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The catalytic effect of inherent and adsorbed metals on the fast/flash pyrolysis of biomass: A review

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A B S T R A C T

Relevant literature which deals with the presence of metals during the catalytic pyrolysis of biomass is reviewed. Only those conditions where the metal was in intimate contact with the biomass components are included. Cellulose, hemicellulose and lignin all fuse during the early stages of pyrolytic heating and the dehydration and decomposition processes begin during this transition. Hemicelluloses such as xylan are more labile and difficult to isolate, whereas both cellulose and lignin produce mostly bio-oils when demineralised and flash pyrolysed. The dominant primary products from 'pure' cellulose are anhydrosugars as well as smaller oxygenates. Lignin gives aromatics based on the syringol and guaiacol molecules. The alkali and alkaline earth metals are found to curtail the yield of bio-oil and modify product distribution, even in the low concentrations naturally found in biomass. All other metals act to catalyse cross-linking reactions, with the nickel and zinc most studied. The electropositivity of the metal tends to correlate with the extent of catalytic activity. The presence of metals causes little change to the production of gases, but more char is formed at the expense of liquids. If the aim of pyrolysis is bio-oil for fuel, prewashing of biomass to remove metals is beneficial.

Keywords:

Metals
Fast pyrolysis
Flash pyrolysis
Biomass
Catalyst

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1. Background

In the current energy climate, the thermal processing of biomass receives a great deal of attention, with pyrolysis being studied as a route to liquid fuels and chemicals. Ten years ago the predominant route under consideration was simple pyrolysis, followed by catalytic upgrading of the pyrolysate. Recently the focus has changed to catalysing the devolatilisation process itself. In addition, there is increasing interest in the processing of lignin, which had generally been neglected because of its refractory nature.

Pyrolysis conversion mechanisms have been well studied by many researchers, and an excellent diagrammatic summary of the decomposition processes of biomass components is available [1]. Generally, the reaction pathways include the cracking, decarboxylation, decarboxylation, hydrocracking, hydrodeoxygenation and hydrogenation of the biomass components.

During any thermal processing, be it pyrolysis, gasification or combustion, the feed material will first devolatilise as it is raised to process temperature. As discussed in Ref. [2], there is extensive loss of volatiles before any gasification reactions occur in either the gas or solid phases. It is therefore important to understand this initial process, especially as catalysis in some form will be involved. It is known that inorganic materials naturally present within biomass act as catalysts that limit the yield of bio-oil and alter the product distribution e.g. Ref. [3]. This consideration has prompted the production of the present article.

This review will be restricted to the action of the metals on the thermal processing of solid biomass, and will not be concerned with the subsequent, independent upgrading of the bio-oils produced by pyrolysis. Many reviews are available on this topic e.g. [4–6].

The devolatilisation process will take place in an environment where many other variables, such as type of feed material, particle size, water content, temperature, heating rate, mode of heat addition, and ambient pressure and atmosphere will influence the result. The effect of these must be considered when evaluating the amount and composition of products.

1.1. Metal-biomass association

All biomass contains inherent mineral matter, particularly alkaline and alkaline earth elements (AAEM), which will influence subsequent processing as the tarry materials and other organics are released during devolatilisation. For example, when corn stover containing 7–8% of ash was washed and leached with dilute acid, up to 97% of the physiological ash species that negatively affect pyrolysis was removed [7]. It is claimed by Bradbury and al. [8] that the observed catalytic effect of metals on the pyrolysis of cellulose is due to ionic species.

Biomass can be considered as a matrix comprised of predominantly three constituents, namely cellulose, hemicellulose and lignin in various amounts, together with small amounts of “extractives” and mineral matter which becomes ash on combustion. The analyses of an extensive range of biomass types have been published by Saidur et al. [9], and Godin et al. [10]. For example, hardwoods are typically high in cellulose content at 40–50% by mass, while nut wastes (walnut, hazelnut, olive) tend to return similar values for lignin. Straws and other grasses lie in an

intermediate region. According to current understanding, lignin, cellulose, and hemicellulose are not just individual units in a plant cell wall, but are intimately interrelated and associated with each other [11].

Cellulose is comprised of linear, long chain macromolecules constructed from different sugars linked by 1–4 glycosidic bonds, while hemicelluloses are polysaccharides of variable composition, including monosaccharide units with both 5 and 6 carbon members. Lignin is an irregular aromatic polymer synthesized from methoxy-phenylpropane units. In general, soft wood lignin is composed of coniferyl alcohol units, while hardwood lignin is composed of coniferyl and sinapyl alcohol units ([11,12]). Lignins from grasses contain guaiacyl, syringyl and *p*-hydroxyphenyl (H) units. Ultimate analyses plotted on a van Krevelen diagram show that hemicellulose is slightly higher in oxygen-to-carbon (O/C) ratio than cellulose, which in turn is much higher than lignin.

The disposition of metals naturally found in biomass is reviewed by Leijenhurst et al. [13]. The simplest form of the alkali metals Na and K is as free ions with counter-ions, dissolved in cytoplasmic fluid inside the cell volume, but they also appear in structured mineral (solid) form e.g. NaCl. Covalent bonds between inorganic elements and the organic biomass structure are seen as well (e.g. proteins). Attachment of the alkali metals to the organic matrix, for example as carboxylate, is less common.

In contrast, the alkali earth metals Ca and Mg predominately form bonds with the organic parts of the biomass, and are less commonly present in free ionic form. Transition metals such as Fe, Cu, Ni, Cd, Cr, Co, Mn and Zn are not always found in biomass, nor are the post transition metals Al and Pb. When present, their concentrations are usually in trace amounts.

One can impregnate the biomass with a metal in solution, and then pyrolyse the treated material. Metal ions in a solution used to impregnate biomass may undergo ion exchange, presumably with alkaline earths, or simply diffuse into the cellular liquid. Most metals used for promoting pyrolysis such as nickel are added as readily soluble salts, e.g. chlorides, nitrates or acetates, which liberate the cations by ionisation or decomposition. For the purposes of this discussion, natural, ion-exchanged and adsorbed metals were considered as homogeneous or in-situ catalysts. Any interaction between metal and organic substrate during thermal decomposition must take into account the physical changes involved, as well as the chemical. All three lignocellulosic components undergo a phase transformation and liquefy at temperatures between 200 and 400 °C [14], as do coals. Lignin liquefies more readily and over a greater temperature range than xylan, while cellulose is far more refractory. It is the elasticity of the crystalline cellulose, in combination with the mineral skeleton, which maintains the structural integrity of the cell [15]. This collapse of cell structures and the consequent fluidity of the mass should facilitate contact between metal and substrate. The accessibility of the metals themselves should also be considered, as catalysis in this application involves ionic species [8]. Surface mobility is generally correlated with the Tamman temperature (taken as half the melting temperature in K), where atoms in the bulk become mobile [16]. Because biomass pyrolysis takes place at comparatively low temperatures, the Tamman temperature of most metals would seldom be reached until the latter stages of the process. However, metal mobility could be achieved by two other effects: (1) the liquefaction

of the lignocellulose materials as noted above, and (2) the release of metal ions from either free or loosely bound sources [13].

1.2. Fast/flash pyrolysis

The rate of devolatilisation for large particles is controlled by heat conduction through the particle. For small particles, the heating is rapid and the rate is controlled by the chemical reactions involved. During the pyrolysis of wood, the decomposition of hemicellulose occurs between 200 and 260 °C, cellulose at 240–350 °C and lignin at 280–500 °C [17]. Comprehensive reviews of the chemical, heat transfer and mass transfer processes involved has been presented by Di Blasi and Paulsen et al. [18]. The latter demonstrate that particle size must be less than 10 µm for the process to be truly isothermal and kinetically controlled.

Since rapid heating rates yield more bio-oil than slow pyrolysis, it has become the preferred technique, and the present review will be restricted to this approach. Fast pyrolysis is considered to apply at heating rates of hundreds of degrees per second, and flash pyrolysis when it is in thousands [19]. Various pyrolysis and fast pyrolysis technologies have been extensively developed in the literature over the past 10 years ([20–22]). The devices which produce such high heating rates may be fluidised beds, entrainment reactors, ablative reactors such as cyclones, or on a smaller scale commercial pyroprobes, which are generally connected to a gas chromatograph/mass spectrometer (Py-GC/MS) for product identification [23].

A suitably small (in particle size and quantity) biomass sample dropped into a fluidised or spouted bed the high bed-to-particle heat transfer rates will ensure fast pyrolysis [24], as will a carefully implemented ‘dump’ of the sample onto a pre-heated fixed bed of inerts, e.g. Ref. [25]. An entrainment reactor exposes individual particles to an intense radiant environment when pneumatically conveyed by an inert carrier gas. When these particles impact against and then slide over a heated surface with significant velocity, they undergo flash pyrolysis under ablative conditions. Ablation is observed if the rates of physical and chemical transformation of the solid and of the external heat transfer are much faster than heat conduction through the solid [26]. Pyroprobes use a maximum sample size of 20 mg held in a quartz tube between quartz wool plugs, which is rapidly inserted into a pre-heated furnace [23]. The usefulness of pyroprobe results in replicating performance in larger pyrolysis units is demonstrated in Fig. 1 [27], which displays the similarity between the GC (gas chromatograph) trace of beech wood subjected to Py-GC/MS (gas chromatograph/mass spectrometer), and that of its pyrolysis oil produced in a pilot

scale reactor. The traces serve to illustrate the product slate obtained from biomass pyrolysis.

As a guide to the comparative pyrolysis behaviour of the three lignocellulosic units, the performance at various temperatures of a small sample rapidly introduced into a preheated furnace under an inert atmosphere is summarised in Fig. 2 [28]. Of the three, cellulose produces the most liquid and lignin the most solid (char), with hemicellulose in between. Carbon dioxide is the dominant gaseous product from all three, with carbon monoxide production increasing rapidly above 500 °C, as the rate of secondary reactions increases.

2. Fast/flash pyrolysis of mineral-free biomass

Ash can be removed from biomass either by acid or simple water-washing. For example, metallic species in rice husk, especially AAEMs (Alkaline and Alkali Earth Metals), were effectively removed by washing even with the aqueous fraction of bio-oil. Amorphous silica with a purity of 99.33% was obtained from combustion of the resulting biochar [29].

In order to categorise and group the various experimental results using a demineralised feed, the information has been arranged in terms of the biomass type, beginning with ‘pure’ i.e. demineralised components. It should be noted that the composition of these natural, polymeric components will vary from source to source ([30,31]), so that any attempted comparisons may be compromised. In addition, residual mineral matter may be present and significantly modify the devolatilisation process; for example, the xylan used in Ref. [32] contained 8.5% ash (db).

Another caution must be introduced in reviewing the data, as particle size exerts an unexpected influence on the product distribution under similar conditions i.e. the same material loadings in a pyrolyser micro-crucible. For example, under flash pyrolysis in a pyroprobe, powder samples of cellulose (bed thickness of 780 µm of 50 µm median microcellulose particles) and a thin-film deposit of 3 µm behaved differently [18]. The yields of the anhydrosugar levoglucosan (LG) at 500 °C were 48% for powder and only 27% for the thin-film case. Hence the authors conclude that the yield of LG is a function of sample mass and therefore sample dimension, indicating that sample dimension affects the interplay of transport and kinetics on product yields.

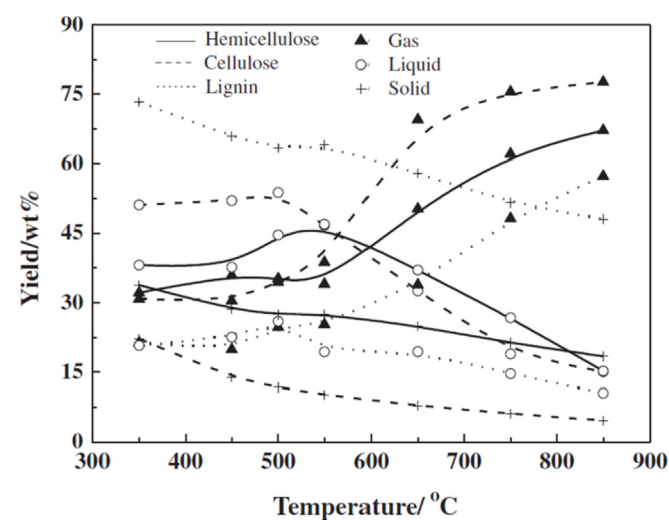


Fig. 2. Effect of temperature on product yield (gas, liquid solid) during the fast pyrolysis of commercial cellulose, xylan and lignin [28].

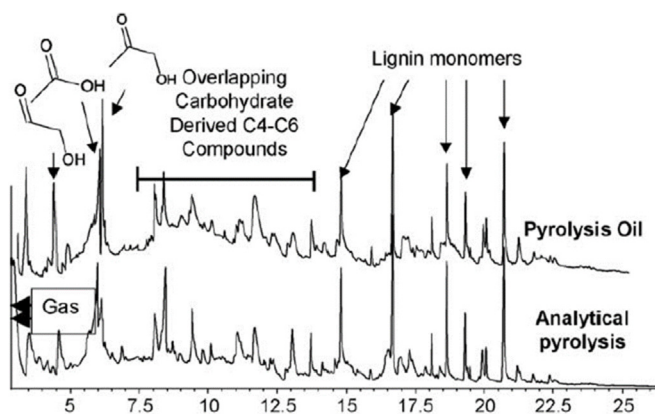


Fig. 1. Typical chromatogram of the light oils from pine pyrolysis [27].

2.1. De-mineralised lignocellulose components

In order to establish the catalytic effect of any metals present, the literature concerning the pyrolysis behaviour of isolated, ash-free samples of cellulose, hemicellulose and lignin was first reviewed. Many of the samples recorded in the literature contain amounts of ash up to 2%, which can significantly influence product distribution during pyrolysis. In view of the sensitivity of this process towards minerals as discussed later, this is a major concern, and only those samples with a demonstrated freedom from mineral matter are included.

2.1.1. Cellulose

A comprehensive review of cellulose pyrolysis can be found in Ref. [33], where it is noted that the process can be engineered to target a desired product distribution. There is a discussion of the nature of “active cellulose”, which has been proposed as an intermediate during some models of cellulose devolatilisation. It is regarded [34] as cellobiosan and heavier oligomers with a degree of polymerisation, which melt and remain non-volatile even under a low vacuum. This fusion should presumably be equated with the phase change described in Section 1.1. The possible reaction pathways for primary and secondary thermal cracking and re-arrangement are described.

Cellulose fast pyrolysis vapours consist of permanent gases (CO , CO_2 , CH_4 , H_2 , etc.), volatile compounds and non-volatile oligomers [35]. The condensation of the latter two classes of compound provides the liquid bio-oil, while GC/MS is able to determine only the organic volatile compounds. It was found that the formation of CO strongly depended on the temperature, whereas CO_2 was mainly produced by the primary pyrolysis and barely affected by additional heating, which is consistent with [28]. Although the list of potential products is vast, a tabulation of the most common product molecules is presented by Lu and co-workers [36].

From a chemical point of view, Balat [19] notes that the thermal degradation of cellulose proceeds through two types of reaction: a gradual degradation, decomposition, and charring on heating at lower temperatures; and a rapid volatilization accompanied by the formation of levoglucosan on pyrolysis at higher temperatures.

Flash pyrolysis trials of pure cellulose by Py-GC/MS at a number of temperatures (400–700 °C) and holding times (5–30s) identified [36] the optimum conditions for the overall yield of organics and of nine specific components, mostly six-member rings based on pyran (see Fig. 3 for examples), as well as furan, furfural, acetic

acid and of acetone-based compounds. The thermodynamics underlying the formation of various kinds of derivatives such as levoglucosan are discussed.

A breakdown of the condensable products tabulated for a number of fast pyrolysis temperatures [28] indicates that under 600 °C the major product is levoglucosan (1,6-anhydro- β -glucopyranose or LG) at about 50% yield, with lesser amounts of 1,4:3,6 dianhydro- α -D-glucopyranose and furfurals. Similar results are reported in Refs. [24,37]. It is claimed that practically all of the levoglucosan retained in cellulose during pyrolysis exists in the form of the chain ends [34].

In a number of cases, the cellulose tested was a microcrystalline commercial product in which the mineral contents are unspecified ([38–42]). In view of the sensitivity of the pyrolysis process to small metal contents, these results may be ambiguous.

Fast heating of commercial cellulose to 450 °C produced 12% char, 8% gas and ~80% bio-oil, which was dominated by LG [38]. High purity commercial microgranular cellulose subjected to analysis in a microprobe to 500 °C returned low values of anhydrosugars [39], the most prevalent being 10.5% LG and 3.7% levoglucosenone (LGO), see Fig. 3. A heating rate estimated to be 600 °C/s was applied to microcrystalline cellulose particles [40] with a view to producing the 1,6-anhydrosaccharides LG and LGO. At 500 °C, the yields were 20.4 and 1.2% respectively.

Fast isothermal pyrolysis at 500 °C [41] gave 3% solid (char), 39% gas which included water, and 59% organic liquids, predominantly LG. At higher temperatures the liquids tend to be converted into gases, while the char yield was unchanged. Similarly, the fast pyrolysis of 50 μm cellulose particles at the same temperature [42] returned 8% solids, with approximately half of the products consisting of levoglucosan. Results consistent with these were found with both powder and thin film trials [3].

At a much higher heating rate of 6000 °C/s [29], the liquid yield is 95%, most of which is classified as containing CH_3O -, $-\text{CH}_2\text{O}$ - and $=\text{CHO}$ groups, and some sugars larger than LG were also detected. It is apparent that the heating rate and the composition of any biomass will strongly influence the product yield under pyrolysis conditions.

According to Chan et al. [43], the literature cites two major pathways in the fast pyrolysis of cellulose: one leads to the selective formation of glycolaldehyde (GA), and the other leads to the formation of levoglucosan. Higher heating rates favour the formation of glycolaldehyde, which has a lower boiling point than LG, and produces the higher volatile fractions compared to lower heating rates. It is also known from the literature that higher heating rates lead to lower apparent activation energies. Li et al. [35] found that the FTIR (Fourier Transform InfraRed spectroscopy) signals from the pyrolysis of pure cellulose and levoglucosan were very similar, with the exception that LG did not furnish hydroxyacetaldehyde (HAA). Any reaction scheme should therefore place these on separate paths.

As a result of entrainment flow experiments, Shen and Gu [24] propose four primary pathways for cellulose pyrolytic decomposition, producing predominantly levoglucosan via two different intermediates, hydroxyacetone (HA) and HAA, and 5-hydroxymethylfurfural (5-HMF). A scheme for the further pyrolysis of the LG to the same smaller molecules is then suggested. Levoglucosan acts as not only a competitor with the other fragments in the primary cracking of cellulose, but also as a precursor for secondary decomposition, giving char through polymerisation and crosslinking reactions. Its formation is viewed as competitive with the formation of a tarry material (Tar 1, leading to HAA, HA, GA and similar, and Tar 2 giving furfural and 5-HMF). CO formation occurs mainly from the secondary reaction of the tars, while CO_2 is produced in the initial low temperature stage through

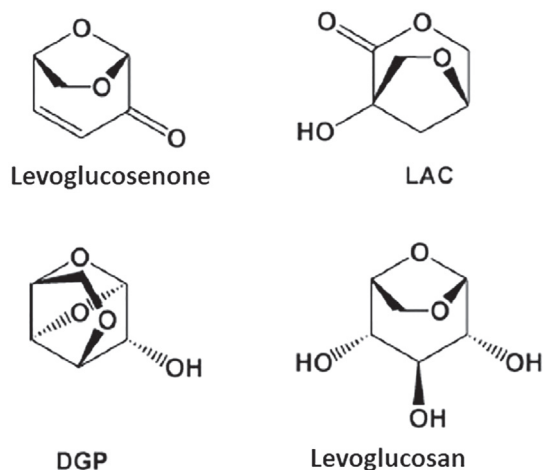


Fig. 3. Pyrolysate molecules from cellulose including levoglucosan (LG), DGP, LAC and levoglucosenone (LGO) [39].

decarboxylation of the ketene structure. The two approaches are then combined into an overall network based on competitive depolymerisation, ring opening and carbonisation processes, which proceed through tar intermediates to the final products. The maximum tar yield of 72% occurred at a reaction temperature of 570 °C.

Shen further develops this system to encompass five primary pathways with the following products [30]: (1) anhydrous hexoses, (2) LG, (3) HAA and HA, (4) CO/formaldehyde with glyoxal and other fragments, and (5) an unsaturated straight chain sugar which cyclises to 5-HMF.

Ab initio modelling of possible chelated structures indicates that any alkali metal ions will form multiple interactions with hydroxyl and ether groups in the cellulose structure [41]. The results of a theoretical study [42] on the non-catalyzed process underpin the important role played by water in the formation of pyrolysis products of cellulose, where proton transfer is a key mechanistic step [45]. Kinetic data are reported, but owing to the substantial differences in the experimental methods, operating conditions, chemical composition of raw materials, and the models used, these kinetics data are consistent only within a particular study, and cannot be compared with one another. Nevertheless the authors opt for a pseudo first-order reaction model.

2.1.2. Hemicellulose

As hemicellulose has a more diverse chemical nature than the other two components, it has not received as much attention from researchers; xylan is usually selected as representative of the group. Its chemistry is much more variable than the other two, such that it is not described in the same detail, and only general results were found. The hemicelluloses reacted more readily than cellulose during heating. Of the hemicelluloses, xylan is the least thermally stable, because pentosans are most susceptible to hydrolysis and dehydration reactions [13]. It is the main source of volatile products from biomasses (essentially furfurals and acetaldehyde) and plays an important role in the initiation and propagation of pyrolysis reactions [46].

The preparation of mineral free hemicellulose is evidently more difficult than with the other lignocelluloses, and the two results found report 4% “residue” in the ultimate analysis [44] and 8.5% mineral matter [32] respectively. In contrast to the behaviour of cellulose, the high-rate results for xylan in Fig. 4 are little different from those presented in Fig. 2 for moderate pyrolysis rates. The gases are dominated by CO₂. The authors speculate that because of the 8.5% mineral content of the xylan, the high char yield is likely to be caused by (very fast) mineral catalyzed (cross)-linking reactions [32].

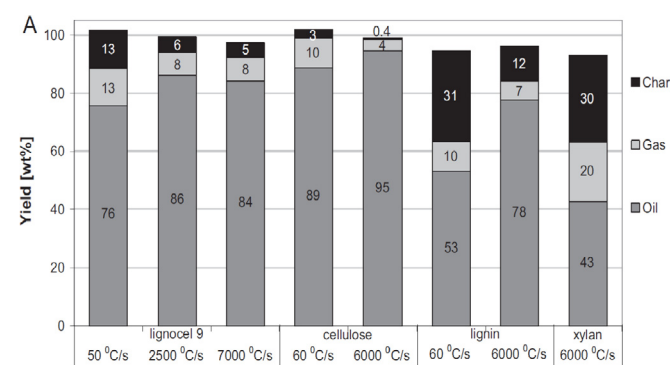


Fig. 4. Yield from biomass components at various heating rates [32].

2.1.3. Lignin

As mentioned above, there has been a rising interest in utilising lignin, which is appearing in greater quantities as reject from the biological processing of biomass. The composition of lignin varies depending on source and method of preparation e.g. alkali, Kraft, Organosolv and Granit materials. Organosolv pulping processes are relatively environmentally friendly, since the lignin extracted during this process contains very little sulphur and ash, and is less likely to be contaminated by carbohydrates [47,48]. It is claimed that Organosolv is representative of the native material [49].

An examination of lignins extracted from a hardwood and a softwood using 3 different solvents, namely aqueous ethanol, aqueous formic acid and a two-step acid (Klason) hydrolysis revealed significant differences [31]. The content of ether linkages in the hardwood lignins was approximately three times higher than that in the softwood lignins because of the presence of the sinapyl alcohol unit in the former. In addition, the number of ether linkages was ranked formasolve > ethanosolv > Klason.

A review of the thermal behaviour of intermediate pyrolysis products [50] traces possible decomposition pathways for lignin, with a number of intermediate products identified. The abundance of phenyl groups leads to the production of more aromatics than holocellulose. It is more resistant to decomposition than the other components of biomass because of the presence of high-energy carbon-carbon bonds between lignin units, such as 5-5' links [51]. Dehydration reactions are initiated around 200 °C, and between 200 and 400 °C cleavage of α - and β -aryl-alkyl-ether linkages (β -O-4 and α -O-4 bonds) occurs [15]. Around 300 °C, aliphatic side chains start splitting off from the aromatic ring, resulting in the production of light hydrocarbons as well as small oxygenated compounds. The prevalence of aromatic rings in lignin led Cheng et al. [48] to review the possibility of extracting jet fuel by a range of methods, both by thermal decomposition and solvent dissolution.

Guaiacols (2-methoxy phenol), and syringols (2,6-dimethoxy phenol) are intermediate degradation products, their amount decreasing with increasing pyrolysis temperature [52]. Highly-substituted phenols are selectively formed by cracking of the phenyl–propane units from the macromolecular lattice of lignin, because the syringyl–propane units are not linked as extensively to the lignin skeleton as the less substituted ones: guaiacyl–propane and phenyl–propane.

Lignins from three different ill-defined sources, extracted by various methods, were pyrolysed at 650 °C using flash pyrolysis methods (Py-GC/MS) [53]. For the three samples, the mean yields were ~18% of non-condensable gases, ~15% of char and ~65% of condensable gases. The liquid product yield hierarchy revealed that in general: phenol < cresol < guaiacol < 4-methyl guaiacol < syringol. The concentration range of these compounds fell within the limits of 0.2–1.7% of the feed. The gases evolved in descending abundance were CO₂ (9%), H₂O, CO (5%), CH₄ (1.4%), CH₃OH and smaller amounts of higher hydrocarbons. Various decomposition mechanisms are proposed.

When lignin was prepared with dilute sulphuric acid to hydrolyse most of the polysaccharides into fermentable sugars [54], the principal products of pyrolysis were syringol, guaiacol and catechol. Of the classes of compounds analysed, the phenolic compounds were the most abundant, contributing over 40% of the total compounds detected. Benzene, styrene, and *p*-xylene were formed in significant amounts throughout the entire temperature range.

In the 6000 °C per second wire-mesh trials mentioned above [32], an exceptionally high tar yield of 78% was obtained (Fig. 4), with 12 wt% of char. Compared to the pyrolysis of cellulose, xylan and softwood, the methane yield was high at 2 wt%. When the high-rate result in Fig. 4 is considered alongside the 60 °C/s test, as well as the result from Ref. [53] and the lignin plot in Fig. 2, it can be

concluded that unlike xylan, lignin will respond favourably to high heating rates.

Dufour et al. [14] link the chemical behaviour with rheological changes as follows. The chemical structure of lignin is affected by the thermal treatment above 200 °C through homolytic cleavage of aryl ether linkages (mostly β -O-4 linkages). Small lignin fragments with a high molecular mobility are produced. With increasing temperature from 225 to 350 °C, the thermal depolymerisation of lignin is associated with the well-known demethoxylation and re-condensation reactions. From 350 °C, the mobile fraction decreases due to the formation of solid compounds from cross-linking and growth of aromatic domains. The decrease in the mobile H fraction evidenced from 350 °C is in accordance with the solidification stage within the lignin char observed at 350–400 °C.

2.1.4. Comment

During pyrolysis all three constituents fuse to various extents, and devolatilisation behaviour is sensitive to heating rate, with cellulose the most responsive. Rapid pyrolysis leads to higher liquid yields and lower char, with an optimum temperature for liquid yield during flash pyrolysis of around 500 °C for cellulose [38], and 400–450 °C for lignin [54]. There is little literature available describing the flash pyrolysis of hemicellulose, probably because of the variability of its chemistry, and the difficulty in preparing samples of the comparatively labile material.

Under thermal treatment, cellulose breaks down into a range of molecules, including derivatives of the oxygen-containing ring compounds pyran and furan, anhydrosugars (mainly levoglucosan), and smaller fragments associated with acetone, such as hydroxyacetaldehyde and acetol. The dominant product is levoglucosan, but only when pyrolysis is rapid, minerals are absent, and there is insufficient time for secondary reactions to take place. With extreme flash pyrolysis, pure cellulose returns a char yield of only a few percent. Lignin forms more char than cellulose, but like cellulose, generates increased liquid products as the heating rate increases. Lignin is the major source of aromatic and phenolic compounds during biomass pyrolysis, derived from the phenylpropane structures found in guaiacyl and syringyl.

2.2. De-mineralised biomass

The effect of metals in biomass pyrolysis can only be understood by comparing the changes brought about by their presence, which calls for tests on de-mineralised natural biomass materials. As a preliminary, some studies on the behaviour of synthetic mixtures have been carried out in order to establish whether interactions take place between cellulose, hemicellulose and lignin during pyrolysis. The pyrolysis reaction for cellulose is claimed to be endothermic, whereas pyrolysis of xylan and lignin is exothermic [24].

2.2.1. Tests on physical mixtures of cellulose, hemicellulose and lignin

The structural models for lignocellulose presented in Refs. [14,33] depict separate, interlacing strands of each polymer which would hinder interaction. Tests in a TGA (Thermogravimetric analysis), which would permit more time for reaction, found no interaction between the three lignocellulosic components under gentle heating conditions ([55,56]). Under flash pyrolysis [24], reaction rates, between the three components suggest that there is not a great deal of interaction, but this must be qualified when the product distribution is considered.

With fast pyrolysis, the evolution rate of gas from dry eucalyptus powder was similar to that predicted by the superposition of cellulose, lignin, and xylan [53]. On the other hand, the evolution rate of the tars from the eucalyptus was different from the estimated tar

evolution rate of the three components. In a 50:50 mixture of cellulose with lignin, the presence of the cellulose did not greatly influence the behaviour of the lignin.

Flash pyrolysis by Py-GC/MS (20 °C/ms) of a synthetic mixture of 50% cellulose, 30% lignin and 20% xylan to 600 °C [55], permitted the major product molecules to be identified, with a distinction between guaiacol and syringol lignins. Cellulose is rate-limiting when mixed with xylan and lignin to simulate biomass, probably due to its highly-ordered crystalline structure. The char yield of the mixture was a weighted average of the components. The demineralised synthetic mixture produced less LG and furans than a coppiced willow sample [55]. Substituted phenols from lignin pyrolysis are more dominant in the pyrolysis profiles of the synthetic biomass than of the wood, implying that the extracted lignins used in the synthetic biomass yield a greater fraction of monomeric type species than the lignocellulosic cell wall material of willow. However, Couhert et al. [30] report modified reaction between cellulose, xylan and lignin in natural biomasses when assessed in terms of the yields of product gases, which were not additive. It is possible that the minerals in the biomass used confounded the results, and the issue is still open [33]. One would expect some interaction between the materials during the overlapping fluid stages, but during rapid pyrolysis this would be brief.

2.2.2. Structural changes resulting from demineralisation

It has been noted that contradictory results have been reported for the performance of metallic catalysts during biomass pyrolysis. These ambiguities can be assigned to the morphological and structural modifications of the reacting biomass by the various demineralisation and impregnation methods [57]. Demineralisation of biomass is carried out by an aqueous wash, generally with acid, which not only removes minerals, but can also modify its organic composition. For example, the volatile matter contents of some acid-washed miscanthus samples were 8–10% higher than those of the raw material, thereby depleting the biomasses in fixed carbon [25].

Tests on rice straw [58] reduced the original ash content of 14.8%–9.85% by water washing, and to around 7.5% by a range of acids mineral acids diluted to 5% by mass. After leaching by nitric, sulphuric and hydrochloric (i.e. strong) acids, Ca and Mg were almost completely removed, and the plant stomata and epidermis wrinkles were modified. Weaker acids led to a decrease in BET surface area and pore volume, while H₂SO₄ produced the opposite effect. Variations produced in the FTIR spectra indicate that some constituents undergo changes in cross linking between the C–OH, C–O–C and other functional groups.

The removal of minerals and extractives from rice husk and dissolution of hemicellulose and cellulose produced increases in surface area and pore volume [59]. Changes to FTIR spectral bands associated with the lignocellulosic elements indicate that some changes have occurred in cross linking between different functional groups. Similar changes were observed to the structures of residues from palm oil production (kernel, bunch and mesocarb fibre). When observed by SEM, they were slightly affected by treatment with mineral acids, with removal of some features and a general flattening of the surfaces [60]. Changes in FTIR scans were also noted, particularly with hydrofluoric acid.

The effect of citric acid on cane bagasse was studied [61], where changes to the FTIR spectra could be attributed to the modification of the xylan fraction and to the substitution of C=O by OH groups. These mild structural changes, caused by hydrolysis, led to the disappearance of the hemicellulose decomposition peak in the DTG curve. Demineralisation of willow wood with hydrochloric acid removed 99% of the ash present [62], and reduced the hemicellulose content of the sample from 19.4% to 3.5%. The cellulose content

also fell significantly, but these changes increased the thermal stability of the remaining cellulose during pyrolysis.

Some organic acids, namely formic, oxalic, tartaric, and citric were found to be ineffective for demineralising 8% ash corn stover [63], whereas sodium citrate, a chelating agent, removed 75% of the minerals. However the cellulose and hemicellulose were unaffected by this milder treatment.

3. Fast/flash pyrolysis of natural versus de-mineralised biomass

Since the small amounts of mineral matter naturally present in biomass exhibit a catalytic action on the pyrolysis process, it is difficult to make a distinction between any added and the inherent material. The technique of adsorbing or exchanging metals onto biomass involves treatment with aqueous solutions, which will inevitably lead to the loss of some metallic ash components, particularly the alkalis. Thus the best way of addressing the impact of catalyst is first to directly compare the behaviour of the two biomasses, natural and demineralised.

An early study at a moderate heating rate to 350 °C [64] examined sapwood from the cottonwood tree (mineral analysis not supplied), and its acid-washed derivative. After acid treatment, the tar yield from room temperature condensation rose markedly from 25 to 45%, and the "distillate" (condensate at -50 °C) fell from 24 to 16%. Since the char yields were little-changed, the increase in tar production was at the expense of fixed gases.

Four materials, namely two woods (eucalyptus and oak), miscanthus and wheat straw were partly de-ashed by a mild acid wash [25]. The acid treatment increased the standard volatile matter content of each sample as the fixed carbon fell, and on fast pyrolysis caused the bio-oil content to increase at the expense of char, gas and water. The CO, CO₂ and (C₁-C₃) gas yields increased monotonically with increasing potassium content of the various biomasses.

Indigenous metals barely affected the bio-oil oxygen content, which indicates that mineral components are not really effective for bio-oil deoxygenation. They mainly promote the formation of additional char, which retains about 40% of the chemical energy contained in the raw biomass.

When pine sawdust was washed in various dilute mineral acids and subjected to fast pyrolysis in a fluidised bed of quartz at 400 °C [65], the type of acid used made little difference to the product slate. The char comprised 20–22% of the feed and the bio-oil organics 57–61%, with 4.5–6% water and 4–5% gases. With the original wood, which was estimated to contain 59% xylan, the char yield was similar, but the organics fraction was less at 49%. Among the multitude of organic products analysed, the most prevalent were 23% acetic acid methyl ester and 7% dimethoxy benzene for the untreated wood, whereas for the acid-leached sample the major molecules were 41% of 1,6 anhydro-2,3,4-tri-O-methylgalactose, 17% butanoic acid methyl ester and only 7% acetic acid methyl ester.

In the quest for LG and LGO from analytical pyrolysis [40], the volatile products obtained from natural and demineralised (sulphuric acid) pine wood were analysed. The yields after treatment increased from 5.3% to 17 for LG and from zero to 0.8% for LGO. The authors attribute this to depolymerisation of the glucane chains in cellulose, and the decrease in overall polymerisation. In an extension of this work, the wood was further impregnated with increasing concentrations of phosphoric acid (0.5–3%), which caused an initial jump in LG followed by a return to the natural value. The value for LGO increased enormously and then also fell away.

As-received, water-washed and acid-washed corn stover with an original ash content of 6.7% (23 mg g⁻¹ potassium) was fast-pyrolysed in a fluidised bed of quartz sand over a range of temperatures [66]. At the only temperature available for comparison,

~335 °C, the yields (dry) of char, oil and gas were 33, 47 and 20% respectively for the original biomass. The washed and acid-leached samples (in which the potassium concentration was reduced to ~5 mg g⁻¹) returned almost identical results to each other, but with much higher bio-oil yield (55/59%) and slightly lower char than the natural corn stover. The bio-oil composition of the washed samples is not provided.

A commercial PY-GC/MS pyrolyser set to 600 °C was used to examine coppiced willow in untreated and demineralised form [55]. The distribution of products is extensive and presented as chromatograms, which makes interpretation difficult. The most obvious change produced by demineralisation is the suppression of acetic acid formation and the promotion of furfural, LG and some phenols. A greater variation in pyrolysis products was observed from acid-washed willow compared to a number of the different synthetic biomass samples.

An alternative to leaching the metals is to convert them into less-active salts by treatment with mineral acids. Through acid infusion into the biomass to convert the AAEMs into thermally stable salts (particularly potassium sulphates and phosphates), the yield of sugars from thermal treatment can be significantly increased [67]. These salts not only passivate AAEMs that normally catalyse the fragmentation of pyranose rings, but also buffer the system at pH levels that favour glycosidic bond breakage.

Zhang and Liu [68] modelled reaction pathways using a density function thermodynamics package, considering cellulose with and without K⁺ and Na⁺ present. The energy barriers applicable to transformations in various proposed pathways were examined. With pure cellulose, the formation of molecules like levoglucosan, which resemble the original polymer units, is favoured. Adding K⁺ and Na⁺ lowers the energy barrier of the dehydration reaction and accelerates the generation of other small molecules like hydroxyacetaldehyde, formic acid, acetic acid and ketones. Spatial orientation can also play a part the reaction process. It is noted [44] that metal atoms co-ordinated in the C6 position can interact with four oxygen atoms, whereas those at C2 can do so with only two.

Organic volatiles can form bonds with inorganic elements on the solid (pore) surface, after which the composed molecule can be released to the vapour phase. Experimental work on the transfer of natural inorganic elements during pyrolysis of 16 biomass materials showed that alkali earth metals (Ca, Mg), transition metals (Fe, Cu, Ni, Cd, Cr, Co, Mn, Zn) and post transition metals (Al, Pb) remain largely on the solid char by-product [13]. The concentrations found in the bio-oils were always less than 1% of the value in the parent biomass. A diagram of potential reaction paths is presented.

3.1. Comment

Strong acids tend to attack hemicellulose and some forms of cellulose, while lignin remains unaffected. Washing with water is almost as effective as with acid, because, as discussed in the next section, the most common and active of the inherent metals is readily-removed potassium. Demineralisation will decrease charring and gas formation during biomass pyrolysis, with a corresponding increase in the yield of organics. Most significantly, the product slate changes with the molecules having a greater resemblance to the basic units of the parent polymers, and LG becomes the predominant constituent. The inherent alkali metals appear to catalyse the initial depolymerisation and dehydration reactions, promoting ring scission and char formation.

4. Fast/flash pyrolysis of metal-loaded biomass

There is a plethora of studies of the kind specified in this section. At the operating temperatures of fast pyrolysis (400–600 °C),

inorganic metals are retained within the char, which indicates that they likely interact with the biomass to catalyse biopolymer degradation [3]. This can be anticipated when it is considered that all components of the biomass will fuse to some extent in the 200–400 °C range, thus capturing and incorporating the mineral matter. For example, when switchgrass was fast pyrolysed at 550 °C, over 90% of K and Na was retained in the char [69].

4.1. Alkali metals

The pyrolysis of 150–180 μm pine particles effected by dropping samples onto a pre-heated metal plate would be barely classified as ‘fast’ [70], but the results are indicative. The pine was infused with potassium in solutions containing 0.1, 0.3 and 0.5 mol kg^{-1} of the metal. At set temperatures ranging from 500 to 800 °C, the char yield from the untreated sample rose monotonically from 24% to 30%, while the tar fell from 18% to 8%.

The char from the treated samples also increased, but was less than untreated and decreased with increasing K content. Tar yield was severely diminished by the presence of the metal, but recovered slightly at 800 °C with the 0.5 M sample. An explanation for the latter anomaly was suggested by an SEM micrograph of the chars produced. The most severe conditions imposed i.e. 0.5 M K at 700 and 800 °C, led to irreversible fusion of the samples which exhibited smooth surfaces with a few blowholes, in contrast to the other chars which retained a cellular structure. The reason why this should occur is unclear.

Pinewood particles treated by leaching or infusion of K^+ , Na^+ , Ca^{2+} and Mn^{2+} solutions to give metal concentrations ranging from 0.1 to 87 $\mu\text{mol g}^{-1}$ were pyrolysed by addition to a fluidised bed of quartz at 400 °C [65]. It was found that the two alkali ions performed similarly, as did the other two metals. When the yield from each product category, namely char, bio-oil and gas was plotted against metal concentration, the char value was almost constant for all metals at ~23%. The organics yield fell from 59 for the demineralised sample to 50% for low K^+ and Na^+ concentrations, and to only 40% for high values. At the high K^+ concentration, the predominant organic products were acetic acid methyl ester and 1,2-dimethoxybenzene.

When cottonwood having several different metal ions incorporated by ion exchange was subjected to fast vacuum pyrolysis [64], potassium and lithium induced the formation of high char and low tar yields, with LG formation almost completely suppressed.

In trials on coppiced willow samples of 0.15–0.18 mm size with potassium infused to a level of 17.0 mg g^{-1} (vis-à-vis 3.8 in the natural timber) flash pyrolysis in a Py-GC/MS system produced concentrations of furfural and LG well below the values from the untreated sample [55]. The potassium present suppressed these in favour of acetic acid and some phenols, such as 2-methoxyphenol and 2,6-dimethoxyphenol, which were greatly augmented. In contrast, the organics after acid-washing were dominated by LG and furfural. The more complex phenols found in the demineralised tests appear to be further degraded by the presence of potassium. These results were not duplicated in tests on a synthetic biomass mixture (50 wt% cellulose, 15 wt.% lignin alkali, 15 wt.% organosolv lignin and 20 wt.% xylan). Although the character of the phenols was similar, it seems that the cellulose experienced inhibition, while the lignin behaved in typical fashion.

De-ashed Organosolv lignin infused with the metals Li, Na, K, Cs, Mg, Ca, Ba and Cu and then fast pyrolysed to temperatures ranging from 400 to 800 °C led to an increase in char, light oxygenates, and volatile aromatics compared to the control [49]. The yield of volatile aromatics peaked at 400–500 °C for all metals. Alkenyl side chains on volatile aromatics decreased, and in general, the effect on

pyrolysis products correlates with electro-positivity of the alkali metals. Increases in volatile aromatics, decreases in alkenyl side chains, and increases in light oxygenates for lignin infused with alkali metals suggests that they alter the cleavage of linkages within the lignin structure.

Fast pyrolysis of pine chips by Py-GC/MS found that the type of AAEM as well as the concentration was significant, with Mg appearing to be relatively inert when compared to the stronger catalytic activity of the other three, with the order $\text{Na} > \text{K} > \text{Ca} > \text{Mg}$ [68]. Even the lowest concentration of AAEMs (0.1 wt %) was observed to have a significant influence on the thermal decomposition behaviour of biomass, promoting the formation of lower molecular weight cellulose and lignin-derived products. However, the addition of NaCl did not present an important effect on pyrolysis products from soybean hulls [72].

The influence of volatile K inside a cellulose sample was investigated in terms of hydrogen production and catalyst stability using a two-stage fixed-bed reaction system in the presence of a Ni/ Al_2O_3 catalyst [71,73]. When the content of K in the cellulose sample was increased from 0 to 15%, the deposition of K on the surface of the reacted catalyst remained constant at around 0.5 wt % in terms of the weight of the catalyst.

4.2. Alkaline earths

Metal ion concentrations of calcium and magnesium ranging from 0.0125 to 0.5 mmol g^{-1} were doped into cellulose to simulate those present in lignocellulosic biomass [3]. Thin-film (3 μm) and powder (780 μm) pyrolysis was performed to 500 °C using a single shot micro-pyrolyzer, with the results depicted in Fig. 5. A large difference in yield between the two techniques was observed with and without the metals. Increasing calcium concentrations generated increasing amounts carbon oxides, whereas magnesium was less active. Without catalyst the LG yield was about 45%, but this fell with added metals. Overall, magnesium was less active than calcium, and the metal oxides were ineffective.

During trials with soybean hulls, it was observed [72] that

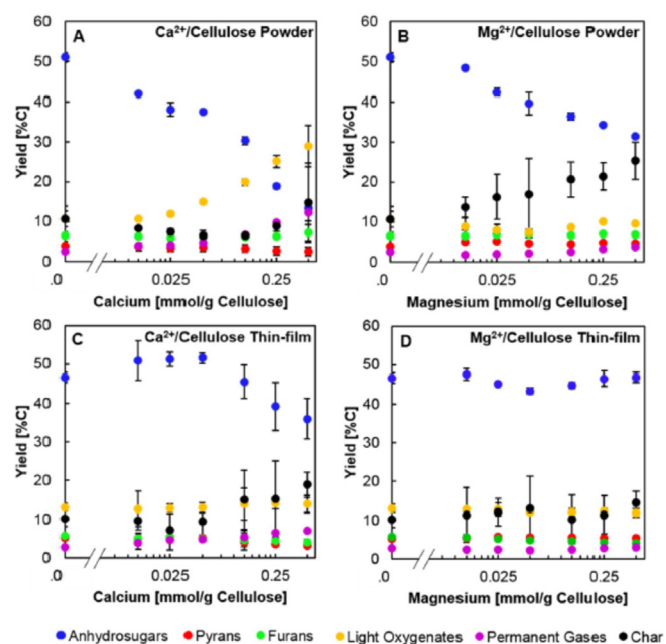


Fig. 5. Product yields from cellulose for calcium and magnesium catalysis as a function of metal loading; two substrate densities [3].

magnesium chloride generated an increase in the yield of aldehydes, but a decrease in acids and esters. It may act on hemicellulose, promoting dehydration, depolymerisation and ring opening, thus leading to the formation of light oxygenate products such as furans.

Trials with pine particles added to a fluidised bed held at 400 °C [65] included Ca^{2+} at $52 \mu\text{mol g}^{-1}$ (2.1 mg g^{-1}) and Mg^{2+} at $13 \mu\text{mol g}^{-1}$ (0.3 mg g^{-1}). These behaved in similar fashion, giving char yields of 22 and 20% respectively, and 55% organics each, but no organic product breakdown is recorded. The untreated pine yielded 22% char and 49% organics. Slightly lower char yields were found with cottonwood at 350 °C [64], and the Mg^{2+} tars contained 10% levoglucosan on daf wood.

When a comparatively slow pyrolysis rate to 700 °C was applied to three agricultural residues (maize stalk, rice husk, and cotton stalk), higher percentages of alkali metals were retained in the char than alkaline earths [74]. As with the alkali metals, over 90% of the inherent Ca and Mg remained in the char after the rapid pyrolysis of switchgrass [75].

4.3. Other metals

Biomass exposed to metals in solution can undergo ion exchange between the solvent cations and those bound to the substrate by ionic bonds, principally the alkaline earth metals [13]. It can be assumed that the tests discussed below involved ions both exchanged at AAEM sites and adsorbed into the cell cytoplasm.

Nickel has been trialled frequently in pyrolysis experiments, as its promise resides in its high activity for C–C and C–H bond cleavage [75]. The conditions for loading nickel onto dried oil-palm mesocarp fibre were examined by grinding and then sieving it to a particle size between 125 μm and 300 μm , and subjecting it to nickel solutions at various concentrations [76]. The adsorption rate kinetics are reported as pseudo second-order.

When nickel nitrate was impregnated into beech wood and pyrolysed to 500 °C at moderate heating rates, it was found that the nickel was reduced Ni^0 nanoparticles, which were catalytically active during subsequent combustion [77]. A thorough study of the formation of these nanoparticles during the pyrolysis of nickel (II)-impregnated wood in the temperature range of 400–500 °C had already been undertaken [78]. During the wood impregnation step, the numerous oxygenated groups present in the bi-macromolecules act as adsorption sites for metal cations in aqueous medium, yielding very high metal precursor dispersion into the wood matrix. The nanoparticles act as the active phase for enhancing both H_2 production and tar conversion during biomass pyrolysis.

The CIRAD group in France then selected seven metals – Ce, Mn, Fe, Co, Ni, Cu and Zn – and impregnated them into eucalyptus particles using nitrate salts [79]. After moderate pyrolysis to 500 °C, the resulting distribution of products is depicted in Fig. 6. All seven caused less oil production than the catalyst-free sample, and there is little to distinguish between them on yield. The metals tended to form nanoparticles, particularly Ni^0 , Cu^0 and ZnO , and it seems that they are closely related to LAC production (see Fig. 3).

Nickel-impregnated kraft lignin (14% ash) was prepared by either the careful addition of nickel nitrate solution, or by adsorption of colloidal nickel from its suspension [80]. Since the heating was by microwave, a carbon adsorbent was added, but even so, the heating rates were modest at 10 °C/s. Both sample types led to Ni^0 particles being present, of mean diameter about 6 μm . Hydrogen, carbon monoxide and methane were the dominant gaseous products.

As rice husk with 25% ash was being infused with iron and nickel [81], the potassium content fell during the infusion process. The

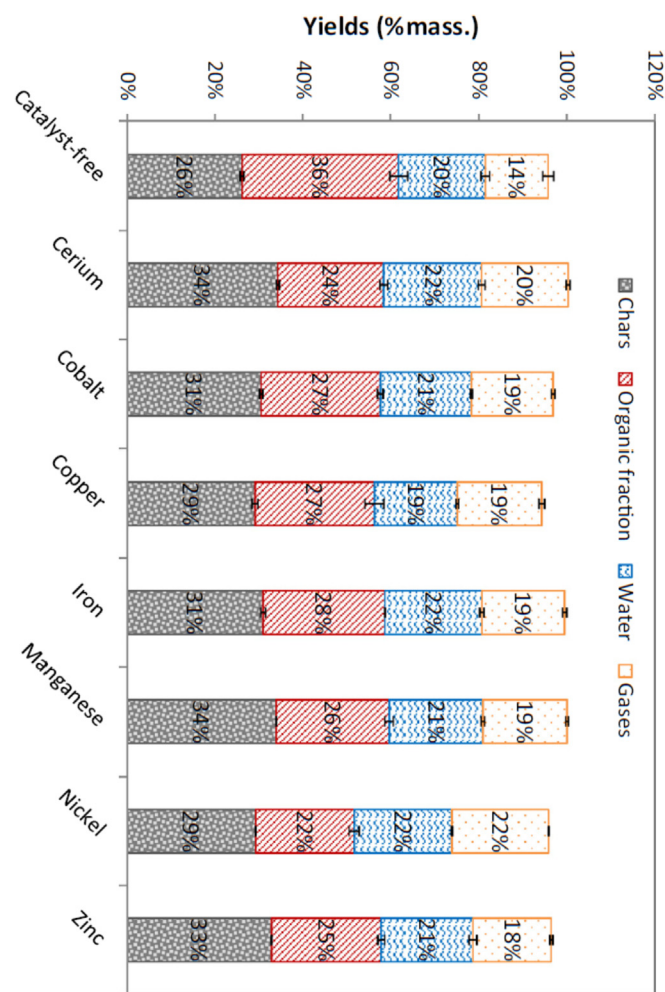


Fig. 6. Pyrolysis product distribution from eucalyptus wood for a range of metal catalysts [78].

resulting samples were fast-pyrolysed to 700 and 850 °C, but only the fixed gas emissions were monitored. Iron promoted the formation of H_2 and CO_2 , and inhibited the formation of CO and CH_4 , while Ni showed positive catalytic effects on H_2 , CO , and CO_2 and a negative effect on CH_4 . Reaction kinetics based on gas formation rates are derived. FeCl_3 on cellulose increased formation of formaldehyde and carbon oxides.

Collard et al. [82] studied the effect of $\text{Ni}(\text{NO}_3)_2$ and $\text{Fe}(\text{NO}_3)_3$ on the pyrolysis of cellulose, xylene, and lignin. The results showed that the impregnated iron catalysts caused an increase in char yield but a decrease in tar formation. In contrast, the impregnated nickel catalyst promoted the depolymerisation of amorphous xylan resulting in a 27-fold increase in furfural yield. Nickel is more effective in the formation of aromatics, contributing to the increase in hydrogen production.

A thermodynamic analysis [83] of the effect of nickel in beech subjected to high temperatures concluded that: (i) Ni has a noticeable catalytic activity even at low contents (between 0.016 and 0.086 mol per kg of wood), (ii) due to the low oxygen potential of the system $\text{C} + \text{CO}_2$, Ni stays in an active metal form as long as some carbon is left in the reactor, and (iii) Ni prevents the volatilization of sulphur during gasification, due to the formation of a stable Ni_3S_2 solid phase. These three conclusions were basically confirmed by experiment.

Lewis acids also contribute to the process of depolymerisation:

for example ZnCl_2 is a Lewis acid that catalyses heterolytic scission of C–O and C–C bonds [84,85]. Following their discussion of the mechanisms of lignocellulosic decomposition in diagrammatic detail in a previous publication [36], Lu and co-workers examined the effect of ZnCl_2 on the pyrolysis of cellulose and xylan [86]. A Py-GC/MS study of poplar wood, corncob, microcrystalline cellulose and xylan revealed that the presence of ZnCl_2 decreased the temperature for the complete decomposition of biomass. It inhibited the devolatilisation of lignin and pyrolytic ring scission of holocellulose, but promoted the depolymerisation and dehydration of holocellulose to form furfural and three anhydrosugars, LGO, LAC and DGP as the major primary products. High zinc concentrations up to 42% promoted furfural formation, but strongly suppressed the formation of other organics, to the point of extinction.

Analytical pyrolysis was also used to investigate the decomposition of pure soybean hulls, and hulls impregnated with the metal chlorides ZnCl_2 and MgCl_2 [72]. Each additive was studied at contents of 10, 20 and 30% in mass. The metals produced increases in the yield of aldehydes and reductions in acid and ester contents. The same effects were noted with rice straw [2], while these additives also improve the water-gas shift reaction to further raise the yields of H_2 and CO_2 .

The tests with corn stover mentioned in Section 2.2 [66] were extended to infuse zinc into the demineralised biomass at a high loading of 18.5%. At 345 °C, the zinc caused the yield of char to rise from 33% for the natural biomass to 47%, while the bio-oil yield fell from 47 to 42%. More water was formed. However the most significant change was found in the bio-oil product distribution, with furfural content rising from zero to 38%, LG from zero to 25% and acetic acid falling from 16 to 14%.

A program to investigate the activity of copper and aluminium adsorbed as chlorides onto cellulose was undertaken [87]. The yield of bio-oil falls with metals present, although that of LGO increases slightly. The secondary decomposition paths for cellulose are explored based on a primary product of glucopyranose. The major non-catalytic path goes through levoglucosan, with one minor route to furan-based molecules, and another to pyrans. In contrast, the major catalytic path passes to the furan groups directly and secondarily via LG.

A pyrolysis trial of pine wood in a fluidised bed with manganese as catalyst at $82 \mu\text{mol g}^{-1}$ of Mn^{2+} returned an organics yield at 400 °C of 56%, which is less than the demineralised sample, but more than raw wood value [65]. No product breakdown is given.

The use of plants for the phytoremediation of contaminated soil can produce high concentrations of heavy metals in the biomass, which is generally processed by thermal treatment. It was shown from equilibrium thermodynamics that the lead in willow at a concentration of about 135 mg kg^{-1} is mostly found under its metal form in the gaseous phase at temperatures above 800 °C, and as liquid below that [87].

4.4. Comment

Alkali metal salts catalyse charring reactions and the formation of fragmentary molecules. The role of potassium in cellulose decomposition is to favour the production of small oxygenates such as hydroxyacetaldehyde, acetol, and formic acid over levoglucosan and furans. The more electropositive cations such as lithium and potassium are more active than the alkaline earths. They act by catalysing the primary dehydration of cellulose and strongly increasing the yield of furanic and pyranic compounds from xylan.

The trends noted for slow pyrolysis [46] seem to be relevant to much higher rates of pyrolysis. Manganese, iron, nickel, cobalt and copper as chloride affect the pyrolysis of biomass components by increasing significantly the char residue, decreasing the maximum

pyrolysis temperature and changing the composition of the evolved gases, see in addition ([39,68]).

It is also concluded that ZnCl_2 is a catalyst in all pathways of cellulose degradation: dehydration, depolymerisation and ring opening, leading to light oxygenated products and CO, CO_2 formation. Apparently NiCl_2 does not contribute much to catalysis of cellulose degradation reactions. Nevertheless, both Zn and Ni catalysts favour anhydrosugar formation at the expense of formic acid, formaldehyde and general furanic derivatives.

There is evidence that cations like nickel and iron tend to be reduced to nanoparticles of the metal, and most metals are retained in the char. The pH of the anion solution associated with adsorbed metals must also be taken into consideration, as an acidic environment either suppresses the positivity of the cation, or actively catalyses the process e.g. phosphoric acid [88].

5. Conclusions

During pyrolysis cellulose, hemicellulose and lignin all pass through a fusion process, and retain most of the metals present. Pure cellulose produces relatively more bio-oil, which is dominated by the pyran levoglucosan, while lignin generates more char and aromatics. Although present in only slight concentrations in natural biomass, alkali metals can strongly influence the process of pyrolysis. Potassium, the most common naturally-present metal, is also one of the most active, as activity is generally correlated with electro-positivity. It serves to catalyse the dehydration and depolymerisation of holocellulose, tending to favour the formation of furans and aldehydes in the form of light oxygenates. Most other metals act in a similar but less effective way. Cations like nickel and iron tend to be reduced to nanoparticles of the metals mostly retained in char that makes the less active. Solid compounds of the metals such as oxides are inactive. The product molecules which result from biomass after catalytic action, being oxygenated fragments, are not favourable for upgrading to liquid fuels. As a result, biomass intended for pyrolysis to bio-oil would benefit from acid or even water washing to remove naturally-occurring mineral matter. Other targeted products such as aromatics may benefit from the application of metallic catalysts, but there is no obvious route to efficient production.

References

- [1] Tong X, Chen H, Hu J, Bi Y, Sun Z, Fan W. The efficient and sustainable pyrolysis and gasification of biomass by catalytic processes. *ChemBioEng Rev* 2015;2:157–74.
- [2] Xie YR, Shen LH, Xiao J, Xie DX, Zhu J. Influences of additives on steam gasification of biomass. 1. Pyrolysis procedure. *Energy Fuels* 2009;23:5199–205.
- [3] Zhu C, Maduskar S, Paulsen AD, Dauenhauer PJ. Alkaline-earth-metal-catalyzed thin-film pyrolysis of cellulose. *ChemCatChem* 2016;8:818–29.
- [4] Grams J, Ruppert AM. Development of heterogeneous catalysts for thermochemical conversion of lignocellulosic. *Biomass Energies* 2017;10:545–70.
- [5] Gollakota ARK, Reddy M, Subramanyam MD, Kishore N. A review on the upgradation techniques of pyrolysis oil. *Renew Sustain Energy Rev* 2016;58:1543–68.
- [6] Chen J, Sun J, Wang T. Catalysts for steam reforming of bio-oil: a review. *Ind Eng Chem Res* 2017;56:4627–37.
- [7] Aston JE, Thompson DN, Westover TL. Performance assessment of dilute-acid leaching to improve corn stover quality for thermochemical conversion. *Fuel* 2016;186:311–9.
- [8] Bradbury AGW, Sakai Y, Shafizadeh F. Kinetic model for pyrolysis of cellulose. *J Appl Polymer Sci* 1979;23:3271–80.
- [9] Saidur R, Abdelaziz EA, Demirbas A, Hossain MS, Mekhilef S. A review on biomass as a fuel for boilers. *Sustain Energy Rev* 2011;15:2262–89.
- [10] Godin B, Lamaudière S, Agneessens R, Schmit T, Goffart JP, Stilmant D, Gerin PA, Delcarte J. Chemical composition and biofuel potentials of a wide diversity of plant biomasses. *Energy Fuels* 2013;27:2588–98.
- [11] Laskar DD, Yang B, Wang H, Lee J. Pathways for biomass-derived lignin to hydrocarbon fuels. *Biofuels Bioprod Bioref* 2013;7:602–26.
- [12] Dutta S, Wu KC, Saha B. Emerging strategies for breaking the 3D amorphous network of lignin. *Catal Sci Technol* 2014;4:3785–99.

- [13] Leijenhorst EJ, Wolters W, Van de Beld L, Prins W. Inorganic element transfer from biomass to fast pyrolysis oil: review and experiments. *Fuel Proc Technol* 2016;149:96–111.
- [14] Dufour A, Castro-Díaz M, Marchal P, Brosse N, Olcese R, Bouroukba M, Snape C. In-situ analysis of biomass pyrolysis by high temperature rheology in relations with ¹H NMR. *Energy Fuels* 2012;26:6432–41.
- [15] Montoya J, Pecha B, Janna FC, Garcia-Perez M. Identification of the fractions responsible for morphology conservation in lignocellulosic pyrolysis: visualization studies of sugar cane bagasse and its pseudo-components. *J Anal Appl Pyrolysis* 2017;123:307–18.
- [16] Argyle MD, Bartholemew CH. Heterogeneous catalyst deactivation and regeneration. A review. *Catalysis* 2015;5:145–269.
- [17] Di Blasi C. Kinetic and heat transfer control in the slow and flash pyrolysis of solids. *Ind Eng Chem Res* 1996;35:37–46.
- [18] Paulsen AD, Mettler MS, Dauenhauer PJ. The role of sample dimension and temperature in cellulose pyrolysis. *Energy Fuels* 2013;27:2126–34.
- [19] Balat M. Mechanisms of thermochemical biomass conversion processes. Part 1: reactions of pyrolysis. *Energy Sources, Part A* 2008;30:620–35.
- [20] Bridgwater AV, Meier D, Radlein D. An overview of fast pyrolysis of biomass. *Organic Chemistry* 1999;30:1479–93.
- [21] Abnisa F, Ashri Wan Daud WM. A review on co-pyrolysis of biomass: an optional technique to obtain a high-grade pyrolysis oil. *Energy Conversion and Management* 2014;87:71–85.
- [22] Bridgwater T. Biomass pyrolysis. IEA Bioenergy; 2017. task 34.
- [23] Miller K. Pyroprobes. accessed September 2018, <http://www.summons.mit.edu/the-pyroprobe-how-it-works-and-what-it-can-do/>.
- [24] Shen DK, Gu S. Pyrolytic behaviour of cellulose in a fluidised bed reactor. *Cellulose Chem Technol* 2010;44:79–87.
- [25] Feroso J, Hernando H, Jiménez-Sánchez S, Lappas AA, Heracleous E, Pizarro P, Coronado JM, Serrano DP. Bio-oil production by lignocellulose fast-pyrolysis: isolating and comparing the effects of indigenous versus external catalysts. *Fuel Proc Technol* 2017;167:563–74.
- [26] Lédé J. Comparison of contact and radiant ablative pyrolysis of biomass. *J Anal Appl Pyrolysis* 2003;70:601–18.
- [27] Torri C, Reinikainen M, Lindfors C, Fabbri D, Oasma A, Kuoppala E. Investigation on catalytic pyrolysis of pine sawdust: catalyst screening by Py-GC-MIP-AED. *J Anal Appl Pyrolysis* 2010;88:7–13.
- [28] Xin S, Yang H, Chen Y, Wang X, Chen H. Assessment of pyrolysis poly-generation of biomass based on major components: product characterization and elucidation of degradation pathways. *Fuel* 2013;113:266–73.
- [29] Zhang S, Chen T, Xiong Y. Effect of washing pretreatment with aqueous fraction of bio-oil on pyrolysis characteristic of rice husk and preparation of amorphous silica. *Waste Biomass Valorization* 2018;9:861–9.
- [30] Couhert C, Commandre J-M, Salvador S. Is it possible to predict gas yields of any biomass after rapid pyrolysis at high temperature from its composition in cellulose, hemicellulose and lignin? *Fuel* 2009;88:408–17.
- [31] Park J, Riaz A, Insyani R, Kim J. Understanding the relationship between the structure and depolymerisation behavior of lignin. *Fuel* 2018;217:202–10.
- [32] Hoekstra E, Van Swaaij WPM, Kersten SRA, Hogendoorn KJA. Fast pyrolysis in a novel wire-mesh reactor: decomposition of pine wood and model compounds. *Chem Eng Journal* 2012;187:172–84.
- [33] Shen D, Xiao R, Gu S, Zhang H. The overview of thermal decomposition of cellulose in lignocellulosic biomass. <https://doi.org/10.5772/51883>.
- [34] Mamelev V, Bourbigot S, Le Bras M, Yvon J. The facts and hypotheses relating to the phenomenological model of cellulose pyrolysis. Interdependence of the steps. *J Anal Appl Pyrolysis* 2009;84:1–17.
- [35] Li S, Lyons-Hart J, Banyasz J, Shafer K. Real-time evolved gas analysis by FTIR method: an experimental study of cellulose pyrolysis. *Fuel* 2001;80:1809–17.
- [36] Lu Q, Yang X, Dong C, Zhang Z, Zhang X, Zhu X. Influence of pyrolysis temperature and time on the cellulose fast pyrolysis products: analytical Py-GC/MS study. *J Anal Appl Pyrolysis* 2011;92:430–8.
- [37] Patwardhan PR, Satrio JA, Brown RC, Shanks BH. Product distribution from fast pyrolysis of glucose-based carbohydrates. *J Anal Appl Pyrolysis* 2009;86:323–30.
- [38] Rutkowski P. Pyrolytic behavior of cellulose in presence of montmorillonite K10 as catalyst. *J Anal Appl Pyrolysis* 2012;98:115–22.
- [39] Fabbri D, Torri C, Baravelli V. Effect of zeolites and nanopowder metal oxides on the distribution of chiral anhydrosugars evolved from pyrolysis of cellulose: an analytical study. *J Anal Appl Pyrolysis* 2007;80:24–9.
- [40] Dobeles G, Rossinskaja G, Dizhbite T, Telysheva G, Meier D, Faix O. Application of catalysts for obtaining 1,6-anhydrosaccharides from cellulose and wood by fast pyrolysis. *J Anal Appl Pyrolysis* 2005;74:401–5.
- [41] Nieva ML, Volpe MA, Moyano EL. Catalytic and catalytic free process for cellulose conversion: fast pyrolysis and microwave induced pyrolysis studies. *Cellulose* 2015. 22/215–228.
- [42] Zhang J, Choi YS, Shanks BH. Catalytic deoxygenation during cellulose fast pyrolysis using acid–base bifunctional catalysis. *Catal Sci Technol* 2016;6:7468–76.
- [43] Chan FL, Umeki K, Tanksale A. Kinetic study of catalytic steam gasification of biomass by using reactive flash volatilisation. *Chem Cat Chem* 2015;7:1329–37.
- [44] Saddawi A, Jones JM, Williams A. Influence of alkali metals on the kinetics of the thermal decomposition of biomass. *Fuel Proc Technol* 2012;104:189–97.
- [45] Marforio TD, Bottoni A, Calvaresi M, Fabbri D, Giacinto P, Zerbetto F. The reaction pathway of cellulose pyrolysis to a multifunctional chiral building block: the role of water unveiled by a DFT computational investigation. *Chem Phys Chem* 2016;17:3948–53.
- [46] Di Blasi C. Modeling chemical and physical processes of wood and biomass pyrolysis. *Prog Energy Comb Sci* 2008;34:37–46.
- [47] Khelifa A, Bensakhri A, Weber JV. Investigations into the pyrolytic behaviour of birch wood and its main components: primary degradation mechanisms, additivity and metallic salt effects. *J Anal Appl Pyrolysis* 2013;101:111–21.
- [48] Cheng F, Brewer CE. Producing jet fuel from biomass lignin: potential pathways to alkylbenzenes and cycloalkanes. *Renew Sustain Energy Reviews* 2017;72:673–722.
- [49] Dalluge DL, Kim KH, Brown RC. The influence of alkali and alkaline earth metals on char and volatile aromatics from fast pyrolysis of lignin. *J Anal Appl Pyrolysis* 2017;127:385–93.
- [50] Amen-Chen C, Pakdel H, Roy C. Production of monomeric phenols by thermochemical conversion of biomass: a review. *Biores Technol* 2001;79:277–99.
- [51] Fan L, Zhang Y, Liu S, Zhou N, Chen P, Cheng Y, Addy M, Lu Q, Omar MM, Liu Y, Wang Y, Dai L, Anderson E, Peng P, Lei H, Ruan R. Bio-oil from fast pyrolysis of lignin: effects of process and upgrading parameters. *Biores Technol* 2017;241:1118–26.
- [52] Brebu M, Vasile C. Thermal degradation of lignin – a review. *Cellulose Chem Technol* 2010;44:353–63.
- [53] Mullen CA, Boateng AA. Catalytic pyrolysis-GC/MS of lignin from several sources. *Fuel Proc Technol* 2010;91:1446–58.
- [54] Kibet J, Khachatryan L, Dellinger B. Molecular products and radicals from pyrolysis of lignin. *Environ Sci Technol* 2012;46:12994–3001.
- [55] Nowakowski DJ, Jones JM, Brydson RMD, Ross AB. Potassium catalysis in the pyrolysis behaviour of short rotation willow coppice. *Fuel* 2007;86:2389–402.
- [56] Yang H, Yan R, Chen H, Zheng C, Lee DH, Liang DT. In-depth investigation of biomass pyrolysis based on three major components: hemicellulose, cellulose and lignin. *Energy Fuels* 2006;20:388–93.
- [57] Haddad K, Jeguirim M, Jellali S, Guizani C, Delmotte L, Bennici S, Limousy L. Combined NMR structural characterization and thermogravimetric analyses for the assessment of the AAEM effect during lignocellulosic biomass pyrolysis. *Energy* 2017;134:10–23.
- [58] Jiang L, Hua S, Sun L, Su S, Xu K, He L, Xiang J. Influence of different demineralization treatments on physicochemical structure and thermal degradation of biomass. *Biores Technol* 2013;146:254–60.
- [59] Aslam U, Ramzan N, Iqbal T, Kazmi M, Ikhlaf A. Effect of demineralization on the physicochemical structure and thermal degradation of acid treated indigenous rice husk. *Polish J Chem Tech* 2016;18:117–21.
- [60] Asadieraghi M, Daud WMAW. Characterization of lignocellulosic biomass thermal degradation and physicochemical structure: effects of demineralization by diverse acid solutions. *Energy Conv Manage* 2014;82:71–82.
- [61] Rodríguez-Machin L, Arteaga-Pérez LE, Pérez-Bermúdez RA, Casas-Ledón Y, Prins W, Ronsse F. Effect of citric acid leaching on the demineralization and thermal degradation behavior of sugarcane trash and bagasse. *Biomass Bioenergy* 2018;108:371–80.
- [62] Mayer ZA, Apfelbacher A, Hornung A. Effect of sample preparation on the thermal degradation of metal-added biomass. *J Anal Appl Pyrolysis* 2012;94:170–6.
- [63] Reza MT, Emerson R, Uddin MH, Gresham G, Coronella CJ. Ash reduction of corn stover by mild hydrothermal preprocessing. *Biomass Conv Bioref* 2015;5:21–31.
- [64] Richards GN, Zheng G. Influence of metal ions and of salts on products from pyrolysis of wood: applications to thermochemical processing of newsprint and biomass. *J Anal Appl Pyrolysis* 1991;2:133–46.
- [65] Aho A, DeMartini N, Pranovich A, Krogell J, Kumar N, Eränen K, Holmbom B, Salmi T, Hupa M, Murzin DY. Pyrolysis of pine and gasification of pine chars – influence of organically bound metals. *Biores Technol* 2013;128:22–9.
- [66] Oh S-J, Choi G-G, Kim J-S. Fast pyrolysis of corn stover using ZnCl₂: effect of washing treatment on the furfural yield and solvent extraction of furfural. *Energy* 2015;88:697–702.
- [67] Kuzhiyil N, Dalluge D, Bai X, Kim KH, Brown RC. Pyrolytic sugars from cellulose biomass. *Chem Sus Chem* 2012;5:2228–36.
- [68] Zhang Y, Liu C. A new horizon on effects of alkalis metal ions during biomass pyrolysis based on density function theory study. *J Anal Appl Pyrolysis* 2014;110:297–304.
- [69] Mullen CA, Boateng AA. Accumulation of inorganic impurities on HZSM-5 zeolites during catalytic fast pyrolysis of switchgrass. *IEC Res* 2013;52:17156–61.
- [70] Guo F, Liu Y, Wang Y, Li X, Li T, Guo C. Pyrolysis kinetics and behaviour of potassium-impregnated pine wood in TGA and a fixed-bed reactor. *Energy Conv Manage* 2016;130:184–91.
- [71] Mahadevan R, Adhikari S, Shakya R, Wang K, Dayton D, Lechrich M, Taylor ME. Effect of alkali and alkaline earth metals on in-situ catalytic fast pyrolysis of lignocellulosic biomass: a microreactor study. *Energy Fuels* 2016;3:3045–56.
- [72] Santana JA, Sousa NG, Cardoso CR, Carvalho WS, Ataíde CH. Sodium, zinc and magnesium chlorides as additives for soybean hulls pyrolysis: influence on the temperature range of reactions and product selectivity. *J Therm Anal Calorim* 2016;125:471–81.
- [73] Zou J, Yang H, Zeng Z, Wu C, Williams PT, Chen H. Hydrogen production from pyrolysis catalytic reforming of cellulose in the presence of K alkali metal. *Int J Hydrogen Energy* 2016;41:10598–607.
- [74] Jiang L, Hu S, Xiang J, Su S, Sun L, Xu K, Yao Y. Release characteristics of alkali

- and alkaline earth metallic species during biomass pyrolysis and steam gasification process. *Biores Technol* 2012;116:278–84.
- [75] Chen J, Sun J, Wang Y. Catalysts for steam reforming of bio-oil: a review. *Ind Eng Chem Res* 2017;56:4627–37.
- [76] Syed-Hassan SSA, Nor-Azemi SNI, Fuadi FA. Adsorption and dispersion of nickel on oil palm mesocarp fiber. *Chem Eng Trans* 2014;37:709–14.
- [77] Richardson Y, Blin J, Volle G, Motuzas J, Julbe A. In situ generation of Ni metal nanoparticles as catalyst for H₂-rich syngas production from biomass gasification. *Appl Catal A: General* 2010;382:220–30.
- [78] Richardson Y, Tanoh ST, Julbe A, Blin J. Improving the kinetics of the CO₂ gasification of char through the catalyst/biomass integration concept. *Fuel* 2015;154:217–21.
- [79] Eibner S, Broust F, Blin J, Julbe A. Catalytic effect of metal nitrate salts during pyrolysis of impregnated biomass. *J Anal Appl Pyrolysis* 2015;113:143–52.
- [80] Tsodikov MV, Ellert OG, Nikolaev SA, Arapova OV, Konstantinov GI, Bukhtenko OV, Vasil'kov AY. The role of nanosized nickel particles in microwave-assisted dry reforming of lignin. *Chem Eng Journal* 2017;309:628–37.
- [81] Liu Y, Guo F, Li X, Li T, Peng K, Guo C, Chang J. Catalytic effect of iron and nickel on gas formation from fast biomass pyrolysis in a microfluidized bed reactor: a kinetic study. *Energy Fuels* 2017;31:12278–87.
- [82] Collard F-X, Bensakhri A, Drobek M, Volle G, Blin J. Influence of impregnated iron and nickel on the pyrolysis of cellulose. *Biomass bioenergy* 2015;80:52–62.
- [83] Said M, Cassayre L, Dirion JL, Nzihou A, Joulia X. Influence of nickel on biomass pyro-gasification: coupled thermodynamic and experimental investigations. *Ind Eng Chem* 2018;57(30):9788–97.
- [84] Di Blasi C, Branca C, Galgano A. Products and global weight loss rates of wood decomposition catalyzed by zinc chloride. *Energy & Fuels* 2008;22:663–70.
- [85] Lu Q, Dong C, Zhang X, Tian H, Yang Y, Zhu X. Selective fast pyrolysis of biomass impregnated with ZnCl₂ to produce furfural: analytical Py-GC/MS study. *J Anal Appl Pyrolysis* 2011;90:204–12.
- [86] Rutkowski P. Catalytic effects of copper(II) chloride and aluminium chloride on the pyrolytic behaviour of cellulose. *J Anal Appl Pyrolysis* 2012;98:86–97.
- [87] Said M, Cassayre L, Dirion JL, Nzihou A, Joulia X. Behaviour of heavy metals during gasification of phytoextraction plants: thermochemical modelling. *Computer Aided Chem Eng* 2015;37:341–6.
- [88] Dobele G, Rossinskaja G, Telysheva G, Meier D, Faix O. Cellulose dehydration and depolymerization reactions during pyrolysis in the presence of phosphoric acid. *J Anal Appl Pyrolysis* 1999;49:307–17.