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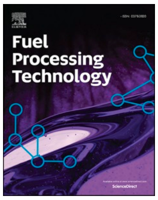

Multi-stage pretreatment of hydrothermal liquefaction biocrude oil as a precursor for sustainable aviation fuel production

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ABSTRACT

A major challenge for upgrading hydrothermal liquefaction biocrude into sustainable aviation fuel is the presence of inorganic material. Unlike commercial crude oil or biofuel from energy crops, excessive amounts of contaminants such as salt, water, and ash in biocrude oil from hydrothermal liquefaction can cause catalyst deactivation during hydroprocessing, decreased distillation efficiency, and equipment fouling from alkali deposits. Therefore, efficient removal of these impurities in HTL biocrude oil is essential. This work investigated a novel 3-stage pretreatment process, removing water, salt, and ash without chemicals, to produce a HTL biocrude oil precursor suitable for hydroprocessing. The influence of water to oil (W:O) ratio, temperature, and time on desalting efficiency was determined. After pretreatment, 81% of salt was removed, reducing total salt content to <0.1%. Improvements in elemental composition and physicochemical fuel properties were observed in biocrude oils from two feedstocks, with up to 39.8% decrease in oxygen content, 55% decrease in sulfur content, 22.2% decrease in nitrogen content, 9.86% increase in higher heating value, 73.4% decrease in total acid number, 99.9% decrease in viscosity, and 17.0% decrease in density. Compared with a single-step distillation as pretreatment, 3-stage pretreatment resulted in increased salt and heteroatom removal, improved heating value, and lower acidity. The precursor quality was viable for subsequential hydrotreating and other downstream refinery processes.

1. Introduction

Rising global population and urbanization have created global challenges, including the need for sustainable energy. The United Nations Sustainable Development Goals (SDG) 7 highlights access to affordable, reliable, sustainable, and modern energy for all—although renewable sources supplement 28.2% of electricity, just 4% powers transportation [1]. In particular, the aviation industry has set a goal to reach net zero carbon emissions by 2050, potentially reducing lifecycle greenhouse gas emissions by 94% by using sustainable aviation fuel (SAF) instead of conventional jet fuel [2,3]. Numerous methods, such as Fischer-Tropsch, hydroprocessing, alcohol-to-jet, fermentation, petroleum co-processing, and hydrothermal liquefaction (HTL) have been explored and approved as SAF production pathways [4]. HTL converts biomass feedstocks into biocrude oil under elevated temperature (200–375 °C) and pressure (5–28 MPa) [5,6]. Using the inherent water content of the feedstock, HTL is suitable for a wide range of wet biowaste feedstocks, including food waste, algae, sewage sludge, and manure, avoiding the costly and energy-intensive drying step prior to conversion [5]. However, impurities in the biocrude oil (water, alkali, sediment, ash) along with presence of heteroatoms (nitrogen, oxygen, sulfur) cause undesirable properties such as low heating values, high acidity, and poor stability, limiting its suitability as a drop-in fuel [7]. Therefore, the use of upgrading methods, such as hydroprocessing, is required to facilitate the removal of heteroatoms from biocrude oil, improvements in chemical composition, and better fuel quality.

Impurities in the HTL biocrude oil pose serious problems in downstream upgrading processes. Chlorides that remain in the biocrude oil can hydrolyze and form corrosive HCl that forms acids or alkali in the crude oil or be deposited onto equipment [8–11]. Furthermore, alkali content in oil may be deposited onto the catalyst surface during hydroprocessing, resulting in pore plugging and then catalyst

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deactivation [12,13]. Biocrude oil with high moisture has reduced higher heating value (HHV) and other affected physicochemical properties [14,15]. In addition, residual water in the biocrude oil can affect the lifetime of hydroprocessing catalysts, cause unstable boiling during distillation, and reduce efficiency of other downstream processes in refineries [16,17]. Similarly, the removal of ash and other suspended sediment in the biocrude oil is also important to improve fuel stability and prevent catalyst plugging [14,18]. A report by Pacific Northwest National Laboratory recommended total salt concentration in HTL biocrude oil to be reduced to 100–1000 ppm prior to downstream upgrading [19]. Therefore, HTL biocrude with high inorganic content should be pretreated to remove salt, water, and ash prior to hydroprocessing to prevent catalyst deactivation, corrosion, and equipment fouling during downstream activities [20,21].

Salt removal methods used for petroleum crude oil can also be applied to HTL biocrude oil [22,23]. Salt contained in crude oil, most often present as organic or inorganic chlorides, are dissolved in water emulsified with the oil phase and are conventionally removed in a “desalting” step by washing the salt from the crude oil with fresh water [9,11]. Typical refinery operations use electrical desalting, in which a mixture of 3–10% wash water is combined with crude oil and surfactant, agitated to coalesce dispersed water, then enters a desalter at moderate temperature (90–150 °C) and pressure (1.9–2.4 MPa), where oil is separated from the salt-containing water phase under an electric field [8,9,11,24]. Other desalting methods include the use of filters, guard beds, centrifugation, polar solvent extraction, acid washing, and ultrasonic agitation [7,8,25–30]. Solvent refining and blending with uncontaminated crude oil may also be used to produce fuels that meet physicochemical standards and environmental specifications [6,11].

For HTL biocrude oil, there are just a handful of published studies and patents on inorganics removal, that involve either the use of acid washes, solvent-assisted separation, or filtration. Gevert and Otterstedt demonstrated the effectiveness of solvent extraction alone to pretreat HTL biocrude oil, using acetone, xyelene, octane, and pentane to separate oil from salts [31]. However, Gevert and Andersson found that the addition of a water-wash step after dissolving the oil in solvent helped further reduce the sodium content in oil, and produced a biocrude oil that was more readily hydroprocessed than the solvent-extracted biocrude oil [32]. Diebold et al. utilized hot-gas filtration after HTL to obtain low alkali, metal, and char-content in biocrude oil [33]. Kilgore et al. investigated the use of a formic acid-aqueous wash, at elevated temperature (60–120 °C), acid concentrations of 1.5–8 wt%, 17–50 wt% wash water and retention times up to 30 min, achieving >90% removal of inorganic material in HTL biocrude oil from food waste [34]. A 2016 patent also published the removal of salts and metals in HTL biocrude oil from algae, using a 1–50 wt% sulfuric acid in an aqueous solution such that the water-biocrude oil mixture had a pH $\leq$ 1 and was mixed for 0.5–8 h at temperatures 4–25 °C [35]. Other patents outline the design of separation systems to remove inorganics and HTL by-products from the biocrude oil, making use of washing agents and settling or separation tanks to remove water-soluble contaminants, dissolved salts, and suspended particles like ash [36,37]. Haider et al. successfully removed 93% of minerals using a solvent-assisted acid wash to remove inorganics from lignocellulosic (*Miscanthus*) HTL biocrude, by first dissolving the biocrude in acetone and performing vacuum filtration, then further dissolving the filtered biocrude oil in a 1:1 *w*/w ratio of acetone and a 1:3 w/w ratio of 0.1 M sulfuric acid [38]. The same method was also applied to HTL biocrude from sludge, achieving 89% demineralization, but noted significant organics loss (up to 20%) [39]. Solvent-assisted water washes have also been applied to extract water-soluble nitrogen compounds from HTL biocrude oil [40,41].

Although most of the water is removed from biocrude oil after separation of the brine phase during desalting, further treatment may be necessary to obtain complete dehydration. Low temperature distillation as described in ASTM 2892 Annex X1 has been used to show improved biocrude oil homogeneity and more stable distillation [15,16,42]. Lastly, the use of distillation to process HTL biocrude oil has demonstrated increased stability and improved fuel characteristics due to removal of moisture and isolation of ash and inorganics in the residue [14,18,43]. But the distilled biocrude oil still contains significant amounts of nitrogen and maintains high viscosity and acidity [44].

This work aimed to develop a method for reducing the inorganics content of food waste derived HTL biocrude below 1000 ppm, thereby producing a viable hydroprocessing precursor without the use of harsh chemicals. HTL biocrude oil from food waste typically contains high inorganic concentration (>5000 ppm), which is detrimental to downstream hydroprocessing and biorefinery processes, causing a major bottleneck for the commercialization of HTL technology. To address this challenge, a novel 3-stage pretreatment approach applied to remove salt, water, and ash contained in the biocrude oil. Additionally, the 3-stage pretreatment approach was compared to a single stage distillation step, exploring the possibility of a more simplified pretreatment method for precursor preparation. The results of this study provide a biocrude oil pretreatment method that does not require the use of acids or solvents, producing a suitable precursor for hydroprocessing.

2. Methods

2.1. Pilot HTL production of biocrude oil

The biocrude oil used in this work was produced as described in a previous study [15]. In summary, a 28.88 L pilot-scale continuous plug flow HTL reactor was operated at 300 °C and 12.4 MPa for an average residence time of 20 min. The biomass feedstocks were food processing waste (FPW) from a salad dressing producer and grocery food waste (GFW) from a grocery store in Champaign, IL. Each feedstock was adjusted to a 20 wt% solids content. The HTL biocrude oil and aqueous phase were collected by gravitational separation and filtered to remove solids.

2.2. Desalting (DS) stage

A set of experiments (Table 1), designed using Taguchi method, was completed to identify the effects of water:oil (W:O) ratio (1:1 to 1:9 *w*/w), retention time (RT) (20–60 min), and temperature (80–120 °C) on desalting efficiency.

During each experiment, biocrude oil and deionized water were combined in a 100 mL batch microstirred reactor (Parr Instrument Series 4590, Moline, IL < USA) according to the ratio in Table 1. The biocrude oil had not yet been dewatered. The mixture was heated to the set temperature and agitated with a stirring impeller at 350 rpm for the selected retention time. Subsequently, the mixture was centrifuged to facilitate fast gravitational settling and the salt-containing aqueous phase was readily separated from the biocrude oil.

2.3. Dewatering (DW) stage

After desalting, the biocrude oil was dehydrated using a B/R Instrument Dewatering System 7400 (Easton, MD, USA) according to

Table 1
Experimental design for desalting.

Sample	W:O (w/w)	RT (min)	Temp (°C)
1	1:1	20	80
2	1:1	40	100
3	1:1	60	120
4	1:3	20	100
5	1:3	40	120
6	1:3	60	80
7	1:9	20	120
8	1:9	40	80
9	1:9	60	100

ASTM D2892 Annex X1 to remove any residual moisture [42]. A quantity of biocrude oil was distilled under atmospheric pressure and a reflux ratio of 0 until reaching a vapor temperature of 130 °C. The dry biocrude oil was collected and the mass fraction of water removed was calculated according to Eq. 1

$$W = (A/B) \times 100 \tag{1}$$

where W = mass % of water, A = mass of water recovered (g), and B = mass of initial biocrude oil (g).

2.4. Deashing (DA) stage

Ash and other solid residue were removed from the biocrude oil with short-path simple distillation under atmosphere according to previous studies [43,44]. The biocrude oil was loaded into a round-bottom flask and heated with a mantle (BIPEE, 98-2-B-1000) with an average heating rate of 2.5 °C/min until 350 °C. 5 mm glass beads (Fischer Scientific, 11-312-10C) were added to prevent violent boiling, and glass wool was wrapped around the flask and column for insulated heating. A J-type thermocouple monitored the temperature of vapor entering the condenser, circulated with tap water at 21 °C. Condensed distillate was collected and weighed in a secondary flask.

2.5. Analytical methods

The elemental composition for carbon (C), hydrogen (H), and nitrogen (N) was measured with an Exeter Analytical Model CE440 CHN analyzer (Coventry, UK). A PerkinElmer ICP-MS (Model NexION 350D) was used to measure sulfur, sodium, calcium, potassium, and silicon. Oxygen was calculated by difference. The removal efficiency of sodium, calcium, potassium, silicon, and total salt was calculated by the percent change in value from the original and desalted biocrude oil. The higher heating value (HHV) was calculated according to Eq. 2 with Dulong's formula [45]:

$$\text{HHV (MJ/kg)} = 0.3516\text{C} + 1.16225\text{H} - 0.1109\text{O} + 0.0628\text{N} \tag{2}$$

The density was determined with a 2 mL glass Gay-Lussac bottle (Core-Palmer, EW-34580-40 at 20 °C. The kinematic viscosity was measured at 20 °C with a size 100 Cannon-Fenske glass capillary viscometer according to ASTM D446 [46]. The total acid number (TAN) was measured according to ASTM D974, the sample was dissolved in a toluene-isopropanol-water solvent with a small amount of added phenolphthalein indicator and titrated with 0.1 M potassium hydroxide until reaching the end point [47]. The chemical composition of the biocrude oil was acquired by gas chromatography–mass spectrometry (GC–MS) using a Micromass 70-VSE (Waters Corporation, MA, USA). The sample (2 μL) was injected in split mode to the GC–MS system with a ZB-5MS column. The initial oven temperature was increased from 30 to 80 °C at a rate of 25 °C/min, held for 2 min, then heated to 220 °C at 8 °C/min, and to 280 °C at 25 °C/min. The electron ionization voltage was 70 eV and the spectrums were scanned from 30 to 800 *m/z* and analyzed with the MassLynx Mass Spectrometry Software (Waters Corporation, MA, USA). Peaks were then identified with Waters ChromaLynx software for non-targeted analysis: automated peak detection and mass library scoring was used to determine the composition of significant ions in the spectra and compared to matches in the NIST Mass Spectral Database (NIST08) [48]. Information on boiling point information and distillate ranges were obtained with a TA Instruments Q50 thermogravimetric analyzer (New Castle, DE, USA). The sample (15 mg) was heated from 20 to 600 °C at 20 °C/min with a nitrogen flow rate of 60 mL/min. Characteristics of the aqueous phase samples were measured by the following methods using a HACH spectrophotometer (Model DR3900): pH was measured by electrode (HACH Method 8156); conductivity was measured directly by meter (HACH Method 8160); chemical oxygen demand (COD) was digested in dichromate solution and measured by visible light absorbance (HACH Method 8000); total organic carbon (TOC) was measured using a persulfate digestion (HACH Method 10,173); ammonia nitrogen (N) was measured using the salicylate method (HACH Method 10,031); and total N was measured using the persulfate digestion method (HACH Method 10,072).

3. Results/Discussion

3.1. Three-stage pretreatment

3.1.1. Desalting efficiency

The sodium (Na), calcium (Ca), potassium (K), silicon (Si), and total salt removal was calculated and displayed in Fig. 1a. The best results were achieved in Sample 3, with 64.1% total removal at 1:1 W:O, 60 min, and 120 °C. The water wash was most effective for potassium and sodium, but not as much for calcium and silicon. This may be because the potassium and sodium compounds in the biocrude oil were more water soluble and existed in larger quantities than the calcium and silicon. In general, samples with the same W:O ratio had similar desalting effect and it was observed that desalting, for both individual and total salt removal, generally decreased as the water ratio decreased. Within each W:O group, there was also a slight increase in salt removal as the retention time increased.

The Taguchi results were averaged for each parameter level to determine the values of W:O ratio, RT, and temperature that yielded the highest total salt removal. It was found that the best results were achieved with a 1:1 W:O ratio (*w*/w), 60 min RT, and 100 °C temperature, with total removals of 61.3, 57.8, and 56.1 wt%, respectively. Seen in Fig. 1b, changes in the W:O ratio resulted in the greatest changes in total salt removal, followed by RT, and then temperature in order of most to least significant parameter. It was observed that salt removal increased with higher amounts of wash water used and longer retention times. Although increasing the temperature from 80 to 100 °C increased the salt removal, further increasing to 120 °C resulted in a decreased salt removal, indicating that there was no benefit to the desalting effect at temperatures beyond 100 °C. These results may be attributed to the parameters affecting droplet dispersion and settling velocity, along with density and viscosity of the biocrude oil.

Increasing the W:O ratio may increase contact between the wash water and salt droplets in the biocrude oil, helping to improve droplet dispersion and coalescence [48]. Especially in the case where there is only a small amount of salt droplets dispersed in the biocrude oil sample, a higher W:O ratio may be required. Increased total salt removal with increased RT could be caused by the additional time aiding demulsification between the oil and aqueous phase after the initial mixing with repeated agitation causing emulsified micelles to break apart, therefore improving the salt removal from the oil phase [50,51]. While changes in temperature had the least significant effect on total salt removal, it was notable that an optimal temperature was identified at 100 °C. The density and viscosity of the crude oil affects the ease of separation and desalting efficiency [9]. Higher temperatures increased the density difference between the biocrude oil and water, while also decreasing the viscosity of each phase. Based on Stokes' Law, the larger density difference and lower viscosity of fluid caused a higher settling velocity of droplets in the dispersed water phase, resulting in better separation of the biocrude oil and salt-containing water [51]. Increasing the temperature also helped decrease the surface tension which allowed better mixing, causing greater coalescence of the dispersed salt droplets in the water phase. Less salt removal was achieved when the temperature was too low or high, so identifying the optimal temperature is important for efficient desalting biocrude oil. At 80 °C, the oil remained too viscous to both mix efficiently and fully separate with the water, causing some of the salt-containing water to be retained in the biocrude oil after the process [48]. However, at 120 °C, water vaporization may have occurred and caused incomplete separation of the oil and water phases [49,51]. Based on Stokes' law, excessive temperature could also cause

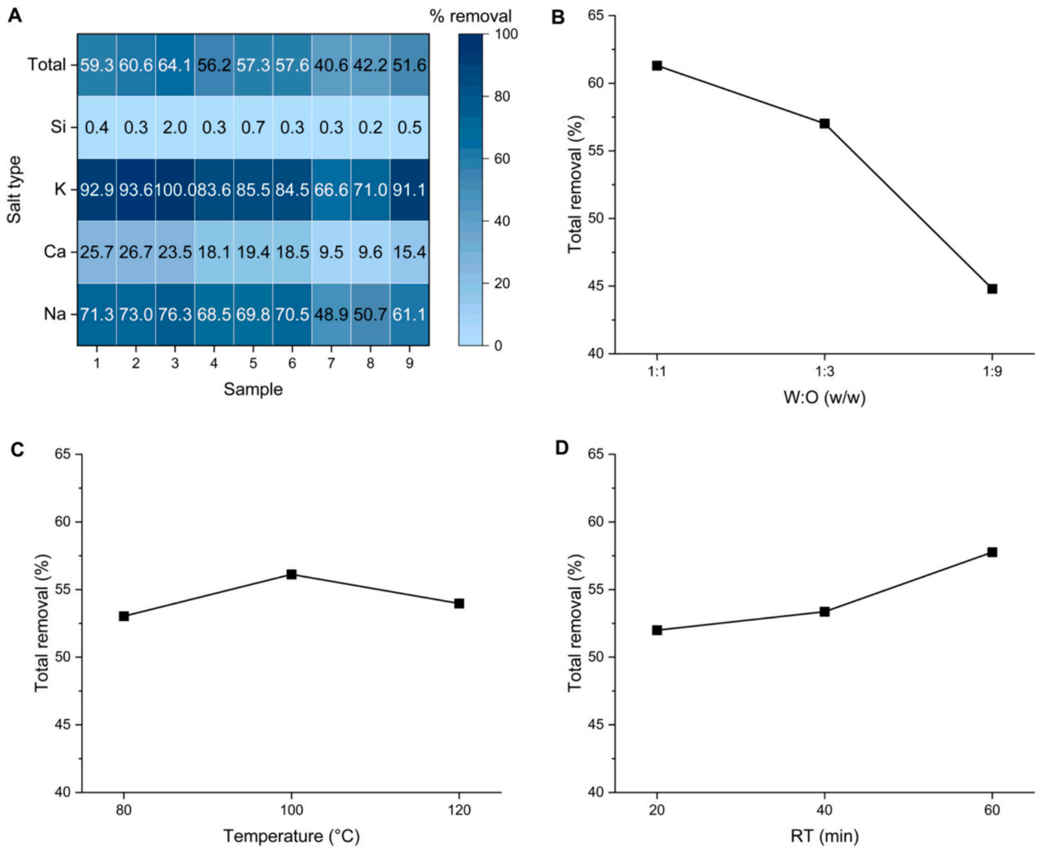


Fig. 1. Taguchi desalting results for a) salt removal and the mean response of total salt removal on changes in a) W:O ratio, b) RT, and c) temperature.

slip between dispersed water droplets, resulting in shrinkage and limiting their cohesion [51].

A comparison of desalting methods was also carried out with a repeated desalting stage, low moisture biocrude oil, and formic acid aqueous wash (Fig. S1). However, these alternative methods, besides being more intensive, were not as efficient as the procedure described previously. In brief, performing dewatering before desalting reduced desalting efficiency, the acidic wash created emulsions not readily separable, and repeated desalting demonstrated little improvement in salt removal. Accordingly, it was determined that the highest salt removal was achieved by desalting the biocrude oil prior to dewatering, using a pure water wash, and performing only a single stage desalting at 1:1 W:O ratio for 60 min at 100 °C.

3.1.2. Chemical composition

The salt concentration in the biocrude oil was determined in Fig. 2 before pretreatment ("initial"), the intermediate stage after desalting and dewatering ("DSW"), and the completed 3-stage pretreatment after deashing ("DSWA"). The concentration was measured after the desalting and dewatering steps instead of each separately so that the biocrude oil could be fully dehydrated prior to analysis. Salt content was reduced by 69.7% after DSW, bringing down the concentration to 1080 ppm, still slightly above the 1000 ppm threshold. After completing the deashing stage, total salt content was 640 ppm, for a total removal of 82.0% compared to the untreated biocrude oil. The greatest amount of Si was removed, followed by Ca, and Na with 91.6, 88.3, and 67.2% removal, respectively. The concentration of K slightly increased in the DSW measurement, which may be attributed to a low K-removal after the water wash, causing the concentration to increase when the mass of K in the biocrude oil stayed the same while the water was removed during dewatering, therefore decreasing the volume. Meanwhile, the further reduction of salt after DSWA could be caused by the removal of the

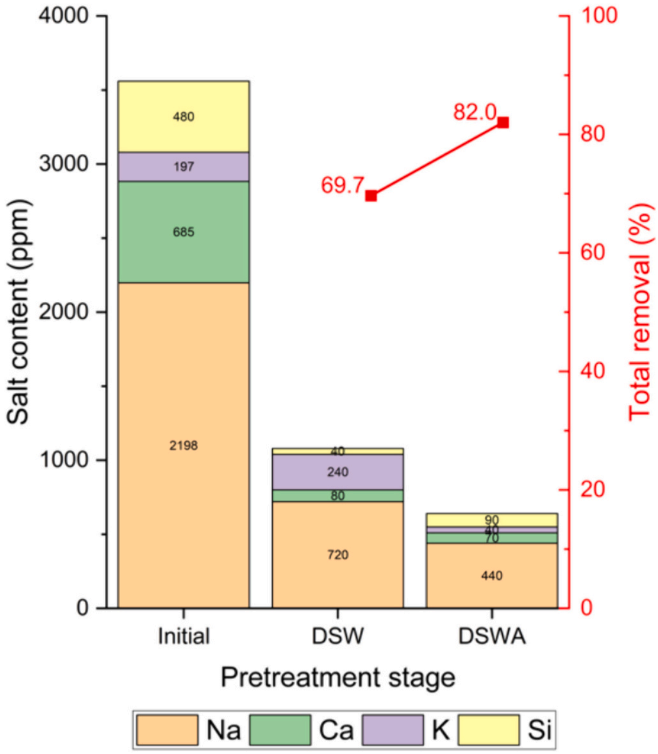


Fig. 2. Concentration of salt in the FPW biocrude oil after each pretreatment stage.

biocrude oil's heavy fraction during distillation. It has been previously observed that distillation was effective in reducing the heteroatom content, and it is likely that a significant portion of salt, metal, and ash were contained within the heavy fraction [13].

Additionally, the GC–MS analysis shed light on changes in the chemical composition of the biocrude oil during the pretreatment stages. Due to the significant presence of compounds with high boiling points and molecular weights in the HTL biocrude oil, these relative abundances only represent compounds that could volatize within the temperature range suitable for GC–MS (up to 350 °C) [52]. The identified compounds for the major abundant components were listed in Tables S1–3. It was observed that after DSW, the amount of oxygen-containing compounds decreased from 82.3 to 21.0% (Fig. 3), which was likely due to degradation of saturated and unsaturated fatty acids contained in the biocrude oil [15]. At elevated temperatures, saturated fatty acids are more soluble in water, which may have allowed some water-soluble oxygen-containing compounds to be separated from the biocrude oil during the desalting process [53]. On the other hand, the relative abundance of oxygen-containing compounds slightly increased after DWSA to 28.3%. This increase in the relative amount of oxygenates may be due to occurrences of thermal and oxidative degradation of biocrude compounds during the high temperature distillation process. Distillation has been demonstrated to reduce heteroatoms leading to lower levels of oxygenated compounds, which could be attributed to decarboxylation and deamination reactions occurring at higher temperature [14,17,18]. For instance, fatty acids in the initial biocrude oil, such as n-Hexadecanoic acid, may undergo decarboxylation to form n-alkanes after distillation, such as hexadecane seen in the DWSA sample. The final pretreated project also has a much higher amount of hydrocarbons compared to the initial and intermediate stages, with greater amounts of aromatics, n-alkanes, isoalkanes, cycloalkanes, and alkenes. These hydrocarbon compounds are ideal for hydrotreating, as the alkenes can undergo double bond saturation and long carbon chains can be hydrocracked or isomerized [54,55]. Similarly, the heteroatom-containing compounds can undergo hydrogenation to remove oxygen, nitrogen, and sulfur.

Beyond the composition of the biocrude oil, characterization of the water recovered after each pretreatment step provided further insight. The water properties were listed in Table 2. Notably, high conductivity of water separated from the biocrude oil after desalting (DS) indicated the presence of dissolved salt removed during the water wash. Low conductivity (<5% of DS) in residual water removed after dewatering (DSW) showed that some dispersed salt droplets remained in the biocrude oil after water wash. Therefore, future work may explore more efficient demulsification and separation methods. Comparably, there was a much lower conductivity from the inherent water content removed without any desalting (DW), supporting the importance of the separate desalting step. The measurement for total nitrogen in the DS sample was out of range for the spectrophotometer due to its dark color, however both ammonia nitrogen and total nitrogen in the water samples were very low, indicating that nitrogen-containing components in the biocrude oil were generally not water-soluble and not removed during pretreatment. All water samples were acidic with pH <4, likely due to the composition of the biocrude oil feedstock and short-chain acids dissolved into the wash water [5]. Meanwhile, the chemical oxygen demand (COD) and total organic carbon (TOC) values of the pretreatment water samples showed presence of organics in the removed water, which may have potential for downstream valorization [5].

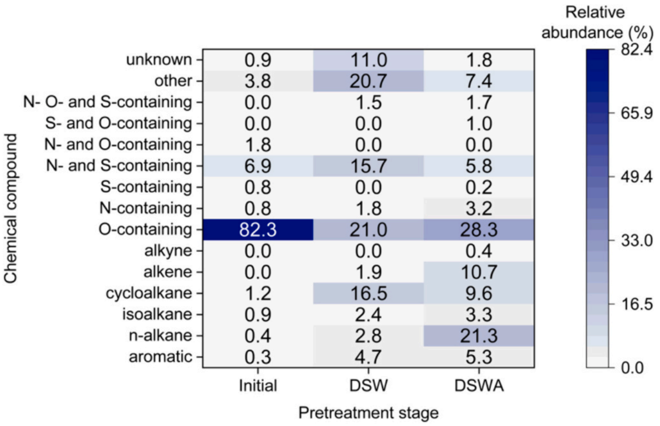


Fig. 3. Chemical composition of the FPW biocrude oil before and after pretreatment stages.

Table 2
Characterization of water samples from each pretreatment stage.

	DS	DSW	DW
pH	3.63 ± 0.02	2.98 ± 0.11	2.95 ± 0.01
Conductivity (μS/cm)	8470 ± 14	423 ± 1	530 ± 3
COD (mg/L)	17,490 ± 1216	11,275 ± 318	5245 ± 92
TOC (mg/L)	5195 ± 573	2815 ± 7	1495 ± 78
Ammonia N (mg/L)	0.22 ± 0.01	0	0
Total N (mg/L)	[a]	7.80 ± 0.01	23.25 ± 0.21

[a] Out of range.

3.1.3. Physicochemical and thermal properties

The elemental composition of the biocrude oil remained relatively the same after DSW, but increases in carbon and hydrogen along with decreases in oxygen content were observed after DSWA (Table 3). The pretreatment was also effective at removing a majority of sulfur present in the initial biocrude oil, with a 55.0% decrease. It was observed that after the DSW stage, both the nitrogen content and TAN of the biocrude oil slightly increased. Higher TAN after DSW may be due to increased abundance of phenol derivates which had relatively low acidity in comparison to other compounds in the biocrude oil such as hydrocarbons, along with acetic acid compounds that proportionately affect TAN value (Table S2) [56]. Meanwhile, decreased TAN after the deashing stage may be attributed to loss of oxygenates and nitrogenates from fatty acids during biocrude degradation. Overall, the physicochemical properties were improved after completed pretreatment, with a 5.3% increase in HHV, 23.5% decrease in TAN, 87.7% decrease in kinematic viscosity, and 7.2% decrease in density. These improvements are likely attributed to the removal of ash and heavy oil fraction after the DSWA stage, which helped isolate heteroatoms contained in the heavier fractions and provide a more stable biocrude oil composition [14].

TGA confirmed the removal of ash and some heavier components from the oil after desalting and deashing (Fig. 4). The initial biocrude oil had 3.16 wt% residue, along with a major derivative weightloss peak at 300 °C and a minor derivative weightloss peak at 400 °C indicating that its fuel components were mainly in the diesel and fuel oil range [57]. After the DSW stage, the TGA curve in Fig. 4a moved slightly up and the minor weightloss peak in Fig. 4b also decreased and shifted to the left. The shift in boiling point distribution to the left reflects the removal of higher boiling point compounds from the biocrude oil. The most significant change in boiling point distribution was after the DSWA stage, in which the ash and residue were completely removed from the oil and 100% recovery was achieved after distillation. Furthermore, the minor weightloss peak at was nearly eliminated, with just the major weightloss peak at 300 °C remaining.

The distillate composition of the biocrude oil (Table 4) across pretreatment was determined based boiling point distribution for weightloss between temperature ranges [56]. The initial biocrude oil was mainly in the diesel range, followed by fuel oil. After desalting, the amount of biocrude oil in the diesel range increased, corresponding to decreases in the heavy gas oil and kerosene ranges. Meanwhile, the amount of residue was decreased from 3.16 to 0.20 wt% after deashing, demonstrating the successful removal of ash from the biocrude oil.

Table 3
Physicochemical properties of initial and pretreated FPW biocrude oil.

	Initial			DSW			DSWA		
Carbon (wt%)	75.57	±	0.23	75.44	±	0.07	77.97	±	0.11
Hydrogen (wt%)	11.31	±	0.03	11.25	±	0.06	12.02	±	0.02
Nitrogen (wt%)	0.64	±	0.02	1.03	±	0.04	0.72	±	0.02
Oxygen (wt%)	12.45	±	0.23	12.26	±	0.17	9.28	±	0.11
Sulfur (wt%)		0.040			0.035			0.018	
HHV (MJ/kg)	38.37	±	0.14	38.30	±	0.12	40.39	±	0.03
TAN (mg/g)	185.17	±	5.92	223.26	±	2.44	141.60	±	2.18
Viscosity (mm^2/s)	119.87	±	2.01	86.53	±	2.55	14.79	±	0.13
Density (g/mL)	0.926	±	0.00	0.912	±	0.001	0.859	±	0.001

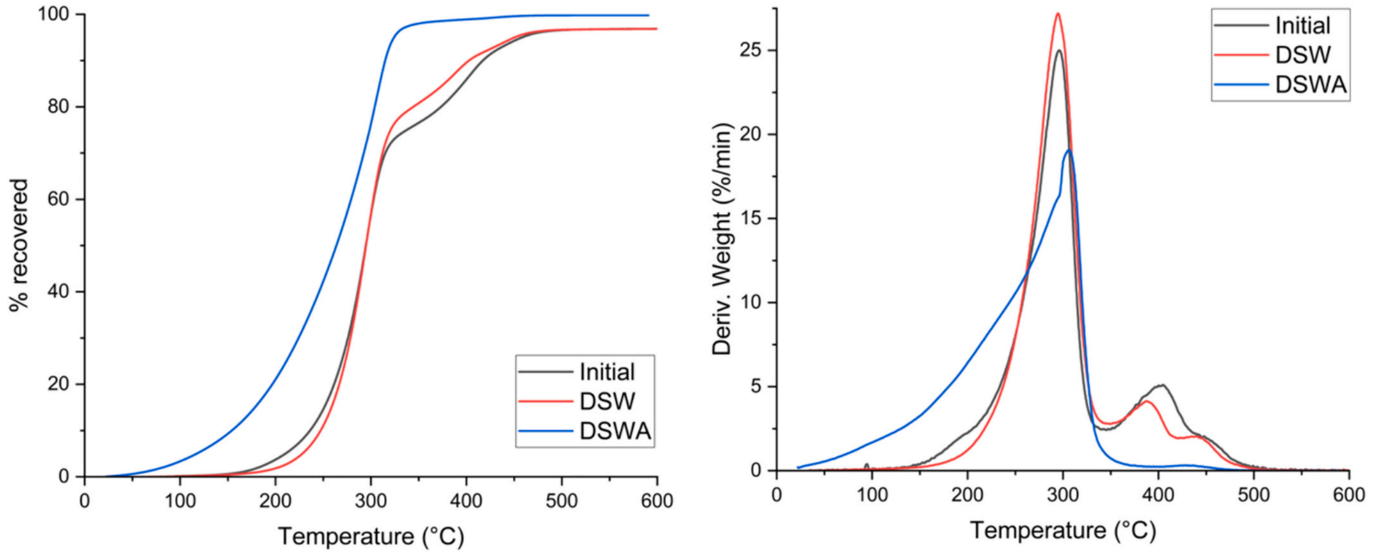


Fig. 4. Thermogravimetric a) boiling point distribution and b) DTGA peaks of the initial and pretreated FPW biocrude oil.

Table 4
Distillate composition of initial and pretreated FPW biocrude oil derived from thermogravimetric analysis.

Distillate range (°C)	Fuel type	wt%		
		Initial	DSW	DSWA
15.5–149	Gasoline	0.59	0.43	9.13
149–232	Kerosene	8.37	5.33	24.30
232–343	Diesel	66.74	74.06	64.27
343–371	Lubricating oil	3.90	4.16	0.82
371–566	Fuel oil	17.24	12.84	1.28
>566	Residue	3.16	3.18	0.20

Moreso, the DSWA stage significantly increased the amount of light and medium distillate fuel, with the gasoline, kerosene, and diesel range accounting for 97.7 wt% of the biocrude oil, compared to just 79.82 and 75.7 wt% in the DSW and initial biocrude oil, respectively. The increase of kerosene and gasoline fractions from diesel after deashing can also be attributed to fatty acid degradation during distillation. The decrease in the heavy fraction also explains the decreased density of the pretreated biocrude oil. Therefore, while desalting aided in the reduction of heavy components, deashing removed nearly all of them and improved the distillate composition and stability of the biocrude oil. It is important to note that this thermogravimetric approach for characterizing the boiling point distribution and distillate ranges of biocrude oil is limited by its procedure under atmospheric conditions. Therefore, thermal decomposition of biocrude components is likely, making the cut points less accurate.

The mass and carbon balances across pretreatment steps (initial, DSW, and DSWA) were depicted in Fig. 5. A significant amount of water was removed during dewatering due to the high moisture content of the HTL biocrude oil used for these experiments. During deashing, the heavy fraction (residue) of the biocrude oil (about 30%) was separated from the light and medium fractions (about 70%). Therefore, a final yield of 29.3% initial biocrude oil was obtained after pretreatment, but this represented about 70% of the actual biocrude oil. High carbon recovery in the DSW biocrude oil was observed, with nearly no carbon transferred to the aqueous phase. However, 28% of carbon was isolated in the residue portion after deashing, resulting in a final carbon recovery of 72% in the pretreated DWSA biocrude oil.

3.2. Single-stage pretreatment

The 3-stage pretreatment was applied to a second biocrude oil derived from GFW (grocery food waste) to determine the effectiveness of this method on removing salt, water, and ash from other feedstocks. Additionally, the results were compared to a single-step pretreatment “DA”, in which GFW biocrude oil was directly distilled for water and ash removal. It was found that the desalting effect was 10.6% less for DA in comparison to DWSA (Fig. 6). This showed that although deashing alone can remove a significant portion of salt contained in the heavy fraction of biocrude oil, the intermediate water wash step provides more effective desalting. Therefore, a 3-stage pretreatment including a desalting step is recommended in order to maximize salt and metal removal and reduce chance of catalyst deactivation during hydroprocessing.

Similarly, the physicochemical characteristics of the DA pretreated biocrude oil were also improved from the initial biocrude oil, but slightly less so compared to DWSA (Table 5). 3-stage pretreatment biocrude oil had slightly better elemental composition, with higher carbon and lower heteroatom (nitrogen, oxygen, and sulfur) content,

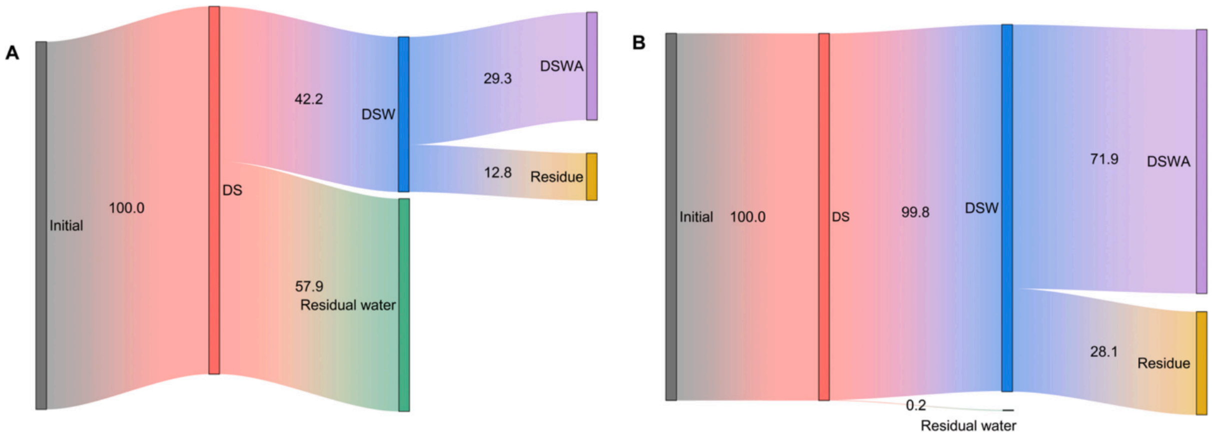


Fig. 5. Balances for a) mass and b) carbon during the 3-stage pretreatment method.

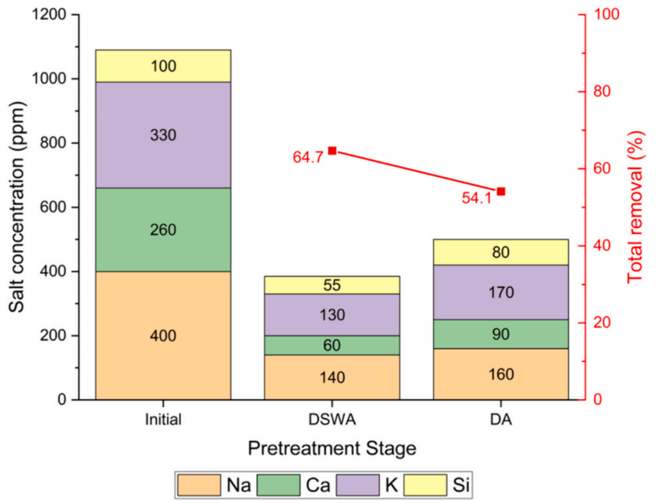
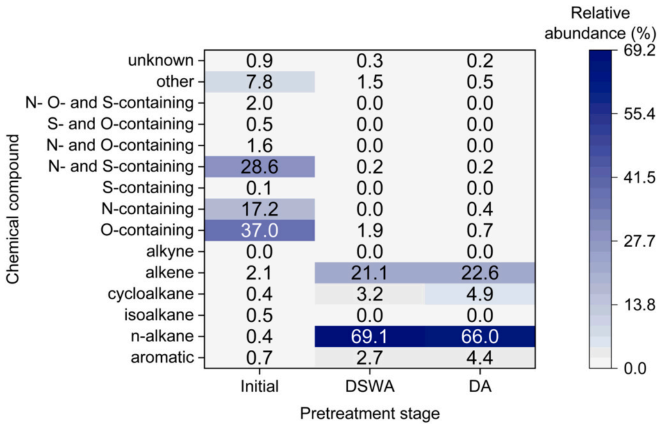


Fig. 6. Salt concentration and total salt removal in the GFW biocrude oil.

compared to the 1-stage pretreatment. Further, the greater presence of nitrogen and oxygen in the DA biocrude oil caused it to have a lower HHV and higher acidity. It was also observed that the DA biocrude oil had a higher viscosity and density compared to DWSA, indicating that the desalting step could help remove some heavy fractions that could not be removed by distillation alone. Both DWSA and DA pretreated biocrude oil had similar GC–MS compositions (Fig. 7). The 1-stage pretreatment produced biocrude oil with lower amounts of O-containing components, but slightly higher amounts of N-containing compounds, alkene, cycloalkane, and aromatic compounds. Comparatively, the 3-stage pretreatment produced biocrude oil with higher amounts of alkanes. Both DWSA and DA biocrude oil were highly composed of hydrocarbons, including n-alkanes, cycloalkanes, and alkenes. Similar to the deashed FPW biocrude oil, fatty acids in the GFW biocrude oil likely underwent decarboxylation and decarbonylation reactions to form n-alkanes and alkenes. For example, 8-heptadecene present in the DWSA and DA could have been derived from decarbonylation of oleic acid in the initial biocrude oil. Decarboxylation of tetradecanoic acid and dodecanoic acid could have also led to the formation or tridecane and undecane, respectively. This degradation could also explain the decreased TAN (Table 5) and increased amount of gasoline and kerosene fractions (Table 6).

Although there were no isoalkanes present in either pretreated biocrude oil, the high amount of n-alkanes could be valuable precursors for hydroprocessing. During hydrotreating, n-alkanes undergo isomerization to form isoalkanes, which improve the cold flow properties of diesel and jet fuel without compromising the fuel properties [54,58,59].

Thermogravimetric analysis of the pretreated biocrude oil showed



	Initial	DSWA	DA
unknown	0.9	0.3	0.2
other	7.8	1.5	0.5
N- O- and S-containing	2.0	0.0	0.0
S- and O-containing	0.5	0.0	0.0
N- and O-containing	1.6	0.0	0.0
N- and S-containing	28.6	0.2	0.2
S-containing	0.1	0.0	0.0
N-containing	17.2	0.0	0.4
O-containing	37.0	1.9	0.7
alkyne	0.0	0.0	0.0
alkene	2.1	21.1	22.6
cycloalkane	0.4	3.2	4.9
isoalkane	0.5	0.0	0.0
n-alkane	0.4	69.1	66.0
aromatic	0.7	2.7	4.4

Fig. 7. Chemical composition of GFW biocrude oil pretreated with 3-stage (DWSA) vs. 1-stage (DA).

Table 5
Physicochemical characteristics of the initial and pretreated GFW biocrude oil.

	Initial			DSWA			DA		
Carbon (wt%)	75.24	±	0.32	79.49	±	0.40	78.79	±	3.73
Hydrogen (wt%)	10.64	±	0.01	12.07	±	0.69	12.21	±	0.44
Nitrogen (wt%)	2.12	±	0.06	1.65	±	0.02	1.75	±	0.12
Oxygen (wt%)	12.00	±	0.27	6.77	±	1.07	7.22	±	0.29
Sulfur (wt%)		0.010			0.025			0.035	
HHV (MJ/kg)	37.62	±	0.15	41.33	±	1.06	41.20	±	2.31
TAN (mg/g)	242.74	±	19.09	64.61	±	1.72	79.87	±	0.74
Viscosity (mm^2/s)	3384.17	±	126.85	4.40	±	0.02	8.98	±	0.07
Density (g/mL)	0.977	±	0.013	0.811	±	0.001	0.832	±	0.001

Table 6
Distillate composition of pretreated GFW biocrude oil.

Distillate range (°C)	Fuel type	wt%		
		Initial	DSWA	DA
15.5–149	Gasoline	0.73	21.19	15.26
149–232	Kerosene	8.44	56.77	44.21
232–343	Diesel	65.85	18.08	39.78
343–371	Lubricating oil	4.59	0.10	0.14
371–566	Fuel oil	12.58	0.33	0.26
>566	Residue	7.71	3.53	0.34

that both 3-stage and 1-stage pretreatment methods reduced the ash in the biocrude oil with <3% residue left in each (Fig. 8a). Pretreatment of GFW biocrude oil also affected the boiling point distribution more significantly than FPW. The minor weightloss peak seen in the initial biocrude oil (Fig. 8b) was removed after both pretreatments, indicating the removal of heavier compounds after distillation. The major weightloss peak at 300 °C in the initial biocrude oil shifted to 200 °C for DSWA and a broader peak at 250 °C for DA, indicating that the fuel composition consisted of lighter fractions after both pretreatments.

This shift in boiling point distribution was reflected in the distillate composition of the biocrude oils (Table 6), where it was observed that the majority of DSWA distillate was within the kerosene range. Meanwhile, major composition of the DA distillate was relatively even between kerosene and diesel, reflecting its broader derivative weightloss peak. While both methods improved the biocrude oil's boiling point distribution, 3-stage pretreatment was superior in increasing light fractions (gasoline and kerosene range) compared to 1-stage. Therefore, DWSA biocrude oil was better qualified for hydroprocessing to produce drop-in fuels.

Lastly, the mass and carbon balances were compared between the single-stage DA pretreatment (Fig. 9a,b) and the 3-stage DWSA pretreatment process (Fig. 9c,d). Notably, the low water content of the GFW biocrude oil (<10%), resulted in high mass yields. However, the DWSA had about 7% higher mass yield compared to DA, along with 3% higher carbon recovery, which would further improve performance measures in technoeconomic and life cycle analyses [60]. This indicated the capability of 3-stage pretreatment method for efficient biocrude recovery. Furthermore, the amount of mass and carbon lost to the distillate residue fraction after deashing was minimized in the 3-stage method, with about 10% less mass and 6% less carbon compared to the DA pretreatment. Therefore, performance of the developed 3-stage pretreatment remained better than distillation only, with higher mass and carbon balance, as well as improved physicochemical composition and fuel properties.

4. Conclusion

This study aimed to develop an economically viable biocrude pretreatment method to produce precursors for hydroprocessing. A 3-stage pretreatment method was used to effectively remove salt, water, and ash from HTL biocrude oil without the aid of acids or solvents. It was found that W:O ratio had the most significant effect of desalting efficiency and the following deashing step further removed salt contained in the heavy fraction and residue of biocrude oil. The 3-stage pretreatment removed up to 81% of inorganics and had better removal compared to a direct distillation. The elemental composition improved due to heteroatom removal. The fuel properties of the biocrude oil were also more desirable following pretreatment with increased HHV, along with decreased TAN, viscosity, and density. Changes in chemical composition across pretreatment steps reflected the removal of oxygenates and nitrogenates, with increased in hydrocarbon content, likely due to the degradation of fatty acids through decarboxylation, deamination, and decarbonylation during distillation in the deashing stage. Furthermore, TGA confirmed the removal of higher boiling point components from the biocrude oil, leaving a pretreated biocrude oil largely consisting of lighter fuel fractions. Meanwhile, the extent of pretreatment may vary based on the biocrude oil's initial composition and properties. Although the 3-stage pretreatment produces higher-quality biocrude oil for hydrotreating precursors, it also requires additional steps and produces a saline wastewater in comparison to a direct distillation. Future work may investigate the economic and lifecycle differences in incorporating each pretreatment method. Overall, the intermediate desalting step in pretreatment played an important role in achieving higher salt and heteroatom removal, while the 3-stage pretreatment method refined the biocrude oil for viable hydroprocessing.

CRediT authorship contribution statement

Sabrina Summers: Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Conceptualization. **Siyu Yang:** Writing – review & editing, Investigation. **Zixin Wang:** Writing – review & editing, Visualization, Investigation. **Buchun Si:** Writing – review & editing, Visualization, Investigation. **Harshal Kawale:** Writing – review & editing, Resources. **Yuanhui Zhang:** Writing – review & editing, Supervision, Resources, Project administration, Funding acquisition.

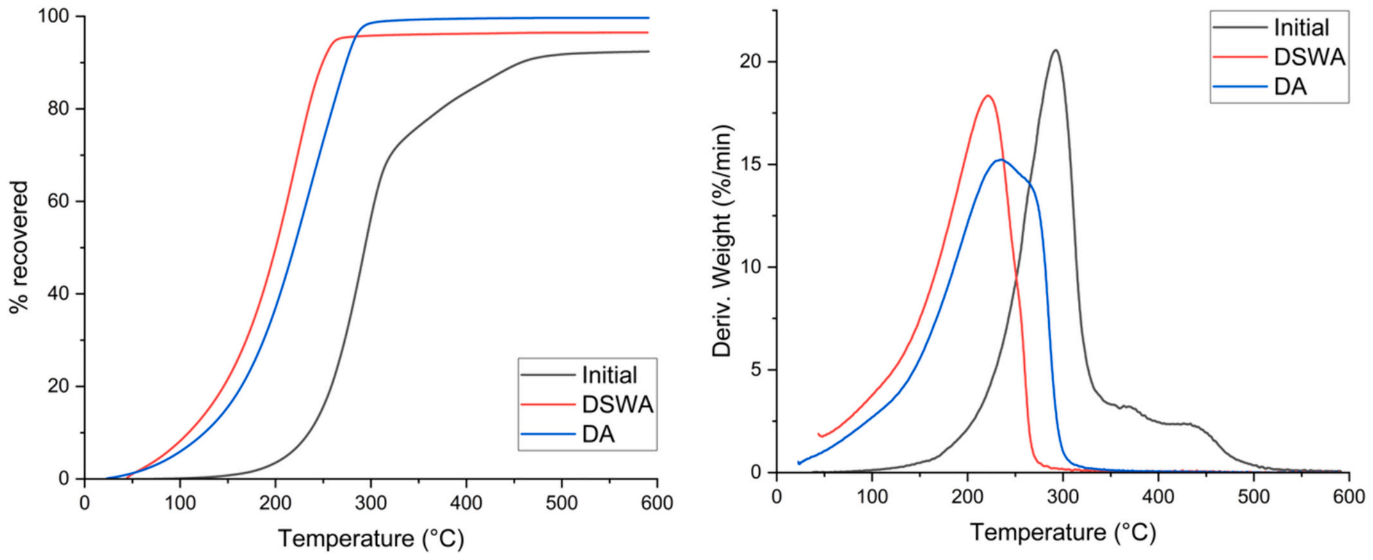


Fig. 8. Thermogravimetric a) boiling point distribution and b) DTGA peaks of pretreated GFW biocrude oil.

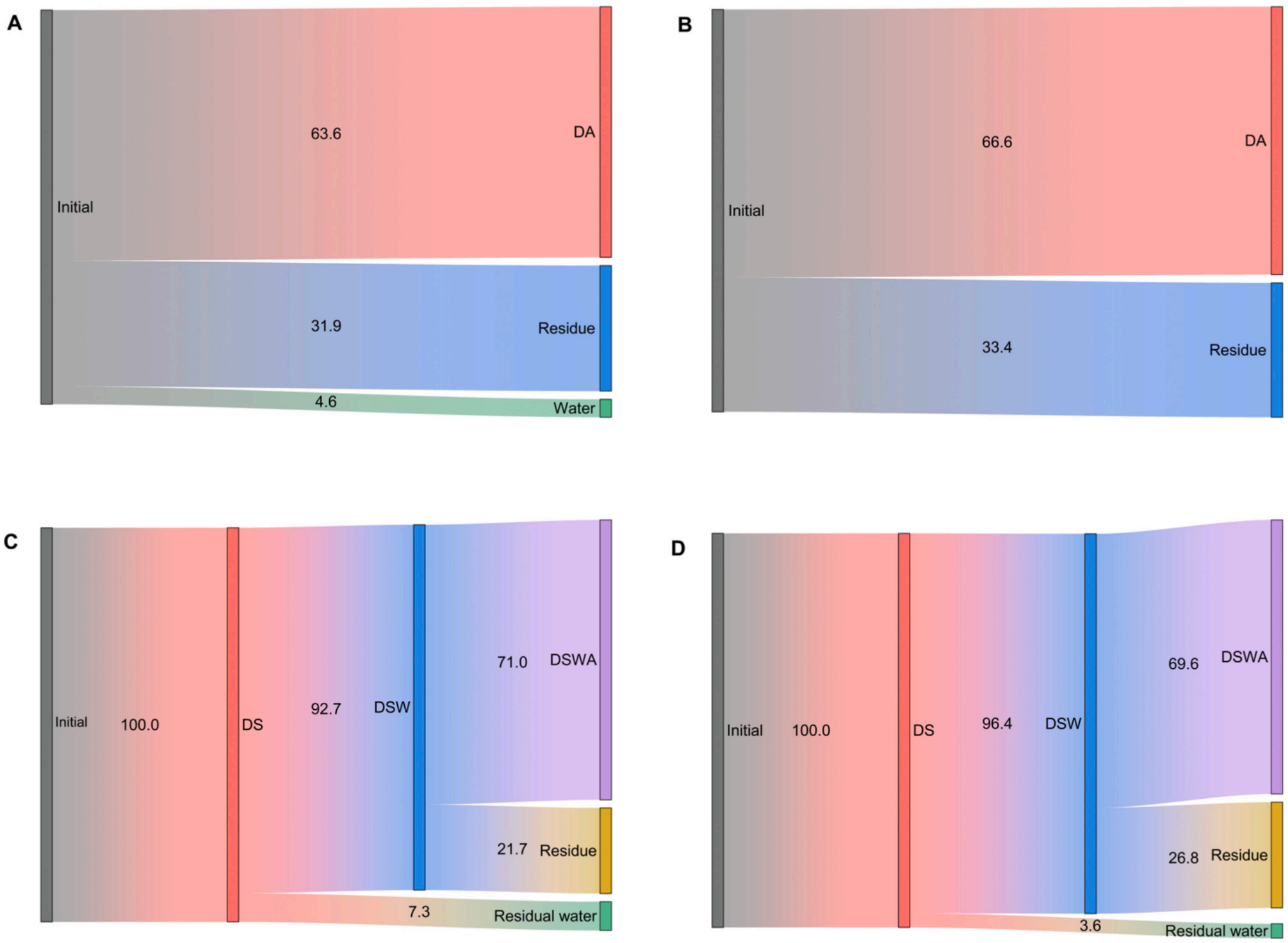


Fig. 9. 1-stage DA pretreatment a) mass and b) carbon balance compared to 3-stage DWSA pretreatment c) mass and d) carbon balance.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Yuanhui Zhang reports financial support was provided by US Department of Energy. Sabrina Summers reports financial support was provided by National Science Foundation. If there are other authors, they 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

No data was used for the research described in the article.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.fuproc.2024.108118.

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