Detailed compositional analysis and structural investigation of a bio-oil from microwave pyrolysis of kraft lignin

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ABSTRACT

This work investigates composition and structure of a bio-oil produced form microwave pyrolysis of kraft lignin at different conditions. The studied variables were content of microwave-absorber (20–40 wt%) and nominal setting power (1.5–2.7 kW). The measured temperatures after applying the selected conditions for 800 s were 900, 980, 1065, 1150, and 1240 K. The obtained yields of the aqueous phase, oil phase, non-condensable gas, and solid were 17–21%, 15–20%, 21–27%, and 32–40%, respectively. To investigate the extracted chemicals quantitatively and qualitatively, GC–MS and GC–FID were performed on the liquid samples. In addition, ^{31}P and ^{13}C NMR spectroscopy were implemented to provide detailed structure information for the whole oil phase and the raw material. Furthermore, different degradation pathways were suggested to represent the thermal-decomposition of lignin bonds.

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1. Introduction

Recently, biomass has been employed as a renewable resource of value-added bio-chemicals. Developing bio-chemicals is one opportunity for dealing with the unexpected challenges that have faced the forest industry in North America for the past few years, such as decreasing demand and competition with low cost sources of wood. As well, generating energy from biomass is one way to compensate for the rapid increase in energy demand expected in the next few years.

Lignocellulosic biomass is composed of three intertwined components: cellulose, hemicellulose, and lignin. The dry basis weight of each is 35–45%, 25–30%, and 20–35%, respectively [1–3]. This distribution depends on the species, the environment in which it was grown, and other factors. Lignin is recognized to result from the polymerization of three aromatic alcohols: *p*-coumaryl, coniferyl, and sinapyl alcohol, as depicted in Fig. 1 [1,3,4].

Even though lignin is the only renewable source of aromatics in nature and the third-most abundant natural polymer after cellulose and hemicellulose, it has received less attention in research than the other biomass components. In addition, the annual production of lignin in the US paper industry is over 50 million tons, yet only

2% of this material is converted to bio-products, whereas the rest is combusted to recover energy and chemicals Farag et al. [5].

Lignin can be converted into chemicals and/or energy using chemical, biological, or physical technology. One of the techniques applied in thermal technology is pyrolysis. Pyrolysis is a thermal decomposition of chemical bonds by supplying heat energy in an oxygen-free environment. The main pyrolysis products are: (1) solid, mostly carbon, which can be used as a solid fuel, soil additive, and other applications. (2) Condensable gas, which is a potential source for value added chemicals that could replace petrochemicals; and (3) non-condensable gas [1,6]. The needed heat energy for pyrolysis can be provided by heat transfer from a heating source. Otherwise, it can be generated within the heated material by an electromagnetic exposure (microwave heating). This pyrolysis is called "microwave pyrolysis" (MW-P).

Microwave heating (MWH) is a volumetric energy conversion mechanism within the target material rather than superficial heat transfer as in conventional heating (CH). MWH has been established in different sectors as it can eliminate several issues/limitations in contrast to CH such as formation of a temperature gradient inside and outside the heated material, and char layer formation of pyrolysis material. Furthermore, it has been demonstrated that a desired temperature gradient and/or hot or cold spots can be generated within the payload in a simple way, compared to CH [7]. Further details regarding MWH can be found in Farag et al. [7].
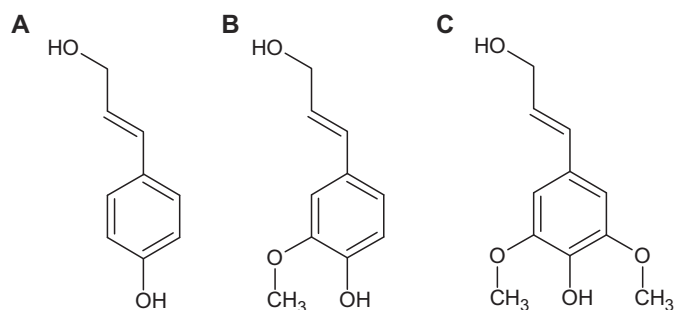
Fig. 1. The three monolignols of a lignin network: (A) coumaryl alcohol, (B) coniferyl alcohol, and (C) sinapyl alcohol.

Table 1
The coded vales and the corresponding actual values and final temperatures applied in MW-P of kraft lignin.

Run #	Coded value		Actual value		Final temperature [K]
	Char wt%	Nominal Power	Char wt%	Nominal power [kW]	
1	−1	−1	20	1.5	900
2	−1	1	20	2.7	980
3	0	0	30	2.1	1065
4	1	−1	40	1.5	1150
5	1	1	40	2.7	1240

Pyrolysis of lignin and characterization of the liquid product have been investigated over the past two decades. Zheng et al. [8] have examined fast pyrolysis of lignin under the catalytic effect of Mo_2N/γ-Al_2O_3, using a pyrolysis–gas chromatography/mass spectrometry system (Py–GC–MS). The same analytical technique was used by Lou et al. [9] to study the effect of temperature and catalysts (sodium chloride, permutite) on the pyrolysis of bamboo lignin and Jiang et al. [10] to discuss the temperature dependence of the composition of lignin pyrolysis products. Choi and Meier [11] investigated the pyrolysis of kraft lignin under the effect of different temperatures and catalysts (Zeolite HZSM-5, FCC and Olivine), employing GC–MS/GC–FID to analyze the liquid product. Py–GC–MS and TGA/FTIR were used by Zhang et al. [12], to study the pyrolysis of three lignin types: prairie cord grass, aspen, and synthetic kraft lignin. De Wild et al. [1] examined the pyrolyis of lignin from two different biomass sources using a fluidized bed reactor, employing GC–MS to analyze the liquid product. Luo et al. [13] have discussed the thermal behavior of organosolv lignin under the catalytic effect of zeolites, using TGA-FTIR.

As has been shown, most of the previous work has been done by employing GC–MS and/or FT-IR to analyze the obtained liquid. Nevertheless, the complexity of the pyrolysis crude liquid limits the use of these instruments due to different issues and consequently many chemical components could not be identified. Therefore, the main goal of the present study was to investigate the structures of kraft lignin pyrolysis liquids under different MW-P conditions. This was accomplished using quantitative NMR to analyze the liquid products and the raw material as it can provide detailed structural information. Such investigations improve understanding about MW-P mechanisms, which leads to more control in the degradation pathways.

2. Experimental work

2.1. Raw material

The raw material used in this work was softwood kraft lignin supplied by FPInnovations, Pointe-Claire, Quebec, Canada. It was precipitated from a Canadian kraft mill using The LignoForce System, a patent-pending process that was developed by FPInnovations and licensed to NORAM Engineers and Constructors, Vancouver, British Columbia, Canada, for commercialization.

Lignin was characterized via CHNS analysis: C = 63.27%, H = 5.79%, N = 0.07%, and S = 1.56%, and proximate analysis: fixed carbon = 37%, volatiles = 62%, and ash = 1%. In addition, it was analyzed using quantitative ^{13}C NMR and ^{31}P NMR spectroscopy as will be shown later.

Indeed, lignin does not interact well with electromagnetic waves (EMW). Therefore, it was homogeneously mixed with a good microwave-to-heat convertor, the solid product after MW-P of kraft lignin, which is a strong microwave-to-heat convertor [14-16]. If

char is absent, the extracted product is expelled from the lignin particles, forming an exceedingly sticky material. Finally, after cooling, the formed material converts into a very strong block, which is extremely difficult to break down [5].

2.2. Experimental design

To study the effect of MW-P conditions on product distribution and crude liquid structure, a central composite experimental design method was applied. This method gave the optimal number of experiments as well as the conditions of each. In this work, two independent parameters were chosen (A_i): (1) the concentration of a MW-thermal-catalyst (A_1 [wt%]) with $A_{1,min} = 20$ and $A_{1,max} = 40$ in the total initial mass (lignin + char) and (2) the MW-nominal setting power (A_2 [kW]) with $A_{2,min} = 1.5$ and $A_{2,max} = 2.7$. The variables A_i were coded as a_i according to Eq. (1).

$$a_i = \frac{A_i - A_o}{\Delta A} \tag{1}$$

where a_i is a dimensionless coded value, A_i is the real value of an independent variable, and A_o is the real value of the independent variable at the center point (0,0). ΔA is the step change, which equals 10 for the first parameter and 0.6 for the second one. Table 1 shows the coded and actual values for the independent parameters. In order to guarantee the reproducibility, each experiment was repeated three times, and the average value was represented as will be shown later.

2.3. Experimental setup

The experimental work was carried out in a bench scale Microwave-oven (MW-O) (Microwave Research Inc; Model: BP-211, 230 V, 2.45 GHz, and setting power up to 3.2 kW). The oven cavity has inner dimensions of 510 × 250 × 320 mm. As electronic devices are highly affected by the surrounding temperature, an alumina box (muffle) with the dimensions of 390 × 180 × 170 mm was kept inside the oven cavity during the heating. This muffle protects the oven's electronic devices from most of the emitted heat and unwanted/unexpected explosions, or combustion during MW-P. A quartz semi-batch cylinder reactor with the dimensions of ID: 70 mm and L: 250 mm was used after connecting it to a condensation system to collect the condensable gas while the non-condensable gas passes directly through, as shown in Fig. 2.

The employed condensation system consists of a set of vertical metallic tubes. These tubes were connected in series at one end while the other ends were connected via a 500 mL two neck Pyrex flask. The reactor outlet was connected to the condensation system via a metallic connection. This connection was kept at 200 °C, to avoid any condensation before the freezing zone.

Temperature measurement was done using the innovated thermometer that was used in Farag and Chaouki [17]; refer to that