

## From waste to wealth using green chemistry\*

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**Abstract:** The availability of chemically rich food supply chain waste (FSCW) gives it considerable potential as a resource for the manufacture of chemicals including materials and fuels. By applying clean chemical technologies to the extraction and conversion of molecules from FSCW, we can aim to produce genuinely green and sustainable products to help meet the legislative and consumer-oriented demands of a sustainable society. Low-temperature microwave (MW) processing is a particularly powerful technology to achieve this aim and is shown to be effective for several different high-volume, geographically diverse biomass types.

**Keywords:** biomaterials; food waste; green chemistry; microwaves; orange peels; waste biomass.

### INTRODUCTION

Our society is facing the twin problems of insufficient resources to feed a growing population and the industry that supports it—at least based on our existing pattern of consumption, and too much waste—again based on existing consumption habits whereby allowing items that were originally paid for and treasured to become burdens that need to be disposed of. Thus, it is tempting to conclude that a change is needed: our society needs to consume fewer virgin resources. The problem with this “solution” is that it is considered to be the idea of the developed world, and the developing world either will not listen or believe that they are entitled to enjoy the benefits of (over) consumption that the wealthier segments of society have indulged in for many years.

Our society’s consumption pattern is not simply about quantity, it is more about resource management. A linear model based on extraction of resources (oil, minerals, etc.) processing (e.g., chemical manufacturing then formulation), use, and disposal has now been applied for some time. This model is “resource stupid” and can only be sustainable if the disposal returns the resource to us in a useful form and on a reasonable timescale, typically measured within a human lifetime (<100 years). This result is rarely the case. With metals, for example, original virgin materials have been dispersed in the form of waste into landfills where recovery is difficult [1]. With organic materials, the situation is somewhat more complex—some are recycled by nature through biodegradation but much is not (e.g., many non-biodegradable plastics). Our own efforts at recycling are not to be dismissed but are woefully inadequate (e.g., only about 1 % of the 260 million t of plastics produced each year is recycled). Also, by stepping outside of the natural quick cycles of fast-rotation bioresources (plants, trees, etc.), and using a large proportion of bioresources with very long cycles measured in millions of years (oil, coal, etc.) an unsustainable economic model has been created.

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\**Pure Appl. Chem.* **85**, 1611–1710 (2013). A collection of invited papers based on presentations at the 4<sup>th</sup> International IUPAC Conference on Green Chemistry (ICGC-4), Foz do Iguaçu, Brazil, 25–29 August 2012.

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A change in our consumption pattern is needed through adoption of a circular economy [2] whereby resources should be consumed only in a way that can return them in a useful form and on a sensible timescale. This model is being “resource intelligent”! With a circular economy in place, our society’s rate of consumption will then be limited by our efficiency—the closer we get to 100 % efficiency the more we can enjoy the benefits of our planet!

Herein, three case studies of large-volume and geographically diverse food supply chain waste (FSCW) are used to show how FSCW can be diverted from landfill and used to develop new sustainable routes to chemicals and related products, thus giving value to what is currently seen as a problem or at best a marginal resource (e.g., compost). In these cases, it is important that large quantities of material are already collected (e.g., citrus for juicing) so that there are no added logistical issues and no need to add any additional transport costs to the overall economic cost and environmental footprint of any waste valorization model.

### WHEAT STRAW: MAKING MORE FROM AGRICULTURAL BY-PRODUCTS

Wheat straw is one of the most abundant types of renewable biomass on the planet. It is grown in very large quantities in countries from Europe to America and Asia and provides a good model for a possible future single-feedstock biorefinery employing a range of clean (bio-) chemical technologies that could be employed in several locations around the globe [3]. Figure 1 describes the concept of a wheat straw biorefinery.

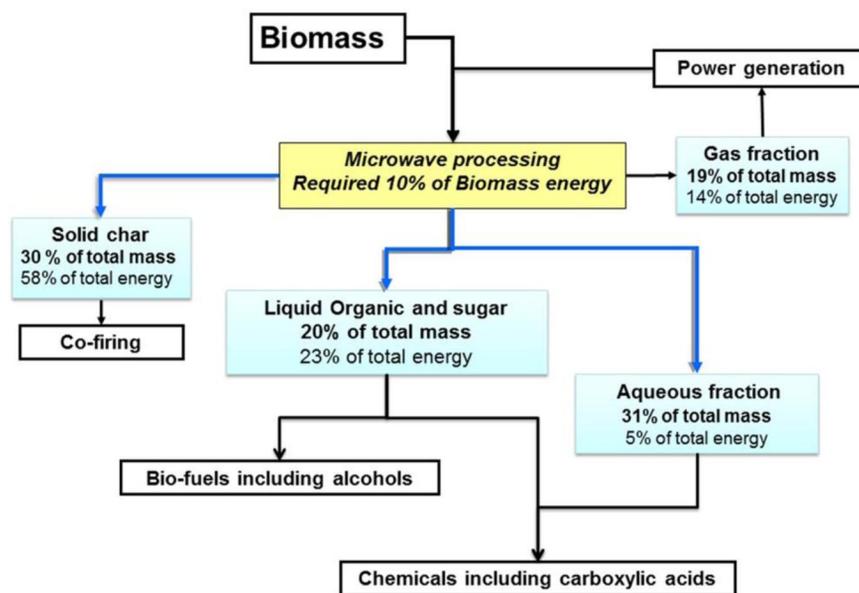


Fig. 1 A possible wheat straw biorefinery based on clean (bio-) chemical technologies and multiple products.

Initial extraction of surface waxes could be carried out using supercritical CO<sub>2</sub>, a benign chemical that will be readily available in most future biorefineries (e.g., from bio-ethanol production). These waxy chemicals include alcohols, aldehydes, and esters. Compared to traditional extraction solvents such as hexane (which is under increasing legislative pressure and is unlikely to be available for commercial processes in the near future), CO<sub>2</sub> extractions give fewer unwanted co-extracted components such as pigments, polar lipids, and free sugars [4].

In keeping with the zero-waste biorefinery target [5], the residues are not wastes but can be transformed into chemical and fuel products using microwave (MW) processing [6,7]. In contrast to most MW pyrolysis precedents, the pyrolysis is carried out at relatively low temperatures (below 200 °C). Under a moderate vacuum, an initial fraction of volatiles is condensed—this is found to be composed of water and acids such as acetic acid (36.4 % of the total weight of wheat straw, significantly higher than the ca. 10 % moisture content of the pelletized wheat straw, indicating a significant production of water and acids through decomposition reactions of the biomass even at low temperature). Subsequently, a fraction of bio-oil can be collected after 2 min irradiation, amounting to 21 % of the total mass of wheat straw used. What is notable is that the oil has a remarkably low water content (<1 %, in contrast to most pyrolysis oils, where at least 10 % is common) and low acidity with an acid value of 1.4. Calorific value was reported to be up to 22 MJ kg<sup>-1</sup>. The composition of the oils has also been investigated by gas chromatography (GC), GC-mass spectrometry (MS), and by NMR with levoglucosan being the largest component (ca. 28 %) and with benzofuran (ca. 10 %) and phenols (total ca. 11 %) also being prominent. Char yields are ca. 30 % with the remainder (14 %) being gases. Our results from the MW pyrolysis of biomass are further discussed below.

### RAPEMEAL: SQUEEZING MORE VALUE OUT OF OIL CROP RESIDUES

Rapeseed is widely grown in regions including Europe, North America, China, India, and Australia, with a total world production just under 60 million t per annum (2010 data) [8]. It is grown as a source of oils for applications including animal feed and vegetable oil for human conversion as well as conversion into biofuels. Processing of rapeseed for oil production produces rapeseed meal as a by-product that can be used as animal feed and a fertilizer, but it is widely recognized that the oil extraction process is inefficient and leaves valuable oil in the meal. In an attempt to gain higher oil yields from the cake, the use of low-temperature MW processing of cake was studied. Starting with MW steam distillation at 100 °C gives an impressive additional oil yield of 18 % (Fig. 2). Interestingly, raising the temperature of the MW process yielded more oil, though clearly of a different nature.

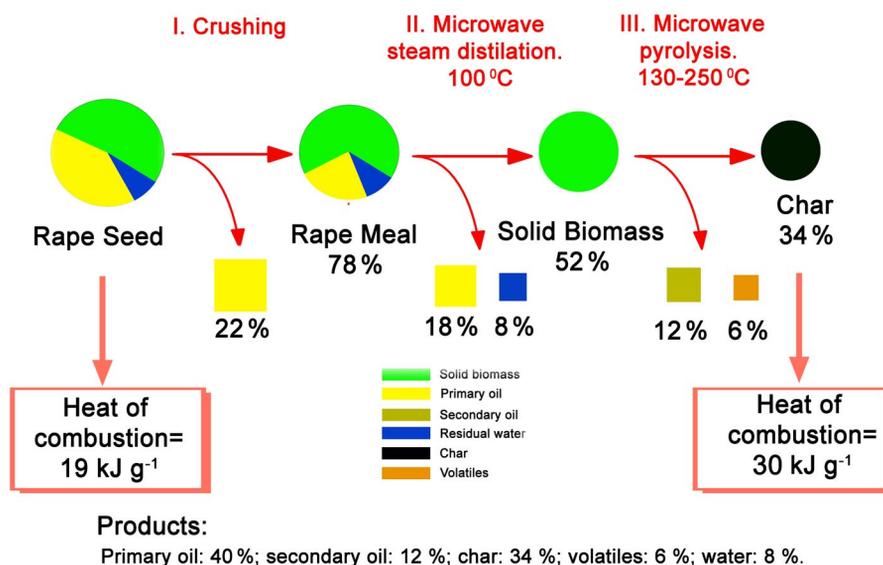


Fig. 2 Mass balances for low-temperature MW processing of rapeseed meal.

Our work on straws, rapemeal, and other biomass shows the development of a novel low-temperature (typically 120–180 °C) MW-based process for continuous thermochemical decomposition of biomass into solid biochar, liquid fractions, aqueous and organic bio-oil fractions (separated in situ during the process), and fuel gas [9,10]. MWs enable processing rates comparable to fast/intermediate high-temperature conventional pyrolysis, but at much lower temperature (see Table 1) [11].

**Table 1** Comparison of pyrolysis techniques for converting biomass.

Mode	Conditions	Weight %			
		Water	Oil	Solid	Gas
Fast	ca. 500 °C, 1 s	–	75	12	13
Intermediate	ca. 500 °C, 10–30 s	–	50	25	25
Slow torrefaction	ca. 290 °C, 30 min	–	–	82	18
Slow carbonization	ca. 400 °C, days	–	30	35	35
Gasification	ca. 800 °C	–	5	10	85
Microwave <sup>1</sup>	ca. 120–180 °C	13–28	7–28	25–80	9–29

<sup>1</sup>As reported here for 2–180 s.

The distribution and chemical characteristics of products can be controlled by varying processing conditions and using additives. The biochars have a calorific value and physical properties similar to coal, making them highly valuable in cofiring applications. The low-temperature MW thermochemical decomposition is based on MW interactions with specific biomass components [12]. It is also enhanced by predensification of biomass.

The oils obtained at low temperature (ca. 200 °C) MW pyrolysis from a range of biomass types, including rapemeal, wheat straw, barley straw, paper, and wood, have been analyzed, paying particular attention to their suitability for catalytic upgrading to liquid transport fuels (Table 2).

**Table 2** Key properties for bio-oils produced by the low-temperature MW conditions reported here.

Property specification	Range for MW pyrolysis oil	Specifications
Heat of combustion (MJ/Kg)	22–25	15 min
Water content (mass %)	3.5–5.7	30
Kinematic viscosity (20 °C) (mm <sup>2</sup> /s)	20–34	125 max.
Sulfur content (mass %)	< 0.02–0.22	0.05 max.
pH	2–4	–

All oil samples provided meet the requirements for pyrolysis liquid biofuels laid out in ASTM D7544-09 in terms of gross heat of combustion and water content. In fact, the majority of heating values are in excess of 20 MJ/Kg, well above the minimum specification of 15 MJ/kg. Similarly, water contents are all less than 6.5 wt %, well below the maximum specification of 30 wt %. Most oils meet the specification in terms of sulfur content (i.e., <0.05 wt), and pH contents are in the range ca. 2–4 [13].

## CITRUS WASTE: THE NEW OPEC

The use of MWs clearly opens the door wider for a future based on renewable biomass as a primary carbon source rather than non-renewable fossil resources. The debate over what proportion of fuels can be obtained from biomass continues, and it may well be that the intrinsic chemical functionality of bio-

mass means it is better suited as a feedstock for making chemicals, which generally require functionality, rather than fuels, which generally do not. A good example of this is citrus waste, a very large-volume, geographically diverse, and chemically interesting resource that offers considerable potential as a renewable source of a number of interesting chemicals.

Citrus fruits are widely harvested around the world and are considered as a commodity product such as coffee and tea in terms of international trade (FAO). 85 440 000 t of citrus fruits (oranges, tangerines, lemons, limes, grapefruit) were produced in 2010–2011 by the major citrus-producing countries (Brazil, China, India, USA, EU-27, Mexico, Egypt, Turkey, Vietnam, Argentina, Australia, Costa Rica, Israel, Guatemala, Japan, Korea, S. Africa, Philippines, Cyprus) [14]. It has been estimated that 31.2 million t of citrus fruit are processed every year in the world, yielding 15.6 million t of waste annually (50 % wet basis of waste) [15]. The United States and Brazil are the leading producing countries of oranges: each, respectively, produces over 18 and 7 million t of oranges [16]. The processing industry creates a large amount of waste by-product in the form of peel, seeds, rag (the membranes between the citrus segments), and pulp (juice sacs), representing ca. 50–60 % [17] of the whole fruit being discarded after juicing, for example. Citrus-processing waste (CPW) poses severe environmental problems as its high carbohydrate content is highly fermentable, leading to rapid degradation and methane production when this type of waste is not managed appropriately [18]. Citrus peel waste is also rich in soluble sugars (glucose, fructose, sucrose), and together with its high moisture content, it is prone to quick bacterial contamination [19]. Overall, waste treatment represents a significant cost, and waste is often misjudged regarding its value. Transformation of waste into value-added products would allow companies to cut treatment costs, generate some profits, and improve their competitiveness. Moreover, the recovery and valorization process of by-products is becoming a necessity as part of the existing sustainable development and environmental protection required by legislation and by the consumer [20]. Residues obtained from citrus processing can yield: dried pulp and molasses, fiber, pectin, dietary fibers, cold-pressed essential oil, essences, D-limonene, juice pulp, pulp wash, ethanol, seed oil, limonoids, and flavonoids (hesperidin, narirutin, naringin, eritrocin). They are used in the production of human food and food supplements, as a fermentation substrate for single-cell protein production, as silage, and as mosquito repellent [18,21].

The challenge is to develop a biorefinery process that will allow using the most valuable components of citrus waste with a maximum efficiency in an integrated process with the least steps possible. One key component is limonene, a chemical with proven value in areas such as cleaning and as an additive to consumer products. D-limonene has been shown to be a useful solvent for process chemistry capable of replacing traditional aromatic solvents such as toluene in important chemical reactions such as amidations [22]. This could be especially useful as new legislation such as REACH (Registration, Evaluation, Authorization, and Restriction of Chemical substances) systematically examines and will often prohibit some of the most widely used solvents. D-limonene is also a useful bioplatfrom molecule that can be converted into bio-*p*-cymene, for example (another useful solvent), and further to the new solid acid catalyst bio-*p*-cymene sulfonic acid [23].

We have developed an MW biorefinery for orange peel whereby in a single process step we separate the limonene from the pectin (useful as a food and cosmetic additive), sugars, and cellulose [24]. Two additional interesting features of the process, and taking advantage of the important process variables referred to earlier, are that the limonene can be converted in situ into other chemicals by altering the temperature, and that the cellulose produced at certain temperatures is mesoporous (giving it possible value as an adsorbent, e.g.). The overall biorefinery scheme is shown in Fig. 3.

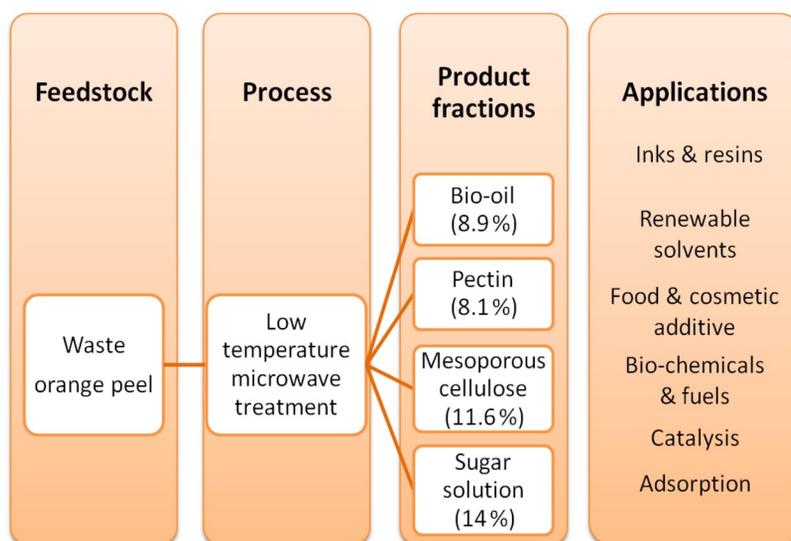


Fig. 3 Orange peel biorefinery scheme.

## CONCLUSION

Biomass and especially large-volume geographically diverse food supply chain residues such as cereal straws, oil seed crops, and citrus fruits that are already collected to give locally high concentrations, have an enormous potential as a source of renewable carbon for making chemicals and fuels.

The MW pyrolysis of biomass has been shown to be an effective, low-temperature route to valorize such biomass in terms of solid and liquid fuels, and also for the production of valuable chemicals that can help replace the many common solvents and other chemicals that will become restricted under legislation such as REACH. Continued efforts to develop larger-scale continuous systems within biorefineries will help to drive the field forward, as will studies aimed at a detailed description of the mechanisms of activation and interaction of MWs with biomass.

## ACKNOWLEDGMENTS

We thank our colleagues in the Green Chemistry Centre for their support for the work described here as well as our sponsors including the EPSRC, BBSRC, and EU (including ERDF).

## REFERENCES

1. (a) T. Graedel. *Ann. Rev. Mater. Res.* **41**, 323 (2011); (b) J. R. Dodson, A. J. Hunt, H. L. Parker, Y. Yang, J. H. Clark. *Chem. Eng. Process.* **51**, 69 (2012).
2. Ellen MacArthur Foundation (online). Available at: <http://www.ellenmacarthurfoundation.org> (accessed 1.09.12).
3. World Wheat Facts, Western Organization of Resource Councils, November 2002 (online). Available at: <http://www.worc.org/userfiles/WorldWheatFacts.pdf> (accessed 01.09.12).
4. A. J. Hunt, E. H. K. Sin, R. Marriott, J. H. Clark. *ChemSusChem* **3**, 306 (2010).
5. V. L. Budarin, P. Shuttleworth, J. R. Dodson, A. J. Hunt, B. Lanigan, R. Marriott, K. Milkowski, A. J. Wilson, S. W. Breeden, A. Fan, E. H. K. Sin, J. H. Clark. *Energy Environ. Sci.* **4**, 471 (2011).
6. A. Dominguez, J. A. Menendez, M. Inganzo, J. J. Pis. *Bioresource Technol.* **97**, 1185 (2006).

7. F. Yu, S. Deng, P. Chen, Y. Liu, Y. Wan, A. Olson, D. Kittelson, R. Ruan. *Appl. Biochem. Biotechnol.* **137–140**, 957 (2007).
8. FAO STAT, Food and Agriculture organization of the United Nations (online). Available at: <http://faostat.fao.org/site/567/DesktopDefault.aspx?PageID=567#ancor> (accessed 15.11.12).
9. V. L. Budarin, J. H. Clark, B. A. Lanigan, P. Shuttleworth, S. W. Breeden, A. J. Wilson, D. J. Macquarrie, K. Milkowski, J. Jones, T. Bridgeman, A. Ross. *Bioresource Technol.* **100**, 6064 (2009).
10. P. Shuttleworth, V. L. Budarin, M. Gronnow, J. H. Clark, R. Luque. *J. Nat. Gas Chem.* **21**, 270 (2012).
11. D. J. Macquarrie, J. H. Clark, E. Fitzpatrick. *Biofuels, Bioprod. Biorefin.* **6**, 549 (2012).
12. V. L. Budarin, J. H. Clark, B. A. Lanigan, P. Shuttleworth, D. J. Macquarrie. *Bioresource Technol.* **101**, 3776 (2010).
13. ASTM International. ASTM D7544-09. Standard specification for pyrolysis liquid biofuel (2009).
14. Department of Agriculture and Consumer Services, *Florida Citrus Statistics 2010–2011*, 2011 (online). Available at: [http://www.nass.usda.gov/Statistics\\_by\\_State/Florida/Publications/Citrus/fcs/2010-11/fcs1011.pdf](http://www.nass.usda.gov/Statistics_by_State/Florida/Publications/Citrus/fcs/2010-11/fcs1011.pdf) (accessed 29.08.12).
15. S. Djilas, J. Canadanovic-Brunet, G. Cetkovic. *Chem. Ind. Chem. Eng. Q.* **15**, 191 (2009).
16. FAO STAT database, 2010 data for production quantities of oranges (online). Available at: <http://faostat.fao.org/site/567/DesktopDefault.aspx?PageID=567#ancor> (accessed 27.08.12).
17. J. A. Siles Lopez, Q. Li, I. P. Thompson. *Crit. Rev. Biotechnol.* **30**, 63 (2010).
18. V. Ferreira-Leitão, L. M. Fortes Gottschalk, M. A. Ferrara, A. Lima Nepomuceno, H. B. Correa Molinari, E. P. S. Bon. *Waste Biomass Valorization* **1**, 65 (2010).
19. K. Grohman, R. Cameron, Y. Kim, W. Widmer, G. Luzio. *J. Chem. Technol. Biotechnol.* **88**, 395 (2013).
20. D. A. Kimball. *Citrus Processing, A Complete Guide*, Aspen Publications (1999).
21. J. M. Bonnell. US 4.497.838, Filed 20 April 1983, Issued 5 Feb 1985.
22. J. H. Clark, D. J. Macquarrie, J. Sherwood. *Green Chem.* **14**, 90 (2012).
23. J. H. Clark, E. M. Fitzpatrick, D. J. Macquarrie, L. A. Pfaltzgraff, J. Sherwood. *Catal. Today* **190**, 144 (2012).
24. A. M. Balu, V. Budarin, P. S. Shuttleworth, L. A. Pfaltzgraff, K. Waldron, R. Luque, J. H. Clark. *ChemSusChem* **5**, 1694 (2012).