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Research paper

Impact of the heating mechanism on the yield and composition of bio-oil from pyrolysis of kraft lignin

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ABSTRACT

The aim of this work is to differentiate between the yield and composition of bio-oils obtained from microwave and conventional pyrolysis of kraft lignin. Four different conditions were performed, microwave and conventional pyrolysis with and without mixing the raw material with a strong microwave receptor. The key findings of this work include that applying microwaves in pyrolysis applications leads to preserving the structure of the obtained products, which consequently enhances the product selectivity. As a result, the liquid product from the pyrolysis of lignin contains 40% more chemicals, and 27% less water than that of the conventional pyrolysis. The impact of electromagnetic waves on the quantitative aspect is not considerable as the difference between the liquid yields from both techniques is slight. Increasing the heating rate and/or the residence time, particularly in conventional pyrolysis, makes secondary reactions play a vital role in decomposing and/or combining the obtained aromatic hydrocarbons.

1. Introduction

As a consequence of the shortage of traditional resources and escalating stringent environmental constraints, the feedstocks of several industrial processes are swiftly changing. For example, blends of different materials, such as wastes, biomasses, coal, etc., are the typical feedstocks for the production of energy and/or chemicals. This aspect makes developing new technologies that can conserve natural resources, accept the intrinsic variability of feedstocks, and be safe and green, in addition to other demands, a must to fulfill the increasing needs of society. To achieve this objective, it is extremely important to well understand the proposed new technologies and carefully evaluate their performance and impacts on the end-products compared to the traditional processes.

Converting electromagnetic radiation into heat energy within the target material is one of the most promising technologies that can replace conventional heating (CH) to avoid many issues and limitations in numerous applications [1,2]. In the case of non-magnetic material, the mechanism of microwave heating (MWH) depends on the reorientation of the dipoles of the exposed payload that try to be in phase with the alternating field. Since the agitated molecules do not have the ability to reorient themselves as rapidly as the reversing field, a phase shift is created between the orientation and electric field. This creates random collisions between the oriented molecules and each other, which is the major mechanism responsible for releasing heat energy from the target. Respecting the penetration limits of the applied waves and the dimension of the heated material, the conversion of electromagnetic energy to heat takes place within the whole volume of the irradiated object, which explains the main reason why MWH is defined as "a volumetric energy conversion mechanism" [3,4].

The mechanism of MWH, which is different from the superficial heat transfer of CH, has been established in a broad range of applications because employing electromagnetic waves in traditional processes can avoid many issues and limitations associated with CH. The most important ones include temperature gradients inside and outside the heated material and char layer formation, which is common in conventional pyrolysis (CP). The fact that electromagnetic waves only interact with particular types of materials makes the process selective in addition to reducing the amount of heat energy needed to achieve a particular end. Certainly, the latter

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benefit will consequently lead to decreasing the operating costs as well as the potential for thermal hazards. Besides the above-mentioned advantages, MWH is a rapidly initiated and terminated, environmentally friendly, energy-efficient heating process and the most promising technique for enhancing product quantity and quality compared to traditional processes [5–13].

The non-uniformity of the electromagnetic waves inside the oven-cavity affects the temperature gradient within the object, which is one of the rather complex issues related to electromagnetic heating. In addition, if the payload is not a good microwave-to-heat convertor, hybrid heating (i.e., mixing the material with a good microwave-receptor) is required in order to achieve the desirable temperature [14]. Further advantages and disadvantages of MWH can be found in Refs. [1,2,14–16].

Over the last few decades, applying electromagnetic waves in chemical processes has received a staggering amount of attention in academia, which is evident in the growing number of publications in the field. These papers have revealed numerous phenomena that could be fundamental to establishing microwave-based technologies in several industrial sectors. The key conclusions of those investigations of MWH have led to greater reaction rates, higher product yields, and lower energy consumption compared to traditional heating [1,6,11,16–18]. These remarkable findings, consequently, make further efforts essential to understand the differences between the impacts of CH and MWH on chemical reactions. In fact, although plenty of studies aimed to examine the influence of the process parameters on the yield of the end-product, only a modest effort has been made to investigate the effects on selectivity. Therefore, the aim of this work is to compare the products from CP and microwave pyrolysis (MWP) of kraft lignin, which should improve the fundamental understanding of MWH for biomass conversion. Such discussions would provide insight into achieving conversion with less energy input and/or achieving reactions that are not initiated by CH. This, consequently, will facilitate and expedite the development of establishing electromagnetic waves in pyrolysis applications.

2. Experimental work

2.1. Raw material

Softwood kraft lignin was the virgin material used for both MWP and CP experiments, 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, Montreal, Quebec, Canada. The proximate analysis of the virgin material is as follows: fixed carbon = 37% ± 1.41%, volatiles = 62% ± 1.56% and ash = 1% ± 0.14%; the elemental analysis is carbon content = 63.27% ± 0.08%, hydrogen = 5.79% ± 0.10%, nitrogen = 0.07% ± 0.00%, and Sulphur = 1.56% ± 0.01%. The presented standard deviations in the above-mentioned analyses were calculated based on two repetitions, in total three measurements. To identify the concentration of the carbon atoms and OH groups, ^{13}C and ^{31}P NMR analyses were performed on the virgin material and reported in Ref. [19] and, therefore, not be presented here.

Since lignin does not have excellent dielectric properties, in particular dielectric loss factor, it does not interact well with electromagnetic waves. The measured dielectric loss factor of lignin is 0.5 compared to 2.3 for char, using a "microwave and millimeter-wave vector network analyzer" (Anritsu 37369D Microwave, 2-Port Vector Network Analyzer, 40 MHz to 40 GHz), and a circular resonance cavity at 2.45 GHz. This means, if enough heat energy is not provided for decomposing the lignin network, the extracted product is expelled from the lignin particles in the form of a tar-like product. After cooling, eventually the heated material is converted into an extremely sticky block with expanded dimensions that is very difficult to break down. Fig. 1-A shows the starting material, which fills two thirds of the spherical volume of the reactor, before performing MWP. Fig. 1-B displays the virgin material after applying MWP when no char was first mixed with it before performing the pyrolysis process. The volume of the material expanded up to twofold the initial volume and became one block taking the same form as the reactor. Fig. 1-C demonstrates the char product that is shown in Fig. 1-B after breakdown the reactor in order to extract the char.

To overcome this issue, a hybrid heating technique was applied. The starting material was first mixed with the solid product from the pyrolysis of lignin (char) as it contains 90% carbon and, thus, is an excellent microwave receptor, Fig. 1-D. A certain concentration of char (C_{ch}) was used to fulfill the requirements of two aspects, enhance the microwave-to-heat conversion, and achieve the same heating rate, 50 °C min^{-1}, maximum temperature, 800 °C, and holding time, 10 min, as the CP0. In addition, to better understand the effect of char on the obtained products, two other experiments were performed, CP with char and MWP without char.

To calculate the yield of the solid product, the mass of char that is initially mixed with the raw materials is deducted from the remaining solid. Thus, the solid product yield = (the mass of the remaining solid after the experiment − the mass of the char that is initially mixed with lignin)/the initial mass of lignin.

2.2. Experimental setup

Microwave pyrolysis of lignin was carried out using a bench-scale microwave oven (Microwave Research Inc.; Model BP-211, 230 V, 2.45 GHz, and power setting up to 3.2 kW), Fig. 2-A. In order to connect the inlet and outlet lines to the reactor, two opposing holes were drilled into the oven's side-walls. The dimensions of these holes were specifically chosen to prevent any microwave leakages during the irradiation period. To protect the oven's electronic devices from any unexpected combustion and the emitted heat during the pyrolysis process, an alumina box (muffle) was used inside the oven cavity. Temperature measurements were done using an innovated thermometer that was presented in Farag and Chaouki 2014 [16]. This thermometer is called air-thermometer and measures the bulk temperature of a material exposed to electromagnetic irradiation. It is based on the relationship between the pressure and temperature of a constant volume of gas. The air-thermometer is made of quartz and, therefore, there is almost zero interaction between the thermometer's probe and the microwaves. Kindly refer to reference [16] for a detailed description, calibration, and validation of the thermometer.

In both MWP and CP, a quartz semi-batch reactor was used after connecting it to a condensation system. The limitations of the penetration depth, in the case of MWP, were carefully considered while designing the reactor and choosing the sample vol/wt. A set of vertical heat exchangers connected in series and maintained at −18 °C was used to collect the condensable pyrolysis vapour, as shown in Fig. 2-C. The connection between the outlet of the reactor and the condensation system was kept at 200 °C to ensure that there was not any condensation prior to the quenching zone.

As demonstrated in Fig. 2-B, a conventional furnace was used to perform the CP experiments. Several thermometers were distributed at different positions within the target material in order to record the transit temperatures. In the CP experiments, the oven was first heated to the target temperature and then kept at its value. The reactor was then introduced inside the oven after perfectly purging it with nitrogen to avoid the potential impact of oxygen. A defined flow rate, 100 cm^3 min^{-1}, of the inert gas, N_2, was

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