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The potential of microwave technology for the recovery, synthesis and manufacturing of chemicals from bio-wastes

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ABSTRACT

Through a series of case studies it is demonstrated that microwave dielectric heating can be a powerful tool to recover and synthesize valuable molecules from a wide range of biomass types. In addition, under microwave irradiation the production of chemicals from biomass proceeds at markedly lower temperatures (up to 150 °C) compared to conventional heating. This has a secondary benefit in that molecules with a high degree of functionality are produced while conventional heating tends to produce a great proportion of lower value gases. Furthermore, the technical set-up of a microwave reactor can easily accommodate for an *in-situ* separation of acids and valuable products therewith improving the shelf life of the latter. The benefits of combining hydrothermal conditions with microwave irradiation are also illustrated. In addition, a specialized case of selective heating in a biphasic reaction system is discussed, allowing for improved yields and selectivity.

1. Introduction

1.1. Biorefineries concept

The global concern over the future oil supplies is fuelling the return to a bio-based economy with an emphasis on the use of non-food related lignocellulosic waste material [1]. This approach has two principle strategic ambitions: (a) the replacement of imported petroleum by renewable domestic raw materials (the energy goal) and (b) the establishment of a robust bio-based industry (the economic goal). The former is already addressed through the current push for bio-fuels (*e.g.* ethanol, butanol, (algal) biodiesel) displacing a part of the transportation related gasoline and diesel. Despite the high volumes of fuel produced, its relatively low value strongly limits the possible return-on-investment for new bio-fuel related technologies [2]. Therefore, there has also been a push towards the production of value-added chemicals from biomass. These drivers for bio-fuels and bio-derived chemicals are powering the development of new zero-waste biorefinery technologies [3]. Conceptually, a biorefinery applies a hybrid of technologies from different fields including (polymer) chemistry, bio-engineering and agricultural research [4]. In very general terms the biorefinery approach encompasses two major techniques: thermochemical (see Fig. 1) and biochemical [5]. The former is able to accept a wide range of biomass types and convert them into a broad spectrum of chemicals and materials, and as such, forms the basis of this paper. The thermochemical treatment of biomass also holds vast potential to apply cleaner technologies, promoting the use of greener chemical practices [6]. It is typically conducted at elevated temperatures under (a) pyrolytic conditions *i.e.* inert atmosphere or vacuum and with only a limited amount of water present or (b) hydrothermally *i.e.* under significant pressure and in the presence of an excess of water (see Fig. 1).

The products of the thermal treatment of biomass span solids (char), liquids and gases. The yield of these fractions can be controlled by parameters such as rate of heating, temperature, pressure and the presence of additives. Typically, increasing the heating rate facilitates the production of volatiles.

Chemicals can be obtained from both gas and liquid fractions. However, the complete deconstruction of the original biopolymer matrix to gaseous molecules followed by their recombination is energy intensive and less sustainable compared to a tuned direct manufacturing approach. At present the thermochemical route requires high initial capital costs despite the fact that it is fast and able to accept a wide variety of biomass types. The costs relate to the micronization of the biomass, a very intensive pre-treatment,

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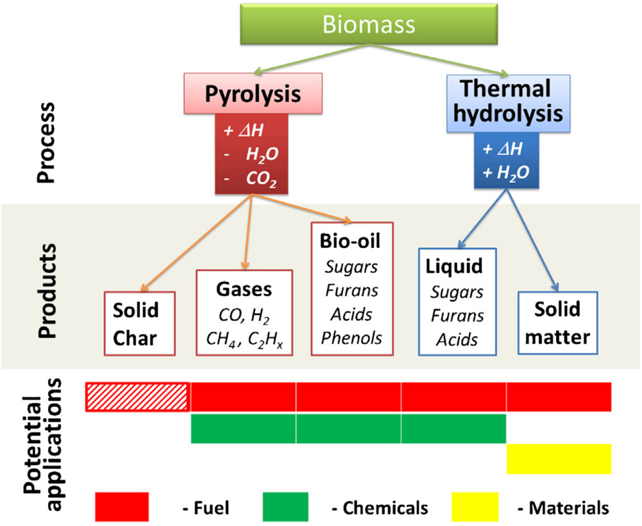

Fig. 1. The thermochemical approach in a hypothetical biorefinery. The striped block refers to a more limited application scope.

and the high temperatures involved (>500 °C). In addition, conventional pyrolysis is unable to separate the acidic aqueous fraction from the organic one *in-situ*, thus requiring additional upgrading steps. This, combined with a low degree of functionality of the products, restricts the industrial application of conventional pyrolysis of biomass. Currently microwave-assisted pyrolysis of biomass is gaining interest as *in-situ* separation of the products is possible. Hydrothermal processing on the other hand requires often the presence of strong acids and/or high pressures.

1.2. Microwave heating

Many routes have been explored to improve the pyrolysis process including the use of catalysts, more uniform temperature distributions and increased rates of heating. These though are not yet allowing the processing of larger particles. Microwave (MW) activation is a more recent approach holding great potential to overcome these issues. The use of microwave irradiation is well established in many industrial and commercial applications for over sixty years: industrial scale microwave systems [7] are available for wood drying [8] and food processing [9,10]. However, there are still a number of drawbacks *e.g.* the limited penetration depth of microwaves and the overall energy consumption. As such further refinement of the equipment and operating procedures is necessarily and this particularly towards pyrolysis [11,12].

The microwave region of the electromagnetic spectrum lies between the infrared and radio frequencies, and corresponds to wavelengths between 1 cm and 1 m (*i.e.* frequencies of 30 GHz to 300 MHz, respectively). Microwave dielectric heating uses the intrinsic potential of (polar) compounds to transform electromagnetic energy into heat, therewith provoking and driving chemical reactions. In contrast to conventional heating this method does not involve radiant heat and indeed the materials themselves absorb and dissipate the “energy” making the heating process more volumetric and hence appreciably faster and selective (see Fig. 2). This feature of microwaves is very important for the processing of poorly thermal conducting materials such as wood.

It has been shown recently that microwave technology can be an energy- and cost-efficient method of heating [13]. As such it has gained wide acceptance as a mild and controllable processing tool both at the laboratory and industrial scale [14]. Microwave heating can be controlled instantly and the power applied can be regulated accurately [15]. This allows for a safe and precise control, even when applying very high heating rates. A large number of examples highlighting the efficiency of microwave-mediated reactions have been described in the literature and then particularly in the areas of organic synthesis [16], polymers [17], and green chemistry [18]. The advantages of microwave technology in terms of mobility, using small scale processors, and towards waste remediation have also been highlighted [19].

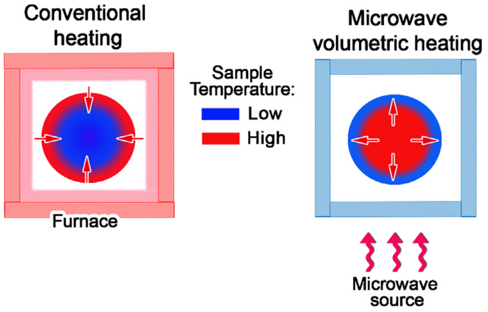

Fig. 2. Comparison of convection and microwave heat distributions within a sample matrix.

Typically, microwave-assisted processing of biomass is conducted at high temperatures (between 450 and 600 °C), which is similar to conventional pyrolysis (>350 °C), with the prime focus being on pyrolysis, gasification and liquefaction to fuels. However, microwaves are not only useful as an alternative method of heating, there is also good evidence that they allow for different pyrolytic mechanisms [20]. In this respect, the fact that microwave irradiation already interacts with different types of biomass (including wood, grasses, agricultural residues and food waste) at relatively low temperatures (<200 °C), producing bio-char and bio-oil, is of significant importance [21–23]. These mild pyrolysis conditions can substantially change the composition of the produced bio-oils and benefit future bio-refineries.

This article explores these emerging microwave-assisted biorefinery technologies/opportunities for processing a wide range of biomasses.

2. Material and methods

2.1. Microwave processing of materials

2.1.1. Microwave rape meal and wheat straw pyrolysis

2.1.1.1. CEM discovery laboratory microwave. Samples of rape meal or wheat straw (typically 300 mg) were weighed out into a microwave tube, and then sealed using the microwave tube lid. The sample was placed in the microwave and irradiated under varying conditions: typical power outputs and temperatures were, respectively between 100–300 W and 100–300 °C. After microwave treatment, the sample was removed from the microwave and washed with acetone to remove condensed (non)-volatile components.

2.1.1.2. Microwave biomass pyrolysis. Larger scale microwave pyrolyser. Milestone ROTO SYNTH rotative solid phase microwave reactor (Milestone Srl., Italy) (2 L vessel). Average sample mass was around 200 g. Samples were exposed to a maximum microwave power of 1200 W with an operating microwave frequency of 2.45 GHz (wavelength 12.2 cm). The process temperature was maintained below 200 °C, as measured by *infrared* temperature probes. The process vacuum was less than 100 mbar and monitored continuously. Liquid fractions were collected in a series of round bottom flasks fitted within the vacuum line.