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THERMAL STUDY OF DECOMPOSITION OF SELECTED BIOMASS SAMPLES

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Abstract

Fears of climate change and increasing concern over the global warming have prompted a search for new, cleaner methods for electricity power generation. Technologies based on utilising biomass are attracting much attention because biomass is considered to be CO_2 neutral. Co-firing of biomass fuels with coal, for example, is presently being considered as a mean for reducing the global CO_2 emissions. Biomass is also applied in thermal conversion processes to produce fuels with higher calorific values and adsorbents. In any case, thermal decomposition is essential stage where volatiles and tars are evolved followed by consequent heats of reactions.

In this work sawdust biomass samples were selected in order to study their thermal conversion behaviour. Heats of decomposition for each sample were measured during continuous heating at a prescribed heating rate under inert atmospheric conditions. The decomposition generally commenced in all samples at 150°C and was completed at 460°C in a series of endo and exothermic reactions influenced by its lignin and cellulosic content. Single biomass sample was subjected to heating rates ranging from 10 to 1000°C min^{-1} and the effect of heating rate on decomposition was studied. The origin of reactions for each thermal sequence is herein discussed in detail.

Keywords: biomass, computer aided thermal analysis, pyrolysis, reactions, specific heat

Introduction

Thermal conversion of wood to produce charcoal and volatiles is very old technology, which over the years declined seriously with the utilisation of liquid fuels and coal. However, the recent concerns over global warming and requirements to reduce greenhouse gas emissions [1] have placed biomass fuels, such as wood, straw, bagasse, peat and municipial solid waste at the forefront in reduction of the pollution as biomass is considered to be CO_2 neutral. These fuels have advantage of being renewable and, as they primarily consist of wastes [2], their conversion to energy provides a sustainable waste management practice. Current research trends in biomass utilisation are based on designing co-firing technologies in which biomass is combusted in

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mixtures with other fuels, mainly coal. Biomass conversion technologies can also consist of pyrolysis and gasification of the renewable energy sources in order to produce higher calorific value fuels i.e. oil liquids, hydrocarbon rich gases [3] and/or hydrogen [4]. In these technologies biomass undergoes thermal treatment and decomposition where volatiles and tars are evolved followed by consequent heats of reactions [5]. Therefore, to be able to understand and design the conversion processes during biomass decomposition, thermal investigation of the devolatilisation is essentially an initial stage. Current work is a part of the broader research in a study of biomass applications in reduction of metallic oxides and is concerned in measurement of thermal properties and reaction stages during decomposition of sawdust samples.

Experimental

Four sawdust samples were selected for the thermal study of their decomposition behaviour. The samples were first dried under vacuum for 2 h at 80°C and packed inside a furnace to the average density of 400 kg m^{-3}. The proximate and ultimate analysis of the selected sawdust samples are shown in Table 1.

Table 1 Analysis of sawdust samples

	Pinus lambertiana (Sugar pine)	Pinus radiata (Radiata pine)	Shorea spp. (Meranti)	Eucaliptus obliqua (Tasmanian oak)
		Proximate analysis		
Ash/%	0.3	0.3	0.2	0.2
Volatile matter/%	86.3	87.5	82.1	83.8
Fixed carbon/%	13.4	12.2	17.7	16.0
		Ultimate analysis		
Carbon/%	52.2	50.1	51.9	49.8
Hydrogen/%	6.14	6.07	5.87	5.79
Nitrogen/%	0.22	0.21	0.31	0.16
Oxygen/%	41.1	43.2	41.6	44.0
Total sulfur/%	0.07	0.08	0.09	0.08

Computer aided thermal analysis based on the inverse numerical modelling [6] was applied for the thermal analysis. The experimental apparatus used in this work was a modified Infrared Image Furnace shown in Fig. 1. The sample was packed manually in a silica tube and heated by radiation from a surrounding graphite cylinder. Heating rate of the furnace was typically maintained at 10°C min^{-1}. The sample was kept under inert atmosphere with an argon flow of 5 mL min^{-1} through the glass sample tube. Sample temperatures were continuously measured by thermocouples positioned at the surface and in the centre. Measured data were continuously acquired

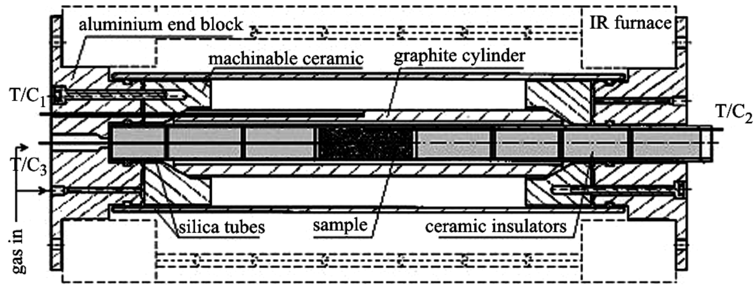

Fig. 1 Cross section of apparatus used for performing Computer Aided Thermal Analysis

at a frequency of 1 Hz. The heat flux at the surface of the sample was calculated by assuming the heat transferred from the graphite tube to the sample was predominantly by radiation:

$$Q=F_{1-2}\sigma(T_g^4-T_s^4) \tag{1}$$

where Q is the heat flux, F_{1-2} is the radiation shape factor, σ is the Stefan–Boltzmann constant and T_g and T_s are the temperatures of the graphite and surface of the sample, respectively. Radiation shape factor was an equipment specific calibration constant and its estimation procedure has been described elsewhere [6, 7]. Furthermore, the heat conduction Eq. (2) was solved simultaneously for ρC_p using an inverse numerical technique.

$$\rho C_p\frac{\partial T}{\partial t}=k\frac{\partial}{\partial r}\left(r\frac{\partial T}{\partial r}\right) \tag{2}$$

where ρ, C_p and k are the density, specific heat and thermal conductivity, respectively.

Quantitative analysis of the reactions could be obtained by determination of the inert specific heat in consecutive heating and cooling cycles as discussed elsewhere [7], however in this study only a qualitative background of the thermal sequences of biomass decomposition is outlined.

The cellulose studied in this work was an ash-free filter paper Whatman CF-41. Sigma Aldrich hydrolytic lignin and xylan from beechwood were applied as representatives for lignin and hemicellulose, respectively. Significant swelling was observed when performing the thermal analysis of hemicellulose. To ensure constant volume during the heating, the sample was mixed with alumina in 1:1 mass ratio.

Results

The apparent specific heats for the four sawdust samples were measured at a heating rate of 10°C min^{-1} under argon atmosphere, as shown in Fig. 2. The apparent specific heat was found to be around 1E6 J m^{-3} K^{-1} at room temperature, which corresponds to 2.5 kJ kg^{-1} K^{-1}. The specific heat measured in this work felt in the reported range of 2.3 and 2.6 kJ kg^{-1} K^{-1} [8].

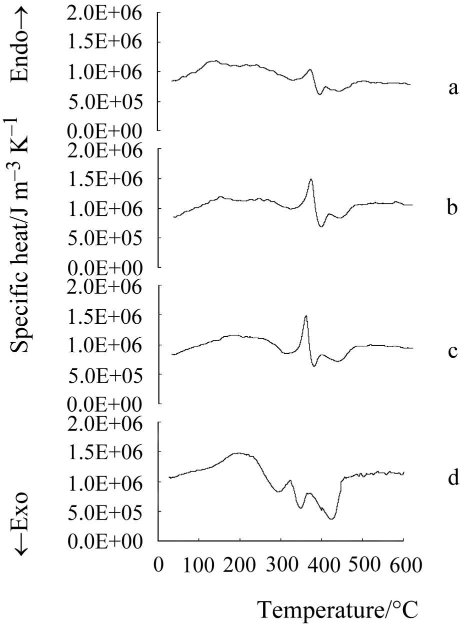

Fig. 2 Specific heat of sawdust as obtained by the Computer Aided Thermal Analysis, a – Pinus lambertiana, b – Pinus radiata, c – Shorea spp. and d – Eucaliptus obliqua

All of the samples showed similarities in their thermal behaviour with a number of exothermic and endothermic reactions. Generally, decomposition commenced at around 150°C with an endothermic reaction, which shifted towards the exotherm when reaching temperatures of around 250°C. From this temperature until 470°C, the thermal decomposition was found to be predominantly exothermic with a single endothermic peak also observed in the region of 320 to 360°C.

Wood pyrolysis can be assumed as a simultaneous pyrolysis of its three main constituents - cellulose, lignin and hemicellulose. Therefore, to clarify the origin of each of the thermal reactions the major wood constituents were also subjected to the thermal study with the results shown in Fig. 3. The endothermic behaviour for the temperatures up to 200°C, similar to the sawdust samples, was also found in the three constituents. The decomposition of hemicellulose was completed at 320°C, a considerably lower temperature than with cellulose and lignin. Hemicellulose and lignin exhibited double trough exotherm, while cellulose showed a strong distinguished endotherm at 330°C, followed by an exotherm with a trough at 370°C. The decomposition of cellulose was completed at 400°C, while in case of lignin it was 470°C.

Comparisons of the thermal decomposition and devolatilisation of wood with its major constituents has been a subject of debates in earlier works [9–11]. The decomposition of wood and its constituents takes place through reactions consisting of competitive and parallel reactions. The sawdust samples as well as their major constituents inevitably decompose to primary gases, which mainly consist of noncombustable volatiles, and tars. The tars can further crack forming secondary volatiles as shown in Fig. 4 [12]. All of the

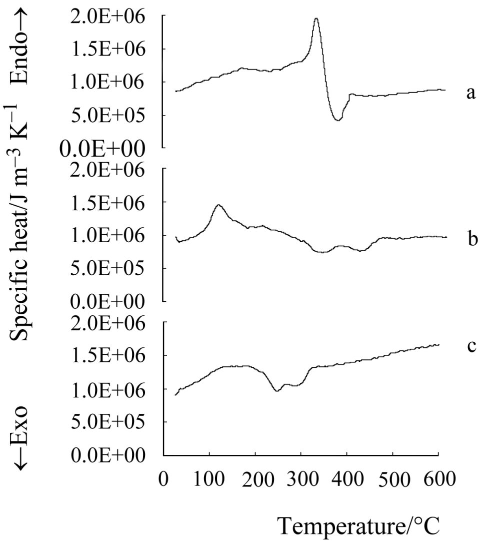

Fig. 3 Volumetric specific heat of major biomass constituents determined through Computer Aided Thermal Analysis method, a – cellulose, b – lignin and c – hemicellulose

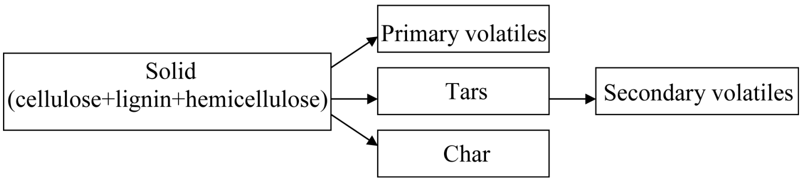

Fig. 4 Thermal decomposition of sawdust

major constituents, similarly, decompose to primary volatiles and tars, and the overall thermal decomposition of the sawdust during primary decomposition and tar formation could be assumed as a simple summary of the individual thermal curves. However, at elevated temperatures the thermal behaviour of sawdust decomposition undergoes through a complex matrix of cracking and secondary decomposition. Grønli and Melaaen suggested that primary decomposition is followed by an endothermic behaviour while tar decomposition is an exothermic process. The current study similarly suggests in all sawdust samples as well as cellulose, lignin and hemicellulose that thermal decomposition is endothermic at early stages of devolatilisation followed by predominantly exothermic behaviour. The exotherm will mainly be dependant on temperatures at which tars are evolved from the main wood constituents and the extent of their chemical reformation and further cracking. Furthermore, from the results shown in Figs 2 and 3 it is apparent that decomposition of biomass samples and corresponding peaks can occur at slightly different temperatures. Therefore, thermal behaviour of biomass will also depend on its chemical composition e.g. amount of each of the constituents represented in the wood, chemical bond structure and catalytic effect of the ash inorganic matter.

The endothermic reaction at early stage of devolatilisation of the sawdust samples could appear as a two-peak endotherm where the first peak represents dehydration of water. The primary devolatilisation, mainly oxides of carbon, is responsible for the second endothermic peak, mostly due to the decomposition of hemicellulose and to some extent lignin. The beginning of the exothermic reaction in all sawdust samples at 250°C could be related to its hemicellulose content, which generally contains high levels of pentosans and upon heating decomposes to furfurals and furthermore to acetic acids as a result of the secondary cracking [13]. The higher temperature exotherm in sawdust, which is evident in temperature range between 350°C, in case of Eucaliptus obliqua and 390°C in Pinus lambertiana and Pinus radiata, appears to be related to its lignin content. The exothermic character of the lignin relies on liberation of hydrocarbons, phenolic and neutral oils [14]. Some of these products are unstable and polymerise. Decomposition of cellulose can be clearly distinguished in the sawdust thermograms with endothermic peak appearing in temperature range of 320 to 360°C. Upon heating cellulose forms dehydrocellulose evolving tars in a process which is significantly endothermic [15, 16]. The dehydrocellulose further decomposes to char and gases. When the release of tars decreases, pyrolysis of cellulose predominantly favours formation of oxide gases shifting to an exotherm.

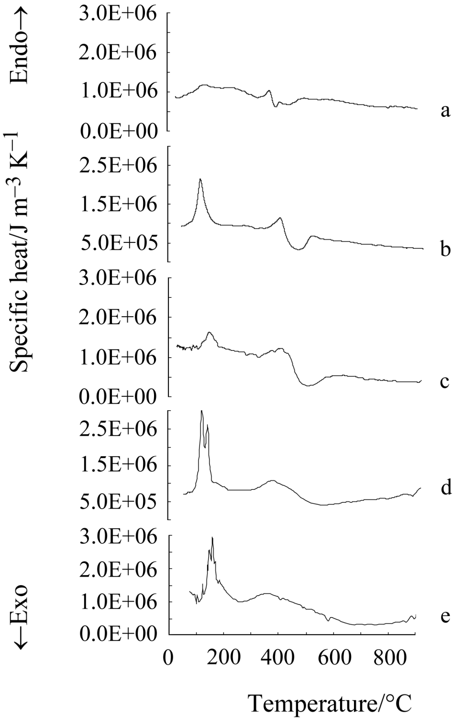

Fig. 5 Effect of the heating rate on the thermal decomposition of Pinus lambertiana sawdust, a – 10°C min^{-1}, b – 50°C min^{-1}, c – 100°C min^{-1}, d – 200°C min^{-1} and e – 1000°C min^{-1}

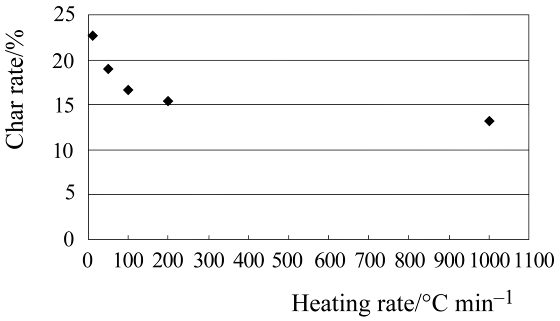

Fig. 6 Char rate variations with the heating rate during heating of Pinus lambertiana

The effect of heating rate on specific heat and pyrolysis reactions is shown in Fig. 5. Pinus lambertiana was heated under heating rates ranging between 10 and 1000°C min^{-1} to the maximum temperature of 900°C. The highest heating rate was achieved by adjusting the furnace power to the maximum. The maximum heating rate was found to vary significantly with time and the estimate of the average value was around 1000°C min^{-1}. At heating rates larger than 10°C min^{-1} the effect of decomposition of cellulose becomes the most pronounced. The distinguished endothermic decomposition of cellulose was apparent at temperatures between 360 and 400°C followed by exothermic char formation. At 50°C min^{-1}, the high temperature exotherm became broader and smaller due to reduction in secondary devolatilisation of the cellulose and lignin. The exothermic trough was delayed towards higher temperatures during pyrolysis and appeared at a larger temperature range. As mainly char formation occurs during this event it is clear the resultant char was affected with the altered heating conditions. For this matter, the char was weighted before and after each heating and results are shown in Fig. 6. Char rate significantly changes with the heating rate ranging from 22% at 10°C min^{-1} to 13% for heating rates close to 1000°C min^{-1}. Decreasing trend in the char yields with increased heating rate was similarly observed in the cellulose pyrolysis [17]. Rapid heating rates enhance transfer of volatiles reducing the time available for primary gases to undergo tar cracking and repolymerisation, which are responsible for the char formation. As a result, high molecular mass tars and volatiles are driven off the matrix leaving low char yields as a final product of pyrolysis.

Conclusions

Thermal analysis was performed on four sawdust biomass samples and the analysis compared with its major wood constituents cellulose, hemicellulose and lignin. Thermal decomposition of biomass sawdust was found to be slightly endothermic at temperatures lower than 250°C, mainly due to dehydration and primary devolatilisation of hemicellulose and lignin. At elevated temperatures the secondary devolatilisation and char formation evolved shifting the reactions towards an exotherm. The exothermic behaviour depends on tar evolution, thermal cracking and tar reformation of the main wood constituents. The decomposition of cellulose exhibited a significant endothermic reaction at temperatures between 320 and 360°C followed by a strong exotherm. In this case, tar evolution was endothermic while the further decomposition to low molecular weight gases and char formation was an exothermic process. The char formation was found to be strongly dependent on heating conditions and at higher heating rates the char yield was significantly reduced from 22% at 10°C min^{-1} to 13% at 1000°C min^{-1} with a reduction of the time available for repolymerisation and cracking of the primary volatiles.

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