**Supercritical Carbon Dioxide Extraction of Value-Added Products and Thermochemical Synthesis of Platform Chemicals from Food Waste**

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**Abstract**

Immense global generation of food waste calls for advanced technologies to maximise the use of such renewable carbon-based resources. In this study, corn, taro, lettuce, and bean sprout, were valorised for the production of value-added chemicals via sequential supercritical CO2 (scCO2) extraction and thermochemical conversion. The scCO2 extraction was performed at 350 bar and 50 °C for 60 min. The extracts of the lettuce contained sterols (764 μg g-1) that have potential anticancer properties. While bean sprout extracts had a higher content of saturated fatty acids (641 μg g-1), corn extracts comprised polyunsaturated fatty acids (405 μg g-1) as one of the major compounds, which are beneficial to cholesterol control. There were also notable amounts of wax esters (75-774 μg g-1) in these food waste extracts. Taro extracts were rich in both saturated (2313 μg g-1) and unsaturated fatty acids (1605μg g-1) and, in particular, contained difatty acids that exhibit pharmaceutical activities. Moreover, the solid residues after scCO2 extraction served as the substrates for platform chemical production. The starch-rich substrates, *i.e.,* taro and corn, resulted in 11-20% hydroxymethylfurfural (HMF) after microwave heating at 140 oC for 5-10 min using SnCl4 catalyst. In comparison, due to the high fibre content, lettuce and bean sprout required a higher temperature of 170-190 °C for chemical decomposition over H2SO4, generating a levulinic acid yield of ~7%, in company with glucose and fructose as the co-products. This study on the combined technologies suggested good compatibility between scCO2 extraction and subsequent thermochemical conversion, producing a wide spectrum of value-added chemicals from biomass waste. We herein highlight the vast potential of integrated technologies for food waste valorisation in achieving sustainable and carbon-efficient biorefineries.

**Keywords**: Thermochemical conversion; biomass decomposition; waste valorisation/recycling; hydroxymethylfurfural; levulinic acid; sustainable biorefinery.

# Introduction

Food waste has a global generation rate of 1.3 billion tonnes per year.1 It has emerged as a valuable and renewable resource, from which a wide diversity of materials and chemical products can be derived through extraction and conversion.2-4 Such resource recovery from the food waste could reduce our dependence on fossil feedstocks and fulfil the concept of a circular economy for achieving sustainable development.5-6 In particular, it is advantageous to extract the pre-synthesised biochemicals from food waste for use in high-value applications (*e.g.,* nutritional and pharmaceutical purposes), because the products generated from non-food substrates are generally subjected to more stringent restriction by international safety regulations.7 The extraction of fatty acids, waxes, polysaccharides, *etc.* can be an important initial step in the valorisation of biomass wastes.8

Traditional extractions are performed using volatile organic solvents, due to their low cost, low boiling points, and suitable solvation properties. However, the solvents could contaminate the extracted products as well as raise environmental and toxicity concerns. For example, the extraction of lipids and fats is commonly undertaken in hexane, which has been reported as a neurotoxin and is regarded by the US EPA as an air pollutant.9-12 Solvent residual guidelines have been developed to restrict the maximum residual levels of hexane in products in the food and pharmaceutical industries. In view of the ever-increasing legislative restrictions or even bans on the use of conventional solvents, it is imperative to look for alternative extraction means.

Supercritical CO2 (scCO2) is an emerging and green alternative to the traditional solvent extraction.13-14 As a non-polar solvent, it has been demonstrated effective for the recovery of lipids including high-value oils and plant waxes from agricultural residues.15 Plant waxes refer to the collection of plant lipids such as fatty acids, alcohols, aldehydes, wax esters, sterols, and β-diketones, which can be applied in hydrophobic coatings, polishes, detergents, nutraceuticals, and cosmetics. Besides being readily available and non-toxic, one crucial advantage of scCO2 extraction is that it leaves no solvent residuals in the extraction products, which addresses the major problem in conventional solvent extraction.16 Such residual-free feature also allows for the direct downstream processing of post-extraction biomass to generate additional products, without the need for any energy-intensive and costly solvent removal/drying procedures.17 ScCO2 extraction has been reported to be cost-effective when the biomass remains are further utilised for energy, material, or chemical production.18-19

ScCO2 treatment of lignocellulosic biomass is usually performed prior to biological processing.20 In an integrated maize stover biorefinery, scCO2 extraction as the first step not only provided extracts for detergent and nutraceutical applications, but also improved the downstream hydrolysis and fermentation of the post-extraction stover in terms of a 40% increase in ethanol production.17 A 20% increase in total sugars was reported in the enzymatic saccharification of scCO2-treated*Miscanthus*,4 which is similar to a study examining scCO2-assisted organosolv pretreatment of sugarcane bagasse.21 While the beneficial effects of scCO2 on enzymatic saccharification/fermentation are recognised,20 there is limited investigation of thermochemical conversion following scCO2 extraction.

ScCO2 extraction may enhance the accessibility of catalysts via the removal of small components as well as partial structural destruction under high-pressure and high-temperature conditions. However, it is uncertain if the structural changes are important to thermochemical treatments, where moderately high temperature (> 100 °C) is usually employed enabling faster mass transfer than that in biological treatments (< 50 °C). Liu *et al.* reported 18-51% increase in the yield of reducing sugars from dilute acid hydrolysis of scCO2-pretreated corncob, cornstalk, and rice straw.22 In addition, the effects of scCO2 treatment could be feedstock-dependent, *e.g.,* relatively small improvement of enzymatic hydrolysis of rice husk (< 10% increase in sugar yield) 23 compared to > 100% increase for sugarcane bagasse, wheat straw, switchgrass, etc. 8, 20

This study aims to evaluate scCO2 extraction for the recovery of useful chemicals from taro, corn, bean sprout, and lettuce wastes, which are common waste residues in fresh markets and food supply chains. The significance of scCO2 extraction was examined in determining the efficiency of a downstream thermochemical process, *i.e.,* catalytic production of hydroxymethylfurfural (HMF) and levulinic acid from the post-extraction food wastes. They are among the top value-added biomass-derived chemicals, potentially serving as the building blocks of polymers, resins, pharmaceuticals, biofuels, *etc*.24-25 The chemicals are generated via the hydrolysis of starch or cellulose to glucose, isomerisation of glucose to fructose, and dehydration of fructose to HMF. Levulinic acid appears as a rehydration product of HMF under intensive conditions. Previous studies reported the promising catalytic conversions of rice and bread wastes to HMF over metal chloride catalysts such as Sn(IV) and Al(III), which provide Brønsted and Lewis acid sites in an aqueous medium to catalyse the tandem reactions.26-28 In this study, the evaluation of scCO2 extraction-thermochemical process highlights the vast potential of integrated technologies in realising sustainable and carbon-efficient biorefineries.

# Materials and Methods

## Food waste and chemicals

The pre-consumer food wastes from restaurants in the Hong Kong International Airport and local fresh markets were used in this study. Taro, lettuce, and bean sprout wastes were individually collected as the raw leftovers and trimmings from daily business. Corn waste refers to the cooked corn-based salad leftovers from buffets, which contained impurities such as oil and seasonings. Taro and corn represent starch-rich feedstock, whereas lettuce and bean sprout represent fibre-rich substrates. The collected waste was freeze-dried, ground, sieved (0.2-mm mesh), and stored in an air-tight container at 4 °C. The dried and sieved samples were characterised, including dietary fibre (AOAC 985.29), protein (N x 6.25, Kjeldahl Nitrogen Method, AOAC 928.08), total fat (acid hydrolysis and gravimetric method, AOAC 922.06), and ash (AOAC 923.03). The content of available carbohydrates (wt%) was calculated as below 29:

(1)

where alcohol was omitted in view of its negligible concentration according to the USDA National Nutrient Database.30 Water content was referred to the difference in food waste mass before and after freeze-drying.

All solvents (ethanol, methanol) used were high-performance liquid chromatography (HPLC) grade and purchased from Fisher Scientific. Standard alkanes (mixture of C12-C60), 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 CO2 cylinders (99%) were obtained from BOC.

As for catalytic conversion, the catalysts, SnCl4∙5H2O (98%) and H2SO4 (95%), were purchased from Sigma Aldrich and BDH Prolabo, respectively. Acetone (99.5%) from Duksan Pure Chemicals was used to make the reaction medium. Model compounds were used in the calibration of analytical equipment, including cellobiose (≥98%), levulinic acid (98%), and formic acid (98%) from Alfa Aesar; fructose (≥ 99%) and maltose monohydrate (≥98%) from Wako; glucose (≥99.5%), HMF (≥99%), and furfural (99%) from Sigma Aldrich; and levoglucosan from Fluorochem. All the chemicals were used as received.

## ScCO2 extraction

The scCO2 extraction was conducted according to the previously published method by Attard *et al*.17 Typical extract conditions were conducted as follows: scCO2 extraction was conducted using a Thar Technology (Pittsburgh, PA, USA) SFE 500 system, at 350 bar and 50 °C with a CO2 flow rate of 40 g min-1 for 60 min. The extracted wax and lipids were collected from the stainless-steel separator vessel for further analysis, and residual biomass was recovered from the extraction vessel for additional catalytic conversion.

## Catalytic conversion

The catalytic conversion of dried food waste (with and without scCO2 pretreatment) was conducted following the procedures reported in previous studies.26-27, 31-32 The substrate (5 wt/v%) and catalyst (55.5 mM SnCl4 or 1 M H2SO4) were added to water or a mixture of acetone and water (acetone/H2O, 1:1 v/v) with a total volume of 10 mL. The mixture was heated to 140-190 °C in 5 min in an Ethos Up Microwave Reactor (Milestone, maximum power: 1900 W). The reaction last for 1-20 min with stirring maintained, followed by 40-min cooling by mechanical ventilation. The use of microwave heating enables more efficient heat transfer via dipole rotation and ionic conduction, consuming less energy compared to the conventional conductive heating.33-34 Therefore, using a microwave reactor could facilitate rapid and energy-efficient catalytic conversions in this study. All trials were carried out in duplicate. The sample was diluted with deionised (DI) water (1:3 v/v) and filtered through a mixed cellulose ester filter (0.22 µm) before product analysis.

## Sample analyses

Gas chromatography–mass spectrometry (GC/MS) analysis of extracts was conducted on a Perkin Elmer Clarus 500 Gas chromatograph coupled to a Perkin Elmer Clarus 560 Mass spectrometer in electron ionisation mode at 70 eV. Typically, 0.5 μL of sample (25 mg mL-1 in DCM) was injected onto a ZB5HT column (30 m× 0.25 mm× 0.25 μm). The flow of helium carrier gas was 1 mL min-1. Initially the temperature was held at 60 °C for 1 minute, prior to ramping at 8 °C min-1 to 340 °C, at which point the temperature was held for 30 min. Derivatisation of samples was achieved by addition of 200 μL N,O-bis-(trimethylsilyl)-trifluoro-acetamide in 1 mL toluene to a vial containing 25 mg of sample. The resulting mixture was heated at 75 °C for 30 min and allowed to cool prior to analysis.

HPLC was adopted to determine the concentration of products from catalytic conversion of food waste, *i.e.,* disaccharide, glucose, fructose, HMF, levoglucosan, levulinic acid, formic acid, and furfural. Chromaster was equipped with a refractive index detector (Hitachi, Japan) and an Aminex HPX-87H column (Bio-Rad) operating at 50 °C, with 0.01 M H2SO4 at 0.5 mL min-1 as the mobile phase.31 Blank and spiked samples (*i.e.,* standard compounds with known concentrations) were injected before each analytical run for quality assurance. The yield of the products was calculated on the basis of dry mass as shown in the equation below.

(2)

where *Pf* represents the concentration of final products and *Si* is the dry mass of food waste added.

# Results and discussion

## Food waste characterisation

The characterisation of food wastes in this study is shown in **Table 1**. The content of available carbohydrates, including starch and sugars, was the highest in taro waste (81.7%), followed by corn waste (49.9%), lettuce waste (31%), and bean sprout waste (19.1%). A reverse order appeared in the content of total dietary fibre (*i.e.,* cellulose, hemicellulose, lignin, and pectin): bean sprout (38.4%) > lettuce (33.1%) > corn (18.9%) > taro (7.6%). Most of the studied food wastes contained a significant amount of protein, *e.g.,* bean sprout (34.4%), lettuce (20%) and corn (15.4%), whereas the total fat content was low in general (≤ 3%) except for corn (11.8%). The fat in corn waste may be contributed by seasoning oil added for salad preparation, based on visual observation during food waste collection. Ash content was higher in lettuce (12.9%) compared to that in the rest (≤ 5%).

## ScCO2 extraction

Previous optimisation studies have demonstrated that suitable conditions for the extraction of waxes were determined to be 350 bar and 50 °C,17, 35 which were therefore adopted for the extraction in this work. The extraction time of 60 min was selected, beyond which further extraction was diffusion-controlled and took place to limited extent, according to our previous kinetic study.4 The extraction time of 60 min has also demonstrated to provide the optimal economic benefit with regards to extraction time and yield of lipids.18 The yields of waxes and lipids were consistent with previous studies on scCO2 extraction of agricultural residues and the highest yield of 1.3% was obtained from taro (**Table 2**).15 One of the biggest challenges in biorefinery is the development of efficient separation processes. As scCO2 is a selective extraction method compared to traditional solvents, this method offers further advantages for downstream application of the extracts. It is noted that the chemical compositions and the potential applications of these extracted products varied considerably between the studied food waste sources.

As observed in **Table S1** (Supporting Information), the extracts presented different compounds of various quantities. The majority of compounds in the lettuce included sterols (763.9 ±23.4 μg g-1 of plant), with the major sterol being stigmasterol (288.8 ±13.6 μg g-1 of plant). Phytosterols have been utilised as efficient compounds in the fight against cancer, it has also been suggested that phytosterol-enriched diet can reduce the risk of cancer by 20%.36 These molecules are known to also be involved in the cholesterol metabolism, reducing plasma LDL-cholesterol levels with minimal side-effects.37 Significant quantities of *n-*policosanols were observed in the extracts of lettuce, with the major alcohol being C26 and extracted in concentrations of 241.0 ±18.0 μg g-1 of plant. Policosanols can act as potent antioxidants, inhibiting low-density lipoprotein (LDL)-cholesterol peroxidation.38-39 The compounds have also demonstrated beneficial uses in the prevention of a variety of cardiovascular-related conditions.

In comparison, the predominant family of compounds in the bean sprout extracts was determined to be saturated fatty acids (C16 saturated fatty acid were dominant) (**Table S1**). Saturated fatty acids have been utilised for years in the production of soaps, detergents, cleaning polishes, and lubricating oils.40-41 Considerable quantities of wax esters were found in both the lettuce and bean sprout extracts, compared to the taro extracts (where minimal quantities were detected). Due to the high wax ester content, it could be possible to utilise this extract of bean sprouts in coatings, hard wax polishes, lubricants, or even in food applications as organogels.42-43

By contrast, the corn extracts demonstrated a low content of saturated fatty acids when compared to the other biomass extracts (**Table S1**). Polyunsaturated fatty acids are the major component of this extract, which are also known to have a beneficial effect on serum cholesterol in humans and reduction of cholesterol levels in the blood.44 Furthermore, polyunsaturated fatty acids could be used as platform molecules in a variety of applications.

The results of the taro extraction are consistent with the literature, which indicate that saturated and unsaturated fatty acids are the dominant compounds in the taro extract (**Table S1**). Large quantities were present in the extract (2313.10 ±45.8 and 1604.9 ±18.7μg g-1 of plant for saturated and unsaturated fatty acids, respectively). The presence of diacids such as azelaic acid (169.3 ±4.2 μg g-1 of plant) was observed, which can display significant pharmaceutical properties, including treatments for comedonal and inflammatory acne.45 Interestingly, in contrast to all other extracts, a considerable amount of xylene was detected in taro. Future work could further enhance the value of such extracts by using fractional separators, set at sequentially lower temperatures and pressures. Thus, such work could enable further separation in one process at the point of collection.

## Synthesis of HMF from scCO2-treated starch-rich food waste

The effects of scCO2 extraction on the efficiency of thermochemical conversion were evaluated, by comparing raw food wastes and their scCO2-treated counterparts in the Sn(IV)-catalysed HMF synthesis. The catalytic conversion of corn waste in acetone/H2O was faster than that in water regardless of scCO2 treatments, i.e., 10% HMF in acetone/H2O > 2% HMF in water under microwave heating at 140 °C for 10 min (**Fig. 1**). The faster conversion kinetics in the presence of acetone has been reported in homogeneous and heterogeneous catalytic systems.26, 46 In this study, it was possibly because the hydrolysis of active Sn(IV) species to inactive SnO2 was suppressed in the presence of acetone.47-48 Acetone/H2O was used as the reaction medium in subsequent experiments for the sake of more vivid observation on the difference between various catalytic systems.

Without prior scCO2 treatment, conversion of raw corn waste resulted in ~40% total products after 1-min heating at 140 °C, with monosaccharides being the major products including 25% glucose and 5.6% fructose (**Fig. 2a**). The products were derived from acid hydrolysis of glucans (*i.e.,* glucose-based polymers such as starch) in corn waste. The HMF yield of 10.3% can be obtained at 5 min as the produced sugars underwent dehydration. The HMF yield did not increase given a longer reaction time of 10 min, probably because further HMF formation was offset by HMF loss to side reactions such as rehydration and polymerisation.49 Changing the substrate to raw taro waste resulted in a higher total product yield of 73% (1 min), in which glucose was the dominant species (yield of 52%) (**Fig. 2b**). As the reaction time increased, HMF emerged with a yield of 12.3% at 5 min and 18.9% at 10 min. These results suggested that more products (sugars and HMF) can be generated from taro than from corn, probably due to the higher content of available carbohydrates in the former (**Table 1**). In contrast, lettuce and bean sprout that were rich in fibre gave a low HMF yield (≤ 3%), demonstrating the hurdle in utilising fibre and lignocellulose for HMF synthesis (**Table 3**).

Catalytic conversions of scCO2-treated lettuce and bean sprout gave product profiles resembling that of the raw substrates (**Table 3**). Similar observation was noted for corn wastes, *e.g.*, ~10% HMF at 5-10 min regardless of scCO2 extraction (**Fig. 2a&c**), suggesting that scCO2 extraction did not compromise the performance of the downstream thermochemical conversion. As for the conversion of taro wastes for 1 min, scCO2 pretreatment improved the glucose yield by 9% (**Fig. 2b&d**). After 5-min conversion, scCO2-treated taro gave a higher HMF yield of 15.2% and a lower glucose content of 31.9% compared to its untreated counterpart (12.3% HMF and 34.3% glucose), suggesting faster thermochemical reactions in the former. Such observation still held as the conversion prolonged to 10 min. These results indicated that scCO2 extraction could potentially improve the efficiency of the downstream catalytic process, depending on the food waste substrates. Taro was relatively rich in saturated and unsaturated fatty acids (**Table S1**), which were found to reduce the solubility of starch due to gelatinisation in the co-presence of protein.50 Therefore, the significant removal of fatty acids by scCO2 could have increased the starch solubility, improving the accessibility of catalysts in the subsequent process.

The advantage of scCO2 in enhancing our catalytic systems was less significant compared to a previous study reporting scCO2-improved acid hydrolysis of biomass.22 The latter employed water during the scCO2 treatment. Carbon dioxide dissolves in water under high pressure to form carbonic acid promoting acid hydrolysis of biomass and formation of small molecules,51 and CO2 enhances the diffusion of water into biomass structure to cause its swelling.8, 20 In comparison, the dry condition in this study that aimed to extract non-polar compounds (*i.e.,* waxes and fatty acids) cannot facilitate the carbonic acid formation and swelling effects, resulting in limited changes in the food waste structures. This speculation corroborated a previous report that scCO2 pretreatment of dry corn stover showed negligible improvement of enzymatic hydrolysis.52 Nonetheless, in field-scale applications, water in the as-received food wastes (30-90% water content 48, 53) is expected to cooperate with scCO2 to enhance their downstream thermochemical processing. Another possible reason was that the release of CO2 in this study was not fast enough to induce CO2 explosion for disrupting the food waste structures. The significance of the structural changes by physical means deserves further study in the future.

The current findings also differ from a recent study, in which similar scCO2 extraction conditions (dry, 80-400 bar, 40-60 oC) resulted in 20% increase in the enzymatic hydrolysis of *Miscanthus*.4 This was plausibly because of the higher content of wax in *Miscanthus* (e.g., ~2% in leaves) compared to the food waste in this study (< 0.1%; **Table S1**). Wax coated on substrate surface was hydrophobic, which may act as a physical barrier against biological and chemical degradation. In addition, as the temperature for enzymatic hydrolysis (55 °C) was lower than that for the thermochemical conversion (140 °C), waxes could have been more soluble in the latter case,54 leaving limited physical barrier on the surface of food waste substrate. The higher temperature may also facilitate mass transfer compensating the potential barrier effects. scCO2-assisted removal of waxes may also aid in the removal of small molecules that may inhibit enzymatic hydrolysis or fermentation. Therefore, the scCO2-assisted removal of waxes from *Miscanthus* played a more significant role in its downstream biological treatment, compared to scCO2 extraction for enhancing thermochemical treatment of food wastes in this work. This current study highlights the divergent consequences of scCO2 application and, most importantly, emphasise the importance of tailoring purpose-driven scCO2 extraction/treatment system for specific biomass and its utilisation. As for low-wax biomass, such as food waste used to serve human consumption, scCO2 could be applied as a pretreatment with the aim to improve downstream thermochemical processes, in which the water in the as-received substrates can be retained without the energy consumption for drying.

## Synthesis of levulinic acid from scCO2-treated cellulose-rich food waste

As bean sprout and lettuce did not degrade over the SnCl4 catalystfor HMF production, a strong Brønsted acid, *i.e.,* 1 M H2SO4, was then evaluated as the catalyst, in order to examine the effects of scCO2 on acid hydrolysis. Conversion of the untreated lettuce and bean sprout generally resulted in more products (~20 wt%) over H2SO4 compared to using SnCl4, due to the strong Brønsted acidity of the former (**Fig. 3**). However, the substrates contained 57-64 wt% glucans in terms of available carbohydrates and dietary fibres (**Table 1**), which was approximately three-fold higher than the sum of acid hydrolysis products. This suggested that the majority of the glucans cannot be utilised. The crystallinity of the cellulose, resulting from the hydrogen bond network, plausibly made the chemical attack difficult. In contrast to our initial hypothesis, the conversion feasibility was not improved with prior scCO2 extraction, in view of the similar chemical profiles of raw and scCO2-treated food wastes (e.g., trials 1&2 vs 3-6 in **Fig. 3**). The results may imply that the recalcitrance of fibre/cellulose-rich food waste was mainly contributed by the glucan polymer structure itself, rather than the barrier effects by non-polar components such as wax and fatty acids. More intensive conditions, for example, increasing the temperature enhanced the formation of levulinic acid (~7% for trials 2&8 in **Fig. 3**) as a product of rehydration of HMF. Therefore, it is highlighted that for applications aiming to pretreat fibre-rich food waste, it is critical to reduce its crystallinity using more vigorous conditions, such as CO2 explosion and scCO2 pretreatment in the presence of water or organic solvents.20

The residues from the integrated scCO2 extraction-thermochemical conversion were estimated to be 50-80 wt% of the initial substrates (**Fig. 2 & 3**). In additional to the recalcitrant fibre discussed above, the residues contained proteins, fats, and ashes (**Table 1**), which are not glucans and thus cannot serve the production of HMF or levulinic acid. Therefore, further utilisation of the proteins and fats can be incorporated in the integrated biorefinery. The presence of humins, a polymerisation by-product, was also expected in the residues from the taro and corn conversions, in view of the loss of soluble products with the increasing reaction time (**Fig. 2**).

# Conclusions

Value-added compounds were produced from four representative types of food wastes, including corn, taro, lettuce, and bean sprout, via sequential scCO2 extraction and thermochemical conversion. The food waste extracts contained compounds with high nutritional and pharmaceutical values, such as sterols with potential anticancer properties, polyunsaturated fatty acids for cholesterol control, and difatty acids for acne treatment. The scCO2-extracted food wastes remained as feasible substrates in the thermochemical conversion. The starch-rich food wastes, *i.e.,* taro and corn, allowed the facile production of HMF (11-20%) over SnCl4 as the catalyst under microwave heating (140 °C, 5-10 min). Comparatively, more intensive conditions were needed for the conversion of the fibre-rich food wastes, lettuce and bean sprout, which produced levulinic acid, fructose, and glucose as the major products at 170-190 oC over H2SO4 catalyst. This study underscores the good compatibility between scCO2 extraction and the subsequent thermochemical conversion, which advocates the innovation of integrated technologies to capitalise biomass wastes, achieving sustainable biorefineries of high carbon efficiency.

**Supporting Information**

Quantification of scCO2 extracts from the studied food waste

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**Table 1.** Characterisation of food waste samples used in this study.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  | **Component (wt% dry basis)** | | | | | **Water content (wt%)** |
| Sample | Available carbohydratesa | Total dietary fibreb | Protein (Nx6.25) | Total fat | Ash |
| Corn | 49.9 | 18.9 | 15.4 | 11.8 | 4 | 76.8 |
| Taro | 81.7 | 7.6 | 5.9 | 1 | 3.8 | 60.5 |
| Bean sprout | 19.1 | 38.4 | 34.4 | 3.3 | 4.8 | 93.9 |
| Lettuce | 31 | 33.1 | 20 | 3 | 12.9 | 94 |

a Available carbohydrates were calculated according to HK FEHD (2008): 100 – [dietary fibre + protein + fat + water + ash + alcohol(ethanol)] g / 100 g substrate; alcohol was omitted in view of negligible concentration shown in the USDA National Nutrient Database;

b including cellulose, hemicellulose, lignin, and pectin.

**Table 2**. ScCO2 extraction yields and major compounds for lettuce, bean sprouts, corn and taro.

|  |  |  |
| --- | --- | --- |
| **Biomass** | **Crude Yields (wt% a)** | **Major compounds in extract** |
| Lettuce | 0.51 (±0.03) | Wax esters, sterols, policosanols, saturated and unsaturated fatty acids. |
| Bean Sprout | 0.48 (±0.02) | Saturated fatty acids, wax esters and unsaturated fatty acids. |
| Corn | 1.08 (±0.05) | Wax esters and unsaturated fatty acids. Low content of saturated fatty acids when compared to the other biomass extracts. |
| Taro | 1.30 (±0.07) | Saturated and unsaturated fatty acids, xylene and diacids such as azelaic acid. |

a On dry mass basis.

**Table 3**. Product yields resulted from the catalytic conversion of lettuce (LE), scCO2-treated lettuce (TLE), bean sprout (BS), and scCO2-treated bean sprout (TBS) over 55.5 mM SnCl4 (conditions: 5 wt/v% substrate in acetone/H2O mixture (1:1 v/v); yield = productwt/substratewt × 100%).

|  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Trial** | **Substrate** | **Temperature (oC)** | **Reaction time (min)** | **Product yield (wt%)** | | | | | | | |
| Glucose | Fructose | DS+LG | HMF | Furfural | LA | FA | Sum a | |
| 1 | BS | 140 | 5 | 4.8 | 4.0 | 1.3 | 1.9 | 2.2 | 1.4 | 1.8 | 17.4 | |
| 2 | BS | 140 | 20 | 3.0 | 2.4 | 0.2 | 2.0 | 2.1 | 1.2 | 0.9 | 11.8 | |
| 3 | TBS | 140 | 20 | 2.6 | 1.9 | 0.0 | 2.2 | 2.2 | 1.3 | 1.7 | 11.9 | |
| 4 | TBS | 180 | 5 | 0.0 | 1.4 | 0.9 | 2.1 | 2.7 | 3.1 | 2.3 | 12.6 | |
| 5 | LE | 140 | 5 | 1.9 | 2.6 | 0.2 | 2.5 | 1.9 | 1.2 | 0.0 | 10.2 | |
| 6 | LE | 140 | 20 | 0.9 | 2.2 | 0.0 | 2.2 | 2.0 | 1.5 | 1.7 | 10.5 | |
| 7 | TLE | 140 | 5 | 2.1 | 2.7 | 0.8 | 2.9 | 1.9 | 1.2 | 0.0 | 11.7 | |
| 8 | TLE | 140 | 20 | 0.9 | 2.1 | 0.0 | 2.4 | 2.0 | 1.6 | 1.8 | 10.7 | |

a The remainder was deduced to be a mixture of fibers, proteins, ashes, and oligosaccharides/humins. Abbreviation: disaccharide (DS), levoglucosan (LG), levulinic acid (LA), formic acid (FA).



**Figure 1**.Product yields resulted from the catalytic conversion of (a) corn and (b) scCO2-treated corn over 55.5 mM SnCl4 in water or acetone/H2O mixture (1:1 v/v) (conditions: 5 wt/v% substrate at 140 oC for 10 min; yield = productwt/substratewt × 100%).



**Figure 2.** Product yields resulted from the catalytic conversion of (a) corn, (b) taro, (c) scCO2-treated corn, and (d) scCO2-treated taro over 55.5 mM SnCl4 (conditions: 5 wt/v% substrate in acetone/H2O mixture (1:1 v/v) at 140 oC; yield = productwt/substratewt × 100%).



**Figure 3**. Product yields resulted from the catalytic conversion of lettuce (LE), scCO2-treated lettuce (TLE), bean sprout (BS), and scCO2-treated bean sprout (TBS) over 1 M H2SO4 (conditions: 5 wt/v% substrate at 140-190 oC for 10 min; yield = productwt/substratewt × 100%).

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Food wastes are valorised for value-added chemical synthesis via the integrated supercritical CO2 extraction-thermochemical processes for sustainable biorefineries.

