Full Length Article

Cellulose, xylan and lignin interactions during pyrolysis of lignocellulosic biomass

Jie Yu, Nigel Paterson, John Blamey, Marcos Millan *

Department of Chemical Engineering, Imperial College London, London SW7 2AZ, United Kingdom

HIGHLIGHTS

- The interaction was not observed before cellulose started degradation.
- Interactions were observed between cellulose and the other two components.
- The trend of product yields between synthetic samples and biomass was opposite.
- The morphology of biomass provided a release route for pyrolysis vapours.

ABSTRACT

The three primary lignocellulosic biomass components (cellulose, xylan and lignin), synthetic biomass samples (prepared by mixing the three primary components) and lignocellulosic biomass (oak, spruce and pine) were pyrolysed in a thermogravimetric analyser and a wire mesh reactor. Different reactivities were observed between the three biomass components. Cellulose mainly produced condensables and was less dependent on heating rate, while xylan and lignin contributed most char yields and were significantly affected by heating rate. While xylan and lignin pyrolysed over a large temperature range and showed the behaviour characteristic of solid fuels, cellulose decomposition is sharp in a narrow temperature range, a behaviour typical of linear polymers. Comparison of the pyrolysis behaviour of individual components with that of their synthetic mixtures showed that interactions between cellulose and the other two components take place, but no interaction was found between xylan and lignin. No obvious interaction occurred for synthetic mixtures and lignocellulosic biomass at 325 °C, before the beginning of cellulose pyrolysis, in slow and high heating rate. At higher pyrolysis temperatures, more char was obtained for synthetic mixtures containing cellulose compared to the estimated value based on the individual components and their proportions in the mixture. For lignocellulosic biomass, less char and more tar were obtained than predicted from the components, which may be associated with the morphology of samples. The porous structure of lignocellulosic biomass provided a release route for pyrolysis vapours.

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1. Introduction

Lignocellulosic biomass is mainly composed of three organic constituents: lignin, cellulose and hemicellulose. The ratio of these three components varies, depending on the type of biomass and the part of the plant sampled. For example, Hazelnut shell contains up to 51.3% lignin [1] while tree leaves are lignin-free [2]. Typically, softwood has a higher amount of lignin and grasses have the lowest [3]. In addition to these main components, biomass also contains small amounts of pectins, inorganic compounds, proteins and extractives. Cellulose is a linear polysaccharide, typically consisting of thousands of D–glucose monomers, and is the largest single component of lignocellulosic biomass. Three hydroxyl groups in each monomer are able to interact with one another forming intra- and intermolecular hydrogen bonds which give cellulose a crystalline structure [4] and its unique properties of mechanical strength and chemical stability. Hemicellulose is a polysaccharide composed of various carbohydrate monomers, mainly xylose, arabinose, mannose and glucose in varying ratios in different biomass samples. The degree of polymerization (DP) of hemicellulose is 50–200 monomers, which is much lower than that of cellulose [5]. Because of its amorphous structure, hemicellulose is less stable. Lignin is a random, three-dimensional network polymer comprised of linked phenylpropane units making it more difficult to decompose.

* Corresponding author.
  E-mail address: marcos.millan@imperial.ac.uk (M. Millan).

Physically, cellulose microfibrils are coated with hemicellulose, whose empty spaces are filled up with lignin [6]. Lignin plays a binding role between hemicellulose and cellulose within the cell wall. It has been suggested that hemicellulose is hydrogen-bonded to cellulose, while lignin and hemicellulose are covalently bonded, more specifically, via ester bonds [7]. These bonds will influence the pyrolytic behaviour of biomass and may cause differences in performance respect to that of synthetic mixtures.

The interaction between the three components during pyrolysis can be examined by studying product distribution, tar characteristics and gas composition. Some researchers have predicted lignocellulosic biomass pyrolysis profiles based on the lignocellulosic composition with some degree of accuracy in thermogravimetric analyser (TGA), concluding that no detectable interactions between the three components took place during pyrolysis [8–10]. By contrast, some other reports claimed that the pyrolysis behaviour of lignocellulosic biomass cannot be explained by the simple superposition of three components due to their significant interactions [11–15], different for example from the additive behaviour found in coal macerals [16]. In terms of product distribution, the interaction between intermediate products from pyrolysis of cellulose powder and lignin extracted from Japanese cedar accelerated tar production, while reducing char and water formation [12]. A significant observation during biomass pyrolysis is the levoglucosan deficit phenomenon compared with pure cellulose. For lignocellulosic biomass, such as olive husk, hazelnut shell, spruce wood and beech wood, less than 3% levoglucosan in the liquid fraction of pyrolysis products was found, even though the spruce wood and beech wood tested contained more than 50% cellulose, which can produce up to 48% levoglucosan [17,18]. The interaction among cellulose, xylan and lignin may have suppressed the evolution of levoglucosan and significantly increased the evolution rate of 5-methylfurfural [19]. Compared with a binary physical mixture of cellulose-hemicellulose, the levoglucosan deficit phenomenon is more obvious for a native mixture of cellulose-hemicellulose [13]. Moreover, the product yields from the pyrolysis of lignocellulosic biomass are also closely linked to the detailed sample morphology [11]. The above discussion shows that the three components of lignocellulosic biomass cannot necessarily be assumed to pyrolyse independently.

When considering the interactions within lignocellulosic biomass, it is necessary to examine the pyrolysis products by simultaneously considering the difference in the chemical structure and morphological characteristics. Couhert et al. [20] prepared two mixtures of three components: the so called simple mixing and the intimate mixing, then pyrolysed them in an entrained flow reactor at 950 °C. It was found that the intimacy of the mixing played a role on the interactions: the more intimate the mixture, the higher the CO_2 yield. Therefore, the effect of interactions between components may differ in a physical mixture from an actual biomass sample as the structure of biomass will affect the outcome of pyrolysis, altering the selectivity towards certain products [21]. A further level of complexity is added by reactions between pyrolysis products, which are determined by the type of contact between particles in the reactor and depend on the configuration of the pyrolysis reactor.

Most studies on these interactions employed TGA, Pyrolysis-Gas Chromatography/Mass Spectroscopy (Py-GC–MS) and fixed beds. However, secondary reactions cannot be avoided in these reactors [22], and therefore interactions between biomass components may be caused by reactions between primary tars and chars. Moreover, most reactors used are only capable of slow heating rates. At low heating rate, intra-particle secondary reactions may be more significant due to the increased retention of liquids within the char residues, changing product yields and tar characteristics [23,24]. On the other hand, the wire mesh reactor, used in this study, was designed to minimise secondary reactions and achieve fast heating rates.

This study sets out to establish the relative contributions of these three phenomena (reactions between biomass components, effect of biomass structure on these reactions, and reactor-related effects) during biomass pyrolysis. It compares the pyrolysis behaviour observed during pyrolysis of synthetic biomass samples (prepared from commercially available constituents) and actual lignocellulosic biomass. During pyrolysis of biomass, different components decompose at different rates and temperature ranges and this difference in reactivity between the three basic components makes pyrolysis complex. It is clear that the use of commercial constituents cannot represent real biomass [1]. The structures and reaction pathways during pyrolysis of individual components alone should be different from those in wood because of the physical associations and interactions among them [25]. Moreover, isolation of biomass constituents from cell wood is commonly achieved by methods that result in alteration of their original structures. Despite these clear limitations, the use of isolated or commercial biomass constituents can be a useful tool to investigate interactions occurring during the pyrolysis of biomass and has been part of the approach in the present work. This study focused first on the pyrolysis of the three biomass components independently and then studied the pyrolysis behaviour of synthetic samples and raw biomass. The effect of reactor configuration is investigated by comparing pyrolysis in a TGA, where sample particles are in contact, and in a wire mesh reactor (WMR), which provides segregation between particles and therefore data can be interpreted as representing single particle behaviour. The data obtained are used to link the decomposition of cellulose, hemicellulose and lignin and the possible interactions within lignocellulose in order to better understand biomass behaviour from primary reactions in the thermal processing of different biomass fuels.

2. Experimental section

2.1. Samples

Commercial microgranular powder cellulose (Whatman, UK; Part No. 4061-050), xylan (from Birchwood, Sigma-Aldrich) to represent hemicellulose, and lignin (Alkali, Sigma-Aldrich) were used in this work. Four composite pellets were prepared by mixing fine cellulose, xylan and lignin in an agate mortar. They were ground using a ball mill for 2 h prior to mixing. All samples were pressed and then crushed into 106–150 μm size for use in wire mesh reactor and TGA. Three biomass feedstocks, pine, spruce and oak, were also studied in this work. Full compositional analysis of these original feedstocks was performed using protocols developed by NREL [26] and modified by Ray et al. [27] (Table 1). The moisture content was determined by oven drying at 105 °C for 12 h [28] and the dried material was used for subsequent analysis. The fraction of extractives was established by treating the dried biomass with 95% ethanol using a Dionex® Accelerated Solvent Extractor (ASE200) [29]. The structural sugars, acid soluble lignin and ash were then determined using a method established by Sluiter et al. [30]. The biomass post-drying and extraction was subjected to a two-step sulphuric acid digestion: (i) in 72% sulphuric acid at 30 °C for 60 min; (ii) in 4% sulphuric acid at 121 °C for 60 minutes. The acid soluble lignin and sugars dissolved in the resultant liquor were determined by UV absorbance and HPLC analysis respectively. The HPLC analysis was performed using a Bio-Rad Aminex HPX-87P column at 80 °C using a mobile phase of water, at a flow-rate of 0.6 mL min^{-1}. The solids resulting from the acid digestion were considered a mix of acid insoluble lignin