**Exploring catalytic potential of red mud for upgrading beechwood fast pyrolysis vapour products**

Jyoti GUPTA,*a* Konstantinos PAPADIKIS,*b* Ivan V. KOZHEVNIKOV, *c*   
Elena Yu. KONYSHEVA *a*,\*

*a* Department of Chemistry, Xi'an Jiaotong-Liverpool University, 215123 Suzhou, China

*b* Department of Civil Engineering, Xi'an Jiaotong-Liverpool University, 215123 Suzhou, China

*c* Department of Chemistry, University of Liverpool, L69 7ZD Liverpool, UK

**Highlights**

* Thermal treatment of red mud impacts fast pyrolysis product distribution.
* Total yield of phenols reduced during catalytic vapour upgrading.
* Good selectivity of red mud to furfurals revealed.
* Red mud catalyst facilitates formation of new ketones and sugars.

**Abstract**

Red mud, a by-product of the Bayer process in the aluminium industry, was applied as a catalyst for *in-situ* upgrading of vapour products of beechwood fast pyrolysis. Thermal pre-treatment of red mud enhanced the catalytic upgrading effect. Individual oxides (α-Al2O3, Fe2O3, SiO2, and TiO2) co-existing in red mud were also tested for fast pyrolysis upgrading. A biomass/catalyst weight ratio of 1:4 had the strongest catalytic effect on the product distribution. Red mud was found to reduce the yield of phenolic compounds and promote the formation of cellulose-derived furfurals and acetic acid, which can be used for the production of a broad range of chemicals and liquid transportation fuels. α-Al2O3 and Fe2O3 also reduced the yield of phenols, whereas the formation of furfurals was promoted by Fe2O3 and TiO2. SiO2 showed negligible effect on fast pyrolysis vapours. The impact of catalysts on the product distribution is discussed for the product groups, such as phenols, furfurals, and acids, displaying the strongest catalytic effect.

**Keywords**: Biomass conversion; Catalytic fast pyrolysis; Py-GC/MS; Red Mud (Bauxite mining waste); Beechwood; α-Al2O3, Fe2O3, SiO2, and TiO2.

**1. Introduction**

Limited resources of fossil fuels have become a great concern in recent years [1]. Abundant and environmentally friendly lignocellulosic biomass is the possible alternative to fossil fuels in the future [2]. Bio-oil is regarded as a viable substitute to petroleum fuel. The production of liquid bio-oil through fast pyrolysis of biomass is considered as one of the promising conversion technologies that offers an alternative way to solve liquid fuel shortage problems [3]. Three main groups of products form during the fast pyrolysis of biomass: non-condensable gases, pyrolysis vapours, and chars. The condensed pyrolysis vapours form the liquid bio-oil is a complex mixture of oxygenated organic compounds derived from the depolymerisation of cellulose, hemicellulose, and lignin, including acids, alcohols, ketones, aldehydes, phenols, ethers, esters, sugars, furans and nitrogen containing compounds. High oxygen content, acidic nature, corrosiveness for common metals, instability and immiscibility with petroleum derived fuels make the bio-oil a low grade liquid fuel [4]. Therefore, it is necessary to upgrade the bio-oil by decreasing the level of undesired oxygenates and converting them into useful products. Several upgrading methods have been developed in recent years. One of the most important methods is the catalytic cracking, which can be applied on pyrolysis vapours as well as on liquid bio-oils. Catalytic upgrading of pyrolysis vapours may be a more desirable approach as instability problems can be avoided [5]. The cracking reactions enhance the decomposition of heavy molecules to lighter molecules and also induce deoxygenation reactions to remove oxygen in the form of H2O, CO, and CO2 [6] to obtain more stable liquid bio-oil with a higher calorific value.

In addition, bio-oil consists of value added products, which could be the source for various chemicals. During biomass fast pyrolysis, furfural is formed as a typical pyrolytic product from both cellulose and hemicellulose. Furfural is a valuable chemical, which is widely used as an organic solvent and an organic reagent for the production of food additives, medicines, fuel additives and other chemical products. Previous studies have confirmed that the formation of furfurals could be promoted in acid-catalysed pyrolysis, using catalysts such as ZnCl2, MgCl2, CaCl2, Al-MCM-41, and SO42−/M*x*O*y* (M = Ti, Zr, Sn) [7-10]. Further, liquid C7 – C15 alkanes can be selectively produced from furfurals by aldol condensation followed by dehydration/hydrogenation over solid bifunctional catalysts (e.g. Pt/SiO2 - Al2O3) [11].

Another main component of bio-oil, acetic acid, is an important industrial chemical applied in many industrial processes with a world demand of about 6 million tonnes per year. It is mostly produced by carbonylation of methanol, which accounts for 60 % of the total world acetic acid manufacturing capacity [12]. Among other uses, acetic acid can be utilised for hydrogen production by catalytic steam reforming [13-15].

Phenolic compounds are widely used for the production of resins, and steroids are natural products with pharmaceutical applications. Separation of steroid [16] and phenol [17] bio-oil fractions has been reported. Several methods have been developed for the recovery of pure chemicals from bio-oils, such as acetic acid and levoglucosan [18, 19]. However, the recovery of pure chemicals from bio-oils is economically unattractive at present, because most of the compounds are present in bio-oils in low concentrations. Utilisation of bio-oils for value-added chemicals requires selective control of biomass pyrolysis pathways to produce specific bio-oils with high contents of target products, known as the selective fast pyrolysis technique. Many studies have been carried out through specific pre-treatment of biomass or catalytic pyrolysis of biomass to increase the content of the target products in bio-oils. For example, levoglucosan and levoglucosenone formation could be facilitated from fast pyrolysis of cellulose or biomass pre-treated with phosphoric acid and Fe3+ ions [20]. The catalytic cracking of pyrolysis vapours with NaOH or Na2CO3 can produce bio-oils rich in acetol, while the application of the Fe2(SO4)3 catalyst favours furfural formation [21]. Besides, for the production of levoglucosan, acetic acid, and monomeric phenols additional studies have been performed [22-24]. However, those entail high production cost, which would have negative impact on the economic viability of the process. Thus, the need for the development of chemically feasible and cost effective catalysts that can facilitate the production of stable pyrolysis oils or valuable chemicals in high yields becomes of great significance.

Red mud (RM) is a solid waste residue of the Bayer process formed after the caustic digestion of bauxite ores during the production of alumina [25]. It is a complex mixture based on oxides such as Fe2O3, Al2O3, TiO2, MgO, CaO and SiO2, also containing minor inclusions of other compounds. The alkaline nature of RM poses significant negative impact on the environment, thus proper disposal of the RM waste is a challenge [26]. Alternative applications of RM can provide significant economic and ecological benefits.

Previously, RM has been considered as unsintered construction material and cementitious material [27, 28] for surface treatment of carbon steel prior to painting [29] and as an adsorbent for the removal of pollutants from solutions [30-33]. In addition, RM can also be employed as a catalyst for pyrolysis of waste plastics [34], for production of valuable chemicals through hydrogenation of naphthalene to tetralin [35, 36], hydrodechlorination of tetrachloroethylene to ethylene [37], and for hydroliquefaction of rye straw [38].

Previously, several oxides were employed as catalysts for the bio-oil upgrading. Torri et al. [39] have investigated the catalytic pyrolysis of pine sawdust over various metal oxides (Fe2O3, CuO, and ZnO) and found that heavy organic compounds were reduced in the final bio-oil. Solid acid 40SiO2/TiO2-SO42- and solid base 30K2CO3/Al2O3-NaOH catalysts have been applied for esterification reactions in bio-oil [40]. Lu et al. [10] have employed three sulphated metal oxides (SO42-/TiO2, SO42-/ZrO2, and SO42-/SnO2) over cellulose fast pyrolysis vapours and found that levoglucosan and hydroxyacetaldehyde were reduced, while 5-methylfurfural, furfural and furan were greatly increased.  Therefore, the RM, which is a mixture of oxides, can be potentially applied as a catalyst for upgrading pyrolysis vapours.

The aim of the study is to explore the red mud as a catalyst for upgrading the beechwood (BW) fast pyrolysis vapour products, looking at the effect of thermal pre-treatment of RM and variation of the BW/RM ratio on product selectivity. Besides the RM, its individual constituent oxides, such as α-Al2O3, Fe2O3, SiO2, and TiO2, were also applied for catalytic cracking of the pyrolysis vapours. This research is therefore related to the co-processing of two waste streams, namely, biomass derived from forestry waste and red mud from bauxite mining. Thus, the utilisation of RM can reduce the amount of solid waste polluting the environment and at the same time provide an economic benefit in the fast pyrolysis process.

**2. Materials and experimental techniques**

**2.1. Materials**

In this study, beechwood (BW) was used as the biomass material. Prior to use, the BW was dried at 105oC for 24 h in an oven and further stored in a desiccator. Red mud was obtained from the Chinese Aluminium industry and was thermally treated in the temperature range of 300-950oC. The following RM powders were used for experiments: as received (RM-initial), after calcination at 600oC (RM-600) and 950oC (RM-950). To better understand the catalytic behaviour of red mud, its constituent individual oxides α-Al2O3, Fe2O3, SiO2, and TiO2 (>99.9% purity and micron particle size) were also investigated as catalysts.

**2.2. Materials characterisation techniques**

Elemental analysis of beechwood was performed on a Vario MACRO (Elementar, Germany) cube elemental analyser to identify C, H, N, and O content. Helium was used as the carrier gas. Three measurements were conducted for each sample. The elemental composition of the dried BW was (wt.%) C 45.8 ± 0.8, H 6.1 ± 0.1, and N 0.04 ± 0.005. In this setup, the sulphur content could not be measured, however the typical content of sulphur in lignocellulosic biomass is quite low (< 1 wt.% [41]), and thus, considered as negligible. Oxygen was assumed to be the balance (48.1 wt. %).

Scanning electron microscopy (SEM) in combination with Energy Dispersive   
X-ray analysis (EDX) was used to identify the chemical composition of red mud after its calcination at 950oC for 5 h. Analysis was performed on JEOL JSM-6510 (JEOL, Japan) equipped with INCA ENERGY 250 X-Act elemental analyser (Oxford Instruments, UK). According to SEM/EDX analysis, RM‑950 contained (at.%) Al 18.8, Fe 7.6,   
Si 6.5, Ti 0.9, Ca 0.2, K 0.1, and O 65.8.

The surface area of red mud powders was measured by the Brunauer-Emmett-Teller (BET) nitrogen adsorption method on a 3H-2000PS2 analyser (Beishide Instruments, China) in the static volumetric mode. Three measurements were conducted for each sample. Thermogravimetric analysis (TGA) was performed on a STA 449 F3 Jupiter instrument (Netzsch, Germany) to determine the mass changes of red mud on heating. The analysis was performed under air flowing atmosphere in the temperature range of 25-950 oC with the heating and cooling rate of 10 and 20oC/min,respectively. The TGA data are presented after subtraction of the buoyancy effect. The X-ray powder diffraction patterns were collected before and after experiments on a Bruker D8 Advance diffractometer with Cu-Kα radiation (Bruker AXS, Germany) with a Lynxeye detector at 1o/min scanning speed in the *2θ* range of 15-110o. Infrared spectra of all catalysts, fresh and spent after fast pyrolysis experiments, were recorded on an FTIR spectrometer (Agilent technology Cary 600 series, USA).

**2.3. Fast pyrolysis analysis (Py-GC/MS)**

A CDS Pyroprobe (Py) 5200 pyrolyser (CDS Analytical, USA) in combination with 7890A/5975C gas chromatograph (GC)/mass spectrometer (MS) (Agilent technology, USA) was used to carry out non-catalytic and catalytic fast pyrolysis of BW. The fast pyrolysis of the samples took place in the pyrolyser, where a sample was thermally decomposed into various chemical compounds. The decomposed pyrolysis vapours were mixed in the pyrolysis interface with a helium carrier gas (30 ml/min flow rate) and transferred into the GC/MS system for identification. Each type of experiments (i.e. non-catalytic pyrolysis, catalytic pyrolysis with red mud and individual oxides, different ratio RM/BW) was repeated three times to ensure reproducibility.

The samples were heated with a heating rate of 20°C/ms to 500°C and then pyrolysed at this temperature for 20 s. The fast pyrolysis temperature was chosen to be 500°C, as it was found optimal in the previous work [42]. Helium was used as the carrier gas with a constant flow rate of 1 mL/min and the split ratio 1:50. The chromatographic separation was performed in the HP5MS capillary column (30 m length with 0.25 mm inner diameter). The GC oven temperature ramp was set from 50°C to 300°C with a heating rate of 5°C/min. The interface temperature of the GC/MS was maintained at 250°C and the pressure was set at 10 psi. The transfer line temperature, ion source temperature, and the auxiliary heater temperature of mass spectrometer were set at 150, 230, and 280°C, respectively. The mass spectra were obtained in the range of m/z ratio between 35-400 amu.

In the non-catalytic pyrolysis experiments, 1 mg of BW was introduced into the quartz tube, packed by a small amount of quartz wool on both sides of the BW. For *in-situ* catalytic fast pyrolysis (CFP) experiments, biomass was mixed with RM powders in a mortar in weight ratios of 1:1, 1:2, and 1:4 before the mixture was loaded into the quartz tube.

The identification of the compounds in the chromatograms was performed by comparing the mass spectra of the peaks with standard spectra of organic compounds from the NIST library to obtain the most probable matches. The chromatographic peak area of the detected compounds is proportional to its quantity and their peak area percentage in the vapour mixture was used for the quantification. The total peak area of the recorded chromatograms was within the same order of magnitude for all experiments in the present study. In order to understand the changes in the yields of the products, all the detected compounds were classified into twelve groups, including CO2, acids, esters, furfurals, aldehydes, ketones, alcohols, phenols, alkoxybenzenes, sugars and other compounds (OC). Small, unidentifiable peaks were grouped together as the non-identified (NI) compounds.

**3. Results and discussion**

3.1. Effect of red mud on beechwood CFP

Beechwood typically contains 45.8 % cellulose, 31.8 % hemicellulose, and 21.9 % lignin [43]. The major compounds detected during the non-catalytic fast pyrolysis of BW are listed in Table 1. The yields of different groups are presented in Fig. 1. In the non-catalytic fast pyrolysis of BW, phenols were found in the largest yield (23.7 %), followed by acids (16.9 %) and ketones (16.6 %). Furfurals were found in a small yield (3.0 %).

**Table 1.** Main identified products from non-catalytic fast pyrolysis of beechwood.

|  |  |  |  |
| --- | --- | --- | --- |
| No. | Retention time | Compound | Group |
| **1** | 1.417 | Carbon dioxide | CO2 |
| **2** | 1.552 | Acetaldehyde | Aldehyde |
| **3** | 1.828 | Ethylenediamine | *a)* OC |
| **4** | 2.056 | Acetic acid | Acid |
| **5** | 2.196 | 1-Hydroxy-2-propanone | Ketone |
| **6** | 3.210 | Succinaldehyde | Aldehyde |
| **7** | 3.292 | 3-Amino-2-oxazolidinone | Ketone |
| **8** | 3.837 | Furfural | Furfural |
| **9** | 4.299 | 2-Furanmethanol | Alcohol |
| **10** | 4.474 | 5-Hexen-2-one | Ketone |
| **11** | 4.794 | 3-Hydroxycyclohexanone | Ketone |
| **12** | 5.610 | 2(5H)-Furanone | Ketone |
| **13** | 5.855 | 1,2-Cyclopentanedione | Ketone |
| **14** | 6.572 | 5-Methyl-2-furancarboxaldehyde | Furfural |
| **15** | 7.596 | 2-Methyliminoperhydro-1,3-oxazine | *a)* OC |
| **16** | 8.443 | 3-Methyl-1,2-cyclopentanedione | Ketone |
| **17** | 9.602 | 2-Methylphenol | Phenol |
| **18** | 9.925 | 2-Methoxyphenol | Phenol |
| **19** | 12.148 | 2,3-Dihydroxybenzaldehyde | Aldehyde |
| **20** | 12.899 | 2-Methoxy-4-methylphenol (Creosol) | Phenol |
| **21** | 14.736 | 5-Hydroxymethylfurfural | Furfural |
| **22** | 15.222 | 3-Methoxy-1,2-benzenediol | Phenol |
| **23** | 15.338 | 4-Ethyl-2-methoxyphenol | Phenol |
| **24** | 16.382 | 4-Ethenyl-2-methoxyphenol | Phenol |
| **25** | 17.560 | 2,6-Dimethoxyphenol | Phenol |
| **26** | 17.810 | 3-Hydroxy-4-methoxybenzyl alcohol | Phenol |
| **27** | 18.913 | 4-Hydroxy-3-methoxybenzaldehyde (Vanillin) | Aldehyde |
| **28** | 20.081 | 4-Methoxy-3-(methoxymethyl)phenol | Phenol |
| **29** | 20.454 | 2-Methoxy-4-propenylphenol (Isoeugenol) | Phenol |
| **30** | 21.186 | 4-Hydroxy-3-methoxyacetophenone (Apocynin) | Ketone |
| **31** | 22.051 | 1,2,3-Trimethoxy-5-methyl-benzene | *b)* AB |
| **32** | 22.307 | (+)-s-2-Phenethanamine,1-methyl-N-vanillyl | Phenol |
| **33** | 23.125 | 3′,5′-Dimethoxyacetophenone | Ketone |
| **34** | 23.987 | 4-Allyl-2,6-dimethoxyphenol | Phenol |
| **35** | 25.509 | 4-Hydroxy-3,5-dimethoxybenzaldehyde | Aldehyde |
| **36** | 25.732 | 2-Allyl-1,4-dimethoxy-3-methyl-benzene | *b)* AB |
| **37** | 27.171 | 1-(4-Hydroxy-3,5-dimethoxyphenyl)ethanone | Ketone |
| **38** | 27.696 | Tetradecanoic acid | Acid |
| **39** | 27.998 | Desaspinidol | Ketone |
| **40** | 29.961 | Pentadecanoic acid | Acid |
| **41** | 30.292 | Hexadecanol | Alcohol |
| **42** | 31.668 | Hexadecanoic acid | Acid |
| **43** | 32.597 | 3,5-Dimethoxy-4-hydroxycinnamaldehyde | Aldehyde |
| **44** | 34.168 | Octadecanol | Alcohol |
| **45** | 35.28 | Oleic acid | Acid |
| **46** | 35.696 | Octadecanoic acid | Acid |
| **47** | 38.568 | 2-Ethylhexyl 4-methoxycinnamate | Ester |
| **48** | 42.352 | Diisooctyl phthalate | Ester |

*a)* Other compounds. *b)* Alkoxybenzene.

Fig. 1. Effect of red mud on product distribution of beechwood (BW) fast pyrolysis: uncatalysed pyrolysis (BW), untreated red mud (RM-initial), calcined RM at 600oC (RM-600) and 950oC (RM-950); BW/RM = 1:4 w/w; alkoxybenzene (AB); other compounds (OC); non-identified compounds (NI).

Fig. 2. Product distribution of beechwood CFP with RM-950 at different weight ratios: 1:1, 1:2, and 1:4.

**Table 2.** New compounds formed in catalytic fast pyrolysis of beechwood with RM-950 catalyst.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| No. | *a)* R.T. | Compound | Group | BW:RM-950 weight ratio | | |
| 1:1 | 1:2 | 1:4 |
| **1** | 4.324 | 3-Methyl-4-penten-2-one | Ketone | Present | Present | --- |
| 2 | 4.537 | 4-Cyclopentene-1,3-dione | Ketone | Present | --- | --- |
| 3 | 5.076 | 5,6-Dihydro-2H-pyran-2-one | Ketone | --- | Present | --- |
| **4** | 5.151 | 2-Acetylfuran | Ketone | --- | Present | --- |
| **5** | 5.59 | 2-Hydroxy-2-cyclopenten-1-one | Ketone | Present | Present | --- |
| **6** | 5.927 | Dihydro-3-methylene-2,5-furandione | Ketone | Present | Present | Present |
| **7** | 6.753 | 3-Methyl-3-cyclohexen-1-one | Ketone | --- | Present | --- |
| **8** | 10.486 | Maltol | Sugar | Present | --- | --- |
| **9** | 10.573 | Levoglucosenone | Sugar | Present | Present | Present |
| **10** | 11.999 | 5-Hydroxy-9-oxabicyclo[3,3,1]nonan-2-one | Ketone | Present | --- | Present |
| **11** | 13.003 | 6-Hydroxyhexahydrocyclopenta(b)furan-2-one | Ketone | Present | Present | Present |
| **12** | 14.784 | 3,4-Anhydro-d-galactosan | Sugar | Present | Present | Present |
| **13** | 20.684 | 4-n-Propylacetophenone | Ketone | Present | Present | Present |

*a)* Retention time.

RM powders after thermal pre-treatment at different temperatures were applied as the catalyst for upgrading the beechwood CFP vapour. These include RM-initial, RM-600, and RM-950.The following general trend was observed: a drop in the yield of phenol fraction was accompanied by an increase in the yields of furfurals, acids, and aldehydes (Fig. 1). Other product groups remained either unaffected or showed very small variations in their yields. High temperature pre-treatment of RM clearly makes an impact on the product distribution. The higher the temperature of RM calcination, the stronger the reduction in the phenols yields and the stronger the increase in the yields of furfurals and acids. CO2 elimination from the pyrolysis products in general decreases with the increase in the calcination temperature of RM catalyst, however this effect is within experimental error. The strongest effect was observed with the RM-950. The yields of furfurals and acids increased up to 13.3 % and 22.3 %, respectively, whereas the yield of phenols decreased to 11.8 %. The effect of the catalyst loading on the product distribution is presented in Fig. 2. The highest impact was observed for the BW/RM weight ratio of 1:4. Note that after CFP with red mud, most of the original products were still detected (Table 1), while new ketones and sugars were also formed in small yields (Table 2).

After thermal treatment, the specific surface area of RM powder was found to decrease from 14.1±1.5 m2/g (RM-initial) to 9.9±0.1 m2/g (RM‑950), however the catalytic impact became more intense, which could be associated with phase evolution. XRD analysis indicates that red mud is a multiphase composition (Fig. 3). The AlO(OH) phase significantly dominates in the XRD pattern of RM-initial, although several other phases can also be identified, including α-Fe2O3, TiO2 (anatase), SiO2, and hydrous aluminium silicates (kaolinite). Several phase transitions associated with the thermal stability of hydrous aluminium silicates and AlO(OH) occur in red mud during heating to 950°C. The RM-950 powder contains α-Al2O3, SiO2, α-Fe2O3, and TiO2. XRD data are in a good agreement with the TGA/DSC results shown in Fig. 4. The gradual weight loss during heating to about 250oC is associated with desorption of physisorbed water. The significant weight loss in the range of 250-350oC and 475-572oC accompanied by exothermic peaks could be attributed to the release of chemically absorbed water [44] from aluminium silicates and the transformation of AlO(OH) to the more stable α-Al2O3 phase with corundum structure.

The XRD and TGA results indicated low chemical stability of AlO(OH) at intermediate temperatures. Therefore, phase transitions in RM-initial would be likely to occur during BW CFP at 500oC.



Fig. 3. XRD patterns of red mud: untreated (RM-initial) and after calcination at 600oC (RM-600) and 950oC (RM-950) for 5 h.

The XRD patterns of RM-initial before and after CFP were found to be very similar (supporting information, Fig. S1). The IR-spectra of RM-initial after CFP of BW shows only a partial disappearance of bands at 3446 cm-1 and 3528 cm-1 associated with vibrations of OH groups in AlO(OH) phase (supporting information, Fig. S2). This indicates that a longer exposure time of RM-initial at 500oC is required for complete transformation of AlO(OH) to another phases. The XRD patterns and IR spectra of RM-950 were very similar before and after CFP (supporting information, Figs. S1 and S2).



Fig. 4. TGA/DSC curves of RM-initial under air in the temperature range of 25-900oC.

To better understand the catalytic effect of RM, the RM constituent oxides (α-Al2O3, Fe2O3, SiO2, and TiO2) were also tested in the CFP of beechwood. It was found that after CFP with α-Al2O3, Fe2O3, SiO2, and TiO2, the distribution of the pyrolysis products was significantly affected (Fig. 5). In general, Fe2O3 and α-Al2O3 had an effect on the pyrolytic products, increasing the formation of CO2 and furfurals, whilst decreasing the yield of phenols. TiO2 also promoted the formation of furfurals, whereas aldehyde formation was promoted by all these oxides. Overall, the acid yield was not altered by all individual oxides constituting red mud. XRD patterns and IR spectra of all individual oxides were recorded before and after CFP of beechwood (supporting information, Figs. S3 and S4).

The catalytic effect of the applied catalysts (RM-950 and individual oxides with the BW/catalyst ratio of 1:4 w/w) will be further discussed for the most highly affected groups of compounds.

Fig. 5. Product distribution for CFP of beechwood (BW) with α-Al2O3, Fe2O3, SiO2, and TiO2 in 1:4 weight ratio.

**3.2. Catalytic effect on the distribution of phenolic compounds**

The decomposition of lignin primarily generates various phenolic compounds [45]. These phenolic compounds are considered to be responsible for the high molecular weight and high viscosity of bio-oils. Therefore, cracking of the primary phenolic products to lighter derivatives is necessary for improvement of the bio-oil properties.

Fig. 6. Catalytic effect on the distribution of some phenolic compounds.

As shown in Figs. 1 and 5, the overall phenolic content is significantly reduced with RM and Fe2O3. In contrast, α-Al2O3, SiO2 and TiO2 had little impact on the reduction of phenolic compounds. However, the application of these catalytic materials showed a different upgrading effect on the yields of identified compounds within the group, as shown in Fig. 6 and Fig. S5. The yields of 4-ethenyl-2-methoxyphenol, 2,6-dimethoxyphenol, 4-methoxy-3-(methoxymethyl)phenol and 4-allyl-2,6-dimethoxyphenol were greatly reduced during CFP with RM (Fig. 6). Except for 4-ethenyl-2-methoxyphenol, the rest of the affected compounds contain two methoxy groups in their side chains. The impact of Fe2O3 on these four phenolic compounds was similar to the impact of RM. This indicates that the catalytic properties of RM are similar to those of Fe2O3 for phenolic compounds, in spite of the red mud containing noticeably lower fraction of iron oxide (7.6 at.%). The reduction of phenolic compounds in CFP showed that the application of the catalysts inhibited the devolatilisation of lignin, as reduction in the total yield was observed without any obvious transformations between compounds within this group. On the other hand, re-polymerisation reactions associated with transformation of pyrolysis vapours with phenolic motive to chars [46] cannot be completely ruled out.

**3.3. Catalytic effect on the distribution of furfural compounds**

Cellulose, in which D-glucose units are linked by β-1,4-glycosidic bonds, starts its decomposition at lower temperatures than lignin, forming various products, including furfurals. Three furfurals are formed during the fast pyrolysis of BW (Fig. 7). The yield of furfurals increased significantly with RM-initial and RM-950 (RM/BW ratio 1:1 w/w), and it also increased with increasing RM/BW ratio (Fig. 2). The yields of furfural, 5-methylfurfural, and 5-hydroxymethylfurfural (5-HMF) increased up to 8.89%, 3.08%, and 1.29%, respectively (Fig. 7), indicating good selectivity of RM to furfurals and efficien depolymerisation reaction through selective cleavage of specific C–C or C–O bonds in glucose molecules. Furfurals, the dehydration products of fructose, were also promoted by Fe2O3 and TiO2, indicating their good furfural selectivity. The results clearly indicate that red mud, Fe2O3 and TiO2 promote the dehydration reactions of the depolymerisation products of cellulose. The peak area percentage of furfurals was increased steadily to 7.88% and 7.08% for Fe2O3 and TiO2 respectively.

The possible pathways for the conversion of cellulose to furfurals are presented in Fig. 8. The dehydration of fructose is required for the production of 5-HMF. 5-HMF could be converted to 5-methylfurfural and furfural by fragmentation as shown in Fig. 8c. Fe2O3 and TiO2 behave similarly to the red mud with respect to furfural formation. However, for RM-950, containing 7.6 at.% iron and around 1 at.% titanium the overall increase in furfurals yield was almost 2 times higher than for Fe2O3 and TiO2 oxides. Despite Al2O3 and SiO2 barely facilitate furfurals formation (Fig. 5), their acidic nature should be taken into consideration as acid sites can catalyse the decomposition of cellulose into furfurals.

**Fig. 7.** Catalytic effect on the distribution of furfurals.

(a)



(b)



(c)



Fig. 8. Possible reaction pathways for the conversion of cellulose to 5-HMF [47] (a);   
dehydration of hexoses [48] (b); and transformation of 5-HMF into furfural and 5-methylfurfural (c).

**3.4. Catalytic effect on the distribution of acidic compounds**

Fast pyrolysis of beechwood primarily produced acetic acid and hexadecanoic acid (Fig. 9). Full list of the identified acids is presented in the supported information (Fig. S6). Acetic acid is known to be mainly formed from the deacetylation of acetyl groups in hemicellulose during fast pyrolysis of BW [49]. The yield of acetic acid was found to increase with RM catalyst, reaching 20.2%. Individual oxides also favoured acetic acid formation, however, their effect was not as strong as with the red mud. The red mud increased noticeably the yield of acetic acid, while decreasing the yield of hexadecanoic acid (Fig. 9). The change in the yield of acetaldehyde in CFP is also presented in Fig. 9 for comparison.

Cracking of hexadecanoic acid at 500oC into acetic acid and alkene compounds followed by oxidation of alkene into acetaldehyde (Fig. 10) could contribute to the observed increase of yield. A fraction of the produced acetaldehyde could be further transformed by oxidation into acetic acid. The proposed pathway correlates with the increase in the yield of acetaldehyde. One mole of hexadecanoic acid produces one mole of acetic acid and seven moles of alkene. Therefore, the increase of acetic acid and acetaldehyde yields could be in favour of less decrease in hexadecanoic acid yield. In addition, one cannot rule out that the observed decrease in the phenols yield is associated with their

Fig. 9. Catalytic effect on the distribution of acetic acid, hexadecanoic acid, and acetaldehyde.



Fig. 10. Possible reaction pathway for transformation of hexadecanoic acid into acetic acid and acetaldehyde.

conversion to acetic acid through a series of consequtive and parallel reactions. Previously, it was found that phenols could decompose into acetic acid and other acids in the presence of catalysts [50].

Acids are not generally considered as desirable compounds in the liquid bio-oil. However, acetic acid is important organic volatile product, which is applied in many industrial processes, and can be recovered as a by-product from the pyrolytic liquid.

**3.5. Catalytic effect on the distribution of ketonic compounds**

1-Hydroxy-2-propanone, 1,2-cyclopentanedione, 3',5'-dimethoxyacetophenone and 1-(4-hydroxy-3,5-dimethoxyphenyl)ethanone were the most abundant ketones in the non-catalytic fast pyrolysis of beechwood (Fig. 11). The full list of the identified ketones is presented in the supported information (Fig. S7). There was no significant effect of catalysts on the overall yield of ketones in CFP of BW: 16.6 % for the BW alone and 15.4 % for the BW with RM-950 (Fig. 1). α-Al2O3, Fe2O3, SiO2, and TiO2 also showed a moderate effect on the overall ketone yield in CFP. However, the yields of some specific ketones were altered during the catalytic upgrading of pyrolysis vapour (Fig. 11), whilst some new ketones in minor quantities below 1 % were formed (Table 2 and Table S1). The yield of 3',5'-dimethoxyacetophenone was reduced by all catalysts, in particular by RM-950 and Fe2O3. All the catalysts had small effect on the yield of 1-(4-hydroxy-3,5-dimethoxyphenyl)ethanone, while the yield of 1,2-cyclopentanedione barely increased. α-Al2O3 and SiO2 specifically favoured the formation of 1-hydroxy-2-propanone.

Fig. 11. Catalytic effect on the distribution of selected ketones.

4. Conclusions

Red mud (RM) was employed as the catalyst for the fast pyrolysis of beechwood (BW). Thermal pre-treatment of red mud at 950oC (RM-950) was found to be effective for BW pyrolysis vapours upgrading, as at this temperature all unstable phases, such as AlO(OH) and hydrous aluminium silicates, transformed into more stable phases, resulting in a higher selectivity of pyrolysis products upgrading. BW/RM-950 weight ratio 1:4 was found to be the optimum pyrolysis condition. In this system the yields of furfurals and acetic acid increased to their highest values and the fraction of phenols almost halved. Cellulose decomposition into furfurals was significantly promoted in the catalytic fast pyrolysis with RM-950 as well as with individual constituent oxides Fe2O3 and TiO2. Phenols and ketones with two methoxy groups in their side chains underwent strong conversions during catalytic fast pyrolysis with RM-950 and Fe2O3. The reduction in phenolic content can improve the quality of bio-oil in terms of its calorific value and lower viscosity.

The potential application of red mud as a catalyst and a schematic overview of processes occurring during catalytic fast pyrolysis are presented in Fig.12. The reduction in the total yield of phenols is related to the low molecular weight and lower viscosity of pyrolytic liquid. The conversion of higher molecular weight ketones into lower molecular weight and new ketones could further improve the heating value of the pyrolytic liquid. Both transformations are important for obtaining high quality bio-oil. Furfural is widely used for the production of chemicals and can also be further converted in liquid transportation fuels [11, 51]. The recovery of furfural and acetic acid from bio-oil can be considered as a platform for the production of a broad range of chemicals. The composition of red mud can be further optimised for targeted production of valuable chemicals.

BW fast pyrolysis with RM-950, α-Al2O3, Fe2O3, SiO2, and TiO2

Decreased Phenols

Increased Acetaldehyde

Increased Acetic acid

Increased Furfural Phenols

Fig. 12. Catalytic impact on fast pyrolysis products.

**Acknowledgement**

Authors gratefully acknowledge for financial support the SIP JinjiLake Double-Hundred Talents Program (01414892X/2012-00460) as well as Research Development Fund (RDF-13-02-14) and PhD Scholarship (PGRS-13-02-10) at Xi'an Jiaotong-Liverpool University.

**5. References**

[1] D. Mohan, C.U. Pittman, P.H. Steele, Pyrolysis of wood/biomass for bio-oil: a critical review, Energy & fuels. 20 (2006) 848-889.

[2] P. McKendry, Energy production from biomass (part 1): overview of biomass, Bioresource Technology. 83 (2002) 37-46.

[3] A.V. Bridgwater, G.V.C. Peacocke, Fast pyrolysis processes for biomass, Renewable and Sustainable Energy Reviews. 4 (2000) 1-73.

[4] Q. Lu, W.Z. Li, X.F. Zhu, Overview of fuel properties of biomass fast pyrolysis oils, Energy Conversion and Management. 50 (2009) 1376-1383.

[5] Q. Lu, W.Z. Li, D. Zhang, X.F. Zhu, Analytical pyrolysis-gas chromatography/mass spectrometry (Py–GC/MS) of sawdust with Al/SBA-15 catalysts, Journal of Analytical and Applied Pyrolysis. 84 (2009) 131-138.

[6] A.V. Bridgwater, Second Japan-EC Joint Workshop on the Frontiers of Catalytic Science and Technology for Energy, Environment and Risk Prevention Production of high grade fuels and chemicals from catalytic pyrolysis of biomass, Catalysis Today. 29 (1996) 285-295.

[7] C.D. Blasi, C. Branca, A. Galgano, Products and global weight loss rates of wood decomposition catalyzed by zinc chloride, Energy & Fuels. 22 (2007) 663-670.

[8] N. Shimada, H. Kawamoto, S. Saka, Different action of alkali/alkaline earth metal chlorides on cellulose pyrolysis, Journal of Analytical and Applied Pyrolysis. 81 (2008) 80-87.

[9] J. Adam, M. Blazso, E. Meszaros, M. Stöcker, M.H. Nilsen, A. Bouzga, J.E. Hustad, M. Grønli, G. Øye, Pyrolysis of biomass in the presence of Al-MCM-41 type catalysts, Fuel. 84 (2005) 1494-1502.

[10] Q. Lu, W.M. Xiong, W.Z. Li, Q.X. Guo, X.F. Zhu, Catalytic pyrolysis of cellulose with sulfated metal oxides: A promising method for obtaining high yield of light furan compounds, Bioresource Technology. 100 (2009) 4871-4876.

[11] G.W. Huber, J.N. Chheda, C.J. Barrett, J.A. Dumesic, Production of liquid alkanes by aqueous-phase processing of biomass-derived carbohydrates, Science. 308 (2005) 1446-1450.

[12] J.H. Jones, The cativa™ process for the manufacture of acetic acid, Platinum Metals Review. 44 (2000) 94-105.

[13] C. Rioche, S. Kulkarni, F.C. Meunier, J.P. Breen, R. Burch, Steam reforming of model compounds and fast pyrolysis bio-oil on supported noble metal catalysts, Applied Catalysis B: Environmental. 61 (2005) 130-139.

[14] E.C. Vagia, A.A. Lemonidou, Hydrogen production via steam reforming of bio-oil components over calcium aluminate supported nickel and noble metal catalysts, Applied Catalysis A: General. 351 (2008) 111-121.

[15] K. Takanabe, K.I. Aika, K. Seshan, L. Lefferts, Sustainable hydrogen from bio-oil-steam reforming of acetic acid as a model oxygenate, Journal of Catalysis. 227 (2004) 101-108.

[16] H. Pakdel, C. Roy, Separation and characterization of steroids in biomass vacuum pyrolysis oils, Bioresource Technology. 58 (1996) 83-88.

[17] C. Amen-Chen, H. Pakdel, C. Roy, Separation of phenols from Eucalyptus wood tar, Biomass and Bioenergy. 13 (1997) 25-37.

[18] F. Mahfud, F. Van Geel, R. Venderbosch, H. Heeres, Acetic acid recovery from fast pyrolysis oil. An exploratory study on liquid-liquid reactive extraction using aliphatic tertiary amines, Separation Science and Technology. 43 (2008) 3056-3074.

[19] L. Moens, Isolation of levoglucosan from lignocellulosic pyrolysis oil derived from wood or waste newsprint, in, Google Patents, 1995.

[20] G. Dobele, G. Rossinskaja, T. Dizhbite, G. Telysheva, D. Meier, O. Faix, Application of catalysts for obtaining 1,6-anhydrosaccharides from cellulose and wood by fast pyrolysis, Journal of Analytical and Applied Pyrolysis. 74 (2005) 401-405.

[21] M.Q. Chen, J. Wang, M.X. Zhang, M.G. Chen, X.F. Zhu, F.F. Min, Z.C. Tan, Catalytic effects of eight inorganic additives on pyrolysis of pine wood sawdust by microwave heating, Journal of Analytical and Applied Pyrolysis. 82 (2008) 145-150.

[22] X.L. Zhuang, H.X. Zhang, J.Z. Yang, H.Y. Qi, Preparation of levoglucosan by pyrolysis of cellulose and its citric acid fermentation, Bioresource Technology. 79 (2001) 63-66.

[23] W.Y. Qi, C.W. Hu, G.Y. Li, L.H. Guo, Y. Yang, J. Luo, X. Miao, Y. Du, Catalytic pyrolysis of several kinds of bamboos over zeolite NaY, Green Chemistry. 8 (2006) 183-190.

[24] C. Amen-Chen, H. Pakdel, C. Roy, Production of monomeric phenols by thermochemical conversion of biomass: a review, Bioresource Technology. 79 (2001) 277-299.

[25] Q. Liu, R. Xin, C. Li, C. Xu, J. Yang, Application of red mud as a basic catalyst for biodiesel production, Journal of Environmental Sciences. 25 (2013) 823-829.

[26] S. Sushil, V.S. Batra, Catalytic applications of red mud, an aluminium industry waste: A review, Applied Catalysis B: Environmental. 81 (2008) 64-77.

[27] J. Yang, B. Xiao, Development of unsintered construction materials from red mud wastes produced in the sintering alumina process, Construction and Building Materials. 22 (2008) 2299-2307.

[28] N. Zhang, X. Liu, H. Sun, L. Li, Evaluation of blends bauxite-calcination-method red mud with other industrial wastes as a cementitious material: Properties and hydration characteristics, Journal of hazardous materials. 185 (2011) 329-335.

[29] A. Collazo, D. Fernández, M. Izquierdo, X.R. Nóvoa, C. Pérez, Evaluation of red mud as surface treatment for carbon steel prior painting, Progress in Organic Coatings. 52 (2005) 351-358.

[30] A. Tor, Y. Cengeloglu, M.E. Aydin, M. Ersoz, Removal of phenol from aqueous phase by using neutralized red mud, J. Colloid Interface Sci. 300 (2006) 498-503.

[31] R. Apak, E. Tütem, M. Hügül, J. Hizal, Heavy metal cation retention by unconventional sorbents (red muds and fly ashes), Water Res. 32 (1998) 430-440.

[32] Y. Li, C. Liu, Z. Luan, X. Peng, C. Zhu, Z. Chen, Z. Zhang, J. Fan, Z. Jia, Phosphate removal from aqueous solutions using raw and activated red mud and fly ash, Journal of hazardous materials. 137 (2006) 374-383.

[33] S. Wang, Y. Boyjoo, A. Choueib, Z.H. Zhu, Removal of dyes from aqueous solution using fly ash and red mud, Water Res. 39 (2005) 129-138.

[34] A. López, I. de Marco, B.M. Caballero, M.F. Laresgoiti, A. Adrados, A. Aranzabal, Catalytic pyrolysis of plastic wastes with two different types of catalysts: ZSM-5 zeolite and Red Mud, Applied Catalysis B: Environmental. 104 (2011) 211-219.

[35] K.C. Pratt, V. Christoverson, Hydrogenation of a model hydrogen-donor system using activated red mud catalyst, Fuel. 61 (1982) 460-462.

[36] J. Álvarez, S. Ordóñez, R. Rosal, H. Sastre, F.V. Dı́ez, A new method for enhancing the performance of red mud as a hydrogenation catalyst, Applied Catalysis A: General. 180 (1999) 399-409.

[37] S. Ordóñez, H. Sastre, F.V. Dı́ez, Catalytic hydrodechlorination of tetrachloroethylene over red mud, Journal of hazardous materials. 81 (2001) 103-114.

[38] B. Klopries, W. Hodek, F. Bandermann, Catalytic hydroliquefaction of biomass with red mud and CoO-MoO3 catalysts, Fuel. 69 (1990) 448-455.

[39] C. Torri, M. Reinikainen, C. Lindfors, D. Fabbri, A. Oasmaa, E. Kuoppala, Investigation on catalytic pyrolysis of pine sawdust: Catalyst screening by Py-GC-MIP-AED, Journal of Analytical and Applied Pyrolysis. 88 (2010) 7-13.

[40] Q. Zhang, J. Chang, T. Wang, Y. Xu, Upgrading bio-oil over different solid catalysts, Energy & Fuels. 20 (2006) 2717-2720.

[41] C.Q. Dong, Z.F. Zhang, Q. Lu, Y.P. Yang, Characteristics and mechanism study of analytical fast pyrolysis of poplar wood, Energy Conversion and Management. 57 (2012) 49-59.

[42] A.V. Bridgwater, D. Meier, D. Radlein, An overview of fast pyrolysis of biomass, Organic Geochemistry. 30 (1999) 1479-1493.

[43] A. Demirbaş, Calculation of higher heating values of biomass fuels, Fuel. 76 (1997) 431-434.

[44] I. Hassan, The thermal behavior of cancrinite, The Canadian Mineralogist. 34 (1996) 893-900.

[45] D.J. Nowakowski, A.V. Bridgwater, D.C. Elliott, D. Meier, P. de Wild, Lignin fast pyrolysis: results from an international collaboration, Journal of Analytical and Applied Pyrolysis. 88 (2010) 53-72.

[46] Q. Lu, Y. Zhang, Z. Tang, W.Z. Li, X.F. Zhu, Catalytic upgrading of biomass fast pyrolysis vapors with titania and zirconia/titania based catalysts, Fuel. 89 (2010) 2096-2103.

[47] W. Deng, Q. Zang, Y.Wang, Catalytic transformations of cellulose and its derived carbohydrates into 5-hydroxymethylfurfural, levulinic acid, and lactic acid, Science China Chemistry. 58 (2015) 29-46.

[48] Y. Román-Leshkov, J.N. Chheda, J.A. Dumesic, Phase Modifiers Promote Efficient Production of Hydroxymethylfurfural from Fructose, Science. 312 (2006) 1933-1937.

[49] P.R. Patwardhan, B.H. Shanks, R.C. Brown, Product distribution from the fast pyrolysis of hemicellulose, ChemSusChem. 4 (2011) 636-643.

[50] A. Santos, P. Yustos, A. Quintanilla, S. Rodrı́guez, F. Garcı́a-Ochoa, Route of the catalytic oxidation of phenol in aqueous phase, Applied Catalysis B: Environmental. 39 (2002) 97-113.

[51] A. Corma, S. Iborra, A. Velty, Chemical routes for the transformation of biomass into chemicals, Chemical reviews. 107 (2007) 2411-2502.