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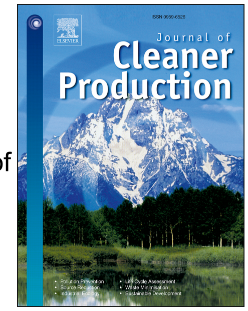

Optimisation and economic evaluation of the supercritical carbon dioxide extraction of waxes from waste date palm (*Phoenix dactylifera*) leaves

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Date palm leaves
ScCO2 extraction
Valuable chemical composition
High yield
High melting point
Green extraction technology
Efficient process
Selective fractionation
Low cost of manufacture
Abundant low value agricultural-waste
Waxes

Optimisation and economic evaluation of the supercritical carbon dioxide extraction of waxes from waste date palm (*Phoenix dactylifera*) leaves.

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Abstract

Wax extraction has been achieved from an abundant and sustainable waste residue, date palm leaves (or leaflets). Supercritical carbon dioxide extraction was utilised as a clean and efficient extraction technology in this process. Extraction conditions including pressure and temperature have been optimised using response surface methodology (*via* a 2x2 factorial experimental design). The highest yield obtained was 3.49% at 400 bar and 100 °C, which is significantly higher than other reported agricultural residues. The wax obtained at optimum condition (400 bar, 100 °C) exhibited a comparable melting point (78 °C) to carnauba wax, making it a suitable alternative or replacement for this overexploited commercial plant wax. The supercritical process required significantly shorter extraction times (with a 97% isolated wax yield after 120 min), as compared to soxhlet systems which typically required extraction times of up to 5 hours to obtain comparable yields. Supercritical carbon dioxide was utilised to tailor the extraction process and obtain waxes with different textural properties, chemical composition and melting profile (35 -78 °C). An economic study for the date palm leaf wax extraction estimated a lowest cost of manufacture (COM) at €3.78 kg^{-1} wax. The low cost of the manufacturing, combined with high wax recovery, the thermal properties of the extract

and abundance of this waste resource, makes date palm leaf an attractive feedstock for the natural wax industry.

Keywords: wax; date palm; supercritical; economic; extraction; carbon dioxide

1. Introduction

The demand for natural waxes is steadily increasing, motivated by preferences towards greener, sustainable and natural products by consumers, particularly in cosmetics and healthcare products (Attard et al., 2018a). Furthermore, the increase in catalytic dewaxing technologies has led to supply issues with petroleum waxes, currently the main source of wax supply. Natural waxes have many applications including cosmetics (Arraudeau et al., 1989; El-Nokaly et al., 2001), pharmaceuticals (Puglia et al., 1982), coatings (Hagenmaier and Shaw, 1992; Bagaria and Lordi, 1991) and detergents (Goffinet, 1983; Chambers et al., 1997). Currently, the sources of commercially available natural plant waxes are limited, with some key waxes being exclusively produced in certain geographical regions of the world, such as candelilla in Mexico and South America ((Hodge and Sineath, 1956) and carnauba in Brazil (Taube, 1952).

The use of agricultural residues and wastes has received growing attention in the scientific literature as a promising route to generate natural waxes and lipids (Sin et al., 2014). However, the reported yields of wax obtained from agricultural residues have been low and it is therefore important to explore other agricultural residues as alternative feedstocks for waxes (Attard et al., 2015a, Attard et al., 2016a). Agricultural pruning waste from date palm (*Phoenix dactylifera*) could be another potential source of natural plant waxes. The date palm tree is one of the most cultivated palm tree varieties across the globe. It is commonly found in the dry band stretching from North Africa to the Middle East (Segal, 2014; Chao and Krueger, 2007). According to the Food and Agriculture Organisation of the United Nations (FAO), the total harvested area of date palm trees around the world was 1.1 million ha in 2014 (FAO, 2014).

Date palm is grown primarily for the fruits (dates) and the leaves are a by-product of the date production industries. In order to assure the healthy growth of the date palm tree and the quality of date fruits, certain parts of the tree need to be pruned annually such as dry fronds (leaves) and trunk fibres (Chandrasekaran and Bahkali, 2013). As a consequence, a huge amount of waste is generated, which is typically disposed of through burning in the field or in a small number of cases burnt for energy (Figure S1 in supplementary information). Each tree produces on average 13-20 Kg of dry fronds (leaves) annually, resulting in an estimated worldwide annual volume of 1.5-2.8 million tons.

Traditionally, lipids and cuticle waxes are extracted using conventional organic solvents such as hexane, dichloromethane (DCM) and chloroform which possess many health, safety and environmental concerns. Furthermore, they are non-selective, extracting a number of unwanted co-extractives (Deswarte et al., 2006). In previous studies, surface waxes composed of *n*-alkanes, triterpenoids, fatty acids, fatty alcohols and ketones were extracted by maceration in hexane and methanol from date palm leaf (Khelil et al., 2016). However, for the majority of the applications where natural waxes are utilised, minimal solvent residues must be present in the extracts and it is therefore paramount that cleaner, more efficient extraction technologies are utilised. No work has focussed on the use of green alternative solvents for the extraction of date palm waxes nor investigated the economic feasibility of such processes.

Supercritical carbon dioxide (scCO_2) has been demonstrated to be an alternative for the extraction of the cuticle waxes from plants (Hunt et al., 2010). ScCO_2 has low surface tension, high diffusivity and low viscosity which make it an ideal solvent for extraction processes (Mark and Val, 1994). Tuning the temperature and pressure of the extraction alters the strength of the solvent, which gives the solvent an extra advantage in the extraction of natural products (Mark and Val, 1994). In addition, scCO_2 provides solvent free extracts making it an ideal extraction technique for industries including pharmaceutical, food and cosmetic sectors, where eliminating trace solvent contamination is crucial (Mendes et al., 2003; Chemat et al., 2012). Furthermore, scCO_2 treatment has been shown to be an effective first step in an integrated biorefinery improving the downstream processing of the biomass (Attard et al., 2015c; Attard et al., 2016b).

Several studies have used a response surface methodology for optimisation of supercritical extraction, whereby a two-level factorial design used to design the experiment and mathematical model was constructed to relate the extract yield to the process variables such as temperature and pressure of the extraction. One advantage of the two-level factorial design, over other methods such as the one-factor-at-a-time method (OFAT), is that it enables the determination of factors influencing extraction and also the interactions between them with minimum numbers of experiments (Sharif et al., 2014; Montgomery et al., 2005). In contrast, the OFAT approach requires a large number of runs, especially when the variables or factors increase (Sharif et al., 2014; Montgomery et al., 2005). A second order factorial design has recently been used to optimise the $scCO_2$ extraction of hemp and spruce (Attard et al., 2018b; McElroy et al., 2018).

Herein, cuticle waxes from date palm leaves were extracted with $scCO_2$ and compared to conventional soxhlet extraction using heptane in order to provide a sustainable source of natural waxes using clean technology. Process optimisation is vital and therefore the extraction conditions were optimised using a second order factorial experimental design and the hydrophobic waxes were characterised by GC, GC-MS and DSC. Finally, it is important that the process is economically viable and thus an economic study was conducted in order to assess the viability of the process, whilst potential applications of the waxes have been identified.

2. Experimental

2.1 Materials

All solvents (toluene, DCM, heptane, ethanol, methanol) used were HPLC grade and purchased from Fisher Scientific. Standard alkanes (mixture of C_{12}-C_{60}), hentriacontane, oleic acid, stigmasterol, stearyl palmitate, dodecanal, 1-octacosanol, phytol and N,O-*bis*-(trimethylsilyl)-trifluoro-acetamide with trimethylchlorosilane were purchased from Sigma-Aldrich. Liquid CO_2 cylinders (99%) were obtained from BOC.

2.2 Sample preparation

Samples of date palm leaves (*Phoenix dactylifera L.*) were sourced from Oman. The leaves were removed from the stalk, rinsed with water in order to remove dust and dried in sunlight for 3 weeks. The leaves were milled using a Glen Creston Ltd. SM1 hammer mill by passing through a 2 mm screen, prior to scCO_2 extraction.

2.3 Extraction of date palm wax with ScCO_2

ScCO_2 extraction was conducted using a Thar Technology (Pittsburgh, PA, USA) SFE 500 system. Milled date palm leaves (100-140 g) were loaded in the extractor vessel and heated to the desired extraction temperature (40-100 °C). A flow of CO_2 was applied at 40 g min^{-1} and the pressure was set to the desired value (80-400 bar). ScCO_2 was passed through the extractor vessel for 4 hours and then depressurised over 60 minutes. The extracted wax was collected from the stainless-steel separator vessel for further analysis. For the time optimisation experiments, the scCO_2 extraction was carried out at 400 bar and 100 °C for 4 hours with a flow rate of 40 g min^{-1}. Samples were collected every 30 minutes and weighed to determine the yield.

2.4 Soxhlet extraction

Milled dry palm leaves (10 g) were extracted with heptane using a soxhlet apparatus for 5 hours. The resultant extract was filtered to remove residual biomass and concentrated to dryness *in vacuo*. The sample was allowed to dry further at room temperature for 48 hours prior to recording the weight to ensure removal of traces of solvent.

2.5 GC analysis

15-25 mg of wax was dissolved in 1 mL toluene containing 2 mg of internal standard tetradecane. The samples were analysed by GC (Agilent Technologies 6890N Network GC) with a Zebron DB-5HT column with (30.0 m× 0.25 mm× 0.25 µm). The inlet temperature was set at 340 °C with a total flow of 26.4 mL and a split ratio of 5:1. The initial oven temperature was 60 °C held for 1 min and ramped at 8 °C min^{-1} to 360 °C, after which the temperature was held for 30 minutes. The carrier gas was He with a flow of 2.2 mL min^{-1} and an average velocity of 55 cm sec^{-1}. A flame ionisation detector was used with its detector temperature set to 360 °C. Nitrogen was used as the makeup gas with a flow of 32.8 mL min^{-1}.

2.6 Derivatisation for GC analysis

A total of 15-20 mg of wax extract was silylated by adding N,O-bis-(trimethylsilyl)-trifluoro-acetamide (200 µL) and toluene (1 mL). The vial was heated at 75 °C on a hot plate for 30 min. The sample was allowed to cool prior to GC and GC/MS analysis.

2.7 GC/MS analysis

The extracted wax samples (15- 25 mg mL^{-1} toluene) were analysed by GC/MS using a Perkin Elmer Clarus 500 Gas chromatography coupled to a Perkin Elmer Clarus 560 Mass spectrometer equipped with a split injector and an auto sampler. The high temperature capillary column used for the analysis was a DB5HT column (30 m× 0.25 mm× 0.25 µm). Helium was used as the carrier gas with a flow rate of 1 mL min^{-1}. The initial oven temperature was 60 °C, held for 1 min and ramped at 8 °C min^{-1} to 360 °C, where it was held for 30 min. The injection volume was 0.5 µL. The mass spectrometer was used in electron ionisation mode at 70 eV.

2.8 IR analysis

Infrared spectrum was obtained by a Bruker Vertex 70 spectrometer fitted with diamond ATR. The spectrum was collected in the wavenumber range 4000–500 cm^{-1} at a resolution of 2 cm^{-1}. The IR spectrum for date palm wax extracted with $scCO_2$ at 100 °C and 400 bar is displayed In Figure S2 of supporting information.

2.9 Scanning Electron Microscopy (SEM) for date palm leaf

The leaf specimens were sprayed with palladium nanoparticles in order to make them conductive in the SEM. A fully computer-controlled scanning electron microscope (SEM - JEOL JSM-6490LV) with a tungsten heated filament was used to scan each palladium-coated specimen. A specimen was sealed in the SEM chamber and the air was evacuated. Each specimen was scanned with an electron beam 30 kV in high vacuum.

2.10 Saponification value and iodine value for date palm wax

Test methods for saponification value, iodine value and acid value have been previously reported by Sin (Sin, 2012) and were carried out for the wax sample extracted with $scCO_2$ at 400 bar and 100 °C listed in Table S2(supporting information).

2.11 Economic analysis

The economic analysis was carried out using an economic model by Turton *et al.* (Turton et al., 2008). A detailed method for the economic analysis of supercritical extraction has been reported by Attard *et al.* (Attard et al., 2015c)

2.12 Differential scanning calorimetry (DSC) analysis

Thermal analysis was conducted with a modulated DSC; TA Instruments MDSC Q2000 Thermal Analysis. The samples (3-6 mg) were weighed in T-Zero standard aluminium hermetic pans and placed in the test cell along with a reference pan. The samples were heated to 25 °C and ramped at 10 °C min^{-1} to 100 °C, held for 1 min at 100 °C and then cooled to -80 °C at a rate of 5 °C min^{-1}. After the samples were held at -80 °C for 1 min, they were heated to 100 °C at a rate of 5 °C min^{-1}. The DSC curve of the last DSC cycle was used in the melting point determination.

3. Results and discussion

$ScCO_2$ extraction of date palm leaf wax was optimised using a 2x2 factorial design (fig 1), whereby the effect of varying the temperature and pressure on the % yield was investigated. Equation 1 is a first order polynomial fit for the experimental study where Y is the % yield, X_1 is a temperature factor and X_2 is a pressure factor:

$$Y = 1.15 + 0.61X_1 + 1.07X_2 + 0.65X_1X_2 \qquad \text{Equation 1}$$

The temperature range of the study was selected as 40-100 °C and the pressure range was 80-400 bar. The highest temperature of 100 °C was crucial in order to obtain the greatest yield of large molecular weight compounds from date palm such as wax esters and long chain alcohols.

Equation 1 demonstrates a linear relationship between the extraction temperature, pressure and the extraction yield. As the pressure increases at a given temperature, the density of CO_2 also increases. Previous studies have described the importance of density on extraction rate or yield (Salgin et al., 2006; Stahl et al., 2012). Interestingly, for date palm leaf wax extraction, all the coefficients in equation 1 are positive, which confirms that temperature, pressure and their combination have positive effects on the extraction process. However, the coefficient of pressure (X_2) is the largest amongst the other coefficients in equation 1 (the coefficient of temperature (X_1) is almost half that of the pressure (X_2), 0.61 compared to 1.07 respectively). This indicates that pressure has the greatest effect on the extraction process. This was observed in an enhanced recovered yield of 0.97% *w/w* at 40 °C and 400 bar compared to 0.10% *w/w* at 40 °C and 80 bar. The effect of temperature on the extraction rate seems to be in agreement with previous solubility studies conducted on minor hydrophobic molecules in $scCO_2$. It has been reported that two mechanisms can explain the effect of temperature on solubility and in both instances the pressure of the system dictates the dominant mechanism (Güçlü and Temelli, 2000). The first mechanism is an increase in solubility with increasing temperature as a result of an increase in vapour pressure. The second mechanism is temperature increase leads to a decrease in solvent density leading to a decrease in lipid solubility. Work has shown that there is a cross-over pressure value, in which solubility decreases with increasing temperature when the pressure is below the crossover value (and hence solvent density is more important) (Friedrich and Pryde, 1984; Güçlü and Temelli, 2000; Hubert and Vitzthum, 1978). A decrease in yield from 0.10% to 0.05% was observed, when increasing the temperature at fixed pressure from (40 °C, 80 bar) to (100 °C, 80 bar). However, once the cross-over value was surpassed, an increase in temperature led to an increase in solubility. This was confirmed by the increase in yield from 0.97% *w/w* at 40 °C and 400 bar to 3.49% *w/w* at 100 °C and 400 bar. At higher temperatures, the system has enough energy to overcome the crystal lattice energy of the wax, resulting in melting and increased extractability of the wax (Sin et al., 2014; Stahl et al., 2012). Therefore, it can be concluded that there are two opposing factors controlling the effect of the temperature on the extraction yield (Stahl et al., 2012; Güçlü and Temelli, 2000; Hubert and Vitzthum, 1978). The coefficient X_1X_2 for the combined effect of both temperature and pressure is substantial (0.65), indicating that the effect of this on the extraction of wax components in CO_2 is significant. The crude yields of date palm waxes ranged from 0.05 to 3.49% *w/w* depending on the extraction conditions, namely temperature and pressure, with the highest yield obtained at an optimal pressure of 400 bar and temperature of 100 °C (Figure 1).

[Figure 1 here]

The highest average yield of wax (3.49% *w/w*) obtained by $scCO_2$ extraction is comparable to the yields of wax obtained using heptane (4.2% *w/w*). Furthermore, since $scCO_2$ extraction leaves no solvent residues, it does not require an energy intensive process to remove the organic solvent (which is required for hexane or heptane as they have relatively high boiling points) making the $scCO_2$ process more efficient, when compared to conventional extraction.

This significant wax yield is considerably higher than reported wax yields from other agricultural residues. Typical yields of waxes extracted from agricultural residues with $scCO_2$ are reported to be less than 2% *w/w* from dry biomass (Attard et al., 2015b; Sin et al., 2014). As such, date palm residues can be an alternative consistent source of renewable waxes. This abundant agricultural residue, coupled with an efficient extraction procedure, makes this process suitable for the cleaner production of waxes.

A time optimisation study was also carried out at 400 bar and 100 °C for 4 hours with a flow rate of 40 g min^{-1}. Results indicate that 90% of the total extractable wax could be recovered after *ca.* 75 min, while 97% could be isolated after 120 min (as shown in figure S3 supporting information). This $scCO_2$ process demonstrated significantly shorter extraction times over soxhlet systems, which typically required extraction times of 4-5 hours to obtain comparable yields.

Table S1 (supporting information) lists the quantified lipid extracts from date palm leaves as determined by GC and GC/MS. The wax obtained in this current study consists of long chain hydrophobic molecules including *n*-alkanes (C_{28}-C_{33}), saturated and unsaturated free fatty acids (C_{10}-C_{34}), fatty alcohols (C_{28}-C_{34}), aldehydes (C_{32}-C_{34}), sterols and wax esters (C_{40}-C_{56}). Increasing the pressure was found to significantly enhance the recovery of certain groups such as free fatty acids, fatty alcohols and wax esters while it also increased yields of other groups of compounds (though not as substantially) including *n*-alkanes and sterols. For example, the recovered quantities of *n*-alkanes doubled from 311.1 ±4.4 μg g^{-1} biomass at (40 °C, 80 bar) to 645.2 ±5.7 μg g^{-1} biomass at (40 °C, 400 bar) while that of long chain aldehydes substantially increased from 50.9 ±0.8 at (40 °C, 80 bar) to 233.8 ±0.6 μg g^{-1} biomass at (40 °C, 400 bar). Increasing the temperature of the extraction resulted in increases in recovered quantities of all the groups of compounds (Table S1 supporting information) including *n*-alkanes, free fatty acids, fatty alcohols, sterols, long chain aldehydes and wax esters. This can be seen in the recovered quantities of fatty alcohols, which increased from 41.5 ±1.1 $μgg^{-1}$ biomass at (40 °C, 400 bar) to 1292.1 ±13.8 $μgg^{-1}$ biomass at (70 °C, 241 bar) and almost tripled to 3115.8 ±27.0 $μgg^{-1}$ biomass at (100 °C, 400 bar). This trend is also observed in the overall crude yield of extraction as discussed earlier. Therefore, elevated temperatures are required to melt and solubilise high molecular weight compounds, leading to much higher extraction rates. Stahl *et al.* stated that the solubility of wax esters in $scCO_2$ increases significantly with temperature (a rise in temperature from 20 °C to 80 °C increased the solubility of the wax esters and triglycerides by a factor of 8) (Stahl et al., 2012). Figure 2 shows the percentage composition of each class of compounds within the extracts obtained in the 2x2 factorial design. Wax esters are the most abundant constituents of the extract obtained at 100 °C and 400 bar, followed by free fatty acids and fatty alcohols. Wax esters are also the most dominant in the extract obtained at 100 °C and 80 bar; however, the overall yield of this extract is very low making the recovered quantity negligible compared to other extracts. Lower temperatures and pressures of extractions (40 °C, 80 bar) resulted in extracts which are rich in *n*-alkanes, comprising 18% of this extract. These *n*-alkanes (C_{28}-C_{33}) are amongst the lowest molecular weight and least polar compounds within the wax composition and therefore they are extracted at relatively milder extraction conditions.

Scanning electron microscopy images in figure S4 highlight the epicuticle waxes on the date palm leaf. Rodlets structure was observed in the intact dry date palm leaf. This is in agreement with reported morphology of date palm leaves (Khelil et al., 2016). Interestingly, milling of the leaf caused destruction of the rodlets and hence there is a potential loss of wax yield by this physical process. The milled leaf extracted with $scCO_2$ showed the absence of these wax which further confirm the effectiveness of $scCO_2$ as a solvent for wax extraction.

[Figure 2 here]

$ScCO_2$ extraction is often compared to hexane or heptane soxhlet extraction since the polarity of these solvents is regarded as being broadly similar to each other (Athukorala and Mazza, 2010; Wang et al., 2007; Ikushima et al., 1991). It was found that the $scCO_2$ extract at 400 bar and 100 °C contained a similar distribution to the heptane extracts, however, significant variation in individual components can be noted in figure 3. The total aldehydes extracted with $scCO_2$ at 400 bar and 100 °C was 1897.8 ±41.4 μg g^{-1} of biomass, which is significantly higher than the heptane extracts, with a total recovery of 368.6 ±26.1 μg g^{-1} of biomass. A similar trend was observed for fatty alcohols, 3115.8 ±27.0 μg g^{-1} of biomass for the CO_2 extract, compared to 1900.2 ±36.0 μg g^{-1} of biomass for the heptane extract. This suggests that the $scCO_2$ extract has enhanced selectivity over heptane in the extraction of aldehydes and policosanols from date palm. Furthermore, higher amounts of phytosterols were obtained with $scCO_2$ as compared to heptane.

In terms of cleaner production, $scCO_2$ has an advantage over heptane in that the extraction leaves no solvent residues in the extracts. Many of the molecules identified above exhibit nutraceutical and medicinal properties and are often integrated in food and pharmaceutical products, where eliminating trace solvent contamination is crucial (Mendes et al., 2003; Chemat et al., 2012). Heptane has a relatively high boiling point (98 ^{o}C), therefore removing trace solvent from the extracts would be an energy-intensive process and thus utilising $scCO_2$ would lead to a more efficient process.

[Figure 3 here].

It is important to determine the melting range of the waxes in order to select a suitable potential application. The DSC profile of the CO_2 extracts and heptane extract are shown in figure 4. Natural waxes contain a mixture of different compounds and therefore a broad melting profile is expected. The highest melting point range for date palm wax was exhibited by the heptane extract at approximately 82 °C. $ScCO_2$ extracts showed a diverse range of melting point ranges depending on the process conditions implemented. This further emphasises the difference in composition when using different extraction conditions (temperature and pressure). Therefore, it is possible to manipulate these conditions to obtain waxes with tailored compositions or thermal properties for specific applications. This is a distinct advantage that $scCO_2$ extraction has over soxhlet extraction, where fractionation at the point of extraction is not possible and only one wax extract can be obtained. Wax extracts obtained from soxhlet extraction would therefore require further separation and purification. Very broad thermal events centred around 30 °C and 43 °C were observed in lower temperature and pressure (40 °C, 80 bar) extracts (figure 4). A similar thermal profile was obtained for extractions at 40 °C and 400 bar, but at higher temperatures of 53 °C and 62 °C. The higher melting point ranges may be due to the greater relative concentration of wax esters compared to the extracts obtained at 40 °C and 80 bar. Moreover, the extract at 70 °C and 240 bar exhibited a very sharp endothermic minimum centred at 71 °C. The highest melting point range (78 °C) was seen for the highest pressure and temperature investigated in this study (100 °C and 400 bar). The exceptionally high content of fatty alcohols, aldehydes and wax esters obtained at this point may have contributed to the high melting profile.

[Figure 4 here]

Figure 5 shows the DSC profile of the date palm leaf waxes compared to other commercial waxes and it can be observed that date palm waxes are versatile and can potentially replace many commercial waxes including candelilla, carnauba and beeswax. The wax extract obtained at 70 °C and 240 bar has a melting point range similar to the candelilla wax, while the extract obtained at (100 °C and 400 bar) showed a thermal profile comparable to carnauba wax. Similarly, the wax extract obtained at 40 °C and 400 bar showed a thermal profile close to that of beeswax.

Compared to other agricultural residue waxes such as stover, rice straw, miscanthus and sugarcane, date palm gave a high yield (3.49%) and an elevated melting point (78 °C). This, in combination with the huge volume of the date palm leaves produced annually, make this a promising natural wax for industry. Also date palm wax exhibited exceptional high content of aldehydes (1897.8 ±41.4 μg g^{-1} biomass), fatty alcohols (3115.8 ± 27.0 μg g^{-1} biomass) and wax esters (3421.1 ±26.1 μg g^{-1} biomass) making it versatile in term of its potential applications. Further analysis of the wax extracted under optimal conditions (400 bar and 100 °C), exhibited an acid value of 20 mg KOH/g of wax, saponification value of 72 mg KOH/g of wax and an iodine value of 8 g/100g of wax (Table S2 supporting information).

[Figure 5 here]

In order to determine the viability of the process, it is important to consider the economics of such an extraction process. An economic study to assess the viability of the extraction process has been conducted based on previous literature studies (Rosa and Meireles, 2005). Due to the high volumes of date palm waste available in the Middle East, it is assumed that the facility will be built in this region to reduce transportation costs. As such, values relating to the cost of electricity, raw materials, waste treatment and labour cost are based on figures found in this region. The cost of manufacturing (COM) was estimated as a function of fixed capital investment cost (FCI), labour cost (C_{OL}), utility costs (C_{UT}), raw material costs (C_{RM}) and waste treatment costs (C_{WT}) using the following equation (Turton et al., 2013):

$$COM = 0.280FCI + 2.73\ COL + 1.23(CRM + CWT + CUT)$$

The FCI involves the cost of a 2000 tonne per annum input capacity commercial supercritical extraction unit at €1,400,000 (Rosa and Meireles, 2005; de Melo et al., 2014). The C_{OL} was estimated based on 330 days per annum with 24 hours per day shifts and two operators per shift at €5 per hour per person (Attard et al., 2016a; Attard et al., 2015c). The raw material costs, which takes into account the harvesting, storage and transportation of pruned leaves, was estimated to be around €23.79 tonne^{-1} of milled date palm leaves and € 69.74 tonne^{-1} of pelletised biomass (Altarawneh and Ebraheem, 2013; Mani et al., 2006). It was assumed that the C_{WT} associated with the process is negligible due to the fact that the solvent is recycled and the biomass is passed on for further downstream processing and is therefore not considered to be a waste (Attard et al., 2016a; Attard et al., 2015c). Finally, the utility cost C_{UT} was determined to be €23.91 h^{-1} (Dubai Electricity and Water Authority, 2017; Sait et al., 2012). The C_{UT} includes electricity costs associated with the CO_2 pump as well as electricity costs associated with refrigeration (cooling the CO_2 pump heads). Detailed analysis of the energy usage for the supercritical process, volumes of CO_2 utilised per extraction and raw material requirements can now be found in the supporting information.

The COM of $scCO_2$ extraction of milled date palm leaves was estimated to be around €13.62 kg^{-1} wax. This cost can be significantly reduced if pelletizing is utilised to increase the density of the biomass (typically the density increases by around three times) (Deswarte et al., 2007). This results in a greater loading of biomass per extraction. Although the C_{RM} and C_{UT} increase with pelletized biomass, the overall COM decreases to around €8.55 kg^{-1} wax. Furthermore, the above calculated cost was estimated without taking into consideration the utilization of the biomass residue post-extraction. If the extraction of the waxes from date palm is viewed as a first step of a biorefinery system, the date palm residue that remains would be passed along for further downstream processing (as a feedstock for additional chemicals and fuels), which could further lower the COM. As an example of this, a simple calculation was conducted whereby the date palm leaf residues were combusted post-extraction for electricity generation. If the biomass is burnt for electricity generation post-extraction, the COM of the waxes would be reduced to around €3.78 kg^{-1} wax. However, combustion is considered to be a low-added value step, if other downstream processes were taken into account such as hydrolysis for sugars and subsequent fermentation and microwave pyrolysis for chemicals, fuel and energy, then the COM of the waxes may be further reduced. It has been shown in previous studies, that the $scCO_2$ extraction of waxes, when introduced as part of a holistic biorefinery, leads to the enhancement of downstream processing of biomass – leading to improved hydrolysis (to give higher sugar yields) and enhanced fermentation (leading to improved production of bioethanol) (Attard et al., 2015b; Attard et al., 2016b). Therefore, it is proposed that the $scCO_2$ extraction of waxes should not be carried out as a standalone process but as part of a holistic biorefinery in order to make the process economically viable. A one-at-a time sensitivity analysis was carried out (figure 6), in order to determine which parameter had the greatest effect on the COM. The results showed that the FCI followed by the C_{UT} have the greatest effect on the cost while the C_{RM} has the lowest effect (figure 6).

[Figure 6 here]

In 2015, the US wax market import prices for non-petroleum waxes including beeswax, candelilla and carnauba wax were €7.8 /Kg, €2.4/kg and €6.0/kg respectively. Therefore, date palm leaf wax production could be promising as the cost of manufacturing falls within the price range of commercial non-petroleum waxes (Argus Media Ltd, 2015).

4. Conclusion

ScCO_2 extraction of waxes from date palm leaves was successfully achieved, obtaining compounds of potential value from this waste biomass. The optimal extraction conditions were determined to be 400 bar and 100 °C. Compared to other agricultural residue waxes such as stover, rice straw, miscanthus and sugarcane, date palm gave exceptionally high yields (3.49%) and an elevated melting point (78 °C). This, in combination with the huge volume of the date palm leaves produced annually, makes this a promising natural wax for industrial exploitation. Different wax extracts demonstrated diverse thermal profiles, with melting points ranging from 30 °C to 78 °C, making date palm waxes a promising competitor in the commercial wax market. Many of the hydrophobic molecules identified within the date palm leaf wax could have potential applications as nutraceuticals, cosmetic ingredients, detergents and surface coatings (Attard et al., 2018a).

Furthermore, scCO_2 extraction is advantageous over organic solvent extraction as waxes obtained by the latter process require further purification, separation and downstream processing in order to tailor the different thermal properties of the product. ScCO_2 leaves no solvent residues, requires shorter extraction times and can be easily recycled, demonstrating that scCO_2 extraction is a more efficient process for recovery of date palm waxes when compared to conventional solvent extraction.

The economic study for the date palm leaf wax estimated a lowest COM of €3.78 kg^{-1} wax. Date palm waxes may potentially find uses in a host of applications including coatings, lubricants and cosmetics. The high wax yield from waste date palm leaf and the low estimated COM with a clean chemical technology such as $scCO_2$ extraction could create new opportunities for the natural wax industry.

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List of Figures

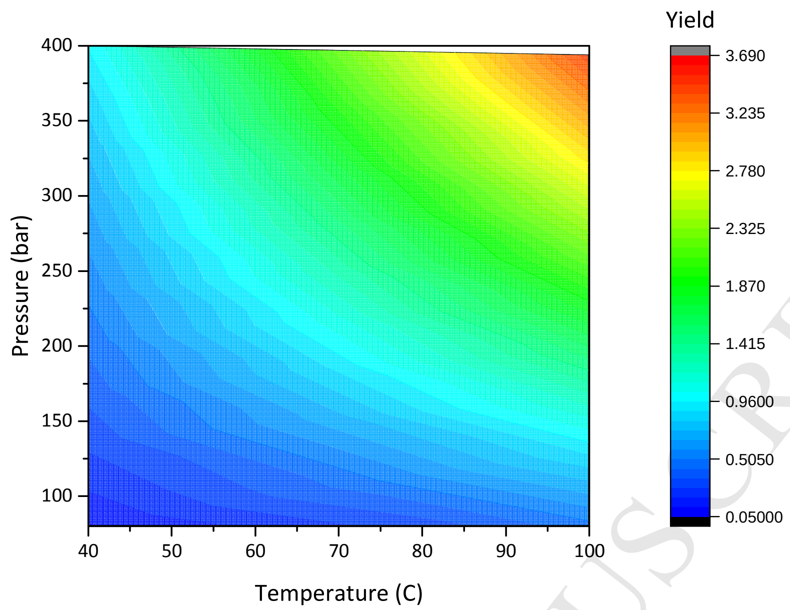


Figure 1 Effect of Pressure and Temperature on the % yield of date palm wax extracted.

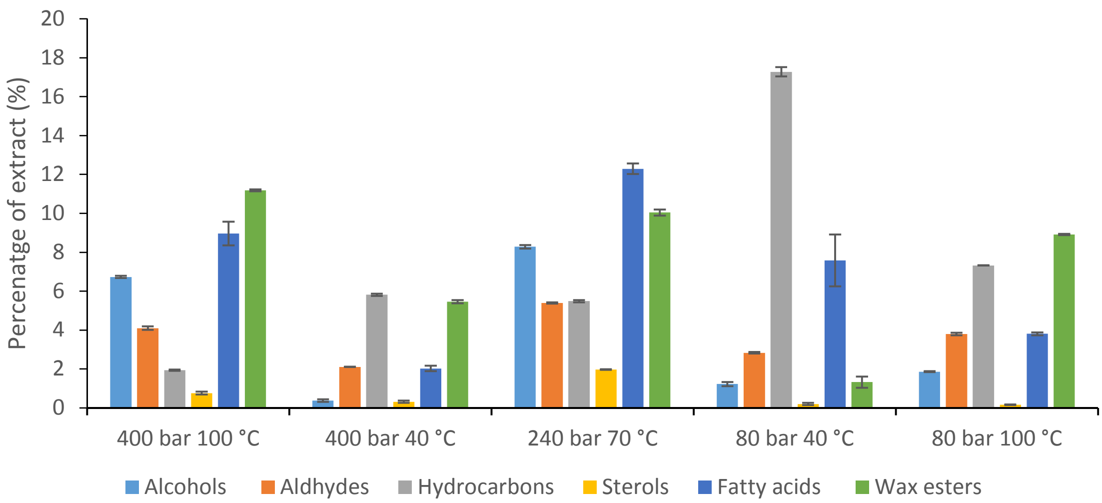


Figure 2 Composition of date palm wax extracted with $scCO_2$ at different temperature and pressure.

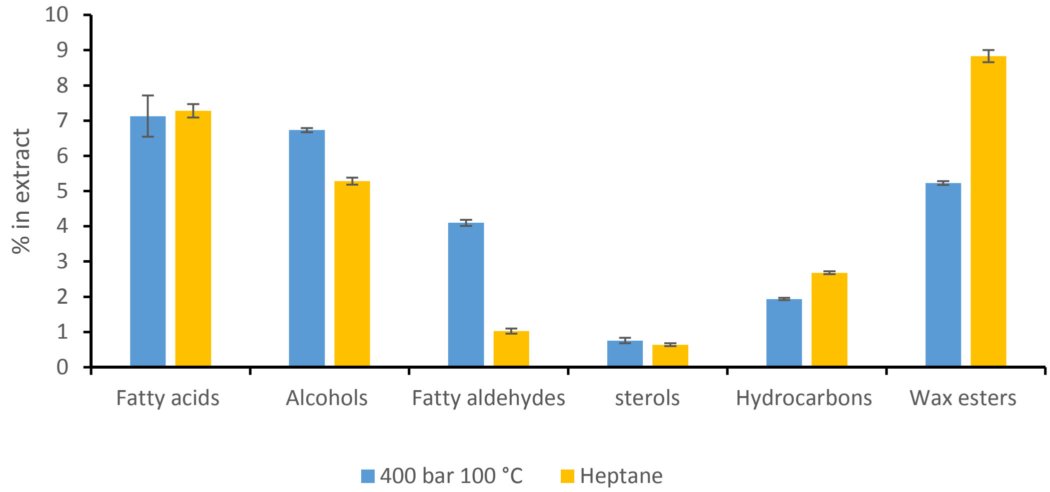


Figure 3 Percentage composition of different wax groups in heptane extract and $scCO_2$ extract at 400 bar and 100 °C.

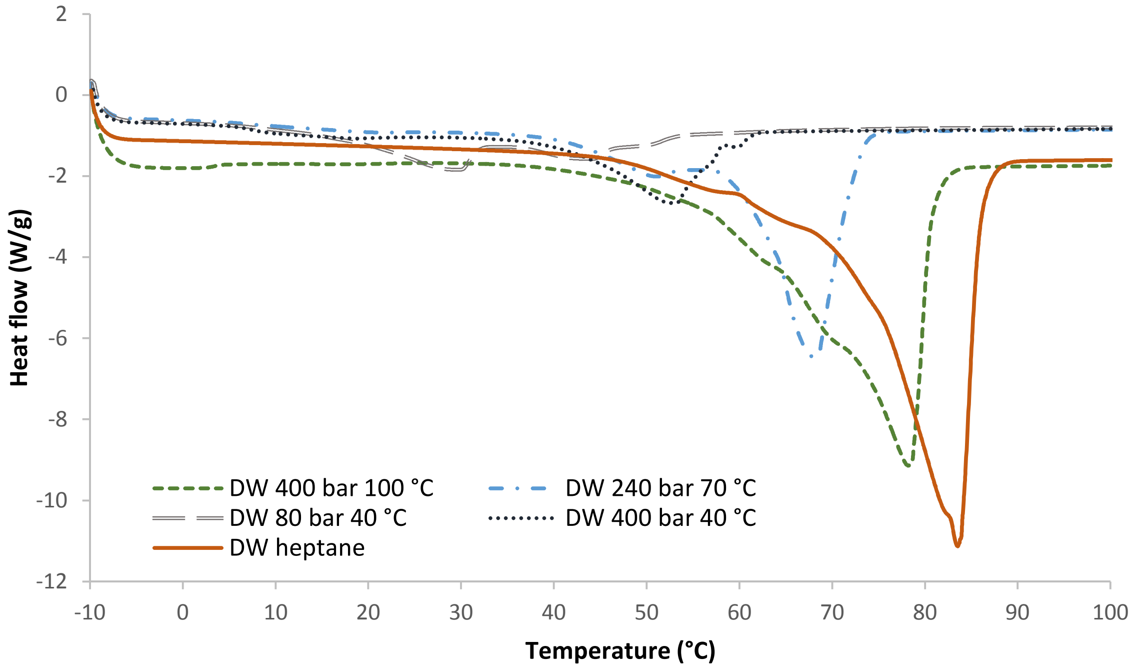


Figure 4 DSC thermograms for date palm wax (DW) extracted with heptane and $scCO_2$ at different extraction temperatures and pressures

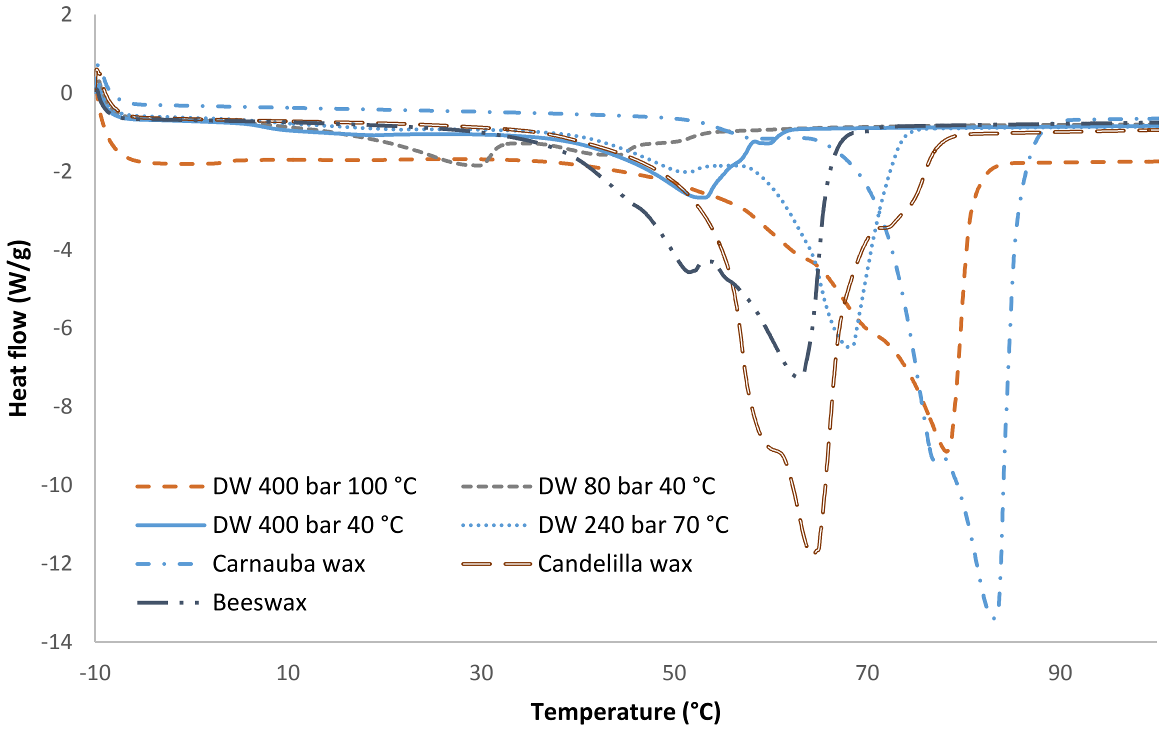
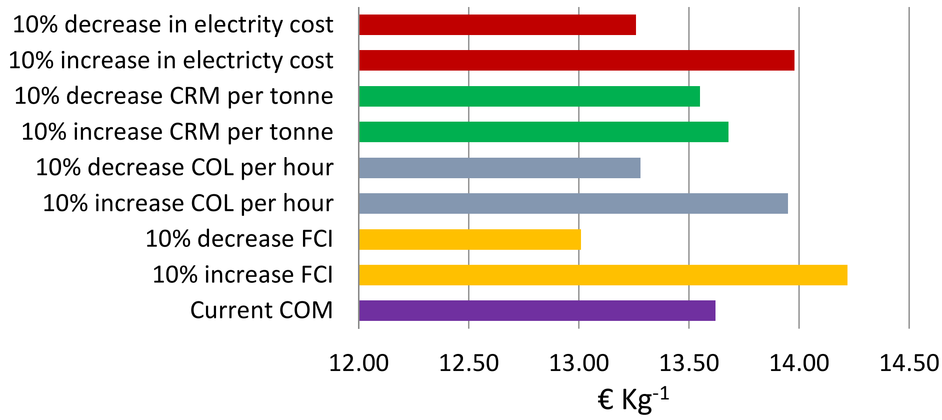


Figure 5 Thermogram showing the melting point profile commercial waxes compared to date palm waxes.



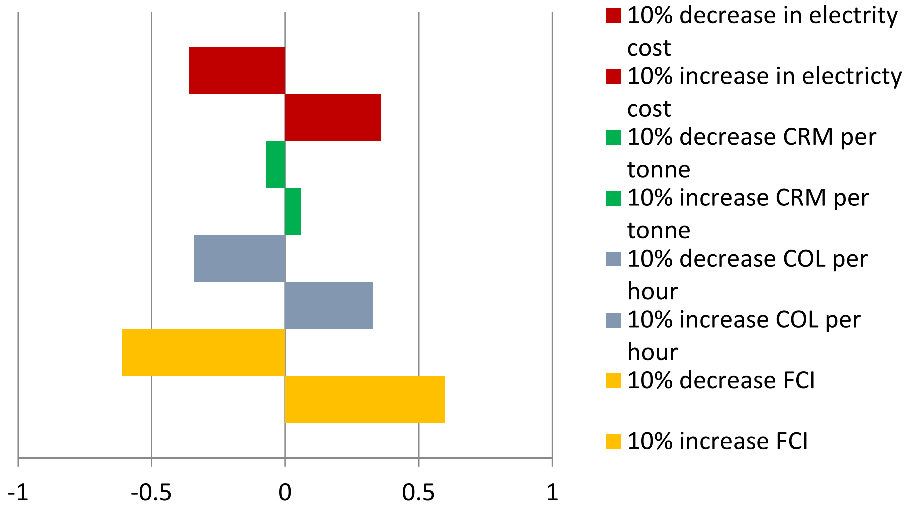


Figure 6 One-at-time sensitivity analysis (Above) total COM per Kg of extracted wax with increasing and decreasing the main parameters by 10% (Below) the difference in COM in respect to the original COM by varying the individual parameters by 10%.

Highlights

- Date palm leaves are an unutilised resource (1.5-2.8 million tons/year)
- Supercritical extraction yields high wax content from waste date palm, 3.49% (w/w)
- Date palm waxes exhibited high melting points (78 ^{o}C), comparable to carnauba wax
- Selectivity was achieved by varying the supercritical carbon dioxide conditions
- Low cost of manufacture highlighting great potential as a sustainable natural wax