



Catalytic effects of copper(II) chloride and aluminum chloride on the pyrolytic behavior of cellulose

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ABSTRACT

The cellulose without and with catalyst (CuCl_2 , AlCl_3) was subjected to pyrolysis at temperatures from 350 to 500 °C with different heating rate (10 °C/min, 100 °C/s) to produce bio-oil and selected chemicals with high yield. The pyrolytic oil yield was in the range of 37–84 wt% depending on the temperature, the heating rate and the amount of metal chloride. The non-catalytic fast pyrolysis at 500 °C gives the highest yield of bio-oil. The mixing cellulose with both metal chlorides results with a significant decrease of the liquid product. The non-catalytic pyrolysis of cellulose gives the highest mass yield of levoglucosan (up to 11.69 wt%). The great influence of metal chloride amount on the distribution of bio-oil components was observed. The copper(II) chloride and aluminum chloride addition to cellulose clearly promotes the formation of levoglucosenone (up to 3.61 wt%), 1,4:3,6-dianhydro- α -D-glucopyranose (up to 3.37 wt%) and unidentified dianhydrosugar (MW = 144; up to 1.64 wt%). Additionally, several other compounds have been identified but in minor quantities. Based on the results of the GC–MS, the effect of pyrolysis process conditions on the productivity of selected chemicals was discussed. These results allowed to create a general model of reactions during the catalytic pyrolysis of cellulose in the presence of copper(II) chloride and aluminum chloride.

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1. Introduction

In last decades there is a big interest in the production and use of biomass as a renewable energy source. The potential recovery of fuels and chemicals from biomass by pyrolysis in relation to process conditions has been widely investigated [1,2]. The influence of process parameters on the product yield and its properties have been widely studied. It was reported that the yield of products, i.e. oil, gas and char depends strongly on the conditions of pyrolysis [3–5]. The liquid products of biomass pyrolysis, called bio-oil, may have various applications [6]. There is a trend to apply bio-oil as fuel or fuel additive but due to its poor quality, bio-oil requires quality improvement [7]. Alternatively, bio-oils containing valuable chemicals in significant concentrations may have also a potential use as a chemical feedstock [8].

Cellulose is the main component of lignocellulosic biomass and the most common biopolymer. It is a linear homopolymer composed of glucopyranose residues linked by β -1,4-glycosidic bonds. Such a chemical structure makes cellulose suitable for the production of monosaccharide derivatives through the depolymerization processes, including pyrolysis [9,10]. The pyrolysis, as a non-oxidative thermochemical conversion process, is a simple

way of cellulose degradation with a formation of various liquid products, mainly monosaccharides, furans and pyrans derivatives [11,12].

The pyrolysis of cellulose has been extensively investigated because bio-oil is considered to be a potential source of chemicals, including anhydrosugars and their derivatives, namely levoglucosan (LG), levoglucosenone (LGO), (1S,5R)-5-hydroxy-3,7-dioxabicyclo[3.2.1]octan-4-one (LAC), 2-furfural (FF), 5-hydroxymethyl-2-furfural (HMF) [13–18]. Various mechanisms of cellulose pyrolysis have been proposed. Shafizadeh and co-workers [19,13] have proposed a three-step mechanism of cellulose pyrolysis. First, cellulose is transformed into “active cellulose”, which decomposes via two major pathways of fragmentation and depolymerization, one yielding anhydrosugars and the other forming char and gas fraction. This general model of cellulose pyrolysis is accepted but there are many efforts undertaken to expand and refine it [20–23] and detailed mechanisms of cellulose pyrolysis are still under investigation.

Levoglucosan is the major component of bio-oil produced from pure cellulose [24]. It was found that impure cellulose during pyrolysis (depending on the type of inorganic impurities) decomposes with the formation of levoglucosenone, 2-furfural, 2-hydroxyacetaldehyde (HA) with high yields accompanied by reduced levoglucosan formation. Therefore, plenty of different type catalysts were used to perform selective pyrolysis of cellulose for chemicals production [25–27]. In general, various acidic

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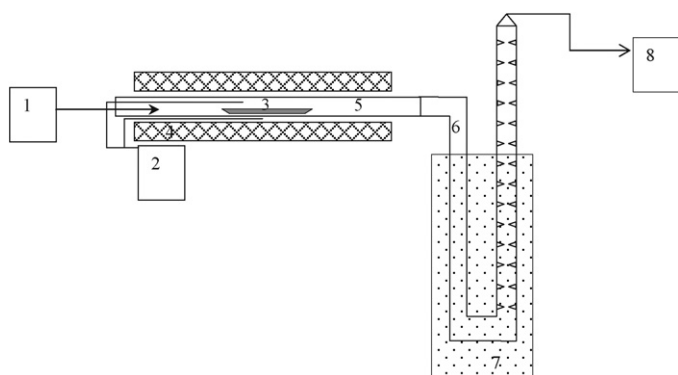


Fig. 1. Scheme of reactor system. 1. gas inlet; 2. temperature controller; 3. sample boat; 4. oven; 5. quartz reactor; 6. condenser; 7. liquid nitrogen reservoir; 8. gas outlet.

compounds promote dehydration reactions, formation of levoglucosenone [28,29] and furfural [30]. Alkali metal salts catalyze charring reactions and the formation of 2-hydroxyacetaldehyde [31]. Nanopowders containing titanate enhance the formation of LGO and LAC [32].

In this paper, the pyrolysis of cellulose in a presence of copper(II) chloride and aluminum chloride is discussed as a way of producing bio-oil with high yield of selected (di)anhydrosugars in comparison to that produced from pure cellulose. The primary objective of this study was to determine the influence of the amount of metal chloride used on the formation of selected chemicals during pyrolysis of cellulose. Furthermore, this study investigated the change in the products distribution as well as individual species yields by changing final temperature and a heating rate of the pyrolysis process.

2. Experimental

2.1. Samples

Commercial microcrystalline cellulose (cellulose powder, Aldrich) was selected for this study. Its characteristics are given in a previous paper [33]. Cellulose blends with 3–30 wt% anhydrous CuCl_2 (powder, purity >98%, Merck) or anhydrous AlCl_3 (powder, purity p.a. >99%, Fluka) addition were prepared in an agate mortar for 10 min. Following abbreviation system for samples was used further in the text: **CxMeXXXy** where **x** is related to the amount (in wt%) of metal chloride (**Me**). **XXX** is a temperature of the pyrolysis process and **y** is a type of heating (f – fast heating, s – slow heating). For example C3Cu450f means cellulose +3% of CuCl_2 heated up 450 °C with a heating rate of 100 °C/s.

2.2. Pyrolysis

The pyrolysis processes of cellulose with and without metal chloride addition were carried out in a horizontal oven with infrared heating system and dynamic cooling system, as given in Fig. 1. A 200 mg of sample was placed in quartz reactor and heated up to 350–500 °C with two different heating rates of 10 °C/min and 100 °C/s and kept at final temperature for additional 5 min. The decomposition products were evacuated in nitrogen flow of 10 dm³ h⁻¹ to the liquid reservoir placed in the liquid nitrogen bath. The pyrolysis process was repeated in triplicate to check reproducibility and to calculate an average yield of products.

Liquid products collected in liquids receiver were transferred with c. 30 ml of benzene–methanol (60:40, vol./vol.) mixture and c. 20 ml of methylene chloride into the measuring flask (50 ml). Next, bio-oil was analyzed by means of GC–MS.

2.3. GC–MS analysis

The bio-oils solutions (2 μl) were analyzed by an HP6890 gas chromatograph equipped with an HP5973 mass selective detector and a HP-1701 capillary column (30 m \times 0.25 mm i.d., 0.25 μm film thickness, 14%-cyanopropylphenyl-86%-dimethyl-siloxane polymer). As a carrier gas helium (purity 99.999%) was used. The column temperature was programmed from 40 to 260 °C at 10 °C/min after an initial 4 min isothermal period and kept at the final temperature for 10 min. The inlet was set at 250 °C. Sample injection was made in the split mode (1:10).

Mass spectrometer was set at an ionizing voltage of 70 eV with mass range m/z 15–400. The identification of organic compounds was accomplished by comparing mass spectra of the resolved components using NIST electronic library search routines and following Refs. [34,12].

2.4. Quantification

To show the productivity of chemicals, the mass yields of selected compounds identified in bio-oils were quantified according to the commercial levoglucosan, LG (99%, Aldrich), furfural (99%, Aldrich), 2(5H)-furanone (98%, Aldrich), 5-hydroxymethyl-2-furaldehyde (99%, Aldrich) quantification. External calibrations using solutions of commercial standards (0–40 mg of compound/100 ml of solvent) were performed in triplicate (average values were used for calibration curve preparation). A mass yield (wt%) of each compound was calculated as a weight of the compound/weight of the cellulose used for the pyrolysis. The quantified compounds with an average yield (based on three or four independent GC–MS analyses) and standard deviation are listed in Tables 1 and 2.

3. Results

This section is divided into three parts. First one concerns the influence of operating conditions of cellulose pyrolysis on the products distribution. The second one describes the composition of bio-oil in relation to operating parameters of the pyrolysis process. The third part combines the composition and the yield of bio-oil to discuss the productivity of selected chemicals.

3.1. Yield of bio-oil

The influence of different parameters of cellulose pyrolysis on the yield of solid, liquid and gaseous products has been investigated. Results are given in Figs. 2 and 3.

Influence of temperature and heating rate. It was found that during non-catalytic pyrolysis of pure cellulose the temperature and a heating rate have a great influence on the products distribution. The results are presented in Fig. 2a. The almost linear increase of liquid product yield from 69 to 84 wt% can be observed with increasing temperature (from 350 up to 500 °C) of the fast pyrolysis process. Increasing temperature of the non-catalytic slow pyrolysis of cellulose enhances the bio-oil formation from 37 to 54 wt% at temperatures applied. This is accompanied by the decrease in both the char and gaseous products yields. In general, these results are consistent with the results of other authors [4,21].

The influence of temperature and a heating rate on the products distribution during catalytic pyrolysis of cellulose has also been evaluated. It was noted that 10 wt% of aluminum chloride addition reduces the yield of liquid product and is independent of the final temperature of the process in the investigated temperature range, Figure 2b. The addition of CuCl_2 in the amount of 10 wt% to cellulose also reduces the formation of liquid product when compared to the non-catalytic process. In the case of 10 wt% CuCl_2 addition to

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