

Understanding heat and mass transfer processes during microwave-assisted and conventional solvent extraction



Yujie Mao, John Robinson, Eleanor Binner*

Department of Chemical and Environmental Engineering, Faculty of Engineering, University of Nottingham, University Park, NG7 2RD, UK

HIGHLIGHTS

- Effect of heat transfer processes on mass transfer during extraction reported.
- Conventional and microwave extraction heating rate incrementally effects yield.
- Step changes in microwave extraction time only for high dielectric loss biomasses.
- Step changes in mass transfer rates achieved above a threshold microwave power.
- Temperature-Induced Diffusion experimentally confirmed to drive mass transfer.

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ABSTRACT

Solvent extraction is a mass transfer process. In this paper, we investigate the role of heat transfer in solvent extraction: in particular, how the heat transfer properties of the solid and the heating method (conventional heating and microwave heating) drive this mass transfer process. Water-based solvent extraction of pectin from orange peel, apple pomace, mango peel and carrot pulp was carried out. The thermal conductivity and dielectric loss were shown as good predictors of extraction performance, with step change increases in mass transfer rates when microwave processing was applied to biomass with dielectric loss significantly higher than water (e.g. 120 mins reduced to 45 mins for optimal pectin extraction from apple pomace). When the loss factor was lower there was no difference in extraction performance between the two technologies (e.g. carrot pulp extraction time was 60 mins in both cases). Further investigations were carried out at different heating rates for both conventional and microwave extraction in order to decouple the effects of microwave volumetric and selective heating. It was shown that below a certain power threshold (within the range of 100–120 W in these experiments), microwave and conventional extraction are equivalent, while above the threshold, microwaves achieved a step-change in extraction time. These findings are the first experimental confirmation of recent theoretical advances in microwave biomass processing, in which Temperature-Induced Diffusion drives mass transfer. It is also the first paper to allow identification of biomass characteristics that will be most amenable to microwave extraction.

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1. Introduction

According to the Food and Agriculture Organization of the United Nations (FAO) data, approximately 1.3 billion tones of food (roughly one-third of total food produced for human consumption) is wasted globally throughout the food supply chain (FSC) from initial agricultural production down to final household consumption or food manufacturing industries (Gustavsson et al., 2011). At the

same time, the development of biorefineries is imperative in order to meet urgent environmental targets such as the UK's commitment to zero carbon by 2050. The need to both avoid waste and find new renewable resources to replace fossil fuels has led to a new and promising research avenue: the use of food supply chain waste (FSCW) as a renewable biorefinery feedstock (Pfaltzgraff et al., 2013). 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, and microwave technology can play a major role in achieving this due to the potential for process intensification afforded by the microwave heating mechanisms alongside their ability to be powered

* Corresponding author.

E-mail addresses: yujie.mao1@nottingham.ac.uk (Y. Mao), john.robinson@nottingham.ac.uk (J. Robinson), Eleanor.Binner@nottingham.ac.uk (E. Binner).

by carbon-free electrical energy rather than traditional fossil fuel heat sources. 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; 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. Microwave-Assisted (Solvent) Extraction (MAE) is promising as a biorefinery unit operation to extract high value chemicals from biomass prior to downstream processing of the solid residues. However, fundamental and systematic understanding of how the microwave heating mechanisms drive mass transfer during MAE is lacking. In this paper, we have used the extraction of pectin from food wastes (specifically food industry co-products) as a case study to address the abovementioned knowledge gaps in solvent extraction. We have investigated experimentally, for the first time, how heat transfer resulting from microwave heating can drive mass transfer in biomass-solvent systems, and the role of the heat transfer properties of the biomass in this process.

Pectin extraction was selected as a relevant case study because although commercial pectin (rich in “smooth” pectin, homogalacturonan (HG)) is already extracted industrially using hot acid extraction, there is no existing industrial process to extract “hairy” pectin, which is rich in rhamnogalacturonan-I (RG-I). The development of commercially viable “hairy” pectin extraction processes is key to the development of novel RG-I derived products (Arrutia et al., 2020), which have a wide range of potential applications, for example as a potential source of a new class of prebiotics (Babbar et al., 2016). The growth of the pectin market is driven by the rising demand for functional food products and increasing use by the cosmetic and pharmaceutical industries. In 2015, the average price of pectin exceeded \$15/kg and the market exceeded 60,000 tons, with 6% of overall annual growth rate reported (Monitor, 2015). Orange peel, mango peel, apple pomace and carrot pulp were selected as industrially relevant co-products with relatively high pectin contents (Table 1).

MAE is a novel extraction process that is widely reported to accelerate or enhance the solvent extraction of pectin compared to CSE (Adetunji et al., 2017), achieved through volumetric and selective microwave heating mechanisms. Microwaves can penetrate throughout the whole volume of material (Li et al., 2013), which makes it possible to achieve rapid volumetric heating with associated extraction time savings and reduced bio-active extract degradation (Venkatesh and Raghavan, 2004). Selective heating can heat different components in a heterogeneous system at different rates, and it is thought that this can lead to rupture of cells within biomass, resulting in higher extraction yields and the ability to treat recalcitrant materials (Adetunji et al., 2017; Chemat et al., 2009). Despite these reported advantages, to our knowledge MAE of pectin has not been applied at an industrial scale, with only two pilot scale examples in the literature. Garcia-Garcia et al. (2019) treated 3 kg of orange peel in water in a 20L recirculating

batch for 1.5 h at 95 °C using a 6 kW microwave power source, yielding 150 g orange peel pectin. Arrutia et al. (2020) developed a semi-continuous MAE process that could treat 250 mL min⁻¹ of 10% w/w potato pulp in water using a 2 kW single mode cavity followed by 20 mins mass transfer time with no heating. Yields in both cases were higher than reported values for batch CSE systems; however, neither were compared under like-for-like operating conditions, so the mechanism by which microwave heating provided advantages could not be assessed.

One small batch-scale study has compared CSE (90 °C water bath) and MAE (maximum applied power 200 W) for pectin extraction from micronised sugar beet pulp using the same processing conditions (including vessel geometry, heating rate and stirring regime), and shown no difference in yield, optimum extraction time or quality of the pectin extracted (Mao et al., 2019). The only other published studies comparing MAE and CSE using the same heating rate are on the extraction of polyphenols from sea buckthorn leaves (Asofiei et al., 2016; Galan et al., 2017). In that case, a higher yield was achieved for microwave heating, while the extraction time was the same for both heating methods. By using the same heating rate (and therefore decoupling the advantages of the faster heating rates that are often achieved using microwave volumetric heating), the studies were able to investigate the effect of microwave selective heating, demonstrating no difference in the case of pectin extraction from sugar beet pulp on one hand, and increased yield in the case of polyphenol extraction from sea buckthorn leaves on the other. Based on these results, we hypothesise that the mass transfer processes during extraction can be enhanced during microwave heating, but only under certain processing conditions and for certain biomasses and/or target extracts. If true, we aim to understand the specific mass transfer processes that can be enhanced by microwave heating, and how they are affected by the heat transfer properties of the biomass feedstock.

To do this, we ask the following research questions:

1. How do the heat transfer properties of the biomass affect temperature during microwave and conventional heating, and does this impact on the extract yield and composition?
2. Can any differences in microwave and conventional heating be attributed to selective or volumetric heating, and if so, under what processing regimes can this be achieved?

2. Theory

2.1. Mass transfer principles in extraction processes

Pectin isolation is conceptualised as a series of mass transfer steps (illustrated in Fig. 1): (i) penetration of solvent at the surface of the solid, (ii) diffusion through the solid, (iii) hydrolysis of the proto-pectin (i.e. the *in situ* pectic polysaccharide, bound to other cell wall compounds like cellulose), (iv) solubilisation of pectin into the solvent, (v) diffusion to the solid surface, (vi) external transfer to the bulk solution, and (vii) degradation and de-esterification of

Table 1
Production quantities and pectin content of selected food waste.

Raw Materials Producing Pectins	Primary nature of waste streams produced	Global annual production of feedstock sources (tonnes/yr) ^a	Pectin Content in biomass (Dry basis % wt) ^b	References
Orange peel	Post juicing and inedible parts	73,187,570	10.9–24.8	(Gomez et al., 2014; Kaya et al., 2014)
Mango peel	Inedible parts	46,508,697	7.6–18.5	(Koubala et al., 2008)
Apple pomace	Apple juice and cider production	89,329,179	4.6–15.8	(Min et al., 2011; Wang et al., 2007)
Carrot pulp	Carrot juice production	41,968,949	5.8–15.6	(Jafari et al., 2017)

^a Data was obtained from Food and Agriculture Organisation of the United Nations database (FAOSTAT, 2016).

^b Pectin content is presented as the yields in dry basis % wt.

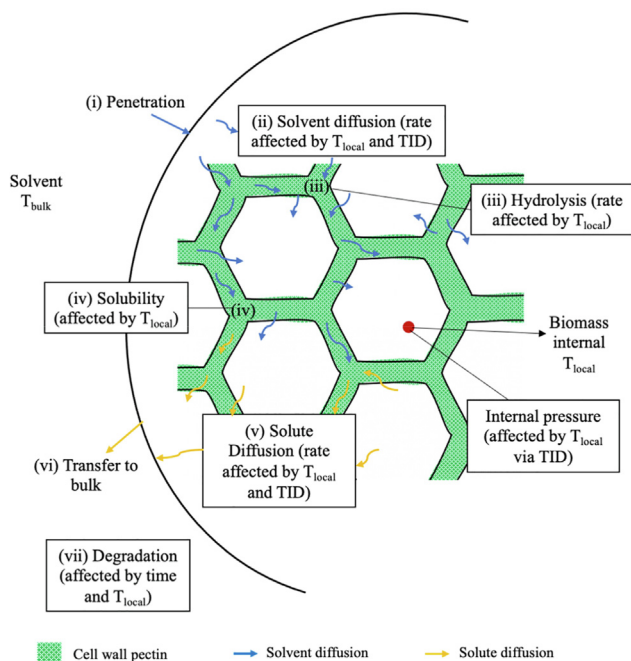


Fig. 1. Conceptual model of pectin extraction from biomass, highlighting (with borders) the steps that could increase yield or extraction rate when biomass internal temperature (T_{local} , which varies with spatial location) at steady state > solvent temperature (T_{bulk}). TID = Temperature-Induced Diffusion.

the extracted pectin (Adetunji et al., 2017; Flórez et al., 2015; Pinelo et al., 2006). Andersen et al. (2017) built a dynamic model of pectin extraction. The model was validated using conventional solvent extraction of lime peel, and the authors concluded that extractions under the conditions investigated appear to be controlled by the transport phenomena, as the hydrolysis (and solubilisation) of proto-pectin was predicted to be fast in relation to the diffusion inside the peel, and this conclusion is in agreement with most publications.

We aim with this work to extend this understanding by interrogating the effect of heat transfer on the aforementioned mass transfer processes in the cases of electromagnetic and conventional heating, and in particular to investigate the effects of differing heat transfer properties of the biomasses themselves under different heating regimes, which has to date been overlooked in the literature. The overall temperature (T_{bulk}) of the system and the solvent type are known to have significant effects on the mass transfer processes. However, in this study we have removed those two parameters as variables in order to focus specifically on the effects of the different local temperature (T_{local}) distributions within the biomass that could be generated using different heating methods and in different biomasses. In the case of CSE, T_{local} will be lower than T_{bulk} until steady state is achieved, at which point the system will be isothermal. In the case of microwave heating, volumetric and selective heating could lead to T_{local} being higher than T_{bulk} even after steady state is achieved, with the highest temperatures expected in the centre of the particle (Taqi et al., 2020).

Fig. 1 highlights the extraction steps that could be influenced by the elevation of T_{local} above T_{bulk} during microwave heating. Compared with the isothermal CSE system at steady state, the rates of diffusion (ii and v) and hydrolysis (step iii) would increase with increasing T_{local} , reducing extraction time. The solubility of pectin is known to be highly temperature dependent (Sila et al., 2009), which means that increased T_{local} could lead to increased pectin yield and/or faster solubilisation at step (iv). Microwave heating could have a positive or negative effect on step vi (pectin degrada-

tion): elevated T_{local} could lead to faster degradation of the pectin once solubilised within the biomass, while reduced extraction time facilitated through speeding up the other steps could lead to reduced time for degradation to take place. The abovementioned changes would be expected to be incremental, as the temperature differences under normal operating conditions are predicted to be in the order a few degrees only (Lee et al., 2016; Taqi et al., 2020).

Microwave heating could also enhance mass transfer through Temperature-Induced Diffusion (TID), in which transport processes are driven by temperature gradients in addition to concentration gradients (Lee et al., 2016; Taqi et al., 2020). This can be understood by considering the chemical potential, which is a universal property that dictates the direction and magnitude of the driving force for mass transfer. The chemical potential of component i (μ_i , J mol⁻¹) in a mixture at given temperature and pressure, and with fixed activity of component i (which is analogous to concentration in non-ideal systems), is given below, which was derived by Robinson et al. (2019):

$$\mu_i = \mu_i^0 + v_L P_L - s_{i(T^0)} (T - T^0) + RT \ln \left(\frac{\alpha_i}{\alpha_i^0} \right) \quad (1)$$

where, μ_i^0 is the chemical potential of the reference solvent in J mol⁻¹; v_L is the specific volume of the liquid state in m³ mol⁻¹; P_L is the specific pressure of the liquid state in bar; T^0 is the baseline temperature and T is the mixture liquid temperature in °C; $s_{i(T^0)}$ is the entropy of component i at temperature T^0 in J mol⁻¹ K⁻¹; R is the universal gas constant ($R = 8.31$ J mol⁻¹ K⁻¹); α_i is the activity of component i and α_i^0 is the baseline activity of component i . In the cases present in this paper, when water is used as the solvent (baseline), the input parameters for the chemical potential expression are: $\mu_w^0 = 0$ J mol⁻¹; $T^0 = 25$ °C; $s_{w(T^0)} = 70$ J mol⁻¹ K⁻¹ (ToolBox, 2005) and $\alpha_w^0 = 1$.

In an isothermal system (such as conventional solvent extraction), T is equal to the baseline temperature T^0 , the temperature term disappears, and the chemical potential becomes analogous to the classical osmotic pressure expression. The inclusion of the temperature-dependent term (which is required in microwave heating) leads to an increase in chemical potential gradients within the biomass, drawing additional water into the cellular structure. This could affect the diffusion rates in steps (ii) and (v), which, as stated above, are likely the rate limiting steps in extraction. It could also theoretically lead to the generation of high enough cellular pressures to disrupt or even rupture the cell walls, leading to increased yields of previously inaccessible protopectin and a step change reduction in extraction time. The experiments presented here were designed to test these hypotheses for the first time.

2.2. Energy transfer principles in MAE and CSE

2.2.1. Effect of thermal conductivity (k)

During CSE, heat is transferred into the solvent from the heating bath by conduction, and therefore the conductivity of the solvent/solute may affect the heating rate of the solvent and hence T_{bulk} . By stirring the solvent-biomass systems, the effect of convection or conduction within the solvent is eliminated and it can therefore be assumed that T_{bulk} is isothermal and the same as the set temperature in all experiments. However, the conductivity of the biomass will affect T_{local} in both CSE and MAE. For CSE, a higher conductivity will lead to a faster equilibration of T_{local} with T_{bulk} . For MAE, any selective heating effects are expected to be enhanced for lower thermal conductivities, as conductive heat transfer from the momentarily hotter phase to the surroundings will be slower. Steady state, however, will not be affected, just the time to steady state.

2.2.2. Effect of dielectric loss factor (ϵ'') and electric field intensity

Dielectric properties describe the response of a material to microwaves. They can be expressed mathematically by the complex relative permittivity of the material ϵ_r (Metaxas and Meredith, 1983):

$$\epsilon_r = \epsilon' - j\epsilon'' \quad (2)$$

where ϵ' as the real part is the dielectric constant, which is defined as the ability of the material to store microwave energy, while ϵ'' as the imaginary part is the dielectric loss factor which quantifies the conversion of microwave energy into heat.

When microwave heating is applied the solvent and biomass are heated directly and instantaneously throughout the bulk (volumetrically). This means that, since the only way for heat to be lost from the system is through the solvent, the temperature difference between the biomass and the solvent at steady state can only be nil or positive (the biomass will likely be hotter than the solvent). Microwave heating is also selective, with the heating rates of the solvent and biomass being affected by their respective dielectric losses. If the dielectric loss of the biomass ($\epsilon''_{\text{biomass}}$) is higher than that of the solvent, ($\epsilon''_{\text{solvent}}$) the heating rate of the biomass by the microwaves will be higher than the solvent.

The heating rate of individual components during microwave heating can be related to the power density, as defined by Eq. (3). From Clark et al. (2000), the power absorbed per unit volume, or power density (P_d , in Wm^{-3}) is given by:

$$P_d = \rho C_p \frac{\Delta T}{\Delta t} = 2\pi f \epsilon_0 \epsilon'' E^2 \quad (3)$$

where ρ is the density of the heated material in kg/cm^3 ; C_p is the specific heat of the heated material in $J/kg\ ^\circ C$; ΔT is the temperature rise in $^\circ C$; Δt is the time increment in seconds and so $\frac{\Delta T}{\Delta t}$ is the heating rate; f is the frequency of the applied field in Hz; ϵ'' is the loss factor of the dielectric material; and ϵ_0 is the free space permittivity ($\epsilon_0 = 8.854 \times 10^{-12} F/m$); E is the root mean square value of the electric field intensity in $V\ m^{-1}$ inside the given volume.

From above Eq. (3), it can be seen that the heating rate of a specific component within a given experimental set-up will be determined by the dielectric loss of the component and E , which is increased with increasing power input. This doesn't account for heat loss to the surroundings, which will be governed by the thermal conductivity and/or convective heat losses.

3. Materials and methods

3.1. Materials and sample preparation

Orange (*Citrus sinensis* 'Jaffa'), mango (*Mangifera indica*), apple (*Malus domestica* 'Gala') and carrot (*Daucus carota* subsp. *sativus*) were bought freshly from the local supermarket (Tesco, Nottingham). All raw biomass samples were washed with deionised water to remove any contaminants. Orange and mango peel were obtained by hand peeling from the raw materials and the peels were then cut in 1 cm slices. Apple and carrot pulp were obtained using a slow masticating juicer (VonShef, UK) to separate the pulp from the majority of the juice.

The moisture contents of the orange peel, mango peel and apple pomace were obtained by oven drying at 60°C until a constant weight was obtained, the results are presented in Table 2. The experiments were designed such that 2 g of biomass on a dry basis was added to 43 mL deionised (D.I.) water in each experiment. Owing to the differing moisture contents, this led to a differing amount of wet biomass being used for each sample type, as detailed in Table 2.

Table 2

Moisture contents of biomasses and their weight of fresh biomass samples and amount of solvent added.

Biomass name	Moisture content (%)	Weight of fresh sample (g)	Amount of solvent added (mL)
Orange peel (OP)	74.2 ± 0.5	8	37
Mango peel (MP)	76.0 ± 0.1	8	37
Apple pomace (AP)	76.1 ± 0.1	8	37
Carrot pulp (CP)	87.2 ± 0.1	15	30

3.2. Heating treatment by MAE and CSE

All extraction experiments were carried out at a set target temperature of 90 °C. CSE was either carried out by adding the extraction vessel to a water bath preheated to 90 °C for the duration of the experiment, or by adding the extraction vessel to an ethylene glycol bath preheated to 120 °C and 150 °C, and transferred to a 90 °C water bath once the set temperature was reached. In doing so, the effect of heating rate on CSE was investigated for the first time. MAE was carried out using a Miniflow 200SS (Sairem, France) single mode microwave heating system at 2.45 GHz, with a fibre optic temperature probe inserted into the reaction vessel. The heating rates of MAE were manipulated by changing the maximum incident power at 200 W, 150 W, 120 W, 100 W and 50 W. The reflected power was adjusted to zero before the treatment, so that the absorbed power can be as close as the incident power. The average heating rates were determined as:

$$\text{Average heating rate } (^\circ C/\text{min}) = \frac{\text{Temperature increase from } 25\ ^\circ C \text{ to } 90\ ^\circ C}{\text{Time required for the temperature increase to } 90\ ^\circ C} \quad (4)$$

After heating, solid residue was removed by filtration. The resulting liquid was centrifuged at 3900 rpm for 40 min and an equal volume of isopropanol (IPA) was added to the supernatant for the precipitation of alcohol insoluble solid (AIS). This precipitation step is carried out to isolate the pectin, although small amounts of hemicellulose can also precipitate if present. Samples were stored overnight at 4 °C then centrifuged for another 40 min at 3900 rpm and the supernatant was discarded. The pellets were either dried overnight at 60 °C to determine yield, or freeze-dried (LyoDry freeze dryer (Mechatech Systems, Bristol, UK)) for sugar analysis. All experiments were performed in triplicate.

3.3. Dielectric loss measurement

Biomass samples were prepared in D.I. water solution at the same sample size and S/L ratio as used in the extraction experiments. This method measures the bulk properties of the system, and therefore indicates the general propensity of the system for volumetric heating. Although it doesn't measure the actual dielectric loss of the biomasses during extraction, the difference between this value and that of the solvent will give a relative indication of the degree of selective heating of the biomass in the system. The mixtures were heated using a hot plate from 20 °C to 90 °C with measurements taken at 10 °C intervals. Dielectric property measurements were performed using an 85070E Dielectric Probe Kit (Agilent, USA). The experimental set-up consisted of a performance coaxial probe equipped with an electronic calibration (ECal) module. The coaxial probe was connected to an Agilent N5232A PNA-L (Purpose Network Analyser) operating at 300 kHz–20 GHz via a high-quality coaxial cable. The probe was immersed into the sample solution and ensure there was no bubble on the probe surface. The dielectric loss was determined at 2.47 GHz, which is within 20 MHz of the MAE equipment used.

3.4. Thermal conductivity measurement

Biomass samples were prepared in D.I. water solution at the same S/L ratio as used in extraction. The samples were heated using a hot plate from 20 °C to 90 °C at 10 °C intervals, and also heated to 90 °C and then held at this temperature for 0, 10, 30, 60, 120 mins. A sample of the extract solution was removed by pipette and the thermal conductivity measured using a modified transient plane source (MTPS) sensor connecting to a TCi analyser (C-Therm, Canada). Thermal conductivities of biomass solids could not be measured using this method as it requires a homogenised system.

3.5. Yield calculations

The extract quantity was determined by AIS yields using the following equations:

$$\text{AIS Yield}(\%) = \frac{\text{Weight of oven dried AIS}}{\text{Weight of raw biomass sample} \times (1 - \text{moisture content})} \times 100 \quad (5)$$

The yield of HG region was determined using the following equation (in other papers, HG yields (%) is also referred as HG region extractability (Kaya et al., 2014)), where DRB represents dried weight of raw biomass:

$$\text{HG Yield}(\%) = \frac{\text{Percentage of HG in AIS} \times \text{AIS Yield}}{\text{Percentage of HG in DRB}} \times 100 \quad (6)$$

Similarly, the yield of RG-I region (as referred as RG-I region extractability (Kaya et al., 2014)) extracted was determined as:

$$\text{RG - I Yield}(\%) = \frac{\text{Percentage of RG - I in AIS} \times \text{AIS Yield}}{\text{Percentage of RG - I in DRB}} \times 100 \quad (7)$$

3.6. Sugar analysis

In order to assess the quality of the extracts, the galactronic acid (GalA) content and the sugar composition were tested. The GalA analysis of pectin extracts using a UV-Vis chromatography was the same as the work published in Mao et al. (2019). In order to allow the break-down of the HGA backbones into GalA, freeze-dried pectin extracts were diluted to give an estimated concentration of 125 μg/mL in D.I. water, after which 40 μL 4 M potassium sulphamate and 2.5 mL of concentrated sulphuric acid were added and the mixture heated to 99 °C in a water bath for 20 mins. The solution was then cooled under running water and an m-hydroxydiphenyl solution (80 μL of a 0.15 wt% m-hydroxydiphenyl in 0.5 wt% NaOH solution) was added, and the samples were left to develop a pink colour over 5–10 mins. The absorbance of the pink solution was determined by UV-Vis chromatography (Jenway model 7315, Cole-Parmer Ltd UK) at a wavelength of 525 nm. Zero absorbance reference was set with deionised water and the GalA standard solution was made at concentrations from 0 – 97 mg/L.

The neutral sugar analysis of rhamnose (Rha.), arabinose (Ara.) and galactose (Gal.) were performed the same way as the work published in Mao et al. (2019) by an ionic chromatography (IC) with a Dionex ICS-3000 system (Thermo Fisher, Loughborough, UK) and a CarboPac PA20 column (3 × 150 mm, BioLC, Thermo Fisher). The freeze-dried pectin extract was hydrolysed with concentrated sulphuric acid using the same method as in the GalA assay in order to allow the break-down of the RG-I region into neutral sugars. After the pre-hydrolysis, 100 μL of supernatant was added to 10 mL of 10 mM NaOH. 1 mL of the resulting solution was added used for sugar analysis. 10 mM NaOH (Solution A)

was used as eluent and 200 mM NaOH (Solution B) as the mobile phase; retention gradient and time as –10 to –5, 0.5 mL/min, 100% Solution A; –5 to 14, 0.4 mL/min, 100% Solution B; stand-by, 0.1 mL/min. Mixtures of sugar standards (L-rhamnose, L-arabinose, D-galactose, D-glucose and D-xylose, all chemicals from Sigma Aldrich (Dorset, UK)) at various concentrations (1–20 mg/L) were used as external standards for identification and quantification.

Please note that the full sugar analysis of the extracts is provided in the supplemental data, with only selected results presented in the paper to support the discussion where relevant.

4. Results and discussion

4.1. Investigation of the effects of biomass heat transfer properties on extraction

4.1.1. Heating rates

To determine whether and how the biomass type affects temperature development during heating, the heating rates during extraction were measured. The heating rates of using only D.I. water under microwave and conventional heating were also measured. The results are shown in Fig. 2A for MAE at 200 W, and in Fig. 2B for CSE heated using the 90 °C water bath. The heating rates were affected by the biomass type, with the apple pomace ≥ orange peel > mango peel > carrot pulp ≥ D.I. water for MAE. Conversely for CSE, the heating rates in descending order were D.I. water ≥ carrot pulp >> orange peel > mango peel > apple pomace. The heating rates were consistently higher for MAE at 200 W than CSE heated using a 90 °C water bath. However, the values for MAE for orange peel, mango peel and apple pomace are significantly higher (e.g. 39.4 °C/min compared with 16.5 °C/min for orange peel), while only incremental for carrot pulp and (34.6 °C/min versus 28.4 °C/min). This indicates that the biomass types does affect heating rates, and the reason for this behaviour will be discussed in the next Section 4.1.2. Additionally, the effect of biomass type on heating rates is larger for CSE (±17.3 °C min) compared with MAE (±6.0 °C/min). This indicates that the heating rate of a scaled-up microwave process should be less sensitive to changes in biomass type, which is favourable for scale-up.

4.1.2. Heat transfer properties

To relate the differing heating rates to the heat transfer properties, the thermal conductivities (k) and dielectric losses (ε'') of the biomass – solvent systems, were investigated.

The thermal conductivity of solute pipetted from the biomass – solvent system at 20 °C are shown in Fig. 3. The thermal conductivity of D.I. water was 0.624 W/m K and that of the biomass solutes at 20 °C were all lower than water, indicating a general reduction in conductivity of the system during extraction to a greater (apple of 0.418 W/m K) or lesser (other biomasses, for example carrot of 0.612 W/mK) extent. This concurs with the CSE heating rates shown in Fig. 2B, showing that the conductivity of the solute correlates with the heating rates of the system (explaining why the carrot pulp heated more than twice as quickly as the apple pomace but had similar heating rate as D.I. water itself) and confirming the hypothesis that conductivity can be used as a predictor of bulk heating rate during conventional heating.

To understand the microwave heating rates, the dielectric loss (ε'') of water and biomass – water systems were measured and are shown in Fig. 4. All biomass – water systems had higher dielectric losses than those of pure water. This explains the results in Fig. 2A and B: while the addition of biomass to the water reduced the thermal conductivity, slowing down conventional heating, it increased dielectric loss, accelerating microwave volumetric heat-

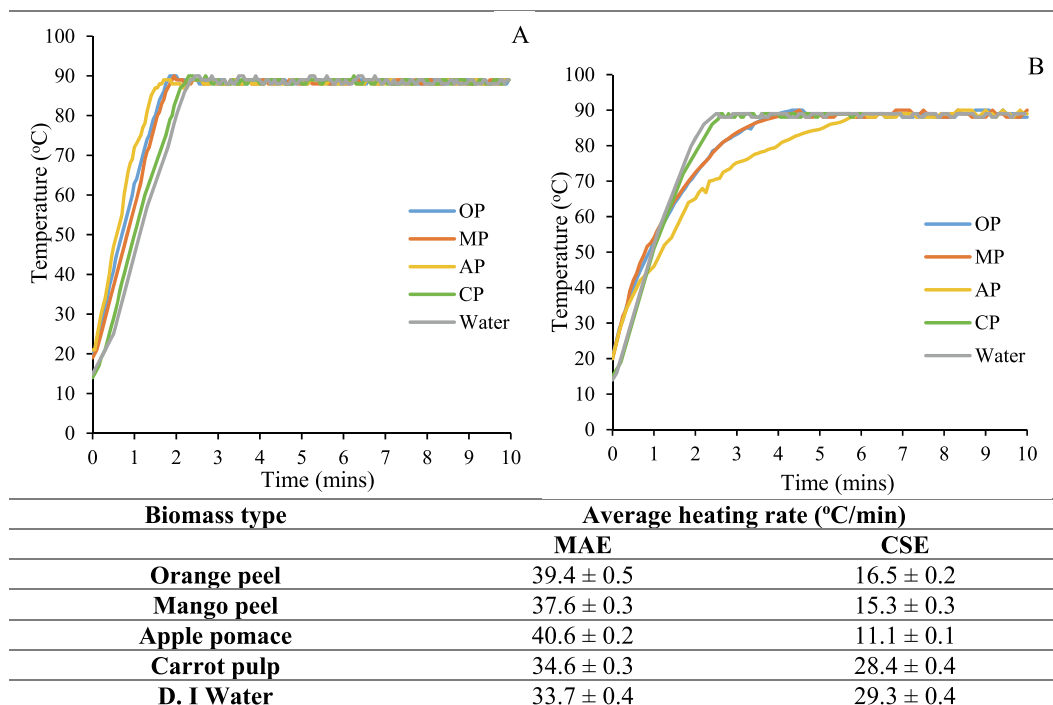


Fig. 2. Bulk heating rates during MAE at 200 W (A) and CSE (B) using orange peel, mango peel, apple pomace, carrot pulp in D.I water and using D.I water only; OP: orange peel; MP: mango peel; AP: apple pomace; CP: carrot peel. All average heating rates were calculated from 25 °C to 90 °C.

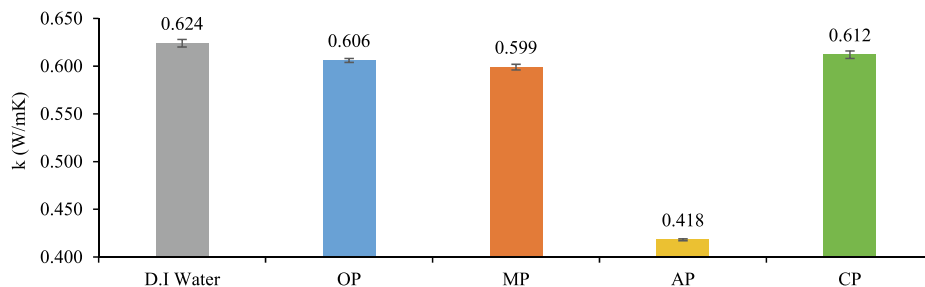


Fig. 3. Thermal conductivities of D.I water and solutes of OP, MP, AP and CP in water. All results measured at 20 °C.

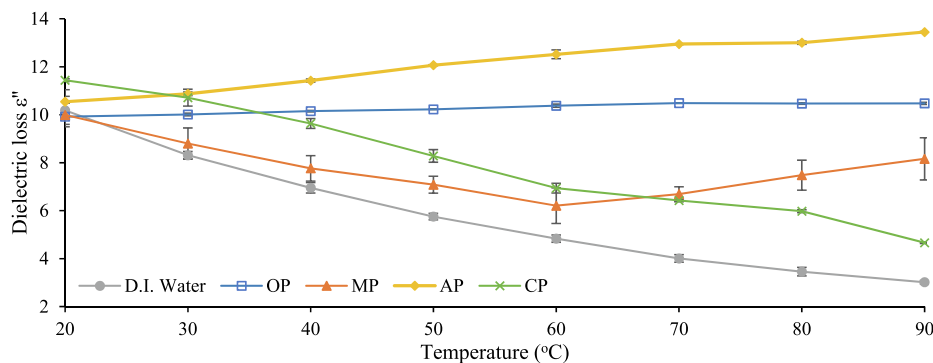


Fig. 4. Dielectric properties of D.I water and solutes of OP, MP, AP and CP in water. All results measured at 2.47 GHz and 20 to 90 °C.

ing. Therefore the fastest microwave heater (apple, $\epsilon''=13.4$ at 90 °C) was the slowest conventional heater, with the opposite true for carrot ($\epsilon'' = 4.7$ at 90 °C).

Looking at the trends in dielectric loss of the biomass-water systems with increasing temperature, it can be seen that apple and orange exhibit a general increase in loss with temperature.

The dielectric properties of the mango peel – water decreased from 20 to 60 °C and then increased from 60 to 80 °C. In addition, the carrot pulp – water system behaved similarly to water, in that the loss decreases with increasing temperature. Based on the fact that losses resulting from dipole polarisation decrease with increasing temperature, with the inverse true for ionic conduction

(Soria, 2015), these results suggest that ionic conduction makes a significant contribution to the dielectric loss under microwave heating for orange peel and apple pomace, and for mango peel above 60 °C. For mango peel below 60 °C and carrot pulp across the whole temperature range, dipolar polarisation appears to dictate the change in dielectric loss with increasing temperature.

4.1.3. Extraction performance

Fig. 5 shows the yield of Alcohol Insoluble Solids (AIS) against treatment time for MAE and CSE for the four different biomasses. AIS yield is used as an indicator of the quantity of pectin extracted, although some hemicellulose could also be present. Other smaller molecular weight extracts remain in the supernatant and so do not contribute to the reported yield (Mao et al., 2020). The results show similar trends for the three fruits (orange peel, mango peel and apple pomace), with significantly different outcomes for the carrot pulp.

For the fruits, the optimum extraction time of MAE was less than that of CSE, while the maximum AIS yields achieved appear unaffected by extraction method. For example, the optimum AIS yield of orange peel extract using MAE was 12.9% at only 45 mins treatment time, with a similar optimum yield of 11.1% achieved at 120 mins treatment time when CSE was used. Similarly, the optimum AIS yields of mango peel extract and apple pomace extract were achieved at 120 mins using MAE and 180 mins using CSE, in all cases with similar yields. Carrot pulp, on the other hand, yielded significantly less AIS, at 6.0% and 6.3% for MAE and CSE respectively, both at an extraction time of 60 min; the optimum

extraction yield and time for carrot pulp were unaffected by heating type.

Sugar analysis of orange peel and carrot pulp extracts using MAE and CSE under their optimum treatment times (i.e. 45 and 120 mins for orange peel MAE and CSE respectively, and 60 mins for carrot pulp) is shown in Fig. 6. Homogalacturan (HG) content is calculated as the total of the galacturonic acid, and represents the “smooth” pectin regions, and RG-I is the total of the rhamnose, galactose and arabinose sugars, representing “hairy” pectin.

For orange peel, the yields of HG and RG-I regions extracted at their optimum condition in both MAE and CSE were very similar, at 25.8% and 27.4% respectively for HG and 12.0 and 10.6% respectively for RG-I. The only difference was that an extra 7.6% unidentified components were yielded from orange peel using MAE that were not extracted using CSE. The unidentified components were most likely protein and ash (Mao et al., 2020). Given that the heating rate and extraction time as well as the heating method were different in these experiments, it is difficult to propose a reason for this discrepancy, which is investigated further in Section 4.2. In the case of carrot pulp, near identical quantities of HG, RG-I, other sugars (xylose and glucose, which are main components of hemicellulose) and unidentified components were extracted using MAE and CSE, and this was expected based on the similar heating rates achieved between MAE and CSE for carrot and the lack of selective heating as indicated by the dielectric loss in Fig. 4 (as discussed in Section 4.1.2). Overall, these results suggest that the biomass predominantly determined the yield and composition of the extract under optimum extraction conditions regardless of the heating method or treatment time.

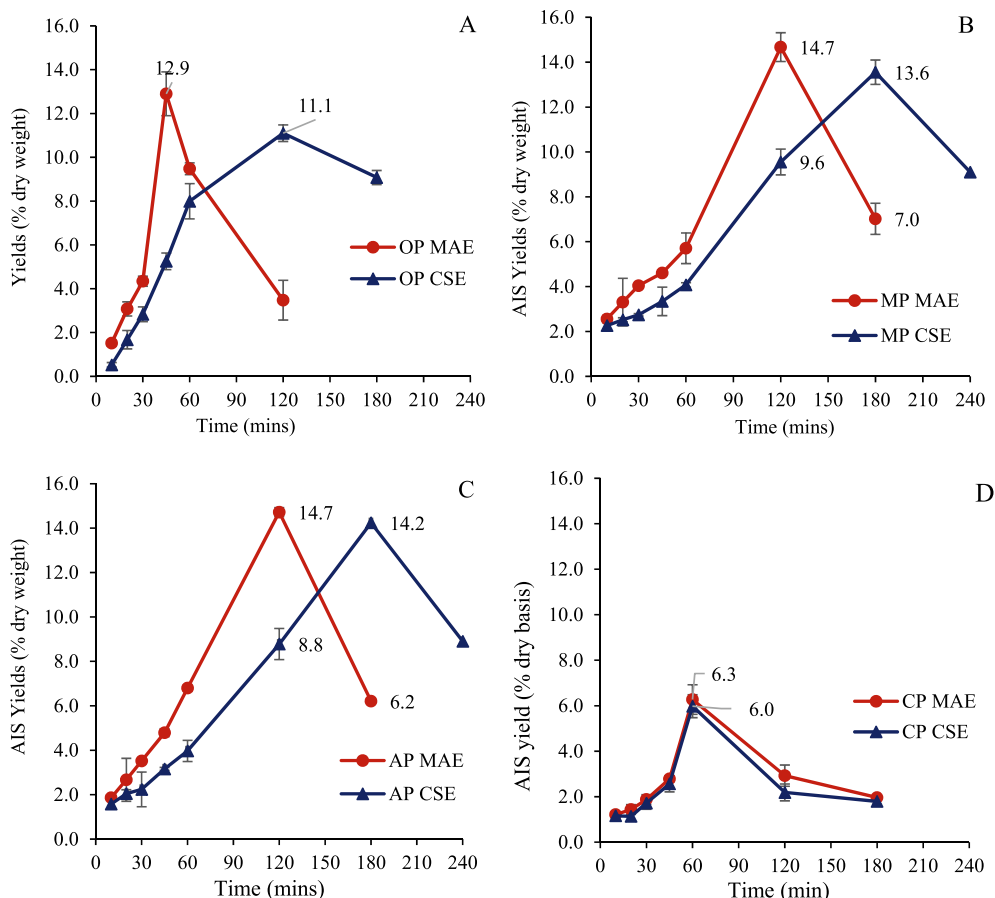


Fig. 5. AIS yields using MAE at 200 W and CSE from orange peel (A), mango peel (B), apple pomace (C) and carrot pulp (D) using water as the solvent at 90 °C.

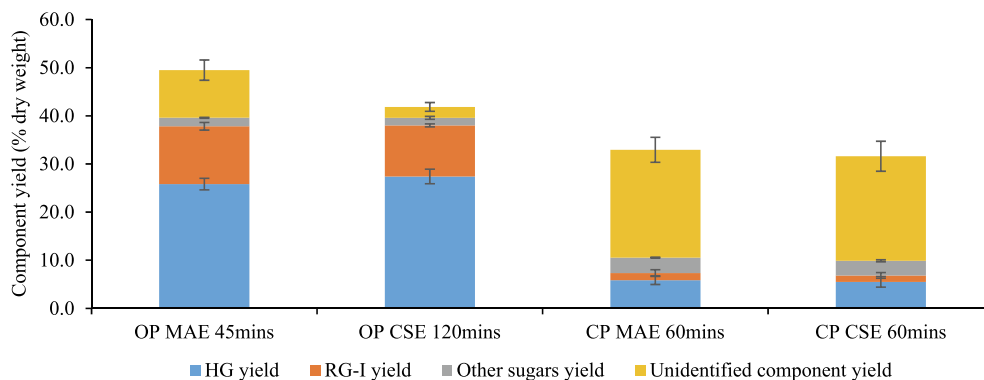


Fig. 6. Yields of HG, RG-I and other components in the extracts of orange peel and carrot pulp from their optimum extraction condition using MAE and CSE.

We can conclude from this section, therefore, that the biomass types does affect the performance of microwave and conventional solvent extraction. Because heating rate in conventional heating is driven by conductivity, and in microwave heating is driven by dielectric loss, and because the presence of extract has a positive effect on dielectric loss and a negative effect on thermal conductivity, a good candidate for MAE is by nature a bad candidate for CSE, and vice versa. This result is a major breakthrough in understanding the huge variation in experimental outcomes of MAE reported in the literature, and a major step forward in terms of enabling the selection of microwave technology where it will offer best advantage.

4.2. Understanding the effect of heating conditions and the role of selective and volumetric heating

4.2.1. Matching heating rate in MAE and CSE experiments

The second research question relates specifically to the mechanisms by which microwave heating leads to processing advantages

in order to be able to predict favourable processing conditions. If the accelerated extraction observed during MAE of the fruits is a result of the faster heating rates caused by volumetric heating, then in theory conductive heating in CSE could lead to the same results if the heating rate of the microwave heating is matched by the conventional experiments. If selective heating plays a role, then there should still be a difference between MAE and CSE even when the same heating rates are applied, and this could impact on the extraction performance in the ways depicted in Fig. 1.

To decouple the effects of heating rate (either by volumetric or conductive heating) and selective heating, heating rate was investigated as an independent variable for orange peel pectin extraction. This was done by varying the microwave input power for MAE (50–200 W), and by using liquid baths of difference temperatures for CSE (90–150 °C) and transferring the reactor to a 90 °C water bath once the set T_{bulk} was reached. The bulk heating rates achieved using these methods are shown in Fig. 7, with the average heating rates calculated between 25 °C and 90 °C tabulated below

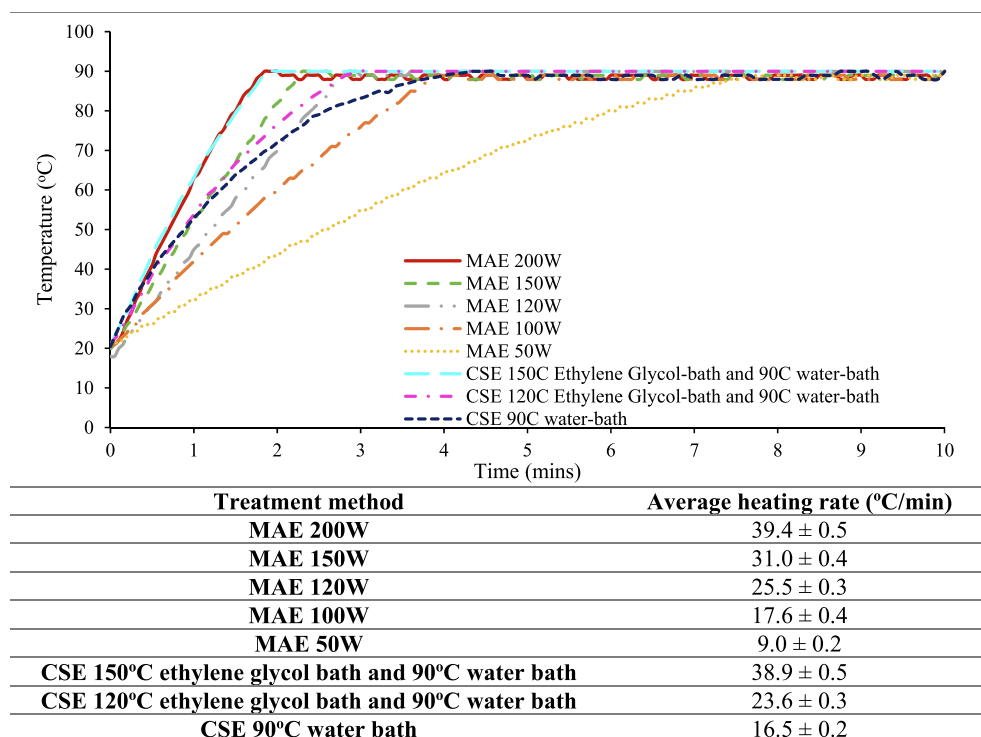


Fig. 7. Bulk heating rates of MAE and CSE at different heating “powers” using orange peel. All average heating rates were calculated from 25 °C to 90 °C.

each figure. It shows that the heating rate increases with increasing applied power for MAE and liquid bath temperature for CSE. MAE at 200 W achieved a similar heating rate to CSE using a 150 °C liquid bath (39.4 °C/min compared with 38.9 °C/min), while MAE at 100 W was close to CSE using a 90 °C bath (17.6 °C/min compared with 16.5 °C/min) and MAE at 120 °C was comparable with the 120 °C bath (25.5 °C/min and 23.6 °C/min). This enables investigation of the performance of MAE and CSE at difference heating rates (and therefore microwave powers) for the first time.

4.2.2. Extraction performance

Fig. 8A shows the AIS yield as a function of extraction time for both CSE and MAE at various heating rates, and Fig. 8B shows the optimal yield as a function of heating rate. Considering the CSE results first, it is clear that the AIS yield increases slightly with heating rate (11.1–12.5%), but that the extraction time appears unaffected, at 120 mins. At the lower microwave powers of 50 and 100 W, the results are similar: increased heating rate increases yield but not extraction time, and comparing MAE at 100 W with CSE and 90 °C water bath, which have very similar bulk heating rates of 17.6 and 16.5 °C/min, the extraction yields and times are very similar. At low heating powers therefore, there is no evidence of a selective heating advantage. It is also important to note that there is fairly low resolution in the data regarding treatment time, especially around 120 mins. Therefore, slight differences in the optimum extraction time cannot be identified.

The MAE results at higher powers show a different trend. Fig. 8A shows that increasing the power from 100 W to 120 W results in a step change reduction in optimum extraction time, from 120 mins to 60 mins. The yields in Fig. 8B and C show a similar incremental increase in optimum extraction yield with increasing heating rate to CSE, except one anomaly 150 W, where it is slightly lower than at 120 W and 200 W (10.5% compared with 12.5 and 12.9%). This is likely due to the lack of resolution in the data coupled with the fact that after the optimum extraction time, the AIS degrades rapidly in the solvent by β -elimination to a molecular weight level too small to be precipitated in alcohol (Fraeye et al., 2007). This degradation is more pronounced in the higher-powered microwave experiments, possibly linked to the selective heating effects causing higher T_{local} temperatures. Therefore, the optimal yield at 150 W was probably closer to 12 – 13% somewhere between 45 and 60 mins. It is noted though that all differences in yields are incremental, likely because the maximum AIS yield with water as the solvent has been achieved (the effect of solvent is known to have a marked effect on extraction yield and composition (Mao et al., 2019), but is not within the scope of this study).

Fig. 9 shows the sugar analysis of the AIS extracted at comparable heating rates for MAE and CSE: ~17 °C/min (MAE at 100 W, 90 °C liquid bath), ~25 °C/min (150 W, 120 °C bath) and ~39 °C/min (200 W, 150 °C bath). It shows, broadly speaking, that the amount of HG and RG-I extracted are similar in all cases. There is a slight decrease in the HG at higher heating rates for CSE, and this could be caused by longer treatment times allowing more time for

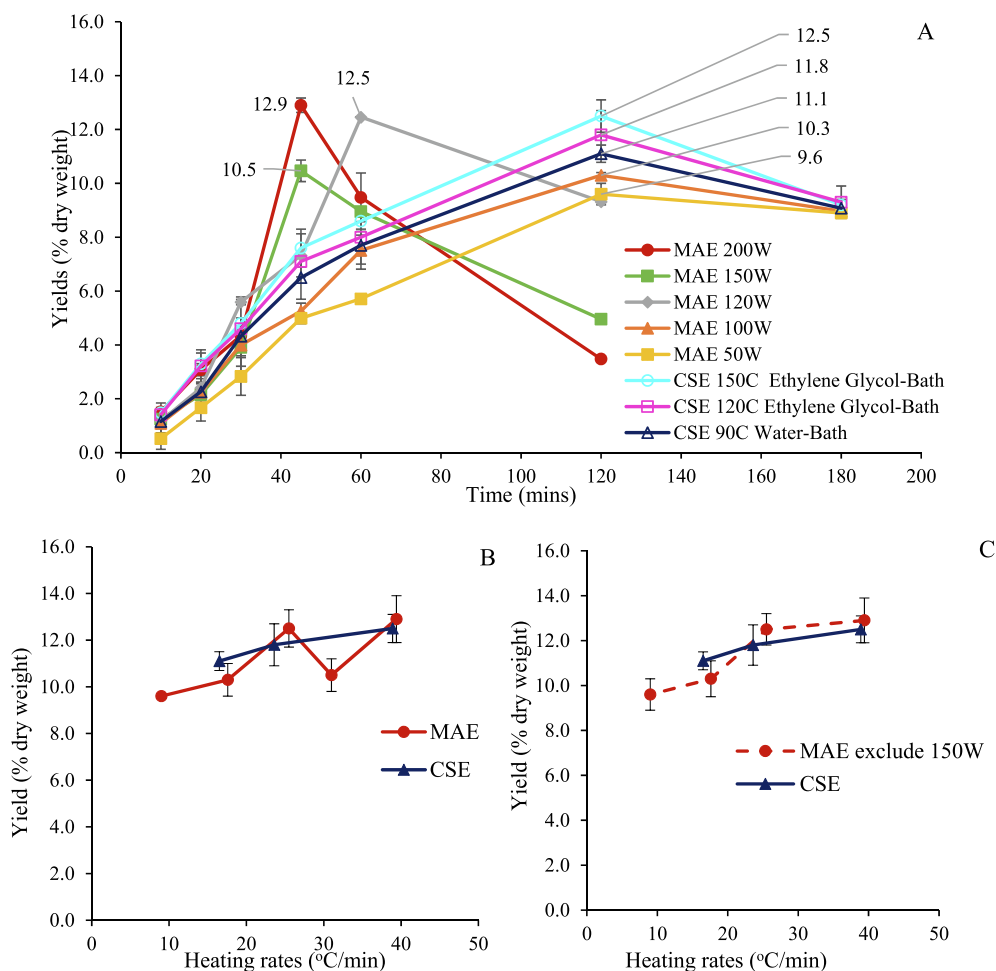


Fig. 8. AIS yields against time (A) and against heating rates (B, C) of MAE and CSE at different heating “powers” using orange peel.

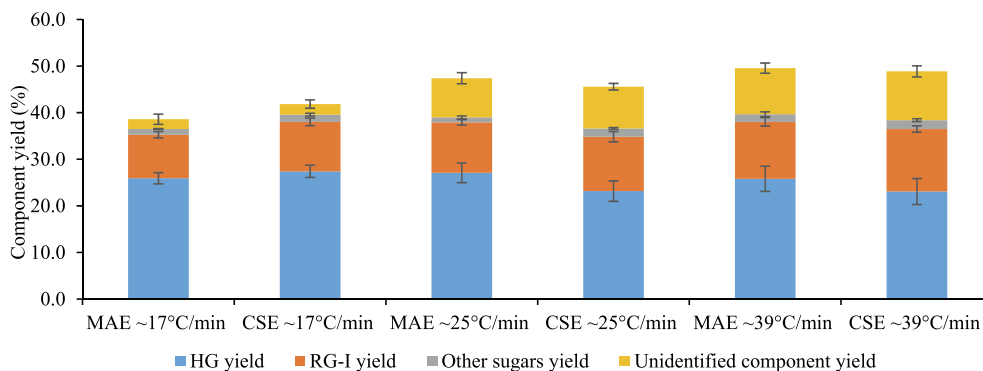


Fig. 9. Yields of HG, RG-I and other components in the extracts of orange peel at different heating rates using MAE and CSE.

HG degradation, but as stated in Section 4.1, yield differences across the board are incremental.

The interesting finding is that the target extract polysaccharides (pectin with some hemicellulose) were expected to predominantly break down into sugar monomers (detected in this analysis). As expected at low heating rates, the total sugar contents in the extracts constituted >900 mg/g AIS. At heating rates above ~20 °C/min, however, the sugar content did not increase in line with the increase in total AIS yield shown in Fig. 8B and C. The increases in yields observed at higher powers were not due to sugars, and were therefore not the result of increased polysaccharide extraction (pectin and hemicellulose), but something else not detected in the sugar analysis (most likely protein and ash). This was the case in both CSE and MAE extraction, and it is therefore concluded that this unidentified components are extracted at higher heating rates, and is not related to any microwave selective heating effects.

The important and novel finding of the experiments in this section is that a microwave power input threshold has been identified. Below the threshold, heating rate has very little effect on results (high heating rates may also lead to the extraction of small amounts of proteins and/or other cell wall components (Mao et al., 2020)) and this finding is independent of heating method (volumetric microwave heating or conductive conventional heating). Above the threshold, there is a step change reduction in extraction time when microwave heating is used: for the highest microwave heating power of 200 W optimal extraction is achieved at 45 mins for MAE, compared with around 120 mins for the equivalent heating rate of ~39 °C/min using CSE. This is compelling evidence that some or all of the selective heating effects caused by elevated T_{local} and Temperature-Induced Diffusion (TID) discussed in Section 2.1 and depicted in Fig. 1 becomes significant at higher microwave powers, and the implications of this finding will be discussed further in the following Section 5.

5. Implications

5.1. Predicting amenable biomasses for MAE

We have shown that the heat transfer properties of the biomass can be linked to conventional and microwave extraction performance. Higher thermal conductivity was favourable for conventional extraction, while higher dielectric loss was favourable for microwave extraction. Because of the contribution of solute to dielectric loss and thermal conductivity, the biomasses that were best suited to microwave extraction were least suited to conventional extraction. Although it seems like an obvious conclusion, this is the first study to investigate the contribution of the biomass

characteristics to heat and mass transfer during extraction. Since the heating rate was found to have a negligible effect on extraction performance, the thermal conductivity of the biomasses did not have a significant impact on the Conventional Solvent Extraction performance. Conversely, the dielectric properties had a significant effect on Microwave-Assisted Extraction performance due to microwave selective heating.

This new knowledge can be tested by relating it to previously published work. Using the same extraction conditions as in Section 4.1 of this paper, Mao et al. (2019) found no difference between pectin yields or extraction times for sugar beet extraction using MAE and CSE. Based on our finding here, the sugar - beet pulp -water system is expected to have a similar dielectric loss to water, and a thermal conductivity closer to carrot pulp than the other samples investigated in this paper. To validate this theory, the dielectric loss and conductivity of the sugar beet pulp - water systems were measured. The thermal conductivity was 6.11 W/mK, almost identical to carrot pulp, and the dielectric loss, shown in Fig. 10, was close to that of water.

5.2. Identification of a power threshold to exploit microwave selective heating

This paper has identified a power threshold, above-which microwaves exhibit a step-change in performance compared with conventional solvent extraction in cases where the dielectric loss factor of the biomass is higher than that of the solvent.

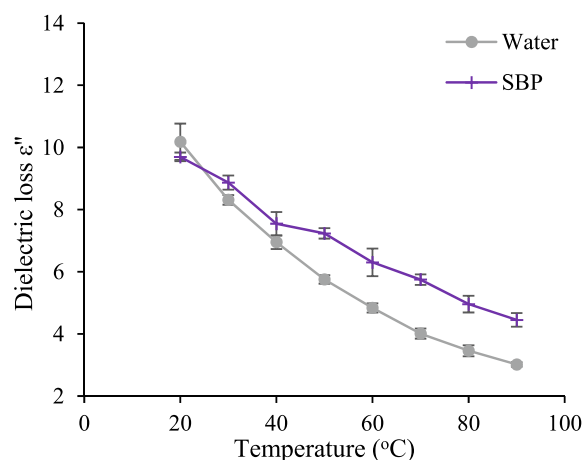


Fig. 10. Dielectric properties of D.I water and solutes of sugar beet pulp (SBP) in water. All results measured at 2.47 GHz and 20 to 90 °C.

The heating rate of a specific component within a microwave heating system is determined by the power density P_d as expressed in Eq. (3). In the case of the experiments reported here, the only experimental variables that could affect the power density are the dielectric loss and the input power (which contributes to the magnitude of the electric field intensity, E). Therefore, in the fruit extraction experiments, the biomass is expected to heat faster than the solvent ($T_{local} > T_{bulk}$) based on the dielectric loss measurements. However, there is also conventional heat transfer happening at the same time, which leads to heat loss from the biomass to the solvent. At low heating powers (low E), therefore, the heat loss matches the difference in microwave heating rates of different parts of the system, and $T_{local} \sim T_{bulk}$ at steady state. This appears to have been the situation below input powers of 100–120 W for the experiments reported here for orange peel extraction.

Increasing the microwave input power (above 100–120 W in this case) increases P_d , and hence the volumetric heating rate exceeds the rate of heat loss, leading to T_{local} exceeding T_{bulk} . At this point, all or some of the selective heating effects identified in Section 2.1 come into effect. The direct effects of elevated T_{local} could be increased rates of diffusion, hydrolysis and dissolution. However, these changes are expected to be incremental, as the temperature differences under normal operating conditions are predicted to be in the order a few degrees only (Taqi et al., 2020), and the changes observed here are step changes in mass transfer rates.

The second, indirect, effect that selective heating could have on mass transfer is Temperature-Induced Diffusion (TID), in which transport processes are driven by temperature gradients in addition to concentration gradients as explained in Section 2.1. The recent work by Taqi et al. (Taqi et al., 2020) investigating the theoretical effects of TID resulting from microwave heating, predicts a threshold in power density above which TID could result in significant differences in mass transfer gradients within the biomass structure. One of the potential outcomes of TID is cell rupture due to pressure increases as more solvent is sucked into the cells (Taqi et al., 2020). However not all extraction is governed by cell rupture, and for pectin in particular it is unlikely that rupture will enhance the extraction of pectin from within cell walls. Other outcomes of TID could include enhanced levels of water activity and corresponding enhanced rates of hydrolysis and/or dissolution, as well as increased diffusion rates due to the higher driving force.

Despite not governing pectin extraction it is possible that cell rupture was achieved in experiments at power levels above the threshold. However, we note that the yields and compositions of the extracts were similar for microwave and conventional experiments carried out at the same heating rates. If cell rupture had occurred, we would have expected this to have had an observable impact on yield and composition of the extract. While the observation of a threshold power is in line with Taqi's prediction, we don't feel that this is conclusive evidence of cell rupture resulting from TID. Rather, we believe on balance that the results are more consistent with a significant increase in activity or diffusion rate resulting from TID. More work is needed to understand the link between the thermal gradient and the extraction rate, however it is beyond doubt that microwave selective heating leads to step changes in mass transfer during solvent extraction, and this

appears to be due to significant acceleration of the rate-limiting diffusion steps.

The power threshold identified for the orange peel extraction experiments presented in Section 4.2 was between 100 and 120 W. This threshold will vary depending on the degree of selective heating (determined by dielectric loss and electric field intensity, which is a function of applied power and microwave cavity design) and heat loss (determined by the heat transfer properties of the biomass and solvent, which are affected by system variables such as the sample mass, particle size and biomass tissue structure). Different microwave heating systems support different electric field intensities depending on the applied power, impedance matching, sample size and location, and as a result we would not expect the 100–120 W threshold to apply directly to other microwave heating systems. However, the general principle is that process variables that affect heating rate will be expected to show a similar threshold no matter what microwave heating system is used, and that higher heating rates can be promoted with higher input power, single-mode cavities, active impedance matching and the appropriate sample size.

6. Conclusion

The results presented in this paper represent major advances in the understanding of how heat transfer properties of different biomasses, as well as the heating method and applied power/heating rate, impact mass transfer during solvent extraction. The new understanding will impact in process selection and design with the following two key findings:

1. Biomass characteristics that are particularly receptive to microwave processing have been identified.
2. A threshold microwave power, above which Temperature-Induced Diffusion leads to a step change mass transfer rates, has been identified.

There is real potential for these findings to contribute to the scale-up of successful microwave processes.

CRediT authorship contribution statement

Yujie Mao: Conceptualization, Methodology, Investigation, Writing - original draft, Visualization. **John Robinson:** Conceptualization, Writing - review & editing, Supervision. **Eleanor Binner:** Conceptualization, Resources, Writing - review & editing, Visualization, Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A

See Table A1.

Table A1

Chemical and physical properties of raw biomass and extracts from orange peel, mango peel, apple pomace and carrot pulp. Where, Total sugars = GalA + Rha + Ara + Gal + Glu + Xyl; RG-I region = Rha + Ara + Gal; RG-I/HG weight ratio = (Rha + Ara + Gal)/GalA, which represents the proportion of HG and RG-I region in ALS extract.

Biomass names	Yields % dry basis	GalA (HG) mg/g biomass	Rha mg/g biomass	Ara mg/g biomass	Gal mg/g biomass	Glu mg/g biomass	Xyl mg/g biomass	Total sugar mg/g biomass	RG-I region mg/g biomass	RG-I/HG Weight ratio
Orange peel	/	301.6 ± 3.1	53.6 ± 0.4	71.1 ± 1.1	47.8 ± 0.8	244.2 ± 1.0	21.7 ± 0.3	740.0 ± 6.7	172.5 ± 2.3	0.57 ± 0.02
Mango peel	/	210.7 ± 2.5	51.5 ± 2.1	68.8 ± 0.3	65.4 ± 1.4	212.0 ± 2.5	18.9 ± 0.6	627.9 ± 9.4	185.5 ± 3.8	0.88 ± 0.04
Apple pomace	/	216.9 ± 2.1	48.2 ± 0.2	63.0 ± 0.6	53.0 ± 0.6	268.2 ± 1.6	37.9 ± 0.2	687.2 ± 6.3	164.2 ± 2.4	0.76 ± 0.03
Carrot pulp	/	428.3 ± 0.2	16.6 ± 1.6	36.8 ± 0.2	62.8 ± 0.7	335.4 ± 1.3	7.5 ± 2.0	887.4 ± 5.9	116.1 ± 2.4	0.13 ± 0.01
Extract names	Yields % dry basis	GalA mg/g extract	Rha mg/g extract	Ara mg/g extract	Gal mg/g extract	Glu mg/g extract	Xyl mg/g extract	Total sugar mg/g extract	RG-I region mg/g extract	RG-I/HG Weight ratio
Pectin extracts using MAE at 200 W from 10 to 120 mins and CSE 120 mins from orange peel.										
OP.MAE.200 W.10 min	1.5 ± 0.1	533.1 ± 4.1	10.0 ± 0.0	10.4 ± 0.1	102.0 ± 0.2	11.4 ± 0.4	6.0 ± 0.2	672.9 ± 5.0	122.4 ± 0.3	0.23 ± 0.01
OP.MAE.200 W.20 min	3.1 ± 0.3	562.3 ± 3.6	10.5 ± 0.0	11.3 ± 0.0	111.4 ± 0.6	13.3 ± 0.3	8.7 ± 0.2	717.5 ± 4.7	133.2 ± 0.6	0.24 ± 0.01
OP.MAE.200 W.30 min	4.3 ± 0.2	592.3 ± 4.7	13.5 ± 0.1	15.5 ± 0.2	116.5 ± 1.0	16.1 ± 0.3	8.9 ± 0.2	762.8 ± 6.5	145.5 ± 1.3	0.25 ± 0.00
OP.MAE.200 W.45 min	12.9 ± 1.0	603.3 ± 2.1	18.6 ± 0.2	24.8 ± 0.1	120.0 ± 0.2	26.9 ± 0.1	6.9 ± 0.0	800.5 ± 2.7	160.8 ± 0.9	0.27 ± 0.01
OP.MAE.200 W.60 min	9.5 ± 0.3	599.0 ± 2.0	16.8 ± 0.1	18.0 ± 0.2	126.0 ± 0.6	28.8 ± 0.4	9.7 ± 0.0	798.3 ± 3.3	163.4 ± 0.5	0.27 ± 0.03
OP.MAE.200 W.120 min	3.5 ± 0.9	585.4 ± 1.6	21.3 ± 0.2	36.2 ± 0.3	126.6 ± 0.7	42.8 ± 0.4	12.1 ± 0.5	824.4 ± 3.7	184.1 ± 1.2	0.31 ± 0.02
OPW.CSE.120 min	11.1 ± 0.4	744.6 ± 2.6	18.8 ± 0.0	30.1 ± 0.1	116.0 ± 0.6	27.9 ± 0.2	9.3 ± 0.0	946.7 ± 3.5	164.9 ± 0.7	0.22 ± 0.01
Pectin extracts of optimum conditions using MAE at 200 W and CSE from mango peel.										
MP.MAE.200 W.120 min	14.7 ± 0.6	502.5 ± 1.3	28.4 ± 1.4	45.7 ± 0.5	107.1 ± 0.4	69.1 ± 0.5	4.2 ± 0.1	757.0 ± 4.2	181.2 ± 2.3	0.36 ± 0.04
MP.MAE.200 W.180 min	7.0 ± 0.6	495.3 ± 2.7	32.6 ± 1.4	56.2 ± 0.0	127.0 ± 0.1	102.6 ± 0.2	6.6 ± 0.0	820.3 ± 4.4	215.8 ± 1.5	0.44 ± 0.04
MP.CSE.120 min	9.6 ± 0.7	568.7 ± 2.5	18.4 ± 0.5	39.4 ± 0.1	99.0 ± 0.2	58.9 ± 0.5	3.8 ± 0.1	816.2 ± 4.8	156.8 ± 0.8	0.28 ± 0.01
MP.CSE.180 min	13.6 ± 0.5	596.7 ± 3.4	19.0 ± 0.9	53.1 ± 0.0	117.6 ± 0.3	77.1 ± 0.5	5.0 ± 0.0	840.5 ± 4.2	189.7 ± 1.2	0.32 ± 0.03
Pectin extracts of optimum conditions using MAE at 200 W and CSE from apple pomace.										
AP.MAE.200 W.120 min	14.7 ± 0.1	411.3 ± 2.9	18.0 ± 0.4	14.3 ± 0.3	92.1 ± 0.7	13.4 ± 0.1	12.4 ± 0.2	604.4 ± 3.0	124.4 ± 1.4	0.30 ± 0.01
AP.MAE.200 W.180 min	6.2 ± 0.2	454.2 ± 1.3	20.0 ± 0.9	35.4 ± 0.1	107.7 ± 0.4	24.9 ± 0.2	17.1 ± 0.0	616.4 ± 4.5	163.1 ± 1.4	0.36 ± 0.03
AP.CSE.120 min	8.8 ± 0.5	609.1 ± 1.4	16.1 ± 0.2	11.4 ± 0.3	75.9 ± 0.6	8.8 ± 0.2	9.7 ± 0.2	731.0 ± 2.9	103.4 ± 1.1	0.17 ± 0.02
AP.CSE.180 min	14.2 ± 0.7	556.8 ± 1.0	16.7 ± 1.0	20.1 ± 0.2	98.5 ± 0.4	18.6 ± 0.1	13.7 ± 0.0	724.4 ± 2.7	135.3 ± 1.6	0.24 ± 0.01
Pectin extracts of optimum conditions using MAE at 200 W and CSE from carrot pulp.										
CP.MAE.200 W.60 min	6.3 ± 0.7	398.2 ± 0.1	1.5 ± 0.1	10.1 ± 0.1	15.5 ± 0.1	133.7 ± 0.3	30.7 ± 0.1	599.7 ± 0.8	27.1 ± 0.3	0.05 ± 0.01
CP.CSE.60 min	6.0 ± 0.5	392.4 ± 0.1	1.3 ± 0.2	9.8 ± 0.3	14.9 ± 0.6	142.4 ± 0.5	31.6 ± 0.1	592.4 ± 1.8	26.0 ± 1.1	0.04 ± 0.01
Pectin extracts of orange peel at various heating rates under MAE and CSE.										
OP. MAE.200 W.45 min	12.9 ± 1.0	603.3 ± 2.1	18.6 ± 0.2	24.8 ± 0.1	120.0 ± 0.2	26.9 ± 0.1	6.9 ± 0.0	800.5 ± 2.7	163.4 ± 0.5	0.27 ± 0.01
OP. MAE.150 W.45 min	10.5 ± 0.7	608.6 ± 4.2	14.1 ± 0.0	16.0 ± 0.3	107.4 ± 0.0	21.4 ± 0.0	6.7 ± 0.1	774.2 ± 4.6	137.5 ± 0.3	0.23 ± 0.03
OP. MAE.120 W.60 min	12.5 ± 0.8	653.1 ± 3.7	16.5 ± 0.1	29.5 ± 0.0	104.0 ± 0.2	16.1 ± 0.3	6.1 ± 0.2	825.3 ± 4.5	150.0 ± 0.3	0.23 ± 0.00
OP. MAE.100 W.120 min	10.3 ± 0.7	759.1 ± 2.1	17.5 ± 0.0	28.1 ± 0.1	110.6 ± 0.8	25.7 ± 0.1	6.3 ± 0.1	947.3 ± 3.4	156.2 ± 0.9	0.21 ± 0.02
OP. MAE.50 W.120 min	9.6 ± 0.1	785.8 ± 2.1	17.1 ± 0.7	24.5 ± 0.1	109.8 ± 1.0	24.9 ± 0.2	5.8 ± 0.1	967.9 ± 4.1	151.4 ± 1.8	0.19 ± 0.01
OP.CSE.150 °C ethylene glycol bath.120 min	12.5 ± 0.6	556.7 ± 1.8	26.7 ± 1.1	34.1 ± 0.8	124.4 ± 0.9	29.7 ± 0.4	10.9 ± 0.2	782.5 ± 5.2	185.2 ± 2.8	0.33 ± 0.02
OP.CSE.120 °C ethylene glycol bath.120 min	11.8 ± 0.9	592.0 ± 2.9	19.3 ± 0.9	32.7 ± 0.3	118.6 ± 0.2	29.1 ± 0.0	10.6 ± 0.1	802.3 ± 5.3	170.6 ± 1.4	0.29 ± 0.02
OP.CSE.90 °C water bath.120 min	11.1 ± 0.4	744.6 ± 2.6	18.8 ± 0.0	30.1 ± 0.1	116.0 ± 0.6	27.9 ± 0.2	9.3 ± 0.0	946.7 ± 3.5	164.9 ± 0.7	0.22 ± 0.01

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