Review

Current status of microwave-assisted extraction of pectin

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A B S T R A C T

There is an urgent need to develop new pectin extraction processes, as the established commercial extraction process damages the pectin (limiting the potential product applications) and is harmful to the environment. Microwave-Assisted Extraction could offer a sustainable route to pectin extraction from a wide range of food wastes and agricultural residues. We present the current state of the art in Microwave-Assisted Extraction of pectin, including the current understanding of the unique heat and mass transfer mechanisms at play during extraction. We review all of the recent literature, testing the commonly held view that microwave heating offers a general improvement in yield and dramatic reductions in processing time compared with conventional solvent extraction. In most of the literature reviewed, there was no evidence that this is the case. However, there is emerging evidence that Microwave-Assisted Extraction can provide processing advantages under some conditions, and that the feedstock dielectric properties and heating rate are important parameters. Preliminary attempts to scale this technology up have shown promise in terms of pectin yield, quality and Life Cycle Analysis compared with conventional extraction. The next steps should be to test more continuous processing concepts for a wider range of feedstocks, and develop more robust Life Cycle Analysis and technoeconomic models. This is the first review paper to focus on the Microwave-Assisted Extraction of pectin.

1. Introduction

Commercial pectin is produced using a well-established industrial process known as hot-acid extraction. This process uses fruit peels and pomace (predominantly citrus and apple juicing co-products) to produce "smooth" pectin, which is rich in homogalacturan (HG) and has favourable properties for gelling and stabilisation of jams and jellies [1]. It is well known that acidic conditions are favourable for extraction of HG-rich pectin. However, pectin that is predominantly rich in rhamnogalacturan-1 (RG1) with some rhamnogalacturan-2 (RG2) cannot be extracted under acidic conditions as the characteristic "hairy" neutral sugar side chains are attacked by the acid. These hairy pectins are known to have functionality that could lead to the development of novel pectin-based products (e.g. as prebiotics or pharmaceuticals) [2]. Another issue with the commercial process is the use of large amounts of acid and high heating requirements, leading to environmental burden of toxic waste streams and CO_2 emissions from electrical, coal or gas burners. Finally, the urge to address food waste and valorise co-products from the food, drinks and agricultural sectors has led to enormous interest in determining the potential to extract pectin from non-conventional sources. This has led to a vast number of papers in

recent years reporting the investigation of novel pectin extraction methods that could:

1. Extract pectin without damaging neutral side chains, thereby increasing the potential applications (e.g. functional food ingredients and medicines).
2. Reduce environmental impact through lower energy use, less toxic solvents and reduced solvent requirements.
3. Extract pectin from a wider range of biomass feedstocks (i.e. food and agricultural wastes and co-products).

One of the emerging technologies of interest is Microwave-Assisted Extraction (MAE). It has frequently been reported that, compared with the conventional hot-acid extraction process used in industry, MAE can provide higher yields in shorter extraction times, requires less energy, may be able to extract pectin without the need for acidic conditions and requires less solvent. It is also generally accepted that the electromagnetic heating mechanisms (which lead to direct, volumetric and selective heating) cause rapid pressure build-up and rupture of the feedstock structure during the extraction process, and this is generally stated as the reason for the enhanced processing outcomes of MAE compared with

Conventional-Solvent Extraction (CSE). Despite the significant research effort in this area, there is a very low conversion of laboratory scale examples to pilot demonstrations and (to the authors' knowledge) no existing industrial-scale microwave-assisted pectin extraction process. The aim of this paper is to critically review the current state of understanding of Microwave-Assisted Extraction of pectin with the hope that this will inform future research and development efforts in this area, increasing understanding and ultimately conversion to industrial demonstration. There have been several recent reviews on pectin extraction, so these are reviewed before our scope is defined to prevent repetition.

2. Review scope

Adetunji et al. [3] carried out a review of emerging pectin extraction methods in 2017, and gave a good introduction to the basics of MAE. Several process parameters and system properties were identified as being important in process outcomes, but quantification of those variables was absent from the existing literature (e.g. the dielectric properties weren't measured, and power, temperature and heating rate were never decoupled as variables). The paper clearly outlined the state of understanding at the time. However, the 2017 literature had limited examples (7 papers), and the underlying heat and mass transfer phenomena had not been investigated in significant depth.

Since 2017, several more reviews have been published in which microwave extraction has been included as part of a wider review of pectin extraction [4–16]. These papers generally reiterated the often-cited advantages of the use of microwaves in solvent extraction. However, they did not interrogate the experimental methods used nor discuss in depth how the results contributed to further understanding of MAE. This is understandable given the broad scope of their reviews, which showcased a range of different extraction technologies and typically included < 10 papers on MAE. Picot-Allain et al. [17] observed that experimental studies to date had been limited to up to 1 kW, and that higher microwave powers would need to be investigated to facilitate scale-up.

From these recent publications, it can be concluded that there is a lot of data detailing the yield and composition of pectin extracted from a wide range of biomass materials under specific processing conditions. It is known that pH, microwave power, extraction time and solid–liquid ratio (SLR) all have significant effects on the extraction results. It is understood that the dielectric properties of the system should influence the processing outcomes, as they determine the heating rate of the solvent and biomass. However, to date none of the literature reviewed quantifies the dielectric properties or correlated them with extraction performance. There is only qualitative, top level description of proposed mechanisms by which microwaves may enhance pectin extraction; since the review in 2017 [3], there has been little new development of understanding of MAE in the review literature. The main reasons for this are that the reviews to date have not focused specifically on microwave technology and that it is only recently that advances in this understanding have begun to be published.

The aim of this paper, therefore, is to focus specifically on the Microwave-Assisted Extraction of pectin: to summarise recent advances in fundamental understanding, to critique experimental practice and design in MAE, to systematically relate the processing conditions and feedstock characteristics to performance, and to report the current state of scale-up attempts. The scope of the review is all literature published since 2017 reporting the extraction of pectin from plant-based materials using MAE. The functionality and potential application of the extracted pectin is outside the scope of this paper: We consider only yield and composition as process outcomes of interest. MAE is the only technology discussed, although conventional solvent extraction results are reported where available for comparison in order to better understand MAE. To this end, we searched "microwave extraction pectin" in Scopus, and downloaded or acquired 50 relevant papers, which are reviewed here.

3. Fundamental understanding of Microwave-Assisted extraction (MAE)

3.1. Solvent extraction

Solvent extraction is a solid–liquid separation process, in which a solid material (biomass in this case) is submerged in a liquid solvent. The extraction of pectin is generally conceptualised as a series of mass transfer steps driven by concentration gradients (osmotic pressure): (i) penetration of the solvent into the biomass, (ii) diffusion through the biomass, (iii) hydrolysis of the proto-pectin (the in-situ pectic polysaccharide), (iv) solubilisation of pectin into the solvent, (v) diffusion to the biomass surface, (vi) external transfer to the bulk solution and (viii) degradation and de-esterification of the extracted pectin [18]. Diffusion and hydrolysis rates and the solubility of the extracts increase with temperature, and therefore temperature is elevated during solvent extraction in order to increase extraction rates and extract yields. During Conventional Solvent Extraction (CSE), the material nearest the walls of the heating vessel is heated first, and heat is transferred throughout the extract mixture via conduction and convection (necessarily enhanced via mixing); once the set temperature is reached, isothermal conditions are maintained. This is not the case in MAE, as microwaves heat using fundamentally different heat transfer mechanisms, which can result in non-isothermal temperature distributions, and this is the key difference between CSE and MAE.

3.2. Microwave heating fundamentals

Microwave energy is delivered directly to materials through molecular interactions with the electromagnetic field [19]. In this case, electromagnetic waves penetrate the material and interact with the molecules, which absorb the energy and convert it to heat. This results in attenuation of the microwave field amplitude with increasing distance from the surface of the material. The two predominant mechanisms for the conversion of microwave energy into heat in dielectric materials are dipolar rotation and ionic conduction. Generally speaking, most biomass materials and aqueous solvents (as in pectin extraction) contain both dipolar and ionic molecules; therefore, dipolar rotation and ionic conduction occur simultaneously, resulting in an almost immediate heating up of the material [20]. It follows that when deionised water is used as the extracting solvent, dipolar rotation is the dominant mechanism, while there is still some effect of ionic conduction due to the free ions in the biomass dissolved into the solution. When solvents like acids, alkalis and/or salty solutions are used, the contribution of ionic conduction to heating would be expected to increase with increasing ionic concentration.

When a material is subjected to microwaves some of the energy is transmitted through the material and some is absorbed, and this is quantified by the dielectric properties [19]. These are used to understand the response of materials to microwaves, predict their heating rates when subjected to microwave electric fields and in the design of microwave reactors.

The dielectric properties of a material are the dielectric constant (ε'), which is the ability of a material to be polarised within an electromagnetic field, and the dielectric loss factor (ε''), which quantifies the conversion of electromagnetic energy into thermal energy. The ratio of the dielectric loss to constant, termed the dissipation factor, loss tangent or tanδ, is also defined:

$$\tan\delta = \frac{\varepsilon''}{\varepsilon'} \tag{1}$$

Tanδ represents a descriptive dielectric parameter that can be used as an indication of the material's general capability to absorb microwave energy and to convert the absorbed energy into heat [21]. A "lossy" material is a material that heats well in a microwave field. When

microwaves are applied to a heterogeneous material, the components with higher dielectric loss or loss tangent will be selectively heated, and they will heat up faster than less lossy components.

The penetration depth d_p is defined as the depth into a sample where the microwave power has dropped to 36.8% of its transmitted value, and materials with higher dielectric properties have smaller penetration depths. Water for example has a penetration depth of 1.3 cm at room temperature and 2.45 GHz. d_p is in the range of 0.6 – 1.0 cm for food products with $\varepsilon^{''} < 25$ [19] and varies with food composition and microwave frequency.

The power density p_d, which equates to sensible heating rate (assuming negligible heat loss), can be expressed as shown in Eq. (2): [22]

$$p_d = \rho C_P \frac{\Delta T}{\Delta t} = 2\pi f \varepsilon_0 \varepsilon^{'} E^2 \qquad (2)$$

where ρ is the density of the material, C_p is the specific heat, ΔT is the temperature rise, Δt is the time increment, f is the microwave frequency, ε_0 is the permittivity of free space, E is the electric field intensity, which in turn is a function of input power and system geometry [22]. From this relationship, it is clear to see that for a given E, the system components with higher $\varepsilon^{''}$ will heat faster than those with lower $\varepsilon^{''}$, and this will give rise to selective heating within heterogeneous systems.

It is evident from Eq. (2) that increasing E by turning up the microwave power leads to an increase in power density and hence heating rate and any selective heating effects.

3.3. Dielectric properties of biomass and solvent-biomass systems

While dielectric properties have been identified as an important variable in MAE, there is little information in the literature on the specific biomass-solvent mixtures of interest. Citrus peel and apple pomace are the most common sources of commercial pectin, but many food and agricultural wastes and co-products are of interest for pectin extraction. Aqueous solvents are used for pectin extraction, most commonly mineral acids, although organic acids and alkalis are also used. Table 1a summarises the dielectric properties of various fruit and vegetables at room temperature and 2.45 GHz. There are several different techiques for measuring dielectric properties that may give different results for the same sample; for consistency, all the data from Table 1a are from the same reference [23]. Table 1b presents the dielectric properties of some common pectin extraction solvents. The data shows that the loss tangent

of all of the biomasses is slightly higher than that of distilled water, indicating that the biomasses would be expected to heat slightly faster than water if heated in a microwave field at room temperature. However, aqueous HCl at pH1 is lossier than all of the biomasses, indicating that biomass would not be expected to accelerate heating in strong acid at room temperature.

As dielectric properties vary with temperature, composition, state, moisture content, bulk density and frequency, it is important to measure them under the conditions at which they will be processed. Mao [24] studied the dielectric properties of various peels and pulps in different solvents as a function of temperature. The results, shown in Fig. 1, show that all of the biomass-water mixtures have a higher dielectric loss than water, indicating that the addition of biomass to water is likely to increase the heating rate. However, the dielectric loss of carrot and sugar beet pulp mixtures were very close to water, so significant increases in heating rate would not be expected. The fruit mixtures would be expected to heat significantly faster than water, especially at higher extraction temperatures. Each extraction mixture showed different trends of dielectric properties as a function of temperature. The data in Fig. 1F shows that the dielectric loss of aqueous HCl is higher before the addition of sugar beet; these results indicate that the addition of sugar beet to acidic solvents is likely to reduce the microwave heating rate, although this may not be the case for all biomasses. We were unable to find any published dielectric property data for biomasses in alkaline solvents, nor for alkaline solvents. As the limited data available suggests that the biomass type and solvent affect the microwave heating behaviour, more research is indicated in this area. However, we note that these measurements only apply to the bulk mixture behaviour; the degree of selective heating of the biomass and any non-ideal mixing behaviour cannot be determined from these results.

3.4. Recent advances in understanding microwave-enhanced mass transfer

A visualisation of how the non-isothermal temperature distribution resulting from microwave heating could affect different extraction steps is presented in Fig. 2 (reproduced from [18]). If the local temperature (T_{local}) at any location within the biomass is higher than the solvent temperature (T_{bulk}), this could lead to build-up of pressure within the cellular structure, enhanced diffusion and hydrolysis rates and increased pectin solubility. Faster extraction and cooler solvent temperatures could also reduce extract degradation.

Rapid pressure build-up leading to swelling and rupture of the

Table 1
Dielectric property data for fruits and vegetables (a) and extracting solvents (b) at room temperature and 2.45 GHz.

Table 1a: Dielectric property data for common fruit and vegetables [23].

Raw Materials producing pectin		Moisture content (%)	Tissue density (g/cm)	Dielectric constant ($\varepsilon^{'}$)	Loss factor ($\varepsilon^{'}$)	Loss tangent tanδ
Citrus	**Orange**	87	0.92	69	16	0.23
	Grapefruit	91	0.83	73	15	0.21
	Lemon	91	0.88	71	14	0.20
	Lime	90	0.97	70	15	0.21
Apple		88	0.76	54	10	0.19
Banana		78	0.94	60	18	0.3
Strawberry		92	0.76	71	14	0.20
Carrot		87	0.99	56	15	0.27
Mango		86	0.96	61	14	0.23
Onion		92	0.97	64	14	0.22
Pear		84	0.94	64	13	0.20
Potato		79	1.03	57	17	0.30

Table 1b: Dielectric property data for common extracting solvents for pectin [24].

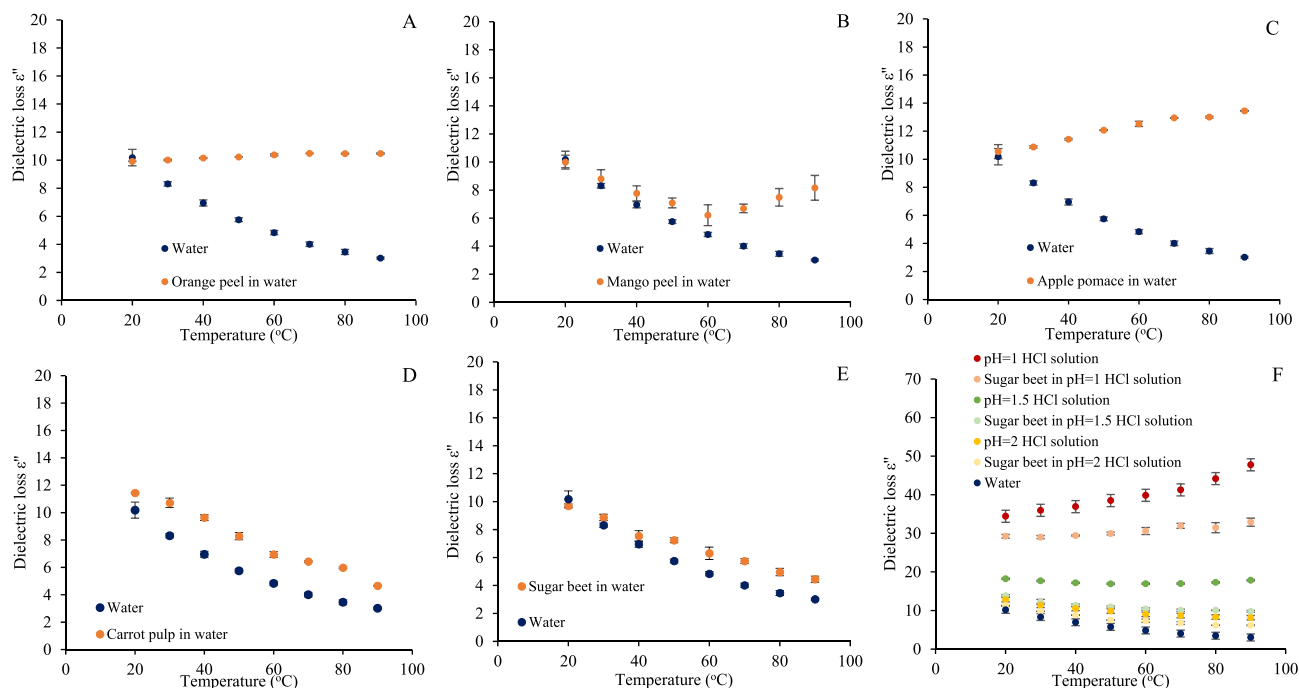| Solvent	Dielectric constant ($\varepsilon^{'}$)	Loss factor ($\varepsilon^{'}$)	Loss angle tanδ
Water	77.0	10.2	0.13
HCl pH = 1	75.3	34.4	0.46
HCl pH = 1.5	76.9	18.2	0.24
HCl pH = 2	77.3	12.8	0.17

Fig. 1. Dielectric properties of orange peel in water (A), mango peel in water (B), apple pomace in water (C), carrot pulp in water (D), sugar beet pulp in water (E) and sugar beet in different pH HCl solutions (F) at 2.47 GHz. Figure adapted from Mao [24] with permission. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
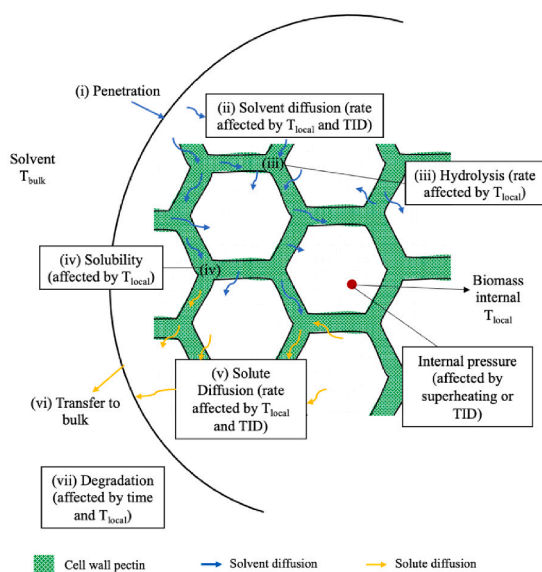

Fig. 2. Conceptual model of pectin extraction from biomass, highlighting (with borders) the steps that could increase yield or extraction rate when biomass internal temperature (T_{local}, which varies with spatial location) at steady state > solvent temperature (T_{bulk}). TID = Temperature-Induced Diffusion. Adapted from Mao et al. [18] with permission.

internal feedstock structure has been generally accepted as the reason for the enhanced processing outcomes when microwave heating is applied during solvent extraction. However, few studies have sought to provide quantitative evidence of how or if this occurs. Some studies have illustrated structural changes to the biomass structure using microscopic imaging before and after processing, e.g. for lime peel powder [25] and eggplant peel [26]. However, evidence of microwave-induced structural changes in these papers is inconclusive, and the lack of ability to observe the biomass at the microscale during processing is a major limitation of

this approach.

To overcome this, some theoretical models to describe physical phenomena during MAE have been proposed. Chan et al. [27] presented a model to link microwave heating with cell pressure due to intracellular steam generation, which until recently was the prevailing theory of how microwaves enhanced solvent extraction. The model, which represented a major step towards a mechanistic description of microwave extraction, was used to predict a cell rupture time consistent with experimental observations of extraction time. However, there was no heat transfer from the biomass to the solvent incorporated into the model, meaning that cell rupture was inevitable under all model input conditions. Lee et al. [28] proposed a new mechanism by which microwave heating could enhance mass transfer during solvent extraction; selective heating of the biomass of only a few degrees above that of the solvent could lead to chemical potential gradients (analogous to osmotic pressure caused by concentration gradients during conventional solvent extraction) that could drive solvent into the plant structure, causing swelling and potentially enough pressure to rupture cells. Taqi et al. [29] developed a mechanistic model to describe the action of microwave heating on biomass-solvent systems, incorporating microwave heating, conventional heat transfer, mass transfer and cellular expansion mechanics. Both cell rupturing hypotheses were tested. Under all but the most extremes of plausible experimental conditions, the temperature difference between the biomass and the solvent was insufficient to induce steam rupturing. Testing the "Temperature-Induced Diffusion" theory proposed by Lee et al. [28], Taqi et al. [29] found that the pressures needed to cause cell rupture could be readily achieved within a range of processing conditions that are consistent with previous laboratory studies. Electric field intensity, dielectric loss factor, thermal conductivity and the number of plant cells were all key parameters in the determination of internal cell temperatures and pressures. It is interesting to note that the model also showed that the biomass temperature is always higher than the solvent temperature regardless of dielectric loss, and this is because the only way to transfer heat away from the biomass is via the solvent, whereas the solvent can also transfer heat to the system boundary (vessel walls).

While these models propose plausible explanations of experimentally observed phenomena, there is still a disconnect between the hypotheses generated by the models and empirical results. To fully validate the models would require in-situ observation of the biomass at the micro-scale during extraction, which would be extremely challenging and to date has not been reported. A more pragmatic approach is to test the hypotheses using evidence from systematic empirical experimentation. Section 4 reviews the literature for such evidence.

4. Progress in empirical microwave extraction of pectin

4.1. Microwave-Assisted extraction experimental methods

Fig. 3 shows the main components and variables of microwave-assisted pectin extraction experiments. The microwaves are supplied to the microwave cavity through a waveguide. The components of the microwave generator and other components of the microwave system are not shown, but are described in detail in Meredith [30] and Metaxas et al. [22].

4.1.1. Microwave energy delivery (controlled variables: Incident power and cavity type)

The incident power shown in Fig. 3 is the power supplied by the microwave generator. Some of this power is absorbed by the sample, and the remainder is reflected. The absorbed power can therefore be calculated by subtracting the reflected power from the incident power. Most papers only report the incident power.

The total energy delivered to the sample is the average absorbed power multiplied by the time. The absorbed power throughout the experiment can fluctuate, and therefore logging the absorbed power as a function of time is essential to attain an accurate energy balance. An important consideration of microwave processes is that a system can have the same energy input at different heating rates, as higher power settings require shorter times to deliver the same energy. Changing the power input changes the power density within system components as calculated by Eq. (2).

The chamber in which the microwaves are applied to the sample is called the cavity or applicator, which typically is of multimode or single mode configuration. Multimode microwave applicators (such as

	Variables
Microwaves	Incident power (absorbed and reflected); Cavity design (e.g. multimode/single mode)
Vessel	Condenser (if boiling); Sealed (if hydrothermal); Open (if not boiling)
Solvent	Solvent types (Mineral acid e.g. HCl/HNO$_3$/H$_2$SO$_4$; Organic acid; Alkali); Solvent Volume
Biomass	Particle Size; Mass; Type; Pre-treatment (e.g. drying)
Process Parameters	Temperature (T); Solid to Liquid Ratio (SLR)

Fig. 3. Main components and variables of microwave-assisted pectin extraction experiments.

domestic microwave ovens) are mechanically simple and can accept a wide range of heating loads. They consist of a closed metal box with some means of coupling power from the microwave power generator, with dimensions of several wavelengths long in at least two dimensions [22]. They support multiple modes, i.e. multiple regions of concentration of electric field, which means that the electrical field pattern during experiments is essentially random. The performance of a multimode cavity depends on the shape, dimensions, configuration of the feeds and accessories of the cavity, and also the workload dielectric properties, dimensions and location in the oven. Minor changes to these parameters can have significant effects on performance [30]. The majority of work reported in the literature was carried out in domestic microwave ovens, some of which were modified and the turntable removed. This means that the sample placement may have had a significant effect on the heating efficiency. Several commercial multimode microwave synthesis/digestion systems have also been utilised for MAE from pectin [31–34]. The inherent variations in the electric field associated with multimode cavities may lead to inconsistencies in heating uniformity. The inability to measure reflected power, and hence calculate the energy absorbed by the sample, is a major limitation of most multimode systems.

The other cavity type used in MAE experiments is a single mode cavity, and commercially available single mode cavity microwave reactors were used in five of the studies reviewed [18,35–38]. Superpositions of the incident and reflected waves lead to the formation of a standing wave pattern, which is very well defined in space. The drawback of single mode cavities is that the standing wave is ½ a wavelength long. In the case of laboratory scale equipment operating at 2.45 GHz, this limits the sample geometry to < 6 cm (around 200 mL in volume). However, the ability to measure the reflected power alongside the well-defined field pattern means that energy and electric field intensity requirements are relatively straightforward to calculate.

Electric field intensity and heating rate are higher in single mode cavities compared with multimode systems, and any selective heating effects are likely to be more pronounced. Most papers did not specify the cavity type or how the sample was positioned.

4.1.2. Extraction regime (variables: temperature, extraction time, vessel type)
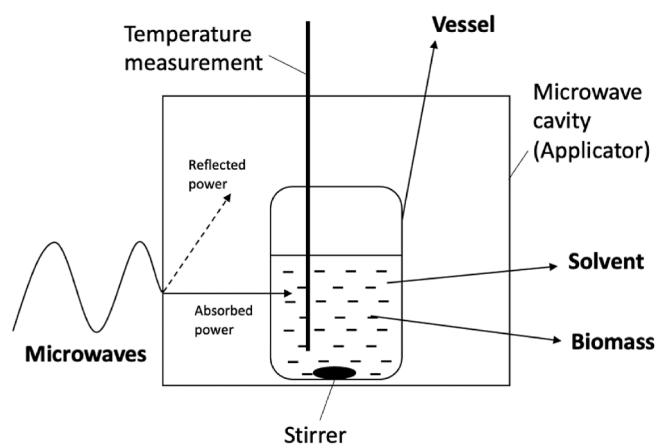
There are three different operating modes: below-boiling, boiling and hydrothermal (e.g. subcritical water extraction). Expected trends in the temperature, applied and reflected power for each operating mode are shown in Fig. 4. The operating mode significantly effects the extraction time, yield and power requirements.

Below-boiling experiments can be carried out in an open vessel. The temperature is set to a value below the boiling point of the solvent, and the maximum incident power is only applied for the heating-up period. After that, the power is reduced or applied intermittently to maintain the set temperature.

During boiling experiments, the incident power is maintained constant throughout the experiment and a condenser should be used to reflux the solvent and prevent solvent loss. Selective heating effects may be more prominent during these experiments due to the longer period of operation at the maximum incident power.

During hydrothermal experiments, the vessel is sealed and heated to a set temperature in the same way as the below boiling experiments. This prevents solvent boiling above the normal boiling point and allows operation at a larger range of temperatures. The physicochemical properties of the system such as diffusion constants, solubility and dielectric properties change under hydrothermal conditions [39,40]. Autoionisation of water into hydronium (H_3O^+) and hydroxide (OH^-) ions above 150 °C increases the dielectric loss through ionic conductivity and results in a lowering of its pH and thus giving water similar properties to dilute acid (Plaza & Turner, 2015).

For the experiments that require a set temperature, the temperature must be measured. This can be done using a fibre optic probe or ruby
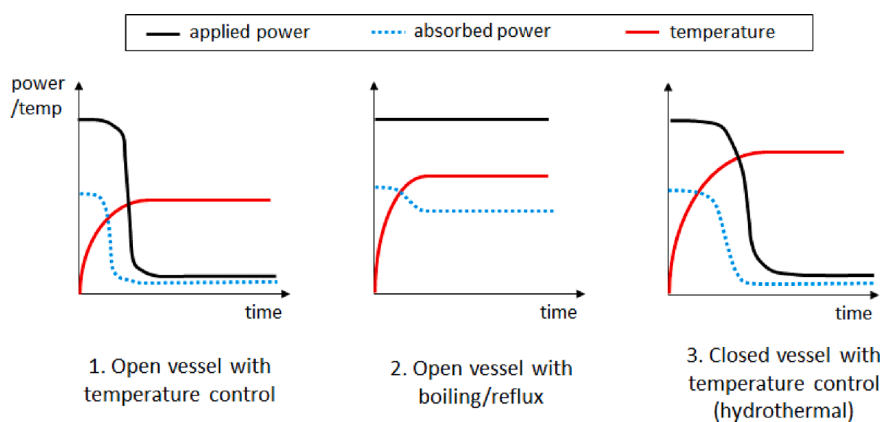
Fig. 4. Trends in power and temperature for different operating modes.

thermometer placed into the sample mixture or using an infrared (IR) thermometer. The temperature may not be the same throughout the mixture due to heating inhomogeneities, although stirring should ameliorate this. If a stirrer or temperature probe are used, it is important to select materials that will not compromise the electric field distribution. IR thermometry is non-invasive, but only measures the surface temperature. None of the abovementioned methods will indicate the degree of selective heating, just the bulk temperature or surface temperature.

4.1.3. Extraction mixture (variables: Biomass type, size and mass; solvent composition and volume)

A large variety of different biomass types have been used. These are usually dried and ground to < 250 μm. However, some researchers report extraction from "fresh" sliced or cubed samples (in the order of mm or cm size), pulps or slurries. The majority of work utilised mineral acid-based extract solvents, which are known to favour HG (smooth pectin) extraction and are used in industrial pectin extraction processes. However, organic acids, aqueous alkaline solvents and water are also used. The choice of solvent and sample preparation method determine the dielectric properties of the system.

The mass of the biomass and volume of the solvent are generally expressed together as the solid-to-liquid ratio (SLR). Penetration depth (D_p) is an important consideration when determining the volume of the extraction mixture. Increasing the load thickness above double the D_p will lead to exponential decreases in heating uniformity. In extreme cases, only the outside of the sample is heated by microwaves and the process relies on conventional heat transfer to heat the bulk of the sample. The penetration depth of extraction mixtures is likely to be within the range of 0.6 – 1.3 cm (Section 3.3), and therefore extraction vessel widths more than a few centimetres will reduce microwave heating rate and uniformity. Although dimensions of the samples are not generally reported, it is reasonable to assume that volumes of > 50 mL would experience heating inhomogeneity; this was the case in 21 of the reviewed papers, while 22 did not report the sample volume.

4.1.4. Determination of yield and composition of pectin

After the extraction experiment, the mixture is filtered, and a pectin-rich fraction is precipitated from the filtrate via the addition of alcohol. This precipitate is either filtered or centrifuged, then dried to form pectin-rich Alcohol Insoluble Solids (AIS). It is convention in the literature to quote the yield of AIS as the pectin yield. Although AIS is rich in pectin, it contains other components such as hemicellulose.

The composition and purity of the pectin extract is determined using a range of analytical techniques, with further details in Section 4.6.

4.2. Summary of experimental data

Table 2 summarises the quoted pectin yields achieved from all papers found presenting MAE pectin extraction since 2017. Note that, unless otherwise specified, the pectin yield reported is actually the pectin-rich Alcohol Insoluble Solids (AIS) yield. GalA denotes galacturonic acid, which constitutes the backbone of smooth pectin and alternates with rhamnose in the backbone of hairy pectin, and is commonly used as a rough indicator of pectin content. Extract yields in Table 2 vary from 2 to 42% (typically between 15 and 25%), optimal extraction times vary from 2.5 to 120 mins, with powers typically applied from 50 to 600 W (although up to 2–6 kW in two papers). A variety of acidic and alkaline solvents as well as water at varying SLRs (typically 1:20 – 1:70 g/mL) are used. Note that the total pectin content and composition vary between different biomass, variety, maturation stage and even within different fruit/vegetables of the same variety and maturation stage.

The following sections review the papers listed in Table 2. Sections 4.3 address the effects of different experimental variables on the overall AIS extraction yield, Section 4.4 compares conventional solvent Extraction (CSE) with MAE, Section 4.5 discusses multi-factor experimental design studies, and section 4.6 discusses the purity and composition of the extracts. Where possible, the effect of each variable as a single factor (i.e. where only one experimental variable was changed at a time) is discussed. Papers where the maximum extraction yield was not identified within the range investigated, i.e. the data indicates yield was still increasing with increasing time (marked* in Table 2) or power**, or there is insufficient data to identify the optimal extraction yield*** are not discussed.

4.3. Key variables in Microwave-Assisted extraction of pectin

4.3.1. Extraction time

Industrial conventional extraction is carried out in batches for > 1hr at ~85 °C using mineral acids pH1 – 3. MAE is often stated to offer faster extraction times, which would lead to higher yields by minimising degradation of the target extracts and smaller processing equipment (smaller batches or continuous processes).

Wandee et al. [41] investigated pomelo peel extraction times of 5 – 15 min, finding very similar extraction yields at all three time-points. The slight increase between 5 and 10 min may indicate optimal extraction between 5 and 10 mins, although more data at < 5 min would elucidate. Sucheta et al. [43] achieved 15% black carrot pomace yield after 5 min. Tongkham et l. [44] achieved almost identical yields from red dragon fruit peel at 5 and 10 min, indicating that optimal extraction may have been achieved in<5 min. Zakaria et al. [34] achieved maximum extraction from pineapple peel at 2.5 min. Sarah [55] achieved a 40% pectin yield from cocoa pod husks within 25 min at 450 W and 30 min at 180 – 300 W. Megawati et al. [62] achieved 40.5% pectin

Table 2

Literature review of MAE pectin papers. Biomass samples were dried unless otherwise stated; NE denotes the parameter had negligible effect; multivariable indicates multiple variables changed at once. *data shows yield still increasing with time; **still increasing with power; ***insufficient data to show trends.

Feedstock	Particle size	Microwave	Parameters investigated	Max Yield (g AIS/100 g dry biomass)	Reference
Pomelo peel	<106 μm	Multimode kitchen microwave	pH 1–2.5 (HCl) pH 11.7–13 (NaOH) Power 550–770 W Time 5 – 15 min	20.5% @pH 1.6 24.2% @pH 12.1 29.8% NE 29.5% NE	Wandee et al. [41]
Apple pomace	125 – 200 μm	Multimode kitchen microwave	Multivariable MAE vs CSE	23.32*** after 180 s at 560 W for MAE 23.26*** after 148 min at 90 °C for CSE	Dranca et al. [42]
Black carrot pomace	<200 μm	Multimode kitchen microwave	Multivariable MAE vs CSE	23%* after 90 min for CSE 15% after 300 s for MAE	Sucheta et al. [43]
Red and white dragon and passion fruit peels	<420 μm	300 W Microwave Synthesis System (CEM), Single mode	multivariable	17.79*** Red DFP 16.72*** White DFP 19.68*** PFP	Dao et al. [35]
Dragon fruit peel	ground	Multimode kitchen microwave	Power 300–600 W Time 5–10 min	23.11 @600 W** 23.11 @10 min	Tongkham et al. [44]
Fig skin	<420 μm	MLS Ethos 1600 Microwave System, Multimode	Multivariable MAE vs CSE	6.05%*** after 60 min, 90 °C for CSE 9.26%*** after 3.5 min, 600 W for MAE	Gharibzahedi et al. [31]
Sweet lemon peel	<420 μm	Multimode kitchen microwave	multivariable	25.31**	Rahmani et al. [45]
Black mulberry pomace	<400 μm	Multimode kitchen microwave	multivariable	9.8*	Khodaiyan and Parastouei [46]
Melon peels	<250 μm	MLS Ethos 1600 Microwave System Multimode	multivariable	32.15*,**	Golbargi et al. [32]
Finger citron pomace	<150 μm	Multimode kitchen microwave	Multivariable MAE vs CSE Acid vs alkali	MAE better than CSE only for alkali e.g. 27.1% alkali @60 °C	Yu et al. [47]
Banana peel	ground	Multimode kitchen microwave	multivariable	2.65*,**	Swamy and Muthukumarappan [48]
Opuntia ficus indica cladodes	<125 μm	Multimode kitchen microwave	multivariable	12.76*,**	Lefsi et al. [49]
Pistachio green hull	<420 μm	Not specified	multivariable	18.13***	Kazemi et al. [50]
Lime peel	<1mm	Multimode kitchen microwave	Multivariable MAE vs CSE	23.59 for CSE @ 95 °C for 1hr 15.91 for MAE @ 700 W for 5 min	Rodsamran and Sothornvit [25]
Eggplant peels and calyxes	<420 μm	Multimode kitchen microwave	Single data point only	29.17*** peel 18.36*** calyx	Kazemi et al. [26]
Raw tobacco stems	59 mesh	Not specified	multivariable	11.27***	Zhang et al. [51]
Dragon fruit peel	<250 μm	Multimode kitchen microwave	multivariable	18.59*,**	Rahmati et al. [52]
American cranberry (*vaccinium macrocarpon*) pomace (	<1.18 mm	MLS Synthwave 402 microwave reactor	pH 13.3, 13.6 84.9, 242.4 W/g	5.0 @pH 13.6*** 5.0 NE***	Spadoni and Karboune [33]
Pineapple peel	<0.6 mm	MAS-II Plus microwave synthesis workstation Multimode	1 – 20 mins 10 – 30 w/v pH 1 – 2.5 400 – 600 W 70 – 100 °C	2.08 @2.5 mins 2.79 @20 w/v 2.27 @pH 2 1.79 @ 500 W 2.55 @ 80 °C	Zakaria et al. [34]
Banana peel	<250 μm	Not specified	multivariable	16.25***	Aklilu [53]
Orange peel	<2mm <5mm	CEM Discover Monowave	Freeze dried versus ground sample	6.2 dried < 2 mm 2.5 freeze dried < 5 mm	Benassi et al. [36]
Mango peel	<600 μm	Multimode	Multivariable	10.45***	Sommano et al. [54]
Cocoa pod husk	<250 μm	Multimode kitchen microwave	10–30 min 180 – 600 W (citric acid/HCl)	40 @25 min/2.2 @15 min 40 @ 450 W/2.2 @ 600 W	Sarah et al. [55]
Banana peel	<180μ	Not specified	5 – 15 min 100 – 300 W	22.65* @15 min 22.65** @300 W	Phaiphan et al. [56]
Watermelon rind	<250 μm	Multimode kitchen microwave	6 – 12 min 120 W – 280 W	5.8* @ 12 min 5.8** @280 W	Sari et al. [57]
Dillenia indica fruit (elephant apple)	ground	Not specified	multivariable	20.36*,**	Kamal et al. [58]
Walnut husks	<420 μm	Multimode kitchen microwave	multivariable	17.40*	Asgari et al. [59]
Cantaloupe rind	ground	Multimode kitchen microwave	multivariable	15*,**	Kazemi et al. [60]
Lemon, mandarin and kiwi peels	ground	Multimode kitchen microwave	1 – 3 min 360 – 600 W Kiwi, HCl vs HNO$_3$	17.97* @ 3 min 17.97 @360 W	Karbuz and Tugrul [61]
Orange peel	<600 μm	Multimode kitchen microwave	10 – 30 min 180 – 600 W	40.5 @ 20 min 40.5 @ 300 W	Megawati et al. [62]
Orange peel	ground	Multimode kitchen microwave	Multivariable MAE vs CSE	15.79 for MAE @540 W for 90 s 8.78 for CSE @80 °C for 10 min	Kute et al. [63]

Table 2 (*continued*)

Feedstock	Particle size	Microwave	Parameters investigated	Max Yield (g AIS/100 g dry biomass)	Reference
Banana peel	ground	MLS Ethos UP multimode microwave digestor	multivariable	13.5***	Rivadeneira et al. [64]
Banana peel	<180 μm	Not specified	multivariable	22.24***	Phaiphan [65]
Cocoa pod husk	<75 μm	Multimode kitchen microwave	multivariable	9.64*	Pangestu et al. [66]
Watermelon albedo (rind)	<250 μm	Multimode kitchen microwave	1 – 3 min 225 – 450 W	5.34* @3 min 5.34** @450 W	Ishartani et al. [67]
Prickly pear peel	<500 μm	Not specified	pH1 – 4 300 – 500 W	13.8 @pH1 13.8 @400 W	Lekhuleni et al. [68]
Kaffir lime pomace	ground	Multimode kitchen microwave	multivariable	30.46***	Akkarachaneeyakorn et al. [69]
Sugar beet pulp	20 – 200 μm	Sairem Miniflow SS200 (atmospheric pressure), Single mode	pH1 – 7	23.1 @pH1	Mao et al. [37]
		Anton Parr Monowave 200 (hydrothermal), Single mode	pH7 – 13 10 – 180 min	23.8 @pH13 23.8 @120 mins	
			90 – 190 °C MAE vs CSE	10.8 @130 °C No statistical difference	
Okra pods	5 – 10 mm fresh	Miniflow SS200 Single mode	pH2, pH7, pH12	10.4 @pH7	Mao et al. [38]
Orange peel Mango peel Apple pulp Carrot pulp	1 cm slice 1 cm slice Pulp Pulp fresh	Miniflow SS200 Single mode	10 – 180 min MAE vs CSE	12.9 @45mins (OP) 14.7 @120 mins (MP) 14.7 @120 mins (AP) 6.3 @60 mins (CP)	Mao et al. [18]
Banana peel	<0.6 mm	Multimode kitchen microwave	0.1 M Citric vs 0.1 M tartaric acid 420, 613 W 5, 10 min	14.74 @613 W** 14.74 @10 min*	Quoc [70]
Banana and Papaya peel	Powder	Not specified	multivariable	23.78%***	Mada et al. [71]
Pomelo peel Mandarin peel Citron peel	Powder	Multimode kitchen microwave	Single data point only	Pomelo 24.19%*** Mandarin 16.13*** Citron 12.44***	Mahmud et al. [72]
Tomato waste	Powder	Multimode kitchen microwave	multivariable	31.58%*	Lasunon and Sengkhamparn [73]
Apple pomace	125–200 μm	Multimode kitchen microwave	multivariable	38% for both MAE and CSE***	Dranca et al. [74]
Whole orange waste Orange albedos	<1mm	Multimode kitchen microwave	MAE vs CSE	19.3% MAE whole orange 22.8% MAE albedos	Zioga et al. [75]
Apple pomace	40-mesh	Multimode kitchen microwave	MAE vs CSE T and t controlled	10–11% MAE 6–7% CSE*	Zheng et al. [76]
Potato pulp	Fresh pulp	Bespoke semi-continuous single mode	250 mLmin⁻¹ 2 kW, 90 °C, Water	40–45% GalA extraction yield	Arrutia et al. [77]
Orange peel	<4mm slurry	6 kW Sairem Labotron Pyro with glass tube cavity	20L batch, 95 °C, 2 hr holding time, Water	150 g/3kg orange peel	Garcia-Garcia et al. [78]

after 20 min extraction from orange peel, with a sharp drop-off in yield by 30 min indicating degradation. The large range of optimal extraction times reported in these papers (2.5 min to 25 min) is difficult to explain. All of them treated dried, powdered biomass samples in multimode cavities. However, experimental details, including the mode of operation (see Fig. 4), were not always provided. None reported temperature control, implying that the temperature was determined either by the microwave power or boiling point of the solvent (which is different for different solvents). The power could have been applied continuously in some experiments, while intermittently (to maintain a set temperature) in others. These variables could all have affected the extraction time and yield.

Mao et al. [18] extracted AIS from fresh orange, mango peel, apple and carrot pulp using deionised water in a single mode cavity at 200 W input power from 10 to 180 min at 90 °C (open vessel, below-boiling). Optimal extraction times and yields were 60 min for orange peel and carrot pulp, and 120 min for mango peel and apple pomace pulp. Using the same MAE set-up, Mao et al. [38] achieved an optimal extraction time around 10 min from okra extracted in alkali, water and acid, and also investigated extraction of pectin from dried, micronised sugar beet using pH 1 – 3 HCl, water and pH 10 – 12 NaOH [37]. In all cases, the maximum sugar beet pectin yield was achieved at 120 min. In most cases, the yield appeared to plateau somewhere between 20 and 40 min before increasing again between 60 and 12 min. At higher temperatures

(hydrothermal, deionised water), optimal extraction was achieved at 130 °C and 10 min. These studies highlight the effect of biomass type on extraction time (from 10 min to 120 min using the same set-up for different biomasses) and temperature on extraction time (extraction time reduced from 120 min to 10 min when temperature increased from 90 °C to 130 °C).

In summary, there is a large variation in reported extraction times for MAE. The available data [18,37] suggests that under atmospheric pressure operating conditions analogous to industrial pectin extraction conditions, extraction times of 1 – 2 h may still be required. Shorter treatment times in the order of minutes can be achieved at higher temperatures than are used in industrial extraction, possibly at- and certainly above-boiling point (i.e. a hydrothermal process operated at 10 – 20 bar) [37]. However, details of temperature and extraction regime are not provided in many of the studies to further elucidate the conditions required. The results of the review also suggest that the common practice of limiting the maximum extraction time to 20 – 30 min (or even 2 – 5 min as is commonplace in RSM studies, see section 4.5) may prevent maximum extraction yield being achieved for some biomasses. The availability of more studies with greater experimental detail, including temperature, heating rate and experimental configuration, would be a valuable addition to the field.

4.3.2. Applied power

It is important to understand the effect of power in order to understand whether the process is power density driven, i.e. the delivery of a high electric field to the sample for short times can lead to better results than a lower electric field for longer times (see Eq. (2)). This means that a better result can be achieved through application of the same amount of total energy at higher powers, and also influences the design of the scaled-up process.

A number of studies have investigated the effect of different power inputs in multimode cavities. Wandee et al. [41] investigated powers of 550, 770 and 1100 W on pomelo peel extraction. "Severe boiling and evaporation" was reported at 1100 W for 2 min. Reducing power to 770 W improved the yield but overheating was still observed. A similar yield (around 30%) was achieved at 550 W without overheating. Pectin extracted at higher power for the same time was found to have a smaller molecular weight (132 kDa at 550 W compared with 76 kDa at 770 W and 5 min). Similar results were achieved by Tongkham et al. [44]: increasing power from 300 to 600 W (and final temperature from 70 to 100 °C) for the same time increased the yield. However, the higher powers (and temperatures) corresponded with a lower viscosity extract, indicating degradation of the pectin. Zakaria et al. [34] varied powers from 500 to 700 W for pineapple peel, finding maximum extraction at 600 W. The temperature and time of operation at each power wasn't reported, so the cause of the result is unclear. Sarah et al. [55] achieved similar results for cocoa pod husk; maximum yields around 47 % were achieved for 180 – 450 W, decreasing at 600 W presumably due to overheating. Karbuz and Tugrul [61] achieved similar maximum yields of kiwi peel pectin at 360 W and 600 W, while Spadoni and Karboune [33] achieved similar yields of cranberry pomace pectin at 85 and 242 W/g. Megawati achieved maximum extraction of orange peel pectin at 300 W out of a range of 180 W – 600 W. However, these were all carried out for 20 min, which was the optimum extraction time for 300 W. Other powers could have yielded higher amounts of pectin at different times. Similarly, Mashau et al. [68] achieved the highest yield of prickly pear peel pectin at 400 W (from a range 300 – 500 W), but only one timepoint was investigated. Phaiphan et al. [56] and Sari et al. [57] observed an increase in banana and watermelon rind pectin extraction respectively by increasing the power from 100 to 300 W, while Ishartani et al. [67] observed increasing watermelon albedo pectin yields when increasing the power from 225 to 450 W; investigation of higher powers was not investigated, however.

In summary, the literature indicates that increasing power initially increases the yield of extraction and that further increases in power decrease the yield. Some studies indicate that the molecular weight of the extract can decrease with increasing power, indicating degradation. However, none reported the temperature or heating rate, and therefore it is possible that where power was seen to affect yield, the higher power settings corresponded to higher energy inputs, heating rates and/or temperatures. Increased temperature increases the yield and decreases the extraction time, while prolonged heating at higher temperatures leads to a reduction in yield, which is usually attributed to degradation. These are well-known thermal effects that would occur in conventional extraction experiments carried out at higher temperatures. These results are therefore unsuitable to investigate if there are any unique effects caused by the application of microwave power to the sample that could be exploited by increasing the electric field intensity applied to the sample.

One study [18] decoupled the effects of temperature and heating rate from microwave power, showing that the increased heating rate provided by increasing microwave power can provide a slight increase in yield of pectin from fresh orange peel: increasing the heating rate from 10 °C/min at 50 W to 40 °C/min at 200 W increased the yield from 9.6 to 12.9 %. Increasing the power above 100 W also led to a step change reduction in extraction time (from 120 min to below 60 min). This is discussed further in section 4.4. These results show that increasing power can increase yield and extraction time for the same set

temperature (and therefore energy input). Further studies are required to understand this effect and investigate whether this is the case for other biomasses and solvents.

4.3.3. Effect of solid to liquid ratio (SLR)

It is often stated that MAE can utilise higher SLRs than CSE, hence reducing the solvent and energy requirements. Rodsamran and Sothornvit [25] reported higher extraction yields of lime peel pectin when decreasing the SLRs from 1:20 and 1:40 g/mL. This is consistent with expectations for CSE, where increased solvent volume compared with solid increases equilibrium extraction yield by increasing the driving force for mass transfer (e.g. the diffusion and solubility of extracts into the solvent) via osmotic potential.

Lefsih et al. [49] observed a steady decrease in yield when decreasing the SLR. Zakaria et al. [34] investigated SLRs of 1:10 to 1:30 and found that the yield was highest at 1:20 g/mL. Rahmani et al. [45] varied SLR from 5 to 35 w/v for pectin extraction from sweet lemon peel, and reported the highest yield at 15 w/v. These results appear to support the theory that reducing the SLR (increasing the relative amount of solvent in the system) above a certain threshold reduces extraction performance in MAE, contrary to CSE. However, the authors [45] attributed this result to the absorption of energy by the excessive amount of solvent at low SLRs. This sheds light on the likely reason for this trend in results: in these experiments, the SLR was decreased by increasing the total volume of the solvent while keeping the solid mass constant. This means that the total amount of energy required to heat the system to a given temperature would be higher, and therefore if the same power was applied for the same time, the extraction temperature would decrease, decreasing the yield and increasing the extraction time. This would not be the case in CSE, where the comparative experiments are always operated at the same temperature (although more energy is applied to achieve that temperature). This is a really important point, which has arisen from a practical difference between microwave and conventional experiments; temperature is harder to control in microwave experiments, but it is still a key variable that has been neglected in the majority of the work reviewed. For fair comparison, the same set temperature and reactor volume should be used in all experiments.

In summary, there is no evidence that the amount of solvent required is lower for MAE than CSE. In both processes, the SLR selected is a trade-off between the yield on the one hand, and the energy required to heat the solvent and size of the downstream separation and recycling/waste disposal steps on the other.

4.4. Studies comparing heating method

4.4.1. Microwave versus conventional heating

It has frequently been reported that, compared with CSE, MAE can provide higher yields in shorter extraction times, requires less energy, may be able to extract pectin without the need for acidic conditions and requires less solvent. In this section, we review the literature for evidence of those claims.

Dranca et al. [42] achieved comparable yields of apple pomace pectin using MAE and CSE respectively, with extraction times of 120 s for MAE compared with 148 min for CSE. MAE appears vastly superior to CSE in terms of extraction time. However, the temperature for the MAE experiments and the vessel type were not reported and the pH of the solvent was different for the two experiments. Gharibzahedi et al. [31] achieved 9.26% yield of fig skin pectin from MAE compared with 6.05% from CSE. MAE was carried out for 3.5 min compared with 60 min for CSE. Kute et al. [63] extracted a higher yield of orange peel pectin using MAE for 90 s compared with CSE for 15 min. Rodsamran and Sothornvit [25] extracted lime peel pectin using CSE with continuous shaking in a water bath for 1 hr compared with 3 min and 5 min in a domestic microwave oven (no shaking) for MAE. In all cases, the CSE yields were higher. Zioga et al. [75] achieved similar yields from whole orange waste, but higher yield from orange albedos. In all of these

papers, several variables had been changed at the same time, preventing fair comparison of the two technologies; usage of different heating rates, set temperatures, extraction pH, agitation and either optimised extraction time or lack of data detailing how the optimisation had been carried out mean that the reason for the differing results between MAE and CSE can't be elucidated. Based on these papers, there is no evidence that MAE can generally achieve higher yields or shorter extraction times than CSE despite frequent claims in the literature to the contrary. This is not to say that there aren't some conditions under which MAE can provide these advantages, as discussed in the following paragraphs.

Sucheta et al. [43] achieved around 16% yield of black carrot pomace pectin for MAE after 180 s compared with around 23% from CSE after 75 min. Intermittent microwave heating was used with the 20% power setting of the 900 W domestic multimode oven being applied for 5 s every 20 s. The data shows that both methods were approaching maximum extraction at the quoted extraction times. The reason for the lower yield in the microwave experiments is unclear, and could possibly be due to overheating caused by the microwave heating method. The difference in extraction times could be due to microwave heating or a result of the use of different sample volumes (not specified) leading to much slower heating rates in the CSE experiment.

Yu et al. [47] extracted finger citron pomace pectin under acidic and alkaline conditions. Experiments were carried out at temperatures ranging from 60 to 80 °C, in CSE for 1 h and MAE for 3 min. The pectin yields were comparable for all conditions with the exception of the alkaline extractions at 60 and 70 °C, for which the MAE yields were considerably higher. This is an interesting result that may indicate a particular advantage of aqueous NaOH as the solvent. It would be helpful to see the temperature measurement method and the extraction yields at different timepoints to elucidate the reason for this result.

Mao et al. [37] compared MAE and CSE of pectin from dried micronised sugar beet at 90 °C for aqueous HCl pH 1–3, deionised water and aqueous NaOH pH 10–12 for extraction times of 10 – 180 min. The MAE was carried out in a single mode cavity with 200 W power applied up to 90 °C then as required to attain 90 °C for the remainder of the experiment. The same heating rate was used in the CSE experiment, while all other variables were the same for both MAE and CSE. The optimal extraction time and yields were found to be the same for all solvent pHs, indicating that for sugar beet at that specific heating power and temperature, microwaves offer no selective heating advantages over conventional heating. However, the contrasting results of Yu et al. [47] and Mao et al. [37] for NaOH-based extraction merit investigation of the dielectric properties of the biomass-solvent mixture under different conditions.

Mao et al. [18] compared MAE and CSE for a range of fresh biomasses (orange and mango peel slices, apple and carrot pulp) in water at 90 °C. CSE was carried out in a 90 °C water bath, while MAE was carried out at 200 W and identical extraction vessel and volume were used. The optimal extraction time was shorter for MAE in the case of the fruits and this corresponded to slightly higher yields for MAE. The optimal extraction time and yield were essentially identical for carrot pulp however. The dielectric loss of the fruit extraction mixtures were found to be significantly higher than the solvent (water), and this corresponded with a faster heating rate for MAE compared with CSE and also the potential for selective heating of the biomass during extraction. Conversely, the dielectric loss of carrot pulp was only slightly higher than that of water and the heating rate for MAE compared with CSE was only marginally higher. This meant that although increased MAE performance was observed for the feedstocks with the highest dielectric loss, the effects of selective heating (leading to some sort of enhanced mass transfer and/or disruption to the cell structure) and volumetric heating (leading to a faster heating rate) could not be decoupled. To elucidate, the authors investigated orange peel pectin extraction at different heating rates for both CSE and MAE. They found that, in general, the optimal yield at any given heating rate was similar for MAE and CSE, and that yield increased with heating rate in both cases. For low heating rates (<18 °C/min) the extraction times were comparable. However, at high heating rates (>23 °C/min), the extraction time was significantly reduced (e.g. 45 mins for MAE compared with > 60 min for CSE at 39 °C/min). This investigation showed that (a) dielectric properties are a good indication of whether MAE should be used for a specific feedstock, (b) increased heating rate (no matter the heating mechanism) increases yield, and (c) selective heating can lead to reduced extraction time, but only above a threshold power density. Zheng et al. [76] compared apple pomace extraction using citric acid and found similar results: the heating rate in a multimode cavity was higher than using a water bath, and this corresponded with faster extraction and higher yield (~7%, still increasing after 35 min for CSE compared with ~11% after 22 min for MAE).

4.4.2. Multimode versus single mode cavities

We note that there are no papers where direct comparison of multimode and single mode is reported. This is because the experimental configurations were typically different, and the effect of the cavity configuration could not be decoupled from other variables. In addition, most papers did not specify the cavity type or how the sample was positioned (which has a significant effect on electric field intensity in multimode cavities). However, from the limited papers that specified cavity type, optimum extraction yields were often achieved in several mins (5–15 mins [56,64,79]) using a multimode cavity, while much longer was required (45–120 mins [80,81]) in a single mode cavity. This might be because in multimode cavities, the maximum power is typically applied throughout the whole extraction period and temperature control is often unavailable, in which case overheating is highly likely to occur. However, single mode microwave reactors usually feedback temperature measurement (e.g. through a fibre optic or ruby thermometer) to a cascade control loop, which allows the precise control of the temperature and microwave power to decrease simultaneously when the desired temperature is achieved. We therefore believe that the different outcomes are more likely to have been a result of other experimental variables (namely continuous power applied to a boiling solvent versus intermittent power applied to maintain a below-boiling point set temperature) rather than the type of microwave cavity.

4.4.3. Energy requirements

Garcia-Garcia et al. [78] (discussed in more detail in Section 5.2) compared the energy requirements of a water-based MAE pectin extraction from orange peel carried out at 95 °C for a 1.5 h hold time and a conventional acid extraction (operating conditions not specified). The microwave process energy requirements were significantly lower than the conventional process (0.12 kWh/g pectin produced for MAE versus 0.50 KWh/g pectin produced for CSE). These results are promising. However, the volume of solvent, solvent type and mass of orange peel, as well as the experimental configurations, were different, so the energy savings may not necessarily be attributed to the heating method.

No other studies compared the energy requirements of MAE and CSE. However, the evidence suggests that similar operating conditions (e.g. temperature and solvent volume) will be required whether the heat is supplied via microwaves or conventionally; this means that the theoretical energy requirements will be similar regardless of heating method (i.e. the sensible heat required to heat the system to the set temperature and any heat of mixing/extraction). Therefore, any differences in energy requirements will result from heat loss and efficiency of power conversion to heat. This was discussed by Galan et al. [82] in the extraction of phenolic compounds from sea buckthorn leaves. Heat losses from a single mode cavity extraction set-up similar to those reported by Mao et al. [37,80] were estimated to be around 30% of the applied power. Comparative data for conventional heating via hot plates or liquid baths is not available. Heat losses are generally lower in scaled up systems compared with laboratory scale systems, and so scaled up processes for conventional and microwave heating are expected to be more efficient.

4.5. Optimisation studies

Given the many often interdependent variables in MAE experiments, it is time-consuming carrying out studies to investigate the effect of each of the experimental variables independently. In order to save time, a popular approach is to use multivariate experimental design; this methodology varies multiple variables (or factors) simultaneously to perform a predefined and limited number of experiments. The stated advantages of this approach are reduced experimental runs, faster determination of optimal conditions, ability to establish a mathematical relationship between independent variables (factors) and dependent variables (responses), and the availability of open-source software to accomplish the entire process in a statistically significant way [83]. The experiments take place in two phases. The screening phase is intended to determine the experimental factors and interactions that have significant influence on the response. From this, typically two levels of each variable are identified to be carried forward to the second phase. The second stage, known as the optimisation phase, uses Response Surface Methodology (RSM) to model an approximate relationship between the response and multiple factors. This is represented graphically and mathematically via a series of polynomial equations obtained through regression analysis [83]. There are various RSM design methods, the most common in the papers reviewed being Central Composite design (CCD) and Box-Behnken design (BBD); these both involve the identification of two levels for each factor plus a central point, such that each experimental variable is limited to three different values that are varied simultaneously with the other variables. As the experimental levels in both phases are predetermined, there is no guarantee that the experimental range investigated approaches the optimal experimental conditions.

Twenty of the 50 papers reviewed used multi-factor experimental design, varying three to four parameters (typically pH, time, power and SLR) simultaneously. Unfortunately, review of these papers (for the large part) has not been helpful in understanding MAE for the following reasons:

- For each pH, power and SLR there is a unique optimal extraction time, below-which extraction is incomplete and above-which product degradation occurs. This yield-time relationship is not linear or polynomial. Using BBD and CCD, a maximum of three (and often only two) time-points under the same conditions were recorded. It is not possible to identify a maximum using two or three data points,

and so the time required for extraction cannot be determined. Restricting each factor (time in particular) to only two or three levels therefore makes identification of the optimal level impossible.
- A limited range of experimental factors was investigated. Even when the data indicated that increases in all factors within the experimental range led to increases in yield (indicating that optimal conditions had not been reached), the model always predicted a maximum yield, usually within the experimental range.
- The optimal conditions identified are only applicable to the specific experimental set-up under investigation; they are not transferable to experiments with different geometries, electric field intensities, fluid dynamic regimes, etc., and so cannot be used in scale-up.
- Presentation of the results in surface response plots obfuscates the data. It took many more hours to unpick the data reported in these papers than the single-factor studies; in order to analyse the data, we manually entered it into spreadsheets and plotted the yield against time for each of the other variables.

To illustrate these points, in Fig. 5 we have plotted data from one of the RSM studies reviewed in Table 2. Each graph includes data where only a single factor was varied at once. The paper modelled optimum conditions of 2.15 min extraction time, 517 W power, solvent at pH 2.26 and SLR of 0.065 g/mL. However, the data clearly shows that those are not the optimum conditions, that higher powers and times and lower SLRs would likely have provided higher yields, and experimental conditions outside the predetermined range should have been investigated.

RSM methodology could be useful in other areas, for example to optimise an industrial system for which there is only limited scope to change the operational parameters, but we recommend against its use in fundamental studies of MAE. Instead, we recommend single factor studies, which investigate one variable at a time while controlling all other independent factors including feedstock type and size, solvent type and pH, extraction temperature, applied power, SLR, reaction vessel geometry and stirring speed. In our experience, optimisation of treatment time for each independent variable (and determination of yield and composition of extract at each time point) is the best way to gain better understanding of the process and identify operating conditions that will be suitable for scaling up.

4.6. Extract characterisation

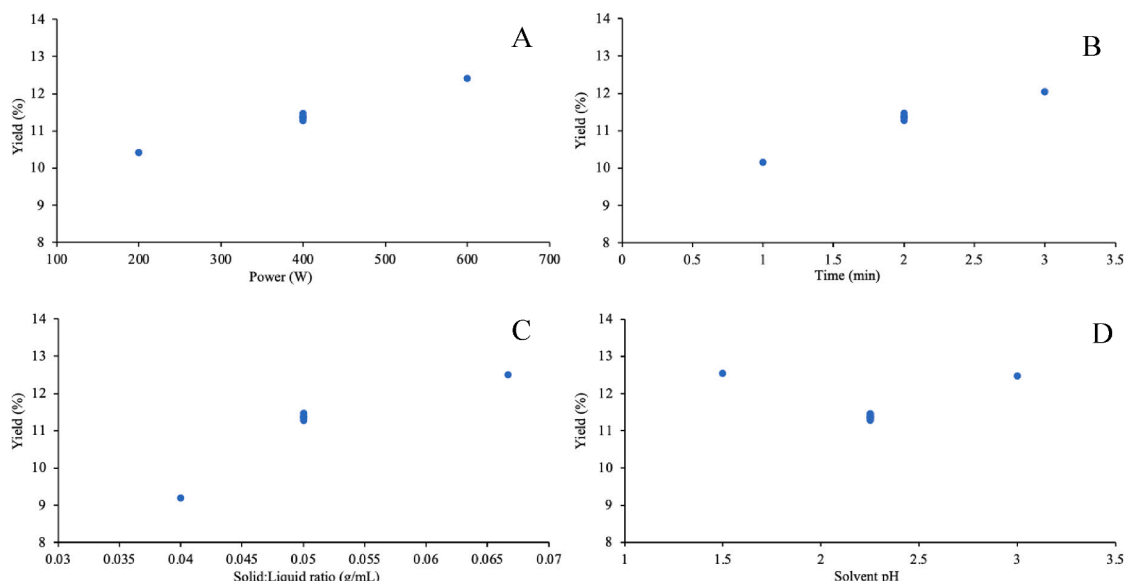There are a variety of methods used to characterise the pectin-rich

Fig. 5. Data plots from an RSM study showing the AIS yields (%) as a function of time (**A**), power (**B**), Liquid:Solid ratio (**C**) and solvent pH (**D**).

Alcohol Insoluble Solid extract, details of which can be found in Table 3. For the most part, the characteristics of the extracted pectin are predominantly a function of the biomass it is extracted from and the pH of the extracting solvent; temperature and time also play a role according to the kinetics of the extraction and degradation mechanisms.

Many of the papers reporting microwave-assisted hot acid extraction succeeded in extracting pectin that met specifications for commercial pectin (GalA content > 65% [92]) in minutes, and in many cases the composition was comparable to pectin extracted using CSE and much longer extraction times [31,41,42,44,46,47,52,65,69]. These results suggest that microwave-assisted hot acid extraction may be able to extract high quality commercial pectin in shorter times than conventional heating, but there are two important caveats. First, many of these papers were not optimised for time (see Section 4.3), and therefore longer treatment times may have increased the yield of pectin with similar quality. Second, the operating temperature used was generally higher than conventional extraction (see Section 4.4), and so conventional heating may have achieved similar results if carried out at the same temperature.

Ishartani et al. [67] observed increasing yield with time and power, and decreasing molecular weight. The different powers would have corresponded with different heating rates and extraction temperatures, and this likely explains the results: higher temperatures increased the amount of pectin extracted but also increased the rate of depolymerisation, decreasing the molecular weight. When Yu et al. [47] compared a 3 min microwave treatment with 1 h conventional, the molecular weight was lower for MAE while the yield was higher. Both studies highlight the importance of fast heating and cooling in order to maximise pectin yield while preserving the quality.

Mao et al. [37] compared extracts of CSE and MAE from sugar beet pulp at optimal extraction time (120 min for all 90 °C experiments, 10 min for 130 °C) under acidic, neutral and alkaline conditions. In all cases, the sugar analysis was very similar for MAE and CSE sugar beet

pectin extracted using the same heating profile. When comparing MAE extracts produced at 90 °C in 120 min and 130 °C in 10 min in water, while the total sugar and pectin content were similar, the RG1 yield was slightly higher at 130 °C. Mao et al. [18] compared MAE and CSE extracts from orange peel and carrot peel, and in both cases the extract contained the same amount of HG and RG1 regardless of the heating method. The authors noted a significant amount of unidentified components and speculated that this could indicate ash or protein. They also reported that the sugar composition for orange peel pectin extracted at different heating rates using MAE and CSE were very similar, but that the amount of unidentified alcohol insoluble components increased with heating rate; even though the extract yield increased with heating rate for both CSE and MAE, the amount of pectin extracted did not increase. This finding requires further investigation.

In summary, the well-documented dependence of pectin composition on the pH of extraction applies equally for MAE and CSE. There is no evidence that the composition or quality of the pectin extracted is affected by the use of microwaves instead of conventional heating. There is evidence that microwaves can extract pectin of similar quality to commercial pectin in very short times (minutes instead of hours). However, in most cases that is attributable to the higher temperatures used in the MAE experiments compared with CSE experiments.

5. Pectin extraction process scale-up

5.1. Current industrial pectin extraction at scale

The current industrial pectin extraction process at scale is described below and its flow diagram is illustrated in Fig. 6. Biomass materials are washed and dried before being treated with a mineral acid at pH 1–3 and heated to 85 °C [93]. The hot pectin extract is separated from the solid residue, although this is not straightforward since the solid becomes soft and the liquid phase increasingly viscous due to the increase in pectin concentration during processing. Therefore, a compromise between efficient extraction, solids separation (both favoured by a large amount of liquid) and operating cost (favoured by producing a more concentrated extract) has to be made [94]. The pectin extract may be further clarified by filtration. Rotary drum vacuum filtration is most commonly applied and the resulting cake is neutralised and sold as cattle feed or put through a re-extraction step before being filtered and disposed of [95]. If necessary, the extract is further treated with carbon to remove colour and with amylase to degrade starch that would otherwise precipitate from the liquid product. The clarified extract is then concentrated under vacuum evaporation at low temperature. To precipitate the pectin from the solvent, the concentrated extract is mixed with an alcohol or aluminium salt solution [96]. The precipitate is often mixed with carbonate salt to neutralise any acid remaining in the extract to give a pH above 4. The precipitate is pressed and washed to remove the extracting solution and finally dried and milled to the desired particle size.

There are several disadvantages associated with the above industrial pectin plant. It is not considered as a sustainable and environmentally friendly process. It uses traditional heating from fossil fuels and hot acid, which has relatively low energy conversion rate (~60% [97]) and generates significant volumes of acidic waste. The hot acid solvent makes the process only suitable for HG-rich pectin extraction, limiting the application of commerically extracted pectin to gelling agents. Therefore, there is an urgent need to develop novel pectin extraction processes using novel heating methods (i.e. microwave heating) and green solvents (e.g. water or weak acids/alkalis) for process intesification and the development of novel pectin-based products. However, the new process is likely to integrate the established up- and downstream unit operations.

5.2. Advances in microwave-assisted pectin extraction scale-up

To our knowledge, there are only two reports of scaled-up MAE

Table 3
Characterisation of pectin-rich Alcohol Insoluble Solid.

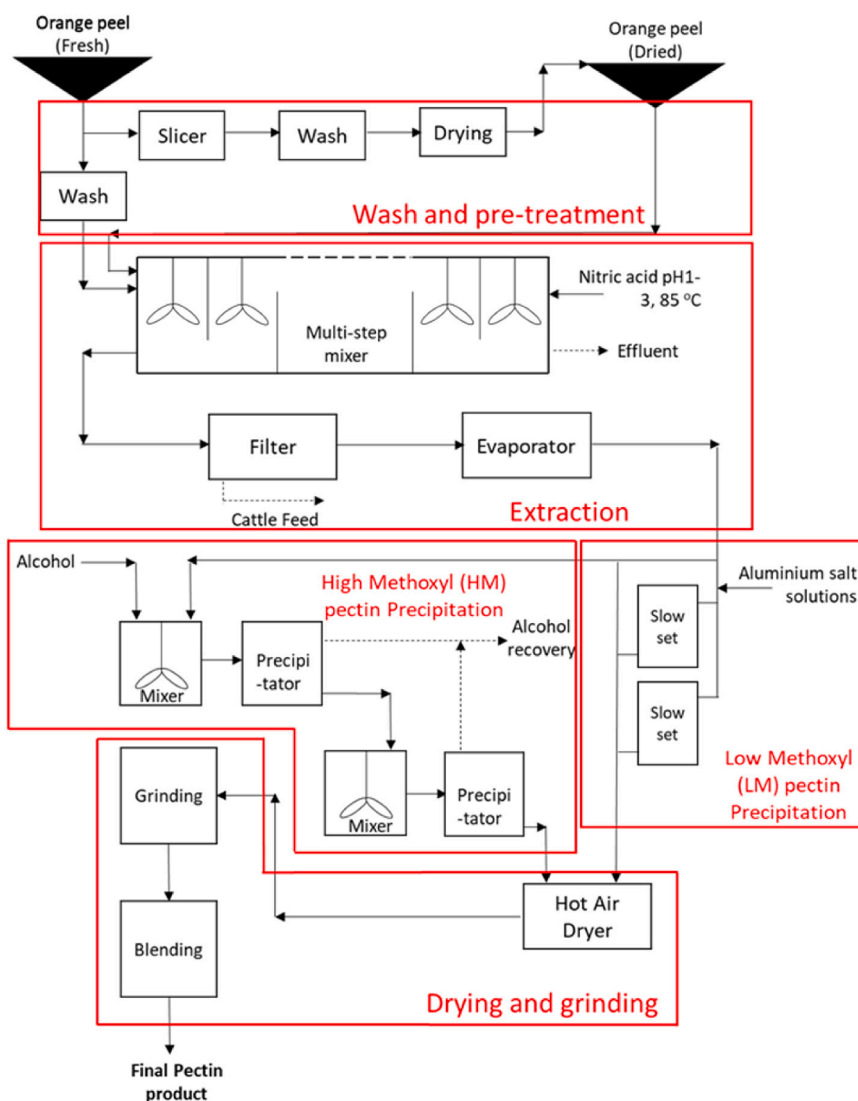| Pectin characterisation	Linked structural information	Analytical techniques	Reference
Galacturonic acid (GalA)	Commercial (HG-rich/"smooth") pectin purity	Colorimetric method and UV–Vis	[84]
Degree of methylation (DM) and acetylation (DA)	Amount of carboxyl groups that exist as methyl or acetyl ester side groups; often used to categorise pectin into high methylated (HM, DM > 50%) and low methylated (LM, DM < 50%)	Titrimetric method (commonly used in food industry to analyse commercial pectins)	[85]
		FTIR	[85,86]
		HPLC	[85,87]
		^{1}H NMR	[88]
Molecular weight (MW); sometimes represented as Equivalent weight EqW	Extract degradation and structural information (HG/RG1 ratio)	Intrinsic viscometer (capillary)	[38]
		Dynamic light scattering (DLS)	[89]
		High performance size exclusion chromatography (HPSEC)	[90]
		Analytical ultracentrifugation (AUC)	[91]
RG1 backbone and neutral sugar side chains (rhamnose, arabinose, galactose, glucose and xylose)	RG1-rich/"hairy" pectin composition and purity; the ratio of HG/RG1	Acid hydrolysis followed by HPLC	[37]

Fig. 6. Industrial process for commercial pectin production from dried citrus peel. Adapted from May [94].

pectin extraction and no examples of industrial operation. Arrutia et al. [77] built a semi-continuous process to extract RG1-rich pectin from potato pulp using water as the solvent. In order to maximise heating rate and microwave selective heating, and provide even heating of the potato slurry, a single mode cavity design was selected. The system featured a feed tank, a peristaltic pump with speed control, a temperature sensor, a single mode microwave cavity which holds the PTFE applicator tube through which the process fluid flows, tuners, a power meter, WR340 waveguides, and a 2 kW microwave generator. A schematic representation of this continuous microwave processing system is shown in Fig. 7. The design limitations were the penetration depth of the potato slurry, which limited the pipe size to 1 – 2 cm to maximise the volumetric heating rate and enable even heating throughout the pipe. The other major limitation was that the high viscosity of the potato slurry caused difficulties with the downstream separation steps using the available equipment, which dictated the SLR of 1:10. A starch removal step was added prior to extraction in order to prevent starch gelation during processing and to add an additional value stream. The 2 kW single mode system processed 250 mL/min potato pulp slurry, achieving stable operation (85 ± 2 °C) within 1 min of operation. The GalA yields achieved with a single pass through the cavity followed by 20 min held at ~85 °C in an insulated container were double those of conventional extraction for 20 min. Furthermore, the MAE pectin was richer in RG1

than the conventionally extracted pectin. These results support the hypothesis that microwave heating advantages will be best exploited in fast, continuous processes.

Garcia-Garcia et al. [78] reported a circulating batch system to extract pectin from orange peel in water. 3 kg of orange peel slurry in 12 L water (total volume 20 L) were continuously circulated through a glass tube cavity using a diaphragm pump. Microwave power of 6 kW was applied until the set temperature of 95 °C was reached. The mixture was then continuously circulated and held at 95 °C using temperature feedback from thermocouples at either end of the cavity to moderate the microwave power, which was recorded each minute. After 1.5 h hold time, the mixture was cooled to 60 °C and decanted from the reactor. The extracted pectin was found to meet the requirements of high-methoxy pectin, and the temperature measurements demonstrated good temperature control throughout the run (95 ± 4 °C). The yield of pectin was found to be 50 g/kg orange peel compared with 30.5 g/kg for lab-scale conventional hot acid extraction.

The results from Garcia-Garcia et al. [78] were used to carry out a Life Cycle Analysis (LCA) of the process compared with lab-scale acid extraction. The analysis indicated that the impact of the microwave process was < 25 % across the entire range of environmental and health factors (such as climate change, ozone depletion, toxicity, etc.). In both cases, the electricity use had the highest environmental impact with the
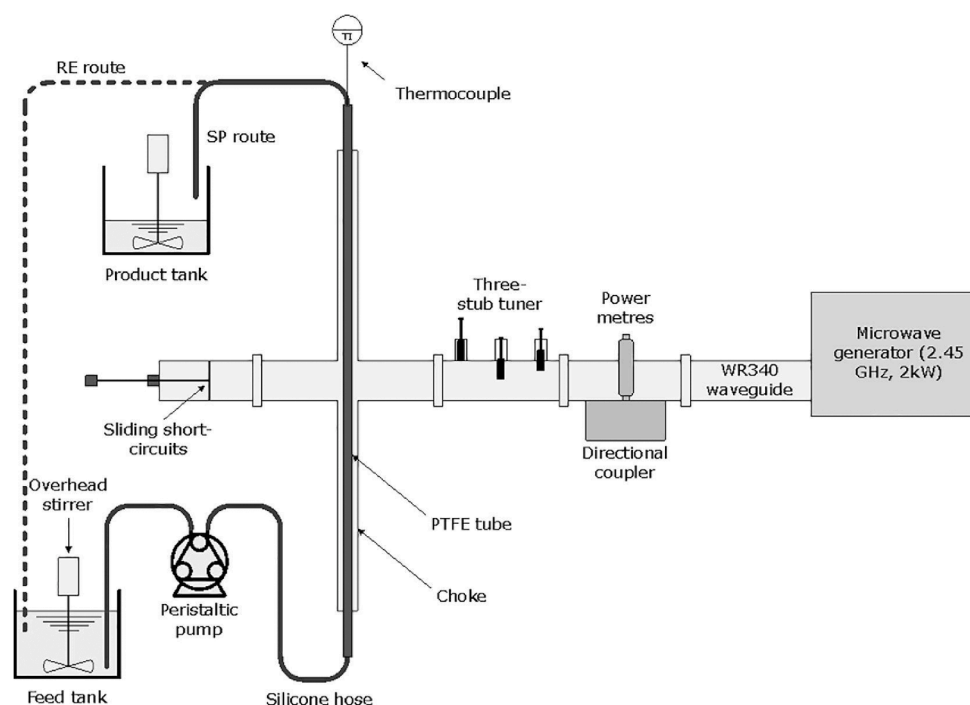
Fig. 7. Schematic representation of the continuous flow microwave system, where RE route: recycle route; SP route: single pass route. Figure reproduced from Arrutia et al. [77] with permission.

highest impact being to human toxicity. These results are the first attempt to quantify the potential impact of the implementation of MAE for pectin extraction in industry and justify further development of the technology. The next step would be to perform LCA studies on industrial-scale designs, for example to see the effect of potentially carbon-free electricity in MAE processes compared with gas-heated conventional hot acid extraction processes (both processes were assumed to use the same electrical energy source in [78]). The actual energy requirements of both processes would also be different at industrial scale, as heat loss in lab scale experiments is much higher. Future work should address these challenges.

These two studies exemplify the potential for microwave processes to provide higher yields of higher quality extracts compared with conventional extraction processes and to decrease the environmental impact of pectin production. The next challenge is to understand the trade-off between the selective heating advantages achieved at very high heating rates, and the limitations that causes in terms of flow rates. Arrutia et al. [77] used a single mode cavity that provides a very high heating rate and even heating, but the very small diameters limited flow rate of the material through the reactor. Further scale-up will require understanding of the trade-off between high electric field intensity and the ability to treat higher flow rates and more concentrated slurries.

6. Future perspectives

Areas for future work in this field can be divided into fundamental studies and commercialisation.

Fundamental studies should focus on understanding which feedstocks are more amenable to microwave heating and how to exploit microwave-enhanced mass transfer. Measurement of dielectric properties of the biomass feedstocks and solvents should become commonplace in MAE studies. Experiments to determine (a) the actual degree of selective heating during MAE and (b) how this affects mass transfer or leads to structural changes are required This will require the ability to monitor real-time changes to the biomass at the microscale during processing. Finally, all future work should diligently report all experimental details, including temperature control, cavity type, sample volume, absorbed power (where possible) etc.

In terms of commercialisation, the next challenge is to propose and evaluate a range of different process concepts. These should seek to maximise the benefits of selective heating demonstrated at laboratory scale by through maximisation of the heating rate while also achieving commercially relevant throughputs. Successful processes will be continuous or semi-continuous systems, but the microwave element of the process must be continuous since the limited penetration depth necessarily limits any batch operations to small scale. Further work on Life Cycle Assessment and Techno-economic Analysis is also required as full-scale process data becomes available. For the commercialisation of novel pectin-based products (which is now possible using MAE), product development is also required: product trials, market research and regulation will need to be explored in parallel with process development.

7. Conclusions

There have been significant advances in the field of Microwave-Assisted Extraction of pectin since the last major review in 2017 [3], and this has led to a definite increase in the body of evidence that MAE: (1) can provide advantages based on its unique heating mechanisms of selective and volumetric heating, (2) can be applied selectively to different feedstocks to exploit the microwave heating mechanisms, and (3) at scale, MAE processes could provide higher yields of higher quality pectins with lower environmental impact than conventional extraction processes.

These advances have put researchers and industry in the position to commercialise this technology and pave the way for the development of a wide range of novel pectin-based products from "waste".

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: [Eleanor Binner reports financial support was provided by Engineering and Physical Sciences Research Council.].

Data availability

No data was used for the research described in the article.

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