Bioresource Technology 102 (2011) 9763–9771

Contents lists available at ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

The comparative kinetic analysis of Acetocell and Lignoboost® lignin pyrolysis: The estimation of the distributed reactivity models

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ARTICLE INFO

Article history:
Received 11 February 2011
Received in revised form 20 July 2011
Accepted 20 July 2011
Available online 27 July 2011

Keywords:
Kinetics
Lignin pyrolysis
Reaction order
Distributed reactivity model
Weibull

ABSTRACT

The non-isothermal pyrolysis kinetics of Acetocell (the organosolv) and Lignoboost® (kraft) lignins, in an inert atmosphere, have been studied by thermogravimetric analysis. Using isoconversional analysis, it was concluded that the apparent activation energy for all lignins strongly depends on conversion, showing that the pyrolysis of lignins is not a single chemical process. It was identified that the pyrolysis process of Acetocell and Lignoboost® lignin takes place over three reaction steps, which was confirmed by appearance of the corresponding isokinetic relationships (IKR). It was found that major pyrolysis stage of both lignins is characterized by stilbene pyrolysis reactions, which were subsequently followed by decomposition reactions of products derived from the stilbene pyrolytic process. It was concluded that non-isothermal pyrolysis of Acetocell and Lignoboost® lignins can be best described by *n*-th ($n > 1$) reaction order kinetics, using the Weibull mixture model (as distributed reactivity model) with alternating shape parameters.

1. Introduction

Lignin is, together with cellulose, one of the main components of the natural organic material from which coal and some other type of solid fossil fuels had been formed. After cellulose, lignins are the most widely occurring compounds of biological origin. However, in contrast to cellulose, which is a polymeric compound with a specific set of characteristics, lignin is a macromolecular organic compound of indeterminate chemical and physical structure. This is an irregular, strongly branched heteropolymer of complex structure, whose empirical formula depends on the type of wood, method of its processing, and recovery prehistory.

Lignin is one of the most important constituents of biomass and, among the group of renewable polymers, only cellulose overcomes its natural abundance. Lignin can be defined as a three-dimensional amorphous macromolecule made of phenylpropane units that arise from the copolymerization of three primary precursors: coniferyl alcohol, sinapyl alcohol and *p*-coumaryl alcohol (Nimz et al., 1981). Coumaryl alcohol, coniferyl alcohol and sinapyl alcohol are called monolignols and are linked together by different ether and carbon–carbon bonds forming a three-dimensional network (Henriksson, 2007). In the lignin structure, the monolignols are presented in the form of *p*-hydroxylphenol, guaiacyl and syringyl residues. The most common lignin bond is the β-*O*-4′ linkage (Henriksson, 2007), which constitutes about 50% in softwood and 60% in hardwood of the total linkages (Sjöström, 1993). Of the hardwood β-*O*-4′ linkages, about 40% are of guaiacyl type and 60% of syringyl type (Sjöström, 1993). About two-thirds of the linkages in a lignin polymer are ether linkages, and about one-third are carbon–carbon linkages. Another important functional group in lignins is the free phenolic group (Henriksson, 2007). The characteristic functional groups in lignin are phenolic hydroxyl groups, methoxyl groups and some terminal aldehyde groups, which are important for the reactivity of the lignin (Sjöström, 1993). Of the aromatic rings in lignin, only about 10–13% of the oxygen in the 4-carbon position are free phenolic and the others form ether bonds (Henriksson, 2007). The content of phenols is important during biodegradation and bleaching since it is the most reactivity site in lignin. The carbon–carbon bonds are generally more stable compared to the ether bonds and often resist processes such as the chemical pulping (Henriksson, 2007).

To use lignin as a material, it must be removed from the wood. The structure of lignin differs with the source of wood, the process of dissolving the lignin from the wood and the isolation process. The dissolving of lignin is often performed by pulping for paper making, where the lignin becomes a by-product. However, only about 1.1 million tons/year of lignin are used commercially – just 2% of the available resource, mostly in very low value applications. Lignin is interesting because it is one of the few naturally-produced aromatic chemical precursors. Several processes are being considered for refining lignin, including supercritical water (Wahyudiono et al., 2008), formic acid hydrolysis (Kleinert and Barth, 2008),

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doi:10.1016/j.biortech.2011.07.080

reactions in a ionic liquids (Binder et al., 2009) and pyrolysis (Iatridis and Gavalas, 1979; Caballero et al., 1996; Ferdous et al., 2002; de Wild et al., 2009; Haensel et al., 2009; Nowakowski et al., 2010; Shen et al., 2010).

Pyrolysis is a thermal degradation process of organic compounds, for biomass example, in the absence of oxygen, which produces gas, tar and char residues. Depending on the conditions (heating rate, temperature, particle size etc.) the product distribution can be adjusted and optimized. Pyrolysis of lignin directly yields useful and valuable products that are currently extracted from non-renewable fossil fuel resources. These include phenolic compounds (such as guaiacol, 2,6-dimethylphenol, phenol and syringol) that are used as precursors and chemical reagents in a wide range of applications. Other derivatives include aromatic hydrocarbon products, such as benzene, toluene, and naphthalene. To increase the renewability and sustainability of chemical-based industries, it would be valuable to increase the proportion of chemicals derived from pyrolysis of lignin.

In most cases, the research efforts focused on lignin pyrolysis to obtain the corresponding kinetic parameters (Jiang et al., 2010a). Understanding kinetics of lignin pyrolysis is important to better explain the underlying processes and to provide useful information for rational design and scaling-up of pyrolysis reactors. Knowledge of kinetics of lignin thermal degradation is fundamental for predicting pyrolysis behavior of this material. Furthermore, TG (thermogravimetric) data reported by different authors (Jiang et al., 2010a) broadly disagree – mostly due to differences in chemical compositions, heating rate, experimental conditions and devices. A further complicating factor is the way in which the lignin is extracted from biomass as the initial lignin structure could be partly modified during the extraction phase.

In this study, using detailed kinetic analysis, the kinetic parameters of pyrolysis processes for two different types of lignin's (the organosolv lignin – Acetocell and Lignoboost® lignin) were derived. The calculated kinetic parameters for both lignins are discussed from the mechanistic point of view. In literature, there is no detailed discussion about kinetic parameters from a mechanistic point of view for Acetocell and Lignoboost® pyrolysis processes. Also, based on the obtained kinetic results, the corresponding distributed reactivity models (DRM) (Burnham and Braun, 1999) for considered lignins were estimated.

In the present work, the comparative kinetic analysis of Acetocell and Lignoboost® pyrolysis processes was carried out, using non-isothermal (dynamic) thermogravimetric (TG) technique at low, medium, and high values of heating rates.

2. Experimental

2.1. Methods

Acetocell lignin (the organosolv lignin) is produced by the so-called Acetocell process, in which Monterey Pine (Pinus radiata D. Don) wood chips received from South Africa (Western Cape) are defiberized, using an aqueous mixture of 87 wt.% acetic acid at 190 °C for two hours (Suess, 2010). The dissolved lignin is precipitated by diluting the spent pulping liquor with water. The filtered lignin is washed with water. Since the pulping method is the sulfur and sodium free, the Acetocell lignin has low ash and contains almost no sulfur.

Lignoboost® is a kraft lignin precipitated from the spent cooked liquor by acidification using carbon dioxide gas (Wallmo et al., 2009). Therefore has a relatively low sodium content and contains the covalently bound sulfur originating from the kraft process (Nagy et al., 2010). The high moisture content of Lignoboost® is due to the hygroscopic nature of kraft black liquor as a result of sodium salts and residual sulfuric acid, which is used in the final washing step of the production process (Wallmo et al., 2009).

The results of the elemental analysis of lignins, which were used for this study are given in Table 1.

2.2. Thermogravimetric (TG) analysis

A thermogravimetric analyzer (TA Instruments SDT 2960 device capable for simultaneous TGA-DTA (DTA abbreviations mean Differential Thermal Analysis, which detects temperature (temperature difference)) analysis) was used to study the pyrolysis of Acetocell and Lignoboost® lignins. All lignins for the measurements were used in powder form. The experiments were conducted with approximately 12 mg samples whose particle size is less than 42.5 μm (after drying, the lignins were crushed and sieved to obtain a particle size less than 42.5 μm), and then transferred onto platinum pans in order to minimize heat and mass transfer effects during measurements. The thermocouple in analyzer used for temperature measurement was located just below the pan in the sample carrier. In order to account for buoyancy effects, a correction curve with empty pans was first obtained and then subtracted from the experimental results. No lids were used on the top of the pans. Temperature calibration, baseline calibration and mass calibration experiments were done as to each condition, according to the manufacturer-provided manual.

Nitrogen (liquid N_2 boil – off) flowing at $\varphi = 20\ \mathrm{mL\ min^{-1}}$ was used as the reaction atmosphere. The non-isothermal scans were performed at selected heating rates (β) of 5 °C $\mathrm{min^{-1}}$ (low value), 15 °C $\mathrm{min^{-1}}$ (medium value) and 40 °C $\mathrm{min^{-1}}$ (high value), through a linear temperature increase with time. Samples were heated from room temperature up to 900 °C. Duplicate runs were made under similar conditions and it was found that the data overlaps with each other, indicating satisfactory reproducibility.

3. Theoretical background

Mass loss data from the thermogravimetric analysis can be recalculated into conversion (α) which is defined as follows (Weerachanchai et al., 2010):

$$\alpha = \frac{m_o - m}{m_o - m_\infty} \tag{1}$$

where m_o is the initial mass of sample (which contains the present moisture), m is the actual sample mass and m_∞ is the residual mass after pyrolysis. It can be pointed out that the moisture content values on the order of 50 to 100% are effective in retarding the rate of pyrolysis process because of the large amount of supplied heat

Table 1
Ultimate analysis of Acetocell and Lignoboost® lignins.

Lignin	Wt% [a]						
	C	N	H	O	S	Ash	Moisture
Acetocell	66.45	Less than 0.5	5.05	26.55	Less than 0.05	1.85	3.35
Lignoboost®	67.36	Less than 0.5	5.59	22.37	2.82	1.35	28.48

[a] Each value is on dry basis except moisture.