The new OPEC
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ABSTRACT

Citrus peels are an ideal feedstock for their use in integrated, resource focused biorefinery activity for the production of high-value bio-chemicals, bio-fuels and biomaterials. Pectin and D-limonene, can be produced together with a rare form of mesoporous cellulose in a single step, without use of added acid, using a low temperature microwave hydrothermal processing of orange peel. A process temperature change enables the conversion of D-limonene to α-terpineol, showing that this process not only enables the separation of the major components but also adds further value to the citrus industry through the production of high-value marketable products.

Keywords: orange/citrus peel waste, pectin, D-limonene, α-terpineol, microwave technology.

1 INTRODUCTION

Orange peel waste (WOP) is a very geographically diverse bio-waste residues, occurring mainly as a result of processing activities for juicing operations.[1] Following juicing, the residual peel accounts for 50 wt. % and is costly to treat due to a high moisture content.[2] However, with high volumes of citrus production (up to 94.8 million tonnes globally),[3] and processing, there is a real opportunity to utilise this resource for mid-scale juicers (typically 50,000 tonnes per annum). Major components of wet WOP include water (80%), soluble sugars, cellulose and hemicellulose, pectin and D-limonene.[4] According to its composition variability, re-use strategies vary greatly: high oil and pectin content varieties have been used for D-limonene[5] and pectin[6, 7] extraction; higher starch and soluble sugars are attractive for bio-ethanol production (in Florida especially).[8] A significant body of literature is available on valorisation strategies for WOP.[1, 4, 8-13] However, single-product applications are almost always envisaged, lowering the cost-effectiveness of those processes and consequently industrial uptake. Limitations include: marginally profitable WOP re-use strategies, low protein content (around 6%) restraining feed applications and high drying cost.[13] Mitigation of expensive drying processes, the design of a sustainable and integrated processing of WOP, including the separation and production of high-value products to allow companies to reduce costs, increase competitiveness and generate additional profits.

Traditional production of pectin requires a two stage process involving the use of mineral acids, generating large amounts of wastewaters, adding to the cost of the final product, for which there is a strong market demand.[14] The price of pectin is of US$10-12/kg. There is a good demand for D-limonene too but its price is variable, dropping from US$ 10/Kg as low as US$1/kg. Microwaves have been used to help break the citrus peel but only in the presence of added acid. Herein we report for the first time the use of acid-free, low temperature microwave heating for the direct production of both highly esterified pectin in good yield, in combination of the production of higher value chemicals: D-limonene or α-terpineol, an important flavour and fragrance additive (US$ 5-6/Kg).

2 RESULTS

Modulated differential scanning calorimetry (MDSC) of WOP under hydrothermal conditions allowed to identify three major critical temperature points of 150º C, 180º C and 200º C for subsequent experiments (see figure 1 below).

Figure 1. MDSC profile showing the overall Heat flow and the Reversing heat capacity signal (Rev Cp).
The organic phase was extracted from the liquid fraction using ethyl acetate (bio-oil, Fraction 1). The remaining aqueous phase was mixed with ethanol to yield a white precipitate (Fraction 2), and the residual ethanol solution concentrated on a rotary evaporator (Fraction 3). The solid fraction (a porous gel) from the initial filtration underwent solvent exchange with lower surface tension solvents (ethanol and acetone) prior to drying (40°C, 12h under vacuum) to yield a porous solid (Fraction 4). All solvents used within this process were collected and dried on a rotary evaporator to produce another fraction (sugars & proteins, Fraction 5). Scheme 1 describes the microwave hydrothermal pyrolysis process as well as products fractions obtained. The total mass of products obtained (optimum conditions) is approximately 60% of the original dry WOP mass, with the residual 40% being converted to water and gas.

Scheme 1. Scheme of microwave hydrothermal pyrolysis of WOP. Mass balance represent the optimum conditions.

Under microwave hydrothermal treatment, large visible differences in the solid products and a significant increase in extracts were observed at 180°C and 200°C. Comparatively, the analysis of the fraction obtained at 150°C revealed a solid visually similar to that of the original material, with the extract containing little oil and no soluble pectin. All fractions were fully characterised and detailed. The temperature variation of the microwave treatment was in good agreement with MDSC data, dramatically changing the pyrolysis mechanism at 180°C, as demonstrated by SEM microscopy. 180°C is known as a key thermodynamic point in which hydrogen-bonded networks break down. [16, 17]

Results from the microscopy of the solids remaining after pyrolysis (Fraction 4) are depicted in Figure 2. The figures below show that, under the conditions used for the microwave hydrothermal treatment, cells are virtually free of pectin, with evidence of increasing black carbonaceous materials forming within the cells when irradiated for longer periods of time by microwaves (Figure 2a and b). The black carbonation material is assumed to be derived from the oil content of the cells. It should be noted that the cell wall structure is intact in all cases, even after microwave treatment (Figure 2c and d).

Figure 2. SEM microscopy images of A) fresh orange peel stained with toluidine blue, turned purple with the presence of pectins (top left image); B) fraction 4 upon microwave treatment (10 mins, 200°C); C) fresh orange peel epidermal tissue treated with CDTA and stained with toluidine blue; D) fraction 4 upon microwave treatment (10 mins, 200°C).

Microscopy data proves that pectin is completely removed from the cell wall showing this method to be a potentially simpler, quicker, less wasteful and overall cheaper process for extracting food-grade pectin, avoiding the need of added acid. [18] pH values before and after microwave treatment being of 5.75 and 4.9 respectively, WOP is not a strong acid. Another observation can be made, leading to improved pectin and oil extraction: the locally bound water within the sample matrix could be locally overheated leading to water vaporisation and cell expansion. The pectin obtained for the low temperature microwave process is remarkable and significantly different from conventional orange pectin. It is white, water soluble and has a high degree of esterification (95%). This is consistent with the use of a gentle and non-acidic extraction method. Nevertheless, the “overheating” mechanism could not explain the in-situ conversion of D-limonene to α-terpineol at temperatures above 180°C (GC-MS, Figure 3) due to endothermicity of water vapour expansion (hot-spot within sample will be immediately cooled down due to water vapour expansion), suggesting another phenomenon is occurring within the microwave process. The influence of electromagnetic fields on acid-base properties is known. For example, in the irradiation of tissue, [19] it was found that the field created a asymmetry of hydrated shells around the charged particles increasing the ion diffusion rate through the reduction of the diffusion layer thickness. Therefore, the conversion of D-limonene to α-terpineol, which normally needs strong acidic conditions, could be explained by polarisation of the inter-cellulose chain hydrogen bonds, enhancing acid-base
equilibrium and proton activation.\textsuperscript{22, 23} \(\alpha\)-Terpineol is a high value chemical and the WOP biorefinery would benefit economically from this transformation.\textsuperscript{24}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure3.png}
\caption{GCMS of orange peel extract after MW pyrolysis at 200\textdegree{}C.}
\end{figure}

FT-IR spectra of the porous solid show good agreement with SEM microscopy and chemical analysis data, confirming the effectiveness of microwave induced separation of the cellulosic (Fraction 4, Figure 4A) and pectin (Fraction 2, Figure 4B) components from the cell wall.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure4.png}
\caption{A) FTIR spectrum of the solid material (fraction 4) and pure cellulose (Aldrich) and B) FTIR spectrum of Fraction 2 in comparison with pure pectin (Aldrich).}
\end{figure}

SEM images of the cellulose sample (Fraction 4), show that after complete extraction of pectin and oil from the orange peel cell wall (at temperature higher than 180\textdegree{} C) the cell organisation in the orange peel has turned into a fibrous macroporous structured cellulose (Figure 5). Liquid nitrogen adsorption data demonstrate a large difference in the mesopore region of cellulose samples obtained at different temperatures: the original non-porous material develops a large macroporous volume upon microwaving at 180\textdegree{} C, switching to a predominantly mesoporous solid at 200\textdegree{} C (see BJH profile, Figure 5). This constitutes a rare, if not unique, example of what we believe to be a mesoporous cellulose-type material which could have a large range of applications.\textsuperscript{25}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure5.png}
\caption{Textural properties of solid Fraction 4.}
\end{figure}

Table 1 summarises the mass balance of the processes. Yields based on dry weight (close to 60\%) clearly show the viability of the proposed approach for the valorisation of citrus waste to value-added products.

\begin{table}[h]
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\begin{tabular}{|c|c|}
\hline
\textbf{N} & \textbf{Fraction composition} \textbf{Yield (\%)} \\
\hline
1 & Ethyl acetate fraction containing D-limonene or \(\alpha\)-terpineol & 8.9 \\
2 & Precipitate from ethanol solution containing pectin & 8.1 \\
3 & Acetone-Ethanol extracts containing sugars & 11.6 \\
4 & Solid fraction/mesoporous cellulose. & 11.6 \\
5 & Water soluble fraction containing sugars & 14.0 \\
\hline
Total & & 54.2 \\
\hline
\end{tabular}
\caption{Mass balance of the microwave-assisted hydrothermal treatment of orange peel waste (40 g) (yield based on dry orange peel weight).}
\end{table}

3 CONCLUSIONS

We have shown that the low temperature hydrothermal microwave treatment of waste orange peel is an effective way to realise the chemical and material potential of this very large, underutilised and geographically diverse resource. The microwave treatment of orange in the presence of water at temperatures above 180º C give an unique opportunity to design a sustainable and integrated process for the production of a range of high-value, marketable chemicals: notably pectin but also α-terpineol and a unique forms of porous cellulose. To the best of our knowledge, this is the first example of a one step in-situ microwave extraction of pectin and conversion of D-limonene to high value α-terpineol in acid-free conditions.

One advantage of this methodology is the production of high quality and highly esterified form of pectin. Continuous microwave processors operating at multi-tonnes per hour are known [23]; they are flexible in size and transportable, offering the exciting possibility of locating the reactors close to the biomass source such as the orange producing regions of Brazil, India, China, North and South Africa and U.S.A.

4 REFERENCES