

# Life-Cycle Analysis of Microwave Assisted Pectin Extraction at Pilot-scale

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ABSTRACT The first Life-Cycle Assessment (LCA) of an acid-free, microwave-assisted process for pectin production at pilot-scale is reported. The properties of the resulting pectin were measured and compared against the criteria for commercial pectin, whilst the energy consumption of the microwave process was measured to compare its life cycle impacts with that of the current commercial process.

Overall, the pectin met all the criteria for food-grade commercial pectin. The microwave unit was estimated to have <25% of the environmental impact of traditional acid-assisted thermal process

in all categories measured and provided an improved yield of 5% (wet weight basis) compared to 3% by thermal heating under normalized conditions. The readouts were comparable with each other over 3 runs indicating a robust and reproducible process, crucial for scale-up purposes.

With the product meeting the relevant criteria and the process being robust and more environmentally friendly, this work demonstrates the practical and commercial potential of microwave technology to succeed conventional acid-based extraction of pectin production.

## **Introduction**

With the continuing depletion of crude oil resources, decreasing landfill space and increasing public awareness of human impact on the environment, waste valorisation and the biorefinery concept are potential solutions to simultaneously address these concerns.<sup>1-5</sup> Citrus peel has been a raw material of particular interest as it is an unavoidable food waste source, inevitably leftover after squeezing for juice or consumption of the flesh. Additionally, it is produced in extremely large quantities by the juicing industry; the Food and Agricultural Organisation of the United Nations estimates that global production of oranges alone has exceeded 65 million tonnes for the last 10 years, peaking at 72 million tonnes in 2014.<sup>6</sup> Even with the most efficient juicing processes, it is estimated that, by mass, 50% of the orange is left behind.<sup>7</sup> Citrus peel (as well as apple pomace) does have some industrial use as the main feedstock for the production of pectin.<sup>8</sup> Pectin is a natural biopolymer comprised largely of galacturonic acid chains, with a certain amount esterified with methoxy groups, found within the cell walls of some plant skins and fibre to help provide structural integrity.<sup>9, 10</sup>

It has long been used as a gelling agent (notably in the production of jam) and viscosity modifier, but is now becoming increasingly sought after<sup>1</sup> both as an alternative to sugar and fat as a bulking agent in food,<sup>11</sup> but also for pharmaceutical applications.<sup>12</sup>

The conventional methods of pectin extraction typically requires boiling in acidic conditions over several hours to rupture the cell walls and release the pectin which subsequently dissolves into the water.<sup>13</sup> Following this, the resulting mixture is filtered and an organic alcohol (typically ethanol or isopropanol) is added to the filtrate. Being a polar molecule due to the galacturonic acid chains, pectin is largely insoluble in organic solvents and the addition of the alcohol, therefore lowers the polarity of the aqueous phase and causes the pectin to precipitate out. From here, the pectin can be filtered or centrifuged off, washed and dried to afford the powder as a product.<sup>7, 8</sup>

The use of microwave technology, in place of thermal heating has the potential to improve this method both economically and environmentally by reducing the heating time needed for the process and eliminating the need for an acid catalyst by having the microwaves interact with the water molecules to heat and expand the aqueous matrix to rupture the cells directly. We have previously published several papers exploring lab-scale (<1L) microwave-assisted extraction of pectin from citrus<sup>2, 3, 7, 14</sup> and other sources,<sup>15</sup> but these have so far largely focussed on yields and optimising conditions. The use of microwaves in place of thermal heating is well established within the food industry for cooking with respect to lowering processing times and subsequent energy costs. However there is a significant discrepancy over the actual values in terms of savings due to a lack of standardisation amongst microwave producers and the variation of foodstuffs that are available for cooking.<sup>16</sup> Additionally, these figures also only concern residential or retail kitchens that rarely exceed heating more than ~1L of material per batch.

To truly succeed conventional acid-assisted thermal extraction of pectin, the microwave biorefinery option, as well as being able to operate at larger scales, must offer demonstrable improvements in terms of product quality, throughput, operating costs or environmental impacts – ideally in all areas. Additionally, the process must be robust and repeatable and the product must perform its function. Herein we present the results of the first pilot-scale microwave-assisted processing of citrus peel to obtain pectin, along with an environmental impact comparison with commercial pectin production.

Working with biomass necessarily creates a number of variables in of itself as seasonal and regional variations can greatly affect composition. Additionally, due to IP and patent applications, whilst the basic process overview is there are same there are variations in the exact details of both the juicing process and pectin extraction processes from company to company. This therefore means that there will always be variation in the orange peel produced in each juicing line and variations in pectin production from plant to plant (providing that the material conforms to specification). For instance, another commercial treatment of citrus peel involves extrusion of the material to produce essential oils – however the effluent ‘yellow water’ from this process is known to contain pectin, therefore the material from such a plant would likely lead to a reduced yield in this particular process and therefore affect the subsequent LCA data.<sup>7, 17, 18</sup>

In order to obtain a more direct comparison of thermal vs microwave heating it has been necessary to control a number of variables to minimise this variation. Firstly, orange peel waste was produced from juicing directly in-house rather than obtained from a commercial juicing plant. Secondly, despite a number of additional processes (e.g. essential oil extraction) being identified as potential steps as part of the citrus biorefinery,<sup>7</sup> this work has assumed no additional upstream processes have been carried out prior to this process. Thirdly, the pre-processing and post-processing steps

were kept identical to both processes to eliminate the need to include them in the comparison and focus only on the heating methods.

## **Experimental**

### **Materials**

Oranges of Spanish and South African origin were purchased from a local supermarket branded as Sainsbury's 'Taste the Difference' range and blended. Ethanol, ethylene glycol (puriss. p.a., absolute,  $\geq 99.8\%$  (GC)) were purchased from Sigma Aldrich and used without further purification. Diethyl ether (analytical reagent grade) iso-propanol (Laboratory reagent grade,  $\geq 99.5\%$ ), hydrochloric acid S.G. 1.18 (Analytical reagent grade), sucrose (laboratory reagent grade) and sodium hydroxide (Analytical reagent grade) were all purchased from Fisher Scientific and used without further purification.

### **Pre-Processing**

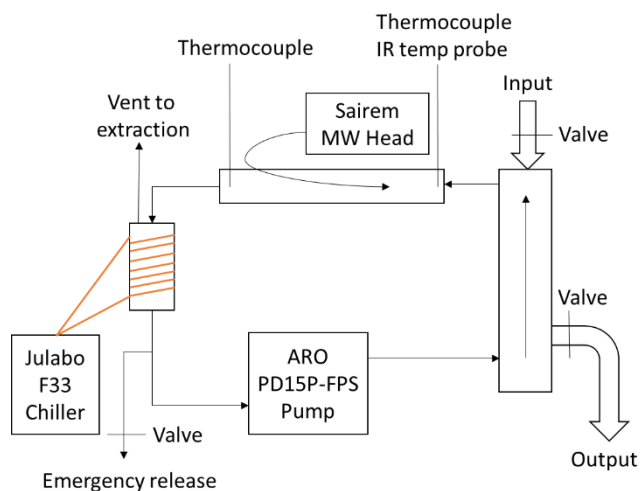
Waste orange peel was added, in portions, to a Retsch GM30 Knife Mill and ground at 2,200 rpm for 2 minutes. The resulting ground orange peel was added, in 0.75 kg portions with 1.5L of deionised water, to a 2L Robocoupe mixer and blended on 3,000 rpm for 30 seconds to form a mobile slurry which was passed through a 4mm sieve to remove any resulting stones or larger particles. Four portions were then combined and an extra 6L of deionised water was added to make the total volume up to 20 L (with the orange peel making up 4 L volume).

### **Microwave Processing**

The mixture was then transferred into the microwave rig consisting of a Sairem Labotron Pyro, 60K Pyro microwave head irradiating a glass-tube cavity connected on either side to an ARO PD15P-FPS diaphragm pump to form a complete circuit, which was then sealed. The temperature

was measured and fed back to the microwave generator via a thermocouple at each end of the cavity and an IR probe at the entrance with a dual emergency release system at the exit end consisting of a vent to the house extraction system in the case of over-boiling and a release valve in the event of pump blockage. The schematic of the system is shown in figure 1, with a photo of the equipment shown in the synopsis).

The pump was activated to ensure continuous flow of liquid and, after checking there were no blockages, the microwave head was activated at a power of 6 kW until a temperature of 95 °C was reached and then held for 1.5 h with the temperature of the mixture (measured at the left of the microwave chamber) and microwave power being recorded each minute (output provided in supplementary information). The microwave was then deactivated and a Julabo F33 chiller (filled with ethylene glycol) was activated to bring the temperature down to 60 °C at which point the exit valve was opened and the mixture decanted into a 20L drum. The rig was then cleaned with another 20 L portion of deionised water.



**Figure 1.** Schematic diagram of the microwave rig used for the procedure.

### Downstream Processing

The material was strained through filter cloth to separate out the cellulosic residues and an equivalent volume of ethanol was added to the filtrate in order to precipitate the pectin out. The pectin was then separated out on a centrifuge at 8,500 G for 30 minutes. The supernatant was removed and the pectin pellet was washed twice in the minimum amount of ethanol and centrifuged at 3,500 G for 30 minutes, before being added to the minimum amount of ethanol at reflux for 10 minutes and then filtered under vacuum, whilst still hot. The solids were then suspended in analytical grade water in an 8:2 water:solids ratio, stirred for 60 minutes at 1,000 rpm and freeze dried at BioPharma industries.

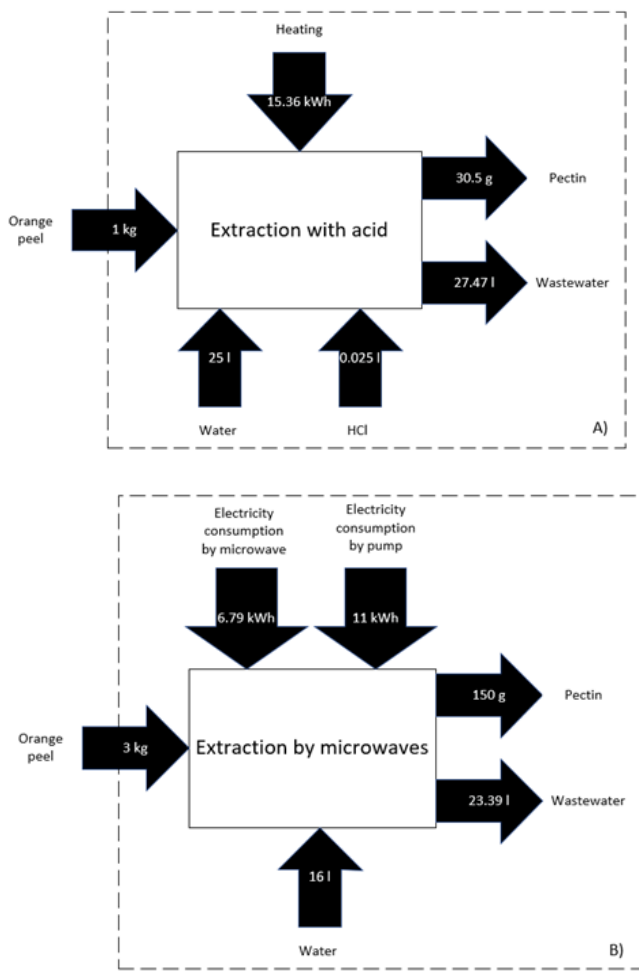
### **Characterisation Tests**

Characterisation of the pectin was largely carried out according to the criteria set out by the World Health Organisation<sup>19</sup> (details provided in supporting information) apart from metals content, which were analysed in triplicate via ICP-OES, courtesy of Yara Analytical Services.

### **LCA analysis**

Upstream and downstream processes are identical to conventional production, thus only the extraction processes are compared in this paper. Since only one process (in each scenario) is assessed, the study presented in this section cannot be considered a full life-cycle assessment (LCA) study of pectin production from orange peel. However, it is expected that the addition of those processes will not significantly change the final results, since the processes in both scenarios are alike, and only the different extraction yields will give proportionally lower environmental impacts for downstream processes per kg of pectin obtained. Nevertheless, the LCA procedure has been applied to study the use of resources and associated emissions of the processes related to the extraction process, e.g. the environmental impact of generating and distributing electricity used in the extraction processes is considered.

The system boundaries of the study are depicted in Figure 2, which also includes the values of the parameters considered. A burden-free or zero-burden approach has been followed to allocate all environmental impacts of the production of the initially targeted product, i.e. orange juice in this study, to that product, thus the raw material entering the system in this study does not carry any environmental load. This is commonly done in LCA studies of waste management<sup>20, 21</sup> as waste is not the targeted product and is a co-product of producing orange juice. On the other hand, the use of other resources in the extraction process is allocated to the production of pectin. Wastewater was the only output considered from the process other than pectin, since the processes were undertaken in closed vessels and air emissions were estimated to be negligible.





**Figure 2.** System boundaries of the two extraction scenarios: A) traditional acid extraction<sup>8</sup>, and B) microwave extraction.

As this paper aims to compare two different methods to produce pectin from the same raw material, it is assumed the pectin manufacturer will adjust pectin production levels to meet demand, and not to meet feedstock availability. Thus, the rest of orange peel will be discarded if there is no sufficient demand for pectin. Consequently, the functional unit has been defined as 150 g pectin obtained, which corresponds to the capacity of the microwave to treat 3 kg of orange peel in one batch. Scenario A in Figure 2 shows 1 kg of orange peel as input to the acid process and 30.5 g of pectin obtained because the data was collected per kg of orange peel, but results shown in this section were calculated per 150 g of pectin obtained, and therefore multiplying values shown in Scenario A (Figure 2) by 4.92.

SimaPro 8.5.2 software was used to aid in the classification, characterisation and normalisation stages of life-cycle impact assessment (phase 3 of LCA). In terms of the modelling framework, attributional LCA was selected to assess the impact associated to the functional unit, since only small-scale interventions were considered. Attributional LCAs can be used to compare different systems producing the same functional unit<sup>22</sup>. Consequently, average data was used to model the background system. Using SimaPro terminology, “Allocation at the point of substitution” (APOS) processes, known as “Allocation, default” in SimaPro 8.5.0 and previous versions, were incorporated into the model. An explanation as to why they were chosen can be found in the supplementary information. In all cases, the geographical scope has been considered to prioritise processes and materials from firstly the UK and secondly Europe.

The International Reference Life Cycle Data System (ILCD) impact assessment method was primarily used in this study, but ReCiPe 2016 Midpoint (H) V1.02 was also used to check

robustness of results. Results obtained by using both methods were similar, with slight differences for marine eutrophication. ReCiPe 2016 method has the advantage of allowing quantification of endpoint indicators, but the disadvantage that it does not support normalisation nor weighting. By using the IMPACT 2002+ V2.14 method, similar results were obtained in terms of the electricity contribution to the total environmental impact.

### **Selection of materials and processes in SimaPro**

The following materials and processes were used to perform the analysis in SimaPro:

- 1) Hydrochloric acid, without water, in 30% solution state {RER}| benzene chlorination | APOS, S

In SimaPro, the processes to produce HCl are:

- a) HCl produced as a primary product by reacting hydrogen and chlorine.
- b) HCl produced as a secondary product of one of the following four processes: allyl chloride production by reaction of propylene and chlorine, tetrafluoroethane production, Mannheim process to produce sodium sulfate, benzene chlorination.

HCl produced as a primary product has not been considered because the majority of HCl (including both its gaseous and solution form) is formed as a co-product.<sup>23, 24</sup> Similarly, the “market for” activities have not been considered because these datasets assumes that HCl is generated from combustion of chlorine with hydrogen. Tetrafluoroethane production has not been considered because recent restrictions to use it due to its high global warming potential.<sup>25, 26</sup> Production of HCl from allyl chloride manufacturing accounts for a proportionally low amount of the total HCl production, around 383,700 metric tonnes.<sup>27</sup> The Mannheim process is a type of process to produce sodium sulfate and HCl as a by-product from salt. HCl production from salt has typically accounted for 3-4% of the total HCl production.<sup>24</sup> Based on the above, production of HCl from chlorination

of benzene has been chosen as the most representative process. The 25 ml HCl/kg orange peel needed corresponds to 0.03 kg, assuming a density of  $1.2 \text{ g mL}^{-1}$  at  $25 \text{ }^{\circ}\text{C}$ .

2) Ethanol, without water, in 99.7% solution state, from ethylene {GLO}| market for | APOS, S

Ethanol is mostly produced by fermentation processes or from catalytic hydration of ethylene. Generally, ethanol produced by fermentation is used in alcoholic beverages and fuel (i.e. bioethanol), whereas ethanol produced from ethylene (i.e. synthetic ethanol) is mostly used industrially as a solvent raw material to obtain other compounds,<sup>28</sup> which is the case described in this paper. In both scenarios considered in the paper, ethanol is used in a volumetric proportion of 1:1 with water, with a density is  $0.7893 \text{ kg L}^{-1}$ . Ethanol use is not included in Figure 7 because in an industrial setting it is recovered after every use for the next batch (although the energy and emissions associated to this process have not been considered in this model), so overall ethanol consumption would be minimal. However, ethanol use has been included in some of the simulations explained in the next section to assess the sensitivity of the model to this parameter.

3) Electricity, medium voltage {GB}| market for | APOS, S

A significant environmental impact of both scenarios could presumably be attributed to energy consumption required for heating. Considering the size of industrial plants to produce pectin, medium voltage and “market for” activity have been selected from Ecoinvent to represent the UK electricity market including energy losses during distribution.

The energy consumption in scenario A, which was attributed to electricity consumption, was modelled as follows. Firstly, a baseline calculation allowed to obtain the theoretical energy needed to heat the sample based on the heat capacities of orange peel and water ( $3300$  and  $4180 \text{ J kg}^{-1} \text{ K}^{-1}$  respectively) for different orange peel amounts. Next, SuperPro Designer software was used to

model the same heating processes plus the energy used for stirring the mixture (“no holding time”), and three different scenarios including the energy needed to keep the temperature at 95 °C for 1.5 h, which is the condition required for the extraction process. These three scenarios were based on different efficiencies to maintain temperature without heat dissipation (100%, 90% and 80% efficiency). Based on our lab experiments on acid extraction of pectin from citrus waste, a 90% efficiency was assumed for the process.<sup>7</sup> Therefore, 15.36 kWh was used as energy consumption to treat 1 kg of orange peel.

**Table 1.** Calculation of energy consumption for scenario A. Baseline is a theoretical calculation, whereas the rest of scenarios were modelled with SuperPro Designer

<b>Mass orange peel</b>	<b>0.01</b>	<b>0.1</b>	<b>0.5</b>	<b>1</b>	<b>3</b>	<b>10</b>	<b>100</b>	<b>1000</b>	<b>kg</b>
<b>Baseline</b>	7.55 E+03	7.55 E+05	3.77 E+06	7.55 E+06	2.26 E+07	7.55 E+07	7.55E+08	7.55E+09	J
	0.0210	0.2096	1.0481	2.0961	6.2883	20.961	209.61	2096.1	kWh
<b>No holding time</b>	1.19	1.42	2.43	3.7	8.76	26.49	254.43	2545.07	
<b>100% efficiency</b>	12.44	12.67	13.68	14.95	20.01	37.74	265.68	2545.07	
<b>90% efficiency</b>	12.57	12.92	13.95	15.36	20.98	40.68	293.93	2826.38	
<b>80% efficiency</b>	12.74	13.02	14.29	15.87	22.2	44.36	329.24	3178.03	

The energy consumption of scenario B was empirically measured from the equipment using a power meter and includes 6.79 kWh for the microwave and 11 kWh for the diaphragm pump in the rig.

1) Water, well, in ground, GB

This seems to be the most relevant water source for the processes analysed in this paper, considering the geographical scope of the assessment.

2) Wastewater, average {Europe without Switzerland}| treatment of wastewater, average, capacity  $1 \times 10^9$  L year<sup>-1</sup> | APOS, S

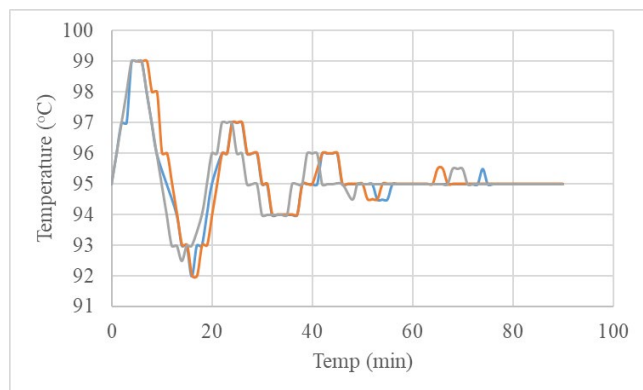
There are different wastewater treatments in SimaPro from Ecoinvent, ELCD, and EU & DK Input Output Database. To keep consistency with the aforementioned processes and materials, and also based on their corresponding descriptions, Ecoinvent database has been selected, specifically the process Wastewater, average {Europe without Switzerland}| treatment of wastewater, average, capacity  $1 \times 10^9$  L year<sup>-1</sup> | APOS, S. Wastewater includes very diluted residual orange peel and HCl in Scenario A, with no HCl in Scenario B. The density of orange peel is 0.406 kg L<sup>-1</sup>.<sup>7</sup>

## **Results and Discussion**

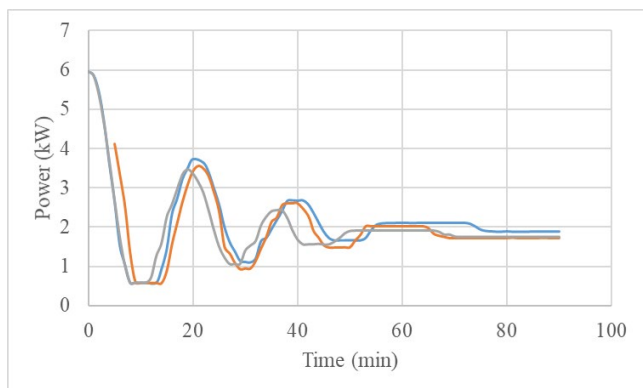
The specification of the pectin versus the commercial criteria is shown in Table 2. As it can be seen, the measured parameters of the material conform to the requirements for commercial pectin. For many of the impurities, the figure is currently <10% of the threshold which also provides a bonus in terms of having significant buffer if the criteria become more stringent following changes in legislation (or other drivers for reduction). Figures 3 and 4 show two of the outputs of the power and temperature from the runs (others available in supplementary data) which show good agreement with each other and indicate a reliable process with good self regulation of desired temperature.

Table 2. The measured specification of the obtained pectin

Criteria	Threshold	Sample Measurement
<b>Degree of esterification</b>	>50%	72.8%
<b>Galacturonic Acid</b>	>65%	72.3%
<b>Degree of Amidation</b>	<25%	None Detected
<b>Loss on Drying</b>	<12%	8.98%
<b>Total Insolubles</b>	<3%	0.29%
<b>Total Nitrogen</b>	<2.5%	0.83%
<b>As</b>	<3 ppm	<0.01 ppm
<b>Cd</b>	<5 ppm	<0.01 ppm
<b>Hg</b>	<1 ppm	0.2 ppm
<b>Pb</b>	<1 ppm	<0.01 ppm



**Figure 3.** Composite temperature profile of 3 runs on the microwave over the 90 minute run.



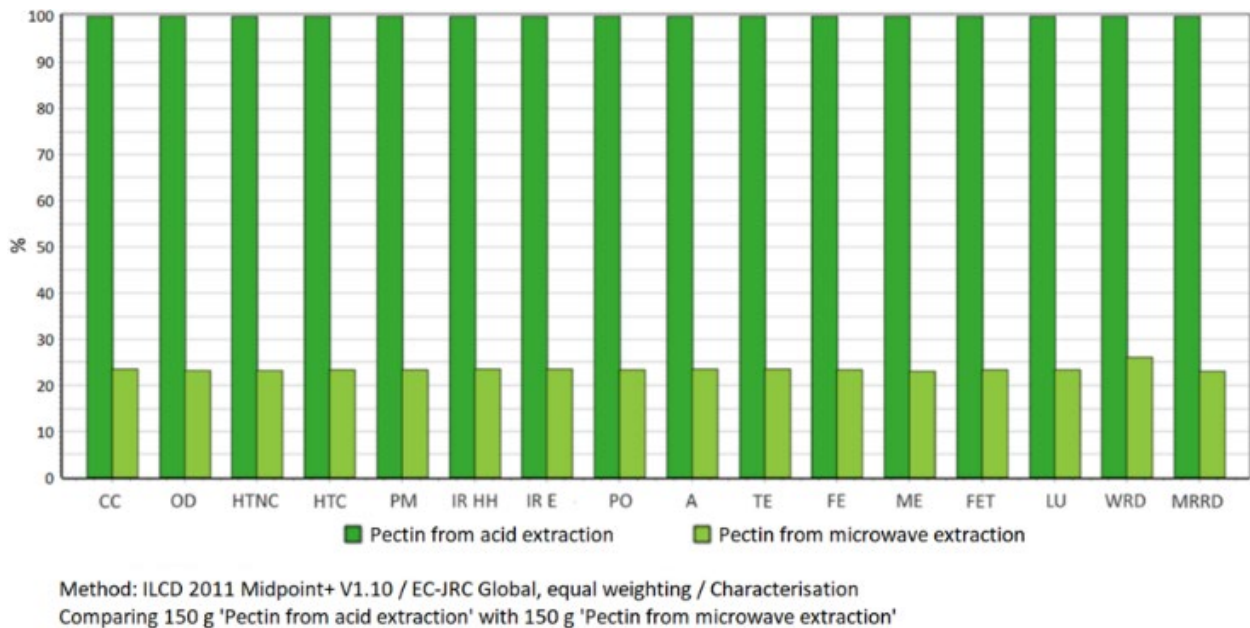
**Figure 4.** Composite power consumption of 3 runs on the microwave over the 90 minute run.

### **Life Cycle Assessment**

The yields of the extraction processes are considered in this LCA analysis, since traditional lab-scale acid extraction allows a recovery of 30.5 g of pectin per kg of orange peel, whereas the microwave extraction proposed in this paper produces 150 g of pectin per 3 kg of orange peel, i.e. a yield increase of a factor of 1.64.

The following processes and materials from Ecoinvent 3.2 database were used to model both scenarios: ‘Hydrochloric acid, without water, in 30% solution state {European data – (RER)} | benzene chlorination | APOS, S’; ‘Ethanol, without water, in 99.7% solution state, from ethylene {Global data – (GLO)} | market for | APOS, S’; ‘Electricity, medium voltage {GB} | market for | APOS, S’; ‘Water, well, in ground, GB’; and ‘Wastewater, average {Europe without Switzerland} | treatment of wastewater, average, capacity  $1 \times 10^9$  L year<sup>-1</sup> | APOS, S’. Although UK materials and processes were prioritised in the model, their use was not always possible, and global (GLO) and European (RER), as well as materials and processes from Great Britain (GB), were used. A justification on the selection of these materials and processes can be found in Supplementary Materials.

Immediate advantages of the microwave extraction are the elimination of HCl use, lower energy (electricity) needed, lower water use and wastewater generated, and higher pectin yield, as can be seen in Figure 5. Figure 6 quantitatively assess the environmental loads of those differences from the results of the impact analysis phase of the LCA procedure by using the ILCD 2011 Midpoint+ V.1.10 method, including long-term emissions. Microwave extraction is significantly better than acid extraction for all impact categories, achieving a reduction of environmental impact of the order of 75%.



**Figure 5.** Impact analysis (characterisation) of both extraction technologies to produce 150 g of pectin. CC: climate change; OD: ozone depletion; HTNC: human toxicity, non-cancer effects; HTC: human toxicity, cancer effects; PM: particulate matter; IR HH: ionizing radiation to human health; IR E: ionizing radiation E (interim); PO: photochemical ozone; A: acidification; TE: terrestrial eutrophication; FE: freshwater eutrophication; ME: marine eutrophication; FET: freshwater ecotoxicity; LU: land use; WRD: water resource depletion; MRRD: mineral, fossil &



renewable resource depletion. A contribution analysis has been performed to elucidate what materials and processes contribute the most to the overall environmental impact in both scenarios.

Next, materials and processes were interchanged one at a time to assess how results are affected.

This procedure is explained below.

The contribution of HCl, electricity and wastewater were compared in Scenario A, finding that electricity accounts for virtually all environmental impact from these parameters (over 98%).

Wastewater generates a minimal environmental impact, with a maximum of around 8% in the impact category marine eutrophication. For water resource depletion, it even generates a negative impact, as the wastewater is finally discharged to the environment. Similar results were obtained when using the process Wastewater, average {Europe without Switzerland} | market for wastewater, average | APOS, S instead. The proportional contribution of electricity is slightly higher in Scenario B (99%), as no HCl is used.

The type of HCl in Scenario A was also substituted with the “market for” activity, producing nearly identical results. Consequently, the selection of the type of HCl from Ecoinvent database is irrelevant when accounting for the total environmental impact.

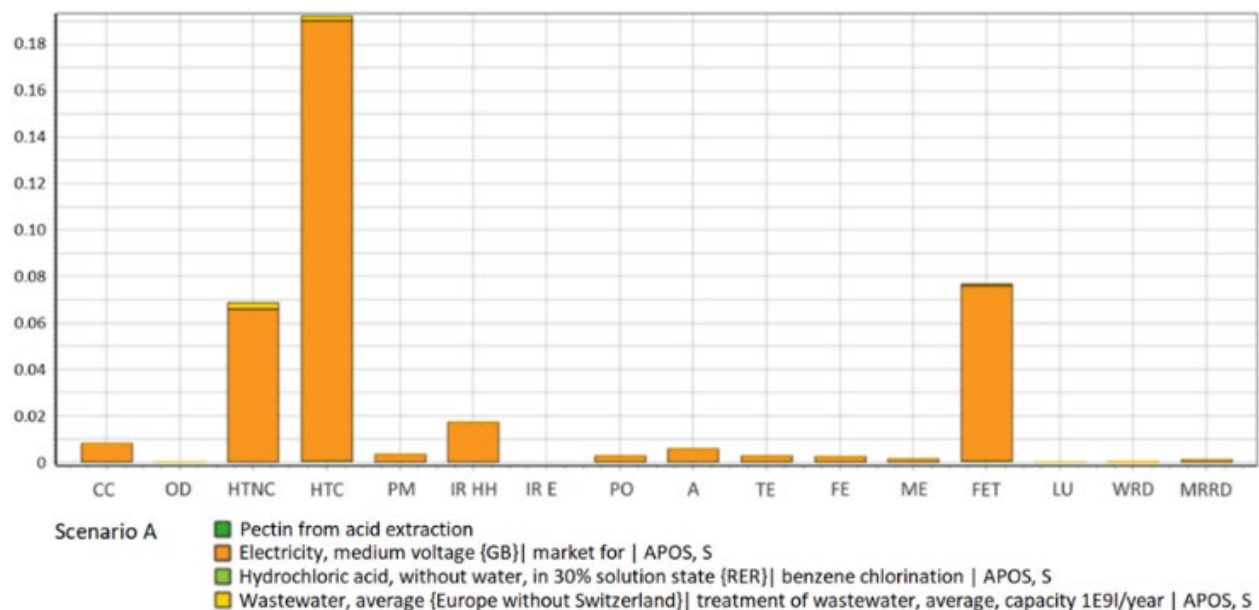
Although it has been assumed ethanol consumption is negligible because it is typically reused in industry, a possible situation in which new ethanol is used for every batch has been modelled as well for both scenarios. Ethanol use would contribute significantly to all environmental categories, principally mineral, fossil & renewable resources, photochemical ozone and particulate matter.

With normalised results obtained by the ILCD method, human toxicity (cancer and non-cancer related) has the largest environmental impact associated. The total contribution of ethanol to overall environmental impact would be larger than that of electricity. Ethanol would make the

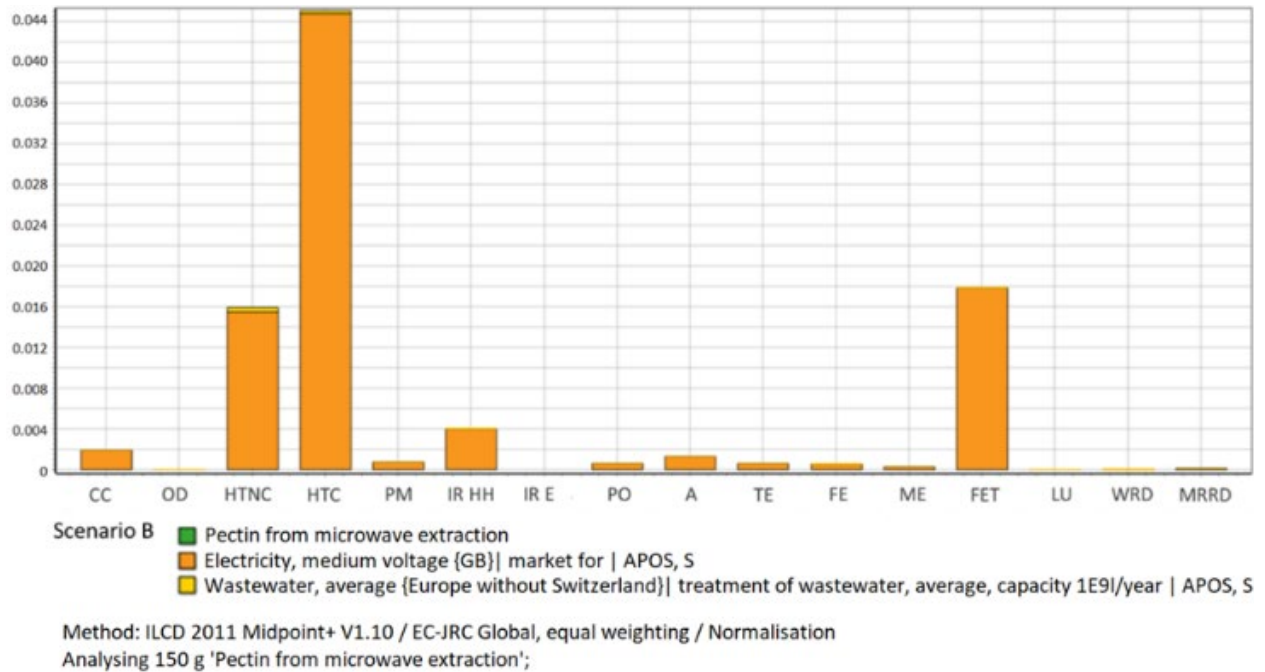
difference in overall results for both scenarios significantly larger, since Scenario A would need more ethanol per kg of pectin obtained.

Although APOS materials and processes were primarily used, the influence of selecting cut-off units was also assessed. Using cut-off units in Scenario A, variations of less than 5% were obtained for all impact categories with the ILCD method, and 2% for all impact categories with the ReCiPe method. Similar results were obtained in Scenario B. Nevertheless, differences were more significant for both scenarios when including ethanol use, particularly for water resource depletion in Scenario A.

From the analysis presented above, it seems the models used for Scenario A and B provide robust and coherent results. It can also be concluded that electricity causes the majority of environmental impact in both scenarios. This can be seen with more clarity with normalised results shown in Figure 6. The most significant environmental impacts caused in both scenarios are human toxicity (cancer related), ionizing radiation, freshwater ecotoxicity and human toxicity (non-cancer related).

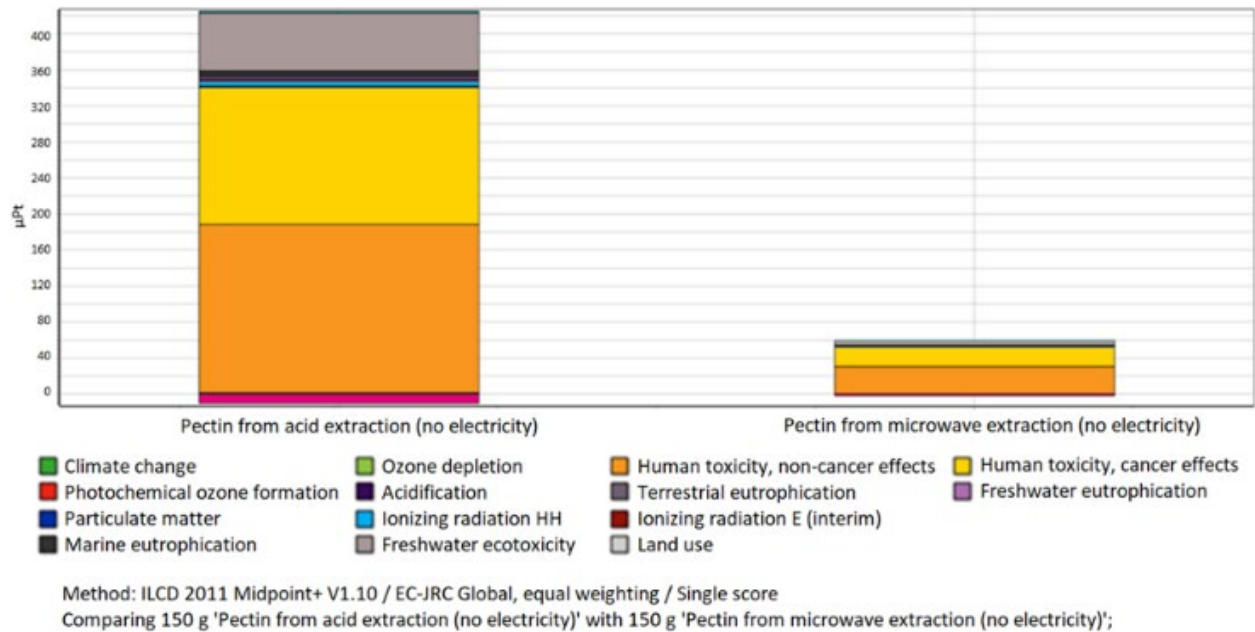


Method: ILCD 2011 Midpoint+ V1.10 / EC-JRC Global, equal weighting / Normalisation  
Analysing 150 g 'Pectin from acid extraction';



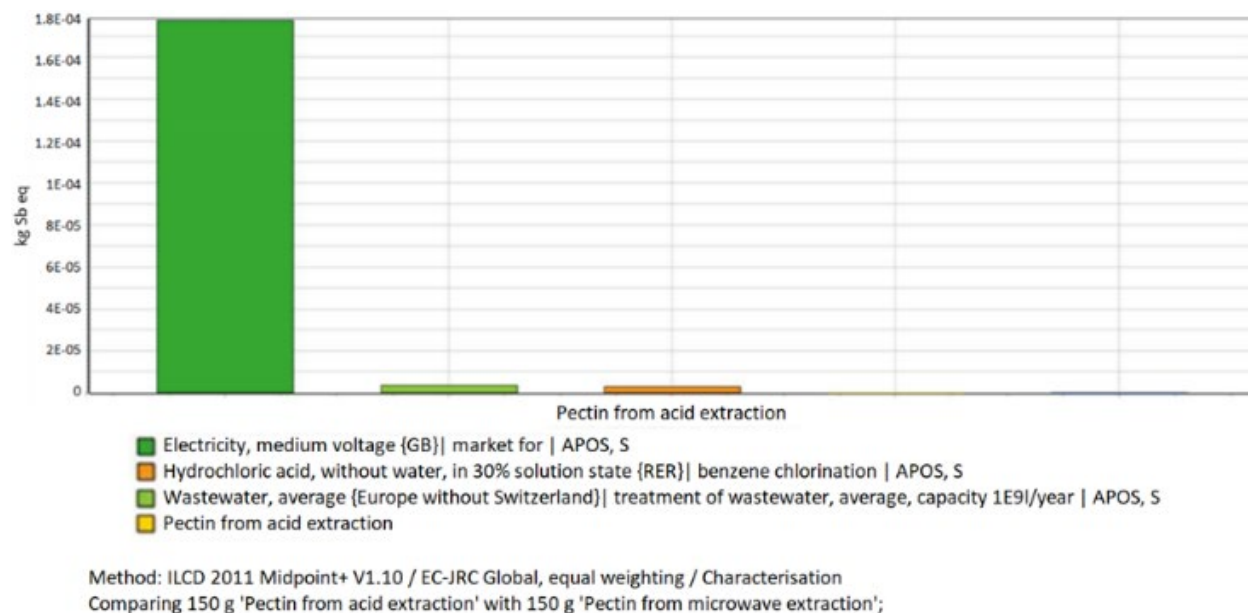
**Figure 6.** Normalised results for Scenario A (top) and B (bottom).

To break down the other environmental contributions from the process, figure 7 shows the contribution of each environmental impact indicator to the overall environmental impact for both alternatives to produce pectin, excluding the contribution of electricity. In absolute values, the most significant reduction is on human toxicity (both non-cancer and cancer effects) and freshwater ecotoxicity.



**Figure 7.** The environmental contributions of the processes excluding electricity.

Figure 8 shows the process contribution for the acid extraction of pectin, for the environmental impact category with the highest proportional contribution of HCl: mineral, fossil and renewable resource depletion. This means that by removing the use of HCl, the environmental impact category that is reduced the most, proportionally, is mineral, fossil and renewable resource depletion. Yet, electricity contribution is much higher.



**Figure 8.** Process contribution for the acid extraction of pectin.

## Conclusions

As previously stated, in order for the microwave procedure to succeed thermal treatment of citrus peel for pectin production the end product must function correctly, the procedure must be robust and must offer an environmental or economic improvement.

With the material meeting all the specification for commercial pectin and passing the gel test, this confirms that the material is on a par (or possibly superior to) what is currently commercially available, meeting the first criteria. Meanwhile, the good agreement in power and temperature readings from the runs indicate that the procedure is robust and reproducible, therefore meeting the second criteria.

In terms of life cycle impacts, the elimination of acid is an immediate environmental benefit as it also eliminates the subsequent acidic waste stream generated when the pectin is filtered off. However, in terms of overall impact this was shown to be negligible in terms of environmental impact compared to the energy savings afforded and the overall benefits achieved from this,

although it must be noted that there is also an economic benefit associated with this as it removes one of the raw materials needed in its entirety. Also, as electricity generation continues to move away from burning of fossil fuels in favour of renewables it is expected that the energy impact would decrease overall and that the HCl usage would then end up making a more significant contribution to the LCA of the product.

This analysis has shown that microwave extraction achieves an approximate reduction of the order of 75% for all environmental impact categories. The main reason for this is the higher energy efficiency of the process to heat the sample, from 15.36 kWh/kg to 5.93 kWh/kg, and the higher pectin yield, from 30.5 g/kg OP to 50 g/kg OP. A contribution analysis and one-at-a-time substitution of materials and processes in the model confirmed the robustness of the results obtained. Due to the markedly different environmental results and the reliability of the model, as discussed above, it has been considered not necessary to undertake further uncertainty analyses, and it can be concluded that scenario B is environmentally (and probably economically due to higher efficiencies and yields) more desirable than scenario A.

Overall, this work has provided the first pilot-scale comparison of microwave heating verses thermal heating for a given process, showing a clear and consistent improvement in all assessed areas whilst still delivering a commercially viable product. Next stages of the research will include the incorporation of all upstream and downstream processes, which will give a fuller LCA picture. The inclusion of other alternative upstream and downstream processes to generate additional products will also be considered, as will other stages where other thermal heating processes could be displaced by microwaves now that this work has shown a much clearer picture of the potential benefits this technology has to provide at industrial scale. Variety of feedstock, including output

from commercial juicing plants will also be considered. This will aim to give a far more robust assessment of the commercial viability of a multi-step citrus biorefinery.

## ASSOCIATED CONTENT

The following files are available free of charge.

Supporting Information.pdf

## AUTHOR INFORMATION

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### **Author Contributions**

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## ABBREVIATIONS

APOS – Allocation at the Point of Substitution

CC – Climate Change

FE – Freshwater Eutrophication

FET – Freshwater Ecotoxicity

GC – Gas Chromatography

HTC – Human Toxicity, Cancer Effects

HTNC – Human Toxicity, Non-Cancer Effects

ICP-OES – Inductively Coupled Plasma-Optical Emission Spectrometry

ILCD – International Reference Life Cycle Data System

IR E – Ionizing Radiation E (interim)

IR HH - Ionizing Radiation to Human Health

LCA – Life Cycle Assessment

LU – Land Use

ME – Marine Eutrophication

MRRD – Mineral, Fossil & Renewable Resource Depletion.

OD – Ozone Depletion

PM – Particulate Matter

PO – Photochemical Ozone

TE – Terrestrial Eutrophication

WRD – Water Resource Depletion

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SYNOPSIS This work describes a less energy intensive means of producing pectin from citrus peel via microwave, rather than thermal, heating.

