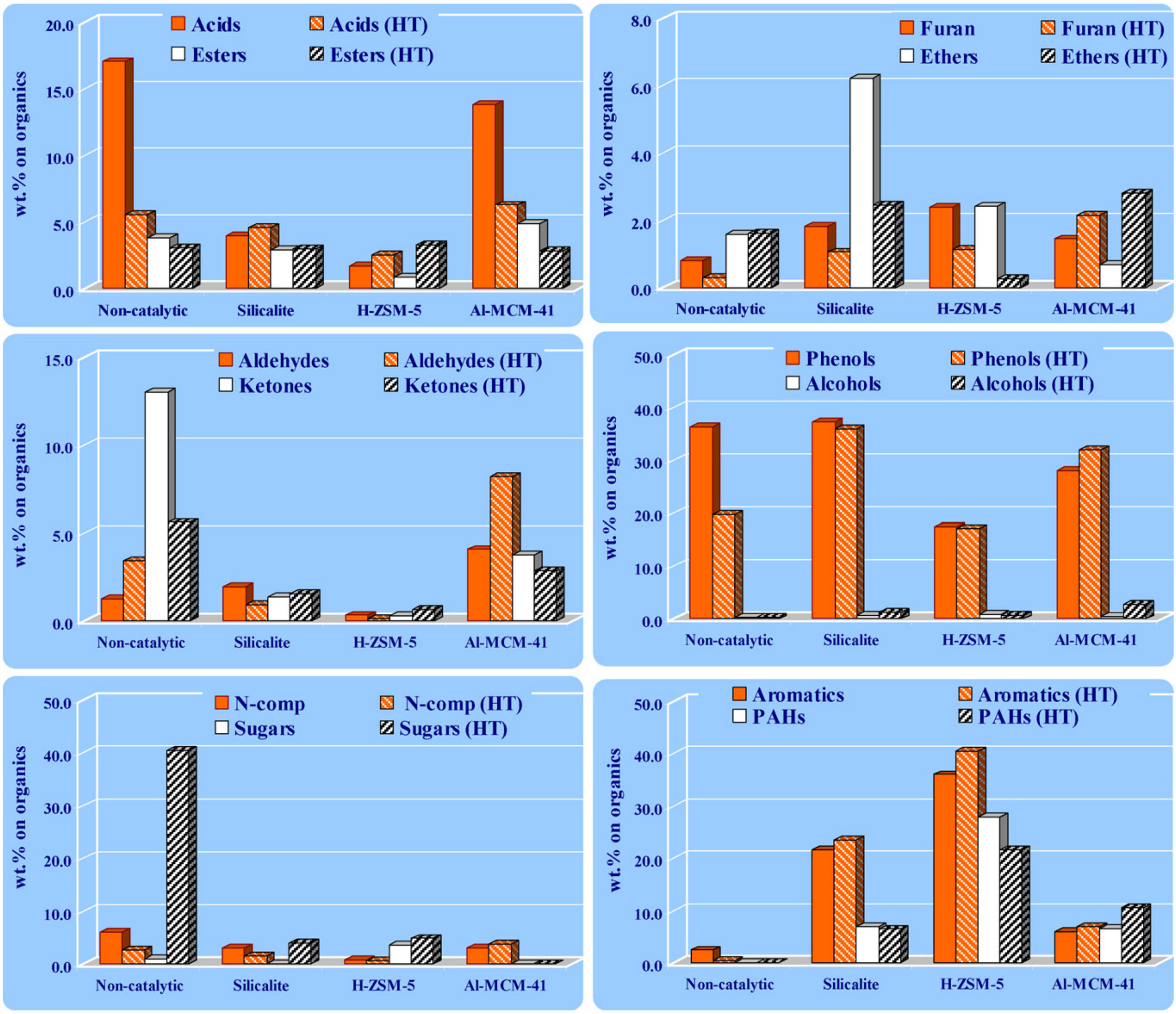

Fig. 1. Composition of bio-oil (wt.% on total organics) produced by non-catalytic flash pyrolysis of lignocellulosic biomass (untreated and hydrothermally pretreated) and by the catalytic upgrading of biomass pyrolysis vapours. The (HT) refers to the experiments with the hydrothermally pretreated biomass.

amount of total liquids (bio-oil), mainly due to the higher content of organics. These organics are not sugars (they were eliminated by the use of catalysts as is shown in Fig. 1 below) but still contain high amounts of oxygen (Table 4). The effects of the three catalysts on the composition of gaseous products when using the hydrothermally pretreated biomass are similar to those observed (see above) in the case of the untreated biomass feed (Table 5).

The composition of bio-oil (wt.% on total organics) produced by the non-catalytic flash pyrolysis of lignocellulosic biomass (untreated and hydrothermally pretreated) and by the catalytic upgrading of the pyrolysis vapours is shown in Fig. 1. The main groups identified in the organic phase of the catalytically upgraded bio-oil/vapours derived from pyrolysis of the untreated biomass were phenols, aromatics and polycyclic aromatic hydrocarbons (PAHs), while acids, esters, furans, ethers, aldehydes and ketones were also present but in lower concentrations. On the other hand, the bio-oil derived from the non-catalytic flash pyrolysis contained high amounts of acids, ketones and phenols, and almost no aromatics and PAHs. From the data presented in Fig. 1, it can be clearly seen that the zeolitic strong acid sites favor decarboxylation (significant decrease of carboxylic acids) in contrast to the mildly acidic Al-MCM-41 which induces only a slight decrease of the acids. Esters are more resistant to both strong and weak acid sites compared to carboxyl group. The formation of ketones is significantly suppressed by both the zeolitic and the mesoporous catalysts, while there is a small increase of aldehydes with all catalysts. Phenols are retained the same with the use of silicalite but decrease with the other two catalysts, especially with H-ZSM-5 zeolite. Furans and ethers are enhanced by the presence of catalysts, especially of the two zeolitic catalysts. From the above results it can be suggested that the lower oxygen content of organics in the bio-oils produced by the catalytic upgrading of the flash pyrolysis vapours compared to the bio-oil of the non-catalytic flash pyrolysis (Table 4) are due to the significant reduction, mainly with the strongly acidic H-ZSM-5 zeolite, of the concentration of acids, ketones and phenols. Zeolites increase significantly the fractions of aromatics, possibly via two routes: either the depolymerization and dehydration of phenols or the condensation-dehydrocyclization-aromatization reaction steps of small alkenes on the strong acid sites of H-ZSM-5. However, the concentration of undesirable PAHs is also significantly increased with the zeolitic catalysts.

Similar catalytic effects can be identified in the upgrading of flash pyrolysis vapours of the hydrothermally pretreated biomass (Fig. 1), as was discussed also above with regard to the effects on total product yields. However, there are some points that need to be emphasized in the composition of the organic phase of bio-oil. In the case of the pretreated biomass, the concentration of acids is not reduced by the use of catalysts (except of a small reduction with zeolite H-ZSM-5) since their concentration in the non-catalytic flash pyrolysis oil of the pretreated biomass is already quite low. The very high concentration of sugars produced by the non-catalytic flash pyrolysis of the hydrothermally pretreated biomass is practically zeroed by the use of all the catalysts, as expected due to acid catalyzed reactions at the relatively high temperature of 500 °C. The removal of sugars affected the relative concentrations of the compounds in the bio-oil, and mainly that of phenols which were actually increased by the use of silicalite and Al-MCM-41. However, the increased concentration of phenols could also be attributed to the higher proportion of lignin in the pretreated biomass compared to the untreated one, which can be converted to phenolic compounds over the less acidic catalysts (i.e. silicalite and Al-MCM-41). The concentration of aromatics and PAHs were significantly increased by the use of both the zeolitic and Al-MCM-41 catalysts, similar to the upgrading of the untreated biomass pyrolysis vapours.

4. Conclusions

The hydrothermal pretreatment of lignocellulosic biomass (beech wood, Lignocel) at a severity factor (Ro) of 3.55 (190 °C at autogeneous pressure for 8 min) led to solubilization of hemicellulose and small part of lignin (~35 wt.% loss of solids). The liquid product of the hydrothermal pretreatment contained mainly acetic acid, pentoses and hexoses from hemicellulose, furfural and HMF from the dehydration of pentoses (xylose) and hexoses (glucose), and few phenolic components. This liquid could be further utilized/upgraded catalytically or (bio)chemically towards fuels (i.e. bioethanol), fuel additives or chemicals (i.e. furfural). The solid product, i.e. the hydrothermally pretreated biomass, exhibited similar C/H and C/O ratios and less amount of ash compared to those of the untreated biomass.

The non-catalytic flash pyrolysis of the hydrothermally pretreated biomass led to the production of substantial amount of sugars, mainly levoglucosan, in the produced bio-oil, compared to the untreated biomass, with a concomitant reduction of the three major groups in the flash pyrolysis oil of beech wood, i.e., carboxylic acids, ketones and phenols. The use of strongly acidic zeolites H-ZSM-5 and silicalite (with very few number of acid sites due to Al impurities) and of the mildly acidic mesoporous aluminosilicate Al-MCM-41, induced similar effects on product yields and on the composition of bio-oil for both the untreated and the hydrothermally pretreated biomass. In general, the strongly acidic H-ZSM-5 zeolite, which contains relatively high number of framework Brönsted acid sites compared to silicalite, leads to increase of water in the bio-oil via dehydration reactions and decrease of organics, increase of gases and coke due to decarbonylation, decarboxylation, dealkylation, cracking and aromatization reactions. The zeolite silicalite with the very low number of strong Brönsted acid sites and the Al-MCM-41 with the relatively higher number of weak (Brönsted and Lewis) acid sites induce similar effects with those of H-ZSM-5 but to a less extent. An exception is the observed significantly higher amount of coke deposited on the Al-MCM-41 mesoporous catalyst compared to the zeolitic ones. Regeneration of all the catalysts by burning off the coke at 550 °C had a relatively small effect on their porosity characteristics, i.e. loss of surface area up to 10% for the zeolites and 20% for the Al-MCM-41 catalyst.

With regard to the composition of the bio-oil, all the catalysts, and mostly the strongly acidic H-ZSM-5 zeolite, reduce the oxygen content of the organics, mainly by decreasing the concentration of acids, ketones and phenols in the bio-oil produced by the catalytic upgrading of the untreated biomass. In the case of the hydrothermally pretreated biomass, the decrease of oxygen content is mainly attributed to the almost complete conversion of sugars present in the non-catalytic pyrolysis oil by the use of all catalysts. For both types of biomass feeds, the use of catalysts leads to a significant increase of aromatics and PAHs in the bio-oil, while the catalytic upgrading of the hydrothermally pretreated biomass vapours by the less acidic silicalite and Al-MCM-41 leads to increase of the concentration of phenols in the bio-oil.

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References

[1] H.B. Goyal, D. Seal, R.C. Saxena, Renew. Sustain. Energy Rev. 12 (2008) 504.
[2] Y.C. Lin, G.W. Huber, Energy Environ. Sci. 2 (2009) 68.
[3] G.W. Huber, S. Iborra, A. Corma, Chem. Rev. 106 (2006) 4044.
[4] B.V. Babu, Biofuels Bioprod. Bioref. 2 (2008) 393.
[5] A.V. Bridgwater, D. Meier, D. Radlein, Org. Geochem. 30 (1999) 1479.
[6] A. Demirbas, Energy Sources, Part A: Recov. Utilization Environ. Effects 31 (2009) 602.
[7] A.V. Bridgwater, G. Grassi, Biomass Pyrolysis Liquids Upgrading and Utilisation, Elsevier Applied Science, London and New York, 1991.
[8] A.A. Lappas, S. Bezergianni, I.A. Vasalos, Catal. Today 145 (2009) 55.
[9] A. Corma, G.W. Huber, L. Sauvanaud, P. O'Connor, J. Catal. 247 (2007) 307.
[10] A.V. Bridgwater, Appl. Catal. A: Gen. 116 (1994) 5.
[11] J. Wildschut, F.H. Mahfud, R.H. Venderbosch, H.J. Heeres, Ind. Eng. Chem. Res. 48 (2009) 10324.
[12] M. Stocker, Angew. Chem. Int. Ed. 47 (2008) 9200.
[13] T.F. Degnan Jr., Stud. Surf. Sci. Catal. 170 (2007) 54.
[14] B.W. Wojciechowski, A. Corma, Catalytic Cracking, Catalysts, Chemistry and Kinetics, Chemical Industries/25; Marcel Dekker, New York, 1986, p. 127.
[15] T.R. Carlson, G.A. Tompsett, Z.W.C. Conner, Z.G.W. Huber, Top. Catal. 52 (2009) 241.
[16] A. Aho, N. Kumar, K. Eränen, T. Salmi, M. Hupa, D.Yu. Murzin, Fuel 87 (2008) 2493.
[17] A. Aho, N. Kumar, A.V. Lashkul, K. Eränen, M. Ziolek, P. Decyk, T. Salmi, B. Holmbom, M. Hupa, D.Yu. Murzin, Fuel 89 (2010) 1992.
[18] A.A. Lappas, M.C. Samolada, D.K. Iatridis, S.S. Voutetakis, I.A. Vasalos, Fuel 81 (2002) 2087.
[19] P.T. Williams, P.A. Horne, J. Anal. Appl. Pyrol. 31 (1995) 39.
[20] P.A. Horne, P.T. Williams, Fuel 75 (1996) 1043.
[21] E.F. Iliopoulou, E.V. Antonakou, S.A. Karakoulia, A.A. Lappas, I.A. Vasalos, K.S. Triantafyllidis, Chem. Eng. J. 134 (2007) 51.
[22] E. Antonakou, A. Lappas, M.H. Nilsen, A. Bouzga, M. Stöcker, Fuel 85 (2006) 2202.
[23] J. Adam, E. Antonakou, A. Lappas, M. Stöcker, M.H. Nilsen, A. Bouzga, J.E. Hustad, G. Øye, Micropor. Mesopor. Mater. 96 (2006) 93.
[24] M.H. Nilsen, E. Antonakou, A. Bouzga, A. Lappas, K. Mathisen, M. Stöcker, Micropor. Mesopor. Mater. 105 (2007) 189.
[25] J. Adam, M. Blazsó, E. Mészáros, M. Stöcker, M.H. Nilsen, A. Bouzga, J.E. Hustad, M. Grønli, G. Øye, Fuel 84 (2005) 1494.
[26] A. Pattiya, J.O. Titiloye, A.V. Bridgwater, J. Anal. Appl. Pyrol. 81 (2008) 72.
[27] K.S. Triantafyllidis, E.F. Iliopoulou, E.V. Antonakou, A.A. Lappas, H. Wang, T.J. Pinnavaia, Micropor. Mesopor. Mater. 99 (2007) 132.
[28] E.F. Iliopoulou, K. Papazisi, S. Stephanidis, K. Kalogiannis, A.A. Lappas, K.S. Triantafyllidis, Energy Environ. Sci., in preparation.
[29] A.T.W.M. Hendriks, G. Zeeman, Bioresour. Technol. 100 (2009) 10.
[30] E.b.M. Hassan, P.H. Steele, L. Ingram, Appl. Biochem. Biotechnol. 154 (2009) 182.
[31] E. Selli, L. Forni, Micropor. Mesopor. Mater. 31 (1999) 129.
[32] Ch. Baerlocher, L.B. McCusker, D.H. Olson, Atlas of Zeolite Framework Types, Sixth ed., Elsevier, Amsterdam, 2007.
[33] T. Chen, A. Men, P. Sun, J. Zhou, Z. Yuan, Z. Guo, J. Wang, D. Ding, H. Li, Catal. Today 30 (1996) 189.

[34] C.A. Emeis, J. Catal. 141 (1993) 347.
[35] C.S. Triantafillidis, A.G. Vlessidis, L. Nalbandian, N.P. Evmiridis, Micropor. Mesopor. Mater. 47 (2001) 369.
[36] S.A. Karakoulia, K.S. Triantafyllidis, G. Tsilomelekis, S. Boghosian, A.A. Lemonidou, Catal. Today 141 (2009) 245.
[37] A. Corma, M.S. Grande, V. Gonzalez-Alfaro, A.V. Orchilles, J. Catal. 159 (1996) 375.
[38] F. Shafizadeh, Y.L. Fu, Carbohydr. Res. 29 (1973) 113.
[39] H. Kawamoto, M. Murayama, S. Saka, J. Wood Sci. 49 (2003) 469.
[40] D.K. Shen, S. Gua, A.V. Bridgwater, J. Anal. Appl. Pyrol. 87 (2010) 199.