

Microwaves in the Biorefinery

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1 Introduction

In order to meet the zero carbon circular economy targets that are increasingly being committed to by governments and industry, biorefineries must replace oil refineries as the mainstream source of chemical feedstocks. To become viable, the efficiency and flexibility of biorefineries must be maximised to cater for the inherently wider range of feedstocks and products compared with oil refineries, as well as the wide geographical distribution of rapidly deteriorating feedstocks. Microwave technology can play a major role in achieving this due to the potential for process intensification afforded by the microwave heating mechanisms. Microwaves therefore offer an exciting double opportunity to enhance the performance and flexibility of biorefineries and to replace traditional sources of fossil heat with carbon-free electrical energy. However, step changes in the approach to the design of microwave processes are required to make this a reality. This is due to the fundamental differences in the way microwaves heat materials compared with conventional heating; as many readers well-know, microwaves cannot simply be “dropped in” to replace conventional heat sources. Bespoke systems must be designed based on an understanding of microwave-material interactions and the role they play in processing. For biomass processing this is only beginning to be understood, and the likely reason for the very low conversion of promising lab-scale microwave technology applications into commercial interests.

This article introduces recent advances in the understanding of microwave-biomass interactions and, more importantly, how this can fundamentally affect mass transfer during microwave processing. We follow with some examples of specific biorefinery applications we’re working on, stressing that the fundamental understanding is absolutely key in helping us design the more applied experiments in

a way that will best exploit the microwave heating mechanisms and inform scale-up.

2 Recent advances in fundamental understanding

It is well-known that microwave processing is driven by the direct heat transfer mechanisms of volumetric (instantaneous heating throughout the bulk of the material) and selective heating (variation in heating rates resulting from differing abilities of system components to store and convert microwaves to heat depending on their dielectric properties). These lead to the development of different temperature profiles compared with conventional heating, which is indirect and in the case of biomass processing typically relies on conductive heating from the outside of the material. A key advantage of microwaves in many biomass processes is their ability to disrupt the cellular structure, enhancing the release of cell wall or intracellular chemicals. There are differing theories on the mechanisms by which this disruption is achieved, and understanding which of them are applicable to any given biomass feedstock and under what range of processing conditions is an absolutely essential input to the basis of design of microwave processes. Figure 1 is provided to illustrate this point. In Figure 1a, the selective microwave heating dominates the internal heat and mass transfer, leading to pressure build-up caused by superheated steam [1]. Figure 1b depicts temperature-induced diffusion, in which microwave-induced temperature differences between the cell, cell wall and solvent drive mass transfer over and above conventional concentration-driven osmotic processes [2]. Both mechanisms could lead to enhanced performance (e.g. faster processing and improved yield/quality), but completely different processing conditions would be required to achieve these: In (a) superheating of steam is required, while in (b) only small degrees of selective heating can effect the pressures required for cell rupture.

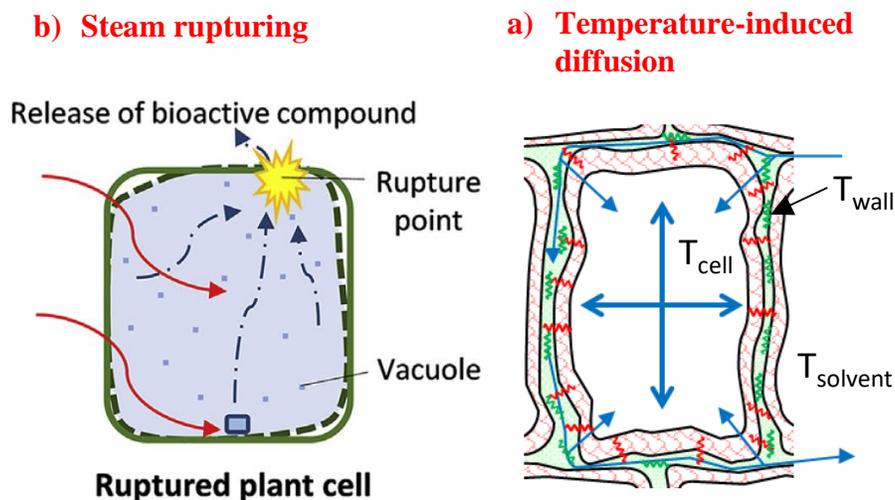


Figure 1: Depictions of possible disruption mechanisms

To better understand how and when these mechanisms may occur, we have recently proposed a cellular scale model of solvent extraction that incorporates conventional and microwave heating, cellular expansion, heat transfer and mass transfer [2]. Using microwave-assisted (solvent) extraction as a case study, we showed that steam-rupture is only possible at the extreme fringes of realistic physical parameters, while temperature-induced diffusion is able to explain cell-rupture across a broad and realistic range of physical parameters and heating conditions. It is interesting to note that, counter to our long-held beliefs, we found that outcomes were far less sensitive to changes in the relative dielectric properties of the solvent and biomass than other system properties such as conductivity. We also note that the study was limited to Microwave-Assisted Extraction (MEA) conditions, and other outcomes may be achievable for other microwave-biomass applications (i.e. steam rupture may be more likely in systems in which the processing conditions achieve significantly higher electric field intensities), and that the model is designed to be expanded and refined to include other processing regimes.

This approach to fundamental understanding can be used to inform the design of processes to exploit the effect of temperature-induced diffusion during microwave heating (i.e. to predict feedstock properties and processing parameters for which microwave heating could enhance process performance).

3 Examples of microwave biorefinery processes

3.1 Green extraction of unconventional polysaccharides

The development of novel products via the green extraction of polysaccharides from co-products and residues of the agri-food industry has received significant attention in recent years. Industrial processes such as commercial pectin extraction typically use hot-acid extraction [3]. However, this leads to large volumes of acidic wastes and is not suitable for the extraction of some polysaccharides, limiting the range of novel bio-based products that can be produced. For example, pectin oligosaccharides (POS), derived from rhamnogalacturan I-rich (branched or “hairy”) pectin have been shown in-vitro to have a bioactive properties that indicate that they could be developed into novel products, including pharmaceuticals [4, 5] or a new class of prebiotic [6]. However, hot acid extraction destroys the neutral sugar side-chains of interest for these applications, rendering commercial extraction useless for hairy pectin extraction. Existing extraction methods are limited to laboratory scale. Enzymatic processes can produce high yields, but the high cost of the enzymes required has stifled scale-up. Many researchers in the past 20 years have reported that MEA can be used to effectively extract a range of materials, and in fact that it can achieve pectin extraction using only water as the solvent, making it a promising green extraction technique. However, until recently, fundamental understanding

of how this process differs fundamentally from conventional solvent extraction has been lacking, and this has led to very low conversion of laboratory-scale experiments into industrial-scale demonstrations. The development of unconventional polysaccharide-based products such as bioactive pectin products has been hampered by the inability to produce them at large enough scale for in-vivo trials.

Many laboratory-scale studies have reported various novel pectin extraction procedures [3, 7, 8]. However, few have considered the effect of extraction method on pectin structure [7], and direct comparison of different technologies and processing parameters using the existing laboratory scale data is challenging due to the difficulty in varying only one process parameter independently. Our recent study [9] systematically investigated the effect of pH, heating type (microwave versus conventional heating), temperature (90 – 150°C) and time on the yield and composition of pectin extracted from sugar beet pulp. Contrary to many studies, which report up to double the yield with microwave heating compared with conventional heating and differences in pectin structure [7], the study showed that the yield and composition of the pectin-rich extract was unaffected by heating type when both methods were carried out using the same processing parameters (including heating rate). The yield and composition were most affected by pH and temperature: the highest yields and purity of “hairy” pectin were achieved at high pHs, while strongly acidic conditions favored the extraction of homogalacturan (HG, “smooth” pectin). This is not to say that different feedstock-solvent combinations would yield the same results (i.e. that microwave heating had no effect on the yield or time), and indeed this is a subject of continuing investigation in our lab. The use of hydrothermal processing conditions (110 – 190°C in a sealed vessel) decreased treatment time and increased yield significantly, but pectin degradation was rapid after peak extraction yield was achieved. The results indicated that while strongly alkaline solvents may achieve the highest yields of “hairy” pectin, hydrothermal processing and atmospheric pressure water extraction may be favorable from a perspective of scale-up. In Mao et al., [10] we used a systematic approach to manipulate pectin structure and composition by varying okra

extraction conditions, and correlating this with the extract’s functionality as a bioflocculant. While previous papers identified okra as a promising bioflocculant and characterized the pectin content in okra mucilage, Mao et al. demonstrated that the HG/RGI ratio could be used to directly predict the flocculating ability of pectin-rich extracts, which processing conditions would achieve this, thereby informing techno-economic assessment of potential feedstocks and processes [11].

We have utilized these advances in the understanding of the effect of processing parameters on experimental outcomes to scale-up a pectin extraction process [12]. The outcomes of laboratory-scale batch experiments were used as a basis of design for the continuous-flow MEA of pectin-derived oligosaccharides from potato pulp in water operating at 85°C. Coupling electromagnetic and process design approaches, the 2kW system developed achieved good temperature control of $\pm 2.5^\circ\text{C}$, and a stable target temperature in ≈ 1 min processing time at a feed flow rate of 250 mL/min. Pectin yields of 40 - 45% were achieved, with a residence time of 0.81 s followed by 20 min cooling-down under stirring, potentially offering a vast improvement on the current batch industrial process, which operates at pH1-3 and a residence time of ≈ 1 hour.

3.2 Microwave pyrolysis

Another area of interest of our research group comes from the unique ability of microwaves to allow materials to be heated whilst maintaining a cold surrounding environment. Microwave transparent liquids are used as the inert media for pyrolysis processes, which regulate the surrounding temperature based on their normal boiling point. The low-temperature environment preserves the quality of primary depolymerisation products, and reduces the risk of thermal runaway that plagues many attempts at microwave pyrolysis [13]. We have also shown that a number of unique products can be obtained in high yield from the pyrolysis of seaweed using microwave heating [14]. The high yields arise from the lack of lignin in the feedstock and the low temperature inert environment, with products that have the potential to form a backbone of a seaweed biorefinery.

4 Outlook

A recent shift in the approach of microwave research and technology is leading to a wider body of evidence and understanding. This is increasingly identifying exactly what advantages microwave can offer in biorefinery processes, and when they can (and can't) be exploited. If embraced by the wider community, microwaves can become an essential tool in the biorefinery, supporting the move from linear petrochemical processes to a sustainable and circular economy.

For further reading

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Eleanor Binner is an Associate Professor in Chemical & Environmental Engineering at the University of Nottingham. She has 15 years' experience in the management and delivery of heterogeneous material processing projects in both industry and academia. She specializes in microwave technologies to convert

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through to establishing a core scientific understanding of microwave-biomass interactions.