Pyrolysis of biomass to produce fuels and chemical feedstocks

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Abstract

This review presents the summary of new studies on pyrolysis of biomass to produce fuels and chemical feedstocks. A number of biomass species, varying from woody and herbaceous biomass to municipal solid waste, food processing residues and industrial wastes, were subjected to different pyrolysis conditions to obtain liquid, gas and solid products. The results of various biomass pyrolysis investigations connected with the chemical composition and some properties of the pyrolysis products as a result of the applied pyrolysis conditions were combined. The characteristics of the liquid products from pyrolysis were examined, and some methods, such as catalytic upgrading or steam reforming, were considered to improve the physical and chemical properties of the liquids to convert them to economic and environmentally acceptable liquid fuels or chemical feedstocks. Outcomes from the kinetic studies performed by applying thermogravimetric analysis were also presented.
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1. What is biomass?

Biomass can generally be defined as any hydrocarbon material which mainly consists of carbon, hydrogen, oxygen and nitrogen. Sulfur is also present in less proportions. Some biomass types also carry significant proportions of inorganic species. The concentration of the ash arising from these inorganics changes from less than 1% in softwoods to 15% in herbaceous biomass and agricultural residues.

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Biomass resources include various natural and derived materials, such as woody and herbaceous species, wood wastes, bagasse, agricultural and industrial residues, waste paper, municipal solid waste, sawdust, biosolids, grass, waste from food processing, animal wastes, aquatic plants and algae etc.

Direct combustion of biomass to take advantage of its heating value has been known for ages, but direct combustion of biomass is not favored any more because it has too high content of moisture to perform stable combustion. Thus, it has highly changeable combustion rates. On the other hand, the density for many kinds of biomass is lower than that of coal, leading to important economic limitations in transportation. In order to overcome these problems, briquetting of low density biomass species before combustion has been considered. Furthermore, it is also possible to blend biomass with coal in various proportions and then produce coal-biomass briquettes.

The total volatile matter content of the briquettes (biobriquette) is proportional to its biomass content. Biomass in the biobriquette makes ignitability easy and increases the burning rate of low grade coals. In general, combustion proceeds in two stages in which the volatile matter mainly evolved and burned to lead the fixed carbon combustion. From this point of view, biomass acts as a promoter in combustion [1].

Both the mechanical strength and combustion characteristics of the biobriquettes closely depend on the briquetting conditions. In order to obtain mechanically strong briquettes, the briquetting pressure and the time applied during the operation must be adjusted properly. Under pressures below an optimum value, firm briquettes cannot be obtained. However, application of excessively high pressures also causes negative effects on the mechanical strength [2,3]. In the combustion of the biobriquettes having very high mechanical strength, another undesirable case happens during combustion due to the limited diffusion of oxygen into the very compact structures.

Other common methods applied to biomass to make use of its energy potential are biochemical and thermochemical conversion methods. Well known biochemical methods are the biochemical liquefaction and microbial gasification processes.

Biochemical conversion methods are based on the conversion of biomass into alcohols or oxygenated products by biological activity. Thermochemical processes involve the pyrolysis, liquefaction, gasification and supercritical fluid extraction methods. The products of the thermochemical processes are divided into a volatile fraction consisting of gases, vapours and tar components and a carbon rich solid residue. The pyrolysis process consists of a very complex set of reactions involving the formation of radicals. The gasification of biomass is a thermal treatment, which results in a high proportion of gaseous products and small quantities of char (solid product) and ash [4]. If the purpose is to maximize the liquid product yield, process conditions are selected as low temperature, high heating rate and short gas residence time. For high char yield, low temperature and low heating rate are required. In order to produce high yield of gas product, high temperature, low heating rate and long gas residence time should be applied [5].

Heating values of the chars obtained from pyrolysis are comparable with those of lignite and coke, and the heating values of liquids are comparable with those of oxygenated fuels, such as CH_3OH and C_2H_5OH, which are much lower than those of petroleum fuels. The heating value of gases is comparable with those of producer gas or coal gas and is much lower than that of natural gas. The heating values of the products are functions of the initial composition of the biomass [6].

Apart from the usage as fuel, the products of thermochemical processes can be used in particular fields. For instance, the char obtained from pyrolysis usually has a porous structure and a surface area that is appropriate to use as active carbon. The liquids obtained from pyrolysis contain many chemical compounds that can be used as feedstock for synthesis of fine chemicals, adhesives, fertilizers etc. [7].

2. The chemical structure and the major components of biomass

The chemical structure and major organic components in biomass are extremely important in the development of processes for producing derived fuels and chemicals. The major organic components of biomass can be classified as cellulose, hemicellulose and lignin. Alpha cellulose is a polysaccharide having the general formula $(C_6H_{10}O_5)_n$ and an average molecular weight range of 300,000–500,000. Cotton is almost pure α-cellulose, whereas wood cellulose, the raw material for the pulp and paper industry, always occurs in association with hemicellulose and lignins. Cellulose is insoluble in water, forms the skeletal structure of most terrestrial biomass and constitutes approximately 50% of the cell wall material. Starches are polysaccharides that have the general formula $(C_6H_{10}O_5)_n$. They are reserve sources of carbohydrate in some biomass and are also made up of some D-glucose units [8].

Hemicelluloses are complex polysaccharides that take place in association with cellulose in the cell wall, but unlike cellulose, hemicelluloses are soluble in dilute alkali and consist of branched structures, which vary considerably among different woody and herbaceous biomass species. Many of them have the general formula $(C_5H_8O_4)_n$. Hemicelluloses usually carry 50–200 monomeric units and a few simple sugar residues. The most abundant one is xylan. The xylans exist in softwoods and hardwoods up to about 10% and 30% of the dry weight of the species, respectively [8].

The lignins are highly branched, substituted, mononuclear aromatic polymers in the cell walls of certain biomass, especially woody species, and are often bound to adjacent cellulose fibers to form a lignocellulosic complex. This complex and the lignins alone are often quite resistant to conversion by microbial systems and many chemical agents. The complex can be broken, and the lignin fraction separated, however, by treatment with strong sulfuric acid, in which the lignins are insoluble. The lignin contents on a dry basis in both softwoods and hardwoods generally range from 20% to 40% by weight and from 10% to 40% by weight in various herbaceous species, such as bagasse, corncobs, peanut shells, rice hulls and straws [8].

3. Outlines of biomass pyrolysis

Pyrolysis of biomass can be described as the direct thermal decomposition of the organic matrix in the absence of oxygen to obtain an array of solid, liquid and gas products. The pyrolysis method has been used for commercial production of a wide range of fuels, solvents, chemicals and other products from biomass feedstocks. Conventional pyrolysis consists of the slow, irreversible, thermal decomposition of the organic components in biomass. Slow pyrolysis has traditionally been used for the production of charcoal. Short residence time pyrolysis (fast, flash, rapid,

ultrapyrolysis) of biomass at moderate temperatures has generally been used to obtain high yield of liquid products. Fast pyrolysis is characterized by high heating rates and rapid quenching of the liquid products to terminate the secondary conversion of the products [8].

Depending on the pyrolysis temperature, the char fraction contains inorganic materials ashed to varying degrees, any unconverted organic solid and carbonaceous residues produced from thermal decomposition of the organic components. The liquid fraction is a complex mixture of water and organic chemicals. For highly cellulosic biomass feedstocks, the liquid fraction usually contains acids, alcohols, aldehydes, ketones, esters, heterocyclic derivatives and phenolic compounds [8]. The pyrolysis liquids are complex mixtures of oxygenated aliphatic and aromatic compounds [7]. The tars contain native resins, intermediate carbohydrates, phenols, aromatics, aldehydes, their condensation products and other derivatives. Pyroligneous acids can consist of 50% CH_3OH, C_3H_6O (acetone), phenols and water. CH_3OH can be produced by pyrolysis of biomass. CH_3OH arises from the methoxyl groups of uronic acid and from the breakdown of methyl esters and/or ethers from decomposition of pectin-like plant materials. Acetic acid comes from the acetyl groups of hemicelluloses [9]. The pyrolysis gas mainly contains CO_2, CO, CH_4, H_2, C_2H_6, C_2H_4, minor amounts of higher gaseous organics and water vapour [8].

In a pyrolysis study performed using bagasse bulk, the yields of condensable matter and gas composition were examined. It was determined that their combined heat of combustion exceeds the upper limit of the heat necessary to carbonise the biomass by 1.6–1.8 times [10].

Primary decomposition of biomass material (<400 °C) consists of a degradation process, whereas the secondary thermolysis (>400 °C) involves an aromatization process [11].

4. Effect of the pyrolysis conditions on the properties of the products

Many kinds of biomass species have been subjected to pyrolysis conditions. Some of these biomass species are as follows: Acacia wood [12], agricultural residues [13–15], almond shell [16–19], apple pulp [20,21], apricot stones [17], Arbutus Unedo (wet biomass) [22], Argentinean hardwood species [23], ash free cellulose [24], Aspidosperma Australe [23], Aspidosperma Quebracho Blanco Schlecht [23], Austrian pine [25], automobile shredder residue (ASR) [26], bagasse [10,12,27,28], bales [29], beech wood [30], birch bark [31], birch sapwood [31], birch wood [28], black liquor [32,33], cellulose [34,35], cherry stones [17], chip piles [29], chlorogenic acid (biomass model comp.) [36], coir pith. [37], corn stover [29], corn–potato starch gel [38], corn stalk [39,40], cotton cocoon shell [41–43], cotton gin wastes [44], cotton stalk [45], cotton straw [45], cottonseed cake [46,47], *Cynara cardunculus* L. [48], D-glucose (biomass model comp.) [36], eucalyptus wood [49], *Euphorbia rigida* [50–52], extracted oil palm fibers [53], filter pulp [54], forest wood [55], grape [56], grape residue [13], grape seeds [17], grass [57], ground nut shell [37], hardwoods (beech, chestnut) [58,59], hazelnut (*Corylus avellans*) shells [50,60–65], herbaceous feedstocks [29], herbaceous residues [15], hybrid poplar [29], Italian sweet sorghum [57], kraft lignin [66], lignin (biomass model comp.) [35], Lodgepole pine [25], lucerne [67], maize [56], Miscanthus pellet [28], mixed wood waste [68,69], municipal solid waste [70–73], natural rubber [74], Norway spruce [25], nut shells [17], oil palm shell [75], old furniture [55], olive husk [13,42,63,76–78], olive stone [16,18,28,79], petroleum residue [80], pine [25,58,82], pine sawdust [81], pinus insignis sawdust [83,84], Ponderosa pine [25], poplar oil [85], pulp black [39], rape plant [86], rape seed [87–91],

rice husks [12,13,37,63,92–98], safflower seed [99], sawdust [16,38,100–102], Scotch pine [25], sewage sludge [12], silver birch [103], sitka spruce [25], soft woods (Douglas fir, redwood, pine) [59], soft wood bark residue [104], spruce [25], stalk of rape seed plant [105], straw [16,58,105,106], straw pellet [28], straw rape [67], straw stalk [86], sugar cane bagasse [49,67,80,103,107,108], sun flower (*Helianthus annulus* L.) pressed bagasse [50,51,56,109], sun flower press oil cake [110], sun flower oil [111], sweet sorghum bagasse [57], swine manure [112], switch grass [67,29], synthetic biomass [37], tea waste [42,113], tobacco [36,56,114], tobacco dust [115], used pallets [55], waste paper [60], waste wood chips [116], wheat straw [13,36,40,60,117,118], white birch wood [54], white spruce [25], wood [14,37,60,63,119–123], wood chips [13,98], wood cylinders [59], wood waste [124], and xylan (biomass model comp.) [35,36].

Fixed bed hydropyrolysis (pyrolysis in the presence of H_2) has been performed on cellulose, sugar cane bagasse and eucalyptus wood using H_2 pressures up to 10 MPa. A colloidal FeS catalyst was used to increase overall conversion. Increasing the H_2 pressure to 10 MPa reduced the O_2 content of the primary oil by over 10–20% w/w. The addition of a dispersed iron sulfide catalyst gave conversions close to 100% for all three biomass samples at 10 MPa. Although NMR indicated that the oils became increasingly aromatic as more oxygen was removed, the increase in H_2 pressure decreased the extent of overall aromatisation that occurs primarily due to the lower char yields obtained [49].

In a study, biomass in the form of oil palm shell was pyrolyzed in a fluidised bed with N_2. The liquid products obtained were highly oxygenated, containing a high fraction of phenol based compounds, but there was no concentration of biologically active polycyclic aromatic hydrocarbons (PAH) in the oil [75].

Pine and spruce samples were pyrolyzed at 550 °C. The pyrolysis products were analyzed using GC methods. The results of this study designated that large amounts of oxygenated organic compounds, such as aldehydes, acids, ketones and metoxylated phenols, were detected. The pine species produced less metoxylated phenols than the spruce species [25].

According to an investigation performing the pyrolysis of mixed wood waste in a fluidised bed reactor at 400–550 °C, the liquid products were homogenous, of low viscosity and highly oxygenated. The gases evolved were CO_2, CO and C_1–C_4 hydrocarbons. Chemical fractionation of the liquids showed that only low concentrations of hydrocarbons were present, and the oxygenated and polar fractions were dominant. The liquids contained considerable quantities of phenolic compounds, and the yield of phenol and its alkylated derivatives was highest at 500 and 550 °C [69].

Tar formation was investigated as a function of temperature during pyrolysis of wood in a free fall reactor operated at near atmospheric pressure. The yields of total tar and phenolic compounds were decreased, whereas aromatic compounds were increased with increasing temperature between 700 and 900 °C [120].

It was reported that tobacco was pyrolyzed in both oxidative and inert atmospheres at atmospheric pressure and temperatures ranging from 150 to 750 °C. NMR analysis results indicated important changes in pectin and sugar constituents of the tobacco and breaking of glycosidic bonds of cellulose at 300–500 °C before the char became predominantly aromatic at high temperatures. Fourier transform infrared spectra (FTIR) analysis results showed a continuous decrease in the intensity of the –OH stretching bonds with increasing temperature and the aromatic character to be at maximum at 550 °C. The H/C ratio of the char decreased with temperature

while the O/C ratio became constant above 300 °C due to the presence of oxide and carbonates in the char [114].

In an investigation, wood powder was pyrolized in a circulating fluidised bed (CFB). It was concluded that the lower heating rate favored carbonization and also reduced the yield of liquid products. Most compounds in bio-oil were non-hydrocarbons and alkanes–aromatics and asphalt were relatively low [101].

Rape seed grains were pyrolized in a fluidised bed reactor. At reactor temperatures of 500 and 600 °C, the presence of fatty acids and fatty acid derivatives was detected, accompanied by aliphatic gases and fluids. At a higher temperature (700 °C), gases were the main products; aromatic oil was obtained and no fatty acids were present [91].

In a study, a two stages fixed bed (hot rod) pyrolysis system was used in the pyrolysis of biomass. Total volatile and tar/oil yields decreased and structural changes took place with increasing sample bed height and pressure, leading to lighter tars/oils. It was observed that the products became more aromatic and less oxygenated [125].

Catalytic pyrolysis of wood chips and rice shell was performed by using a powder-particle fluidised bed (PPFB). This study showed that in the primary pyrolysis of wood chips, the volatile matter content above a temperature of 427 °C mainly consisted of light aromatic hydrocarbons, i.e. C_6H_6 (benzene), C_7H_8 (toluene), $C_{24}H_{30}$ (xylene) and $C_{10}H_8$ (naphtalene), increasing with increasing pyrolysis temperature [98].

Pyrolysis of the samples of sugar cane trash, switch grass, lucerne and straw rape were performed under a N_2 atmosphere, and the Cl_2 content of the residue was measured. Results indicated that 20–50% of the total Cl_2 evaporated at 400 °C, although the majority of the Cl_2 was water soluble and, therefore, most probably ionic species. At 900 °C, 30–60% of the Cl_2 was still left in the char [67].

It is reported that one step and stepwise vacuum pyrolysis of a mixture of birch bark and birch sapwood was performed up to 550 °C. The pyrolysis oil (defined as the total condensates, including water and organics) was analyzed by a gas chromatography–mass spectroscopy (GC–MS) technique, and the quantity of phenols (monolignols) was determined as a function of temperature. The active zone of decomposition and the maximum recovery of phenols were found to be at 275–350 °C [31].

Corn and potato starch gels, wood sawdust suspended in a corn starch gel and potato wastes were treated at temperatures above 650 °C and at pressures above the critical pressure of water (22 MPa). It was determined that the organic content of these feedstocks vaporized under these conditions. A packed bed of carbon within the reactor catalyzed the gasification of these organic vapours in the water. Consequently, the water effluent of the reactor was clean. The gas was composed of H_2, CO, CO_2, CH_4 and traces of C_2H_6. Its composition was influenced by the peak temperature of the reactor and the condition of the reactor wall [38].

Conversion of polymers and biomass to chemical intermediates and monomers by using subcritical and supercritical water was investigated. Reactions of cellulose in supercritical water are rapid and proceed to absolute conversion with no char formation. A significant increase in the yields of hydrolysis products and lower pyrolysis products were observed when compared with reactions in subcritical water. There is an augmentation in the reaction rate of cellulose at the critical temperature of water [126].

The radiant flash pyrolysis method was also reported to apply to biomass. Samples were exposed to brief flashes of a concentrated radiation at the focus of an image furnace operating with a 5 kW xenon lamp associated to elliptical mirrors. The microscopic observations of the sample after the flash indicated the presence of short life time liquid species formed for flash durations lower then 1 s. These products, which are liquid in pyrolysis conditions, were solid at room temperature, and they were soluble in water. For longer flashes, they gave rise to vapours escaping in the gas phase, while practically no char was formed [127].

Three different chemical sewage sludges were treated using a primary pyrolyzer at 700 °C and a secondary reactor operating at 290–650 °C temperatures. CH_4, C_2H_4, C_3H_6, C_3H_8, CH_3OH, $C_2H_4O_2$ (acetic acid), C_2H_4O (acetaldehyde), C_4-hydrocarbons, CO, CO_2 and H_2O were designated as pyrolysis products. It was concluded that this technique allowed the liquid formed in primary pyrolysis to be transformed almost completely into light gases that do not cause important environmental problems. Only about 1–2% of the liquids remained without cracking. The gases formed were mostly CO, CO_2 and water vapour [128].

In an investigation, the thermally induced interrelation between total tar, chemical distribution of principal tar constituents and the three C_2 compounds (ethane, ethene, ethylene) obtained from wood pyrolysis at atmospheric pressure in a continuous bench scale fixed bed reactor was investigated. Total tar and certain tar constituents were determined to exhibit a close correlation with the C_2 compounds over the temperature range 700–900 °C [123].

Application of the fluidised bed system in the study of the formation of gases from municipal solid waste (MSW) pyrolysis at high nominal temperatures (700–850 °C) was researched. Biomass decomposition followed by tar cracking reactions took place inside the reactor. The yields of the gases formed were determined as CH_4, C_2H_6, C_2H_4, C_3H_8, C_3H_6, C_2H_2, C_4H_8, H_2, CO and CO_2 as a function of operation conditions [71].

Another study aimed to convert ASR into chemical products at temperatures between 700 and 850 °C for 0.3–1.4 s residence times by means of fast pyrolysis (ultrapyrolysis) process. It was found that no measurable amounts of liquid pyrolysis oils were produced. The most abundant pyrolysis gases were CO, CO_2, CH_4, C_2H_4 and C_3H_6. The use of a higher organic content ASR feed resulted in less solid residue and more pyrolysis gas. However, no significant changes were noted in the composition of the pyrolysis gases [26].

The primary degradation kinetics of wheat straw and corn stalks were studied by exposing samples to radiative heating under isothermal conditions. The samples were heated at the range 25–70 °C/s. Time–weight loss curves were determined for reaction temperatures between 127 and 375 °C. These curves, for both samples were well interpreted by a two stage mechanism, which takes into account the formation of a solid intermediate and volatiles, followed by further degradation of the intermediate to char and volatiles. For all temperatures, the first stage, where most of the volatiles were released, was about 10 times faster than the second stage [40].

To investigate the first steps of biomass flash pyrolysis, the image furnace technology was applied. The experiments performed using small pellets of cellulose revealed that the reaction primarily passed through the intermediate of short lifetime liquid species (ILC). The quantitative study of the variations of the sample mass loss and of the mass of ILC indicated the existence of a transient period followed by a steady state regime resulting from an equilibrium between cellulose decomposition into ILC and ILC vaporization [34].

The subject of an investigation was to test the simultaneous pyrolysis and gasification of wastes from birch wood, olive stones, bagasse, pellets from straw and miscanthus in a flow of steam or in a mixture of steam and CO_2. This study showed that the oxygen containing functional groups in the solid product were $-COOH$, $=CO$ and $-OH$ [28].

Thermal degradation of sugar cane bagasse was studied between 200 and 800 °C under N_2 gas flow. The effects of temperature, time and heating rate were investigated. The solid residues obtained were then analyzed by elemental analysis and FTIR. The most significant structure modifications appeared between 300 and 400 °C, and they are characterized by the decrease of intensities of the C–O and C=C bonds and the formation of alkyl bonds. The thermal degradation of bagasse is marked by dehydration and the formation of CO and CO_2 molecules. The carbonization is characterized by the disappearance of chemical bonds and the formation of low molecular weight compounds, leading to a char consisting essentially of carbon, hydrogen and mineral oxides [108].

A wire mesh reactor with the capability of eliminating secondary reactions was used in the pyrolysis and hydropyrolysis of sugar cane bagasse at 600 °C up to 70 bar. Structural properties of the bio-oils were examined by size exclusion chromatography and FTIR. The effect of increasing pressure was determined to reduce the bio-oil and total volatile yields. Hydropyrolysis bio-oil yields were higher than pyrolysis yields under equivalent conditions [107].

Reactive gases were tested during the pyrolysis of biomass. Conversions observed during pyrolysis in a He atmosphere were compared directly with gasification in H_2, CO_2 and steam–He mixtures under between 1–20 bar in a fixed bed "hot rod" reactor with heating at 10 °C/s [129].

Thermal decomposition of cellulose in a reactive H_2 atmosphere and in pure argon was studied. It was determined that compared with the yields obtained in pure argon, the CH_4 yield decreased by a factor of 2 in H_2, and the CO yield decreased similarly to 30–35% in H_2 [130].

Thick wood cylinders were pyrolized with applied radiation intensities of 28–80 kW/m^2 to investigate the effect of wood variety on the degradation characteristics (temperature and weight loss dynamics), product (char, gas, liquid) yields and gas composition. Two hardwoods (beech, chestnut) and three softwoods (Douglas fir, redwood, and pine) were used in the experiments. Apart from the higher minimum heat flux needed for softwood pyrolysis, all the varieties presented the similar behavior, and the process dynamics tended to become the same for applied heat fluxes above 40 kW/m^2, when internal heat transfer was the controlling mechanism. However, the qualitative differences remained large in terms of pyrolysis temperature and product yields [59].

The effects of some properties (density, thermal conductivity, permeability to gas flow, specific heat capacity) of the feedstocks on the convective-radiant pyrolysis of cellulosic fuels were investigated. For conversion in a thermally thick regime (intra-particle heat transfer control), it was concluded that variations in the physical properties mainly affected the activity of the secondary reactions of tar vapours and the conversion time. The highest sensitivity was associated with the biomass density and the char thermal conductivity. Physical properties weakly affected only the conversion time in the thermally thin regime (external heat transfer control) [131].

A chain growth model for heterogeneous secondary reaction was developed for the pyrolysis of large wood particles, and the parameters were determined by non-linear optimization. The model takes both the volatiles retention time and the cracking and repolymerization reactions of the vapours with the decomposed solid, as well as autocatalysis, into consideration. The extent of the secondary reaction was strongly influenced by the time and the ratio of the autocatalytic

(propagation) reaction rate to the non-catalytic (initiation) reaction rate. The wood, which has a higher value of the autocatalytic/non-catalytic ratio, also has a higher exothermic heat of reaction and yields a higher amount of final char residue. This fact confirms that the heterogeneous secondary reaction leads to carbon enrichment of the final residue and is accompanied by an exothermic heat of reaction [122].

Biomass fast pyrolysis reactions consist of primary activation and fragmentation reactions, followed by secondary vapour phase cracking reactions. The primary reaction rates exceed those of the secondary reaction by several orders of magnitude [132].

According to an investigation, the product distribution from straw and washed straw pyrolysis showed temperature (387–717 °C) dependence, but the pretreatments made the initial degradation temperature slightly higher and gave rise to larger yields of condensable products. Water washings also affected the decomposition of straw in air. Devolatilization again took place at higher temperatures and with a higher peak rate, but the char combustion reactions were lower. Hot water washing of large (0.5–1 mm) straw char particles was less effective for ash removal than straw washing, independently of the temperature and the atmosphere where chars were formed [106].

Thermal degradation of white birch wood and filter pulp was tested in water and methanol vapour at 2 MPa pressure in a flow through reactor. Char yields in methanol were similar to those in an inert gas atmosphere. However, the presence of water significantly increased the amount of char produced. The product distribution of cellulose was strongly affected by the solvents. In methanol, pyran derivatives dominate besides levoglucosan and glycolaldehyde, whereas the relative abundance of 2-furaldehyde and 5-(hydroxymethyl)-2-furaldehyde increased in the presence of water. Water catalysis was also indicated by lowering the decomposition temperature of the cellulose [54].

5. Characteristics of liquid products

Biomass pyrolysis oils have a potential to be used as a fuel oil substitute. Combustion tests indicate that these oils burn effectively in standard or slightly modified boilers and engines with rates similar to those for commercial fuels. The oils have heating values of only 40–50% of that for hydrocarbon fuels. However, some problems occur in the combustion systems when these liquids are burned without upgrading. They have very high water content that is detrimental for ignition. Moreover, organic acids in the oils are highly corrosive to common construction materials. Solids (char) in the liquids can block injectors or erode turbine blades. Besides, over time, the reactivity of some components in the oils leads to formation of larger molecules that result in high viscosity and in slower combustion [133].

To investigate ignition delay and combustion behavior, experiments with two pyrolysis oils and No. 2 Diesel fuel were performed in a direct injection Diesel engine. The thermal efficiencies of both pyrolysis oils were similar to that of the Diesel fuel. On the other hand, they exhibited excessive ignition delays and required a moderate degree of combustion air preheating to ignite reliably [134].

A procedure was suggested to convert biomass flash pyrolysis liquids (BFPLs) to transportation fuels based on hydrotreatment of a BFPL, both in a thermal and in a catalytic mode. The

liquid product of this process can not be used in the refinery without further upgrading. However, its heavy fraction, mixed with an aromatic hydrocarbonaceous feedstock (LCO) was considered as a potential FCC feedstock. The direct introduction of BFPLs in the FCC process was, so far, infeasible because of their particularly high tendency to coke formation [135].

In order to stabilize pyrolysis oils, a two step processing was also preferred. A low temperature hydrotreatment enables stabilization through reactions like olefin, carbonyl and carboxylic groups reduction. Further hydrotreatment aims at hydrodeoxygenation of phenols and hydrocraking of larger molecules [136].

6. Steam reforming

The term "reforming" was originally used to describe the thermal conversion of petroleum fractions to more volatile products of higher octane number and represented the total effect of many simultaneous reactions, such as cracking, dehydrogenation and isomerization. Reforming also refers to the conversion of hydrocarbon gases and vaporized organic compounds to hydrogen containing gases such as synthesis gas, a mixture of carbon monoxide and hydrogen. Synthesis gas can be produced from natural gas, for example, by such processes as reforming in the presence of steam (steam reforming) [8].

Catalytic steam reforming of some model oxygen containing compounds present in biomass pyrolysis vapours was investigated using a fixed bed microreactor interfaced with a molecular beam mass spectrometer (MBMS). Steam reforming of acetic acid (HAc) and hydroxyacetaldehyde (HAA), two major products derived from the pyrolysis of carbonhydrates in biomass, was examined. Both HAc and HAA undergo rapid thermal decomposition. Complete steam reforming of these two model compounds can be achieved with commercial Ni based catalysts. HAc forms coke on the catalyst surface, which is subsequently gasified by steam. The proposed mechanism for this coke formation involves an adsorbed acetate species that decarboxylates to form the coke precursor, (CH_{1-3}) and also ketene, a dehydration product of HAc that decomposes to form $(CH_{1,2})$. The reforming of HAA by steam does not involve any detectable intermediate and proceeds smoothly with a complete breakdown to CO and H_2 on the catalyst surface [137].

Production of H_2 by catalytic steam reforming of model compounds of biomass fast pyrolysis oil was investigated. Acetic acid, m-cresol, dibenzyl ether, glucose, xylose and sucrose were reformed using a commercial nickel based catalyst for steam reforming naphta. Steam to carbon ratios (S/C) of 3 and 6 and catalyst temperatures from 550 to 810 °C were selected. Rapid coking of the catalyst was observed during acetic acid reforming at temperatures lower then 650 °C. Acetic acid, m-cresol and dibenzyl ether were completely converted to H_2 and carbon oxides above this temperature [138].

Steam reforming of hydrocarbons yields a mixture of H_2 and CO (syngas), followed by the water–gas shift conversion to produce H_2 and CO_2. The steam capability can be significantly improved by permitting the classical Ni–Alumina or Ni–silica/alumina formulations with Ca and/or K [139].

Fast pyrolysis of biomass followed by catalytic steam reforming and shift conversion of specific fractions to obtain H_2 from bio-oil was presented as an effective way to upgrade biomass pyrolysis oils. This process was applied to model compounds and aqueous fractions of poplar oil with a

commercial nickel based steam reforming catalyst. H_2 yields as high as 85% of the stoichiometric value were obtained [85].

The effectiveness of reforming the pyrolysis oils of lignocellulosic biomass was tested under different operational conditions. The results of this study revealed that reforming was possible within a wide range of temperature and steam to carbon ratios, considering thermodynamic modeling of the major constituents of the bio-oil [140].

Sunflower oil was treated by catalytic steam reforming in a fixed bed with a commercial nickel based catalyst at temperatures between 550 and 800 °C. This process provided almost completely conversion of sunflower oil to H_2, CH_4 and carbon oxides. Thermal cracking of the oil in the gas phase was a competing process during steam reforming, especially above 650 °C where it converted fatty acids to a wide array of products, ethylene and aromatics [111].

7. Catalytic upgrading

Some catalyses have been used to improve the characteristics of pyrolysis products. In particular, oxygenates in the pyrolysis liquids can be reduced using zeolite type catalyses.

The pyrolysis oils of rice husks pyrolized in a fluidised bed reactor at 400–600 °C were homogenous, of low viscosity and highly oxygenated. The oxygenated compounds in the oils consisted mainly of phenols: cresols, benzenediols and guaniacol and their alkylated derivatives. In the presence of the zeolite ZSM-5 catalyst, the yield of oil was markedly reduced, although the oxygen content of the oil was reduced with the formation of coke on the catalyst. The influence of catalysis was to convert the oxygen in the pyrolysis oils to H_2O at lower catalysis temperatures and largely CO and CO_2 at higher catalysis temperatures. The catalysed oils were markedly increased in single ring and PAH compared to uncatalysed biomass pyrolysis oils. The concentration of aromatic and polycyclic aromatic species was increased with increasing catalysis temperature [92].

The pyrolysis of mixed wood waste with catalyst upgrading was investigated in a combined fluidised bed pyrolysis unit with online fixed bed zeolite HZSM-5 catalytic upgrading. The concentrations of PAH in the biomass pyrolysis oils were low. However, after catalytic upgrading, an important increase occurred in the concentrations of PAH, and their concentrations reached high levels. The concentration of PAH also increased with catalyst temperature. The freshly activated catalyst gave the highest concentrations of PAH, and successive regenerations caused the catalyst to become progressively less active, producing lower levels of PAH. Extended run time with the catalyst also resulted in a less active catalyst and lower concentration of PAH. Shorter vapour residence times produced lower concentration of PAH. The pyrolysis oils after catalysis contained high concentrations of certain PAHs, which are of known mutagenic and/or carcinogenic activity. For example, the oils contained tri- and tetra-methylphenanthrenes, chrysene, methylchrysenes and benzopyrenes [68].

The vapours from pyrolysis performed in a fluidised bed reactor at 550 °C using waste wood chips were upgraded by passing them over a fixed bed of ZSM-5 zeolite catalysts. The catalysis bed was diluted with stainless steel ball bearings to increase the residence time of the pyrolysis vapours in the bed and to provide additional hot surface for thermal cracking of the vapours. The presence of steel in the catalytic bed appears beneficial in the conversion of the pyrolytic vapours

to hydrocarbon products, with a threefold increase in the form of monocyclic aromatic compounds under certain process conditions [116].

An investigation was focused on the determination of the kinetic modeling of the conversion of a bio-oil over HZSM-5 catalyst in a fixed bed microreactor. The kinetic models showed that bio-oil upgrading was a complex combination of parallel and series reactions. Bio-oil deoxygenation and cracking of the non-volatiles were identified as the rate controlling steps [141].

Flash pyrolysis of wood waste was performed in a fluidised bed reactor at 550 °C. Methanol was injected into the reactor and the subsequent mixture of pyrolysis vapours and methanol was passed over a fixed bed of zeolite ZSM-5 catalyst held at 500 °C. The presence of methanol during the catalytic upgrading of the pyrolysis vapours was found to increase the amount of oxygen expelled from the vapours as water. It was also reported that there was a significant increase in the formation of alkylated aromatic hydrocarbon products [124].

Based on a study, it was concluded that there are natural catalysts in biomass that substantially influence the production of high yielding chemicals. Removal or reinforcement of these catalysts had a dramatic effect on product yield and composition. The pyrolysis vapours can be catalytically cracked over zeolites to give aromatics and other hydrocarbon products [142].

Catalytic elimination of the condensable organic compounds, which are unsuitable for specific applications, was examined. Three main groups of catalysts were used for this purpose. These catalysts are dolomite, alkali metals and nickel [143].

The upgrading of the raw hot gas from a bubbling fluidised bed biomass gasifier was studied using cheap calcined minerals, such as dolomite (MgO–CaO), pure calcite (CaO), and pure magnesite (MgO) [144].

8. Properties of char

The solid products from pyrolysis contain char, ash and unchanged biomass material. The pyrolysis conditions determine the chemical composition of the solid products. The char can be used in the preparation of active carbon when its pore structure and surface area are appropriate.

The pyrolysis of apple pulp exhibits two weight loss steps, ascribable to decomposition of the light fractions (hemicellulose) and cellulose. Changes in pyrolysis conditions had no effect on these two weight loss steps and did not affect the yield of the process. Chemical additives ($AlCl_3$, $FeCl_3$, H_3PO_4, NH_4Cl, KOH and $ZnCl_2$) slightly affect the first step by inhibiting hemicellulose decomposition and accelerating cellulose decomposition through the dehydration reaction. Phosphoric acid exhibited the largest influence on the pyrolysis process. At concentrations higher than 30% H_3PO_4, the two weight loss steps ascribed to hemicellulose and cellulose decomposition overlapped. Impregnation with phosphoric acid can enhance the production of char from apple pulp [20].

Char with an alkaline character of the surface, tar and gas products are obtained by steam pyrolysis of biomass (almond shells, nut shells, apricot stones, cherry stones, grape seeds). The chemical character of the oxygen containing functional groups on the char surface revealed that they are polyfunctional cationities. It was determined that carbon adsorbents obtained by means of pyrolysis from biomass have hydrophilic surfaces and are suitable for removing metal ions and other pollutants from water [17].

The reactivity of char obtained from pyrolysis of wood and agricultural residues by a free fall reactor was investigated. It was concluded that the char reactivity is very strongly influenced by the treatment conditions and may be significantly increased by using high heating rates, small particle size of the biomass and short residence time at higher temperatures [14].

The effects of some pyrolysis conditions, such as reactor temperature, heating rate, porosity, initial particle size and initial temperature, on char yields and conversion times were investigated. High temperature and fast heating rates were determined to decrease the yield of char. Three pyrolysis regimes were identified: (1) initial heating, (2) primary reaction at the effective pyrolysis temperature, and (3) final heating. The relative durations of each regime are independent of the reaction temperature and are approximately 20%, 60% and 20% of the total conversion time [121].

Generation of a microporous structure and determination of char formation kinetics were investigated via pyrolysis of sawdust of pinus insignis in a conical spouted bed reactor in the range 350–700 °C. The BET surface (representative of the physical evolution of the solid) and the C/H ratio of the solid product (representative of the chemical structure change) were taken as conversion indices. From measurement of the C/H ratio of the solid, it has been determined that the reaction order is 0.5 [84].

9. Inorganic constituents

The concentration of ash ranges from less than 1% in softwoods to 15% in herbaceous biomass and agricultural residues. During biomass pyrolysis, these inorganics, especially K and Ca, catalyze biomass decomposition and char forming reactions. Chars formed during these reactions invariably end up in the biomass pyrolysis oils (biocrude oils) as suspended submicron particles. The presence of high concentrations of submicron char particles in biocrude oils makes them problematic for combustion systems due to potential release of the ash and alkali metals during combustion [15].

Studies on wood and 12 other types of biomass showed that, in general, deashing increased the volatile yield, initial decomposition temperature and rate of pyrolysis. However, coir pith. groundnut shell and rice husk showed an increase in char yield on deashing, which is attributed to their high lignin, K and Zn contents. These results were supported by studies on salt impregnated, acid soaked and synthetic biomass. On deashing, liquid yield increased and gas yield decreased for all the biomass samples studied. The active surface area increased on deashing. The heating value of the liquid increased, whereas the increase in char heating value was only marginal [37].

The solid product from pyrolysis of tobacco was examined using the SEM technique. It was reported that pyrolysis of tobacco led to a gradual accumulation of inorganic crystals on the exposed surface, and some constituents also melted, resulting in the formation of bubbles by the evolving gas [114].

Alkali metal release during pyrolysis of biomass was investigated with a surface ionization method. Wheat straw samples were pyrolized under N_2, and two characteristic temperature intervals for alkali metal emission were identified. A small amount of the alkali content was released in a low temperature region (180–500 °C and was attributed to a connection with the decomposition of the organic structure). The major part of the alkali metal release was determined to take place in the high temperature region (>500 °C) from the ash residues [118].

The Waterloo fast pyrolysis in an atmospheric fluidised bed was used for Italian sweet sorghum and sweet sorghum bagasse at 400–560 °C and volatiles residence times from 222 to 703 ms. The sorghum bagasse gave results typical of similar grasses. Because of the high ash content of the bagasse, the char obtained (Ca 13%) had an ash content of nearly 50% [57].

10. Thermogravimetric analysis and kinetic studies

Thermogravimetric analysis (TGA) is a method by which the weight loss of a sample is recorded against temperature under controlled heating rate and gas atmosphere. Differential thermogravimetric analysis (DTG) curves are derived from TG curves, and they have been widely applied to biomass to evaluate pyrolysis kinetics.

To obtain biomass pyrolysis models, the TG–FTIR technique provides useful input in the form of kinetic information under low heating rate conditions. The analysis was applied to wheat straw, three types of tobacco and three biomass model compounds (xylan, chlorogenic acid and D-glucose) [36].

Thermal decomposition of sugar cane bagasse, petroleum residue and their blends was performed under N_2 by TGA. Sugar cane bagasse pyrolysis was described as the sum of cellulose, hemicellulose and lignin. First order equations were used to determine the bagasse component thermal decomposition kinetics. Activation energies were calculated as 235, 105 and 26 kJ/mol for cellulose, hemicellulose and lignin, respectively [80].

Biomass and sewage decomposition was studied by a competitive model consisting of weight loss and char formation reactions. A non-linear optimization technique was used to simulate the experimental curves obtained by TGA by minimizing the sum of the squares functions. Kinetic parameters were calculated for acacia wood, bagasse, rice husk and sewage sludge. The order of the reaction determined for sewage sludge was much higher than that of other biomass materials, whereas the activation energies were lower. Isothermal experimental studies resulted in much higher yields of char for all the four samples, and experiments conducted at various initial N_2 gas pressures confirm that vapour–solid interactions were the cause of the secondary char formation. Rice husk and sewage sludge yield higher amounts of secondary char due to the catalytic effect of the inorganics present in higher amounts in the samples [12].

Thermal degradation characteristics and kinetic parameters of rice husk were examined by TGA and DTG. Two prominent reaction zones were established from the thermogravimetric curves. Thermal degradation rates in the first reaction zone were relatively higher than those in the second reaction zone. The initial degradation temperatures were found as 220–240 °C [94].

Pyrolysis using the TGA technique was applied to rice husk from ambient temperature to 700 °C. It was reported that the higher the cellulosic content of the rice husk, the higher was the thermal degradation rate and the initial degradation temperature [96].

Pyrolysis kinetics of two lignocellulosic materials (olive stones and almond shells) was studied applying the TGA technique. Different kinetic models were tested that consider the thermal decomposition of lignocellulosic materials can be grouped in two or three overall processes (each one being the result of a great number of reactions) corresponding to the hemicellulose, cellulose and lignin decomposition. The best results were reported to be obtained with a model that considers that the biomass decomposes via three independent reactions. There is a qualitative

agreement between the decomposition of hemicellulose, cellulose and lignin with the peaks observed in the TG–DTG diagram [18].

Biomass pyrolysis studies were conducted using both a thermogravimetric analyzer and a packed bed pyrolyzer. Each kind of biomass has a characteristic pyrolysis behavior that is explained based on its individual component characteristics. Studies on isolated biomass components, as well as synthetic biomass, show that the interactions among the components are not of as much significance as the composition of the biomass [145].

Thermoanalytical investigations of biomass samples were conducted to evaluate their thermal behavior in both oxidizing and inert atmospheres. Evaluation of the lignin content was found to be useful to predict biomass thermal behavior and the quality of pyrolysis products obtained [146].

A method for direct determination of the cellulose and lignin content of biomass was developed assuming that negligible interactions exist between biomass macrocomponents, and it is based on the analysis of TGA pyrolysis data [147].

Olive residue was pyrolized at 300–600 °C in a captive sample reactor under atmospheric pressure of helium, with a heating rate of 200 °C/s. As the temperature increased, the percentage mass of char decreased whilst the gas and oil products increased. A simple first order kinetic model was applied to the evolution of total losses and gases [78].

In the same TGA under identical conditions, samples of pure, ash free cellulose undergo pyrolysis. The pyrolysis chemistry of pure cellulose is not governed by a universal rate law, as is the case with a pure hydrocarbon gas (for example). Nevertheless, the pyrolytic weight loss of all the samples is well represented by a high activation energy (228 kJ/mol), first order rate law at both low and high heating rates [24].

Pyrolysis of rice hulls was performed in a TGA. The global mass loss during rice hull pyrolysis was modeled by a combination of the volatile evolution of four independent parallel lumps: one for moisture and the other three for non-moisture volatiles. The decomposition of each lump was characterized by a single reaction of first order with respect to the amount of volatile yet to evolve [97].

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