Catalytic upgrading of biomass pyrolysis vapours using faujasite zeolite catalysts

T.S. Nguyen [a], M. Zabeti [a], L. Lefferts [a], G. Brem [b], K. Seshan [a,*]

[a] Catalytic Processes and Materials, Faculty of Science and Technology, University of Twente, PO Box 217, 7500 AE Enschede, The Netherlands
[b] Laboratory of Thermal Engineering, Faculty of Engineering Technology, University of Twente, PO Box 217, 7500 AE Enschede, The Netherlands

ABSTRACT

Bio-oil produced via fast pyrolysis of biomass has the potential to be processed in a FCC (fluid catalytic cracking) unit to generate liquid fuel. However, this oil requires a significant upgrade to become an acceptable feedstock for refinery plants due to its high oxygen content. One promising route to improve the quality of bio-oil is to pyrolyse the parent biomass in the presence of a catalyst. This work investigates the influence of faujasite catalysts on the pyrolysis of pinewood. Pyrolysis process with Na-faujasite, $Na_{0.2}H_{0.8}$-faujasite, and H-faujasite (Na-FAU, $Na_{0.2}H_{0.8}$-FAU, and H-FAU) were carried out in a fixed-bed reactor at 500 °C. It is shown that, in the same condition, catalytic upgrading of pyrolysis vapour is superior to in-situ catalytic pyrolysis of biomass when it comes to quality of bio-oil. The yields of coke, gas and water increase while that of organic phase decreases proportional with the concentration of protons in catalysts. Compared to the other two catalysts, $Na_{0.2}H_{0.8}$-FAU removes the most oxygen from bio-oil, reduces amount of acids and aldehydes/ketones which result in a higher energy-contained and more stable oil with less corrosive property. However, the biggest contribution to the oxygen removal is via the formation of reaction water, which is not an optimum path. This leaves space for future development.

© 2012 Elsevier Ltd. All rights reserved.

1. Introduction

Declining fossil resources, combined with increased demand for petroleum by emerging economies, as well as political and environmental concerns about fossil fuels are driving our society to search for new sources of fuels. Biomass is a promising sustainable source of green fuels [1]. One option for the production of green fuels is to use biomass-derived feedstocks/fuel precursors in existing petroleum refinery plants. Petroleum refineries are already built and use of this existing infrastructure for the production of biofuels therefore requires little capital investment [2]. These feedstocks/fuel precursors are generated using a number of techniques involving gasification and liquefaction [3]. Among these techniques, fast pyrolysis which involves short vapour residence times (less than 2 s), rapid heating rates (up to 10^4 °C s^{-1}) and moderate temperatures (<550 °C) has drawn much interest since it has been shown to favour the formation of easy-to-handle liquid product (bio-oil) with a higher energy density (19 MJ kg^{-1}) than the original biomass (15 MJ kg^{-1}) [4—7]. The basic conceptual

scheme of the biomass pyrolysis coupled with fuels production is shown in Fig. 1. Biomass pyrolysis results in three fractions, bio-oil, gas and char. In the proposed scheme, solid heat carrier (sand) and catalyst transport char to a regenerator where it is combusted and catalyst regenerated. Heat from regenerator is integrated to the endothermic pyrolysis process similar to FCC scheme in a refinery.

The biggest technical challenge for such a green refinery is that the bio-oil consists of variety of oxygenates, e.g., organic acids, aldehydes, alcohols and ketones. This results in an acidic, corrosive, viscous and unstable oil with a relatively low-energy density compared to that of fossil fuels [5]. Chemical methods for improving the properties and applicability of bio-oil mainly include catalytic de-oxygenation [8,9], hydrogenation/hydrodeoxygenation (HDO) [10–12] and esterification [13,14]. De-oxygenation is an easier and promising route [15,16] as it does not require use of other chemicals, for e.g., alternative HDO process requires hydrogen, which is expensive and not easily available.

In general, de-oxygenation of biomass results in elimination of oxygen as carbon oxides, water and, depending on the extent of oxygen removal, a mixture of oxygen containing organic, aliphatic/aromatic, acids aldehydes, alcohols, etc. Complete de-oxygenation (Eq. (1)) results in an aromatic hydrocarbon mixture (H/C ∼ 1–1.2) due to the low hydrogen content of the starting biomass (H/C ∼ 1.3) [17].

$$C_6H_8O_4 \rightarrow 4.6CH_{1.2} + 1.4CO_2 + 1.2H_2O \qquad (1)$$
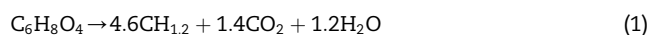
In the case of complete de-oxygenation (Eq. (1)), the organic yield is about 42% (mass fraction), and this corresponds to 50% energy recovery from the biomass feedstock. Incomplete de-oxygenation, i.e, retaining some of the oxygen in the organic fraction, will help enhance the liquid yields, however, this is an option only if the resulting product has properties that are compatible with fossil fuel/fuel additives (see Fig. 1, co-processing section).

The influence of H-MFI (ZSM-5) zeolite catalyst on the pyrolysis of biomass based on rice husks in a fixed-bed system has been investigated [18]. It was found that, in the presence of ZSM-5, oxygen in the feedstock was removed mostly as H_2O at lower temperatures (<500 °C) and as CO/CO_2 at higher temperatures (>550 °C). At the higher temperatures, the bio-oils obtained from catalytic experiments contain significantly higher

amounts of single ring and polycyclic aromatic hydrocarbons (PAH) because of deeper de-oxygenation. The evaluation of different commercial catalyst, including H-MFI, FCC catalysts, transitional metals (Fe/Cr) and aluminas (γ, α) for biomass pyrolysis has been carried out in a fixed bed reactor [19]. It was concluded from this study that H-MFI is a promising catalyst for the selective production of aromatic hydrocarbons while transitional metal catalysts lead to the selective production of phenol and light phenolics from biomass feedstocks. De-oxygenation of glycerol or sorbitol, as model compounds representing bio-oil, has been reported over several catalysts (H-MFI, γ-Al_2O_3, H-FAU (USY), SiC and commercial FCC catalyst) [20] and it was concluded that, at high de-oxygenation levels, achieved with H-FAU (USY) catalyst, aromatic hydrocarbons (fossil fuel compatible) and coke were the major products.

Alkali and alkali earth metals e.g., Na, K, Ca have attracted attention as promising catalysts for upgrading of biomass vapours in recent years [21–24]. This is also because they are naturally present in the biomass. For instance, Na^+ found to be effective for the conversion of biomass by improving the bio-oil energy content [4,25]. In the case of holo-celluloses, degradation is suggested to occur via depolymerization to give compounds such as levoglucosan, or sugars which subsequently undergo ring opening degradation to give aliphatic acids, aldehydes, etc. It is suggested that choice of the type of alkali metal, its content and reaction temperature can influence yields of levoglucosan [24]. Levoglucosan can be further converted to aromatic components via oxygen removal as H_2O [26]. Role for alkali metals on the decomposition of lignin is less discussed since in general these metals are less active to lignin conversion than to holo-cellulose conversion. The nature of working of alkali cations is not well established [16], but basicity of alkali and alkaline earth metals have been suggested to catalyse de-oxygenation, especially de-carboxylation [27,28].

In this work, influence of catalysts on the conversion of lignocellulosic biomass to various organic components is investigated with a view to establishing a catalytic pyrolysis process for a green refinery. Faujasite catalyst, which is the active ingredient in fluid catalytic cracking (FCC) catalyst, was employed because of its price, availability, mechanical/thermal stability, its ability to crack C–C, C–O bonds and regenerability from coke. H-FAU was further modified by Na^+
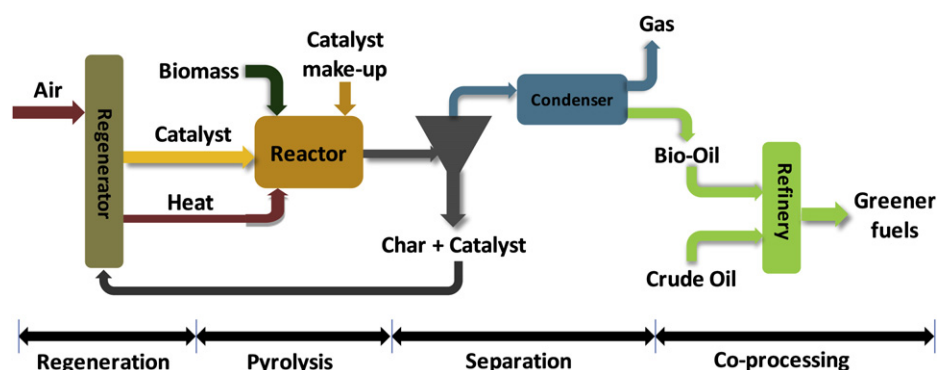

Fig. 1 – Conceptual scheme for green fuels from lignocellulosic biomass. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

ion exchange to probe role for alkali in pyrolytic de-oxygenation. Advantages of using catalyst over the thermal pyrolysis (in absence of the catalysts) is discussed.

2. Experimental

2.1. Biomass

Woodchips from Canadian white pine (*Pinus strobus*) were used as the feedstock in this study (ThoroughBed, purchased from Long Beach Shavings Co.). Prior to all experiments, the chips were ground by milling and sieved to particle sizes of 0.3—0.6 mm. Characteristics of the pinewood is given in Table 1.

2.2. Catalyst

The catalysts used in our study were obtained from Zeolyst (Na-FAU, $Na_{0.2}H_{0.8}$-FAU) and Albermale (H-FAU). The catalysts, which were originally in the form of fine powder, were pelletized and sieved to particle sizes of 0.3—0.6 mm. Before each catalytic experiment, the catalysts were dried at 500 °C for 60 min in the pyrolysis set up (Fig. 2). This allows removal of free water presented in the micropores of the zeolites, and hence, a better estimation of the mass balance of the experiments. Details of the catalysts are listed in Table 2.

X-ray diffraction (XRD) patterns of the catalysts were collected over the range $2\theta = 5-60°$ on a Bruker D2 Phaser XRD device using Cu Kα1 radiation source.

2.3. Pyrolysis experiment

The experimental set-up used in this study is shown schematically in Fig. 2. In all experiments, 2 g of biomass sample was packed inside a tubular quartz reactor. The reactor consists of two compartments: the biomass and the catalyst bed, of which the inner diameter/length are 10/350 mm and 7/250 mm, respectively. Before each experiment, the whole system was purged by a flow of 100 cm^3 min^{-1} of Ar for 30 min to guarantee an inert atmosphere during the pyrolysis. After the flushing period, the flow of Ar was reduced to 70 cm^3 min^{-1} and kept constant during the experiment. Experiments were conducted in one of the two modes: mixing mode or post-treatment mode. In mixing mode, the biomass and catalyst were mixed and packed in the same compartment #5 (biomass bed). In this mode, the electrical furnace #7 was not used. Biomass-catalyst mixture was heated to the desired temperature using the IR furnace #3. Using the IR furnace, it is possible to raise the temperature to 500 °C in less
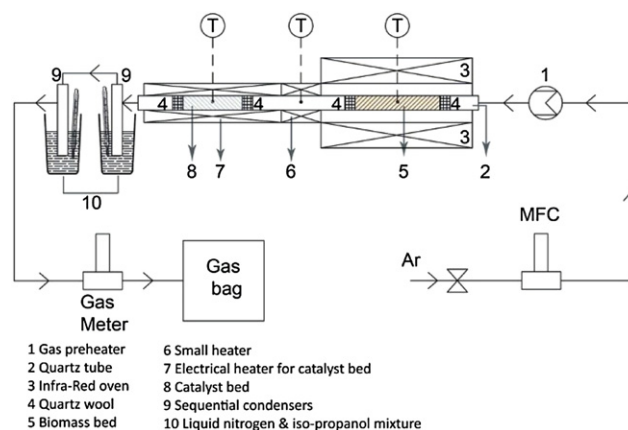

Fig. 2 — Schematic of the packed-bed system for fast pyrolysis of biomass.

1 Gas preheater
2 Quartz tube
3 Infra-Red oven
4 Quartz wool
5 Biomass bed
6 Small heater
7 Electrical heater for catalyst bed
8 Catalyst bed
9 Sequential condensers
10 Liquid nitrogen & iso-propanol mixture

than 10 s. In the post-treatment mode, the biomass and catalyst were kept in compartment #5 and #8 (biomass and catalyst bed), respectively. In this experiment, catalyst in position #8 was brought to the required temperature and maintained there. Pyrolysis experiment begins by activating the IR furnace and the vapours formed in compartment #5 travel through the catalyst bed. Temperature was measured at points marked T in the figure using thermocouples. For all the experiments (in both mixing and post-treatment modes), biomass to catalyst mass ratio of 10 was used. Lower ratios (more catalyst) were not applied because they resulted in bio-oil with very high water contents (>90 mass fraction %) and makes bio-oil analyses susceptible to severe errors. All the tests were conducted at atmospheric pressure at 500 °C. This was also the temperature of the catalyst bed in experiments in post-treat mode. The average temperature ramp and vapour residence time inside the quartz tube (#2) was 40 °C s^{-1} and 4 s, respectively. The average vapour residence time here was calculated based on the Ar flow rate.

Products of pyrolysis reactions were pushed by the Ar flow into two consecutive condensers immersed in isopropanol/liquid nitrogen mixture, at around - 40 °C to make sure that only non-condensable gases escaped for collection in a gas bag. Duration of experiments was set at 10 min to ensure collection of all products. This should not be mistaken with the pyrolysis reaction time (in the order of a few seconds). After each experiment the condensers were rinsed with known amounts of isopropanol to collect all the liquid products for latter analysis. The weight of the liquid products was considered equal to the gain in the weight of the two

Table 1 — Main characteristics of the Canadian pinewood.								
Proximate analysis (mass fraction %)					Ultimate analysis (mass fraction %)			
Fixed carbon	Volatile	Ash	Moisture	HHV[a] (MJ kg^{-1})	C	H	O[b]	N
14.51	78.40	2.59	4.50	16.01	48.34	5.81	45.46	0.40

a Higher heating value.
b By difference.

Table 2 – Basic properties of faujasite catalysts.				
Catalyst	SiO_2/Al_2O_3 molar ratio	Nominal cation form	Na_2O (mass fraction %)	Surface area (m^2 g^{-1})
Na-FAU	5.1	Na$^+$	13	900
Na$_{0.2}$H$_{0.8}$-FAU	5.1	H$^+$/Na$^+$	2.8	730
H-FAU	7	H$^+$	0.2	650

condensers after experiments. The change in the weight of the quartz reactor before and after pyrolysis is equal to the amount of volatiles which has left the reactor during this process (weight of liquid + weight of gas). By applying the mass conservation law (weight of biomass = weight of solid + weight of liquid + weight of gas), it is possible to calculate the amount of solid products. Non-condensable gases collected in the gas bag were injected to a micro GC (using PPQ and MS 5A columns) to analyse the composition (based on volume fraction). The total volume of gas which flows to the bag was measured using a gas flow metre (Fig. 2). This, together with composition analysed by the micro GC, provide the exact volume of each gas in the mixture. The ideal gas law was employed to calculate the molar amount of each gas and close the mass balance.

2.4. Bio-oil analysis

In order to acquire the liquid bio-oil, the condensers were washed with a known amount of 2-propanol. The mass ratio between 2-propanol and the bio-oil was limited at around 1:2 to prevent errors in sequential analyses. All the analyses of bio-oils were reported on a water- and solvent-free basis. The water content of bio-oil (mass fraction) was determined using Karl Fischer titration (using Metrohm 787 KF titrator). The energy content of bio-oil was determined by a bomb calorimeter unit (C2000 Kikawerke). A Flash 2000 (Interscience) instrument was employed to analyse the elemental composition (C, H, and O mass fraction) of bio-oil and char. In this analysis, the samples were completely oxidized in O_2 and the [C], [H] mass fraction were calculated directly based on the amount of CO_2 and H_2O formed, and the [O] mass fraction was obtained by difference.

The total acid number (TAN) of bio-oil was determined according to ASTM standard D664 using the titrator 785 DMP Titrino (Metrohm). In the measurement, the potential of the bio-oil/solvent solution was plotted against the amount of KOH (1 mol L^{-1}) used to titrate. The end point was determined as the point with the highest slope.

The amount of coke formed on the catalysts was determined by Thermogravimetric analysis (TGA) (Mettler Toledo, TGA/SDTA851e) in air. The procedure for the coke determination was the following: the samples were heated from room temperature to 110 °C and maintained there for 30 min to remove all the physically absorbed water, which was followed by a ramp to 800 °C. The analyses were carried out in the flow of 50 cm^3 min^{-1} air and using the heating rate of 10 °C min^{-1}.

The weight distribution of bio-oils was analysed in the Agilent 1200 series gel permeation chromatography (GPC) equipped with a refractive index detector.

The composition of the gas mixture obtained from pyrolysis was measured offline using a micro GC (Varian − CP4500)

consisted of two columns and a TCD detector. The first column (MS 5A) was set at 70 °C and used for determination of H_2, CO and CH_4. The second column (PPQ) was set at 80 °C for the separation of CO_2 and the rest of the H−Cs. Both columns used Ar as the carrier gas. Finally, an Agilent 7890A GC coupled with 5975C MS was used to determine the chemical composition of the bio-oil. The GC was equipped with a capillary column (Varian VF-1701ms 60 m × 0.25 mm × 250 μm) using He as the carrier gas at a constant flow rate of 1 cm^3 min^{-1}. The injection port of the GC was set at 250 °C and a split ratio of 50:1 was employed. The initial oven temperature of 40 °C was held for 5 min. The oven was programmed from 40 to 280 °C at 5 °C min^{-1} and the maximum temperature was maintained for 30 min. Data were collected in the full-scan mode between m/z 25−500 with a solvent delay of 8 min. The compounds were identified by comparing their mass spectra to the mass spectra of the built-in NIST 2008 library, interpreting the observed fragmentation and evaluating the retention times in comparison with standard compounds.

3. Results and discussions

First, results of thermal pyrolysis experiments in the absence of catalysts are discussed. It is intended to use these results to establish the proper choice of laboratory experiments and determine the possibility to carry out catalytic pyrolysis experiments.

3.1. Thermal pyrolysis experiments

Yields of products in the thermal pyrolysis experiments were, based on mass fraction, 20.4% of fast pyrolysis char, 10.3% of gas and 61.2% of liquid which adds up to a total mass balance of 92%. Liquid product contained 36.9% (in mass, based on initial weight of biomass) of organic fraction and 24.3% yield of water. The relatively high liquid yield and low gas and solid yield shows resemblance to those obtained from fast pyrolysis in bigger scale systems [29−32].

Obtained solid char (i.e., excluding minerals/ash), contained carbon (78.7 mass fraction %), hydrogen (2.8%) and oxygen (18.5%). Energy content of this char was measured to be 26 MJ kg^{-1}. This, combined with the yield of 20.4%, provides more than enough energy (by burning the char in air) to drive the pyrolysis reaction without the necessity of external heat, which makes the whole process autothermal (Fig. 1) via proper heat integration.

Carbon monoxide and carbon dioxide are major components in pyrolysis gas (total >90% selectivity) with yields of 4.66 and 4.75% (mass fraction compared to biomass), respectively. There are smaller amounts of (C_1−C_3) hydrocarbons and hydrogen (yields of 0.83 and 0.02%, respectively).

Table 3 lists the differences in the major properties of the obtained liquid (bio-oil) with those of the original biomass and a representative fossil fuel-oil. Compared to the parent biomass, bio-oil contains almost the same amount of hydrogen (~5.8 mass fraction %), slightly more carbon (52.11% of bio-oil compared to 48.74% of biomass) and less oxygen (42.34% of bio-oil compared to 45.6% of biomass).

However, this difference is very small compared to the difference between bio-oil and fuel oil. Compared to bio-oil (H/C 1.3), fuel oil has much higher carbon and hydrogen content (85.30% and 11.47%, respectively, H/C 1.6) and much less oxygen (1.05%). Higher [C], [H] content of fuel oil gives it higher energy content. Table 3 also summarizes the problems when working with bio-oil. Presence of high [O] content in bio-oil results in a corrosive, acidic, viscous, unstable and particulates containing oil with a relatively low-energy density compared to that of fossil fuels.

To have a better understanding of the undesired properties of bio-oil, and the factors that cause them, GC/MS was used to analyse the chemical composition of bio-oil.

Since bio-oil is a complicated mixture of hundreds of different organic compounds, it is reasonable to classify them into different groups based on their chemical functionality. Such a classification of the components of bio oil is shown in Fig. 3. In Fig. 3, the vertical axis shows the relative proportions of different groups in the bio-oil calculated by summing the total ion chromatogram (TIC) area percentages of all the compounds belonging to these groups. This method, commonly used by other authors [33–35], generates semi-quantitative results. It can be used to compare the concentrations of a certain component in bio-oil obtained under different conditions. Fig. 4 shows the components of biomass and the possible products that can be formed from them by pyrolysis. Bio-oil contains a variety of carboxylic acids e.g., formic, acetic acids, mainly formed by the decomposition of cellulose and hemicellulose fractions of biomass [16]. These are the main components that cause acidity of the bio oil [36]. Phenols which form by the decomposition of lignin also contribute to acidity but to a much lesser extent [36]. Carbonyl compounds such as aldehydes and ketones have tendency to undergo condensation reactions causing viscosity increase make the oil unstable [16]. Hydrocarbons and furans (formed from holocelluloses) are the required components due to their high-energy content [16]. In order to improve the properties of bio-oil, it is thus essential to remove/modify the problematic components during de-oxygenation. Essentially de-oxygenation of harmful components can be achieved by converting them to products such as CO_2, CO or H_2O. In
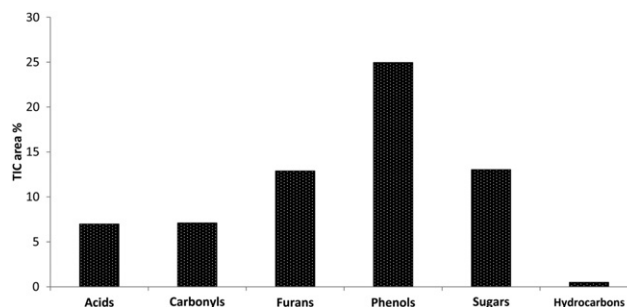

Fig. 3 – Distribution of different chemical groups in non-catalytic bio-oil.

order to illustrate how effective each route is, in an energy content point of view, glucose ($C_6H_{12}O_6$) was chosen as a model compound. From glucose, we can either remove one or more CO_2 or CO or H_2O molecules and obtain corresponding products (Fig. 5). The higher heating values (HHV) of these products can be estimated using Dulong formula, a widely-used model to estimate the HHV of a compound based on its elemental composition ([C], [H], [O]%, mass fraction) [37–39]. The higher heating values and oxygen contents of the products were then compared with those of the original glucose. These comparisons are represented by the energy enhancement (%) and the degree of de-oxygenation (%), respectively (Fig. 5). It is obvious from Fig. 5 that selective de-oxygenation to CO_2 is the most beneficial. This is because per carbon atom lost, two oxygen atoms are removed and thus carbon loss is lower. For the same reason, de-oxygenation as CO is less efficient. Formation of water lowers hydrogen content of biomass, and is thus the least preferred.

Incorporation of a catalyst in the pyrolysis process must have the ability to selectively deoxygenate unwanted pyrolysis product oxygenates and form CO_2. Results of catalytic pyrolysis are discussed next.

3.2. Post-treatment vs. mixing catalytic pyrolysis modes

Catalytic pyrolysis experiments were carried out with three faujasite catalysts, details of which are given in Table 2. Since both catalysts and biomass are solids, there are two ways to introduce the catalysts into the pyrolysis system, namely: (i) mixing mode and (ii) post-treatment mode. The aim of applying catalysts in our work is to reduce the oxygen content of biomass to get a higher quality bio-oil. It is therefore

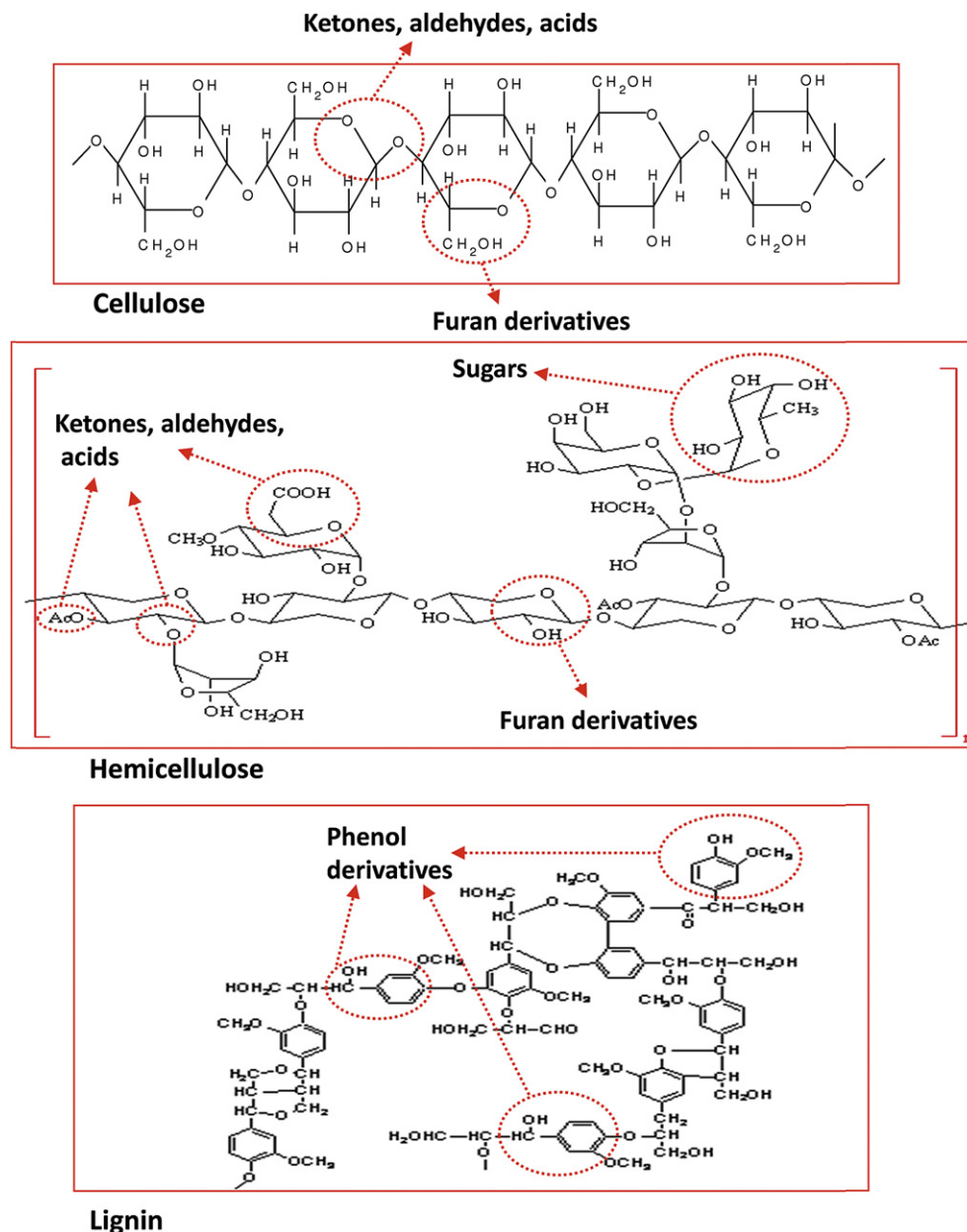| Table 3 – Comparison of main characteristics of bio-oil with those of biomass and fuel-oil.						
Materials	C[a]	H[a]	O[a]	Energy density (MJ kg^{-1})	pH	Water content[a]
Biomass	48.74	5.80	45.46	16	—	5.6
Bio-oil	52.11	5.70	42.34	19	2.4	30.5
Fuel-oil	85.30	11.47	1.05	40	5.7	0.1
a *Data are in mass fraction %.						

Fig. 4 – Origin of components in bio-oil related to chemical functionalities of holocellulose and lignin.

reasonable to use degree of de-oxygenation to compare the efficiency of the two modes. The formula for the oxygen removal degree is shown below.

$$\text{Oxygen removal degree} = \big[1 - ([O]\%_{bio-oil} \\ \times \text{Yield}_{bio-oil}/[O]\%_{biomass})\big] \times 100$$

In this formula [O]% represents the oxygen content (mass fraction) of a specific material. Oxygen removal degree can be used to judge the amount of oxygen that has been removed from the biomass and retained in the bio-oil. In non-catalytic experiment, the bio-oil contains 21% less oxygen than which was originally present in biomass. By using $Na_{0.2}H_{0.8}$-FAU catalyst in mixing mode, it is possible to remove 23% oxygen from biomass, which is slightly better compared to non-catalytic experiment. The same catalyst in post-treatment

mode, however, shows much higher activity in terms of oxygen removal, which is 31%.

In post-treatment mode, the biomass vapours always have to travel through the catalyst bed and contact the catalytic sites at the required temperature. In the mixing mode the situation is different. The problems are (i) solid–solid contact between the catalyst and the biomass (particle size: 300–600 μm) is not ideal, and (ii) since catalyst and biomass are subjected to the temperature ramp simultaneously, biomass vapours that already form at lower temperatures (around 300 °C) pass the catalyst before it has reached pyrolysis temperature (500 °C). For these reasons, not surprisingly, post-treatment mode is superior to mixing mode in terms of oxygen removal, and hence this mode is chosen for further catalytic tests.
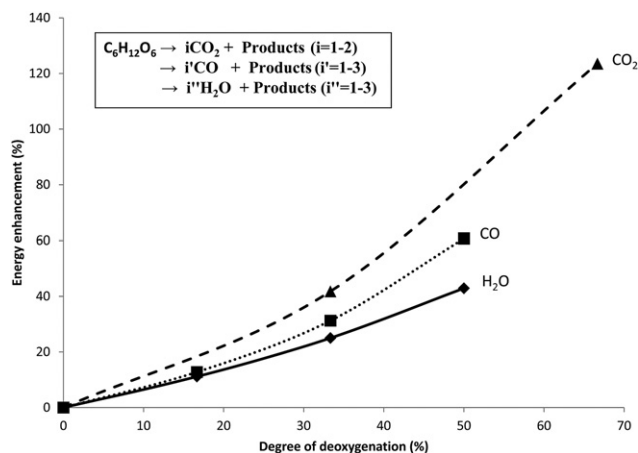
Fig. 5 – Efficiency of different oxygen removal routes, calculated using Dulong formulaHHV (MJ/kg) = (0.3388*[C]) + (1.442*([H] − [O]/8)).**

3.3. Catalytic experiments

3.3.1. Products distribution

In this section the catalytic influences on the yields of pyrolysis products (gas, liquid and solid) and on the composition of solid and gas products are discussed. The catalytic effects on the composition of liquid phase are discussed separately in Section 3.3.2. Fig. 6 shows the yields of pyrolysis products obtained from catalytic and non-catalytic (thermal) experiments. For all the experiments the mass balances are more than 90%. One can see from Fig. 6 that the solid and gas yields increase while that of liquid decreases in presence of the catalysts. H-FAU gave the lowest liquid yield (46.3 mass fraction %, based on initial weight of biomass), highest solid yield (28.6%) and high gas yield (16.3%).

In Fig. 6, solid yields shown are the sum of solid char left in the pyrolysis compartment (>90 mass fraction % of total solid) plus the coke/char formed over the catalyst. Coke/char formed on the catalyst is maximum for H-FAU catalyst with the yield of 1.8% (mass fraction, based on initial weight of biomass) compared to that of 1.6% on $Na_{0.2}H_{0.8}$-FAU and 1.3% on Na-FAU. Among the catalysts, H-FAU also has the highest concentration of acid sites (H$^+$) and the highest cracking activity of C–C, C–H and C–O bonds and it is not surprising
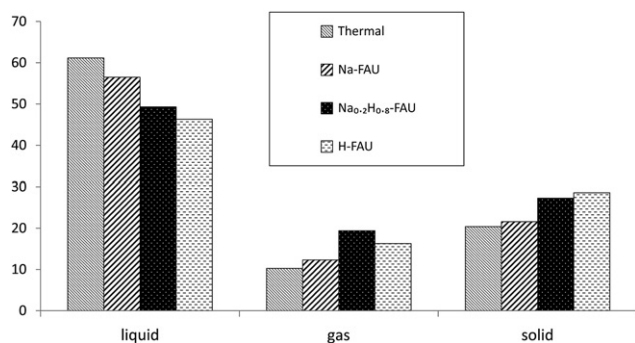
that it produces the maximum amount of coke/char. Comparable experiment with inert material (quartz) in place of catalyst did not produce any char/coke. H-FAU also gave the maximum amount of water (yield of 22 mass fraction %, based on initial weight of biomass) as expected, since dehydration is strongly catalysed by acids.

For all the catalysts, elemental compositions and higher heating value (HHV) of the char and coke were analysed. All the results are based on ash-free calculations, which means that the compositions and heat values were only attributed to the organic fraction of the solid. Elemental composition of char formed in the pyrolysis chamber was, as expected, similar for all experiments (78.7% carbon, 2.8% hydrogen and 18.5% oxygen, mass fraction). Surprisingly, compositions of coke/char formed on the catalysts were also similar, only the amount of coke varied and was maximum for H-FAU catalyst. This coke/char contains 87.5% carbon, 6% oxygen and 6.5% hydrogen, mass fraction. As can be seen, the oxygen content of coke/char formed on the catalyst is much lower than that of char in the pyrolysis chamber, but it still contains 6% of oxygen (mass fraction). This implies that it is not the classical hydrocarbon coke that is formed on the catalyst but oxygen-containing oligomeric species. Moreover, it can be seen that this coke/char is aromatic in nature (H/C ~ 1). Both acidic H$^+$ sites and sodium ions Na$^+$ seem to catalyse this oligomer formation since both H-FAU and Na-FAU resulted in coke/char formation.

The gases formed during catalytic experiments are mainly composed of CO and CO_2, the rest being smaller hydrocarbons (C_1–C_3) and hydrogen. Details are shown in Table 4. As can be seen, the yields of CO and CO_2 increased in the presence of catalysts, especially in the cases of $Na_{0.2}H_{0.8}$-FAU and H-FAU. Using $Na_{0.2}H_{0.8}$-FAU, the yield of CO and CO_2 increased ~1.7 times compared to the non-catalytic experiment. $Na_{0.2}H_{0.8}$-FAU also shows the maximum amount of hydrocarbon and hydrogen compared to all experiments. Consequence of these results on the properties of bio oil is discussed in the next section.

3.3.2. Catalytic effects on the composition of bio-oil

This section discusses the change in bio-oil composition, as analysed by GC/MS, for the various catalytic experiments and the correlations between the composition and properties, namely: acidity/corrosiveness, stability, and energy density of bio-oils.

3.3.2.1. Acidity. Pyrolysis of wood results in the formation of carboxylic acids and other acidic components which make the bio-oil corrosive and negatively affect its applicability as

Fig. 6 – Product yields in catalytic and non-catalytic experiments.

Table 4 – Composition of non-condensable gas yields; data are given in mass fraction %, based on initial weight of biomass.

	Thermal	Na-Y	$Na_{0.2}H_{0.8}$-Y	H-Y
CO	4.66	4.89	8.01	7.25
CO_2	4.75	4.37	7.55	6.03
HC	0.83	1.10	3.66	2.91
H_2	0.02	0.03	0.18	0.09

a fuel. It was shown that among the various components present in bio-oil, carboxylic acids contribute to the acidity of bio-oil the most (60–70%) [36]. Other components which contribute to the acidity of bio-oil are phenols (5–10%) and sugars (20%). For this reason, the acidity of bio-oil can be correlated to the amount of carboxylic acids determined by GC/MS. Validity of this correlation is shown in Fig. 8 by plotting the acidity of several bio-oil samples determined by potassium hydroxide titration (TAN) *versus* the corresponding carboxylic acid concentrations determined by GC/MS.

Fig. 7 shows the influence of catalysts on the amounts of acids, phenols, and sugars formed. All the catalysts reduced the amount of carboxylic acids compared to thermal experiment with H-FAU having the most influence. It is noteworthy to recall that the reduction in carboxylic acids is correlated to the increase in yield of CO_2 in gas stream (Table 4). Since the amount of acids and the acidity of bio-oils is well correlated, it is expected that H-FAU is a good catalyst to reduce the acidity of bio-oil. In the meantime, the amount of phenols increased drastically in the presence of catalysts (Fig. 7). Phenolic components are less troublesome in terms of causing acidity and, together with their high-energy content, are more desired than carboxylic acids. This increase also indicates the ability of FAU catalysts to decompose more lignin-derived vapour.

3.3.2.2. Energy density. Hydrocarbons are the most valuable fuel components from pyrolysis of biomass due to their high heating value. The amount of hydrocarbons formed in bio-oil using each catalyst is compared in Fig. 7. As can be seen from the figure, there is only a slight increase in hydrocarbon concentration when Na-FAU is used compared to thermal pyrolysis. However, when H-FAU and especially $Na_{0.2}H_{0.8}$-FAU were used, the area percentage of hydrocarbons in bio-oil increased significantly from 0.5% (thermal) to 3.4% (H-FAU) and 9.5% ($Na_{0.2}H_{0.8}$-FAU). During catalytic de-oxygenation of biomass, hydrocarbons are proposed to be formed from sugars through several reactions including dehydration of monomer sugars to dehydrated products, i.e. furans, and subsequent decarbonylation, decarboxylation and oligomerization of dehydrated products to aromatics [16]. Another possible pathway for hydrocarbon formation is decarboxylation of organic acids to CO_2 and hydrocarbons. Because the
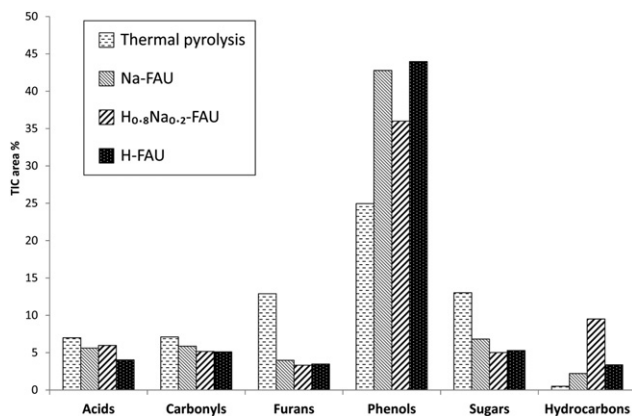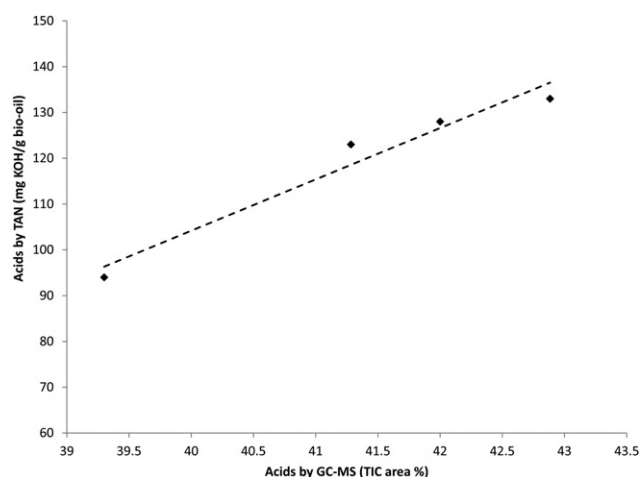
Fig. 8 – Correlation of TAN with total amount of acids in bio-oil; measurement error of TAN analysis calculated to be 1.47% based on 95% confidence level.

hydrogen content of biomass is very low, in the absence of external source of hydrogen most of the hydrocarbons in bio-oil can be found as aromatics. Moreover, aromatic hydrocarbons can also be produced from phenolic compounds by scission of all oxygenate substituents from phenol ring [28,35]. It can be concluded that in the presence of $Na_{0.2}H_{0.8}$-FAU catalyst hydrocarbons are most likely produced from de-oxygenation of phenols and sugars because the amount of phenols and sugars obtained using this catalyst was the lowest (Fig. 7).

3.3.2.3. Stability. Ageing process of bio-oil results in an increase in molecular weight and viscosity of bio-oil due to the presence of reactive components, i.e. aldehydes and ketones. A number of possible reactions responsible for the instability of bio-oil was proposed [40], including reactions of (i) organic acids with alcohols forming ester and water, (ii) aldehydes and alcohols forming hemiacetals or acetals and water, (iii) aldehydes forming oligomers and resins, (iv) aldehydes and phenols forming resins and water, (v) and aldol type of condensation reaction between aldehydes and ketones. Reactions ii, iv and v consume aldehydes, phenols and form water and the fact that the amount of aldehydes and phenols in the old oil decreased and water increased compared to fresh oil supports this (Fig. 9). In order to have an overview of how the molecular weight distribution of the compounds in bio-oil has shifted during ageing process, two bio-oil samples were analysed using GPC technique: one is a sample of a fresh bio-oil and the other is the bio-oil which was produced in the same conditions but has been kept at laboratory conditions for 1 year. The results are shown in Fig. 9. The GPC chromatogram can be divided into 2 regions: low-molecular weight ($M < 400$ g mol^{-1}) and high-molecular weight ($M > 400$ g mol^{-1}). In the low-molecular weight region, the curve corresponding to the old oil has similar shape compared to that of the fresh oil but with lower intensity. The opposite occurs with the high-molecular weight region (similar shape, higher intensity). From these results, it can be concluded that during storage process, the
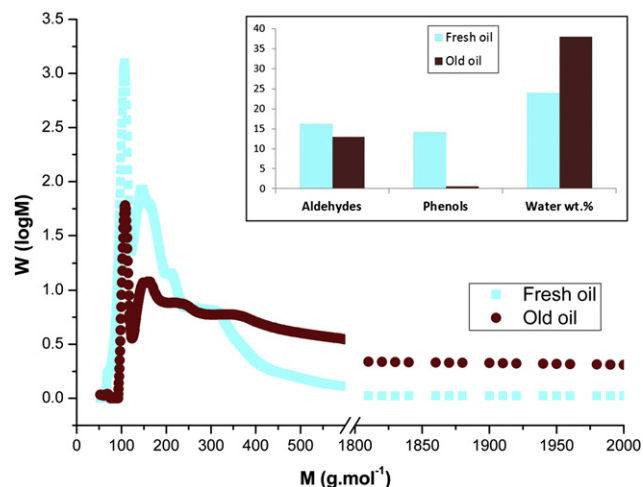
Fig. 7 – Distribution of chemical groups in bio-oils obtained from catalytic and non-catalytic experiments.

Fig. 9 — Molecular weight distribution of fresh and old bio-oils.

low-molecular weight compounds in the fresh oil has reacted with each other to form heavier molecules and increase the viscosity of bio-oil. Fig. 7 compares the effect of each catalyst on the formation of aldehydes/ketones (carbonyls) in bio-oil. It is obvious from the figure that all the catalysts reduce the amount of carbonyls in bio-oil compared to thermal reaction with H-FAU and $Na_{0.2}H_{0.8}$-FAU having the most influence. It can be concluded that the higher the proton concentration of the catalyst is, the more carbonyls are removed from bio-oil and the higher stability of bio-oils is expected.

Highest de-oxygenation extent obtained with $Na_{0.2}H_{0.8}$-FAU, accompanied by the highest amount of CO_2 formation, as expected, also results in a bio oil with higher energy content (24 MJ kg^{-1}, compared to 22 MJ kg^{-1} for Na-FAU and H-FAU). $Na_{0.2}H_{0.8}$-FAU is a promising catalyst because it (i) decreases the acid content of the bio-oil, (ii) removes unstable components such as aldehydes and ketones, (iii) and by increasing
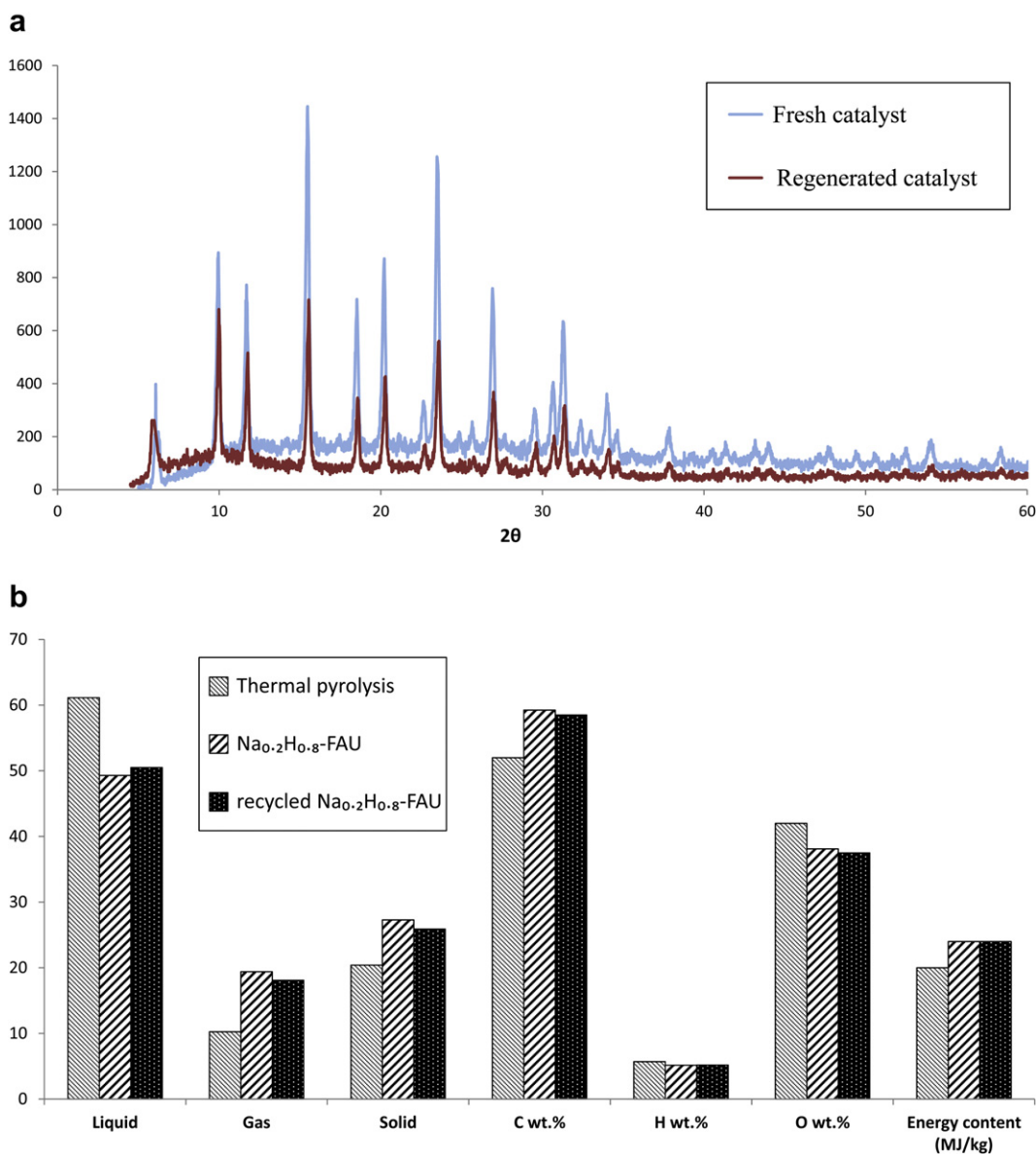

Fig. 10 — (a) XRD analyses. (b) Comparison of activities of fresh and regenerated catalysts; tested after one pyrolysis cycle.

the phenols and hydrocarbon contents it not only improves the energy density of bio-oil but also makes it easier to blend with crude [41].

3.4. Catalyst regeneration/recycle

In our proposed scheme, the catalyst/coke is burnt to generate heat for the process and recycled back to the reactor (Fig. 1) similar to the FCC process. In order to investigate the regenerability of the catalysts, pyrolysis experiments were conducted with fresh and regenerated $Na_{0.2}H_{0.8}$-FAU catalyst.

Regeneration by coke/char combustion was probed in a TGA experiment which showed that complete removal of coke/char is achieved by 600 °C. Catalyst after a single pyrolysis experiment was regenerated at 600 °C in flowing air (30 cm^3 min^{-1}) for 5 h. XRD analyses of the two samples: fresh and regenerated are shown in Fig. 10a. No appreciable differences were observed. Results of catalytic pyrolysis experiments for fresh and regenerated catalyst are shown together in Fig. 10b. As can be seen, the fresh and regenerated catalysts have almost the same performance in pyrolysis reaction. It can be concluded that the catalyst is regenerable. However, this conclusion is only valid for the catalyst which was regenerated after one cycle, while in industry (e.g. in FCC process) catalysts were required to be functional after many cycles. Testing catalytic performance after multiple cycles is, nevertheless, out of scope of this paper.

4. Conclusions

Catalytic upgrading of biomass pyrolysis vapours was carried out in a lab-scale fix-bed reactor at 500 °C. Three zeolite catalysts with different H^+ and Na^+ concentrations including H-FAU, $Na_{0.2}H_{0.8}$-FAU and Na-FAU were tested in the reaction. The results showed that the amount of H^+ and Na^+ of the catalyst plays an important role in the product yields and product distribution. The higher the concentration of H^+ of the catalyst is, the lower the liquid yield, and the higher the solid and gas yields are obtained. It was shown that two of major problems with bio-oil, namely the corrosiveness and instability, were mainly caused by carbonyl and carboxylic acid compounds, respectively. The best catalyst candidate is $Na_{0.2}H_{0.8}$-FAU, which reduced the most acid and carbonyl compounds while boosted the amount of the desirable phenolic and hydrocarbon compounds compared to non-catalytic experiment and to the other two catalysts. $Na_{0.2}H_{0.8}$-FAU also removed the most oxygen as CO_2, resulting in an oil with lowest oxygen content (38 mass fraction %) and highest energy content (24 MJ kg^{-1}). It was shown possible to regenerate the spent catalyst without changing its crystalline structure and catalytic performance.

Acknowledgements

REFERENCES

[1] Lynd LR, Cushman JH, Nichols RJ, Wyman CE. Fuel ethanol from cellulosic biomass. Science 1991;251(4999):1318–23.

[2] Huber GW, O'Connor P, Corma A. Processing biomass in conventional oil refineries: production of high quality diesel by hydrotreating vegetable oils in heavy vacuum oil mixtures. Appl Catal A: Gen 2007;329(0):120–9.

[3] Bridgwater AV, Peacocke GVC. Fast pyrolysis processes for biomass. Renew Sust Energ Rev 2000;4(1):1–73.

[4] Babich IV, van der Hulst M, Lefferts L, Moulijn JA, O'Connor P, Seshan K. Catalytic pyrolysis of microalgae to high-quality liquid bio-fuels. Biomass Bioenerg 2011;35(7):3199–207.

[5] Bridgwater AV, Meier D, Radlein D. An overview of fast pyrolysis of biomass. Org Geochem 1999;30(12):1479–93.

[6] O'Connor P, Stamires D, Daamen S, inventors; Kior, Inc., assignee. Process for the conversion of biomass to liquid fuels and specialty chemicals. United States patent US 2012190062; 2012 Jul 26.

[7] O'Connor P, Corma A, Huber GW, Sauvanaud L, inventors; Kior, Inc., assignee. Fluid catalytic cracking of oxygenated compounds. United States patent US 2012198756; 2012 Aug 9.

[8] Priecel P, Kubicka D, Capek L, Bastl Z, Rysanek P. The role of Ni species in the deoxygenation of rapeseed oil over NiMo-alumina catalysts. Appl Catal A: Gen 2011;397(1–2):127–37.

[9] Stefanidis SD, Kalogiannis KG, Iliopoulou EF, Lappas AA, Pilavachi PA. In-situ upgrading of biomass pyrolysis vapors: catalyst screening on a fixed bed reactor. Bioresour Technol 2011;102(17):8261–7.

[10] Busetto L, Fabbri D, Mazzoni R, Salmi M, Torri C, Zanotti V. Application of the Shvo catalyst in homogeneous hydrogenation of bio-oil obtained from pyrolysis of white poplar: new mild upgrading conditions. Fuel 2011;90(3):1197–207.

[11] Fernández MB, Sánchez M, Jhon F, Tonetto GM, Damiani DE. Hydrogenation of sunflower oil over different palladium supported catalysts: activity and selectivity. Chem Eng J 2009;155(3):941–9.

[12] Fisk CA, Morgan T, Ji YY, Crocker M, Crofcheck C, Lewis SA. Bio-oil upgrading over platinum catalysts using in situ generated hydrogen. Appl Catal A: Gen 2009;358(2):150–6.

[13] Lohitharn N, Shanks BH. Upgrading of bio-oil: effect of light aldehydes on acetic acid removal via esterification. Catal Commun 2009;11(2):96–9.

[14] Mahfud FH, Melian-Cabrera I, Manurung R, Heeres HJ. Biomass to fuels – upgrading of flash pyrolysis oil by reactive distillation using a high boiling alcohol and acid catalysts. Process Saf Environ 2007;85(B5):466–72.

[15] Czernik S, Bridgwater AV. Overview of applications of biomass fast pyrolysis oil. Energ Fuel 2004;18(2):590–8.

[16] Huber GW, Iborra S, Corma A. Synthesis of transportation fuels from biomass: chemistry, catalysts, and engineering. Chem Rev 2006;106(9):4044–98.

[17] Bridgwater AV. Catalysis in thermal biomass conversion. Appl Catal A: Gen 1994;116(1–2):5–47.

[18] Williams PT, Nugranad N. Comparison of products from the pyrolysis and catalytic pyrolysis of rice husks. Energy 2000;25(6):493–513.

[19] Samolada MC, Papafotica A, Vasalos IA. Catalyst evaluation for catalytic biomass pyrolysis. Energ Fuel 2000;14(6):1161–7.

[20] Corma A, Huber GW, Sauvanaud L, O'Connor P. Processing biomass-derived oxygenates in the oil refinery: catalytic cracking (FCC) reaction pathways and role of catalyst. J Catal 2007;247(2):307–27.

[21] Fahmi R, Bridgwater AV, Darvell LI, Jones JM, Yates N, Thain S, et al. The effect of alkali metals on combustion and

pyrolysis of Lolium and Festuca grasses, switchgrass and willow. Fuel 2007;86(10—11):1560—9.

[22] Mullen CA, Boateng AA. Chemical composition of bio-oils produced by fast pyrolysis of two energy crops. Energ Fuel 2008;22(3):2104—9.

[23] Nowakowski DJ, Woodbridge CR, Jones JM. Phosphorus catalysis in the pyrolysis behaviour of biomass. J Anal Appl Pyrol 2008;83(2):197—204.

[24] Patwardhan PR, Satrio JA, Brown RC, Shanks BH. Influence of inorganic salts on the primary pyrolysis products of cellulose. Bioresour Technol 2010;101(12):4646—55.

[25] Zabeti M, Nguyen TS, Lefferts L, Heeres HJ, Seshan K. In situ catalytic pyrolysis of lignocellulose using alkali-modified amorphous silica alumina. Bioresour Technol 2012;118(0): 374—81.

[26] Vispute TP, Zhang HY, Sanna A, Xiao R, Huber GW. Renewable chemical commodity feedstocks from integrated catalytic processing of pyrolysis oils. Science 2010;330(6008): 1222—7.

[27] Selva M, Fabris M, Perosa A. Decarboxylation of dialkyl carbonates to dialkyl ethers over alkali metal-exchanged faujasites. Green Chem 2011;13(4):863—72.

[28] Ding LH, Rahimi P, Hawkins R, Bhatt S, Shi Y. Naphthenic acid removal from heavy oils on alkaline earth-metal oxides and ZnO catalysts. Appl Catal A: Gen 2009;371(1—2): 121—30.

[29] Choi HS, Choi YS, Park HC. Fast pyrolysis characteristics of lignocellulosic biomass with varying reaction conditions. Renew Energ 2012;42(0):131—5.

[30] Bridgwater AV. Review of fast pyrolysis of biomass and product upgrading. Biomass Bioenerg 2012;38:68—94.

[31] Zhang HY, Xiao R, Wang DH, He GY, Shao SS, Zhang JB, et al. Biomass fast pyrolysis in a fluidized bed reactor under N(2), CO(2), CO, CH(4) and H(2) atmospheres. Bioresour Technol 2011;102(5):4258—64.

[32] Pattiya A. Bio-oil production via fast pyrolysis of biomass residues from cassava plants in a fluidised-bed reactor. Bioresour Technol 2011;102(2):1959—67.

[33] Dominguez A, Menendez JA, Inguanzo M, Bernard PL, Pis JJ. Gas chromatographic-mass spectrometric study of the oil fractions produced by microwave-assisted pyrolysis of different sewage sludges. J Chromatogr A 2003;1012(2):193—206.

[34] Marin N, Collura S, Sharypov VI, Beregovtsova NG, Baryshnikov SV, Kutnetzov BN, et al. Copyrolysis of wood biomass and synthetic polymers mixtures. Part II: characterisation of the liquid phases. J Anal Appl Pyrol 2002; 65(1):41—55.

[35] Goncalves AR, Schuchardt U, Meier D, Faix O. Pyrolysis gas chromatography of the macromolecular fractions of oxidized organocell lignins. J Anal Appl Pyrol 1997;40(1):543—51.

[36] Oasmaa A, Elliott DC, Korhonen J. Acidity of biomass fast pyrolysis bio-oils. Energ Fuel 2010;24:6548—54.

[37] Mason DM, Gandhi KN. Formulas for calculating the calorific value of coal and coal chars: development, tests, and uses. Fuel Process Technol 1983;7(1):11—22.

[38] Wanignon Ferdinand F, Van de Steene L, Kamenan Blaise K, Siaka T. Prediction of pyrolysis oils higher heating value with gas chromatography—mass spectrometry. Fuel 2012;96(0): 141—5.

[39] Kathiravale S, Yunus MNM, Sopian K, Samsuddin AH, Rahman RA. Modeling the heating value of Municipal Solid Waste. Fuel 2003;82(9):1119—25.

[40] Diebold J. A review of the chemical and physical mechanisms of the storage stability of fast pyrolysis bio-oils. Golden, Colorado: National Renewable Energy Laboratory; 2000 Jan. p. 60, Report No. SR-570-27613 (Contractor Thermalchemie, Inc).

[41] Anderson BD, Rytting JH, Higuchi T. Influence of self-association on the solubility of phenol in isoctane and cyclohexane. J Am Chem Soc 1979;101(18):5194—7.