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Matharu, Avtar S., Houghton, Joseph A., Lucas-Torres, Covadonga et al. (2016) Acid-free microwave-assisted hydrothermal extraction of pectin and porous cellulose from mango peel waste-towards a zero waste mango biorefinery: Towards a Zero Waste Mango Biorefinery. Green Chemistry. pp. 5280-5287. ISSN: 1463-9270

https://doi.org/10.1039/c6gc01178k

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Journal Name

ARTICLE

Received 00th January 20xx,

Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Acid-Free Microwave-Assisted Hydrothermal Extraction of Pectin and Porous Cellulose from Mango Peel Waste – Towards a Zero Waste Mango Biorefinery

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Mango is the second most consumed tropical fruit after banana and the by-products of mango processing (peel, kernel and seed) roughly comprise 35 – 60% of the total fruit weight, thus representing a potentially high volume resource of exploitable biobased chemicals and materials. Herein, conversion and characterisation of waste mango peels from three different cultivars (Alphonso, Honey and Tommy Atkins) into pectin and porous cellulose using low temperature microwave-assisted acid-free hydrolytic conditions is reported. Microwave-assisted acid-free extraction yielded up to 11.63% (dry weight basis) of pectin which was characterised by IR, NMR (both solution and solid phase) and TGA which showed close similarity to commercial (acid extracted) pectin. The degree of esterification of pectin was determined by 13C NMR (75.6 – 86.2%) and titrimetry (79.3-87.7%) and the pectin showed excellent gelling ability. The molecular weight as determined by GPC was in the range 14130 (Honey) – 25540 (Tommy Atkins). Porosity measurements on the depectinated residue, i.e., residual cellulosic matter showed mesoporous characteristics: average pore diameter, 9.3 nm (Alphonso) – 10.5 nm (Honey), however with poor surface area 16.3 m^2g^{-1} (Honey) – 26.0 m^2g^{-1}. Interestingly, a second microwave hydrothermal treatment on these residues retained mesoporosity whilst significantly increasing surface area (88.8 m^2g^{-1} (Honey) – 124.0 m^2g^{-1} (Alphonso)) and pore volume by approximately six-fold. This is the first detailed combined study of microwave-assisted extraction to yield pectin and mesoporous cellulose towards a potential zero waste mango biorefinery.

Introduction

Globally, 1.3 billion tonnes of food is wasted per annum due to a variety of differing reasons; poor storage post harvesting mainly in developing countries, consumer non-acceptance primarily based on aesthetics, i.e., mis-shaped or blemished produce mainly in developed economies and, as a result of processing from farm to fork.[1-3] The latter generates roughly 35-40% of unavoidable food supply chain waste (FSCW) which can be considered as a potential source of biobased chemicals and functional materials derived from nature rather than synthetically engineered from petroleum refineries.[4-8] For example, pectin is an industrially important natural biopolymer used as a rheology modifier and stabiliser in the food industry. FSCW is a rich source of pectin inasmuch that industrial pectin is obtained mainly from apple or citrus pomace usually under acidic conditions and thus FSCW is an important economic biorefinery feedstock.[9-12]

In this context waste mango is an interesting feedstock because of its increasing global popularity resulting in potential high volumes of pectin and cellulosic matter. Mango is the second most consumed tropical fruit after banana. Mango production has nearly increased by four-fold in the last 50 years to over 42 million metric

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

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tonnes in 2013.[13] The by-products of mango processing (peel, kernel and seed) comprise 35 – 60% of the total fruit weight thus representing a potentially high volume resource of exploitable biobased chemicals and materials within the context of a FSCW biorefinery. Mangos are a rich source of highly esterified pectin, antioxidants in the form of polyphenolic compounds, flavonol *O*- and xanthone *C*-glycosides,[14-16] carotenoids, dietary fibres,[17] and lipids.[18] Soluble dietary fibres from mango peel may help control diabetes.[19] Mango peel is good source of pectin and many researchers have isolated mango pectin but using traditional hot, aqueous acidic conditions ultimately generating large volumes of acidic waste detrimental to any large-scale industrial operation such as a FSCW biorefinery.[10,11,20,21] Researchers have explored replacing conventional heating with alternative energy sources such as microwaves,[22-24] pulsed electric energy,[25] and ultrasound.[26]

Herein, we report the first combined hydrothermal acid-free microwave-assisted processing of waste mango peels to yield pectin and porous cellulose as important biobased materials providing additional value to any potential mango waste biorefinery. We postulate that microwave acid-free processing of waste mango peels will release pectin from cellulosic matter but also create porous cellulose *in situ*.

Materials and Methodology

Unless specified all chemicals, reagents and solvents, for examples, commercial citrus pectin, ethyl acetate, ethanol, acetone, sucrose, citrate buffer, D_2O, etc, were purchased from Sigma Aldrich Chemical Company and used without further purification.

Mangos *(Tommy Atkins, Alphonso and Honey)* were sourced from a local supermarket. The peel removed with a sharp, stainless steel knife and any remaining flesh was removed with the blunt edge of the knife. The peel was left to air dry at slightly above room temperature in a well-ventilated area for 2-3 weeks until a constant mass was recorded. Peels were then milled into small pieces using a mechanical food processor and preserved in sealed plastic bags for further use.

Pectin Extraction and Purification

Pectin extraction was attempted using two separate techniques as described below (a and b). Both methods resulted in an aqueous solution of pectin being obtained; in some of the studies, the aqueous solution was extracted twice with ethyl acetate to obtain pyrolytic oil after solvent evaporation. Pectin was isolated from aqueous solution with the addition of an excess of ethanol (at a ratio of ca. 3:1 ethanol: water) under rapid stirring for 20 minutes. The solution was then left to stand overnight to allow maximum pectin precipitation which was isolated (centrifuge, 20 mins with an acceleration value of 9 and a deceleration value of 3 RCF (relative centrifugal force)). The pectin pellet obtained was purified by washing with ethanol (2 x 100 mL; in some instances, the pectin pellet was washed twice with acetone), boiling in ethanol for 15 mins and hot filtering to afford an off-white solid. The latter was dissolved in the minimal amount of deionised water and subjected to freeze drying (-105 °C and -110 °C at a vacuum of ~27 mT until the flask was room temperature) to furnish the desired pectin as a white solid.

a. Conventional method (aqueous HCl) Traditional acid-assisted pectin extraction was performed on dry powdered mango peel (20.10 g) stirred in 0.03 M-aqueous HCl (600 mL) at pH 1.51 and heated to 85 °C for 1 h (peel:solvent ratio 1:30) Thereafter, the cooled reaction mixture was filtered (Büchner) and the filtrate was treated with ethanol to effect precipitation as described earlier to afford the desired pectin, 1.12 g (5.60 wt%), as a white powder.

Experiments at reflux temperature were also carried out: dry powdered mango peel (5 g) was suspended in 0.01 M-aqueous HCl (50 mL) and heated for 1 h (peel:solvent ratio 1:10). The same reaction was reproduced using deionised water as extraction solvent for the sake of comparison. The amounts obtained, with the use of acid or without it, were 7.50 wt% and 1.30 wt%, respectively.

b. Hydrothermal microwave-assisted acid-free extraction

Microwave-assisted pectin extraction was carried out on dry powdered mango peel from Tommy Atkins cultivar, using a CEM Discovery microwave to allow for closed vessel and thus, pressurised extraction conditions. Powdered mango peel was loaded into the reaction vessel along with a microwave safe stirrer bar and the prescribed amount of water added. The microwave

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reaction temperature was set at 110 °C (unless specified otherwise) for the desired amount of time, setting the maximum power at 300 W, which is self-regulated to keep the required temperature. The conditions of the experiment were altered in an attempt to find the optimal conditions for pectin extraction as summarised in Table 2 of the results and discussion section. For scale-up procedures, these were performed using a CEM Mars 6 closed vessel Microwave, operating to a maximum of 600 W, 2.45 GHz using EasyPrep Plus Teflon 100 mL closed vessels to ensure comparable power densities between small- and large-scale experiments over the same time scales.

Pectin Characterisation

Attenuated Total Reflection Infrared Spectroscopy (ATR-IR): ATR-IR was carried out using a Bruker Vertex 70 spectrometer equipped with a Specac Golden gate. Spectra were taken from 4000 cm^{-1} to 600 cm^{-1} at 64 scans, with a spectral resolution of 2 cm^{-1} with a blank window for background.

Degree of esterification (DE) by titrimetry: Degree of esterification of pectin was determined using the double titration method according to the Food Chemical Codex.[27] Two volumes were recorded as the initial titer (V_1) and the saponification titer (V_2) and %DE was calculated according to equation 1.

$$\% \ DE = \frac{V_2}{V_1 + V_2} \qquad \text{Eq.1}$$

Solution NMR analysis and degree of esterification by NMR: Pectin (100 mg) was allowed to dissolve in D_2O (1 mL) over a period of time, usually 1 h, in a standard bore (5 mm) NMR tube. ^1H and ^{13}C NMR were recorded in a Bruker BioSpin GmbH 500 MHz, operating at 500.23 MHz for the ^1H nuclei and 125.80 MHz for the ^{13}C nuclei. The ^1H NMR were obtained with a spectral width of 8 KHz, a relaxation delay of 2 s and 64 scans. The ^{13}C NMR spectra were obtained with a spectral width of 31.5 KHz, 10 s of relaxation delay and 21000 scans. All the experiments were run at 25 °C. The degree of esterification (%) of pectin was determined using equation 2:

$$\%\,DE = \frac{I(\text{esterified carboxyl group})}{I(\text{esterified carboxyl group}) + I(\text{non-esterified carboxyl group})} x100 \qquad \text{Eq. 2}$$

Gel Permeation Chromatography: GPC analyses were performed independently by the Centre for Water Soluble Polymers at Glyndwr University. The GPC system consisted of a Suprema column (dimensions 300 mm x 8 mm; Polymer Standards Service GmbH) with 10 micron beads with a 3000 Å pore size, protected by a Guard column (Polymer Standards Service GmbH: 10 microns). The eluent used was 0.1 M NaCl containing 0.005 % sodium azide and was filtered with a 0.22 µm Millipore filter and degassed before use (Vacuum degasser Gastorr 153/SFP). 1% solutions of control and experimental pectin samples were prepared in aqueous solutions of 0.1 M NaCl and by tumbling overnight at 25 ˚C. The effluent flow rate was set at 0.5 mL/min. Dawn EOS light scattering and Dawn DSP refractive index detectors were used. Samples were passed through a 0.22 µm pore size nylon syringe filter before being injected onto the column. Measurements were performed in duplicate. The molecular weight was determined using Astra for Windows 4.90.08 QELSS 2.XX. The Debye model was used for all evaluation analyses. A value of 0.146 mL/g was used for the refractive index increment (dn/dc).

Gelation studies: The tests were carried out following a protocol derived from that described by Löfgren *et al.*[28] A solution was prepared using a citrate buffer of different pH (pH 2, pH 3, pH 4) with a 0.75 % of pectin (w/v) and heated under reflux (see details in Table 1). A weighted amount of sucrose was added (60, 70 or 80 % by weight) to the hot solution and re-set to reflux before being transferred in to a dry beaker (50 mL) to encourage gelation at room temperature over 24 – 48 h.

Table 1. Gelling tests carried out on mango pectin

Buffer	Amount of pectin (w/v%)	Amount of sucrose (wt%)
pH = 2	0.75	60
	0.75	70
	0.75	80
	1.5	70
pH = 3	0.75	60
	0.75	70
pH = 4	0.75	70

Thermo-Gravimetric Analysis (TGA): TGA was carried out under a flow of nitrogen (50 mL min^{-1}) using a NETZSCH Themishe Analyse STA 409 cell for pectin analysis (25 – 350 °C at 10 °C min^{-1}).

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Elemental Analyses (CHN): Elemental analysis was performed by an Exeter Analytical CE-440 analyzer used in conjunction with a Sartorius SE2 analytical balance. Selected samples were analysed and the data is given in ESI Table S1. NB. No nitrogen was detected for acid-free microwave processing.

Porosimetry:

De-depectinated mango peels from different cultivars were treated differently in order to evaluate their surface area before and after the treatments. Samples of de-pectinated mango peels (3 g) were subjected to microwave heating at a temperature of 180 ^{o}C for 10 minutes (peel:water ratio 1:20, CEM MARS 6 microwave reactor, operating up to a maximum power of 600 W).

After that, the solid residue was put in a round bottom flask and washed with ethanol (3 x 200 mL) during 1 hour with high stirring at room temperature, followed by subsequent washing with acetone (3 x 200 mL) during 1 hour. The remaining solid was filtered by Büchner and dried under vacuum in a rotory evaporator.

The surface area and porosity of the residues was tested using a Micromeritics ASAP 2020 Surface Area and Porosity Analyser. A measured amount of dry, powdered residue was put inside a clean, dry porosimetry tube and the mass of the glassware and sample recorded; this was then degassed at a temperature of 303K under the extraction temperature (with a ramp rate of 10 °C min^{-1}) and under a vacuum of 50 µmHg (with an evacuation rate of 5.0 mmHg s^{-1}) for between 4 and 6 h depending on the sample. After degas, the mass of the glassware and sample was re-measured and this value used for the analysis. The analysis was run at 77 K using the properties given in the ESI, Table S2 and S3.

Results and Discussion

Pectin Yield

Traditional acid-extracted pectin of mango peel yielded 5.60 wt% at 85 ^{o}C and 7.50 wt% at reflux temperature, respectively, which is comparable with the literature.[29]

Initial screening microwave-assisted extraction (acid-free) Depending on the conditions employed (see Table 2), microwave-assisted (acid free) extraction gave yields ranging from 0.16 (entry 11) – 11.63 wt% (entry 2).

Table 2. Pectin yields obtained from Tommy Atkins cultivar at different conditions under microwave irradiation.

Entry	T (^{o}C)	Sample: Solvent (w/v)	Time (min)	Yield (wt %)
1	110	1:6	2	6.70
2	110	1:6	5	11.63
3	110	1:6	10	6.70
4	110	1:4	5	10.72
2	110	1:6	5	11.63
5	110	1:8	5	5.88
6	110	1:10	5	6.90
7	120	1:10	10	10.37
8	140	1:10	10	11.22
9	160	1:10	10	9.23
10	180	1:10	10	0.65
11	200	1:10	10	0.16
12	140	1:10	1	-
13	140	1:10	5	10.29
14	140	1:10	20	6.86

As can be seen in Figure 1, at fixed irradiation time (5 mins) and temperature (110 ^{o}C) the optimal peel:solvent ratio was found to be 1:6 (entry 2), followed by 1:4 (entry 4), then 1:8 (entry 5) and lowest at 1:10 (entry 6). At optimal sample:solvent ratio solvation improves such that internal microwave absorption is enhanced causing more effective cell rupture and thus easier pectin release. However, too much solvent leads slow mass transfer and reduced dispersion of the pectin into the solution. This relationship although not linear has been observed by other researchers.[30] At fixed peel:solvent ratio (1:10), the optimal conditions were found at 140 ^{o}C and 10 minutes (entry 8).

In contrast, at elevated temperatures (>160 ^{o}C), the degradation process of pectin becomes dominant and faster than the extraction. Consequently, lower molecular weight pectin could not precipitate at the same ratio, which resulted in dramatically reduced yields (entries 9-11).

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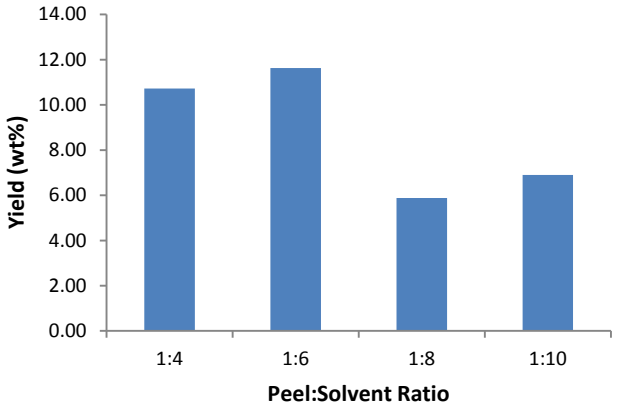

Figure 1. Influence of peel:solvent ratio on pectin yield at fixed irradiation time (5 mins) and temperature (110^{o}C)

Upscaling The extractions were reproduced with peels from three different mango cultivars at a larger scale (CEM-MARS6, see Table 3), using the conditions that showed high yield of pectin (140 ^{o}C, 10 min, peel:solvent (1:10)).

Table 3. Pectin yields obtained from peels of different mango cultivars.

Cultivar	Pectin yield (g)	Pectin yield (wt%)	Peel residue (wt%)
Tommy Atkins	2.98	10.05	33.1
Alphonso	3.78	12.76	31.9
Honey	1.36	9.20	34.0

ATR-IR characterisation Comparison of the ATR-IR of conventional acid extracted pectin and microwave assisted pectin (eg. Entry 8) with commercial pectin (Figure 2) shows excellent correlation with the notable exception of the peaks corresponding to the ester and carboxylic acid, these show that of the three samples shown, commercial pectin has the highest degree of methylation, followed by the microwave extracted mango pectin, and finally the conventional acid extracted mango pectin. The characteristic absorption band at 1700-1740 cm^{-1} corresponding to the methyl ester/acid (-$COOCH_3$/-COOH) group is observed along with the –CH_3 bending adsorption band due to the esterified CH_3 at 1350-1450 cm^{-1}.[31] The absorption band at roughly 1600 cm^{-1} corresponds to the carboxylate salt (–COONa).

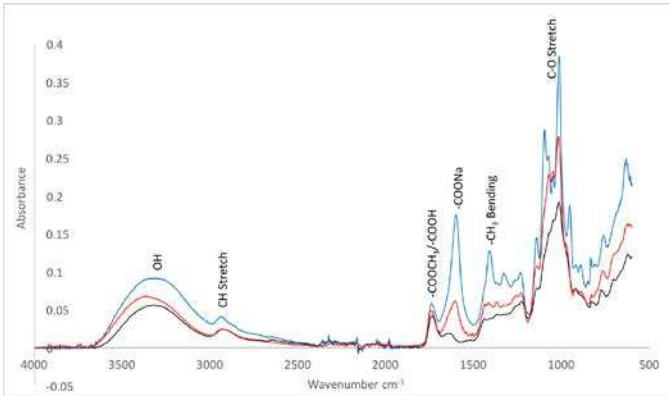

Figure 2. IR spectra of pectin obtained from acid assisted extraction (black) and microwave-assisted extraction (entry 8, red) compared to commercial pectin (blue).

Similarly, the ATR-IR spectra of microwave-assisted pectin (varying solvent:sample ratio (1:4. 1:6, 1:8 and 1:10), fixed irradiation time (5 mins) and fixed temperature (110^{o}C)) with that of commercial pectin show excellent correlation (see ESI, Figure S1), i.e., absorption bands corrosponding to the methyl ester/acid at 1700-1740 cm^{-1}, along with the esterified methyl (-CH_3 bending) absorption band at 1431-1439 cm^{-1} are observed.

Solution NMR and degree of esterification (titrimetry and ^{13}C NMR) The solution ^{1}H NMR of isolated mango pectin (Honey) is shown in Figure 3 and the ^{13}C NMR of each variety is shown in Figure 4. Full quantification is difficult due to different conformers of monosaccharides present in the side chains. Nevertheless, the signals for the methoxy group (OCH_3) and protons on the C1 (anomeric carbon), C2, C3, 4 and C5 are clearly discernible.

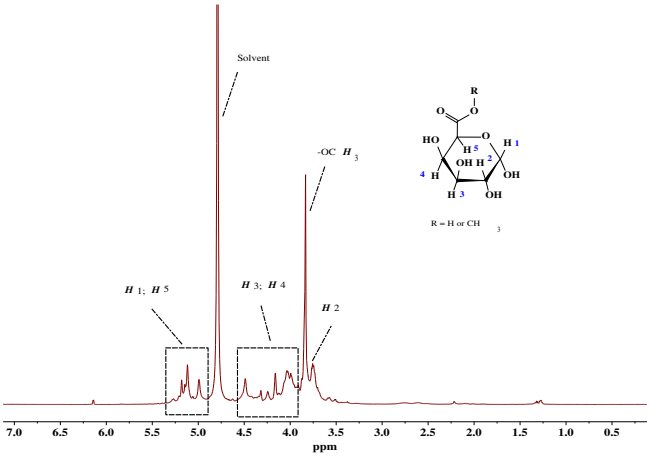

Figure 3. ^{1}H NMR spectrum of isolated mango pectin (*Honey*)

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The calculation of the degree of esterification by the titration was fraught with difficulty (subjective estimation of end point) and thus reproducibility was questionable. Hence, ^{13}C NMR spectroscopy was a better method for quantifying degree of esterification (see Table 4). The degree of esterification was calculated using the integral area of the carbonyl group (free galacturonic acid, 175.1 ppm) and the integral area of the esterified carbonyl group (esterified galacturonic acid, 170.7 ppm) (see Figure 5) and detailed assignments are listed in Table 5.

Table 4. DE (%) determined by titrimetry and ^{13}C NMR for three cultivars of mango

Cultivar	DE (%)	
	Titrimetry	^{13}C NMR
1. Tommy Atkins	87.7 ± 0.5	86.2
2. Alphonso	79.3 ± 6.2	75.6
3. Honey	83.0 ± 4.3	77.1

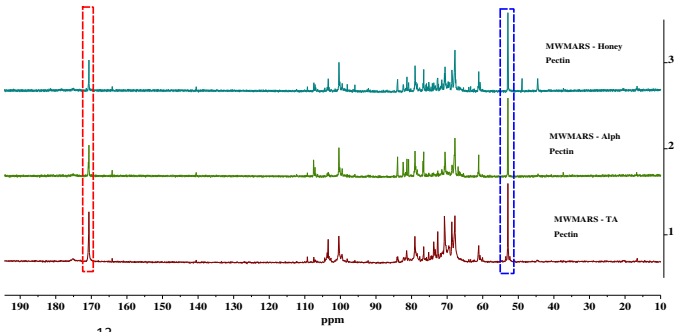
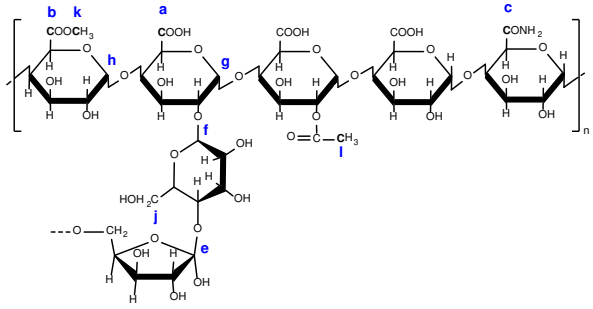
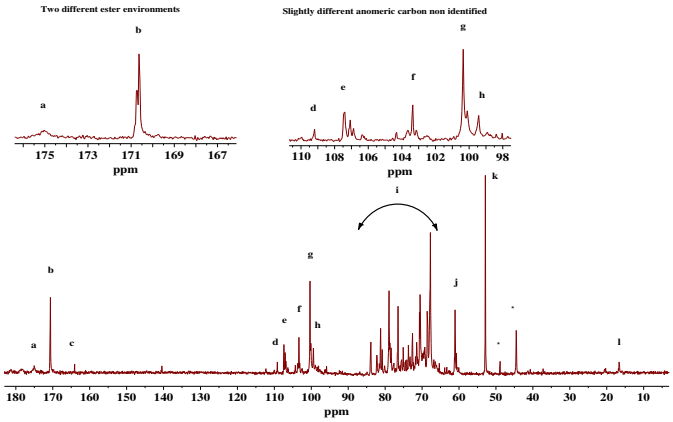


Figure 4. ^{13}C NMR signals MW-extracted pectin from three cultivars (Honey (Top), Alphonso (Middle) and Tommy Atkins (bottom).





** Not identified peaks*

Figure 5. Representative ^{13}C NMR spectrum (500 MHz, D_2O) of microwave-assisted pectin from *Honey* variety (see ESI, Figures S2-S3 for Tommy Atkins and Alphonso varieties)

Table 5. ^{13}C NMR assignments of microwave-assisted extracted pectin (Honey variety) solubilised in D_2O

Signal (refer to Figure 5)	Chemical shift (ppm)	Assignment
a	175.1	Non-esterified carbonyl GalA (-**C**OOH)[32]
b	170.7	Esterified carbonyl GalA (-**C**OOCH$_3$)[33]
c	164.1	Amidated carbonyl GalA (-**C**OONH$_2$)*
d	109.3	Anomeric carbon*
e	107.5	**C**1 (α-L-arabinose)[33]
f	103.4	**C**1 (α-D-galactose)[32]
g	100.5	**C**1 GalA non-esterified[32]
h	99.5	**C**1 GalA esterified[32]
i	84.1-61.1	**C**2 to **C**5 of GalA and rest of residues (esterified and non-esterified)[34]
j	61.1	**C**6 (galactose)[33]
k	52.9	Methyl GalA (- COO**C**H$_3$)[32]
l	16.5	Methyl (- OCO**C**H$_3$)[32]

* *Not verified chemical shifts*

Additionally, the structure of pectin was further characterised using ^{13}C CPMAS solid state NMR, and compared with commercial pectin (Figure 6).

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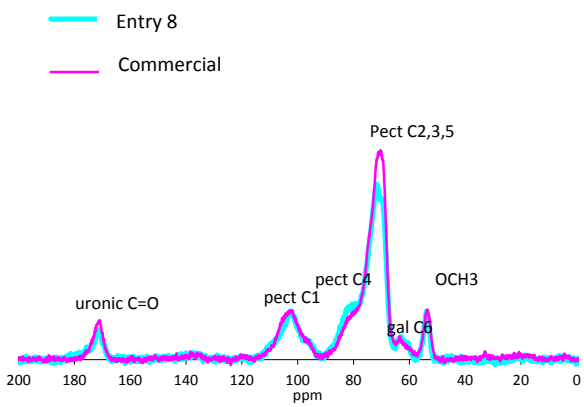


Figure 6. ^{13}C CPMAS NMR of acid-free MW-assisted pectin to commercial pectin (MP pectin acid).

Thermogravimetric analysis. Thermal analysis of microwave-assisted extracted pectin was compared with that of commercial pectin (Figure 7). Each sample showed a main mass loss between 220-240 ^{o}C of approximately 36 %, which is consistent with that of commercial pectin (temperature of maximum rate loss = 231 ^{o}C, 47 %). Commercial pectin also showed a less pronounced mass loss between 260 and 375 ^{o}C, corresponding to a mass loss of 14 %, while MW-extracted pectin loses a higher mass percentage between these temperatures (Honey 28 %, Alphonso 27 %, Tommy Atkins 32 %). Commercial pectin is highly purified compared with our materials. Mass loss between 260-375 ^{o}C may be due to residual low molecular starch or oligosugars still bound to our pectin. Although not evident by ATIR and 13C CPMAS NMR this difference may be manifest in polydispersity and gelation studies (see later: Table 6 and, Figure 9). Our samples have polydispersity than commercial pectin (Table 6) and although they show gelling ability the resultant gel had a light brown hue and took up to 24-48 h to gel (Figure 9). Commercial pectin on the other hand affords a clear, colourless gel within a few hours of cooling.

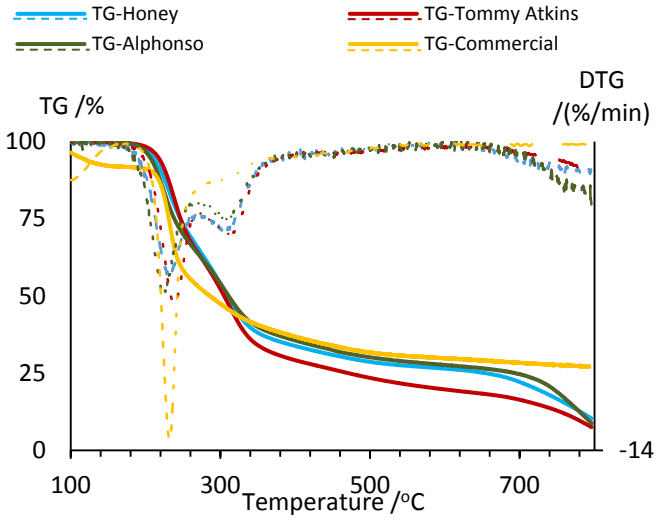
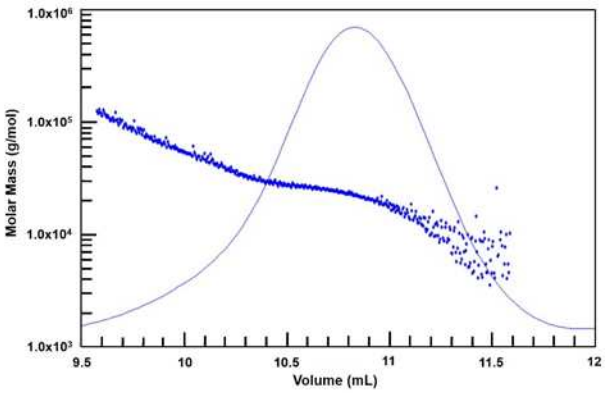


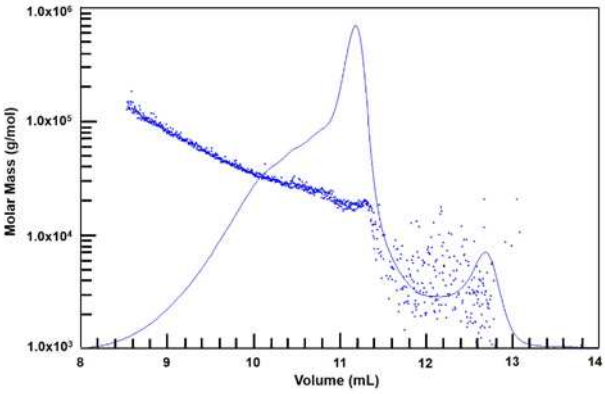
Figure 7. TG (solid line) and DTG (dashed line) traces of microwave-assisted extracted pectin from different varieties, compared with commercial pectin.

Gel permeation chromatography: Molecular weight and polydispersity studies. Refractive index and molecular weight GPC elution profiles for representative samples are shown in Figure 8a and b, and compared with commercial pectin (Figure 8c).

(a) – Tommy Atkins; 140°C, 10 mins



(b) – Tommy Atkins; Conventional acid extraction



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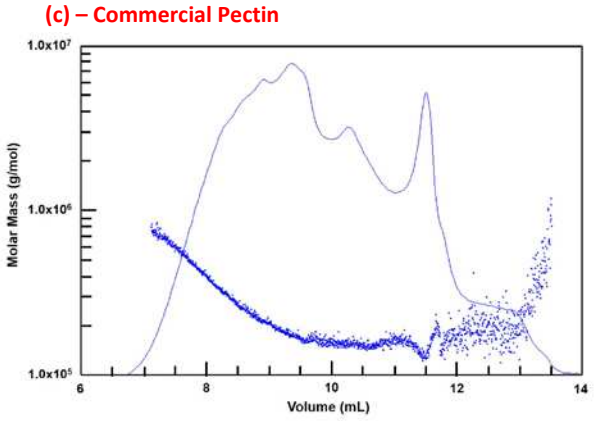

Figure 8. Refractive index and M_w GPC elution profiles of MW-assisted pectin from Tommy Atkins (a), conventional acid extracted pectin from Tommy Atkins (b) cultivars along with commercial pectin (c). See ESI Figure S4 for Honey and Alphonso varieties.

The comparison of number and weight average molar mass (M_n and M_w, respectively) and polydispersity (M_w/M_n) between commercial pectin and microwave extracted pectin as well as conventional acid-extracted pectin is listed in Table 6. Lower M_w and M_n values are obtained in all extracted samples comparing with commercial. This means that both chain length and polymer size are smaller for extracted mango pectin than the commercialised from citrus. Although our comparison is with commercial pectin we must appreciate that the latter is highly refined and thus has low polydispersity. Conventional acid-extraction produces high polydispersity due to its harsh nature causing ready cleavage of C-O bonds. We see a similar effect with acid-extraction of Tommy Atkins (M_W/M_N 2.081). Interestingly, acid-free MW-assisted extraction, deemed a milder method than acid-assisted, produces a lower polydispersity (M_W/M_N 1.365) which at an industrial level may minimise need for further purification. Polydispersity is similar although slightly lower for microwave-extracted Tommy Atkins, which shows more similarity with commercial pectin. The highest polydispersity was seen for conventional extracted mango pectin. Interestingly, we have also noticed approximately 3.72% (see ESI, Table S1) protein in the acid-extracted samples which would also affect polydispersity. The average molecular weight of mango extracted pectin via acid-free MW irradiation is of the same order *of magnitude as those reported by Kratchnova et al.*[10] *for hydrochloric acid soluble pectin.*

Table 6. Molecular weight (g/mol) and polydispersity for pectin samples irradiated at 140°C.

Sample	M_n	M_w	M_w/M_n
Tommy Atkins	18710	25540	1.365
Alphonso	11950	18260	1.529
Honey	8723	14130	1.621
Conventional acid-Tommy Atk	13370	27830	2.081
Commercial pectin	198400	232200	1.170

Gelation studies Different pH provided by citrate buffer solution and different quantities of pectin and sugar (sucrose) were tested in order to find the best gelling conditions. High ester (HE) and low ester (LE) pectin gelled at concentrations between 0.5 and 1.5 % w/w.

The use of an over excessive amount of sucrose at >pH 2 caused the gel to crystallise over time due to the ability of sugar to compete for water with pectin. A too low percentage of sucrose did not allow the pectin to completely gel giving a viscous liquid instead formed also by competition of sucrose and pectin for water but not being enough.

Under the conditions performed, only pectin extracted from *Tommy Atkins* and *Honey* mangos could be gelled. The best conditions were pH = 2, 0.75% pectin and 70% sucrose for *Tommy Atkins* pectin and pH = 2, 1.5% pectin and 70% sucrose for *Honey* pectin (Figure 9). The lower DE of Alphonso extracted pectin could be a reason why this pectin could not be gelled under these conditions. Lower pH could be a solution for this as the viscosity of pectin solutions usually increases with decreasing pH in a calcium-free solution. In this case, as the DE is lower, there are more quantity of free carboxylic acid groups. A decrease in pH will supress the dissociation of carboxylic groups, thus promoting chain to chain association.

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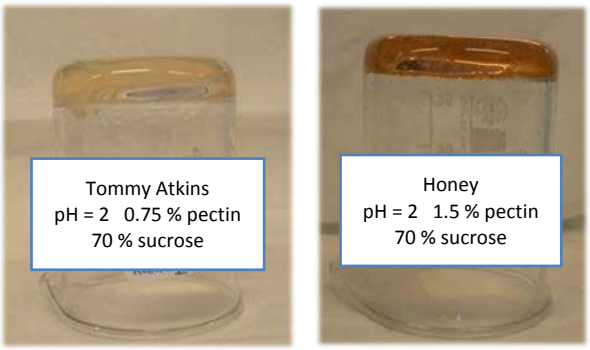

Figure 9. Gels obtained from (left) "*Tommy Atkins*" mango pectin and (right) "*Honey*" mango pectin.

Porosimetry: Mango peel de-pectinated cellulosic residue

Varietal differences. The porosity data (Surface area (S_{BET}), Pore volume, Pore diameter) of mango de-pectinated peels and cellulosic material derived from the residue after a second microwave hydrothermal treatment, for the different cultivars are shown in Table 7.

Table 7. Porosity data of depectinated peel and depectinated peel after a second hydrothermal microwave treatment at 180 °C.

Sample	S_{BET} (m^2/g)	P. vol. (cm^3/g)	P. diam. (Å)
'Alphonso' depectinated peel	26.0	0.06	93.4
'Alphonso' Cellulosic material (second MW)	124.0	0.37	102.8
'Honey' depectinated peel	16.3	0.04	105.0
'Honey' Cellulosic material (second MW)	88.8	0.22	99.7

The cellulosic matter is mesoporous as shown by the average pore diameter (9.3 – 10.5 nm). As expected, it can be seen that there is a significant difference between the properties of the cellulose obtained from each of the mango's peel according to their varieties and origins, *Alphonso* and *Honey*. This difference is probably not only due to its origin, but it also may be related to bio- and physio-chemical changes such as the ripening. Also, an interesting observation is that porosity of peel samples before and after the second hydrothermal treatment enhanced porosity. The surface area increases between 6 and 8 times, increasing the amount of available pores. This is due to the second microwave hydrothermal treatment performed on the samples. This treatment removed the residual pectin and hemicellulose from the samples, then increasing the porosity, as reported in literature for other pre-treatments of biomass.[35,36]

Conclusions

Low temperature microwave-assisted acid-free processing of waste mango peels are a significant source of potentially exploitable biobased chemicals and materials within the context of a future mango waste biorefinery. Depending on cultivar type (Honey, Alphonso and Tommy Atkins) microwave-assisted acid-free extraction yielded up to 11.63% (dry weight basis) of pectin, a widely used commercially important thickener and rheology modifier which is produced under hot aqueous acidic conditions. Mango pectin possesses high degree of esterification (75.6 – 87.7%) with good gelling ability and low polydispersity which again merits its commercial applicability. Pectin-free cellulosic fibres are mesoporous (average pore diameter, 9.3 nm (Alphonso) – 10.5 nm (Honey), but with poor surface area 16.3 m^2g^{-1} (Honey) – 26.0 m^2g^{-1}. A second microwave hydrothermal treatment significantly enhances surface area (88.8 m^2g^{-1} (Honey) – 124.0 m^2g^{-1} (Alphonso)) and pore volume by approximately six-fold. Such materials may be amenable for adsorption-desorption, chromatography and as substrates for catalyst. In conclusion, low temperature microwave-assisted acid-free treatment of waste mango peel yields high DE, gel-labile pectin and mesoporous cellulose a represents an interest future biorefinery feedstock.

Acknowledgements

The Authors wish to acknowledge Ms A Bagaria, Dr M deBruyn, Dr L Pfaltzgraff and Dr V Budarin for technical assistance with microwave experiments, porosimetry and solution NMR spectroscopy. CLTP wishes for assistance with solution NMR studies and Ministerio de Economía y Competitividad (MINECO) and Campus de Excellencia Internacional (CYTEMA) for funding. JAH acknowledges Dr Roger Ibbett, University of Nottingham, for 13C CPMAS solid state data.

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