Green Chemistry

Food waste biomass: a resource for high-value chemicals

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Our society currently faces the twin challenges of resource depletion and waste accumulation leading to rapidly escalating raw material costs and increasingly expensive and restrictive waste disposal legislation. The variety of food processes used in the food and drink industry globally generate food supply chain waste on a multi tonne scale every year. Such resides include wheat straw surpluses, spent coffee grounds or citrus peels, all of which represent a resource for an integrated, product focused biorefinery. Orange peel is particularly interesting: pectin and D-limonene, two marketable components, can be produced together with several flavonoids under the same conditions at a litre scale using low temperature microwave treatment. The running costs for such a process on large scale (50 000 metric tonnes per annum) have been estimated on the basis of the combined production of pectin and D-limonene.

1. Introduction

The need to both avoid waste and find new renewable resources has led to a new and promising research avenue: the use of food supply chain waste (FSCW) as a renewable biorefinery feedstock. FSCW could be defined as "the organic material produced for human consumption discarded, lost or degraded primarily at the manufacturing and retail stages".[1] Our food supply chain (FSC) has recently been recognised as being inefficient, producing large and accumulative quantities of waste.[2,3] The European Union (E.U.-27) produces each year just under 90 million tonnes of food waste (FW), 38% of which is directly produced by the food manufacturing sector.[4] The Food and Agriculture Organization of the United Nations (FAO) estimated last year that up to a third of the food aimed for human consumption is wasted every year globally.[5] The inherent and diverse chemical content of FSCW (see Fig. 1) together with the drive to reduce our environmental footprint and our society's concerns over the depletion of our fossil resources has led to 2nd generation FSCW valorisation initiatives. They include re-using waste as a raw material for the production of marketable chemicals such as silica based bio-derived adhesives from wheat straw or bio-derived surfactants produced from bread waste, gradually helping our society to achieve a circular economy based on zero waste.[6–9]

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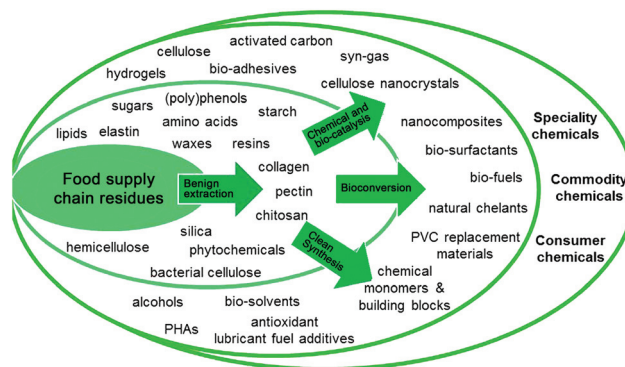*E-mail: james.clark@york.ac.uk; Fax: +44 (0) 1904322705; Tel: +44 (0) 1904322559*

Fig. 1 Components present in FSCW and their uses in common consumer applications, highlighting sectors of the chemical industry that could benefit from the use of such a renewable resource.

2. FSCW as a renewable resource

Residues produced by our FSC contain valuable functionalised molecules such as flavonoids, waxes, biopolymers or fatty acids as shown in Fig. 1. When using FSCW as a feedstock for electricity generation (*i.e.* through anaerobic digestion), fuel generation (*i.e.* conversion of cellulosic biomass to bio-ethanol) or the production of animal feed, those chemical functionalities are lost or at best underutilised. We cannot justify these losses knowing crude oil prices have reached an all time high in the last decade,[10] and that the conversion of these diminished hydrocarbons to functional molecules displays chemistry that is increasingly unacceptable due to hazardous substances, low resource efficiency and large quantities

of waste. Furthermore, it has recently been proven that the conversion of biomass waste to bulk chemicals for example was nearly 7.5 and 3.5 times more profitable than its conversion to animal feed or transportation fuel respectively, highlighting the marginal value of 1st generation FSCW recycling (*e.g.* anaerobic digestion, composting, animal feed).[11]

The variety of processes used in the FSC leads to the production of waste at every single stage.[12,13] Those wastes are mostly of organic nature (although they contain a number of useful inorganic species) and are characterised by high associated chemical and biological oxygen demand (COD and BOD),[14] fluctuating chemical composition and pH due to seasonal variations and changes in food processing,[14] rapid bacterial contamination (*e.g.* fruit and vegetable by-products),[15] high water content,[16] high accumulation rate, all leading to disposal management problems[2,17] and a high disposal cost (£68–111 gate fee in the UK in 2011).[18]

These limitations dictate the logistics needed to allow the production of novel added-value materials, chemicals and fuels from FSCW. The use of transportable continuous processing technology is needed to avoid rapid fermentation/bacterial contamination. This would also allow decentralised valorisation processes to occur where FSCW is produced, limiting the transport of low value material. The high water content often characterising FSCW shouldn't be an obstacle to 2nd generation valorisation strategies and technologies allowing on-site conversion of waste without resorting to a drying stage. The later would especially benefit the economics of the whole process, drying operations being expensive. Those technologies should be coupled with sophisticated extraction techniques capable of selectively removing fragile compounds such as carotenoids or flavonoids from the biopolymer matrix constituting the bulk of FSCW. Such a combination is key to the successful integration of FSCW as a raw material next to non food crops for example, showing how important multidisciplinary research is to gain an edge in this research area. We believe that the integration of clean and safe chemistry in disciplines such as biology, food science, biochemistry, (bio)chemical engineering and biotechnology has the potential to bridge the gap between established valorisation strategies of agro-residues and the biorefinery concept based on FSCW as a renewable feedstock for the production of marketable products.

But however sophisticated the valorisation process, it would be rendered ineffective without careful selection of the type of FSCW used as a raw material. In order to qualify as a feedstock for chemical production, availability is key. High, concentrated volumes of FSCW are needed to fit the large production capacity necessary to achieve economy of scale. Those volumes of FSCW should preferably occur around the globe (strengthening security of supply at a regional scale) and with the least heterogeneous composition as possible (*i.e.* tomato pomace, wheat straw, rice husks, spent Brewer's grain). The variety of extractable chemicals and biopolymers is also important, as the combined production of several marketable components from a single feedstock is essential to ensure the cost-effectiveness of the process.
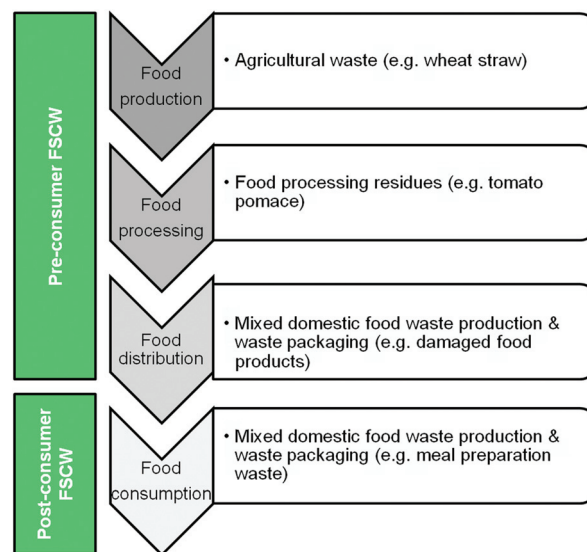

Fig. 2 Simplified food waste chain highlighting the difference between pre- and post-consumer FSCW.

3. Availability of FSCW

As mentioned earlier, the availability of FSCW is a very important criteria: the possibility of securing consistent and regular supplies of a given type of FSCW will determine whether industry will or will not implement the use of such a resource. Fig. 2 describes the four main stages of the FSC and the associated types of FSCW produced.

Although post-consumer waste is often the most visible, especially on a daily basis from the consumer's perspective, it is not only difficult to collect and segregate, but also challenging to valorise given its heterogeneous composition. Preconsumer waste is generated in a more concentrated manner, especially when considering the ever increasing rate of global food production[19] and processing ("more than 70% of the agricultural goods produced in the E.U.-27 are used to be transformed into food industry products"),[20] ensuring as little feedstock variability as possible when using pre-consumer FSCW as a raw material. In terms of logistics, FSCW such as agricultural residues or food processing residues should be preferred.

This is especially relevant as, in the UK for example, the commercial and processing sectors of industry produced together 36% of total industrial waste (excluding Scotland).[21] The food industry is omnipresent in our society: today, the three main sectors of the FSC (agriculture, food and drink production, distribution) generate together €581 billion.[22] In comparison, the chemical sector contributes €491 billion to the E.U.-27 economy,[23] showing the potential of 2nd generation valorisation of FSCW for the production of bio-derived chemicals, materials and fuels. This could boost the efficiency and competitiveness of two major sectors of the European economy, helping the food and chemical industry to form a symbiotic relationship instead of competing against each

other for the same resources, as highlighted by the *food vs. fuel* debate.[24]

Data on the exact amount of waste produced by the FSC is limited. For example, no data is issued on an annual basis by the E.U.-27 given the commercial sensitivity of this information for the food industry. When published data are available, there are often disparities between the numbers published by governmental and non-governmental organisations. They are often due to variations in the definition of waste and by-products used by the food sector. It is also worth mentioning that the variable water content doesn't allow consistent volume estimation. A European founded network (AWARENET network), estimated the amount of by-products and residues produced by the FSC as a percentage of the process input.[25]

Processing operations in the food sector can be classified into two categories: activities processing either animal-derived or plant-derived feedstocks. Fish and meat processing produce waste associated with a high sanitary risk and requires strict handling and waste management legislation, making the valorisation of such agro-industrial residues less feasible. On the other hand, plant-derived FSCW represents a lower risk of bacterial and transmissible spongiform encephalopathies contamination.

Without aiming to report all available types of FSCW, Table 1 lists examples of different pre-consumer types of agro-industrial residues available around the globe. The intention is to illustrate available volumes of this resource, showing how non animal-derived waste issued from the production of processed foods accumulates on a global scale in significant quantities.

4.   Plant-derived FSCW

According to the AWARENET report, when considering production processes, plant-derived waste represents a higher proportion (63%) of FSCW in comparison to animal-derived waste (on a wet basis). Five main operations are applied to the processing of agricultural products and associated wastes are summarised in Table 2.

Exemplary are the huge quantities of fruit pomace produced by the beverage industry: 5 to 9 million metric tonnes from grape and 3 to 4.2 million metric tonnes from apple are estimated to be produced worldwide every year, based on the wet by-product generated while the crop is processed.[40]

Citrus peel represents another important type of FSCW occurring around the world in high volumes, proving to be the perfect candidate for the combined extraction of known marketable chemicals such as D-limonene, pectin and flavonoids. A new biorefinery concept will be further developed in the remainder of this article.

5.   The new OPEC

82 430 000 metric tonnes of citrus fruits (oranges, tangerines, lemons, limes, grapefruit) were produced in 2010–2011 by the major citrus producing countries (Brazil, China, India, US, E.U.-27, Mexico, Egypt, Turkey, Vietnam, Argentina, Australia, Costa Rica, Israel, Guatemala, Japan, Korea, S. Africa, Philippines, Cyprus), of which 60% concern oranges.[43] Over 30% of the citrus fruit production, and more specifically 40% in the case of oranges, is processed.[44] This generates large quantities

Table 1 FSCW mapping

FSCW examples	Volume available/year (metric tonnes)	Geographical location
Europe		
Olive mill residue[26]	30 000 000	Mediterranean basin
Waste vegetable oil[1]	50 000–100 000	U.K.
Tomato pomace[27]	4 000 000	Europe
Wheat straw (surplus)[28]	5 700 000	U.K.
Food waste[4]	89 000 000	E.U.-27
Whey (surplus)[29]	13 462	Europe
Brewer's spent grain[30]	3 400 000	E.U.-27
Pea pods[31,32]	54 000	U.K.
Egg shells[33]	11 000	U.K.
Spent coffee grounds	15 600	U.K.
Tomato pomace[34]	53 800	Spain
Potato peels[30]	100 000 (dry basis)	U.K.
America		
Sugarcane bagasse[35]	194 692 000	Brazil
Grape pomace[36]	15 000 000	U.S.A.
Vegetable crop residue[36]	1 000 000 (dry basis)	California
Nut shells and pits[36]	400 000	California
Corn residue[35]	42 000 000	Brazil
Africa		
Orange peel (post-juicing)[37]	139 724 (2010)	South Africa
Cocoa pods[30]	20 000 000	Ivory coast
Cashew shell nut liquid[1]	20 000	Tanzania
Asia		
Food waste[1]	1 204 500	Hong Kong
Palm shells (from palm oil production)[38]	4 300 000	Malaysia
World		
Rice husks[39]	110 000 000	Global
Citrus fruit processing residues[40]	15 600 000	Global
Apple pomace[40]	3 000 000–4 200 000	Global
Banana processing[40]	9 000 000	Global
Oat straw[41]	11 000 000	Global
Barley straw[41]	58 000 000	Global
Rice straw[41]	731 000 000	Global
Rapeseed meal[42]	35 000 000	Global

Table 2 Main processing activities applied to plant borne FSCW and associated examples of waste streams

Main processing operations	Nature of waste streams produced
Vegetable oil and fat production	Seed meal, oily sludge
Vegetable and fruit processing (juice, preservation)	Peels, pomace
Starch production from corn, potato and wheat	Husks, straw
Sugar production	Dried pulp, vines and leaves
Wine production	Grape pomace, vines and leaves

Table 3 Estimated amounts of WOP produced in main citrus producing countries

Country	Amount of orange fruits produced (metric tonnes)	Orange fruits processing rates (%)	Estimated amount of WOP produced (metric tonnes)
Brazil	21 624 000	72	7 752 000
China	5 900 000	4	90 000
E.U.-27	6 264 000	19	607 500
Mexico	4 100 000	27	560 000
U.S.A.	8 035 000	73	2 947 500

Table 4 Reported composition of WOP[45] (20% dry matter)[51]

Components	wt% on the basis of dry weight
Ash (%)	2.56
Sugar (%)	9.57
Fat (%)	4.00
Protein (%)	9.06
Flavonoid (%)	**4.50**
Pectin (%)	**23.02**
Lignin (%)	7.52
Cellulose (%)	**37.08**
Hemicellulose (%)	11.04

of citrus peel, coming from both the juicing and canning operations. The residual peel accounts for 50 wt% fruit.[45] Estimated quantities of waste orange peel (WOP) produced according to reported amounts of oranges obtained and processed during the 2010–2011 harvesting season are presented in Table 3.[46]

The major components of orange peel are listed in Table 4, highlighting the number of commercial products available from this type of FSCW. In addition, dry citrus peel waste contains 3.8% D-limonene (w/w),[47] a molecule known for its applications as a bio-solvent,[48] a starting material for synthetic resins,[49] a flavour and fragrance component[44] and a chemical intermediate.[50]

Citrus peel and WOP produced by the juicing and canning industry have the potential to be used as a biorefinery raw material, giving rise to the OPEC (Orange Peel Exploitation Company) project. At the Green Chemistry Center of Excellence, research in the area of microwave activation of biomass[52] has led to the application of hydrothermal low temperature microwave process to WOP to produce D-limonene, pectin and a form of mesoporous cellulose using a single process and without any need of a form of pre-treatment (*i.e.* drying).[53] Reaction conditions were then tested on a larger scale given the industrial interest this project attracts. Herein we report the successful use of microwave technology at a larger scale for the production and the separation of D-limonene, pectin and flavonoids.

The use of microwaves instead of conventional thermal heating has increasingly been studied, especially in the last 20 years.[54] Advantages linked with the use of this technology include high heating rates, volumetric and contactless heating as well as a high control of the energy input.[55]

The use of microwave technology was chosen for the particular valorisation of WOP as it allows the design of an integrated conversion process. This technology has many advantages: it is adaptable for use in continuous processes and is easily scalable.

Additionally, this technology isn't limited by the high water content present in WOP (up to 90%),[56] quite the contrary given the dielectric constant of water. This results in a good interaction between microwaves and water-based systems.[57] This is important for future industrial scale applications given the importance of WOP drying costs (Fig. 3).[58]

5.1. Recent developments

Fig. 4A and B show the set-up used for D-limonene extraction at a three litre scale. A 1.52% yield was obtained when working at this scale under the conditions described in the Experimental section. The yield was surprisingly higher than obtained at lower scale (0.19%, 25 ml scale). Steam distillation of the resulting orange oil allowed for the recovery of D-limonene. A ^{13}C NMR spectrum confirmed its identity (see Experimental section) (Fig. 5 and 6).

Following steam distillation, the remaining aqueous orange oil revealed a clear precipitate. Using ESI mass spectrometry it was found to consist of 4 different polymethoxyflavones being

Fig. 3 OPEC project overview.

Fig. 4 (A) Microwave equipment used; (B) three litre round-bottom flask containing macerated orange peel in hexane; (C) closed-vessel set-up used for pectin extraction in the microwave; (D) vial on the left: pectin using method reported in this article; vial on the right: commercial pectin (galacturonic acid content >74.0%, Aldrich).
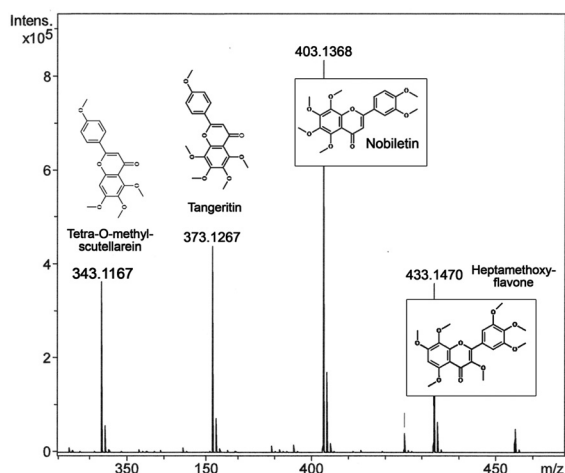
Fig. 5 ESI spectrum of the clear precipitate obtained after steam distillation of the D-limonene containing orange oil.
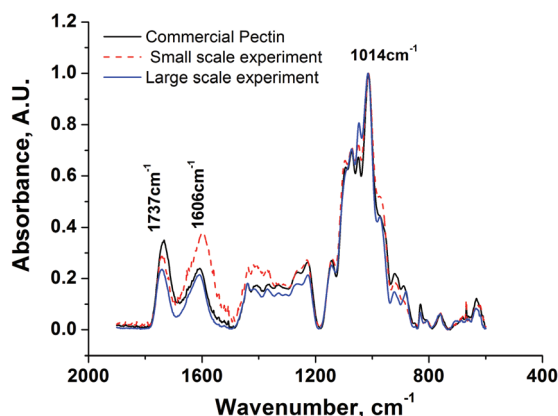

Fig. 6 ATR-IR spectrum comparison of pectin samples obtained at small and large scale together with commercial pectin (galacturonic acid content >74.0%, Aldrich).

tangeritin, nobiletin, tetra-*O*-methylscutellarein and hepta-methoxyflavone. While the detected polymethoxyflavones are present in a mixture, the ^{1}H NMR spectrum couldn't be decisively interpreted but does show a very strong aromatic methoxy signal at ~3.97 ppm.

These aromatic methoxy groups are characteristic of all the above mentioned polymethoxyflavones. Polymethoxyflavones are a subclass of flavonoids. They are of considerable importance as they exhibit a range of interesting medicinal properties such as anti-inflammatory, anti-carcinogenic, anti-atherogenic, anti-diabetic and anti-fungal properties.[59–61] However, their pharmacokinetic properties have rarely been investigated. This is mainly due to their high cost: the current trading price of 3,5,6,7,8,3′,4′-heptamethoxyflavone reached 300$ mg^{-1}.[62] Additionally, some polymethoxyflavones have found application as sweeteners or sweetness enhancers.[63]

Preliminary work in a smaller scale (25 ml) showed that the best quality pectin was produced under the following microwave conditions: 120 °C, 10 minutes, 1 : 10 peel : water. The ATR-IR of this pectin showed how well it compared with commercial pectin (galacturonic acid content >74.0%, Aldrich). A combination of IR, NMR and physicochemical methods allowed us to determine pectin's degree of esterification. The molecular weight was established using GPC equipped with triple detection. This was followed by a large scale microwave-driven hydrothermal extraction in closed vessel. Given the results obtained, microwave-assisted pectin extraction in water was carried out in closed-vessel (6 × 70 ml). As for D-limonene, the yield of pectin obtained was high, being almost 1.5 times higher than at small scale: we obtained a 7.4% and 10.80% of pectin at small and larger scale respectively.

Fig. 4D visually illustrates how well our pectin sample compares in terms of colour against commercial pectin: the colour is almost identical.

6. Economic considerations

In order to estimate the economic feasibility of the OPEC project, production costs of D-limonene and pectin were estimated when using microwave technology. The assumptions made to carry out such an assessment are detailed in the paragraph below.

Knowing citrus juicers operating above 50 000 metric tonnes of fruit are equipped to manage efficiently the citrus peel produced, an opportunity was identified and a scale of 50 000 metric tonnes of citrus processed per harvesting season was chosen (wet basis, 10 000 metric tonnes on a dry basis with a water content of 80%). It is assumed that the microwave plant will be located on the same site as the orange peel producing juicing plant and that it will be running 24/7 over a period of 6 months. The product yields (dry basis) are the ones calculated according to the above reported experiments: 1.52% for D-limonene (£0.62 kg^{-1}) and 10.8% for pectin (£11 kg^{-1}), yielding 152 and 1080 metric tonnes of D-limonene and pectin respectively per annum (1232 metric tonnes of product in total). A summary of the production costs is developed in Table 5. The cost of biomass and biomass transport was assumed to be marginal since the microwave plant is located in the vicinity of the juicing plant providing the WOP.

According to Table 5, the direct cost associated with such a process can be estimated to £4.7 million for the production of 1232 metric tonnes of product. The value generated by selling those products equates to £11.8 million for pectin and £94 032 for D-limonene, generating a profit of £7.3 million per annum. Hence the cost of producing a kilo of pectin and D-limonene is of £3.83, demonstrating the economic feasibility of our WOP based biorefinery concept. It is recognised that these profits are based on the actual market price for the products which may be significantly higher than a producer can expect from an intermediary. Also, our estimations do not include CAPEX for the microwave equipment. Nonetheless it does seem that a WOP biorefinery could be cost-effective.

Table 5 Distribution of costs associated with the production of D-limonene and pectin when processing 50 000 metric tonnes of WOP per harvesting season

Associated direct costs	£/harvesting season
Biomass and transport	0
Labour (4 senior researchers and 8 technicians)	387 675
Microwave energy consumption	1 654 256
Water consumption	135
Solvent consumption	2 427 661
Maintenance and consumables	104 089
Routine quality control analysis	141 627
Total	4 715 443
Total costs associated with the production of pectin (£ per year)	4 133 668
Total costs associated with the production of D-limonene (£ per year)	581 775

7.   Experimental

D-Limonene extraction experiments were carried out using macerated orange peel provided by a London-based juicer (Sundance, New Covent Garden Market). In the case of pectin production, the orange peel provided by Sundance was subjected to size reduction using a food processor. In all cases, the orange peel used was used wet. D-Limonene and pectin production were both carried out using a MARS 6 CEM microwave but different set-ups were designed.

The water content of each type of orange peel was determined by measuring the mass loss observed after heating the peel at 100 °C for 12 hours.

7.1.   D-Limonene production

D-Limonene was extracted at a three litre scale (open vessel), using an average of 3.5 kg of macerated orange peel per run (92.44% water content) in the presence of 250 ml of hexane For each extraction a microwave field of 1800 W was used for 5–9 minutes, depending on how fast the solvent used started to condense. All experiments were done under a blanket of nitrogen. Once the two sets of extractions were done, the hexane fraction was separated and the orange oil recovered by evaporation. This oil was then subjected to steam distillation to isolate D-limonene. The quality of the latter was evaluated using ^{13}C NMR showing only a minor impurity of hexane. This spectrum was recorded on a Jeol ECX-400 NMR spectrometer at 100 MHz using the central resonance of CDCl$_3$ (δ_C = 77.16 ppm). ^{13}C NMR (100 MHz, CDCl$_3$): 20.96; 23.62; 28.07; 30.75; 30.96; 41.24; 108.50; 120.80; 133.89; 150.42.

At a smaller scale, 2.5 g of WOP in 25 ml of distilled water were microwaved in a closed vessel for 10 minutes at 120 °C for 10 minutes (300 W, 300 PSI). After solid/liquid separation, D-limonene was extracted from the aqueous fraction with pentane and D-limonene yield was determined using GC.
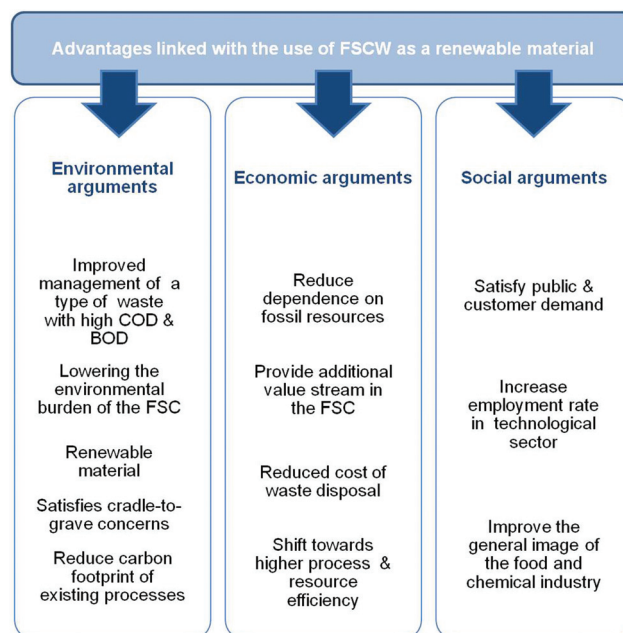
7.2.   Pectin production

Six closed vessel were each filled with 70 g of milled WOP (76.21% water content) and 70 ml of water (1 : 10 peel : water).

The vessels were submitted to microwave heating (dynamic mode, 1800 W) at 120 °C for 15 minutes (10 minutes ramping). The remaining WOP was removed by filtration and the aqueous solution collected. Using an excess of ethanol the pectin could be precipitated. The precipitated pectin was collected by centrifugation and washed twice with twice the volume of acetone. The neutral sugars were removed using a treatment with hot ethanol. The purified pectin was subsequently dried in a rota evaporator to remove any residual ethanol. ATR-IR was performed and the spectrum compared with both commercial pectin and pectin obtained at a lower scale. ATR-IR analysis of samples was carried out on a Bruker Vertex 70 instrument equipped with "Specac" Golden Gate Single Reflection Diamond ATR accessories.

The small scale pectin extraction was done using a Discovery microwave (CEM) under the following conditions: 2.5 g of milled orange peel in 25 ml of distilled water were microwaved for 10 minutes at 120 °C (dynamic mode, 300 W maximum power). Following filtration, the aqueous mixture was extracted with ethyl acetate to remove the organics present in solution. This step was omitted at the larger scale as apparently a fraction of pectin was lost in the ethyl acetate phase. Any remaining organics in the pectin were removed during the acetone washing. This actually allows to obtain a higher grade pectin. The pectin was dried overnight at 40 °C in a vacuum oven.

Conclusions

In summary, the example of a biorefinery based around the use of waste produced by the citrus juicing industry clearly illustrates the importance FSCW can play as an alternative to "virgin biomass". The introduction of different types of

Fig. 7   Advantages linked with the use of FSCW as a renewable feedstock.

renewable feedstocks such as FSCW next to more conventional non-food biomass will reduce the tensions linked to food–fuel conflicts, improve our environmental sustainability and food supply security.[16] Given the much improved yields obtained at a larger scale, compared to the ones obtained at laboratory scale, we intend to pursue this project, looking at the simultaneous production of D-limonene, pectin and flavonoids from WOP at low temperature using hydrothermal microwave.

The key to go beyond 1st generation waste valorisation is to make use of all the valuable components in waste. With respect to WOP this means taking into account also the presence of high-value products such as pectin and flavonoids, and not just limonene. Their isolation and purification adds markedly to the viability of a WOP based biorefinery. Fig. 7 summarises the benefits of using FSCW as a renewable resource according to environmental, economic and social factors.

Acknowledgements

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