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On the effect of hydrothermal pretreatment of biomass and catalytic conversion mechanism in pyrolysis process with a review of flash pyrolysis of lignocellulosic biomass using effective catalyst

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ABSTRACT

The inception of biofuels have induced the need for technologies such as pyrolysis, gasification and related. With flash pyrolysis (non-catalytic) and the obtained product yields 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). A review of catalytic upgrading of pyrolysis vapors of lignocellulosic biomass (beech wood) in its parent state or after being subjected to hydrothermal pretreatment is taken up in the concluding part.

Keywords: pyrolysis; catalyst; bio-oil; biomass

1. INTRODUCTION

There are several reasons for biofuels to be considered as relevant technologies by both developing and industrialized countries. These include energy security, environmental concerns, foreign exchange savings, and socioeconomic issues, mainly related to the rural sector. A large number of research projects in the field of thermochemical and biochemical conversion of biomass, mainly on liquefaction, pyrolysis, and gasification, have been carried out.

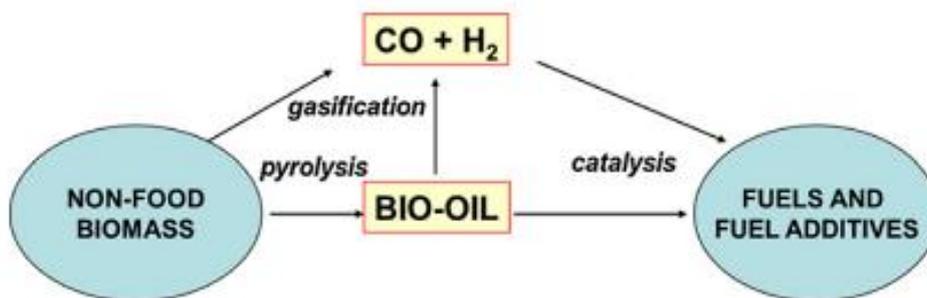


Figure 1. Thermochemical/catalytic approaches for transformation of non-food biomass to fuel additives [1]

Pyrolysis products are divided into a volatile fraction, consisting of gases, vapors, and tar components, and a carbon-rich solid residue. The gasification of biomass is a thermal treatment, which results in a high production of gaseous products and small quantities of char and ash. Bioethanol is a petrol additive/substitute.

Bridgwater [18,19] has classified the different modes of pyrolysis as shown in Table 1.

Table 1. Modes of Pyrolysis adapted from Bridgwater [18,19]

Mode of pyrolysis	Temperature/°C	Residence time	Yields/%		
			Liquid	Char	Gas
Slow	400	Very long	30 (70% water)	35	35
Intermediate	500	Moderate (10-20s)	50 (50% water)	25	25
Fast	500	Short (<2s)	75 (25% water)	12	13
Gasification	800	Long	5	10	85

Pyrolysis seems to be a simple and efficient method to produce gasoline and diesel like fuels. Hydrocarbons from biomass materials were used as raw materials for gasoline and diesel-like fuel production in a cracking system similar to the petroleum process now used. Pyrolysis is the thermal decomposition of biomass by heat in the absence of oxygen, which results in the production of char, bio-oil, and gaseous products. Thermal decomposition in an oxygen-deficient environment can also be considered to be true pyrolysis as long as the primary products of the reaction are solids or liquid. Three-step mechanism reactions for describing the kinetics of the pyrolysis of biomass can be proposed:

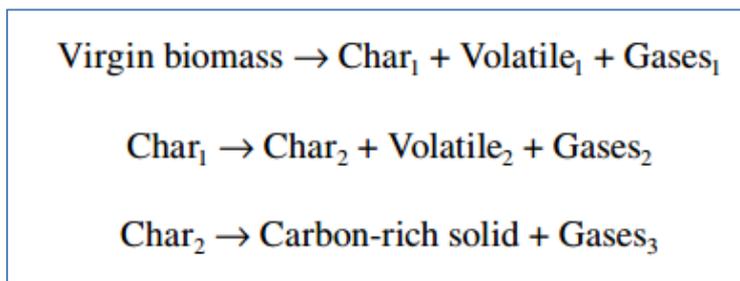


Figure 2. Three step mechanism for Pyrolysis [2].

The most interesting temperature range for the production of the pyrolysis products from biomass is between 625 and 775 K. The charcoal yield decreases as the temperature increases. The production of the liquid products has a maximum at temperatures between 625 and 725 K. Conventional pyrolysis is defined as pyrolysis that occurs at a slow rate of heating. The first stage of biomass decomposition, which occurs between 395 and 475 K, can be called pre-pyrolysis. During this stage some internal rearrangement, such as water elimination, bond breakage, appearance of free radicals, and the formation of carbonyl, carboxyl, and hydro-peroxide groups, takes place. The second stage of the solid decomposition corresponds to the main pyrolysis process. It proceeds at a high rate and leads to the formation of the pyrolysis products. During the third stage, the char decomposes at a very slow rate and carbon-rich residual solid form.

Pyrolysis of biomass may proceed through radical or catalytic mechanisms. Different salts and acids present in biomass and formed during pyrolysis may affect the reactions taking place at increased temperatures [20].

Bridgwater [14] has indicated that pyrolysis and gasification should be considered as complementary rather than competitive. The advantage of the thermochemical approach is that all the biomass is converted, including the lignin. The disadvantage is that heating to high temperatures is energy intensive. The products of pyrolysis, bio-oils, are more complex than the products of acidic hydrolysis in relation to further conversion to fuels. It is important that when compared to the hydrolysis route, the pyrolysis route gives quite similar carbon yields of products [15,16]. The main pyrolysis applications and their variants are listed in Table 1.

Table 2. Applications and variables for pyrolysis [2].

Main Pyrolysis Applications and Their Variants				
Method	Residence Time	Temperature (K)	Heating Rate	Products
Carbonization	Days	675	Very low	Charcoal
Conventional	5–30 min	875	Low	Oil, gas, char
Fast	0.5–5 s	925	High	Bio-oil
Flash-liquid	<1 s	<925	Very high	Bio-oil
Flash-gas	<1 s	<925	Very high	Chemicals, gas
Hydro-pyrolysis	<10 s	<775	High	Bio-oil

Biomass is a mixture of structural constituents (hemicelluloses, cellulose, and lignin) and minor amounts of extractives which each pyrolyse at different rates and by different mechanisms and pathways. It is believed that as the reaction progresses the carbon becomes less reactive and forms stable chemical structures, and consequently the activation energy increases as the conversion level of biomass increases. Lignin decomposes over a wider temperature range compared to cellulose and hemicelluloses, which degrade rapidly over narrower temperature ranges, hence the apparent thermal stability of lignin during pyrolysis.

2. ENERGY TRENDS AND BIOMASS ENERGY

Most of the energy consumed nowadays originates from nonrenewable 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 [3-5].

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 m² year for example eucalyptus, pseudoacacia, willow, miscanthus, switch grass, cellulosic sorghum, etc. [6]. Also the CO₂ evolved during utilization of biofuels is consumed during photosynthesis for plant growth and so it does not contribute to the problem of greenhouse gas emissions.

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, CO₂, H₂ and gaseous C₁ – C₄ hydrocarbons) and solid (char) products [3,7,8]. 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 vapor contact time (e.g. less than 2-3 s) and fast vapor cooling rates (quenching). Biomass is usually pyrolyzed in the presence of inert solid heat 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) [6].

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. 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 or hydro-processing,

minimization of oxygenated compounds (e.g. acids, furans, ketones, etc.) and increase of hydrocarbons (aromatics, aliphatics, etc.) is required.

3. BIO OIL OR PYROLYSIS OIL

All the products of biomass pyrolysis are valuable and can be used. The most interesting product is pyrolysis oil as it can be converted to fuel additives in a wide variety of ways. The yield of pyrolysis oil under optimized fast pyrolysis conditions may reach 70-80%. It should be noted that this liquid includes up to 25% of water. Slow pyrolysis gives considerably higher concentrations of water. At lower temperatures and with longer residence times, the yield of pyrolysis oil decreases while char is formed in higher amounts. High temperatures lead to the formation of gases.

Bio-oil may consist of more than 300 organic compounds. It is an easily transportable source of chemicals and it has energy content higher than that of biomass. Another advantage is that it is cleaner than biomass. Given below is the comparison of some of the properties of bio-oil with those of conventional transport fuels.

Table 3. Some features of bio-oil, gasoline and diesel [17].

	Bio-oil	Gasoline	Diesel
Carbon chain length	Up to 100	5–10 branched alkanes, aromatics	12–20 linear alkanes
H/C ratio	1.2–1.4	1–2	~2
O/C ratio	0.5	0	0

Bio-oil contains some heavy aromatic compounds and this contrasts with gasoline and diesel which comprise of mixtures of hydrocarbons with relatively low carbon chain lengths of 5-10 and 12-20, respectively. The H/C ratio in bio-oil is in the range 1.2-1.4 and this is closer to that of aromatics than to that of alkanes. The O/C ratio in bio-oil is high (0.5) as this liquid contains significant quantities of water and oxygen-containing groups. There are four main catalytic approaches to transform bio-oil to fuel additives: gasification, hydrotreating, cracking and esterification. Pyrolysis can be also performed in the presence of catalysts, bringing about simultaneous pyrolysis of the biomass and upgrading of the product [17].

An approach to de-oxygenation of bio-oil is catalytic cracking. Catalytic cracking is normally performed over solid acid catalysts such as aluminosilicates and zeolites. This approach does not require added hydrogen and oxygen is eliminated in the form of water and CO₂. As compared to hydro-treating, cracking gives a higher value transport fuel product because of higher aromatic content.

However, the yields are lower and the amount of coke formed is relatively high. The yields obtained in the process reach 50-60% of the theoretical maximum. The liquid product obtained by cracking as the product obtained by hydrotreating demands further refining to produce gasoline or diesel hydrocarbons

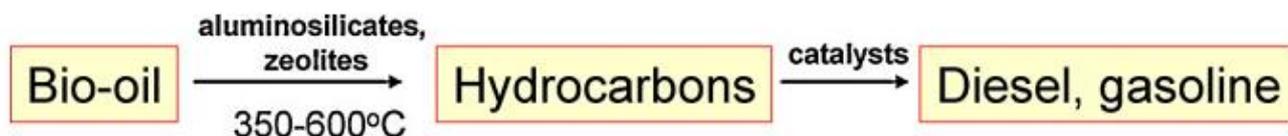


Figure 3. Scheme of bio-oil upgrading via cracking [31].

4. CATALYST UTILIZATION PROCESSES

A current aim of society is to produce fuels from non-food biomass and catalysis is central to achieving this aim [18]. A way to alter and fine-tune the composition of bio-oil specimen is the use of catalysts during pyrolysis, i.e. the catalytic pyrolysis of biomass feeds.

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 [11,12].

The type of biomass and the reactor system/conditions play an important role on product yields; however, it is generally accepted that zeolite 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.

4. 1. Zeolite utilization as catalyst

Zeolites with different porous structure have frequently been used for catalytic biomass pyrolysis and bio-oil upgrading. ZSM-5 zeolites are known catalysts for catalytic cracking and they have been used more often than other zeolites for the cracking of biomass and bio-oil. Gayubo et al. [20] explained the choice of this zeolite by suggesting that it provides a suitable compromise between activity, shape selectivity to <C12 hydrocarbons, limited deactivation by coke, and high thermal stability.

Samolada et al. [21] have used ZSM-5 zeolites as catalysts for pyrolysis of biomass and found that introduction of these to a reactor used for non-catalytic biomass pyrolysis led to a decrease of the concentration of liquid products and to an increase of the quantity of gaseous products. This might be expected as the application of catalysts gives cracking, leading to a decrease of the molecular weight of the product molecules.

Aho et al. [22] have compared non-catalytic (using a reactor with added quartz sand) and catalytic pyrolysis of pine chips in the presence of different zeolites in a fluidized bed reactor. They observed a decrease of the organic fraction in the pyrolysis oil obtained in the experiments using the catalysts and showed that ZSM-5 zeolite gave the highest yield of organic fraction in pyrolysis oil as compared with -, Y- and mordenite zeolites ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 12-25$). The formation of acids was lower with ZSM-5, but the formation of ketones was higher than over the other zeolites. Polyaromatic hydrocarbons were detected with zeolites, but none was observed when only quartz sand was added to the reactor.

Aho et al. [23] have also studied the effect of the acidity of zeolite on the properties of the bio-oil formed by catalytic pyrolysis.

Table 4. The yield of products (wt.%) from the pyrolysis of pine chips over different zeolites at 450 °C. adapted from Aho et al. [22]

	Quartz sand	β -zeolite	Y zeolite	Mordenite zeolite	ZSM-5 zeolite
SiO ₂ /Al ₂ O ₃ ratio	-	25	12	20	23
Pore size/nm	-	0.76 × 0.64, 0.55 × 0.55	0.74 and 1.18	0.70 × 0.65	0.52 × 0.57, 0.53 × 0.56
Organic fraction in pyrolysis oil	27.3	15.1	9.0	17.6	20.7
Water	5.4	13.9	16.7	14.4	13.0
Char and coke	15.3	21.6	23.2	19.9	14.2
Gas	52.0	49.5	51.1	48.1	52.1

Table 5. The yield of products (wt.%) from the pyrolysis of pine chips over -zeolites with different SiO₂/Al₂O₃ content at 450°C as adapted from Aho et al. [23].

SiO ₂ /Al ₂ O ₃ ratio	Concentration of Brønsted acid sites at 450°C/ μ .mol/g	Organic fraction of bio-oil	Water	Char and coke	Gas
25	125	15.8	13.1	21.7	49.4
300	23	17	9.5	20.1	53.4

They reported that an increase in the acidity of the zeolite (decrease of the SiO₂/Al₂O₃ ratio) gave a decrease in the yield of the organic fraction of the pyrolysis oil and that there was concurrently an increase in the water and poly-aromatic hydrocarbons yields. However, as can be seen from the data of Table 4, the effect of the concentration of Brønsted acidic sites, although noticeable, is small. Hence, it seems that additional work on this subject might be useful.

Bridgwater [25] has pointed out that an important step in the reactions of hydrocarbons over zeolites is aromatization. Huber and Corma [26] noticed that this aromatization may proceed via the Diels–Alder reaction in which olefins obtained by cracking combine with each other, forming cyclic and aromatic compounds.



Figure 4. Diels-Alder reaction.

Lignin is the most difficult component of biomass to convert. Thring et al. [27] have reported that it is possible to convert lignin to a liquid product consisting mainly of aromatic hydrocarbons (benzene, toluene and xylene, with toluene dominating) with yields of up to 90% using a ZSM-5 catalyst (Si/Al = 56) at temperatures from 500 to 650 °C. The liquid mixture obtained possessed a high octane number and the gaseous product contained C1 – C5 hydrocarbons, CO and CO₂. These authors suggest that the mechanism involves the initial formation of olefins which then undergo further cyclization, oligomerization and alkylation reactions due to the presence of strong acid sites; this is in accordance with the ideas put forward by Huber and Corma [26]. Jackson et al. [28] have also reported the formation of 46.7% of simple aromatics and 46.2% of naphthalenic ring compounds from lignin using a ZSM-5 zeolite at 600 °C. The same authors found that a Co/Mo/Al₂O₃ catalyst gave a liquid product containing 21% aromatics, 4% naphthalenics and 75% oxygenated aromatics.

It is well known that coke is formed on many catalysts under the reaction conditions used for catalytic pyrolysis and that this leads to catalyst deactivation. Carlson et al. [29] have shown that coke formation can be minimized by using high heating rates of the biomass with the catalyst, high catalyst to feed ratios and proper catalyst selection. Aho et al. [30] have studied the nature of the coke formed on different zeolites by dissolving the zeolite in hydrofluoric acid and then dissolving the coke in dichloromethane. The coke content was highest using Y-zeolites, probably because of the presence of large pores. These authors showed that the coke formed consisted mostly of linear long-chain alkanes and alkenes, ranging from C10 to C28. The number of carbon atoms in the chain was even (10, 12, 14, etc.). The coke formed on Y-zeolite and ZSM-5 contained also branched C18, C20, C22 alkanes and a linear C30 alkene. The same authors [29,30] found that regeneration of the deactivated catalysts was possible in air at high temperatures.

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 [13].

5. EXPERIMENTAL ANALYSIS OF HYDROTHERMAL PRETREATMENT OF BIOMASS

Stephanidis et al., 2011, studied the flash pyrolysis (non-catalytic) and the catalytic upgrading of pyrolysis vapors 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 analyzed here with regard to their work on the discussed with regard to the effect of hydrothermal pretreatment of biomass or the effect of catalyst's type (zeolitic or mesoporous). A review of their work is given below.

5. 1. Catalyst material

The catalytic materials used by Stephanidis et al. for the biomass pyrolysis experiments were the micro-porous 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 [20]. Since the commercial ZSM-5 zeolite was provided in NH₄⁺ form, it was previously calcined at 500°C for 2 h to convert it to H⁺ form.

5. 2. Properties of the feed biomass used and the hydrothermal method

A commercial lignocellulosic biomass (Lignocel HBS 150-500) originating from beech wood was used in the 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 H₂O 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 8min, 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 hydrothermal pretreatment. The severity factor is an expression of combined effect of time and temperature of the hydrothermal pretreatment. It is defined by the equation $Ro = t \cdot \exp[(T - 100)/14.75]$ where *t* is the time of the hydrothermal pretreatment in minutes and *T* is the temperature of the pretreatment in °C [13]. The properties of both the untreated and the hydrothermally pretreated biomass are shown in Table 6.

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

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

The ash content of the 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 12h takes place. The moisture analysis of the samples was done by drying at 105 °C for 6 h. C, H and N content was determined by elemental analysis using a LECO-800 CHN analyzer.

5. 3. Reactor specification for the analysis

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 vapors were then directly transferred with the aid of N₂ (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 N₂ was 15 min. An additional purging with N₂ (50 cc/min) was performed for another 10 min during cooling of the reactor [6]. The inert solid used was silica sand with particle size of 90-180 μm. A typical residence time of the vapor phase in the silica sand bed was <0.1 s. For the catalytic experiments the inert silica and was replaced with the various catalysts under study.

This type of experiments can be referred to as in situ catalytic upgrading of biomass pyrolysis vapors and are of the “ex-bed” type (i.e. there was no mixing of solid biomass with the solid catalyst). 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 (Pre-column: 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.

6. RESULTS AND FURTHER SCOPE

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) as conducted by S. Stephanidis et al. led to solubilization of hemicellulose and a small part of lignin (~ 35 wt. % loss of solids). The liquid product obtained from 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. There is scope for the liquid to be further utilized/upgraded catalytically or biochemically 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 has less amount of ash compared to those of the untreated biomass. 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.

The chemical composition, porosity and acidity characteristics of zeolitic and mesoporous (alumino) silicate catalytic materials for upgrading of biomass flash pyrolysis vapors as conducted by S. Stephanidis et al. can be found at table below.

Table 7. Characteristics of zeolitic and mesoporous silicate catalytic materials.

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)	Brønsted 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

^c At P/P₀ = 0.99.

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 vapors by the less acidic silicalite and Al-MCM-41 leads to increase of the concentration of phenols in the bio-oil [6].

7. CONCLUSION

A review of biomass catalytic pyrolysis is shown as how catalyst efficiency matters in bio-oil production. Biomass from fast pyrolysis is a transportable intermediate which has various utilizations. Upgrading this bio-oil to remove water and oxygen content is necessary. Problems like deactivation of catalyst due to coke deposition can be dealt by optimizing reaction conditions and mode of operation of process, which can be a cost competitive oil alternative in the future. Products from hydrothermal pretreatment consist mainly of acetic acid, pentoses and hexoses which can be further upgraded to bioethanol or fuel additives catalytically or by biochemical reactions. With regard to catalytic activity zeolite based catalyst reduces oxygen content of organics by decreasing concentration of acids, ketones and phenols in the bio-oil produced.

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