



# Controllable production of liquid and solid biofuels by doping-free, microwave-assisted, pressurised pyrolysis of hemicellulose



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## ABSTRACT

Batch, pressurised microwave-assisted pyrolysis of hemicellulose in the absence of any external microwave absorber was found to be a promising route for the production of bio-based chemicals and biofuels. The experiments were conducted in a 10 mL batch reactor using a fixed power of 200 W employing different initial masses of xylan (0.1–0.7 g) for a maximum time, temperature and pressure of 10 min, 250 °C and 200 psi, respectively. The gas, bio-oil and solid (char) yields varied by 16–40%, 2–21% and 40–82%, respectively. Char production is preferential using a low amount of xylan (<0.25 g), while bio-oil production is favoured using a high amount of xylan (0.25–0.7 g). The effect of the sample mass is accounted for by the different physical state of the volatiles released during pyrolysis depending on the pressure attained during the experiment. This permits the process to be easily customised for the selective production of liquid (bio-oil) or solid (bio-char). Regarding the bio-oil, it is composed of a mixture of platform chemicals such as aldehydes, alkenes, phenols, polyaromatic hydrocarbons (PAHC), cyclic ketones and furans, with the composition varying depending on the initial mass of xylan. The char had a higher proportion of C together with a lower proportion of O than the original feedstock. Energy efficiencies of 100 and 26% were achieved for char and bio-oil production, respectively; thus leading to an increase in the HHV of the products (with respect to the original feedstock) of 52% for char and 19% for bio-oil.

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## 1. Introduction

Renewable biomass as sources of chemicals and energy is set to increase with the excessive use and depletion of fossil fuels. In this context, the development of second generation biorefineries and utilisation of renewable resources, such as lignocellulosic biomass, is seen as one of the most efficient ways to achieve this goal [1]. Biofuels produced from lignocellulosic biomass have lower life-cycle greenhouse gas emissions compared to fossil fuels [2]. However, the utilisation of the lignocellulosic feedstock (LCF) is challenging due to both its diversity and variable cost (physical properties, chemical composition, collection logistics, etc.) [3]. This diversity creates challenges to develop replicable biomass supply systems and needs specialised conversion technologies to convert it to bio-power or biochemicals. The properties of LCF can be predicted based on a systematic investigation of the characteristics of the major biomass structural components, such as cellulose, hemicellulose, and lignin [4].

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cellulose, and lignin [4]. Cellulose and its decomposition have been well documented, while further investigation into lignin and hemicellulose pyrolysis is still challenging due to their more varied and complicated structure [5–7].

Hemicellulose is the second most abundant natural biopolymer after cellulose, and it consists of a diverse group of heterogeneous  $\beta$ -(1,4)-linked polysaccharides [8]. As regards to its chemical composition, hemicellulose can be classified into four types: xylans, mannans, xyloglucans, and  $\beta$ -Glucans, depending on its backbone chain composition [9]. Amongst the different types of hemicellulose, xylan is the most abundant, accounting for more than 30% of the total renewable biomass content [10]. Therefore, a detailed investigation into its properties will be essential for modern zero waste biorefinery processes.

One route that has been widely accepted as an attractive way to generate biofuels from biomass is pyrolysis, a thermochemical conversion method [11]. During the pyrolysis of biomass, it is well established that higher heating rates and higher final temperatures favour the production of gases and low molecular weight bio-oil fractions, while low heating rates and lower temperatures favour

the production of char and higher molecular weight bio-oils fractions [12]; thus converting this process into a tailor-made route for the valorisation of biomass. However, the heat efficiency of this thermochemical route is one of its major issues for the development of this technology, and the efficiency of this heating method depends on the thermal conductivity and convection current of the material which converts it into a slow and low efficient process for the valorisation of biomass [11].

Microwave irradiation has been shown to be a promising alternative to increasing the efficiency of the pyrolysis of biomass [13]. This method can provide energy efficient high rates of heating due to its controllability, selectivity as well as its non-contact and volumetric mechanism of interaction with the biomass [14]. This occurs due to the direct interaction of the microwave electromagnetic field with the ions and dipoles within the biomass source [15–17]. In particular, within the biomass, it is commonly assumed that water is the best microwave absorber [18,19] and the dry vegetation relatively microwave passive [20].

A possible solution to overcome this limitation is the use of microwave absorbents, such as, activated carbon, graphite and silica carbide [21,22]. Nevertheless, the addition of these types of external absorbents is a barrier to the industrial development. This impregnation not only is expensive but also it could create heterogeneous distributions within the biomass, resulting in the formation of ‘hotspots’, leading to non-uniform heating process and resultant unpredictable pyrolysis reaction mechanism [23].

Nevertheless, there are several publications that highlight the fact that the structural components of biomass alone and/or their products of decomposition are microwave active at high temperature. In particular, additive free microwave assisted pyrolysis of lignocellulosic feedstocks has been demonstrated for wood pellets [20], rice straw [24], corn stover [25], wheat straw [26] and rice husk [27]. Though, as these biomasses have different amounts of cellulose, hemicellulose and lignin along with some microwave active inorganics, the biomass structural compound or compounds responsible for the microwave activity of these feedstocks is not yet completely understood. Therefore, it is necessary to understand the behaviour of the biomass structural components alone to gain a depth insight into the microwave assisted pyrolysis of biomass. However, the number of works studying the microwave assisted pyrolysis of biomass structural components alone is very limited. Specifically, to the best of the authors’ knowledge, there are only few works studying the microwave pyrolysis of cellulose and lignin without any external microwave absorber, while the microwave pyrolysis of hemicellulose has never been reported. Specifically, Farag et al. [28] analysed the microwave assisted pyrolysis of kraft lignin establishing a comparison between conventional and microwave heating with and without mixing the raw material with a microwave absorber. It was found that microwave heating led to preserving the structure of the obtained products, improving the product selectivity. As regards the microwave assisted pyrolysis of cellulose, Al Shra’ah and Helleur [29] studied the effect of the temperature and the use of external microwave absorbers on the product distribution and the properties of the bio-oil produced from microcrystalline and amorphous cellulose. It was found that an increase in the temperature resulted in an increase in the yield of bio-oil and gas along with a decrease in the biochar yield. While for microcrystalline cellulose higher yields of bio-oil and biochar and a lower yield of gas were obtained in a closed vessel system. Interestingly, no significant differences were found between both setups when using amorphous cellulose. In addition, it was found that for amorphous cellulose the production of biochar and bio-oil was much greater at lower temperatures (<220 °C) than for microcrystalline cellulose due to the stronger intermolecular forces found for crystalline cellulose. This finding was previously reported by other authors [30].

Given this background, the following work addresses pressurised microwave-assisted pyrolysis of hemicellulose in the absence of any external microwave absorber. Different pressurised microwave-assisted pyrolysis experiments were conducted using both, constant microwave power and reaction volume, with various hemicellulose loadings. This permitted the analyses of how and to what extent the reaction pressure and the presence of pyrolysis decomposition products (which can act as good microwave absorbers) affect the microwave process efficiency and product selectivity. Bearing in mind that the absorber-free, microwave pyrolysis of hemicellulose has never been reported before, and the works dealing with the microwave pyrolysis of cellulose and lignin are scarce, this work represents a novel and challenging investigation not only for the valorisation of hemicellulose but also for the understanding of the behaviour of biomass under microwave heating.

## 2. Materials and methods

### 2.1. Feedstock

Xylan extracted from beech wood (cell wall polysaccharide, >90% xylose residues), having a particle size ranged from 50 to 600 µm, was purchased from Sigma-Aldrich and used as received.

### 2.2. Simultaneous thermal analysis (STA)

Mass loss and heat flow were measured using a Stanton Redcroft STA 625. Approximately 2.5 mg of xylan was added to an aluminium STA sample cup and then placed in the STA for analysis. The experimental conditions for the analysis were as follows: temperature 20–625 °C at 10 °C min<sup>-1</sup> in a 20 mL (STP) min<sup>-1</sup> flow of nitrogen.

### 2.3. TG-IR analysis

A thermogravimetric analyser (Netzsch STA-409 C/3/F) coupled to an FTIR spectroscopy (Brüker Equinox-55 FT-IR) via a narrow bore PTFE transfer line set at 180 °C, and a TASC 414/3 system controller was used to study the pyrolysis behaviour of xylan. The experiment was carried out at a heating rate of 10 °C min<sup>-1</sup> from 25 °C to 625 °C under a constant nitrogen flow of 100 mL (STP) min<sup>-1</sup>. The volatiles released during pyrolysis were immediately transferred to the FTIR gas cell and analysed using a FTIR equipped with an MCT detector within the spectral range of 500–4000 cm<sup>-1</sup> at a resolution of 4 cm<sup>-1</sup>. The spectrum was recorded every 30 s.

### 2.4. Proximate and ultimate analyses

Proximate analyses were performed according to standard methods (ISO-589-1981 for moisture, ISO-1171-1976 for ash and ISO-5623-1974 for volatiles). Elemental analysis based on carbon, hydrogen and nitrogen content was carried out using an Exeter Analytical (Warwick, UK) CE440 Elemental Analyser, calibrated against acetanilide with a S-benzyl-thiuronium chloride internal standard.

### 2.5. GC-MS

The bio-oils were solubilised in methanol, and the 1 µl solution was injected in a Perkin Elmer Claus 500 gas chromatograph coupled to a Perkin Elmer Claus 560 s mass spectrometer. A non-polar ZB-5HT (30 m × 0.25 mm *id* × 0.25 µm film thickness) column from Phenomenex (UK) was used. The oven temperature was maintained at 60 °C for 1 min, then ramped at 10 °C min<sup>-1</sup> until

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