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Microwave pyrolysis of cellulose at low temperature

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ABSTRACT

Microwave pyrolysis of cellulose was successfully achieved at low temperature (200–280 °C) using a lab-scale microwave synthesis system. Both closed and open microwave setups were developed to measure yields of pyrolysis products and to characterize the bio-oil. The effect of temperature, type of cellulose (crystalline and amorphous), and microwave absorber were examined. Microwave-derived bio-oil compositions were compared to conventional pyrolysis (microfurnace pyrolyzer–GC/MS) under similar heating rates. Maximum bio-oil yield (45%) was obtained from amorphous cellulose at 260 °C using an open system. Addition of water significantly increased the bio-oil yield to 52% (amorphous) and to 47% (crystalline) while addition of activated carbon had the effect of increasing gaseous products. Microwave-derived bio-oil products varied in chemical nature and abundance depending on cellulose crystallinity and between open or closed microwave pyrolysis and showed significant differences from conventional pyrolysis bio-oil. High yields of levoglucosan were obtained from amorphous cellulose at 260 °C while conventional pyrolysis required a much higher temperature (400 °C).

1. Introduction

Lignocellulosic biomass is an important feedstock for thermo-conversion for fuel and chemical production [1]. Moreover, the products derived from it are a renewable and green source of energy [2]. The main components of biomass are cellulose, hemicellulose, and lignin, cellulose being the most abundant. The pyrolysis behavior of cellulose is thus important in understanding the more complex pyrolytic behavior of lignocellulosic biomass.

Cellulose is a polysaccharide consisting of D-glucose units with glycosidic bonds that are formed between monomeric units at positions 1 and 4. Cellulose material includes high ordered (crystalline) and low ordered (amorphous) regions and ratio between these regions is dependent on its source [3]. Hydroxyl groups in cellulose can create intra and intermolecular hydrogen bonds which greatly affect the crystallinity arrangements in cellulosic structure [4]. The degree of cystallinity affects not just its physical and chemical properties such as accessibility for derivatization, swelling, and water bonding [5] but also its pyrolysis pathway. For example, Py–GC/MS of amorphous cellulose at low temperature produces much higher amounts of levoglucosan than highly crystalline cellulose and at higher temperatures amorphous cellulose shows higher levoglucosenone, and 1,4:3,6-dianhydro-glucopyranose products [6]. The mechanism of lignocellulosic pyrolysis includes dehydration, cracking, isomerization, dehydrogenation, aromatization, condensation reactions, and rearrangements [7]. However for cellulose, according to the Broido-Shafizadeh model, pyrolysis involves two sequential stages: (1) formation of active cellulose and (2) production of char and gases or volatiles [8]. The decomposition of active cellulose produces levoglucosan through the dehydration and condensation mechanism [9,11].

Pyrolysis of biomass can also be achieved by microwave heating. Conventional thermal heating involves energy transfer from source to target via radiation, convection, and conduction, while in microwave heating electromagnetic energy is converted to thermal energy within the sample. Therefore, microwave heating is energy conversion instead of heat transfer [10] and it has been shown to be a viable alternative for biomass pyrolysis [11]. Compared to conventional pyrolysis, microwave pyrolysis (MP) of solids can save time and can be done selectively by heating polar materials and creating hot spots inside the sample. Furthermore, microwave heating can be described as a non-contact, volumetric, rapid, safe [12], clean, and cheap heating method [13].

There are only a few studies on the microwave of cellulose. In one study, low bio-oil yield (8%) was obtained under 12 min irradiation time and 620 W microwave power [14]. Budarin et al. examined the microwave-assisted decomposition of cellulose and it was determined that the amorphous region showed thermal degradation as low as 180 °C producing a useful biochar product [15]. No microwave absorber was used in either study.

In spite of its advantages, MP produces lower yields of bio-oil (<30%) than fast pyrolysis (60–70%) from wood [16]. With a microwave absorber such as char, the bio-oil yield from MP of biomass can reach up to 40% [17]. Microwave irradiation was

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successfully used for pyrolysis of wheat straw [18], sewage sludge [19–21], coffee hulls [22], larch [23], pine wood sawdust [24], peanut shell, maize stalk [25], rice straw [26,27], wheat straw pellets [28], corn stover pellets [29], aspen pellets [30], algae [31], distillers dried grain [32], douglas fir [33] and oil palm fiber [17]. Moreover, microwave heating was used for biomass drying before conventional pyrolysis. This pre-treatment was found to increase the yield of bio-oil and char while decreasing the gas yield [25].

Microwave vs. conventional pyrolysis were compared for biogas production with various feedstocks such as wheat straw, softwood pelletized, waste office paper, and macroalgae. MP was achieved at low temperature (120–180 °C) MP and at 250–400 °C for conventional pyrolysis [11]. The main gaseous components were CO_2, CH_4, CO, acetic acid, formic acid, acetaldehyde, and formaldehyde. These results showed the importance of comparing MP results with conventional pyrolysis and detailing the advantages and drawbacks of MP of biomass.

In contrast to previous work on MP of cellulose, the present work, for first time, compares closed vs open microwave heating of cellulose at low temperatures in addition to comparison of bio-oil products between low temperature MP and conventional pyrolysis. Effect of cellulose crystallinity and microwave absorbers on low temperature MP of cellulose were also examined for first time.

The ability of biomass and cellulose material to absorb microwave irradiation is poor [34]. Therefore, microwave absorbers such as water and carbon-based materials have been used to improve the microwave absorption efficiency. A materials ability to absorb microwave irradiation is dependent on the dielectric loss tangent (tan δ). For example, water is a good microwave absorber and it has tan δ of ~0.1 while carbon materials such as activated carbon have a higher tan δ in the range of 0.1–0.8 [35]. This study examines the differences (and benefits) in yields and bio-oil composition of MP of cellulose with and without the addition of absorbers.

The objectives of this study were to examine the ability of microwave irradiation (300 W; small sample cavity) to pyrolysis cellulose at low temperature (200–280 °C), to determine suitable conditions (i.e. pyrolysis temperature, cellulose type, and microwave system) for bio-oil production and to examine the effect of microwave absorbers. This study also examined the differences in bio-oil composition between MP and conventional pyrolysis.

2. Experimental

2.1. Materials

Microcrystalline cellulose (Sigma–Aldrich, 50 μm), amorphous cellulose from a socklet thimble paper (Fisher Scientific, 1 mm pieces), activated carbon (Fisher Scientific, 50–200 mesh), C_{18} cartridge (Supelco Envi-18, 6 mL tube) and HPLC-grade methanol (Sigma–Aldrich) were used as received.

2.2. Experimental methods

2.2.1. Closed and open microwave system

Pyrolysis was carried out using a microwave synthesis system (CEM Discover SP; Fig. 1) at max. microwave power of 300 W at set

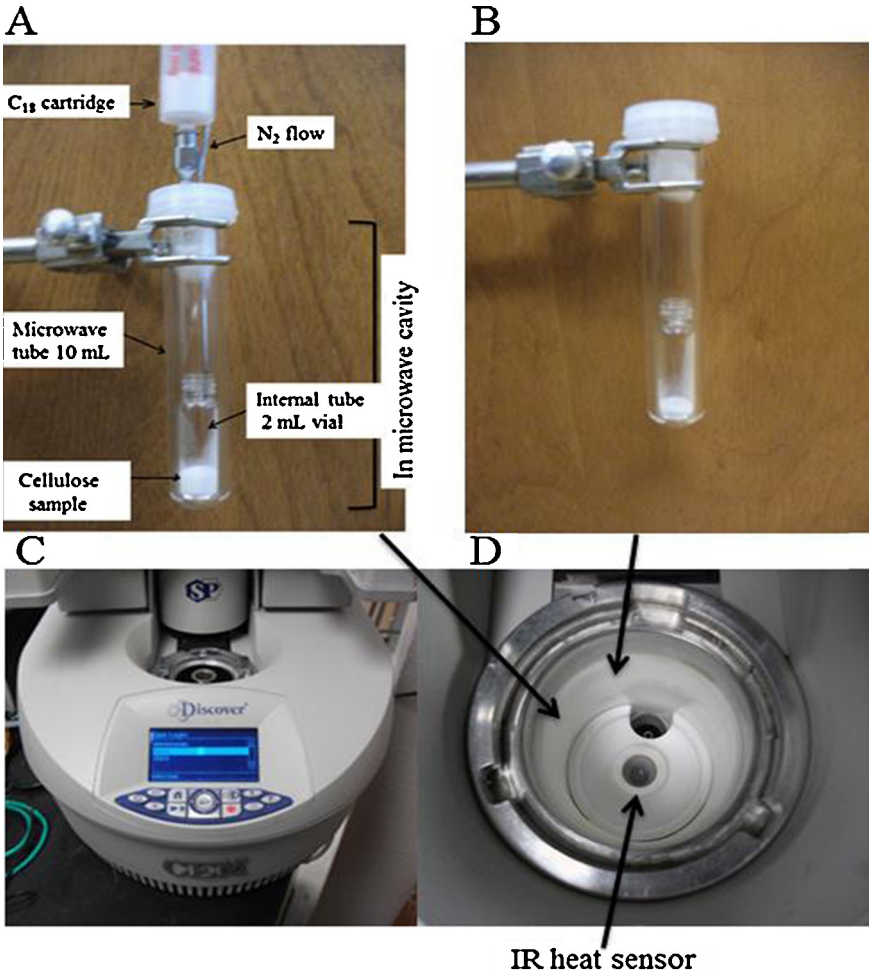

Fig. 1. Microwave apparatus for cellulose pyrolysis. (A) Open system, (B) closed system, (C) the microwave synthesis system and (D) inside microwave cavity. The clamp is used only for illustration purposes.