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Storage stability of biocrude oil fractional distillates derived from the hydrothermal liquefaction of food waste

Buchun Si [a,b], Jamison Watson [b,c,**], Zixin Wang [b], Tengfei Wang [d], Juan S. Acero Triana [e], Yuanhui Zhang [b,*]

[a] Key Laboratory of Agricultural Engineering in Structure and Environment, Ministry of Agriculture and Rural Affairs, College of Water Resources and Civil Engineering, China Agricultural University, Beijing, 100083, China
[b] Department of Agricultural & Biological Engineering, University of Illinois at Urbana-Champaign, Urbana, IL, 61801, USA
[c] Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA, 02142, USA
[d] Faculty of Geosciences and Environmental Engineering, Southwest Jiaotong University, Chengdu, 611756, China
[e] Department of Environmental Sciences, University of California-Riverside, 900 University Ave, Riverside, CA, 92521, USA

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ABSTRACT

Biocrude oil produced via hydrothermal liquefaction (HTL) is a promising precursor for transportation fuels and biochemicals. Present studies have highlighted the inherent instability of the biocrude oil, which poses significant challenges for its subsequent storage, upgrading and transportation. On the other hand, biocrude oil distillates showed the potential to serve as a transportation fuel blendstock. To this end, this study aimed to investigate the influence of the distillation temperature (199–238 °C and 238–274 °C), storage atmosphere (air and nitrogen), temperature (25 °C and 55 °C), and time (0–16 weeks) on the physical, chemical, and boiling point distribution properties of the distillates. Results demonstrated that changes in the stored distillates due to different distillation temperature were drastically higher than that between different storage atmospheres and temperatures. Comparing with the raw distillate, the distribution of compounds with a molecular weight < 300 Da in low-temperature (199–238 °C) distillates (LD) and medium-temperature (238–274 °C) distillates (MD) was improved with the increasing storage time. In addition, storage led to a decrease in O:C ratio (21.6 % and 86.5 %), and an increase in the HHV (3.6 % and 12.3 %) in the LD and MD, respectively. Furthermore, only slight deviations were observed in the density (5.2 % and 7.4 %) and viscosity (5.2 % and 0.8 %) for LD and MD, respectively. In particular, the MD group exhibited comparable characteristics to transportation fuels with decreased acidity (1.8–2.8 mg KOH/g) and increased HHV (46.2–46.8 MJ/kg) after long-term storage. At last, the mechanism of superior distillates stability was discussed. This study indicated that distillation not only presents a potential approach for producing transportation fuel blendstock but also improves the stability of HTL biocrude oil.

1. Introduction

Hydrothermal liquefaction (HTL) is a thermochemical processing technology that operates at elevated temperatures (200–375 °C), pressures (5–28 MPa) [1,2], and uses the intrinsic moisture in the feedstock as a reaction medium for waste processing, yielding a hydrocarbon-rich oil that is similar to petroleum crude oil [3]. Preceding studies have incorporated HTL as a waste-to-energy conversion methodology to valorize food waste. HTL (15 wt% solid loading, 600 °C, 1 min residence time) demonstrated a high energy recovery (46 %) and heating value (42 MJ/kg) for a ternary mixture rich in potato starch [4]. Aierzhati et al. conducted isothermal HTL (280–380 °C, 10–60 min residence time) of dining hall waste and model compounds. Yields ranging from 2 to 79 %, energy conversion ratios (ECRs) ranging from 0.12 to 1.31, and total biocrude oil carbon recoveries of 19–88 % at different reaction conditions were obtained [5]. Despite the advantages of food waste-derived HTL biocrude oil, the disadvantage of the HTL process is that it yields an oil with a high heteroatom content (e.g., O: 5–17 %, N: 1–9%), which leads to the poor physical, chemical, and thermal properties of biocrude oil [5,6]. Watson et al. proposed that the distillation of

* Corresponding author.
** Corresponding author. Department of Agricultural & Biological Engineering, University of Illinois at Urbana-Champaign, Urbana, IL, 61801, USA.
E-mail addresses: watson.jamisont@gmail.com (J. Watson), yzhang1@illinois.edu (Y. Zhang).

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food waste-derived biocrude oil could first be performed to isolate fuel compounds from recalcitrant compounds, thereby paving a path for future oil upgrading on distillate fractions of biocrude oil [7]. The results suggested that distillation increased the H:C (4.2–13.7 %), decreased the O:C (5.5–93.5 %), decreased the N:C (6.0–39.0 %), and augmented the heating value (4.1–21.3 %) compared to the biocrude oil, respectively. Further, Chen et al. verified HTL biocrude oil converted from food waste could be upgraded into a diesel blendstock via distillation combined with esterification, and fuel specification analysis and engine tests with diesel blends indicated promising results in terms of energy efficiency and air emissions [8].

Due to the presence of heteroatoms and unsaturated bonds, biocrude oil is a very unstable mixture of chemicals. The instability of olefins, aldehydes, ketones, and alcohols over time contributes to the changing characteristics of biocrude oil during storage [9]. Stability has been referred to as the resistance of a chemical mixture to avoid reactions contributing to changes in physical and chemical properties [10]. Stability is an important industrial parameter for biocrude oil because it dictates its potential application as a fuel source [11]. A previous study indicated that a variety of reactions contribute to this instability: hemiacetal formation, the formation of glycols from aldehydes/ketones via hydration, acetalization, polymerization of furans, dimerization of nitrogen-containing compounds, etc. [12]. These reactions contribute to the changing of various chemical and physical properties, including the viscosity, acidity, molecular weight, chemical composition, and elemental composition. The formation of a chemically stable biocrude oil is essential because instability can cause the formation of insoluble gums and sediments which results in an unreliable and unusable fuel [13].

Previous studies have investigated both the thermal and oxidation stability of biocrude oil. Meng et al. determined that accelerated aging of biocrude oil derived from the pyrolysis of torrefied wood resulted in an increased water content (9–20 %), total acid number (14–23 %), molecular weight (44–96 %), and viscosity (114–212 %) compared with raw biocrude oil [14]. Wang et al. hypothesized that an "oxidative shell" was formed due to the polymerization of phenols and nitrogen-containing compounds which demarcated an upper oil and an inner oil [10]. Ren et al. separated oil into organic and aqueous phase fractions to better understand the impacts of organic- and aqueous-soluble components on the accelerated aging of biocrude oil [9]. It was determined that water-soluble organics (e.g., alcohols, furans, ketones, and phenols) could be attributed in part to the poor stability of the biocrude oil. Lin et al. determined that the type of oil contributed to oil stability. Specifically, large variations in the acidity and moisture content were observed for swine leather residue-derived biocrude oil (97–140 mg/g and 7–11 %, respectively) than sewage sludge-derived biocrude oil (109–118 mg/g and 3–5%, respectively) [15]. Most recently, Wang et al. expanded upon the study by Lin et al. by examining three different types of biocrude oil: Spirulina-derived biocrude oil, cornstalk-derived biocrude oil, and swine manure-derived biocrude oil [16]. It was determined that the physiochemical properties of biocrude oil derived from high-lipid and high-protein feedstocks were impacted less severely than the oil derived from high-carbohydrate feedstocks.

However, despite the presence of research on the impacts of the thermal environment, oxidative environment, and feedstock on the storability of biocrude oil, limited studies have incorporated techniques to isolate chemical compounds via fractional distillation to better understand if distillation can be incorporated to improve the stability of biocrude oil. This study utilized atmospheric-pressure distillation to separate food waste-derived biocrude oil into low-temperature distillates (Group LD) and medium-temperature distillates (Group MD) to understand how physical isolation of compounds can influence oil stability with respect to oil's physical, chemical, and boiling point distribution properties. Thus, the purposes of this study are threefold: (1) Expose distillates (Group LD and MD) of biocrude oil derived from food waste to different oxidation (air and nitrogen) and thermal (25 °C and 55 °C) environments over sixteen weeks; (2) Quantify the changes in the physical (e.g., acidity, density, viscosity), chemical (elemental, molecular weight, chemical distribution), and boiling point distribution properties to determine how the distillation group, thermal environment, and oxidation environment influence the properties of biocrude oil distillates; (3) Unravel how distillation can augment the stability of biocrude oil.

2. Materials & methods

2.1. Feedstock and materials

Food waste was collected from a food processing plant in Champaign, IL. The collected food waste was first homogenized using a blender and then sieved with a No. 16 wire mesh (1 mm center-to-center) to avoid particles larger than 1 mm. The ultimate and proximate analysis of food waste was conducted and reported in previous studies [7,8]. Food waste was stored in a refrigerator at a temperature of 4 °C to preserve the samples.

2.2. Pilot-scale biocrude oil production and distillation

HTL experiments were conducted using a 30 L pilot-scale continuous plug flow reactor system [17,18] at an average temperature of 280 °C, an average pressure of 10 MPa, and an average residence time of 60 min. The feedstock flow rate was averaged at 0.5 L/min. The mixture of biocrude oil aqueous-soluble organics was released into product collection tanks. The biocrude oil naturally phase-separated from the aqueous-soluble organics, thereby allowing for physical separation of the phases by decantation.

Atmospheric-pressure distillation was conducted by modifying the standard methodology utilized in previous studies [7,8,19]. The biocrude oil was charged into a round-bottom flask which was wrapped with glass wool to reduce heat loss. A J-type thermocouple was used to monitor the vapor temperature entering the condenser unit. The round-bottom flask was then heated using a magnetic stirrer heating mantle (BIPEE, Model Number: 98-2-B-1000). The heating rate was set at approximately 2.5 °C/min. The vapor distillate was refluxed into an inclined condenser by circulating tap water (25 °C) through the condenser unit. The condensed material was dripped into a graduated cylinder.

2.3. Oxidation and thermal stability setup

Groups of distillates were combined based on their similar physical and chemical properties. Fractions 1–6 were considered to be the low-temperature distillates (Group LD), and fractions 7–14 were considered to be the medium-temperature distillates (Group MD). Specifically, Group LD consisted of compounds that eluted from food waste-derived biocrude oil between 199 and 238 °C, and Group MD consisted of compounds that eluted between 238 and 274 °C. Approximately, 35 g of Group LD and Group MD distillates were added to separate serum bottles with a working volume of 160 mL. The two distillate groups were exposed to two thermal environments and 2 atm over sixteen weeks. The thermal environments involved two temperatures: 25 °C and 55 °C. The two atmospheres involved exposure to two gases: air and nitrogen. All distillates were covered to ensure a dark environment, thereby negating the impact of light. During each testing period, the atmosphere gas was vented and then replaced with fresh air or nitrogen. The experimental design is presented in Table 1.

2.4. Product analysis

Elemental analysis was conducted via a CE440 element analyzer (Exeter Analytical; North Chelmsford, MA). The oxygen content was

Table 1
Experimental design for testing the stability of low-temperature distillate (LD) and medium-temperature distillate (MD) groups under different storage temperatures (22 °C and 55 °C) and atmospheres (air and nitrogen). Storage environment: AH-Air-heated; AR-Air at room temperature; NH-Nitrogen heated; NR-Nitrogen at room temperature.

Group	Distillation Temperature Range		Storage Temperature		Atmosphere	
	LD (199–238 °C)	MD (238–274 °C)	25 °C	55 °C	Air	Nitrogen
LD-AH	●	○	○	●	●	○
LD-AR	●	○	●	○	●	○
LD-NH	●	○	○	●	○	●
LD-NR	●	○	●	○	○	●
MD-AH	○	●	○	●	●	○
MD-AR	○	●	●	○	●	○
MD-NH	○	●	○	●	○	●
MD-NR	○	●	●	○	○	●

calculated by difference. The higher heating value (HHV) of the biocrude oil samples was calculated based on Dulong's formula [7]. The elemental ratios (H:C, O:C, and N:C) were calculated by taking the ratio of the element weight percent and the element molecular weight.

The chemical characterization of the biocrude oil samples was conducted via gas chromatography-mass spectrometry (GC-MS) (Agilent Technologies; Santa Clara, CA). The GC-MS conditions were determined based on a previous study [20]. A 2 μL sample was injected in split mode into a system consisting of three components: An Agilent 6890 chromatograph, an Agilent 5973 mass detector, and an Agilent 7683B auto-sampler. The injection temperature was set at 250 °C. The oven temperature was initially set at 70 °C and then ramped at 5 °C/min to 300 °C. The source temperature was set at 230 °C, and the electron ionization voltage was set at 70 eV. Spectra were scanned from 30 to 800 *m/z*, and the characterization of individual peaks was determined by comparing mass fragmentation patterns of the peak to the NIST (NIST08) database.

The mass distribution of the biocrude oil was analyzed via matrix-assisted laser desorption/ionization time of flight mass spectrometry (MALDI-TOF-MS). MALDI-TOF-MS measurements were conducted using a Bruker Autoflex Speed LRF instrument (Bruker Scientific Instruments; Germany) with dual microchannel plate detectors for both linear and reflectron modes. In accordance with the manufacturer's instructions, MALDI-TOF was used with Flexcontrol software 3.0 (Bruker Daltonics) for the automatic acquisition of mass spectra in the reflectron positive mode within the range of 150 to 1,500 Da. The number-averaged molecular weight (M_n), weighted-average molecular weight (M_w), and polydispersity index (I) were determined according to Equation (1), Equation (2), and Equation (3), respectively:

$$M_n = \frac{\sum M_i * n_i}{\sum n_i} \quad (1)$$

$$M_w = \frac{\sum M_i^2 * n_i}{\sum M_i * n_i} \quad (2)$$

$$I = \frac{M_w}{M_n} \quad (3)$$

Where M_i and n_i are the mass and abundance of the ith oligomer, respectively [21]. The polydispersity index represents the total overall spread of chemical compound weights present in the biocrude oil. A large value represents a broad weight distribution, and a value of 1 signifies a homogeneous weight distribution.

The boiling point distribution was determined via thermogravimetric analysis (TGA). TGA conducted in an inert atmosphere has been widely incorporated to construct the true boiling point distillation curve of biocrude oil in a myriad of previous studies [22,23]. To determine the mass fraction vaporized as a function of temperature, approximately 10–20 mg of the sample was placed in a quartz crucible. The crucible was then transferred to a platinum pan and delivered to the Cahn TherMax 500 TGA system. Samples were heated from room temperature up to 650 °C at a ramp temperature of 10 °C/min while under a nitrogen flow rate of 22 mL/min. The boiling point distribution was categorized based on the mass vaporized at five distinct temperature ranges: naphtha (<193 °C), kerosene (193–271 °C), diesel (271–343 °C), vacuum gas oil (343–538 °C), and residue (>538 °C) [24].

The kinematic viscosity of the oil samples was determined using a Cannon-Fenske routine viscometer at 20 °C according to standard methods (ASTM D446-12) [25]. The acidity (total acid number) of the samples in this study was determined via color-indicator titration according to standard methods (ASTM D974-12) [26]. The acidity was reported as the unit mass of KOH needed to neutralize a unit mass of biocrude oil (mg/g). The density was measured using a Gay-Lussac bottle (Cole-Parmer, EW-34580-40) [27]. The change in the color of the distillates over time was quantified using a spectrophotometer (Hach Company, DR 3900). The percent transmittance over the wavelength range of 320–800 nm with a step interval of 1 nm was measured.

3. Results and discussion

3.1. Physical properties

The qualitative color change of the distillates under different storage temperatures and atmospheres is presented in Fig. 1A. The color change was apparent for both Group LD and MD. For the former, the transparent light-yellow tint changed to a semi-transparent bright orange over time, and for the latter, the brown tint changed to an opaque black over time (Fig. 1A). A color change is typically indicative of a chemical change, thereby confirming that storage of the biocrude oil distillates involved some sort of chemical transformation over time. A previous study noted that changes in the liquid solution color can be used to estimate the extent of a chemical reaction [28]. Thus, from the lack of color change after eight weeks, it can be hypothesized that the chemical transformation of the distillates was initially rapid and then decelerated over time.

Within the visible spectrum (~380–750 nm), the relative transmittance trends were opposite for low- and medium-temperature distillates (Fig. 1BC). However, values were similar to the raw distillates below 500 nm, which corresponded to the orange/red tint of the Group LD before and after storage (Fig. 1B). The storage temperature and atmosphere did not seem to accelerate or decelerate the color change. Group MD all had transmittance values far below the raw distillate (Fig. 1C). This corresponded to the brown-to-black color change since low transmittance values signify a high absorbance at all wavelengths.

Raw LD and MD had a viscosity of 5.23 ± 0.01 and 3.86 ± 0.01 mm^2/s (Table S1), which were much lower than the biocrude oil [7]. The viscosity of distillates markedly changed among all storage temperatures and atmospheres (Fig. 2). All groups demonstrated a decrease or slightly elevated viscosity during the first eight weeks and then an increase after sixteen weeks. With regard to Group LD, under an inert nitrogen atmosphere, a hot storage temperature (LD-NH) resulted in a higher increase in viscosity after sixteen weeks (29.0 %) compared to a cool storage temperature (LD-NR) environment (19.5 %). Under a constant storage temperature, an inert atmosphere led to a greater viscosity increase in both hot (30.0 % vs. 7.2 %) and cool storage conditions (19.5 % vs. 11.4 %). As for Group MD, the change in atmosphere resulted in slightly different trends. Under a hot storage temperature, an inert atmosphere (10.6 %) resulted in a less viscous fluid than in an oxidative atmosphere (14.0 %). However, for cool storage conditions, an oxidative environment resulted in a less viscous fluid (7.0 %) than an inert

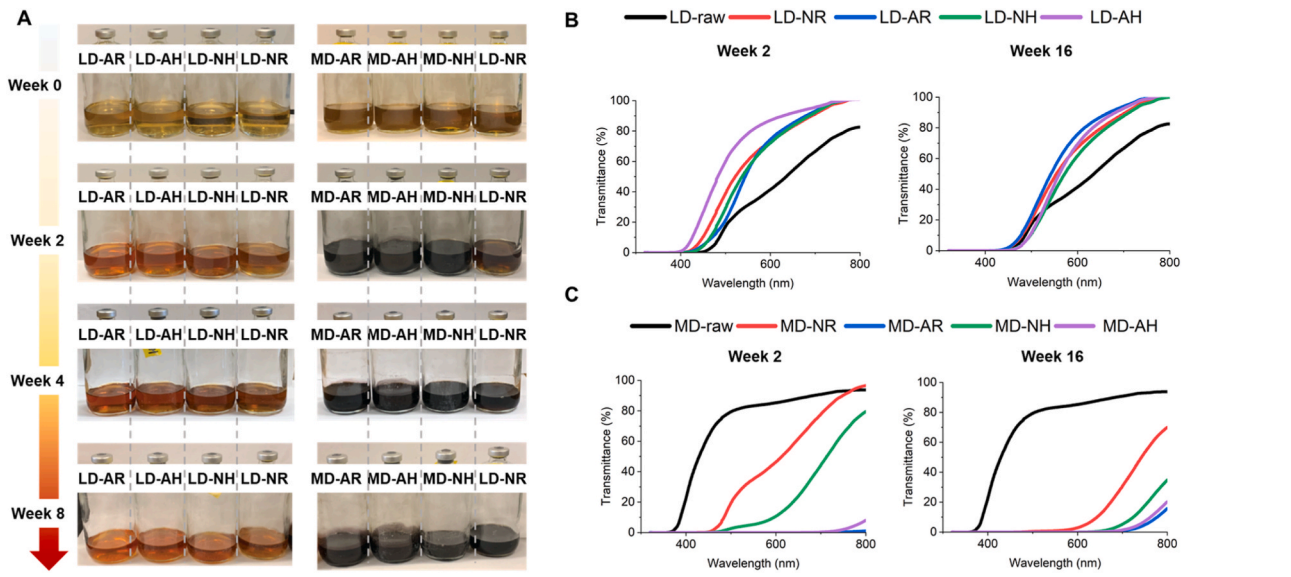

Fig. 1. Influence of storage temperature and atmosphere on the color change of distillates over 8 weeks (A) and relative transmittance of the Group LD (B) and Group MD (C). No further color change was observed after 8 weeks.

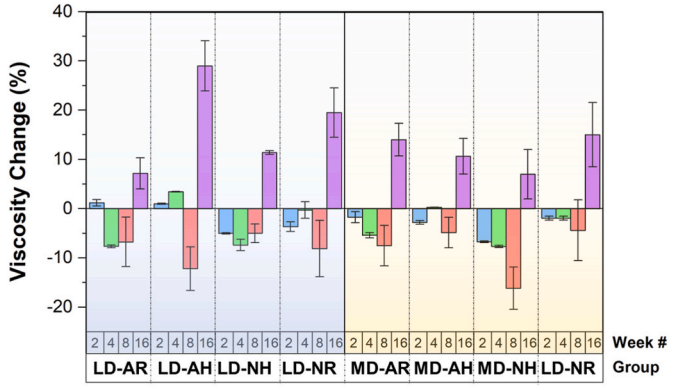

Fig. 2. Influence of storage temperature and atmosphere on the viscosity change of the low-temperature distillate (Group LD) and medium-temperature distillate (Group MD) fractions compared to the raw distillate (week 0).

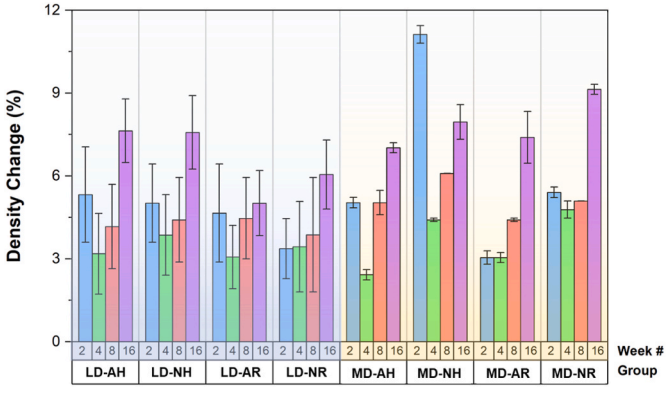

Fig. 3. Influence of storage temperature and atmosphere on the density change of the low-temperature distillate (Group LD) and medium-temperature distillate (Group MD) fractions compared to the raw distillate (week 0).

environment (15.0 %) compared with the raw distillate. Though an increase of viscosity of all distillates after sixteen weeks was observed, the viscosity changes in this study were far less than those reported in previous studies, which previously demonstrated maximum increases of biocrude oil viscosity by up to 454 % after twelve weeks of storage [10,14]. Viscosity increases have been attributed to the accumulation of high-molecular-weight derivatives and the presence the polymerization, condensation, and oxidation reactions [10,29,30]. In comparison, the decrease in viscosity could be attributed to the reduced presence of intermolecular forces (e.g., intermolecular hydrogen bonding) associated with polar functional groups [31]. Since the viscosity did not dramatically change until the final weeks, this may indicate that condensation and polymerization of distillates are slow, kinetically limited reactions that were not appreciably noticeable until the end of the time study.

The distillates suggested a stable density range of 0.82–0.88 g/cm^3 during the storage (Table S1), and a slight increase of less than 10 % of density as the storage time increased for all conditions was confirmed (Fig. 3). Interestingly, the same trend was exhibited for all storage temperatures and atmospheres. Specifically, a local maximum was achieved at week two compared to the raw distillate (4.5–7.1 %); thereafter, the relative change decreased and then increased to an absolute maximum compared to the raw distillate (7.3–8.9 %). The one exception to this trend was the MD-NH condition, which exhibited an absolute maximum at week 2 (11.4 %) compared to the raw distillate. There were no apparent density change differences when comparing the LD and MD. Previous studies have correlated fuel density with its molecular weight and kinematic viscosity [32], and it also noted that density change tends to be a function of storage time and that density change is more rapid in the latter stages of oxidation [33]. These results support the hypothesis that condensation and polymerization reactions may be kinetically limited, thereby not occurring at the onset of storage and not influencing the physical properties until sixteen weeks of storage.

Clear differences of acidity change were observed between the LD and MD groups (Fig. 4). All LD demonstrated a decrease in the acidity throughout the entirety of the storability experiments, amounting to total decreases ranging from −10.5 to −20.2 %. The decreased acidity could be associated with the esterification of fatty acids, dehydration of alcohols, or the polymerization of phenols [10,16]. This indicated a decreased presence of –COOH and –OH functional groups. No clear influence of the specific storage conditions on the influence of the LD was observed. Previous studies have demonstrated mixed results on the influence of storage on acidity [10]. Trends were of greater magnitude for

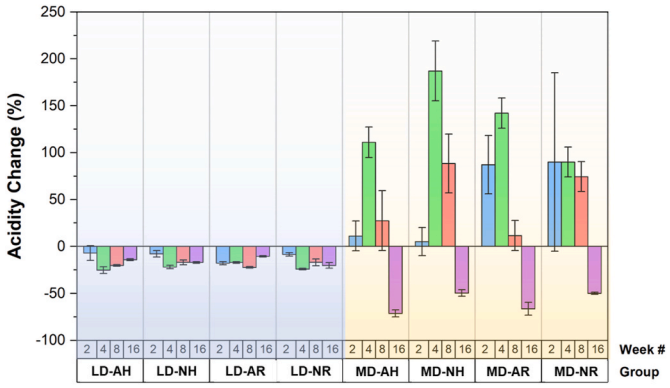

Fig. 4. Influence of storage temperature and atmosphere on the acidity change of the low-temperature distillate (Group LD) and medium-temperature distillate (Group MD) fractions compared to the raw distillate (week 0).

the MD in comparison to the LD. However, the absolute acidity values were significantly lower for the MD than the low-temperature distillates and incurred a greater amount of error; thus, trends for the MD provide directional insight and may not provide reliable quantitative insight (Table S1). Under hot storage conditions when changing the atmosphere (MD-AH vs. MD-NH), the acidity only increased slightly for week two (11.3 % and 5.3 %, respectively) and then increased dramatically to a maximum for week four (111.2 % and 187.2 %, respectively); thereafter, the acidity dramatically decreased. Pattamaprom et al. corroborated this finding by noting that the acid value of biodiesel dramatically increased during storage, and this was particularly noticeable in a hot storage environment [33].

3.2. Molecular weight distribution

The average molecular weight (M_n) first decreased and then increased as the storage time increased for the LD groups (Fig. 5). The abundance of compounds <300 Da and >1,000 Da were most influenced as the storage time increased. A previous study found that over time the accumulation of compounds >1,000 Da increased and compounds <1,000 Da decreased during storage [34]. In an oxidative atmosphere, the inclusion of heat (LD-AH vs. LD-AR) demonstrated a 5.8 %, 0.7 %, and −0.8 % difference in the accumulation of compounds <300 Da, >1,000 Da, and the average molecular weight on average over the entire duration of the experiment, respectively. As for the influence of hot storage conditions in an inert atmosphere (LD-NH vs. LD-NR), the difference was −19.9 %, 23.2 %, and 10.3 %, respectively. Thus, it was clear that the influence of heat was more potent in an inert atmosphere than in an oxidative atmosphere.

As for the MD (Fig. 6), a nearly identical trend was observed; however, the trends were not as extreme as the LD. Most changes were < 10 %, indicating that the MD was not as susceptible to changes in the storage temperature and atmosphere. The exception was the influence of the atmosphere in a hot environment (MD-AH vs. MD-NH) and a cool environment (MD-AR vs. MD-NR). Specifically, the accumulation >1,000 Da increased by 21.6 % in the former and 24.9 % in the latter. Similar results were also found in the biocrude oil the high-molecular-weight material ranged from 1 k to 10 kDa significantly increased after 1-year storage, which could be attributed to the polymerization or condensation reactions [11]. Most MD groups exhibited similar trends, with the one exception being MD-NR, which demonstrated a decreased molecular weight (405 Da) after sixteen weeks compared to the raw distillate (433 Da), indicating that a cool storage environment and a nitrogen atmosphere could reduce the polymerization reaction associated with compounds being transformed from the 200–300 Da range to <1,000 Da range.

The polydispersity index increased for the first eight weeks and then decreased or remained stable thereafter in all distillates. This indicated an increased heterogeneity of chemical compound weights in the oil over time. This could have signified the presence of the polymerization of low-molecular-weight compounds into high-molecular-weight compounds and that this reaction diminished over time as the size distribution became more homogeneous. Meng et al. noted that the change in the average molecular weight correlated well ($R^2 > 0.8$) with changes in viscosity [14]. Wang et al. also proposed that the increased viscosity of the biocrude oils should be attributed to the polymerization of the light fraction [16]. The results in this study found a similar result, indicating a causal relationship between the viscosity, density, and molecular weight distribution of the distillates samples.

3.3. Elemental composition

There was a noticeable difference in the change of the elemental compositions of the LD and MD groups (Table 2). Looking at the relative change, the change in the carbon content of the low-temperature distillates only increased slightly in all cases (<4 %) compared to the raw distillate (Figure S1). However, the MD all demonstrated a greater

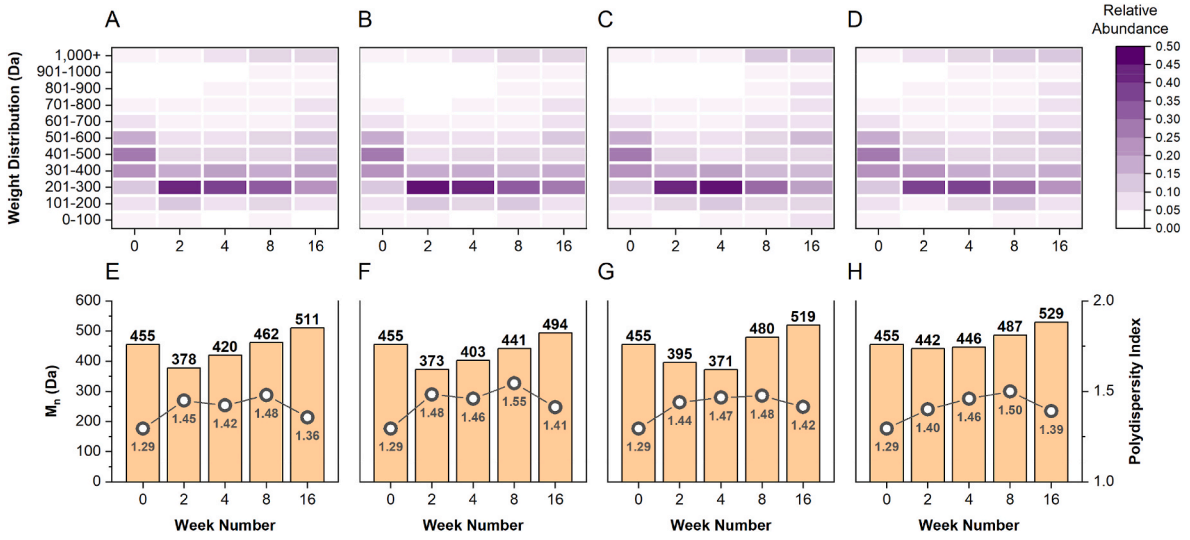

Fig. 5. MALDI weight distribution results for the LD-AR (A), LD-NR (B), LD-AH (C), and LD-NH (D) conditions. The average weight (M_n) and polydispersity index (I) for the LD-AR (E), LD-NR (F), LD-AH (G), and LD-NH (H) conditions.

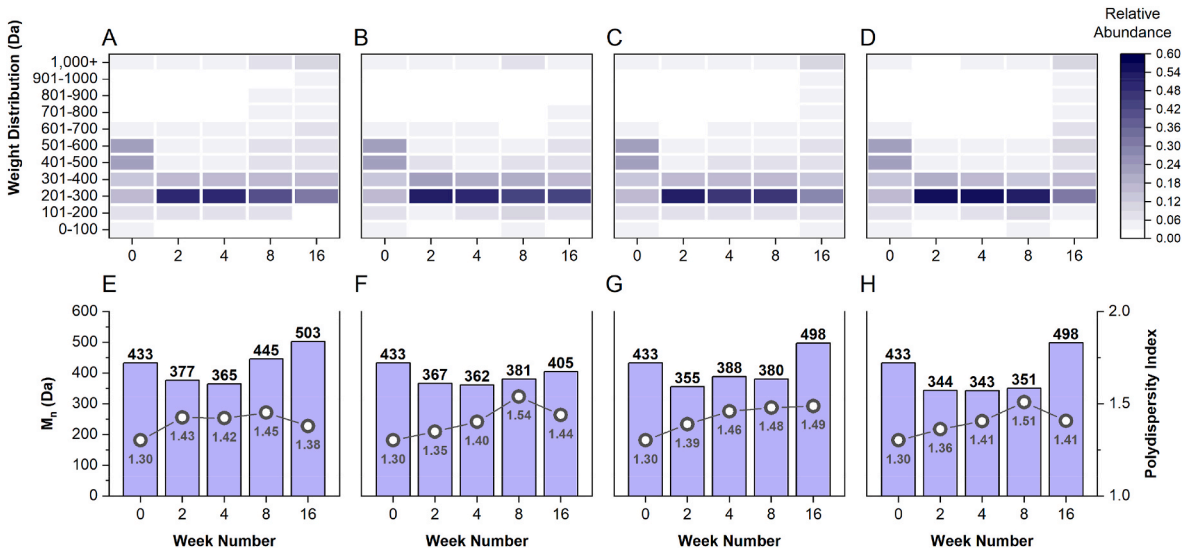

Fig. 6. MALDI results for the MD-AR (A), MD-NR (B), MD-AH (C), and MD-NH (D) conditions. The average weight (M_n) and polydispersity index (I) for the MD-AR (E), MD-NR (F), MD-AH (G), and MD-NH (H) conditions.

Table 2
Elemental analysis of the low-temperature and medium-temperature distillates under different storage conditions.

Group	Week	Carbon (wt.%)	Hydrogen (wt.%)	Nitrogen (wt.%)	Oxygen[a] (wt.%)	HHV (MJ/kg)	H:C	O:C	N:C
LD	0	76.06 ± 0.26	12.41 ± 0.01	0.46 ± 0.04	11.08 ± 0.30	41.41	1.96	0.110	0.0051
LD-AH	2	77.63 ± 0.12	12.64 ± 0.08	0.41 ± 0.03	9.33 ± 0.18	42.58	1.96	0.090	0.0045
	4	78.21 ± 0.03	12.37 ± 0.18	0.31 ± 0.01	9.12 ± 0.15	42.43	1.90	0.087	0.0034
	8	78.05 ± 0.07	12.27 ± 0.15	0.30 ± 0.01	9.39 ± 0.02	42.18	1.89	0.090	0.0033
	16	78.23 ± 0.01	12.52 ± 0.02	0.34 ± 0.02	8.92 ± 0.01	42.68	1.92	0.086	0.0037
LD-NH	2	77.48 ± 0.15	12.73 ± 0.01	0.37 ± 0.01	9.43 ± 0.15	42.64	1.97	0.091	0.0040
	4	78.08 ± 0.06	12.52 ± 0.01	0.30 ± 0.02	9.1 ± 0.05	42.60	1.92	0.087	0.0033
	8	78.23 ± 0.03	12.46 ± 0.05	0.27 ± 0.01	9.45 ± 0.01	42.50	1.91	0.087	0.0030
	16	78.44 ± 0.18	12.50 ± 0.09	0.34 ± 0.04	8.74 ± 0.23	42.76	1.91	0.084	0.0037
LD-AR	2	77.66 ± 0.04	12.81 ± 0.05	0.36 ± 0.01	9.18 ± 0.10	42.86	1.98	0.089	0.0040
	4	77.83 ± 0.10	12.37 ± 0.09	0.34 ± 0.01	9.48 ± 0.19	42.23	1.91	0.091	0.0037
	8	78.07 ± 0.01	12.44 ± 0.01	0.32 ± 0.02	9.19 ± 0.02	42.47	1.91	0.088	0.0035
	16	78.52 ± 0.08	12.55 ± 0.04	0.34 ± 0.01	8.60 ± 0.11	42.88	1.92	0.082	0.0037
LD-NR	2	77.51 ± 0.13	12.78 ± 0.03	0.42 ± 0.03	9.30 ± 0.13	42.74	1.98	0.090	0.0047
	4	78.28 ± 0.04	12.56 ± 0.02	0.31 ± 0.01	8.86 ± 0.01	42.77	1.92	0.085	0.0034
	8	78.19 ± 0.01	12.40 ± 0.01	0.28 ± 0.02	9.15 ± 0.01	42.46	1.90	0.087	0.0030
	16	78.82 ± 0.12	12.44 ± 0.06	0.34 ± 0.01	8.41 ± 0.07	42.86	1.89	0.080	0.0036
MD	0	79.13 ± 1.43	11.93 ± 0.23	0.44 ± 0.01	8.51 ± 1.65	42.22	1.81	0.081	0.0048
MD-AH	2	85.31 ± 0.09	12.99 ± 0.06	0.40 ± 0.01	1.31 ± 0.16	47.10	1.83	0.011	0.0040
	4	85.73 ± 0.01	12.65 ± 0.02	0.31 ± 0.02	1.32 ± 0.01	46.76	1.77	0.012	0.0031
	8	85.74 ± 0.01	12.56 ± 0.05	0.36 ± 0.02	1.35 ± 0.07	46.63	1.76	0.012	0.0036
	16	85.91 ± 0.01	12.67 ± 0.02	0.40 ± 0.04	1.03 ± 0.01	46.90	1.77	0.009	0.0039
MD-NH	2	85.54 ± 0.05	13.12 ± 0.01	0.34 ± 0.01	1.01 ± 0.03	47.42	1.84	0.009	0.0034
	4	86.03 ± 0.06	12.68 ± 0.02	0.35 ± 0.01	0.95 ± 0.08	46.97	1.77	0.008	0.0034
	8	85.69 ± 0.16	12.56 ± 0.12	0.34 ± 0.02	1.41 ± 0.26	46.60	1.76	0.012	0.0034
	16	85.63 ± 0.13	12.50 ± 0.02	0.39 ± 0.01	1.49 ± 0.15	46.48	1.75	0.013	0.0039
MD-AR	2	85.30 ± 0.09	13.02 ± 0.05	0.38 ± 0.01	1.31 ± 0.14	47.14	1.83	0.012	0.0038
	4	85.94 ± 0.11	12.74 ± 0.04	0.33 ± 0.01	1.00 ± 0.13	47.01	1.78	0.009	0.0033
	8	85.57 ± 0.13	12.58 ± 0.07	0.33 ± 0.04	1.53 ± 0.16	46.57	1.76	0.013	0.0033
	16	85.65 ± 0.01	12.67 ± 0.01	0.38 ± 0.04	1.31 ± 0.05	46.76	1.77	0.011	0.0038
MD-NR	2	85.25 ± 0.03	13.15 ± 0.05	0.34 ± 0.03	1.26 ± 0.05	47.32	1.85	0.011	0.0034
	4	85.78 ± 0.03	12.80 ± 0.01	0.35 ± 0.01	1.08 ± 0.03	47.03	1.79	0.009	0.0035
	8	85.81 ± 0.05	12.68 ± 0.11	0.37 ± 0.01	1.15 ± 0.15	46.86	1.77	0.010	0.0037
	16	84.58 ± 0.25	12.49 ± 0.01	0.40 ± 0.05	2.54 ± 0.2	45.92	1.77	0.023	0.0041

[a] O(%) = 100 – C(%) – H(%) – N(%), and the sulfur content was neglected due to its low content in the feedstock.

increase in the carbon content (11.2–13.1 %) compared to the raw distillate. Among all samples, it was clear that the highest rate of change occurred during week two, and then slowly the rate of change became less and less until nearly reaching a steady state. A previous study attributed these changes to the condensation reactions occurring which removed oxygen and increased the carbon content [35].

As for the hydrogen content, an identical trend was apparent. Even more minimal deviations from the raw distillate were exhibited for hydrogen (<3.2 %), and the MD deviations were still much more pronounced (4.7–10.3 %). It was interesting to note that the maximum deviation again occurred during week two, and then the relative rate of change receded. This was apparent in all trial runs. In the future, longer experiments should be conducted to understand if the content will reach a steady state or recede to the original value of the raw distillate. As time progressed the H:C ratio first increased and then decreased in comparison to the raw distillate for both the low-temperature and medium-

temperature distillates (Table 2). Decreasing the H:C ratio is unfavorable because it is attributed to the formation of olefins and cyclic compounds [36].

As for the heteroatom content, both the nitrogen and oxygen content decreased in all distillates. The nitrogen content exhibited maximum decreases ranging between 33.5 and 40.5 % for the LD and 22.5–29.6 % for the MD among all conditions. This was also observed in the aging of algae biocrude [10]. The most interesting trend was the decrease in the oxygen content. A drastic change occurred among all distillates after two weeks, where the effect thereafter was then subdued. The LD exhibited maximum decreases in the oxygen content ranging from 19.4 to 24.0 %. Surprisingly, the MD demonstrated a more dramatic decrease in the oxygen content. Specifically, the oxygen content in the raw distillate was 8.5 wt% and after sixteen weeks, the oxygen content ranged from 1.0 to 2.5 wt%. This represented decreases ranging from 69.4 to 87.4 % in comparison to the raw distillate. The oxygen content in the MD after storage was within the range of acceptable limits for crude oil (0.1–1.8 %) [34]. A previous study also noted a decrease in the oxygen content between 27 and 42 % which was attributed to the condensation and esterification reactions which eliminated water and evaporated volatile compounds [37]. Dramatic decreases in the O:C ratio were also observed (Group LD: 0.11 to 0.08, Group MD: 0.08 to 0.01), which was in agreement with previous studies [38]. Finally, the increase in the carbon content and decrease in the oxygen content led to small changes in the HHV of the Group LD (1.9–3.6 %) and larger changes for the Group MD (8.8–12.3 %) compared to the raw distillates. The different changes in the HHV of distillates should be attributed to the trade-off among a variety of reactions [15].

3.4. Chemical compound distribution

The distribution changes of chemical compounds demonstrate the main groups that were influenced by storage (Fig. 7). Previous studies have also noted significant changes in the oil composition after aging; however, detailed conclusions have yet to be reached regarding the specific reaction mechanisms [10]. It was interesting to note that the distribution of saturated fatty acids increased depending on the storage conditions, amounting to the highest accumulation after eight weeks in the LD-AR condition (83.5 %), and the LD-AH condition led to the lowest of the other conditions (79.0 %). After sixteen weeks, all samples underwent similar transformations, amounting to total distributions of 67.5–68.8 % saturated hydrocarbons and 27.0–28.3 % unsaturated hydrocarbons. The MD exhibited a similar trend as the LD. A previous study noted that a decrease in the carbonyl content was well correlated with an increase in the viscosity over time ($R^2 = 0.93$) [39]. The results in this study supported this finding, demonstrating that the fatty acid concentration and viscosity decreased after sixteen weeks (Fig. 2 and Table 2). The stability of biocrude oil has been directly associated with the composition of fatty acids [40]. It is hypothesized that in both LD and MD that the saturated fatty acids could have undergone esterification and subsequent condensation (e.g., Claisen condensation) to high-molecular-weight moieties which cannot be detect by GC-MS. The production of high-molecular-weight moieties was also verified by the MALDI results, which the accumulation >1,000 Da increased after 16 weeks storage. This lead to the dramatic decrease in the fatty acid content and contributing to the higher density, viscosity, and reduced acidity after 16 weeks (Figs. 3–6). This was supported by the consistent cumulative integral signal over time of the ketones, unsaturated hydrocarbons, and saturated hydrocarbons, but a dramatic decrease in the saturated fatty acids over time in this study.

3.5. Boiling point distribution

TGA was performed to elucidate the impact of storage on the different fuel-like fractions over time (Table 3). As for the LD, minimal differences with the raw distillate were observed for the kerosene fraction (−2.8–5.3 %). Larger changes occurred in the naphtha fraction, amounting to decreases in all experimental runs regardless of storage condition ranging from 7.9 to 22.8 %. Decreases in the naphtha fraction and increases in the diesel, vacuum gas oil, and residue fractions corresponded well with the increase in density, viscosity, and accumulation of compounds >1,000 Da. This was particularly apparent in the diesel, vacuum gas oil, and residue fractions. The changes in these three aforementioned fractions were drastic relative to the raw distillate. For all samples, the vacuum gas oil fraction and residue fraction increased dramatically after 16 weeks. The increased residue fraction corresponded to the viscosity change and molecular weight, which was also confirmed in a previous study [16].

Regarding the MD, trends were nearly similar to the trends present in the low-temperature distillates, except some effects were muted and others were exacerbated for some boiling point fractions. For example, both the naphtha (−15.8–0.2 %) and diesel (−0.4–38.0 %) fractions did not demonstrate a dramatic deviation from the raw distillate Group LD. However, the vacuum gas oil fraction demonstrated increases an order of magnitude higher than the increases present in the low-temperature distillates, amounting to a maximum increase in the different treatments ranging from 12,078.1 to 13,603.7 %. Thus, it is clear that the sensitivity to different boiling point fractions was apparent for the LD and MD. Previous studies corroborated the findings in this study noting that light boiling point fractions decreased and heavy boiling point

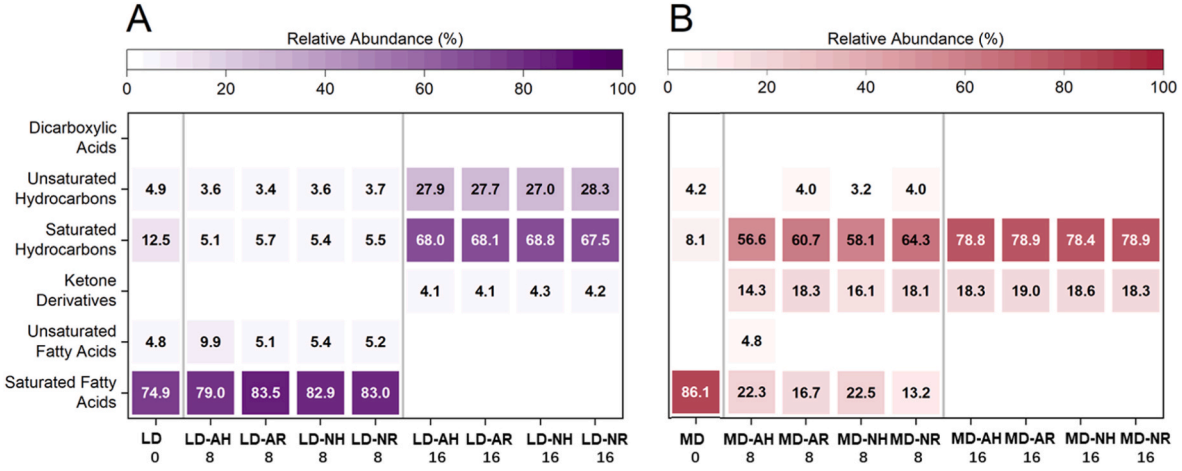

Fig. 7. Influence of storage temperature and atmosphere on the chemical composition of the low-temperature distillate (Group LD) and medium-temperature distillate (Group MD) fractions via GC-MS analysis. The change of chemical composition was based on the relative peak area of each component.

Table 3
Impact of storage on the low-temperature distillate (LD) and medium-temperature distillate (MD) fraction boiling point distributions.

Group	Week	Naphtha (wt.%)	Kerosene (wt.%)	Diesel (wt.%)	Vacuum Gas Oil (wt.%)	Residue (wt.%)
LD	0	42.73	55.93	0.92	0.03	0.02
LD-AH	2	34.51	56.02	9.05	0.16	0.00
	4	39.07	54.57	5.73	0.20	0.01
	8	34.57	58.64	6.20	0.26	0.01
	16	31.70	57.12	10.71	0.27	0.01
LD-NH	2	34.34	56.38	8.79	0.17	0.01
	4	36.03	55.56	7.89	0.17	0.01
	8	35.73	58.86	4.93	0.16	0.01
	16	32.97	56.66	9.04	1.04	0.13
LD-AR	2	35.84	55.70	7.96	0.16	0.01
	4	38.47	54.36	6.77	0.26	0.00
	8	35.71	58.86	4.99	0.15	0.00
	16	38.07	55.11	5.44	1.08	0.06
LD-NR	2	39.34	56.10	4.21	0.07	0.01
	4	36.97	55.48	7.03	0.14	0.01
	8	34.30	58.92	6.35	0.16	0.03
	16	36.54	56.16	5.95	0.96	0.06
MD	0	37.70	48.43	13.61	0.01	0.07
MD-AH	2	35.92	49.10	14.53	0.04	0.03
	4	35.94	47.21	16.34	0.07	0.01
	8	33.24	50.84	15.44	0.10	0.00
	16	32.27	47.53	18.30	1.42	0.28
MD-NH	2	33.28	47.59	18.78	0.03	0.01
	4	36.00	47.02	16.74	0.02	0.00
	8	32.92	50.82	15.84	0.06	0.00
	16	31.76	48.08	18.12	1.57	0.26
MD-AR	2	34.49	47.68	17.51	0.02	0.01
	4	37.79	48.20	13.56	0.02	0.01
	8	34.40	50.24	14.92	0.07	0.00
	16	36.04	47.25	14.70	1.55	0.23
MD-NR	2	33.16	48.23	18.34	0.02	0.01
	4	35.47	47.09	17.04	0.02	0.01
	8	33.17	50.41	16.02	0.08	0.01
	16	34.58	48.09	15.53	1.381	0.18

fractions increased over time in different storage conditions [41].

3.6. Impact of storage atmosphere, temperature, and time

The impacts of the distillates and storage conditions (atmosphere, temperature, time) were averaged over sixteen weeks to understand the comprehensive impact of storage and compare values to the raw distillates (Figure S5) and specific treatment conditions (Fig. 8). In general, trends were identical for the distillates compared with the raw distillate. Specifically, the vacuum oil fraction, diesel fraction, and distribution <300 Da were all impacted to the greatest extent compared to the raw distillate (Figure S5A-D). From the data presented in Fig. 8, it is clear that the storage conditions impacted the LD and MD to different extents. Comparing the influence of hot and cool storage temperatures in the air (Fig. 8A vs. Fig. 8E), although both exhibited increases in the residue fraction to similar degrees, the LD observed a 52.7 % decrease in saturated fatty acids while the MD exhibited a 157.8 % increase. Regarding the influence of storage temperatures in nitrogen, divergent trends were present. LD exhibited an increase in the vacuum oil fraction (42.9 %) and diesel fraction and a decrease in the saturated fatty acids (50.3 %). However, this condition did not have as pronounced of an impact on the MD, amounting to a decrease in the residue fraction (39.5 %) and a decrease in the saturated fatty acids (15.0 %). Comparing the influence of the atmosphere in a constant storage temperature, impacts were similar for the LD and more extreme for MD (Fig. 8C vs. Fig. 8G).

To further reveal the relationship between storage conditions and characteristics of bio-oil from a statistical perspective, a correlation analysis was conducted (Fig. 9). Both of the storage atmosphere and temperature have impacts on boiling point distributions of LD group. The temperature was significantly negative related to naphtha and positive related to the diesel content. Similarly, the storage atmosphere and temperature suggested a significant effect on the boiling point distributions. This may suggest the storage conditions significantly affect the boiling point distributions of distillates. The storage atmosphere was reported to play an important role in biocrude storage. Specifically, Wang revealed that the total acid number of the biocrude oil decreased by 22.6–24 % in an N_2 environment but increased by 9.1–10.1 % in air, regardless of the storage temperature [10]. The differences between the two distillate groups (Group LD and Group MD) were more potent than the differences between individual storage treatment conditions. Storage time had a strong relationship with the changing of the bio-oil characteristics. There was a positive correlation between the heavy oil distribution and molecular weight and a negative correlation with the hydrogen content. Although there was a significant change in distillate characteristics, they presented a much more stable storage performance when compared with that of biocrude oil in previous studies (Table 4). In general, the distillates derived from food waste biocrude after sixteen weeks still had very promising applications for transportation fuels. In particular, the MD group had a lower acidity and viscosity compared to that of the LD group. This suggested that distillation could be used to improve the long-term stability of biocrude oil from HTL. Taghipour et al. also confirmed the stable performance of the viscosity of distillates from algae biocrude which was much lower than raw biocrude [38]. It should be noted that long-term storage of over 100 days was evaluated in this study; however, previous studies argued that storage of 30 days should be enough since the realistic application of bio-oil was usually within 30 days [15]. In that case, the distillates (four weeks) suggested a more stable performance, and even better quality for potential application because of decreased acidity, viscosity, and increased HHV.

The stability of distillates of biocrude from HTL may result in the removal of solid particles, ash and nitrogen. Solid particles and ash in the biocrude could be removed during distillation. Li et al. reported that over 96 % of metals (such as Ca, K, and Pb) were removed in the distillate fraction, and most of the metals were concentrated in the remaining solid residue [43]. Previous studies proposed that the ash in the biocrude contains inorganic elements (e.g., potassium, calcium, sodium, magnesium, silicon, phosphorus, and chlorine) that could act as a catalyst for polymerization and condensation reactions, thereby negatively affecting oil stability during long-term storage [11]. This was also confirmed by Palomino et al., which demonstrated that an increase in the biocrude oil viscosity was observed when in the presence of metal species [35]. In addition, nitrogen could be removed and isolated in the solid residue post-distillation. A previous study reported that the high nitrogen content of bio-oil was more likely to form high molecular weight compounds and complex nitrogenous compounds via condensation and alkylation [16].

4. Conclusions

In this study, the impact of storage conditions (atmosphere, heat, and time) and distillation range (low-temperature and medium-temperature) of biocrude oil derived from food waste was investigated in terms of the changes in the physical, chemical, and boiling point distribution of the aged samples. Results demonstrated that large property changes occurred between the treatment groups and the raw distillate, but these changes were less pronounced when comparing the different changes among different distillates groups. Among both groups of distillates, the boiling point distribution (e.g., vacuum oil fraction, diesel fraction), molecular weight distribution (e.g., distribution <300 Da), and chemical composition (e.g., fatty acids) were the characteristics most influenced by storage, indicating the main cause of the instability of biocrude oil may be associated with fatty acid derivatives. Storage did have several beneficial aspects. For example, for the MD, a dramatic decrease in the O:C, N:C, and an increase in the HHV was observed. Furthermore, the physical properties were not impacted to a great extent, which is in contrast to reports in previous studies. This may

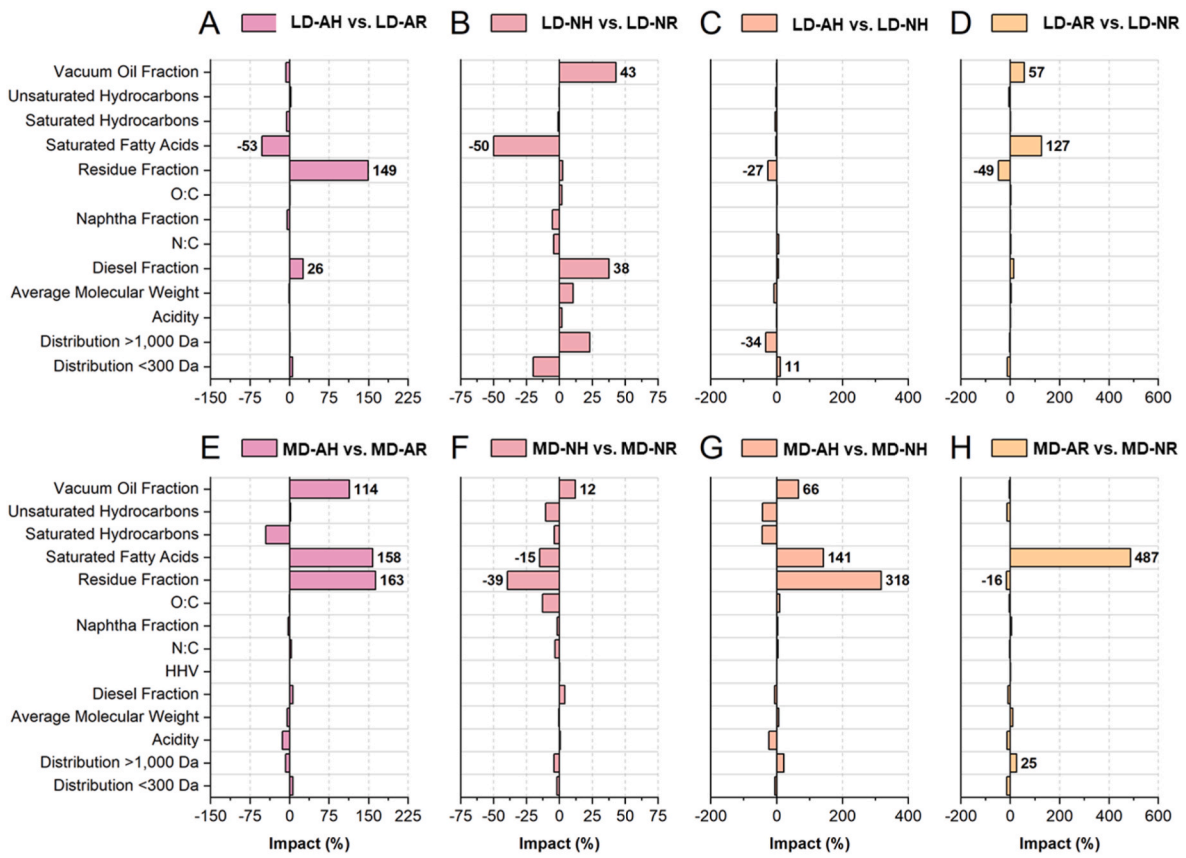

Fig. 8. Summary of the influence of the storage temperature and atmosphere on the characteristics of the biocrude oil distillate fractions. Values were obtained by averaging the relative change between the two trials at each time interval to calculate the comprehensive change over the entire duration of the experiments. Labels are shown for the top three parameters that were influenced the most by the storage condition comparison.

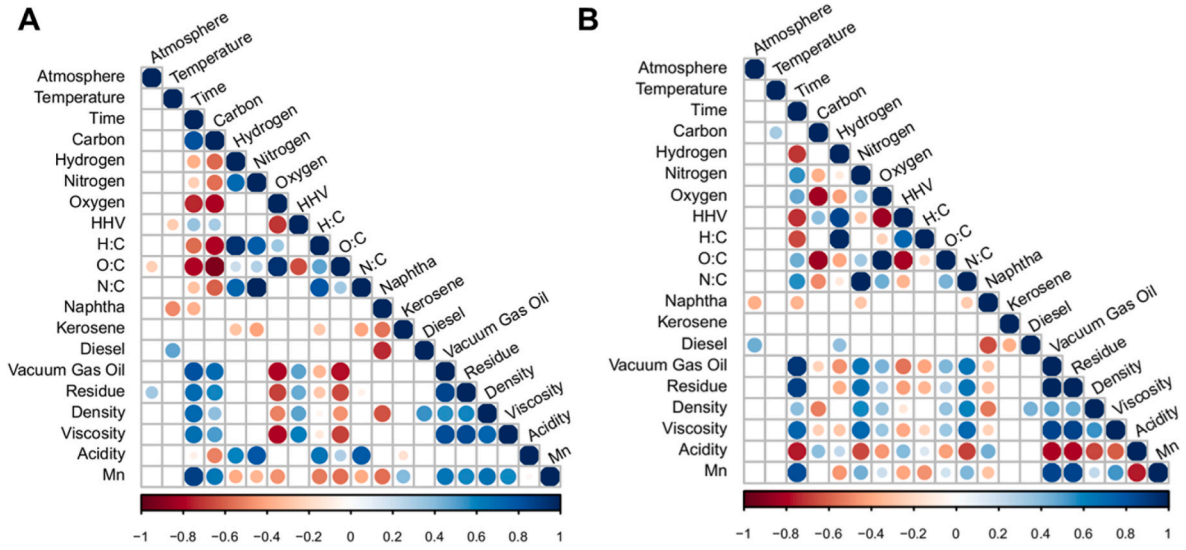

Fig. 9. Correlation plots of storage conditions (atmosphere, temperature, and time) and characteristics of low-temperature distillate (LD) (A) and medium-temperature distillate (MD) (B) (the cutoff line for the selected correlations was at $p < 0.001$ level; Positive correlations are in blue while negative correlations are in red).

indicate that distillation may be an advantageous technique for improving the stability, elemental composition, and longevity of biocrude oil.

CRediT authorship contribution statement

Buchun Si: Storage stability part, Writing – original draft, Writing – review & editing. **Jamison Watson:** Storage stability part, Writing – original draft, Writing – review & editing. **Zixin Wang:** Formal analysis.

Table 4
The comparison of the storage of bio-oil from HTL and transportation fuels.

Feedstock	Storage condition	C (%)	H (%)	N (%)	O (%)	HHV (MJ/kg)	Viscosity (mm^2/s)	Acidity (mg KOH/g)	Mn (Da)	Ref.
Biocrude – swine leather residue	30 day	NA	NA	NA	NA	36.7–36.2	258–136[a]	97.5–139.5	NA	[15]
Biocrude-sewage sludge	30 days	NA	NA	NA	NA	30.2–31.6	326–503[a]	47–39	NA	[15]
Biocrude- Spirulina	15–35 °C, N_2, 84 d	72.4–71.0	9.2–9.0	7.5–7.3	10.9–12.6	35.7–33.8	530–3500[b]	20.8–15.5	NA	[10]
Biocrude- Spirulina	15–35 °C, Air, 84 d	72.4–71.7	9.2–9.1	7.5–7.3	10.9–11.9	35.7–34.1	530–3500[b]	20.8–22.9	NA	[10]
Light Biocrude-sugarcane bagasse	80 °C, Air, 8 d	68.9–69.4	8.0–8.0	0.28–0.30	22.9–22.4	31.2–31.2	NA	NA	NA	[42]
Biocrude-sugarcane bagasse	80 °C, Air, 8	67.2–66.2	7.7–7.8	0.30–0.29	24.8–25.6	29.9–29.7	NA	NA	NA	[42]
Light Biocrude--sugarcane bagasse	80 °C, Air, 8 day	75.0–73.8	8.7–7.9	0.34–0.30	15.1–18.0	35.0–32.5	NA	NA	NA	[42]
Biocrude-sugarcane bagasse	80 °C, Air, 8 d	74.3–73.5	8.7–8.4	0.35–0.32	16.7–17.7	34.4–33.2	NA	NA	NA	[42]
Biocrude- Spirulina	80 °C, N_2, 7 d	69.3–69.9	9.2–8.6	7.5–7.2	14.1–14.3	34.0–33.4	6000–20000[b]	NA	1196–1222	[16]
Biocrude- Cornstalk	80 °C, N_2, 7 day	70.02–70.2	6.9–6.7	1.1–1.5	22.0–21.8	29.6–29.3	12000–46000[b]	NA	370–1008	[16]
Biocrude- Swine manure	80 °C, air, 7 d	75.8–77.0	9.1–9.3	5.0–4.9	10.1–8.7	36.8–37.8	1000–9000[b]	NA	115–98	[16]
Biocrude- Microalgae	25 °C, air, 1 year	70.2–69.8	7.6–7.4	7.5–7.2	14.5–15.4	32.6–32.1	207–308	210–258	1091–1550	[41]
Biocrude- Spirulina	20 °C, air, 60 d	68.2–69.4	8.7–8.9	7.0–7.4	16.1–14.4	32.2–32.3	NA	NA	NA	[35]
Biocrude- Chlorella	20 °C, air, 60 d	70.8–72.8	9.0–9.1	6.6–6.7	13.6–11.5	33.8–34.8	NA	NA	NA	[35]
Biocrude- Chlorella	15–33 °C, air, 70 d	NA	NA	NA	NA	36.0–36.1	NA	NA	313–3300	[38]
Medium Distillates-food waste	25–55 °C, N_2, 102 d	79.1–85.1	11.9–12.5	0.44–0.40	8.5–2.0	42.2–46.2	3.86–4.35	5.6–2.8	433–498	This study
Medium Distillates-food waste	25–55 °C, air, 102 d	79.1–85.8	11.9–12.7	0.44–0.39	8.5–1.2	42.2–46.8	3.86–4.27	5.6–1.8	433–502	This study
Light Distillates-food waste	25–55 °C, N_2, 102 d	76.1–78.6	12.4–12.5	0.46–0.34	11.1–8.6	41.4–42.8	5.23–6.49	202–162	455–529	This study
Light Distillates -food waste	25–55 °C, air, 102 d	76.1–78.4	12.4–12.5	0.46–0.34	11.1–8.8	41.4–42.8	5.23–5.55	202–174	455–519	This study
Gasoline	NA	85.8	11.7	0.03	2.51	45.2	0.53	28.8	270.2	[7]
Diesel	NA	86.7	14.0	0.24	<0.01	49.3	4.09	12.4	278.2	[7]
Jet fuel	NA	85.9	14.4	0.23	<0.01	49.7	2.04	18.6	247.5	[7]

[a] Measured at 100 °C.
[b] Adopted from the picture and calculation which was measured at 40 °C. The change was calculated based on the average value. NA is not available.

Tengfei Wang: Formal analysis. **Juan S. Acero Triana:** Formal analysis. **Yuanhui Zhang:** Writing – original draft, Writing – review & editing.

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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.renene.2023.119669.

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