



## A study of lignocellulosic biomass pyrolysis via the pyrolysis of cellulose, hemicellulose and lignin

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### ABSTRACT

In this study, thermogravimetric (TG) analyses, along with thermal and catalytic fast pyrolysis experiments of cellulose, hemicellulose, lignin and their mixtures were carried out in order to investigate their pyrolysis products and whether the prediction of the pyrolysis behavior of a certain lignocellulosic biomass feedstock is possible, when its content in these three constituents is known. We were able to accurately predict the final solid residue of mixed component samples in the TG analyses but the differential thermogravimetric (DTG) curves indicated limited heat transfer when more than one component was present in the pyrolyzed sample. The limited heat transfer did not have a significant effect on the TG curves but it affected the product distribution in the fast pyrolysis experiments, which resulted in inaccurate calculation of the product yields, when using a simple additive law. In addition, the pyrolysis products of each biomass constituent were characterized in order to study their contribution to the yield and composition of the products from whole biomass pyrolysis. An investigation into the pyrolysis reaction pathways of each component was also carried out, using the bio-oil characterization data from this study and data found in the literature.

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### 1. Introduction

Increased world energy demand and environmental concerns have driven research on alternative energy sources. Lignocellulosic biomass is considered a promising alternative and renewable energy source that can be converted via the biomass fast pyrolysis process into a liquid product, known as bio-oil, which is considered to be a promising biofuel/bioenergy carrier. The bio-oil is a complex mixture of oxygenated compounds and its composition and quality is heavily dependent on the composition of the biomass feedstock. Lignocellulosic biomass is composed mainly of three basic structural components; cellulose, hemicellulose and lignin. The content of these components in biomass varies depending on the biomass type. Woody plant species have tightly bound fibers and are richer in lignin while herbaceous plants have more loosely bound fibers, a fact that indicates lower lignin content. Usually, cellulose, hemicellulose and lignin constitute 40–50 wt.%, 20–40 wt.% and 10–40 wt.% of the plant material respectively [1]. In addition

to these components, lignocellulosic biomass also contains a small amount of inorganic material (ash) and extractives.

It has been suggested that since all lignocellulosic biomass is mainly composed of these basic structural components, the aggregative behavior during pyrolysis of each of those independent components would describe the behavior of any lignocellulosic feed [2]. Therefore, it should be possible to predict the yield and composition of the pyrolysis products of any feedstock, when its composition is known. In order for that to be true however, the pyrolysis behavior of each individual component must be independent of the presence of other components. Otherwise, if synergistic effects were to take place, the prediction of the behavior of a biomass feedstock would be a more complex task. In addition, since biomass pyrolysis proceeds through an extremely complex network of reaction mechanisms, the study of the biomass pyrolysis chemistry can be simplified by studying the pyrolysis reactions of cellulose, hemicellulose and lignin individually.

Several groups in the literature have studied the pyrolysis of biomass on the basis of these three main components. Raveendran et al. [2] studied the pyrolysis characteristics of biomass components in a thermogravimetric analyzer and a packed-bed pyrolyzer and found no detectable interactions among the components during pyrolysis in either experimental setup. Yang et al. [3] also observed negligible interactions among the three biomass components in their study, when using a thermogravimetric analyzer. On

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**Table 1**  
Composition of the biomass feedstocks used in this study (on dry basis).

Sample	C (wt.%)	H (wt.%)	O (wt.%) <sup>a</sup>	Ash (wt.%)
Cellulose	42.27	6.40	51.33	0.00
Xylan	42.07	5.82	45.75	6.36
Lignin	63.41	5.89	28.42	2.28

<sup>a</sup> By difference (oxygen% = 100% – carbon% – hydrogen% – ash%)

the other hand, Worasuwannarak et al. [4] studied the pyrolysis behavior of cellulose, xylan, lignin and mixtures by TG–MS technique and observed significant interactions between cellulose and lignin that caused a suppression of liquid product formation and an increase in solid residue yield. Wang et al. [5] also observed cellulose–lignin interactions, as well as hemicellulose–lignin interactions, while they reported that hemicellulose and lignin did not seem to affect each other during pyrolysis in a thermogravimetric analyzer. More recently, Wang et al. [6] studied the interactions of the biomass components in both a TG–FTIR and an experimental pyrolyzer. They reported no significant differences between the experimental and calculated TG/DTG curves, when using biomass component mixtures, but differences in the evolution curves of the main products (levoglucosan, 2-furfural, acetic acid and 2,6-dimethoxy phenol) were apparent. In addition, the mixed samples exhibited a common tendency to form less liquid and more gas products than what the calculations predicted. To the best of our knowledge, the pyrolysis of mixed biomass components with catalytic upgrading of the pyrolysis vapors has not been studied yet.

In this study, the thermal and catalytic pyrolysis of biomass components (cellulose, xylan and lignin) was studied, both in a TG apparatus and in a pyrolysis reactor and the contribution of each component on the yield and the composition of the biomass pyrolysis products was investigated. Moreover, the pyrolysis of mixtures of cellulose, hemicellulose and lignin was studied in order to investigate the contradictory literature results concerning the interactions between cellulose, hemicellulose and lignin during pyrolysis. Finally, based on the results from the pyrolysis of the individual components and reports from the literature, an elucidation of the reaction pathways in the absence or presence of a catalyst was attempted.

## 2. Experimental

### 2.1. Biomass feedstock properties

The cellulose used in this study was purchased from JRS Pharma with the commercial name VIVAPUR Type 200 Microcrystalline Cellulose. The lignin used was a kraft lignin isolated from a commercial pulp mill using predominantly Norway spruce as a raw material and was purchased from Sigma–Aldrich (Aldrich 370959). Because hemicellulose was not commercially available, xylan purchased from Sigma–Aldrich was used instead (Sigma X4252). Xylan is considered to be an adequate replacement for hemicellulose and it is widely used in the literature for this purpose [3]. All biomass samples were dried at 105 °C for 4 h before use and therefore, all results reported here are on a dry basis. The elemental composition of the dry biomass samples is presented in Table 1.

### 2.2. TG experiments

The TG experiments were performed in a TA Instruments SDT2960 thermogravimetric analyzer to study the decomposition curves upon pyrolysis of the samples. Experiments were carried out with sample masses of about 10 mg using a linear heating rate of 10 °C/min within the temperature range of 28–840 °C and a steady nitrogen flow rate of 100 cm<sup>3</sup>/min.

### 2.3. Pyrolysis experiments

The pyrolysis experiments were performed at 500 °C in a bench-scale fixed bed biomass pyrolysis reactor. The reactor was made of stainless steel 316 and measured 14 mm in internal diameter and 41 cm in height. Heat was provided by a three-zone furnace and the temperature of each zone was independently controlled using temperature controllers. The catalyst bed temperature was considered as the pyrolysis temperature and was monitored with a thermowell. The biomass sample (1.5 g) was loaded in a specially designed piston mounted on top of the reactor, outside of the furnace. After the desired pyrolysis temperature in the reactor was reached, the piston was used to introduce the biomass feedstock into the hot reactor. A constant stream of nitrogen (100 cm<sup>3</sup>/min) was fed from the top of the reactor for the continuous withdrawal of the pyrolysis vapors and maintenance of the inert atmosphere during the experiment. The vapors were carried through the catalyst bed (0.7 g), exited from the bottom of the reactor in gaseous form and were condensed in a glass receiver submerged in a cooling bath that was kept at –17 °C. Non-condensable gases were collected in a gas collection system, while a glass wool filter placed between the glass receiver and the gas collection system recovered any light condensable liquids that were not condensed in the receiver. The above described catalytic pyrolysis experiments can be referred to as *in situ* upgrading of pyrolysis vapors and are of the “ex-bed” type (i.e. there was no mixing of solid biomass with the solid catalyst). In addition, all the experimental parameters (i.e., fast heating of biomass, low residence time, fast cooling of products) resemble those of the biomass fast pyrolysis type of experiments. A schematic representation of the experimental setup can be found elsewhere [7].

Both thermal and catalytic pyrolysis experiments were performed. Inert silica sand was used in place of the catalyst bed in the thermal pyrolysis experiments, while a commercial ZSM-5 formulation diluted with silica alumina (30 wt.% crystalline zeolite, 138 m<sup>2</sup>/g surface area, 4 nm average pore diameter, 0.037 cm<sup>3</sup>/g microporosity and 0.018 cm<sup>3</sup>/g mesoporosity) was used for the catalytic pyrolysis experiments.

The liquid products were collected and quantitatively measured in the pre-weighted glass receiver. The pyrolytic vapors, upon their condensation in the glass receiver, formed multiple phases; an aqueous phase, a liquid organic phase and viscous organic deposits on the receiver walls. Extensive effort has been put in the development of a method for the collection of a representative bio-oil sample for analysis [7]. Towards this goal, the bio-oil was first fully homogenized inside the receiver using ethyl lactate as the solvent and then collected as a solution, which was then submitted for analysis. Ethyl lactate was chosen for its non-volatility, which minimizes errors during weighing. It also proved to be a good solvent for all the bio-oil samples in this study.

### 2.4. Analysis methods

The elemental composition of the biomass samples and the bio-oil was determined with an elemental CHN LECO-800 analyzer. The water content of the bio-oil was measured with Karl–Fischer titration (ASTM E203-08). The water/aqueous phase present in the bio-oil was then separated from the organic phase using an organic solvent (dichloromethane) and the organic phase of the bio-oil was analyzed by GC–MS using an Agilent 7890A/5975C gas chromatograph–mass spectrometer system (Electron energy 70 eV, Emission 300 V, Helium flow rate: 0.7 cc/min, Column: HP-5MS 30 m × 0.25 mm ID × 0.25 μm). Internal libraries were used for the identification of the compounds found in the bio-oil and their categorization into main functional groups. The gaseous products were collected and measured by the water displacement method. The gaseous products were analyzed in a HP 5890 Series

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