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Producing upgradeable bio-oil from food bio-waste via hybrid-assisted pretreatment coupled with catalytic hydrotreatment

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ABSTRACT

Slurry food waste sourced from Renova (Gothenburg, Sweden) was investigated as a model for generating upgradeable bio-oil via a hybrid-assisted pretreatment along with a catalytic hydrotreatment process. Hybrid-assisted pretreatment has been examined for extracting and stabilizing of reactive-derived substances. For the resulting bio-crude and residual solids, the properties of the heteroatoms were also examined prior to the catalytic hydrotreatment experiments. Hybrid-assisted pretreatment is an interesting solution in that it maximizes the bio-crude yield and transfers significant amounts of the nitrogenous content (De-N ~83.3 %, dry basis) into the residual solids. Nearly 87 wt% of the oxygenated monomers were found in the obtained bio-crude, which possessed 52.0 wt% of alcohols. The highest upgradeable bio-oil of 86.0 wt% was achieved during catalytic hydrotreatment of the bio-crude and residual solids jointly: producing blends of up to 78 wt% of hydrocarbons, 14 wt% oxygenated and <6 wt% of cyclic, aromatics, N-containing components.

1. Introduction

The Food Waste Index Report states that 931 million tonnes of food waste were generated each year from households, food service, and retail waste (Amicarelli et al., 2021; Franco et al., 2022; You et al., 2022). The costs associated with the food wasted within the European Union (EU) in 2022 were estimated at around 130 billion euros, two-thirds of which are derived from households (Basnet et al., 2023). In 2022, a call for the revision of the Waste Framework Directive (WFD) was sought due to the increased generation of municipal waste (Olczak and Piebalgs, 2022; Paleari, 2022; Santagata et al., 2021). In line with the European Green Deal, this directive also sets the target of 65 % of municipal waste being recycled by 2035 (Olczak and Piebalgs, 2022). To achieve the action plan established by the EU Commission, households in the EU countries have an obligation to selectively collect bio-waste from December 31, 2023 (Olczak and Piebalgs, 2022; Paleari, 2022; Santagata et al., 2021). The concept of the zero-waste policy includes a 100 % recycling of municipal solid waste and a 100 % recovery of all resources from materials. According to a recent study reported by the Confederation of European Waste-to-Energy Plants (CEWEP) (CEWEP, 2022), Germany is the leading country for recycling in 2020, with 68 % of municipal waste either recycled or composted. While some EU countries (Slovenia, Estonia, Cyprus, and Lithuania) still landfill >10 % threshold set by the Landfill Directive for 2035. More importantly, the contribution made by biomass in achieving low-emission goals, such as those set by the revised Renewable Energy Directive – Recast to 2030 (RED II), must be based on ways of producing advanced biofuels that explicitly ensure significant reductions in the life-cycle of GHG emissions compared to those of fossil fuels (Olczak and Piebalgs, 2022; Paleari, 2022; Santagata et al., 2021).

The advanced biofuels of second and third generation must comply with sustainability criteria from a wide array of different feedstock, ranging from lignocellulosic to microorganism biomass feedstocks, including municipal solid waste: biomass fraction of mixed municipal waste, industrial waste and biowaste from selected private households without competing with food and land supplies (Mizik and Gyarmati, 2022). On the other hand, non-edible sources of biomass, such as food waste from municipal solid waste, are important feedstocks in the production of advanced transportation fuels, as described by European Technology and Innovation Platform (ETIP Bioenergy). Nevertheless, the valorisation of food waste has only focused on using the by-products obtained from some agricultural practices, e.g. landfill, animal feed, fertilizer supply, composting, incineration and anaerobic digestion (AD) (Mizik and Gyarmati, 2022). The recovery capacity, and its effectiveness in creating value in scaling the production from food waste, remain quite limited on a commercial level. Considering a zero-waste policy, the

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efficient exploitation of food waste resources is crucial in supporting the sustainability of the process. In this respect, designing systems for the production of multiple products would boost process competitiveness by lowering manufacturing costs further and assuring a more efficient utilisation of raw materials (Bhatia et al., 2023). Scientific studies have demonstrated that it is possible to generate a wide variety of bioenergy from biomass residues and waste, but also that its cost is not competitive to that of petro-fuels and other kinds of renewable energy (Bhatia et al., 2023; Mizik and Gyarmati, 2022; O'Connor et al., 2021). On-going efforts continue to be made extensively to improve conversion technologies and thereby reduce production costs (Lee et al., 2019). Currently, the two most common types of biofuels available on the market are bioethanol (108.5 billion l/year) and bio-diesel (49.9 billion l/year), produced principally from sugar and starch containing materials and fatty acid methyl ester (FAME) (El-Sheekh et al., 2023), respectively. The efficient use of food waste could help the circular bioeconomy by reducing the gap between waste valorisation and product recovery. This demonstrates the potential of food waste not only in obtaining value-added products but also promoting circular economies and green chemistry. Converting food waste into potential liquid biofuels is nevertheless important, and is currently being investigated by many researchers as fuels in a pure form or as a blend to be added to existing diesel engines (Babalola, 2020; Chen et al., 2019; Hafid et al., 2022; Johansson, 2021; O'Connor et al., 2021; Panzella et al., 2020; Santagata et al., 2021). With every few exceptions, all conversion processes for biomass produce solid, liquid and gaseous products in varying yields and composition. Compared to other thermochemical processes such as torrefaction, pyrolysis and gasification, the pre-drying of biomass is not required in hydrothermal liquefaction (HTL) because water acts as a reaction medium (Hansen et al., 2020). Therefore, feedstocks with high moisture contents, e.g., microalgae, food waste and sewage sludge, are well-suited to HTL and have the added advantage of saving energy in the pre-drying process.

From a technological perspective, the aim of advanced biofuel processes is to produce liquid transport biofuels that can leverage capital expenditures in the existing petroleum distribution infrastructure. However, the utilisation of food waste remains a direct challenge due to its heterogeneous nature, some kind of physical, chemical, enzymatic or combined pretreatment is therefore required to make it more accessible (Maria et al., 2020; Santagata et al., 2021). This applies to both agro-industrial and food waste, as most of these are not in pure liquid form. In their analysis of the HTL process, Zhu et al. (2014) found that the economic performance of HTL is most sensitive to carbon loss to the aqueous phase. The process conditions of HTL that diminish the production of water-soluble organic compounds can potentially improve the energy yield, improve the carbon yield, reduce waste treatment costs and improve the economics of the process. While homogeneous alkali salts, such as Na_2CO_3, have been reported to improve the carbon yield of HTL, and that improvement is attributed to the formation of coke being suppressed (Elliott et al., 2006; Jena et al., 2012; Shah et al., 2022). However, water-soluble organics from HTL experiments produce a non-negligible amount of contaminated water as a co-product, leading to large water handling requirements. Recently, the effect of aqueous phase recirculation (APR) on HTL has received some attention, and few solutions have been suggested (Harisankar et al., 2021; Kohansal et al., 2021; Leng et al., 2020; Zhu et al., 2015). Pedersen's Group investigated a two-stage process by integrating the APR with HTL process for wet biowaste (bio-pulp), and subsequently hydrotreating the bio-crude obtained over sulfided $NiMo/Al_2O_3$ catalyst (Kohansal et al., 2022). Interestingly, the findings showed that the APR exhibited a promising result in terms of bio-crude yield and energy recovery. However, the heterogeneous nature of biowaste remains the main challenge: more hydrogen is necessary to reduce the N-content, using severe hydrotreating conditions, to obtain a suitable drop-in quality of the biofuel. The authors also suggest that the two-stage process requires pretreatment that is capable of extracting N-content before being further processed in the downstream processing step (Kohansal et al., 2022). Slow pyrolysis is another prominently used thermochemical process to produce bio-oil from food waste by depolymerizing cellulose, hemicellulose, lipids, proteins, and lignin (Lu et al., 2020). In comparison with HTL, bio-oil from pyrolysis has the potential to be mixed with other transportation fuels after being catalytically hydrotreated. The bio-oil from slow pyrolysis generally contains a wide range of complex organic compounds, and their decomposition in food waste at the elevated temperature (300–500 °C) leads to an elevated pH of the bio-oil. Furthermore, a few organic nitrogen compounds were also found in food waste, which could produce harmful NOx during thermochemical treatment (Lu et al., 2020; Mansor et al., 2018). Therefore, it is necessary to establish methods of recovering and stabilizing of these organics in bio-waste. Table 1 presents data characterizing the individual types of technology (Ahmed Ebrahim et al., 2022; Déniel et al., 2016; Fadhil, 2017; Harisankar et al., 2021; Kohansal et al., 2022, 2021; Modak et al., 2023; Patra et al., 2021; Qing et al., 2022). The composition of bio-crudes varies depending on the chemical composition of the food waste and the conditions in which the process takes place. Moreover, a combined process is applied to maximize bio-oil production.

Mechanical pretreatment, on the other hand, involves physical processes like chipping, milling and grinding, along with sonication, maceration and microwave. These are used to reduce the size of the waste so as to increase the surface area of the waste, forming so-called slurry biowaste. These methods, when implemented, do not generate odour and consume only moderate amounts of energy. A search of this literature suggests that mechanical pre-treatments lead to rapid solubilization due to the enhancement of biodegradables via intermediate formation (Kondusamy and Kalamdhad, 2014). Izumi et al. (2010) studied the effects of particle size reduction as mechanical pretreatment for anaerobic digestion of food waste. The results revealed that particle size reduced by bead milling enhanced methane yield by 28 % compared with disposer treatment (Izumi et al., 2010). Therefore, the integration of a mechanical pretreatment for municipal solid waste could potentially enhance the solubilization of food waste. For example, Renova's treatment facility for sorting food waste produces a slurry suitable for biogas production after being pulverized, compressed and strained with liquid food waste ("Treatment facility for biological waste in western Sweden", n.d.). Hence, investigating the extraction, separation, and isolation of biowaste slurry as a method of pretreatment should be evaluated in order to enhance the organic recovery prior to further upgrading process. The aim of this research study was to evaluate the effects of the chemical composition of bio-products resulted from a hybrid-assisted pretreatment, and its subsequent co-hydroprocessing into compatible petroleum-biofuel blends. For this purpose, the hybrid-assisted pretreatment is expected to provide exceptional chemical composition with better solubilization of biowaste compared to traditional pre-treatments and thereby enables higher bio-crude production rates. The study also aimed at evaluating the impact of mild and deep catalytic hydrotreatment on the extracted bio-crudes and solid residues. The properties and molecular composition of the products were characterized using various analytical and characterization techniques such as elemental analysis, Karl Fischer, TGA-DSC, GC–MS, and GCxGC–MS/FID.

2. Materials and methods

2.1. Feedstocks and chemicals

The food waste slurry, sourced from Renova AB (Marieholm, Gothenburg, Sweden), was produced from assorted food waste after it was pulverized, compressed and strained. All of the following chemicals and materials were of analytical grade and used with no further treatment: absolute ethanol (~100 %, VWR chemicals), cyclohexane (99 %, Sigma Aldrich), hexadecane (99 %, Sigma Aldrich), pectinase from aspergillus aculeatus, endopolygalacturonase (activity 3800 units/mL, Sigma Aldrich), nickel (II) nitrate hexahydrate (99.99 %, Alfa Aesar),

Table 1
Selected examples and comparison of valorization of food waste at various process conditions.

Feedstock	Catalyst used	Reaction parameters		Products and composition	Reference
		Reaction conditions	Reaction systems		
Food waste	Ru/Al_2O_3, $NiMo/Al_2O_3$, Pd/Al_2O_3, Pt/Al_2O_3 and unsupported Fe.	350 °C, 60 min, 20 MPa of CO_2.	Batchwise, catalytic HTL	Bio-crude, 32–58 wt%	(Ahmed Ebrahim et al., 2022)
Biopulp	K_2CO_3 for HTL	APR-assisted HTL: 400 °C, 15 min, 2 MPa of N_2 (APR-C1 to C4)	Batchwise, APR-assisted catalytic HTL	Bio-crude, 30.7 wt% (C0–400 °C) and 49.3 wt% (C4–400 °C).	(Kohansal et al., 2021)
Biopulp	$NiMo/Al_2O_3$ for hydrotreatment (HT)	APR-assisted HTL: 350 °C, 15 min, 2 MPa of N_2 (APR-C1 to C3) + HT: 350 and 400 °C, 180 min, 8 MPa of H_2.	Batchwise, APR-assisted-HTL-HT	Hydrotreated bio-crude, 45.4 wt% (C3–350 °C) and 40.1 wt% (C3–400 °C).	(Kohansal et al., 2022)
Rice straw	Without catalyst	APR-assisted HTL: 350 °C, 30 min, 18–20 MPa of N_2 + APR-C1 to C3	Batchwise, APR-HTL	Bio-crude, 32.6 wt% (C0–350 °C) and 9.1 wt% (C3–350 °C). Bio-char 64.1 wt% (C3–350 °C).	(Harisankar et al., 2021)
Blackcurrant pomace	Without catalyst	APR-assisted HTL: 310 °C, 10 min, 1 MPa of N_2 + APR-C1 to C5	Batchwise, APR-HTL	Bio-crude, 26 wt% (C0–310 °C) and 31 wt% (C5–310 °C).	(Déniel et al., 2016)
Cooked food waste	Without catalyst	Slow pyrolysis: 300–500 °C, 60 min, 100 mL/min N_2	Continuous mode, slow pyrolysis	Bio-crude, 31 wt% (300 °C), 45 wt% (400 °C) and 41 wt%. (500 °C).	(Modak et al., 2023)
Food waste	Without catalyst	Slow pyrolysis: 400–600 °C, 15 min, 200 mL/min N_2	Continuous mode, slow pyrolysis	Bio-crude, 40.3 wt% (400 °C), 38.6 wt% (600 °C) and 33.4 wt%. (700 °C).	(Qing et al., 2022)
Prunus armeniaca L.	Without catalyst	Pretreatment-Slow pyrolysis: 350–600 °C, 30–150 min.	Semi-batch mode, slow pyrolysis	Bio-crude, 43.7 wt% (450 °C, 60 min).	(Fadhil, 2017)
Agro-food wastes	Without catalyst	Pretreatment-Slow pyrolysis: 300–600 °C, 30–60 min, 30 mL/min N_2	Continuous mode, slow pyrolysis	Bio-crude, maximum 42.4 wt% (500 °C, 60 min).	(Patra et al., 2021)

ammonium molybdate tetrahydrate (99.98 %, Sigma Aldrich) and alumina spheres (1.8/210, Sasol Germany). The Soxhlet extraction thimble 501 (made from pure alpha cellulose) was provided by VWR International.

2.2. Pretreatment and separation of biowaste

Extraction and separation experiments were carried out using various extraction techniques, see Fig. 1. In the extraction process, components were transferred from their source (e.g., slurry biowaste) to, in this case, a liquid bio-crude, and the remainder of which is referred to as residual solid. After extraction, the bio-crude components were then recovered by removing the solvent by means of vacuum evaporation. For separation and recovery, different pretreatment procedures were compared and categorized into conventional (Soxhlet pretreatment (PR-Sox), ultrasound assisted pretreatment (PR-UAE) and enzymatic-assisted pretreatment (EAE)) and hybrid-assisted pretreatment (HAE) (see detailed in Supplementary information).

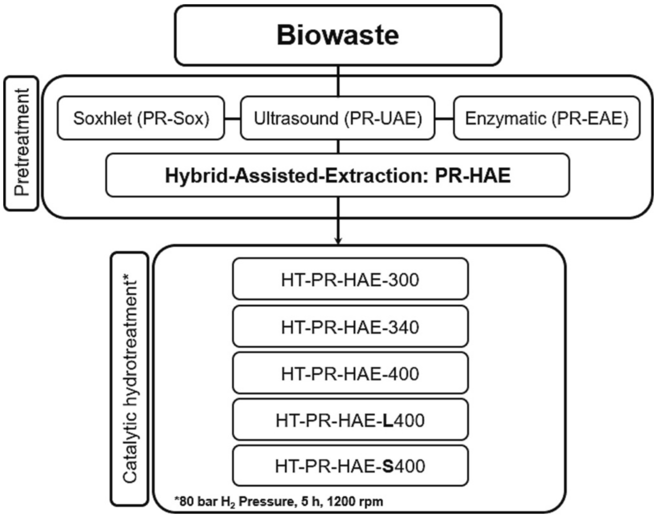

Fig. 1. Schematic diagram of both the pretreatment and post catalytic hydrotreatment experiments.

The yields of the different fractions and mass balances were determined based on the initial biowaste introduced according to the following equations:

$$\text{yield extracted bio}-\text{crude (wt\%)} = \frac{\text{mass of bio}-\text{crude after extraction (g)}}{\text{initial biowaste feed (g)}}\times 100 \tag{1}$$

$$\text{yield extracted residual solid (wt\%)} = \frac{\text{mass of dried solid residues after extraction (g)}}{\text{initial biowaste feed (g)}}\times 100 \tag{2}$$

$$\text{mass balance (wt\%)} = \frac{(\text{extracted bio}-\text{crude (g)} + \text{extracted residual solid (g)})}{\text{initial biowaste feed (g)}}\times 100 \tag{3}$$

2.3. Catalyst synthesis

A hydrotreating $NiMo/\gamma\text{-}Al_2O_3$ catalyst was prepared using incipient wetness impregnation. Alumina spheres ($\gamma\text{-}Al_2O_3$) were calcinated at 450 °C for 4.5 h in air and then crushed and sieved to a ~250 μm. A mixture of metal precursors of nickel nitrate hexahydrate and ammonium molybdate tetrahydrate were dissolved in ethanol while stirring, after which the sieved alumina support was added gradually with constant stirring. After mixing for 2 h, ethanol was evaporated at 60 °C. Finally, the impregnated catalyst was dried at 110 °C for 12 h before being calcined at 450 °C for 4.5 h.

2.4. Catalytic hydrotreatment procedure

The hydrotreatment experiments were carried out in a 450-mL stainless steel Parr reactor. Prior to each experiment, the catalyst was activated at 300 °C under hydrogen pressure of 20 bar for 3 h. 1 g of $NiMo/\gamma\text{-}Al_2O_3$ catalyst, 55 g of hexadecane and 10 g of pre-treated biowaste (namely liquid bio-crude and residual solid) were placed in the reactor and sealed. After purging with nitrogen and hydrogen leak testing, the pre-treated biowaste was hydrotreated in the temperature

Table 2

Catalytic hydrotreatment of the pretreated biowaste and the operational conditions used.

Experiment	Operating conditions M^a–T^b–P^c–t^d–W^e
HT-PR-HAE: jointly hydrotreated	
HT-PR-HAE-300	HAE–300–80–5–W_{10}
HT-PR-HAE-340	HAE–340–80–5–W_{10}
HT-PR-HAE-400	HAE–400–80–5–W_{10}
HT-PR-HAE-L/S: individually hydrotreated	
HT-PR-HAE-L400	HAE-L–400–80–5–W_{10}
HT-PR-HAE-S400	HAE-S–400–80–5–W_{10}

[a] Method used: jointly or individually extracted liquid bio-crude and/or solid residues (M).

[b] Temperature applied (°C).

[c] H_2 pressure applied (bar).

[d] Residence time (h).

[e] wt.% of catalyst loaded based on 10 g of pre-treated biowaste.

range of 340–400 °C and at a pressure of 20–35 bar for 5 h (Table 2); the rate of stirring was 1000 rpm. Once the reaction was complete, the reactor was cooled to room temperature and the gaseous, bio-oils and hydrochar products were recovered as depicted in Fig. S1.

2.5. Analysis of the feedstock and products

The moisture content, volatile carbon, fixed carbon and ash content of the bio-waste were determined using a thermogravimetric technique (TGA/DSC, 3+ Star system, Mettler Toledo, US). The boiling point distribution and ash content of the products from the pretreatment and hydrotreatment experiments were also analysed using a TGA system. The ash content of the dried bio-waste was confirmed using the ASTM D482 standard method; the pH of both the extracted bio-crude and hydrotreated bio-oil samples were determined by a pH meter (704 pH meter, Metrohm). The elemental composition of the bio-waste, bio-crude, hydrotreated bio-oil and residual solid samples were monitored using a CHNS elemental analyser (Vario MACRO cube, Germany), while the oxygen content was determined by the difference according to the following equation:

$$\text{oxygen (wt.\%)} = 100 - (\text{C} + \text{H} + \text{N} + \text{S})\ \text{(wt.\%)} - \text{Ash (wt.\%)} \tag{4}$$

The higher heating values (HHV) of the bio-waste and all of the products were calculated based according to:

$$\text{HHV (MJ/kg)} = 0.335\ \text{C} + 1.423\ \text{H} - 0.154\ \text{O} - 0.145\ \text{N} \tag{5}$$

The energy recovery (ER) from the pretreatment was calculated thus:

$$\text{ER (\%)} = \frac{\text{HHV}_{\text{pretreated product}}}{\text{HHV}_{\text{biowaste}}} \times \text{products yield} \tag{6}$$

The crude fat content (CF) was determined by extracting the fat from the dried bio-waste with a hexane solvent: 5 g of dried bio-waste was subjected to approx. 90 mL of hexane solvent for 6 h. The solvent was then removed by means of vacuum rotary evaporation. The flask was placed in an oven at 70 °C to dry the contents until a constant weight was reached. The crude protein content (CP) was estimated by multiplying the nitrogen content of the bio-waste by a 6.25 (Kohansal et al., 2022; Mariotti et al., 2008). Following the US Food and Drug Administration (FDA) [21 CFR 101.9(c)(6)(i)-(iv)] instructions, the carbohydrate content was calculated based on:

$$\text{Carbohydrate (\%)} = \text{Combustibles (\%)} - (\text{CF} + \text{CP})\ (\%) \tag{7}$$

The extracted bio-crude and hydrotreated bio-oil products were analysed via Agilent comprehensive two-dimensional gas chromatography (GCxGC, Agilent Technologies, Santa Clara, CA, USA) coupled to two different detectors, a flame ionization detector (FID) and a mass spectrometry detector (MSD). The column set consisted of a moderately polar VF1701ms column (30 m × 0.25 mm × 0.25 μm) paired with a non-polar DB-5 MS UI column (3 m × 0.15 mm × 0.15 μm). The column flow was set at 0.8 mL/min, and the temperature of the injector port and MS interface was set at 280 °C. The oven temperature programme was set initially at 40 °C and held for 1 min, before being heated up to 280 °C at 3 °C/min; the modulation time was 6 s. The data were processed via GC image 2.5 (Zoex Corporation) using GC Project and Image Investigator functions. In order to quantify the composition of the monomers in the products, an internal standard was used to measure the relative responses of the monomers, as described in our previous study (Achour et al., 2023).

The gaseous products were analysed by a calibrated GC (456-GC, Bruker) equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD). The detectors were connected to a BR-SWax column (30 m × 320 μm × 1 μm) and a Molsieve 5 Å column (1 m × 3.175 mm), respectively. The gaseous components H_2, CO, CO_2 and CH_4, along with the C_2+ light hydrocarbons, were separated and quantified using reference mixtures. The solids from the hydrotreatment experiments were washed with acetone to remove the adsorbed organic components. The soluble oligomers were extracted by suspending 0.5 g of solids in 15 mL of DMSO and thereafter stirred for 24 h at room temperature. Following filtration of the extracted solution, the hydrochar solids were washed with acetone and dried overnight at 80 °C. The weight difference between the solids before and after the washings was assumed to be the weight of soluble oligomers. The water content in the hydrotreated bio-oils was quantified using a Karl Fischer instrument (Metrohm Titrino 807 KF), as described in our previous study (Achour et al., 2023). All analyses were performed twice, with the average value being given.

The conversion, hydrochar yield, mass balance, monomer yield and the degrees deoxygenation (De-O) and denitrogenation (De-N) were calculated as follows:

$$\text{Conversion (wt.\%)} = \frac{\text{dried extracted bio} - \text{crude} + \text{dried extracted solid (g)} - \text{hydrochar formed (g)}}{\text{dried extracted bio} - \text{crude} + \text{dried extracted solid (g)}} \times 100 \tag{8}$$

$$\text{Hydrochar yield (wt.\%)} = \frac{(\text{total solid fraction (g)}) - (\text{soluble solid (g)} + \text{catalyst (g)})}{\text{dried extracted bio} - \text{crude} + \text{dried extracted solid (g)}} \times 100 \tag{9}$$

$$\text{Mass balance (wt.\%)} = \frac{\sum \text{products (g)}}{\text{dried extracted bio} - \text{crude} + \text{dried extracted solid (g)}} \times 100 \tag{10}$$

$$\text{Monomer yield (wt.\%)} = \frac{\text{monomer (g)}}{\text{dried extracted bio} - \text{crude} + \text{dried extracted solid (g)}} \times 100 \tag{11}$$

Table 3
Properties of the biowaste sourced from Renova's slurry food waste.

Analysis	Value
Proximate analysis (wt%)	
Moisture	78.0
Ash[a]	4.9
Volatile matter[b]	79.0
Fixed carbon[b]	15.9
Elemental analysis[b] *(wt%)*	
C	49.4
H	8.6
N	3.3
S	0.2
O[c]	33.5
Composition analysis[a] *(wt%)*	
Crude fat	19.0
Crude protein	20.6
Carbohydrate[c]	55.3
Higher heating value[a] (MJ/kg)	23.2

[a] Dry basis ASTM D482.
[b] Dry ash-free.
[c] Calculated by difference.

$$\text{De} - \text{O}\ (\%) = \left(1 - \frac{\text{O upgraded oil}}{\text{O bio} - \text{crude}}\right) \times 100 \tag{12}$$

$$\text{De} - \text{N}\ (\%) = \left(1 - \frac{\text{N upgraded oil}}{\text{N bio} - \text{crude}}\right) \times 100 \tag{13}$$

3. Results and discussion

3.1. Characterization of the bio-waste

The proximate and ultimate analyses of the biowaste, including the biochemical compositions and HHV, are reported in Table 3. The proximate analysis shows the biowaste to be composed of 79.0 wt% volatile carbon, 15.9 wt% fixed carbon and 4.9 wt% dry ash (Confirmed by TGA: the red line in Fig. S2). The elemental analysis demonstrates that carbon, oxygen and nitrogen account for 49.4, 8.6 and 3.3 wt.% of the biowaste, respectively. The calculated HHV based on dry biowaste is about 23.2 MJ/Kg. The biochemical composition of the biowaste is 20.6 wt.% crude protein, 19.0 wt% crude fat and 55.3 wt% carbohydrate. The resultant analysis indicates that the actual characteristics of biowaste possess great potential for being valorised and thereby contribute toward a sustainable and circular bioeconomy.

3.2. Pretreatment of bio-waste and analysis of products

3.2.1. Pretreatment of bio-waste

Four extraction techniques were carried out, as described in Section 2.2 (Fig. 1). A key purpose of the pretreatment process was to demonstrate how the extracted bio-crude can be converted into value-added chemicals and fuels. To achieve this, it is of importance to develop efficient and selective procedures to stabilize the upstream components by altering the reactivity of certain components (i.e., compounds containing O and N). This allows the stabilized upstream products to be subsequently upgraded (De-O and De-N) into lighter components to improve both carbon utilisation and waste management capacities. The pretreatment conditions are essentially crucial in optimising the selectivity of the organic and inorganic compounds extracted from bio-crude

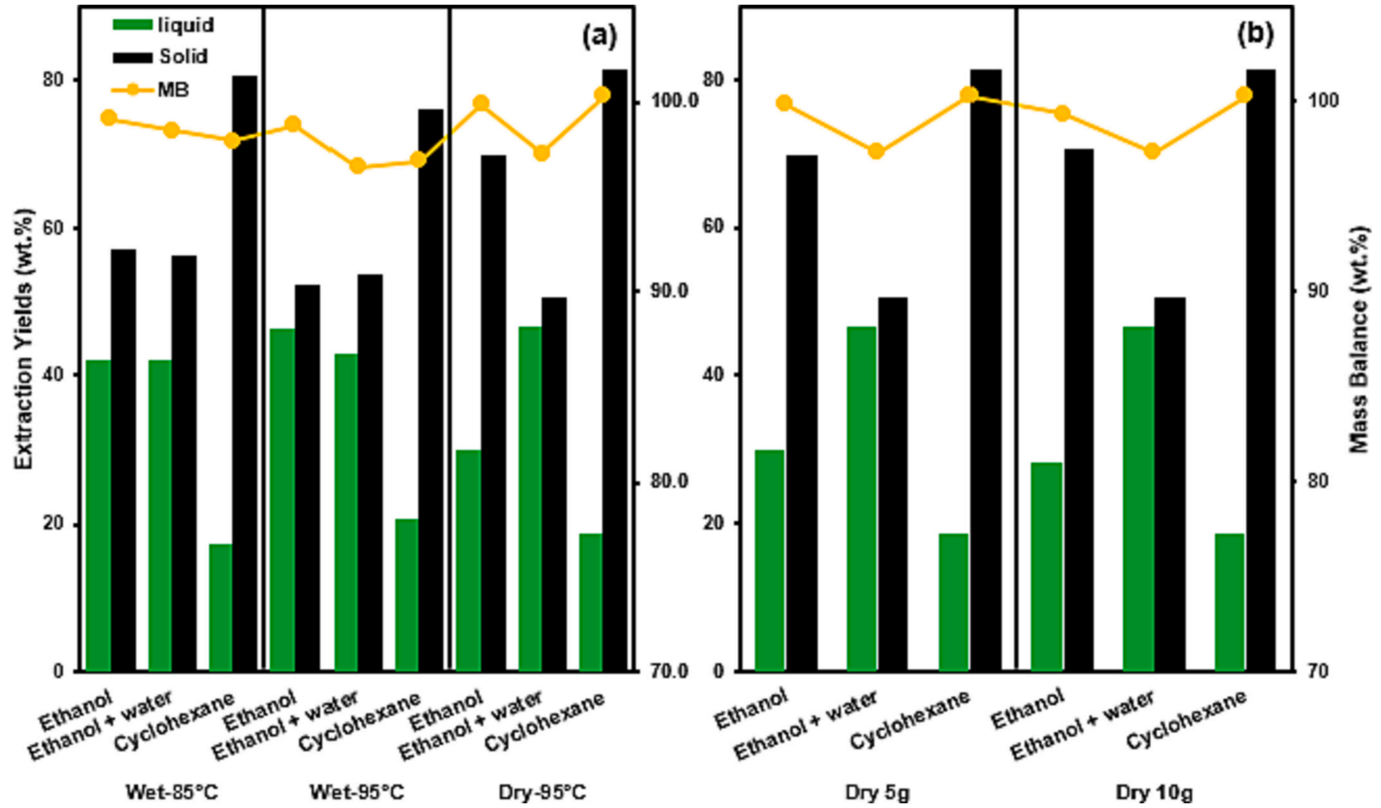

Fig. 2. Recovery of bio-crudes and residual solids using Soxhlet pretreatment (PR-Sox) over various solvents (a) for wet biowaste at 85 °C, wet biowaste at 95 °C and dry biowaste at 95 °C. (b) Feedstock loading effect on the extracted bio-crude and residual solid using Soxhlet pretreatment (PR-Sox) (a) 5 g dry biowaste and (b) 10 g dry biowaste at 95 °C.

and residual solid products. The resultant products highlight the importance of the state of the bio-waste (dryness/wetness), solvent polarity and temperature pretreatment in enhancing the recovery of bio-crude during the extraction process.

The efficiency of the pretreatment process was scrutinised by determining the product distributions, elemental and chemical compositions, mass balance and energy recovery of the products. The overall mass balance for all pretreatment experiments was found to be within the range 96.3–100.6 wt%. Fig. 2 shows the product distributions obtained from the Soxhlet process (PR-Sox) in various solvents under different conditions. It is apparent that the results are favourable for higher yields of residual solids, which is associated with solvent polarity, solvent boiling point and the wetness/dryness of the bio-waste. These results suggest that the solid solutes are less likely to be soluble in non-polar solvents (e.g., cyclohexane), whereas higher yields of bio-crude were observed with large dipole moments in polar solvents. It demonstrated that the Soxhlet process, with ethanol and co-solvent water-ethanol, is able to achieve high and comparable bio-crude recoveries of 46.4 and 46.7 wt% for both wet and dry bio-waste at 95 °C, respectively (Fig. 2a). These solvents are widely employed due to their high polarity, low boiling point, reasonable cost, and non-toxic properties. One exception to these results was observed in ethanol without water as solvent under dry bio-waste condition, indicating an obvious discrepancy on bio-crude recovery that dropped from 46.4 to 30 wt% compared to wet bio-waste condition (Fig. 2a). This implies that water could be effective not only in promoting hydrolysis but also in maintaining a higher level of solubility of the bio-waste (Zhang et al., 2018). In addition to the high polarity that facilitates the extraction, the low boiling point of high polar also enable a less energy-intensive recovery of extractives. Apart from the recovery of products, the mass balance was affected slightly while using polar solvents but was consistently low at 96.6 % based on dried bio-waste. The recovery of both bio-crude and residual solid products was also evaluated by varying the dry bio-waste loadings at 95 °C, as shown in Fig. 2b. Higher loading of dry bio-waste showed no significant improvement in performance compared to low loading. The bio-crude and residual solid yields, along with the mass balance, were all within 0.8–5.0 % STD differences.

Bio-waste was also pretreated using ultrasound-assisted extraction (PR-UAE) with polar and non-polar solvents. The experiments were conducted at 50 and 55 °C with reaction times of 15 and 30 min, because a main aim of this study was to quantify the impact of ultrasound high-frequency at lower temperatures and shorter residence times. Fig. 3 shows that the ultrasound experiments resulted in significant increases in the yields of residual solids of up to 73 wt%, with the least yield of bio-crude being 36 wt% at 55 °C for 0.5 h. Although the Soxhlet process (PR-Sox, Fig. 2a), together with polar solvents, affected the extraction of bio-crude (46.7 wt% at 95 °C for 5 h) significantly, the ultrasound process provided excellent recovery of bio-crude that yielded up to 33.4 wt% at much lower temperatures (50–55 °C) and residence times (15–30 min). The results revealed that the ultrasound pretreatment, along with a non-polar solvent (e.g., cyclohexane), elevated the bio-crude content substantially to as high as 31 wt% (50 °C for 0.5 h) compared to the bio-crude obtained using Soxhlet pretreatment (18.2 wt% at 95 °C for 5 h). Moreover, they also demonstrated that the reason why ultrasound-assisted pretreatment improved the effectiveness of pretreatment could be associated with the mechano-acoustic effects of ultrasound.

Perhaps ultrasound technology, used in combination with enzymatic pretreatment, can lead to a high extraction efficiency of bio-crude. It was therefore suggested that an enzyme (such as pectinase) be involved to accelerate the degradation and depolymerization of the cell wall structure (e.g., polysaccharides), which would promote the release of linked compounds and thus enhance extraction of the bio-crude. Since the solvent was determined as being the major factor in extracting a higher fraction of bio-crude, the enzymatic-assisted experiment was performed based on solvent extraction by varying the polarity of the solvent. Moreover, it was also suggested that the incubation and ultrasound techniques be compared for their mechano-acoustic effects over polar solvents at 55 °C for 30 min. As Fig. 3c shows, the amount of bio-crude produced was found to slightly increase with the enzymatic-incubation process and the polar solvents used. During the vibration extraction-process, these mechanical effects, in turn, cause the breakdown of particles, peeling and erosion phenomena and hence, the improved extraction rate and yield (Oroian et al., 2020). It is important to indicate that a slight decrease in the yield of bio-crude in an ultrasound-assisted process might be due to a difference in the type of vibration (mechanical vs. frequency resonance) that affects the degradation rate of cells attached to surfaces. Liao et al. reported that high-intensity ultrasound could also induce the formation of various free radicals, which could react with polyphenols leading to numerous undesirable reactions such as polymerization (Liao et al., 2015). Therefore, the optimum pretreatment conditions for hydrolysis were obtained at 55 °C with an incubation time of 30 min, yielding 36.6 and 67.3 wt% of bio-crude and

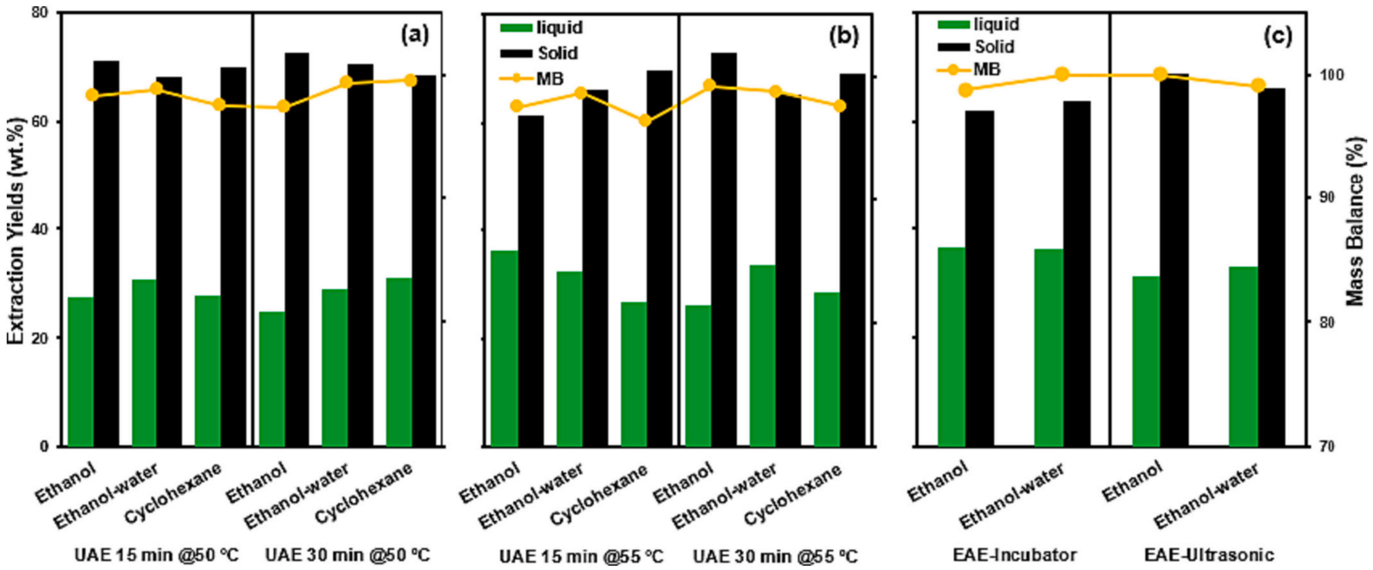

Fig. 3. Bio-crudes and residual solids extracted using ultrasound pretreatment (PR-UAE) over various solvents. Effect of time at (a) 50 °C, (b) 55 °C and (c) effect of incubator versus ultrasonic equipment at 55 °C for 30 min.

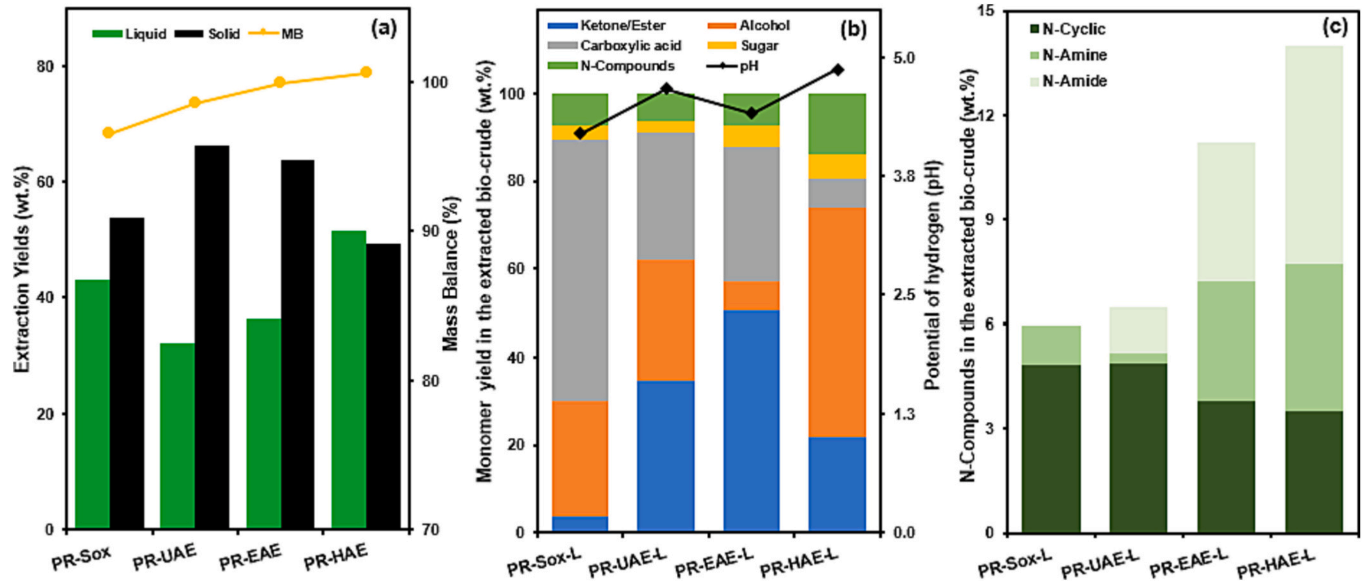

Fig. 4. The influence of the extracted bio-crudes and residual solids on hybrid-assisted pretreatment (PR-HAE) compared to the individual pretreatment methods (a), GCxGC composition of the bio-crudes extracted from the pretreated biowaste (b) monomer yield and pH (c) N-compounds in the extracted biocrude.

residual solids, respectively. Remarkably enough, the ethanol-water solvent showed an excellent mass balance of 99.9 % compared to the 98.8 % of the ethanol solvent. Note that in a recent published study on the effect of incubation duration (up to 20 h) after pulsed electric field (PEF) treatment on the release of carbohydrates from microalgae, the amount of carbohydrate resealed after treatment does not increase further with incubation time (Silve et al., 2018). The longer incubation used in this study, which is less prone to induce intercellular damages might partially explain the observed no differences in bio-crude yields (Fig. 3b and c).

Fig. 4a illustrates a comparative evaluation of the recovery of bio-crude and residual solids between the hybrid-assisted pretreatment and the conventional methods used above. The hybrid-assisted process was performed by combining the enzymatic-assisted process with incubation at 55 °C for 2 h, and then applying the Soxhlet method at 95 °C for 5 h. The yield of the extracted bio-crude subjected to the novel hybrid-assisted method was enhanced to 51.5 wt%, thereby showing improved performance over the conventional Soxhlet (42.9 wt%), enzymatic-assisted (36.3 wt%) and ultrasound-assisted (32.4 wt%) methods, respectively. In contrast, the formation of the solid residue decreased noticeably for the hybrid-assisted method: down to 49.2 %. The increasing trend in the yield of bio-crude for the hybrid-assisted process may have been caused, and facilitated, by various chemical reactions that occurred in parallel and/or in series: decarboxylation, hydrolysis, Strecker degradation in the Maillard reaction, isomerisation, rehydration, Amadori rearrangement, self-condensation, and etc. (Li et al., 2022). As described in the experimental section, the parameters which are of paramount importance for enhancing bio-crude production are the solvent solubility effect, temperature, and residence time. Zeb et al. recently reported that the density, solubility and dispersion properties of solvent/co-solvent affect the decomposition of feedstock macromolecules to promote low molecular-weight liquid in a liquefaction process (Zeb et al., 2017). The consequence of the low solubilities and dipole moments of cyclohexane and ethanol (i.e., dried-biomass) is that the ethanol-water co-solvent is therefore identified as being an eco-friendly method for highly extracting bioactive compounds and bio-crude. In other words, it indicates the effect of higher solubility of polysaccharides and other heavy compounds in water (Bello et al., 2018). Interestingly, this further confirms that for the same combination of biowaste-solvent, namely wet biowaste-ethanol vs. dried biowaste-ethanol-water, showed consistent results, where the bio-crude yield was highly achieved (Fig. 2a). Hence, the bio-crude yield could be mainly attributed to solvent properties since the reaction rate can strongly affected by the mass transfer between phases. Yet, the bio-crude yield obtained from HTL, and pyrolysis depends on several process parameters, including temperature, pressure, residence time, stirring, flow rate, biomass particle size, heating and cooling rates, reactor geometry, and biomass-to-solvent ratio which render the results difficult to interpret. For example, bio-crudes yields presented in Table 1 showed an increase to certain temperature, but further increase in the temperature resulted in decreasing of bio-crude yield and enhancing coke formation and gasification (Harisankar et al., 2021; Izumi et al., 2010; Modak

Table 4
Bio-crudes to residual solids ratio (dry basis) for different pretreatment conditions from food waste.

Pre-treatments	Solvents/co-solvents	Ratio biocrude/solid[a]
PR–Sox–Wet–85 °C	Ethanol	0.73
	Ethanol-water	0.75
	Cyclohexane	0.21
PR–Sox–Wet–95 °C	Ethanol	0.89
	Ethanol-water	0.80
	Cyclohexane	0.27
PR–Sox–Dry–95 °C–5 g	Ethanol	0.43
	Ethanol-water	0.92
	Cyclohexane	0.23
PR–Sox–Dry–95 °C–10 g	Ethanol	0.40
	Ethanol-water	0.87
	Cyclohexane	0.22
PR–UAE–15 min–50 °C	Ethanol	0.38
	Ethanol-water	0.45
	Cyclohexane	0.40
PR–UAE–15 min–55 °C	Ethanol	0.59
	Ethanol-water	0.49
	Cyclohexane	0.39
PR–UAE–30 min–50 °C	Ethanol	0.34
	Ethanol-water	0.41
	Cyclohexane	0.45
PR–UAE–30 min–55 °C	Ethanol	0.36
	Ethanol-water	0.51
	Cyclohexane	0.41
PR–EAE–Incubator–30 min–55 °C	Ethanol	0.59
	Ethanol-water	0.57
PR-HAE	Ethanol-water	1.05

Note: gases might be produced negligibly.
[a] On dry basis.

et al., 2023; Qing et al., 2022). That is one of the reasons, different pretreatments were adopted in this study, and the effect of the enzyme and co-solvent composition were investigated. As reported in Fig. 4a, where it is possible to show that hybrid-assisted extraction has capacity to reach such a threshold. Thanks to the hybrid-assisted extraction. The possibility of performing multi-component reactions under mild conditions with bio-waste as a greener solvent as well as catalysts could enhance their efficiency from an economical point of view. These reactions offer frequent benefits in preparative procedures, such as environmental compatibility, simplifying work-up, formation of cleaner products, enhanced selectivity, reduction of by products, and much improved reaction rates (Tanaka and Toda, 2000).

Table 4 provides details on bio-crude to solid ratios for all above-mentioned pre-treatments. The bio-crude/solid ratio is another relevant marker to identify the efficiency and efficacy of pretreatment for bio-oil energy production from organic waste. Note that the produced gases were merely negligible in comparison to thermochemical methods (Modak et al., 2023). Comparing the bio-crude/solid ratios, a great difference appears, particularly in the co-solvent was enhanced for PR-HAE (bio-crude/solid: 1.05), PR-Sox (0.92), PR-EAE-incubation (0.57) and PR-EAE-ultrasound (0.47), respectively. This concurs with the large dipole moments, solubilities and changes of chemical compositions of bio-waste during the particular pretreatment. Except the bio-crude/solid ratios were nearly same and low at all conditions for PR-UAE. This could confirm Liao et al. suggestion that high-intensity ultrasound induces the formation of various free radicals, which react with polyphenols leading to numerous undesirable reactions such as polymerization (Liao et al., 2015). Accordingly, the bio-crude/solid ratio and bio-crude selectivity clearly identify the potential benefits of emerging pretreatment, especially when using an appropriate co-solvent. The results suggest, to a certain extent, that water is a sustainable solvent for the efficient extraction of bio-crude: it has double hydrogen atoms bonded to an oxygen, whereas ethanol has only one hydrogen and an alkyl group bonded to an oxygen atom. To clarify the effect of pretreated bio-waste, the elemental, chemical composition and monomeric analysis in the following section provide certain comprehensive explanations. It is worth mentioning that the impact of post-treatments, such as the co-solvent HTL process, used to deeply liquefy the residual solid, was not examined in this study and left to be determined in future studies. Furthermore, the bio-crude/solids ratios can be adjusted speculatively to certain degree by altering the water/ethanol ratios, introducing other types of enzymes, using bio-waste as received, and varying the operating conditions, respectively (Vitasari et al., 2011).

3.2.2. Analysis of the bio-crudes and residual solids produced

The elemental and chemical compositions of the extracted bio-crude and residual solids were investigated. The elemental composition was determined after each pretreatment of the bio-waste and extracted bio-crude, along with the residual solids samples, and is presented in Table 5. The elemental composition showed a trend of higher efficiency of heteroatom removal (De-O and De-N) associated with the pretreatment and products. When subjected to enzymatic-assisted (PR-EAE) and hybrid-assisted (PR-HAE) pre-treatments, the carbon and nitrogen contents of the extracted solids were noticeably higher than those of the non-enzymatic (PR-Sox-S and PR-UAE-S), whereas lower contents of oxygen were found for residual solids treated with the enzyme (PR-EAE-S and PR-HAE-S, Table 5). However, the opposite trend was revealed in the bio-crude products, as reported in Table 5. This indicates the importance of PR-HAE in the selective decomposition of bio-waste into intermediates components that are associated with contents of carbon, oxygen, and nitrogen, and particularly so with the higher content of the latter in the residual solids. These results are in accordance with Kaushik et al., who studied the co-production of hydrochar and bio-oil in the enzyme-assisted pre-treatment of food waste (Kaushik et al., 2014). The carbon (C: 43.7 wt%) and nitrogen (N: 3.5 wt%) contents of the hydrochar produced were higher than for those not pre-treated with the enzyme (C: 38.2 and N: 0.5 wt%) at 150 °C, 7 bar for 20 min. However, a lower content of oxygen (46.3 wt%) was obtained in the enzyme-assisted pre-treatment compared to those not pre-treated with enzyme (O: 54.7 wt%), respectively (Kaushik et al., 2014). These demonstrate that an enzymatic pretreatment is a highly efficient approach to removing, to a certain extent, the nitrogen content (De-N) before bio-crude upgrading. However, a common challenge confronted with the enzymatic pretreatment is the high content of oxygen in the upgrading process, overwhelmingly resulting from high yield of oxygenated in bio-crude, as later demonstrated by GCxGC analysis. Note that only 68 wt% of the total compositions in the form of monomer components were quantified by GCxGC analysis (Fig. 3S). Following the enzymatic hydrolysis reaction, the results suggest that long chain carbohydrates were cleaved down into simpler sugars and, subsequently, the fragmentation of sugar became more favourable, giving rise to different soluble products such as furfural derivatives, organic acids, aldehydes and alcohols. This could also indicate that the different distributions of bio-crudes and residual solids were most likely linked to their physicochemical properties and the pretreatment conditions. The calculated calorific values (HHVs) of the extracted residual solids increased with increasing carbon contents, suggesting higher degrees of carbonisation being achieved. The HHV values associated with the extracted solids ranged from 21.8 (PR-Sox-S) to 27.8 MJ/kg (PR-HEA-S, Table 5) and considerably improved the energy recovery, up at 60.3 %, for the hybrid-assisted pretreatment (PR-HAE). Sulphur contents lower than 0.1 and 0.27 wt % were quantified for the extracted bio-crude and residual solid, respectively. No specific trend for ash content could be observed within a range of 0.96 to 3.39 wt%.

Fig. S4 shows a conceptual van Krevelen diagram for the extracted bio-crudes and residual solids, where the deoxygenation (De-O), denitrogenation (De-N) and chemical transformations of the carbon rich materials are clearly promoted for all pre-treatments. Higher H/C and O/C atomic ratios increased linearly for the extracted bio-crudes, especially for those pretreated with enzyme (PR-EAE-L and PR-HAE-L, Fig. S4a), whereas no H/C atomic changes were observed for the residual solids (triangles, H/C: 2.3). Remarkably enough, the O/C atomic ratios were lower than 0.8 for the residual solids, particularly for the hydride-assisted pretreatment (PR-HAE-S, O/C: 0.33). These results

Table 5
Elemental analysis, ash content, higher heating value and energy recovery of extracted bio-crudes and residual solids after the pretreatment of biowaste using various extraction methods.

Samples	C (wt.%)	H (wt.%)	N (wt.%)	S (wt.%)	O (wt.%)	Ash (wt%)	HHV (MJ/kg)	ER (%)	De-N (%)
Biowaste	49.4	8.6	3.3	0.20	33.5	4.9	23.7	–	–
PR-Sox-L	43.9	10.8	1.7	0.03	35.0	2.4	21.4	38.6	50.2
PR-Sox-S	40.1	7.9	2.7	0.12	41.1	2.2	21.8	39.4	19.4
PR-UAE-L	36.8	10.6	1.8	0.10	38.4	3.4	19.3	26.3	46.7
PR-UAE-S	49.6	9.6	2.4	0.10	29.2	2.5	23.6	36.1	27.9
PR-EAE-L	33.3	9.9	1.5	0.05	51.7	0.9	19.2	29.3	54.6
PR-EAE-S	50.6	9.7	4.6	0.20	29.9	1.4	26.5	40.4	–
PR-HAE-L	31.5	9.4	0.6	0.02	52.6	1.6	17.6	38.0	83.3
PR-HAE-S	52.4	10.1	5.8	0.27	22.8	2.4	27.8	60.3	–

indicate that the less oxygen-rich residual solids (reduced H/C and O/C ratios) may follow a carbonisation path, which correlated well with the calculated HHVs (Table 5). In Fig. S4b, the residual solids show a higher N/C atomic ratio when the bio-waste is pre-treated using the hybrid-assisted method (PR-HAE-S, N/C: 0.1). However, the lowest N/C atomic ratios, ranging from 0.06 to 0.015, were observed for the bio-crudes, representing up to 83.3 % degree of De-N when using the hybrid-assisted method (PR-HAE-L). It is worth mentioning here that a reverse sigmoid shape between the O/C and N/C ratios was observed for the bio-crudes. These results suggest that the hybrid-assisted pretreatment (PR-HAE) demonstrated a higher removal efficiency of nitrogen associated with the bio-crude, which was significantly adsorbed into the extracted residual solid. According to literature (Kaushik et al., 2014; Kondusamy and Kalamdhad, 2014; Patra et al., 2021; Saengsuriwong et al., 2021), protein and carbohydrate derivatives were found to dissolve favourably in aqueous phase at mild HTL processing conditions (e.g., >300 °C). These resulted in higher N-concentrations (4 to 10 wt% in bio-crudes). Based on our findings, HTL operating temperature (<200 °C) could be an alternative solution to promote a controllable decrease of the N content when the temperature decreases. Thus, the pretreatment method can be further selective toward a particular application, such as biofertilizer or biochar, for the residual solids obtained, while improving the H/C and marginal O/C ratios is suitable for advanced biofuels applications.

In addition to the elemental composition, the monomer compositions of the bio-crudes after each pretreatment were investigated using GCxGC-MS analysis. Fig. 4b and c displays the organic compounds identified, which are classified into their functional groups, e.g., carboxylic acids, alcohols, ketones, aldehydes, esters, sugars and nitrogenous compounds. In accordance with TGA analysis, about 68 wt% of the total compositions in the form of monomer components were quantified by GCxGC analysis (Fig. 3S). As shown in Fig. 4b and c, the recovery of sugars remains comparatively low regardless of the pretreatment used. The average total sugar yield was 2.6 wt% for PR-UAE-L, followed by 3.3, 4.9 and 5.5 wt% for PR-Sox-L, PR-EAE-L and PR-HAE-L bio-crudes, respectively. These results suggest that sugars from carbohydrates offer a clear insight into the chemical transformation that occurs during pretreatment and gives rise to various different soluble products, such as alcohols. Upon PR-HEA pretreatment, alcohols were obtained in higher yields that might have resulted predominantly from the cleavage of the monosaccharides identified, such as 1,5-anhydro-ᴅ-mannitol, ethyl α-d-glucopyranoside, polygalitol, 3,4-altrosan and sorbide-derivatives. With PR-Sox and PR-EAE pre-treatments, lower yields of alcohols can be explained by the difficulty in breaking down the most dominant dimers and trimers saccharides identified in bio-crudes, namely 4-O-beta-D-galactodosyl-ᴅ-glucopyranose, maltose and melezitose. Although the bio-crude could be improved, the solids development during the decarboxylation was probably due to the presence of a large amount of pyrolytic sugars in water-soluble fraction that critically weakens the bio-crudes extraction (Zhang et al., 2018). Considering that the conversion of the carboxylic acids found in bio-crude into ketones via decarboxylation is highly efficient approach for the bio-oil upgrading. The highest yield of carboxylic acids, sourced from lipids, was easily extracted using the PR-Sox method, whereas a drastic decrease in their yields was observed for PR-UAE, PR-EAE and PR-HAE pre-treatments. This result suggests that the reactivity of the carbonyl group within other given oxygenated components can alter the composition of bio-crudes (Román-Leshkov and Davis, 2011). In the case of PR-EAE pretreatment, it was suggested that the highest yield of ketones was the result of the cross-ketonization of two reactive carboxylic acids. Regarding PR-HAE pretreatment, it is reasonable to suppose that the highest alcohols yields can also be produced via protonation of the carbonyl group that subsequently forces away the alcohol group. It is therefore obvious that the pretreatment processes undertake multiple reaction pathways that reveal the respective effects the oxygen lone pairs (e.g., carboxylic acids and alcohols) and C═O double bonds have upon the mechanism. This means that a great number of different approaches have been made in this regard to understand the importance of combining PR-EAE and PR-Sox pre-treatments. As the results show, the association step of the pretreatment processes altered the biochemistry and chemistry of the bio-crudes significantly, see Fig. 4b.

As described earlier in Table 3, the biochemical composition of the bio-waste is of 19.0 wt% crude fat and 55.3 wt% carbohydrate. The production of short (C_2-C_4) and long-chain carboxylic acids, including fatty acids, were mainly observed through the PR-UAE (28.9 wt%), PR-EAE (31.0 wt%) and PR-Sox (59.4 wt%). Whereas a combination of these pretreatments is preferably suggested to produce alcohols. More importantly, this provides insights and suggests on future directions of producing alcohols for food waste utilisation. Although theoretically alcohol production from biowaste appears to be feasible, however in practice, it requires further research to conclude. This also suggests that effective utilisation of food wastes in alcohol production can significantly affect the production economics by not requiring to grow crops for raw materials or acquiring biomass at a high cost. Biowaste materials also consist of organic matter that contains N, including aliphatic proteins linked by the condensation of amine and carboxylic acid. Nitrogenous organic compounds identified by GCxGC analysis were categorized as N-amine, Ni-amide and N-cyclic groups, see Fig. 4c. Consequently, PR-EAE and PR-HAE pre-treatments exhibited compounds with higher amounts of N than those pretreated without enzymes (PR-Sox and PR-UAE), comprised of six-fold N-amino/amide and their derivatives (light green, Fig. 4c), respectively. These results suggest that countless conversion reactions, via cleavage of C—N bonds in the bio-crudes, have resulted from the aldol reaction, Strecker reaction, Michael tandem reaction, allylation of aldehydes, reduction of N-Aryl mines, opening of epoxides, asymmetric hydrogen transfer and N-specific nitrosobenzene reaction with aldehydes (Reddy et al., 2022). It was more apparent for the N-amide yield, which was more dominant than the N-amine and N-cyclic components in PR-HAE pretreatment (Fig. 4b). The higher yield of N-amide in the PR-HAE showed more pronounced chemical inertness and stability than the carboxylic acids and other carbonyl derivatives (ketones/esters), due to its lower electrophilicity derived from resonance effects (Cabrero-Antonino et al., 2020).

3.2.3. Reaction pathway

Based on the above analysis, there are diverse reactions of chemicals components during the pretreatment process and several possible reaction pathways for the decomposition of biowaste have been reported. However, mechanism explanation is limited and relies on GCxGC analysis in this study to explain the reaction pathways that connected the chemical products obtained from the biowaste. Particularly the generated intermediate substance that are chemically unstable and prone to undergo decomposition, deamination, dehydration, reforming, or polymerization. While this approach, GCxGC analysis, fails to describe the undetectable reactive condensed phase, particularly the molecular-level intermediates pathways and barriers for driving nitrogen to each phase. With this respective, it is better understanding how biomolecules block, mainly consisted of lipids, proteins and carbohydrates, can be hydrolysed to their precursors mono-units to form the bio-crude, and specifically how nitrogen becomes incorporated into the bio-crude and residual solids.

In this study, bio-waste contains significant quantity of lipids (Table 3). Lipids can initially undergo hydrolysis to produce higher fatty acids, and glycerol under all pretreatment conditions, particularly higher under PR-Sox conditions. Under enzymatic pretreatment, part of higher fatty acids are converted directly into alcohols and ketones/aldehydes and esters through deoxygenation, hydrolysis and esterification, respectively. For PR-EAE, we detect a pronounced increase of the fatty acid esters, which is remarkably due to subsequent esterification of fatty acids with carbonyl and/or alcohols. It can also suggest that the formed esters can be reverted back through deoxygenation when Soxhlet was processed after enzymatic-assisted via incubation (PR-HAE). The co-solvent can also act as a hydrogen donor for deoxygenation that influence the pretreatment process. It is also noteworthy to mention that the limitation of bio-crudes yield significantly depends on the contribution of lipids from biowaste.

Biowaste also consists of 20 % crude proteins. Generally, proteins would firstly hydrolyse into amino acids by breaking the peptide bond under all pretreated conditions. The C—N bond presents in all amino acids between the carbonyl and amine groups (Yang et al., 2015). With enzymatic effect, the depolymerization of proteins is more rapid under an acidic environment that weakens the peptide bond and subsequently may generate various side-chain groups. Moreover, different amino acids can undergo cyclodehydration, leading to the formation of cyclic imides and cyclic dipeptides as detected by GCxGC. Because of the presence of other components in bio-crudes, the recondensation reactions can happen and heavily depended on the type of amino acid, operating conditions, and the effect of pH solution. From elemental analysis, the highest content of nitrogen in residual solids can explain their higher molecular weight that might be enhanced via recondensation, cyclisation and cyclodehydration reactions. Yang et al. studies the reaction HTL processes of crude proteins with an acid catalyst (Yang et al., 2017). The authors found that the extracted bio-crude yield was much lower in the catalytic system due to the enhancement of the residual solids than without the catalyst.

Carbohydrates fraction may experience a similar pathway as lignocellulose for the hydrolysis of polysaccharides to simple sugars (Questell-Santiago et al., 2020). Biowaste mainly comprises of 55 wt% carbohydrates, which are reported to have higher bio-crudes yields than protein and lipid substrates. When glucose was used as source of carbohydrate, studies were undertaken to evaluate how the variable contents of carbohydrates in organic waste are associated to bio-crudes yield (Questell-Santiago et al., 2020). Generally, monomer units of sugars hydrolysed from carbohydrates can decompose mainly into three derivatives: furan derivatives, short-chain unsaturated organic acids, and Maillard products (Lin et al., 2020; Mohd Thani et al., 2020; Questell-Santiago et al., 2020). Whether synergetic or antagonistic effects exist between these three main groups of organics depends strongly on the operating conditions.

3.3. *Hydrotreatment of the extracted products*

In this section, the bio-crude and residual solids resulting from PR-HAE pretreatment were upgraded via catalytic hydrotreatment (Fig. 1 and Table 2). Deep hydrotreatments were also performed separately for the extracted bio-crude and residual solids for comparative studies. Prior to the hydrotreatment, the bio-crudes obtained were concentrated using a vacuum rotary evaporator at 45 °C; the distillates were analysed by GC-MS and showed no traces of volatile organic matter. After each hydrotreatment experiment, the resulting gases, bio-oil and hydrochar products were identified and analysed.

3.3.1. *The effect of hydrotreatment and distribution of products*

Fig. 5a and b shows the yield of products obtained from the catalytic hydrotreatment of bio-crudes and residual solids. The mass balance closure of the hydrotreatment experiments always exceeded 93 %. The hydrotreatment experiments, along with the bio-crude and residual solids, were performed under different temperatures. It is clear that the yield of bio-oil and the conversion rate increased significantly, i.e., from 63.3 to 86.0 wt% and 87.4 to 97.0 %, respectively, as the reaction increased from 300 °C to 400 °C while the hydrochar decreased significantly, from 26.4 to 5.0 wt% (Fig. 5a). These results indicate that the higher temperature accelerated the hydrolysis, hydrogenation and depolymerization reactions, which enhanced the carbon content via

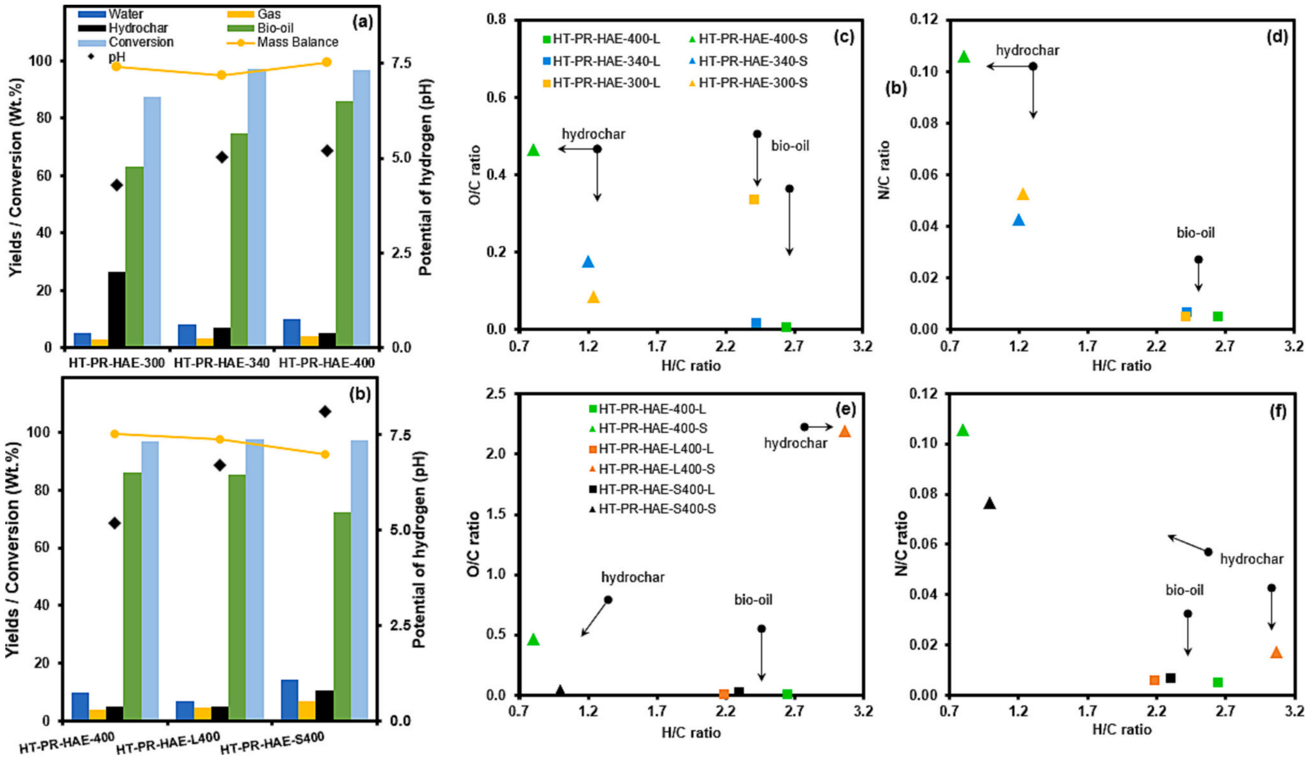

Fig. 5. Product distribution of the catalytic hydrotreatment of the extracted bio-crude and the solid residues resulting from the hybrid-assisted pretreatment of the biowaste. (a) Joint hydrotreatment of biocrude and solids as a function of temperature; (b) comparison of joint and individual hydrotreatment of the extracted bio-crude and solid residues. (c) O/C and H/C ratios (d) N/C and H/C – Van Krevelen plot of the bio-oils and hydrochars produced after catalytic hydrotreatment of the extracted bio-crude liquid and solid residues using PR-HAE. Mild hydrotreatment: 300 °C; deep hydrotreatment: 340 °C and 400 °C, 80 bar H_2, 5 h and 1200 rpm. (e) O/C and H/C ratios and (f) N/C and H/C – Van Krevelen plot of the bio-oils and hydrochars produced after the catalytic hydrotreatment of bio-crudes and solid residues jointly or individually. Conditions: 400 °C, 80 bar H_2, 5 h and 1200 rpm.

deoxygenation and suppressed the yield of hydrochar. The gas yield (mostly methane and carbon dioxide) showed no significant changes from 3.1 to 4.0 wt% as a function of temperature, respectively. This is in line with the study reported by Kohansal et al., where HTL bio-crudes are subjected to hydrotreatment (Kohansal et al., 2022). However, the effect of hydrotreatment temperatures significantly affected the bio-oil yield and composition, which resulted in higher gas and coke formation as a function of temperature (Kohansal et al., 2022).

The feed conversion and product distributions were also investigated when the hydrotreatment was applied together and individually to the bio-crude (PR-HAE-L) and residual solids (PR-HAE-S) at 400 °C, Fig. 5b. It is evident that, in terms of conversion and product distributions, the catalytic activity of the hydrotreated bio-crude (HT-PR-HAE-L-400) showed a trend similar to those of the hydrotreated bio-crude and residual solids (HT-PR-HAE-400). It is notable that the acidity of the bio-oil produced increased for the hydrotreated bio-crude: this is probably due to the high carbonyl content of the bio-oil and will be discussed in due course. A lower yield of bio-oil (72.2 wt%) and higher yield of hydrochar (10.7 wt%) resulted, however, when the residual solids were hydrotreated separately, under identical conditions (HT-PR-HAE-S-400). This is expected, since condensation reactions lead to more recalcitrant polymers being present in the residual solids extracted (PR-HAE-S, Fig. S3b). Moreover, the results also suggest that mild hydrotreatment (e.g., at 300 °C) of the same residual solids might make more upgrading difficult and lead to further increases in the formation of hydrochar. Based on the above results and analyses, the degradation rate of the residual solids accelerates when they are hydrotreated jointly with the bio-crude, resulting in a higher yield of bio-oil (86.0 wt%) and lower yield of hydrochar (5.0 wt%) at 400 °C (HT-PR-HAE-L400, Fig. 5b).

Thermochemical studies with food wastes and algae, report limited bio-crude yields with a focus dependent on treatment conditions, which maybe require a suitable pretreatment to hydrolyse the biowaste prior to HTL (Ahmed Ebrahim et al., 2022; El-Sawy et al., 2020; Paritosh et al., 2017; Patra et al., 2021; Qing et al., 2022; Saengsuriwong et al., 2021). As shown in this study, the integration of the pretreatment method of bio-waste significantly influenced the downstream operations, leading to an increase in the quantity and quality of valuable products from biowaste. Overall, an increase in the yield of bio-oil may be well considered if HTL accompanied by an improvement in the quality and quantity of bio-crude throughout an appropriate pretreatment.

3.3.2. *Analysis of bio-oils and hydrochar*

The elemental compositions of the bio-oils and hydrochars produced from the hydrotreated bio-crude and residual solids are shown in Table S1 and represented by van Krevelen diagram, Fig. 5c–f. The bio-oil resulting from mild hydrotreatment had the highest O/C ratio of 0.33 (HT-PR-HAE-300-L, Fig. 5c), which is consistent with the high number of oxygen-containing molecules found by GC analysis. In comparison to deep hydrotreatment conditions, the hydrotreated products displayed greater H/C and lower O/C values, and particularly so at 400 °C (H/C: 2.65 and O/C:0.004), which lowers the quantity of oxygen-containing molecules significantly. Also, it can be seen that the O/C atomic ratios increased for the hydrochars and were much accentuated at 400 °C (HT-PR-HAE-400-S, Fig. 5d). These results indicate that the H/C and O/C atomic ratios were proportionally consistent with bio-oils and hydrochars produced as a function of their hydrotreated temperatures. Moreover, the N/C ratios were suppressed in bio-oils upon hydrotreatment (N/C: 0.005, Fig. 5d) and, surprisingly, the N/C ratios in the hydrochars were twenty-fold higher than in the bio-oils, particularly under severe hydrotreatment conditions (N/C: 0.11). Contents of both sulphur and ash are relatively at trace levels for all of the bio-oils produced. In this respect, it seems that PR-HAE pretreatment, accompanied by catalytic hydrotreatment, is more effective for the removal of nitrogen (HDN) and oxygen (HDO). It can be appreciated that hydroprocessing of PR-HAE bio-crude differs from HTL because of the importance of deoxygenation as well as nitrogen or sulphur removal (Kohansal et al., 2022). A negligible nitrogen removal was reported by Kohansal et al. whom reasonably claimed due to resistance of some nitrogenous organics toward hydrotreating (Kohansal et al., 2022). Furthermore, APR-assisted HTL process led to a significant decrease of the carbon content and increase nitrogen between C0 and C3 (Kohansal et al., 2022).

Bio-oils and hydrochars produced by hydrotreating the bio-crude (HT-PR-HAE-L400) and residual solids separately (HT-PR-HAE-S400) were also investigated. The elemental compositions are compared in Fig. 5e and f. The carbon content of the bio-oils increases slightly when they are hydrotreated individually (HT-PR-HAE-**L**/**S**400-L) compared to being hydrotreated jointly (HT-PR-HAE-400-L, Table S1), leading to lower H/C and O/C values. The H/C and O/C atomic ratios of the hydrochars produced were much higher when the bio-crude was hydrotreated separately (HT-PR-HAE-L400-S, Fig. 5e). This is likely due to the higher condensation reactions of bio-crude to form complex oxygenated heterocycles molecules triggered by heating rate (Nejad-moghadam et al., 2023). On the other hand, the H/C and O/C atomic ratios were lower when the residual solids were hydrotreated separately and extremely low for the O/C ratio (HT-PR-HAE-S400-S). This can be explained by a deep hydro-liquefaction conversion of the residual solids into rich-carbon (81.7 wt%) and low-oxygen (2.0 wt%) products in the resulting bio-oil. It is interesting to note that a concurrent decrease in the O/C ratios was observed for both bio-oil (O/C: 0.004) and hydrochar (O/C: 0.47) when the bio-crude and residual solids were hydrotreated jointly. It could be suggested that residual solids could primarily act as co-catalyst and stabilizer to restrain the recondensation reactions at mild temperatures prior to $NiMo/Al_2O_3$ being activated at higher temperatures. This resulted in a reasonable reduction (De-O: 98.0 %) in the oxygen content of the bio-oil produced (O: 0.4 wt%, HT-PR-HEA-400L). In terms of nitrogen content, hydrotreating bio-crude and residual solids jointly appeared to adsorb more nitrogen onto/into the hydrochar that was produced (N/C: 0.11, HT-PR-HEA-400S) compared to being hydrotreated individually, Fig. 5f. This result is consistent with the amount of nitrogen in the bio-oil produced, which decreased significantly to 0.4 wt% (De-N ~ 83.7 %, HT-PR-HEA-400L). In this respect, the pretreatment of bio-waste (PR-HAE) accompanied by a hydrotreatment process results in a bio-oil of sufficiently good quality (HT-PR-HAE400: H/C > 2.6, O/C > 0.004, N/C > 0.005, and ash ~0 wt%) and a rich amount of N is adsorbed onto the hydrochar product. It can therefore be predicted that upgradeable bio-oils can promote the production of high-quality components that can be used as alternatives to fossil-based transport fuel.

The bio-oils produced were analysed by GCxGC-MS to clarify their organic composition, Fig. 6: this analysis provides only the detectable low-molecular weights and monomeric compositions. The TGA analysis in Fig. S5 shows complete decomposition of the hydrotreated bio-oils (<250 °C), which fits well with GC analysis range. Fig. 6 shows that aliphatic compounds were largely detected in the bio-oils, including alkanes, olefins, alcohols, ethers and ketones, and that these increased significantly as a function of the temperature. The yield of hydrocarbons increased from 54 wt% at 300 °C to 78 wt% at 400 °C, Fig. 6a. It is interesting to observe that the content of olefins to alkanes ratio increased (but not shown for brevity), but it should be also noted that higher branched alkanes (> C20, alkyl substituted) were seen to increase. These results suggest that the hydrodeoxygenation of carboxylic acids was followed by hydroisomerisation-hydrocracking of the alkanes/olefins. According to the results obtained, cycloparaffin and aromatic-naphthalene were the minor products of deoxygenation, possibly generated from the lignin-carbohydrate complex (Cassoni et al., 2022). As shown in Fig. 6b, more phenolics and furanic derivatives were generated in the bio-oil from the hydrotreated residual solids (HT-PR-HAE-S400L) than in the hydrotreated bio-crude (HT-PR-HAE-L400L).

A higher temperature also contributed to nitrogenous organic transformation into hydrocarbon compounds (8.5 wt% to 1.3 wt%, Fig. 6a). These results agree with the elemental compositions above-

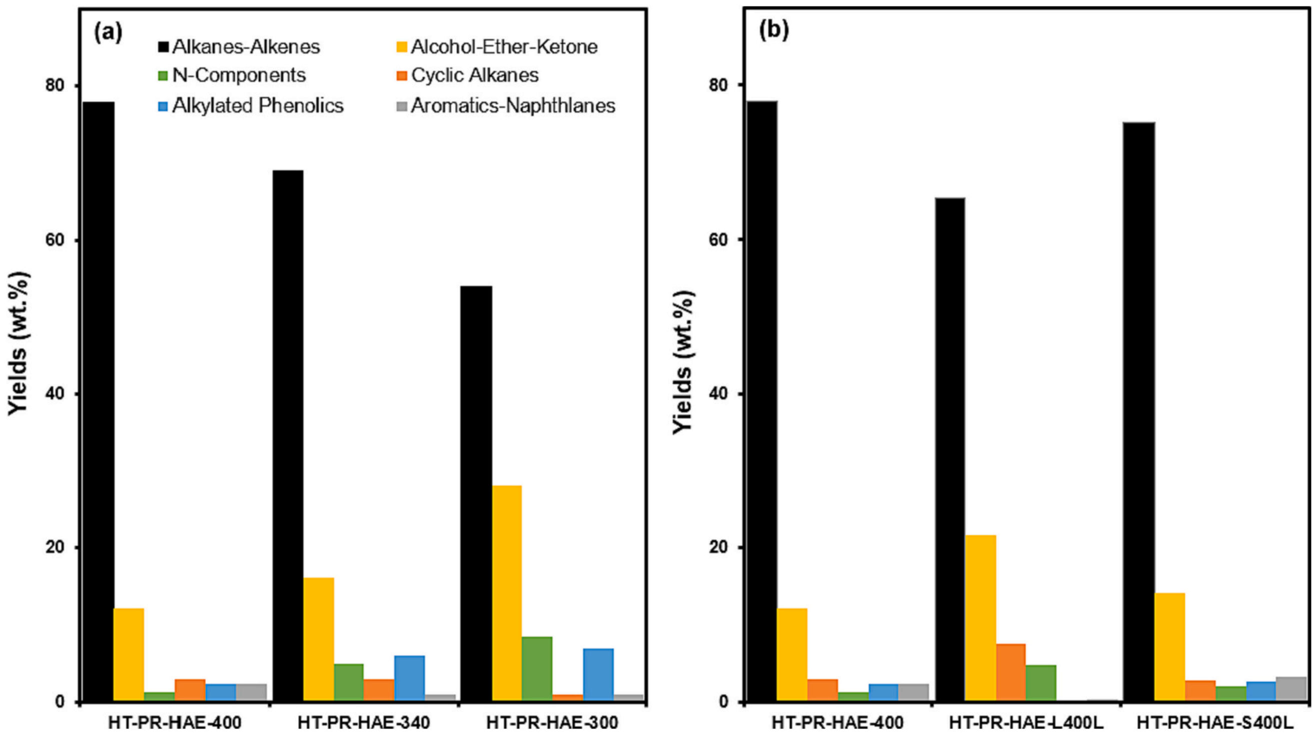

Fig. 6. GCxGC composition of the bio-oil products after catalytic hydrotreatment of biocrude and residual solids: (a) monomer yield of bio-crude and solids hydrotreated jointly as a function of temperature, and (b) comparison of the bio-crude and solid residues hydrotreated jointly and individually.

mentioned, particularly when the bio-crude and residual solids were being jointly hydrotreated at elevated temperature. The ash fraction of the bio-oil was found to be <0.01 %. Calorific (HHVs) values of bio-oils vary from 32.4 to 48.0 MJ/kg and increase as a function of the bio-crude and residual solids compositions with their hydrotreatment temperatures. The increment of HHVs suggests increasing in organic molecule content at higher temperature, where the hydroisomerisation-hydrocracking of longer molecule leads to the production of branched-alkyl, which are likely hydrophobic (as miscible with n-hexadecane) and higher in energy. Hence, most of carboxylic acids, monosaccharides and N-cyclic mixtures in the extracted bio-crude and solids were converted to rich aliphatic hydrocarbons yields, via subsequent hydrogenation reactions of oxygenated and nitrogenous aliphatic components as a function of temperatures and hydrogen consumption.

4. Practical applications and future research

Food waste contains carbon organic matter is a promising feedstock by converting these materials into upgradeable bio-oil. But, compared with heavy petroleum fuel oil, it has several undesired properties for fuel applications such as high oxygen, high nitrogen, water content, and corrosiveness. There are several pre-treatment and treatment techniques for biomass. Every technique has its own advantages and disadvantages. Hydrotreating process seems to be a promising approach for post-treatment of bio-waste since it is well-established and has been used in refineries for several years, however, further efforts are required to resolve the problem of bio-crude recovery, and high nitrogenous component content. Generally, upgrading of bio-oil from biomass has appealed attention of many researchers, but little work has been published on upgrading of crude-oil extracted from food waste which opens a new route for future research work, particularly when emerging pre-treatment technologies. More importantly, there is not comprehensive research on both the bio-crude recovery and techno-economic evaluation of all upgrading methods which are essential for large scale implementation of bioeconomy. Hence, these could be one of the interesting topics for further research to determine the most economic method of bio-oil production via food waste. The authors also suggest that future research should consider the quantities and types of food waste that are available, patterns of generation of these materials and the qualitative and quantitative characteristics of such food waste, as well as the variability of its generation. More interestingly, it is worth mentioning that the impact of post-treatments, such as co-solvent HTL process, used to deeply liquefy the residual solid, was not examined in this study and left to be determined in future studies. Moreover, there is still scope for improving the hybrid-assisted pretreatment, e.g. introducing other types of enzymes, using bio-waste as received and varying the operating conditions.

5. Conclusions

The main purpose of the present study was to demonstrate the feasibility of pre-treating food biowaste and then catalytically hydrotreating to generate bio-products. A series of pretreatment methods were employed in order to evaluate the bio-crudes and residual solids in terms to their fraction yields, elemental and chemical compositions modifications. The findings were rationalized by a higher total extracted bio-crude yield with the lowest N-containing components (De-N ~ 83.3 %), and a larger amount of elemental N content of 5.8 wt% in the extracted residual solid and a high density of ketone-ester-alcohol comprised of 87 wt% extracted bio-crude. Bio-oil from hydrotreatment of extracted materials was comprised primarily of 78 wt% hydrocarbons, 6 wt% cyclic and aromatics, 14 wt% oxygenated and <5 wt% N components. This demonstrates that food biowaste can be used as a feedstock for upgradeable bio-oils using a two-stage process combining hybrid-assisted pretreatment and catalytic hydrotreatment.

CRediT authorship contribution statement

Prabin Dhakal: Investigation, Formal analysis, Review & editing. **Emma Olsson Månsson:** Formal analysis. **Abdenour Achour:** Conceptualization, Investigation, Formal analysis, Writing original draft - review & editing, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.biteb.2023.101626.

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