

Diesel blends produced via emulsification of hydrothermal liquefaction biocrude from food waste

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ABSTRACT

Hydrothermal liquefaction (HTL) is a promising method for producing biocrude oil from wet biowaste. However, the complex composition of the HTL biocrude has several undesirable qualities, including high viscosity, total acid number (TAN), oxygen and nitrogen heteroatom content, and lesser higher heating value (HHV) in comparison to petroleum fuels. This study investigated the production of diesel blends and their fuel quality by emulsification of HTL biocrude with the aid of a block copolymer surfactant through centrifugation and ultrasonification. Four emulsion treatment variables were considered: biocrude fraction, surfactant fraction, retention time, and RPM (rotations per minute) for centrifuge or temperature for ultrasonic. Emulsification produced fuel blends with better HHV, viscosity, and TAN in comparison to HTL biocrude oil, and high solubility levels were achieved with surfactant addition and increased retention time. Maximum biocrude solubilities of 65.43 and 75.67 wt% were obtained for centrifugation and ultrasonification, respectively. Meanwhile, the highest HHV of centrifuge and ultrasonic emulsions was 45.39 and 45.73 MJ/kg, respectively. Emulsification led to viscosities as low as 5.91 and 6.06 mm²/s for centrifuge and ultrasonic samples, respectively. The TAN of emulsions were much lower than the biocrude: 14.18–41.31 and 16.22–50.31 mg KOH/g for centrifugation and ultrasonification, respectively. Thermogravimetric analysis, elemental analysis, combustion characteristics, and thermal properties gave further insight into the fuel quality of the emulsions and any deviations from the predicted HHV, viscosity, and TAN fuel properties, as well as comparison to ASTM specifications for biodiesel blends. The results show that emulsification of HTL biocrude could be an efficient and economical pathway for producing renewable diesel blends.

1. Introduction

Increased energy demand and sustainable management of wet biowastes, such as food waste, presents global challenges. It is estimated that about 931 million tons of food waste is generated globally [1], with about 60.7 million wet tons of food waste generated in the U.S. annually [2]. Overall, 61% of this food waste comes from households, 26% from food service, and 13% from retail [1]. Food waste disposed of in landfills releases greenhouse gases during decomposition and can also cause soil and water contamination [3]. On the other hand, this carbon-rich biowaste could be a resource for the generation of sustainable fuel. One promising approach for sustainable fuel production from wet organic waste is hydrothermal liquefaction (HTL) [4,5,6,7], where water serves as both a solvent and reactant. Moreover, HTL is particularly suitable for wet feedstocks because they can be used directly without drying as pretreatment [4], which is energy intensive. The use of HTL to convert

food waste into fuel contributes to a waste biorefinery concept where bioprocessing can generate valorized products and lead toward a sustainable circular bioeconomy. However, the complex chemical composition of HTL biocrude results in several undesirable properties, including high oxygen and nitrogen heteroatom content, high viscosity, and high acid number, all of which require the biocrude be upgraded prior to use as a transportation fuel [8]. Its high viscosity and acidity in comparison to conventional fuels like gasoline or diesel [9] limits its use as a drop-in fuel due to engine problems such as corrosion and increased wear [10,11]. Multiple processes, including distillation, hydrotreating, and emulsification have been applied to decrease the viscosity, oxygen, and nitrogen content of biocrude oil [12,13,14].

Emulsification is a simple and inexpensive physical method that takes place without chemical reactions [13,15,16,17,18]. With the aid of surfactants and agitation, emulsification allows immiscible liquids to be mixed [14,19,20]. Therefore, emulsification can be an effective method

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Table 1

Literature summary of biocrude oil/diesel emulsification work consisting of different feedstocks, biocrude production methods, biocrude content, emulsification methods, and surfactants.

Pyrolysis feedstock	Biocrude Content	Emulsification Method	Surfactant	Ref.
Oak, beech wood, pine wood	25–75 wt %	Variable speed electrical motor	Polymeric surfactants/ short chain additives (n-octanol)	[5]
Pineapple pine	10 wt%	Ultrasonic: 20 kHz, 2 min Ultrasonic-mechanical: 20 kHz, 2 min; 5000 rpm, 5 min 1200 rpm, 15 min	Span-80, Tween-80, Span-85	[19]
Softwood residue	20–50 wt %		Octanol	[8,21]
Hardwood	10–30 wt %	Micro-emulsifier: 800–1750 rpm, 5–20 min	Hypermer B246SF/2234 (Croda International)	[26]
Rice hull	16–19 wt %	Emulsifier: 20–60 °C, 5,000–25,000 rpm, 2–8 min	Span-80, Tween-80	[27]
Palm kernel shell	10–30 wt %	Magnetic stirrer: 350 rpm, 25 °C, 30 min	Brij-80, Tween-80	[28]
Liquefaction feedstock	Biocrude Content	Emulsification Method	Surfactant	Ref.
<i>Chlorella pyrenoidosa</i>	5 wt%	Ultrasonic: 25 °C, 30 min Centrifuge: 3000 rpm, 30 min	Span-80	[4]
Sewage sludge	5 wt%	Manual shaking: 1 min Centrifugation: 6000 rpm, 20 min	Span-80	[29]
Food waste	5–30 wt%	Vortex mixer: 3000 rpm, 2 min	Atlox 4914, Methanol	[30]
Sewage sludge, swine leather residue	10 wt%	Vortex mixer: 3000 rpm, 2 min	Atlox 4914	[31]
Waste wheat flour, canola meal	5–20 wt%	Stirrer: 500–1750 rpm, 5–60 min	Octanol	[34]
Synthetic feedstock	Biocrude Content	Emulsification Method	Surfactant	Ref.
Model compounds ^a	20–70 wt %	Magnetic stirring: 1000 rpm, 15 min	Span-80	[24]

^a Including methanol, acetaldehyde, acetic acid, glyoxal, acetol, glucose, guaiacol, furfural, vanillin, and DI water.

to adapt HTL biocrude for fuel applications through the production of diesel blends. The high fraction of diesel distillates in HTL biocrude makes it an ideal blending component for commercial diesel. The emulsion of biocrude and diesel results in calorific value comparable to diesel, as well as decreased viscosity, decreased acidity, and decreased oxygen content compared to biocrude [21]. There are two types of emulsions: water-in-oil (W/O) and oil-in-water (O/W) [15]. The type of emulsion formed depends on the hydrophilic-lipophilic balance (HLB) of the surfactant. Non-ionic surfactants are widely used as emulsifiers for complex mixtures due to their low sensitivity to electrolytes and

compatible nature with cationic and anionic surfactants [15]. The HLB classification system for non-ionic surfactants was created by Griffin, where low values (4–8) are lipophilic surfactants that create W/O emulsions and high values (9–12) are hydrophilic surfactants that create O/W emulsions [5,22,23,24].

Several studies have explored emulsification to upgrade biocrude produced from a variety of methods, including pyrolysis, liquefaction, and synthetic biocrude from model compounds, along with a wide range of emulsifiers. These studies are summarized in Table 1 with their feedstock, biocrude content, emulsion method, and surfactant type. The most common emulsion methods employed are ultrasonification and mechanical agitation such as homogenizers or centrifugation. Zhang and Wu (2017) found that elevated stirring speeds led to rapid separation and high energy consumption [25], therefore high-speed stirring is not necessary. In regard to temperature effects, Zhang et al. (2018) observed that moderate increases in temperature during ultrasonification can improve the emulsion stability [26]. In previous studies, it was observed that after emulsification, a top and bottom layer was formed—with the lighter, top layer taken as the emulsification product, since the bottom layer had heavy products from the biocrude [8,26]. It has also been shown that mechanical mixing did not provide enough energy to produce a stable emulsion, suggesting that ultrasonic emulsion be performed instead so that the generation of smaller droplets can improve the stability of the emulsion [28]. Guo et al. [19] combined ultrasonic and mechanical methods, resulting in improved stability.

There have also been multiple emulsification studies performed with hydrothermal liquefaction biocrude derived from biowaste feedstocks including algae [4], sewage sludge [29], food waste [30], swine leather residue [31], waste wheat flour and canola meal [32]. The biocrude content of the emulsions varies greatly in literature, ranging from 5% up to 75%. However, studies experimenting with emulsions consisting of high biocrude content found that they had extremely high viscosities: >4000 cS for 75% biocrude content emulsions compared to 10.62–11.59 cS for 25% biocrude content emulsions [5]. Due to their high viscosities, these emulsions would be difficult to use in many applications [5]. Moreover, the high acidity and nitrogen, sulfur, and oxygen content of HTL biocrude oil led to high TAN and heteroatom content in the emulsion [34]. Pretreating the biocrude with methods such as esterification, transesterification, or hydrotreating can reduce these components [34].

Many previous emulsification studies selected their surfactant concentration based on a study by Wang et al., where a synthetic biocrude was used to create microemulsions in diesel with Span-80 as a surfactant [24]. Based on surface tension measurements, 0.15 M was found to be the critical micelle concentration (CMC) of Span-80 in diesel—the surfactant concentration at which micelles start forming. Based on this value, surfactant concentrations of 0.19–0.98 M in diesel solution have been commonly investigated.

As seen in Table 1, several common surfactants such as Tween and Span series surfactants have been used for biocrude and diesel emulsification. While Atlox 4914, a random copolymer-structured surfactant has been previously used in biocrude emulsions [30,31], Atlox 4912 can tolerate high levels of organic materials in the aqueous phase and has not yet been extensively studied for its applications in fuel blends, so a CMC value for this surfactant has not yet been identified. Atlox 4912 is an opaque, polymeric, non-ionic surfactant produced by Croda International. It is solid at room temperature, with a melting point of 40 °C. The surfactant has a mean molecular weight of 5,000, and an HLB value

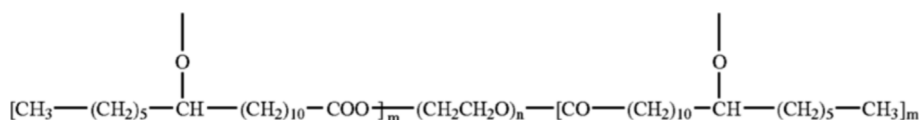


Fig. 1. Chemical structure of Atlox 4912 where $n = 34$ and $m = 7$. The central polymer section of polyethylene oxide ($\text{CH}_2\text{CH}_2\text{O}$) is hydrophilic. The outer 12-hydroxystearic acid ($\text{C}_{18}\text{H}_{36}\text{O}_3$) polymer blocks are lipophilic.

Table 2

Taguchi method experimental design and emulsion treatment variable levels for (a) centrifuge experiments and (b) ultrasonic experiments.

(a)	Sample	Biocrude fraction (wt %)	Surfactant fraction (wt%)	Time (min)	RPM
	C1	10	1	20	1200
	C2	10	5	30	2400
	C3	10	10	40	3600
	C4	20	1	30	3600
	C5	20	5	40	1200
	C6	20	10	20	2400
	C7	30	1	40	2400
	C8	30	5	20	3600
	C9	30	10	30	1200

(b)	Sample	Biocrude fraction (wt %)	Surfactant fraction (wt%)	Time (min)	Temperature (°C)
	U1	10	1	20	20
	U2	10	5	30	40
	U3	10	10	40	60
	U4	20	1	30	60
	U5	20	5	40	20
	U6	20	10	20	40
	U7	30	1	40	40
	U8	30	5	20	60
	U9	30	10	30	20

of 6. Fig. 1 depicts the general formula of Atlox 4912, where the central, hydrophilic section is composed of polyethylene oxide and the two lipophilic side arms are 12-hydroxystearic acid [27]. Its block copolymer design allows Atlox 4912 to create stable emulsions through steric stabilization. Furthermore, its medium polarity and low HLB value makes it an effective surfactant to produce W/O emulsions with average droplet sizes of 3–5 μm that are stable to high heat and shear [27].

The primary objectives of this study were to 1) explore the quality of HTL biocrude-diesel blends produced with a block copolymer emulsifier and deviations from predicted trends of fuel properties, and 2) identify sensitivity of the emulsion fuel properties, including biocrude solubility, calorific value, viscosity, and acidity, to treatment variables. Traditional experimental method designs, such as full-factorial and one factor at a time experiments, are typically used to determine optimal experimental conditions, but can be time consuming and costly. Rather than performing and analyzing all possible combinations of treatment variables, a Taguchi design was used in this study to examine a subset of them, optimize design parameters and determine their sensitivity to response variables [33]. The obtained results can elucidate the application of block copolymer surfactants for emulsification of HTL biocrude, as well as provide useful insights into the effects of different emulsion parameters on fuel quality.

2. Materials and methods

2.1. Materials

Atlox 4912 (Croda International, USA) is a polymeric, non-ionic surfactant that has a solid form and a hydrophilic lipophilic Balance (HLB) value of 6 (Fig. 1). HTL biocrude was produced with a food waste from a local food processing plant. Commercial No. 2 diesel from a local gas station in Champaign, IL was used as the base to produce the diesel blends.

2.2. Experimental procedure

2.2.1. Biocrude/diesel emulsification

The production of biocrude was performed in a plug-flow continuous HTL reactor at 300 °C and 9.2 MPa with a 1 h retention time. The method is detailed in our previous study [35]. The emulsification

experiment was designed using the Taguchi method including the following treatment variables with three levels each (Table 2): biocrude fraction (of entire mixture), surfactant fraction (of biocrude), retention time, and mixing intensity (RPM/temperature).

The biocrude/diesel emulsions were prepared with two instruments: a Thermo IEC Centra CL3 centrifuge and a Kendal Ultrasonic Cleaner (model HB-S-49DHT). In efforts to avoid extremely high viscosities of the biodiesel blends, biocrude fractions of 10–30 wt% were chosen for the emulsion experiments. Since a CMC has not yet been identified for Atlox 4912, low levels of surfactant fraction (1–10 wt%) were chosen in order to determine if biodiesel blends could be effectively produced with minimal amounts of Atlox 4912, even below the 0.15 M level. Emulsification by centrifuge was performed at speeds of 1200, 2400, and 3600 RPM in order to evaluate mixing speeds across the full range of the instrument, which had a maximum speed of 4000 RPM. The emulsification experiments carried out by centrifugation were performed at room temperature (20 °C). Ultrasonification was performed at 20, 40, and 60 °C in order to produce emulsions below, at, and above the melting temperature of Atlox 4912. An L27 (3⁴) orthogonal array was selected to have 9 experiments each performed in triplicate. A total of 10 g biocrude, diesel, and Atlox 4912 were combined and hand-shaken for 1 min in a 50 mL centrifuge tube with mass fractions according to the experimental design. After the emulsification, the tubes were hand-shaken again for 1 min.

2.2.2. Emulsion characterization

After each emulsification experiment, the mixtures were centrifuged at 3600 rpm for 40 min to facilitate fast separation mimicking a natural gravitational stratification. The resulting two layers were a dark, solid fraction of insoluble biocrude precipitated at the bottom and a lighter-colored liquid layer of emulsified biocrude in diesel, which was collected separately as the emulsion sample. The biocrude solubility (wt%) in emulsion is determined by Eq. (1) according to a previous work by Ding et al. [36]:

$$S = (m_0 - m_f)/m_0 \times 100\%. \quad (1)$$

where m_0 is the initial mass of biocrude, m_f is the final mass of the solid, insoluble fractions after centrifugation, and $m_0 - m_f$ represents the diesel-soluble fraction of biocrude in the emulsion.

The kinematic viscosity of samples was measured at 20 °C with a size 100 Cannon-Fenske glass capillary viscometer according to ASTM D446. The density was determined using a 2-mL glass Gay-Lussac bottle (Core-Palmer, EW-34580–40) at 20 °C. Moisture content of samples was determined by Karl-Fischer coulometric titration using a Metrohm 917 Coulometer (Riverview, Florida, USA). Thermal properties and boiling point distribution analysis of samples were obtained using a TA Instruments Q50 thermogravimetric analyzer (New Castle, Delaware, USA) with an N₂ flow rate of 60 mL/min. During each experiment, the sample (15 mg) was heated from 20 °C to 700 °C at a rate of 20 °C/min. The calculated cetane index (CCI) and calculated flash point (CFP) were determined using methods ASTM D4737 and ASTM D7215, respectively. Combustion characteristics of samples were obtained with a TA Instruments Q50 thermogravimetric analyzer with an air flow rate of 60 mL/min. For each experiment, the sample (15 mg) was heated from 20 °C to 700 °C at a rate of 20 °C/min. The total acid number (TAN) of samples was measured by titration with 0.1 M potassium hydroxide and phenolphthalein indicator according to ASTM D974. The elemental contents of samples (carbon, hydrogen, and nitrogen; oxygen by difference) were measured by an Exeter Analytical Model CE440 CHN analyzer (Coventry, United Kingdom). The higher heating value (HHV) was calculated according to Dulong formula [35] in Eq. (2) based on the elemental analysis of each sample:

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

For each emulsion process, the energy input of the centrifuge and

Table 3
Physicochemical properties of base fuels, surfactant, and emulsion fuels.

Sample	Biocrude solubility (wt%)	HHV (MJ/kg)	Viscosity (mm ² /s) @ 20 °C	TAN (mg KOH/g)	C (wt%)	H (wt%)	N (wt%)	O (wt%)
No. 2 Diesel	–	45.93 ± 0.01	5.32 ± 0.04	0.43 ± 0.03	86.18 ± 0.08	13.44 ± 0.04	0.35 ± 0.03	0.04 ± 0.01
HTL biocrude	–	38.52 ± 0.02	122.60 ± 2.80	184.08 ± 2.15	75.77 ± 0.06	11.38 ± 0.01	0.48 ± 0.02	12.39 ± 0.08
Atlox 4912	–	35.12 ± 0.05	–	–	69.06 ± 0.01	11.16 ± 0.04	0.40 ± 0.02	19.39 ± 0.03
C1	18.39 ± 3.15	45.26 ± 0.03	5.91 ± 0.20	15.21 ± 0.71	85.35 ± 0.08	13.21 ± 0.06	0.35 ± 0.04	1.09 ± 0.07
C2	38.35 ± 7.88	45.39 ± 0.10	6.09 ± 0.17	14.82 ± 0.52	85.54 ± 0.01	13.20 ± 0.09	0.34 ± 0.05	0.88 ± 0.03
C3	23.48 ± 3.72	45.28 ± 0.01	6.10 ± 0.03	14.18 ± 0.28	85.20 ± 0.04	13.29 ± 0.01	0.31 ± 0.01	1.21 ± 0.02
C4	48.59 ± 3.03	44.91 ± 0.02	6.79 ± 0.11	24.65 ± 0.36	84.70 ± 0.01	13.18 ± 0.02	0.29 ± 0.00	1.84 ± 0.01
C5	37.38 ± 3.48	44.82 ± 0.02	7.44 ± 0.18	29.22 ± 1.57	84.61 ± 0.04	13.14 ± 0.04	0.32 ± 0.01	1.94 ± 0.01
C6	50.24 ± 4.13	44.90 ± 0.04	7.38 ± 0.05	28.13 ± 0.99	84.65 ± 0.00	13.20 ± 0.03	0.30 ± 0.01	1.87 ± 0.04
C7	44.26 ± 1.01	44.67 ± 0.21	8.51 ± 0.06	39.88 ± 1.87	84.37 ± 0.18	13.11 ± 0.10	0.30 ± 0.00	2.22 ± 0.28
C8	65.43 ± 4.16	44.72 ± 0.14	8.53 ± 0.40	40.65 ± 1.63	84.24 ± 0.29	13.20 ± 0.00	0.29 ± 0.02	2.28 ± 0.31
C9	52.38 ± 2.34	43.22 ± 0.41	9.87 ± 0.10	41.31 ± 1.58	81.81 ± 0.61	12.89 ± 0.10	0.34 ± 0.01	4.97 ± 0.70
U1	18.74 ± 5.30	45.70 ± 0.10	6.06 ± 0.16	16.22 ± 0.17	85.72 ± 0.04	13.43 ± 0.06	0.33 ± 0.02	0.53 ± 0.08
U2	65.37 ± 4.00	45.73 ± 0.13	6.37 ± 0.34	16.73 ± 0.06	85.64 ± 0.15	13.50 ± 0.05	0.31 ± 0.01	0.58 ± 0.18
U3	70.68 ± 6.79	45.68 ± 0.16	6.73 ± 0.34	16.85 ± 0.12	85.50 ± 0.15	13.49 ± 0.07	0.30 ± 0.03	0.72 ± 0.25
U4	70.49 ± 2.84	45.02 ± 0.13	7.62 ± 0.23	32.51 ± 1.39	84.79 ± 0.10	13.23 ± 0.07	0.31 ± 0.04	1.68 ± 0.13
U5	42.94 ± 1.62	44.87 ± 0.09	7.89 ± 0.17	34.06 ± 1.75	84.47 ± 0.11	13.23 ± 0.04	0.31 ± 0.02	2.00 ± 0.13
U6	75.67 ± 4.28	44.64 ± 0.26	8.79 ± 0.33	36.54 ± 1.31	83.93 ± 0.66	13.20 ± 0.04	0.30 ± 0.01	2.54 ± 0.63
U7	71.81 ± 7.73	44.55 ± 0.06	9.21 ± 0.23	50.31 ± 2.10	84.14 ± 0.06	13.10 ± 0.07	0.30 ± 0.00	2.47 ± 0.01
U8	52.26 ± 2.43	44.53 ± 0.14	9.59 ± 0.03	43.87 ± 0.48	84.00 ± 0.14	13.14 ± 0.06	0.30 ± 0.02	2.57 ± 0.18
U9	65.74 ± 0.70	44.37 ± 0.04	10.28 ± 0.17	43.88 ± 0.26	83.76 ± 0.06	13.10 ± 0.01	0.29 ± 0.02	2.87 ± 0.09

ultrasonic instruments was calculated from their given voltage, amperage, and heater power, and was defined as E_{proc} . The energy yield of emulsions was defined as.

$$EY = S \times \frac{HHV_{\text{emul}}}{HHV_{\text{bio-oil}}} \times 100\% \quad (3)$$

where S is biocrude solubility (effectively the mass yield of HTL biocrude in the emulsion) as defined in Eq. (3), HHV_{emul} , and HHV_{biocrude} are the higher heating values of the emulsion sample and raw HTL biocrude, respectively. The energy of the emulsion was defined in Eq. (4) as

$$E_{\text{emul}} = m_{\text{emul}} \times HHV_{\text{emul}} \quad (4)$$

where m_{emul} is the mass of the emulsion sample. Lastly, the energy

return ratio was defined in Eq. (5) as

$$\xi = E_{\text{emul}}/E_{\text{proc}} \quad (5)$$

The fuel properties of the final emulsions were compared with the ASTM properties of diesel to determine their viability as a drop-in fuel. The fuel specification properties were compared according to ASTM D6751 and D7467 for biodiesel blends.

2.2.3. Sensitivity of treatment variables

Several characteristics of the emulsions, including biocrude solubility, higher heating value (HHV), kinematic viscosity, and total acid number (TAN) were selected as response variables. To identify treatment variable levels that produced emulsion with the most desirable fuel

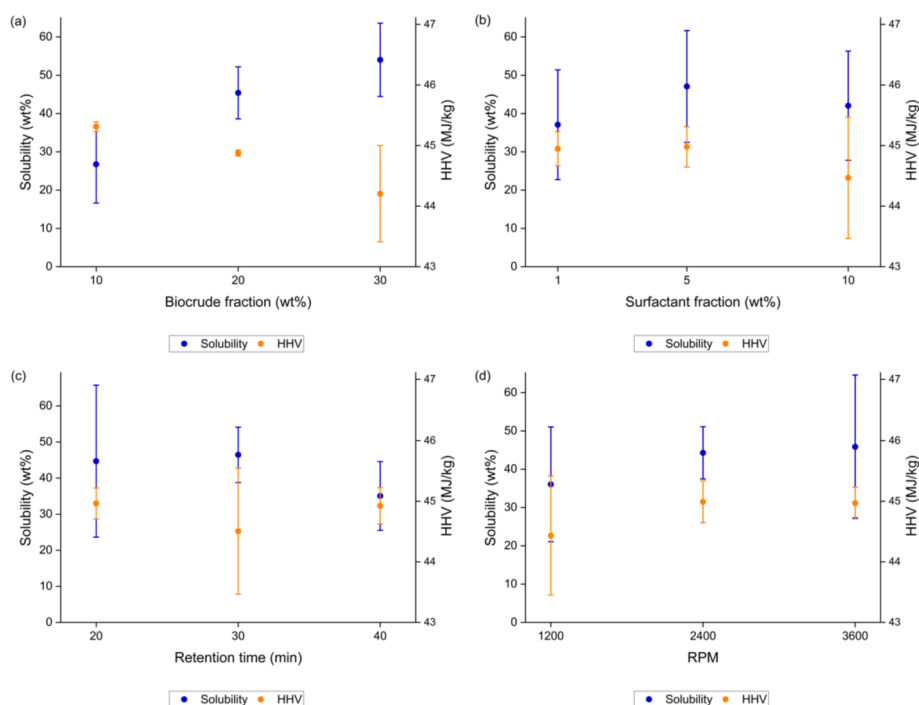


Fig. 2. Mean of response for solubility and HHV of centrifugation emulsion samples vs. treatment variables (a) biocrude fraction, (b) surfactant fraction, (c) retention time, and (d) RPM. The error bars in the figure represent deviation in the data due to differences in other treatment variables.

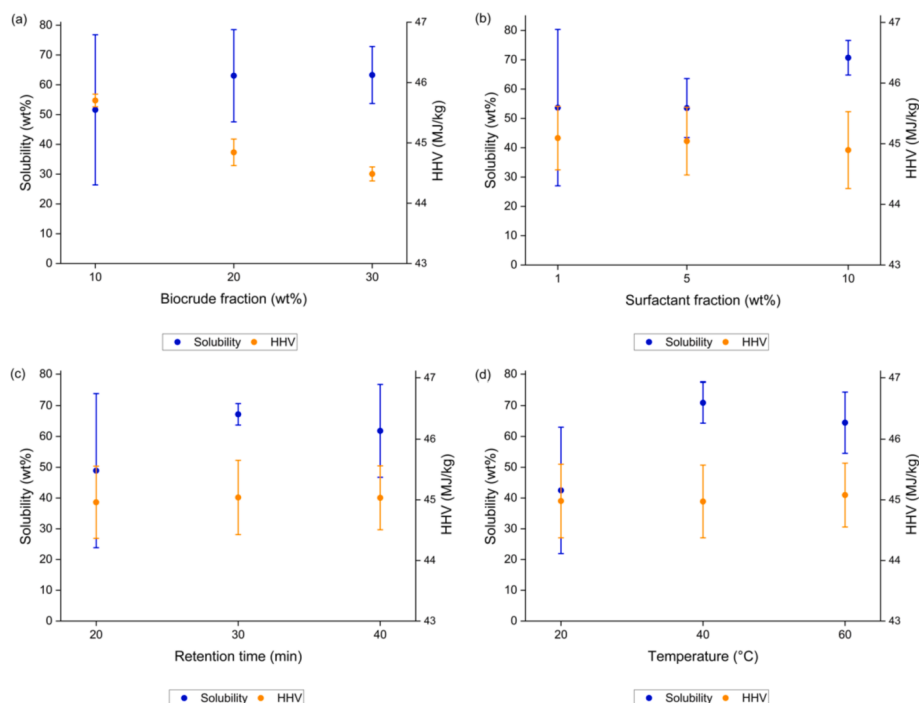


Fig. 3. Mean of response for solubility and HHV of ultrasonification emulsion samples vs. treatment variables (a) biocrude fraction, (b) surfactant fraction, (c) retention time, and (d) temperature. The error bars in the figure represent deviation in the data due to differences in other treatment variables.

qualities, the analysis was divided into three objectives: first, to maximize desirable response variables (biocrude solubility and HHV); second, to minimize undesirable response variables (viscosity and TAN); and lastly, identify the overall sensitivity and ideal level of each treatment variable on the response variables. A statistics software, Minitab, was used to carry out the data analysis.

To determine the influence of treatment parameters on the response variables, a mean of response was calculated vs. level of emulsion treatment variable. For example, the average solubility was calculated for the samples with biocrude fractions of 10, 20, and 30 wt% in order to elucidate a relationship between the biocrude fraction and solubility. To calculate the average solubility for the biocrude content level of 10 wt%, the solubilities of samples C1, C2, and C3 were used. While their biocrude fractions were the same, each sample had a different level of the other emulsion treatment variables (surfactant fraction, retention time, and RPM) as seen in Table 2. The same was done for the other three response variables (HHV, viscosity, and TAN) and each of the other treatment variables (surfactant fraction, retention time, and RPM/temperature). Since these averages are calculated from different samples, rather than replications of a single sample, the SD values were used to indicate the range of data and sensitivity of response to the corresponding emulsion treatment variable, instead of a traditional statistical standard deviation. Therefore, the deviation in the solubility values was evaluated as an indicator of how sensitive the response was to changes in the control parameter, i.e. a small deviation indicates that the biocrude content is the most significant factor in the solubility response, while a large deviation indicates that the solubility depends is more sensitive to changes in the other treatment variables.

The mean of response was also calculated to determine the most significant treatment variable. The averages of response variables for each level of the treatment variable can then be graphed to create a main effects plot. Delta is the difference between the lowest and highest average response values for each variable. The delta values are then ranked to indicate the relative effect of each variable on the response; where Rank 1 is the highest delta value and Rank 4 is the lowest. The mean of individual response variables was also determined to identify the best treatment variable levels to maximize or minimize the response.

3. Results and discussion

3.1. Maximized response variables

3.1.1. Biocrude solubility

The biocrude solubility of centrifuge emulsions was 18.39–65.43 wt %. For ultrasonification treatment, the biocrude solubility was slightly higher, ranging from 18.74 to 75.67 wt%. The individual solubilities and standard deviations of the centrifuge and ultrasonic emulsion samples are listed in Table 3. The average of response for solubilities of emulsion samples are listed in Supplementary Tables S1 and S2 and the corresponding plots are in Figs. 2 and 3. Higher solubility achieved by ultrasonic emulsion may be attributed to the high frequency sound waves emitted by the instrument, which promote mixing and allow small, stable droplets to form. The lowest solubility for both methods occurred when all treatment variables were at their lowest levels (samples C1 and U1), i.e. the biocrude fraction, surfactant fraction, retention time, and RPM/temperature were only 10 wt%, 1 wt%, 20 min, and 1200 RPM/20 °C, respectively. Interestingly, the variable with most significant influence on the biocrude solubility differed between the two methods. For centrifugation, biocrude content was the most influential, while for ultrasonification, temperature had the most significant influence. As explained in section 2, this was determined by calculating the differences, referred to as “delta”, between the highest and lowest average solubilities for each emulsion treatment parameter. The delta can be observed visually in Figs. 2 and 3 and calculated from the values in Tables S1 and S2. For centrifuge emulsions, the largest delta occurred in the response to biocrude fraction, while for ultrasonic emulsions the largest delta was in the temperature response. For emulsions produced by centrifugation, the solubility was positively correlated to the biocrude fraction. In Fig. 2a, it is shown that increasing the biocrude fraction level from 10 to 20 wt% increased the average biocrude solubility from 26.74 to 45.41 wt%, and again for 20 to 30 wt% where the solubility further increased to 54.02 wt%. There was a similar albeit less drastic trend seen in the ultrasonic emulsions (Fig. 3a), where increasing the biocrude fraction from 10, 20, and 30 wt% resulted in average solubilities of 51.60, 63.03, and 63.27 wt%, respectively. As seen in Fig. 2b

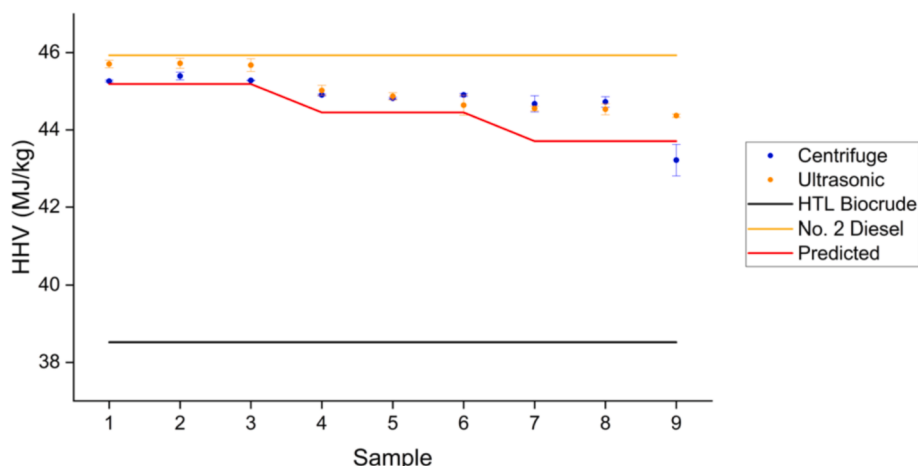


Fig. 4. Comparison of the HHV of each emulsion sample and the predicted values based on biocrude content.

and 3b, further addition of Atlox 4912 resulted in increased solubility for both centrifugation and ultrasonification, reflecting the surfactant's ability to help emulsion formation. Atlox 4912 can promote emulsion formation by decreasing interfacial tension between the two immiscible phases and promote the solvation of biocrude compounds into the diesel [4]. The average solubility of emulsions with surfactant fraction levels of 1, 5, and 10 wt% were 37.08, 47.06, and 42.04 wt% for centrifuge, and 53.68, 53.52, and 70.70 wt% for ultrasonic, respectively. For retention times of 20, 30 and 40 min, the average biocrude solubility was 44.69, 46.44, and 35.04 wt% for centrifugation and 38.89, 67.20, and 61.81 wt% for ultrasonification. While increasing the retention time from 20 to 30 min resulted in a greater biocrude solubility, further increase to 40 min led to a decreased solubility. As agitation goes on, changes in fluid direction and velocity can lead to separation by breaking the surface tension of micelles and preventing further emulsion. Therefore, a 30 min retention time may be ideal for maximum biocrude solubility before emulsion separation begins. The average biocrude solubilities were

44.69, 46.44, and 35.04 wt% and 48.89, 67.20, and 61.81 wt% for centrifuge and ultrasonic emulsions, depicted in Fig. 2c and 3c, respectively. While increasing the RPM levels of the centrifuge led to a slight increase in the average values of biocrude solubility (36.05, 44.28, and 45.84 wt% for 1200, 2400, and 3600 RPM, respectively), there was a significant increase in the solubility with increased temperature in the ultrasonic. As seen in Fig. 3d, increasing the temperature from 20 to 40 °C resulted in the average biocrude solubility increasing from 42.47 to 70.95 wt%, but further increase to 60 °C slightly decreased the solubility, falling to 64.68 wt%. This may be due to the physicochemical and kinetic properties of the surfactant. The melting point of Atlox 4912 is 40 °C, so upon reaching this temperature, the polymer surfactant can be fully extended in the solution and promote optimal emulsion performance. However, high temperatures adversely effects biocrude solubility due to decreased interfacial tension, deteriorating the emulsions [37,38]. Increased kinetic energy of droplets due to the increased temperature results in increased collision. Therefore, coagulation occurs and

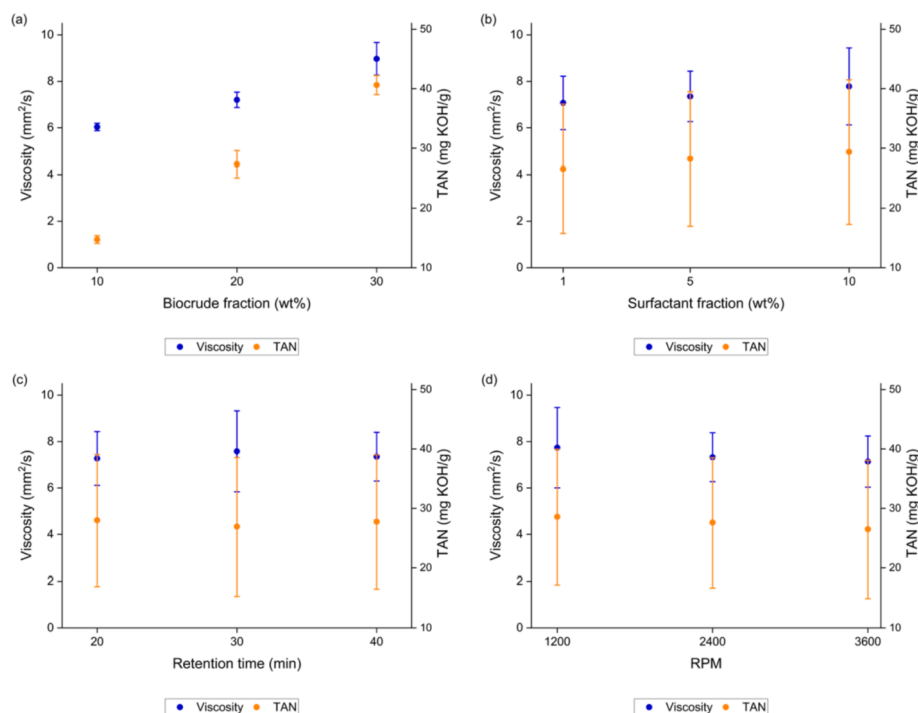


Fig. 5. Mean of response for viscosity and TAN of centrifugation emulsion samples vs. treatment variables (a) biocrude fraction, (b) surfactant fraction, (c) retention time, and (d) RPM. The error bars in the figure represent deviation in the data due to differences in other treatment variables.

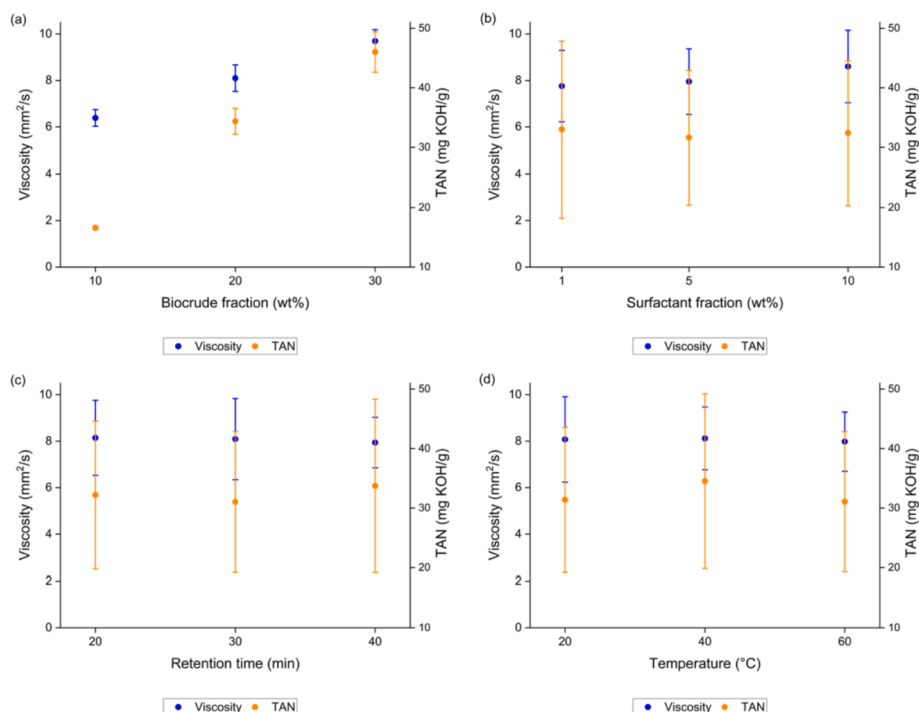


Fig. 6. Mean of response for viscosity and TAN of ultrasonification emulsion samples vs. treatment variables (a) biocrude fraction, (b) surfactant fraction, (c) retention time, and (d) temperature. The error bars in the figure represent deviation in the data due to differences in other treatment variables.

the amount of emulsion decreases, reflected in a lesser biocrude solubility. Even with the highest observed solubility values, at least 24.33 wt % of the biocrude remains as a water-insoluble fraction, which should be addressed to maximize downstream utilization. These heavy, insoluble biocrude fractions can be treated by thermocatalytic upgrading [39,40], solvent extraction, distillation, column chromatography, and membrane filtration [41].

3.1.2. Higher heating value (HHV)

Emulsification effectively combined HTL biocrude and diesel without sacrificing the calorific value. The HHV of the HTL biocrude, No. 2 diesel, Atlox 4912, and each emulsion sample are listed in Table 3. The HHV of emulsions from centrifuge treatment were 43.22–45.39 MJ/kg, and 44.37–45.73 MJ/kg from the ultrasonic treatment. In comparison to the HHV of the HTL biocrude, 38.52 ± 0.02 MJ/kg, the HHV of the emulsions was 12.2–17.8% and 15.2–18.7% larger for centrifuge and ultrasonic methods, respectively. The HHV of each emulsion was also comparable to the HHV of the No. 2 diesel, which was 45.93 ± 0.01 MJ/kg. The average HHV for the levels of each treatment variable are listed in Supplementary Tables S1 and S2. In Fig. 2a and 3a, there was a

negative correlation between the biocrude fraction and HHV for both treatments. For biocrude fractions 10, 20, and 30 wt%, the average HHV was 45.31, 44.88, and 44.20 MJ/kg, and 45.70, 44.84, and 44.48 MJ/kg for centrifuge and ultrasonic, respectively. This is due to the lower HHV of HTL biocrude compared to diesel; as the biocrude fraction increases, the overall HHV of the emulsion will decrease.

Compared with biocrude fraction, the HHV of emulsions for both treatments did not change as significantly in response to other variables (surfactant fraction, retention time, and RPM/temperature) (Figs. 2 and 3). This indicated that the calorific value of the emulsions is most sensitive to the fraction of biocrude oil in the mixture. Depicted in Fig. 4, the HHV of each emulsion was predicted based on the fraction of HTL biocrude and diesel in the mixture. A majority of the emulsion HHVs were slightly higher than the predicted values. This deviation may be attributed to Atlox 4912 promoting the solubility of biocrude compounds into the diesel. Since the maximum biocrude solubility was 65.43%, it is possible the compounds that dissolved in the emulsion were of higher calorific value than the whole raw biocrude, resulting in an HHV greater than the predicted value.

3.2. Minimized response variables

3.2.1. Kinematic viscosity

The kinematic viscosity of the HTL biocrude, #2 diesel, and each emulsion sample was measured at room temperature (20 °C) after the insoluble biocrude fractions were separated and are listed in Table 3. The average viscosity for the levels of each treatment variable are listed in Supplementary Tables S3 and S4. The viscosity of the HTL biocrude was 122.6 ± 2.80 mm²/s compared to diesel 5.32 ± 0.04 mm²/s. The viscosity of the centrifuge emulsions ranged from 5.91 to 9.87 mm²/s while the ultrasonic emulsions ranged from 6.06 to 10.28 mm²/s. Biocrude fraction and average kinematic viscosity were positively correlated (Fig. 5a and 6a). For biocrude fractions of 10, 20, and 30 wt%, the average viscosity was 6.03, 7.20, and 8.97 mm²/s, and 6.39, 8.10, and 9.69 mm²/s, for centrifuge and ultrasonic, respectively. The higher viscosities of the ultrasonic emulsions are likely due to the increased

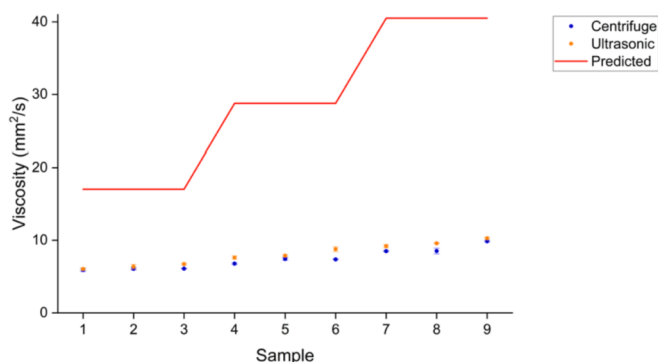


Fig. 7. Comparison of the viscosity of each emulsion sample and the predicted values based on biocrude content.

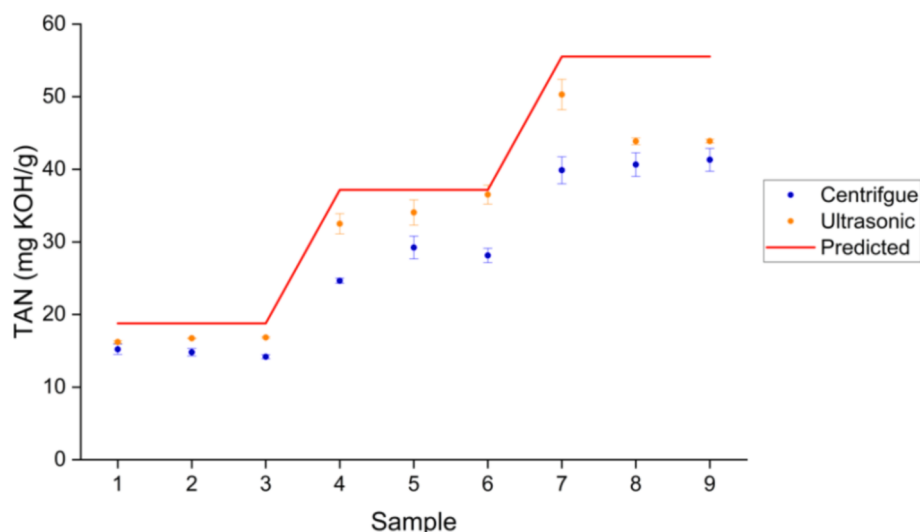


Fig. 8. Comparison of the TAN of each emulsion sample and the predicted values based on biocrude content.

biocrude solubility achieved, resulting in greater fractions of HTL biocrude in the emulsion. However, there were not any significant trends with the other treatment variables, indicating that viscosity is most sensitive to changes in the biocrude fraction. From Figs. 5 and 6 b-d, the standard deviations for viscosity vs. surfactant fraction, retention time, and RPM/temperature are much greater than the standard deviations for biocrude fraction, further indicating that these response variables depend greatly on biocrude fraction. With larger standard deviations, the viscosity values are more spread out across each level, possibly due to having more dependence on other treatment variables.

Like the HHV, viscosities of the emulsion samples were predicted based on the viscosities of the HTL biocrude and diesel. As seen in Fig. 7, the actual viscosities were notably lower than the predicted values, even with increased biocrude fraction. Due to the extremely high viscosity of HTL biocrude, the emulsion viscosity was expected to greatly increase with the biocrude fraction. However, it was observed that the emulsion viscosities remained more similar to that of diesel. This may be explained by the heavier, more viscous, biocrude components being separated out as compounds in the insoluble fractions, leaving only the lighter components dissolved in the emulsion, resulting in viscosities lower than the predicted values. Overall, the emulsification of HTL biocrude into diesel produced a diesel blend with a reasonable range of viscosity (5.91–9.69 mm²/s) compared with the commercial No.2 diesel (5.32 mm²/s).

3.2.2. Total acid number (TAN)

The emulsification process produced biocrude diesel blends with much lower acidity than the raw HTL biocrude. As seen in Table 3, the TAN of HTL biocrude was 184.08 ± 2.15 mg KOH/g, significantly higher than the centrifuge emulsions which ranged from 14.18 to 41.31 mg KOH/g and ultrasonic from 16.22 to 50.31 mg KOH/g. It was observed in Fig. 8 that acid numbers of the emulsified biocrude and diesel were slightly lower than the calculated values, but generally followed the predicted trend. The lower TAN of centrifuge emulsions compared to ultrasonic may be a result of less biocrude in the mixture because of their lower solubility.

With an acid number of just 0.43 ± 0.03 mg KOH/g, the diesel contributed significantly toward the improvement of the HTL fuel emulsion's acid number. The TAN was most influenced by changes in the biocrude fraction. As seen in Figs. 5 and 6, TAN values were positively correlated with biocrude fraction. The average TAN for the levels of each treatment variable are listed in Supplementary Tables S3 and S4. For biocrude fractions of 10, 20, and 30 wt%, the average TAN was 14.74, 27.34, and 40.61 mg KOH/g, and 16.60, 34.37, and 46.02 mg

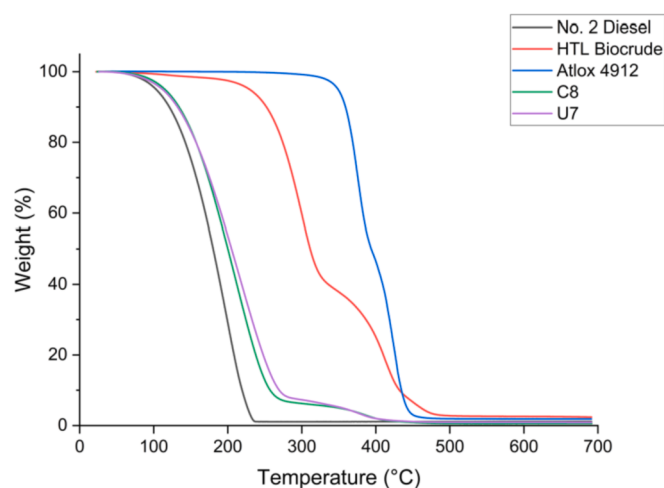


Fig. 9. TGA curves of base fuels, surfactant, and emulsions under N₂.

KOH/g, for centrifuge and ultrasonic, respectively. The standard deviations of the average TAN for each biocrude fraction level were also much smaller than the other treatment variables, further indicating that

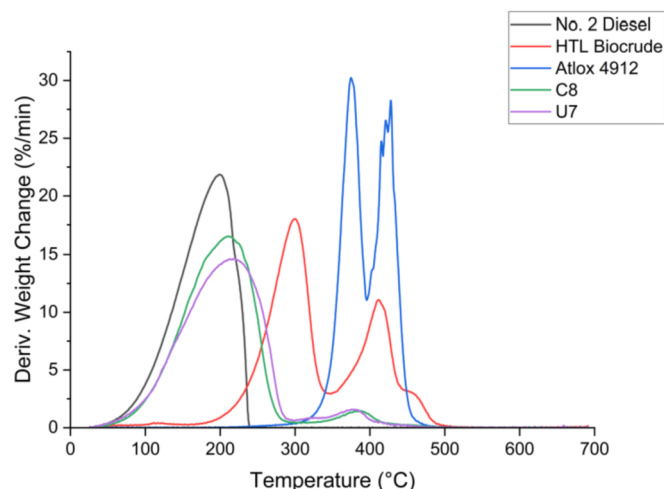


Fig. 10. DTG curves of base fuels, surfactant, and emulsions under N₂.

Table 4

Boiling point distribution of HTL biocrude, No. 2 diesel, Atlox 4912, and emulsions.

Distillate range (°C)	Oil type	wt%				
		No. 2 Diesel	HTL Biocrude	Atlox 4912	C8	U7
15.5–149	Gasoline	23.98	1.43	0.03	15.86	16.30
149–232	Kerosene	73.70	3.94	0.13	59.98	53.21
232–343	Diesel	1.24	55.75	3.43	18.93	24.91
343–371	Lubricating oils	0.00	4.77	19.50	1.25	1.67
371–566	Fuel oils	0.03	31.50	75.09	3.43	2.99
> 566	Residue	0.02	0.21	0.02	0.01	0.03

the TAN was most sensitive to this parameter. A low acidity in the fuel is beneficial to improve the engine performance in terms of preventing corrosion and enhancing fuel efficiency.

3.3. Physicochemical properties

3.3.1. Boiling point distribution

Thermogravimetric analysis (TGA) in a nitrogen atmosphere were used to determine the boiling point distribution of No. 2 diesel HTL biocrude, Atlox 4912, and a selected emulsion sample from each treatment method. Samples C8 and U7 (specific emulsification treatment parameters in Table 2) were selected to analyze for their boiling point distribution because they achieved the greatest biocrude solubility for the experiments at the highest level of biocrude fraction (30 wt%). Both emulsion samples were also produced with the lower levels of surfactant fraction: 5 wt% and 1 wt% for centrifuge and ultrasonic, respectively. Figs. 9 and 10 overlay the TGA and DTG curves of each sample. The boiling point distribution was characterized by the distillate range of six fractions [42] and the results are summarized in Table 4. Compared to No. 2 diesel whose largest weight loss fraction was 73.70% in the kerosene range (149–232 °C), the HTL biocrude composition was dominated by heavier compounds; 55.75% of weight loss occurred from 232 to 343 °C (diesel distillates) and 31.50% occurred from 371 to 566 °C (fuel oils distillates). Meanwhile, the main weight loss in the emulsion samples occurred in the kerosene range (149–232 °C), with weight losses of 59.98 and 53.21% for C8 and U7, respectively. These results confirm that emulsification with a surfactant can effectively dissolve the lower weight components of HTL biocrude with diesel, leading to improved ignition performance [4].

The HTL biocrude contained two major weight loss peaks in the DTG curve (Fig. 10), the first from 200 to 350 °C and the next from 350 to 500 °C. For diesel, there was one major weight loss peak from 200 to 250 °C. The major weight loss of the Atlox 4912 surfactant occurred between 300 and 500 °C. This suggests that the HTL biocrude and surfactant was composed of heavier components than diesel. The emulsion samples had similar DTG curves, each with two weight loss peaks. In Fig. 10, a dominant weight loss peak from 200 to 300 °C and a second minor weight loss peak from 300 to 450 °C indicated that while a majority of biocrude components dissolved in the diesel emulsion were lighter fuel fractions, heavier weight components were also able to be dissolved. It was observed that the composition of sample U7 had less kerosene and higher amounts of diesel fractions in comparison to C8 (Table 4). Therefore, ultrasonic agitation may be more effective than centrifugation at emulsifying heavier HTL biocrude components, due to its high frequency sound waves that allow small, uniform droplets with long-term stability to form emulsions. The boiling point distribution indicates that during emulsification, the lighter biocrude fractions dissolved more readily in diesel than the heavier fractions, meanwhile the addition of Atlox 4912 as a surfactant can also help dissolve heavy biocrude fractions during emulsification.

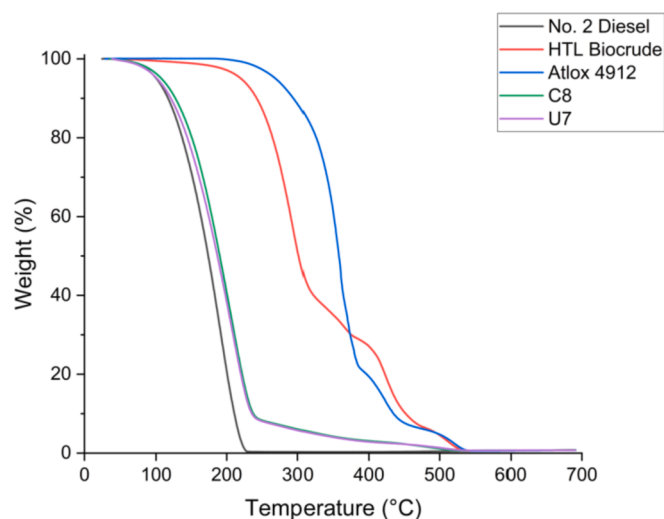


Fig. 11. TGA curves of base fuels, surfactant, and emulsions under air.

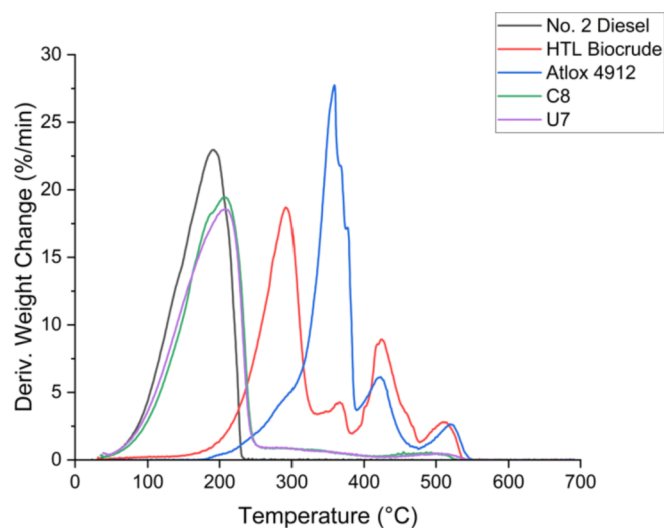


Fig. 12. DTG curves of base fuels, surfactant, and emulsions under air.

3.3.2. Combustion characteristics

Thermogravimetric analysis was also conducted to assess the combustion characteristics of No. 2 diesel, HTL biocrude, Atlox 4912, and emulsion samples C8 and U7 through oxidation with air. The TGA and DTG curves of each sample are depicted in Figs. 11 and 12, respectively.

The DTG curve of HTL biocrude oil (Fig. 12) showed four weight loss peaks located in 20–325 °C, 325–375 °C, 375–475 °C, and 475–550 °C. These weight loss peaks were mainly attributed to the complex composition of the biocrude. Based on the weight loss peaks, combustion of the HTL biocrude can be divided into three stages [14,43,44]: low temperature oxidation from 20 to 375 °C, fuel deposition from 375 to 475 °C, and high temperature oxidation from 475 to 550 °C. In the low temperature oxidation stage, oxygenated compounds such as aldehydes, ketones, and acids are formed [43]. The fuel deposition stage follows the oxidation mechanism of hydrocarbons, in which oxidation transitions from low to high temperature mechanisms [43]. Lastly, traditional complete combustion reactions occurred in the high temperature oxidation stage, where oxygen reacts with the heavier hydrocarbons to produce carbon dioxide, water, and heat [43]. Compared to the weight loss peaks of HTL biocrude, diesel had a single peak at a lower temperature (20–225 °C). This weight loss at low temperature suggested that the combustion reactions occurring in diesel were cracking and

Table 5

Empirical calculation of emulsions and base fuels based on thermogravimetric analysis.

	No. 2 Diesel	HTL Biocrude	C8	U7
IBP (°C)	61.00	91.08	69.29	61.37
T ₅ (°C)	103.22	229.48	115.08	111.79
T ₁₀ (°C)	121.10	252.31	134.18	132.14
T ₅₀ (°C)	180.26	311.28	200.11	205.13
T ₉₀ (°C)	219.41	431.97	257.30	269.57
CCI	25.70	n/a ^a	27.13	30.28
CFP (°C)	15.62	76.40	23.70	19.53

^a Value outside limit for CCI equation.

oxidation of hydrocarbons [43,45]. The weight loss peaks of both C8 and U7 emulsions were more similar to diesel than HTL biocrude, consisting of a major weight loss peak from 20 to 250 °C, along with two minor peaks from 250 to 425 °C and 425–525 °C. This further supported that most of the biocrude dissolved in the emulsions was of lower weight components, while the addition of Atlox 4912 promoted solubility of higher weight components into the diesel as well.

3.3.3. Thermal properties

TGA results, including boiling point distribution and recovery temperatures, were employed to calculate thermal properties of the diesel, HTL biocrude, and emulsions. These methods were derived from empirical relationships of fuel property correlation assessments [46,47]. The CCI and CFP of the emulsions and base fuels are listed in Table 5. Based on ASTM D4737 and D7215, these values were calculated using the initial boiling point (IBP) and recovery temperatures (T_i) obtained from TGA. The recovery temperatures indicate the temperature at which a certain wt% (i) of the fuel was volatilized. The CCI ranges from 0 to 100, with the maximum being the CCI of the reference fuel, cetane. The emulsions had slightly higher CCI (27.13 and 30.28 for C8 and U7, respectively) compared to No. 2 diesel (25.70). This improved CCI could be due to the contribution of heavier components in the HTL biocrude that were dissolved in the diesel during emulsification. Both improved emulsions (C8 and U7) indicated that the auto-ignition characteristics are improved compared with No. 2 diesel. However, the CCI calculation does not consider fuel additives commonly used in industry, such as nitrates or nitroalkanes, for cetane improvement, so the CCI value is equal or less than the true cetane number for tested fuel [48]. As for the CFP, HTL biocrude (76.40 °C) was significantly higher than the diesel (15.62 °C), C8 emulsion (23.70 °C), and U7 emulsion (19.53 °C). This could be attributed to the composition of HTL biocrude, consisting of unsaturated, high molecular weight, oxygenated compounds [48]. The CFP of both emulsion samples were slightly higher, but more like diesel, due to their compositions with lighter weight components compared to HTL biocrude. The CFP is an important thermal property because it affects the transportation and storage conditions of the fuel. The low CFP of C8 and U7 emulsions would require the storage temperature to be below 19.53–23.70 °C in order to prevent fuel vapors from reaching flammability limits [48,49].

3.3.4. Elemental analysis

The carbon, hydrogen, nitrogen, and oxygen content of the feedstock components and the emulsion products can be found in Table 3 and the tabulated atomic ratios are in Supplementary Table S5. The carbon content of the emulsion samples ranges from 81.81 to 85.54 wt% for centrifuge and 83.76–85.72 wt% for ultrasonic, an increase compared to 75.77 wt% for biocrude. After emulsion, the nitrogen and oxygen contents decreased. The nitrogen and oxygen content of the HTL biocrude was 0.48 wt% and 12.39 wt%, respectively. Centrifuge samples had nitrogen contents 0.29–0.35 wt% and oxygen contents 0.88–4.97 wt%, while ultrasonic samples had nitrogen contents 0.29–0.33 wt% and oxygen contents 0.53–2.87 wt%. Therefore, emulsification effectively increased carbon content, and reduced nitrogen and oxygen contents.

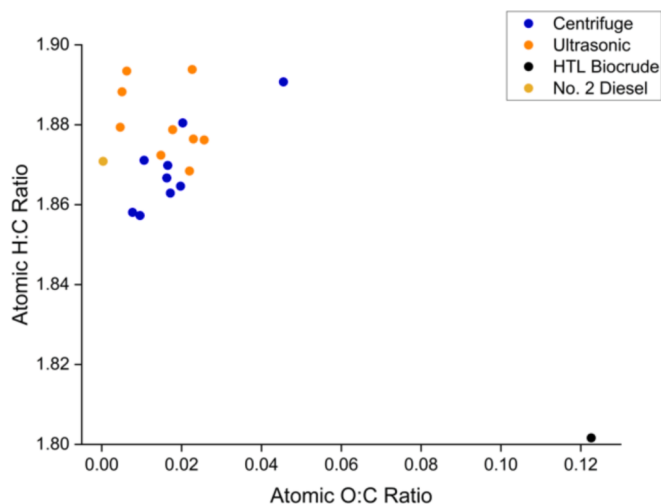


Fig. 13. Van Krevelen diagram of atomic H:C vs. O:C ratios.

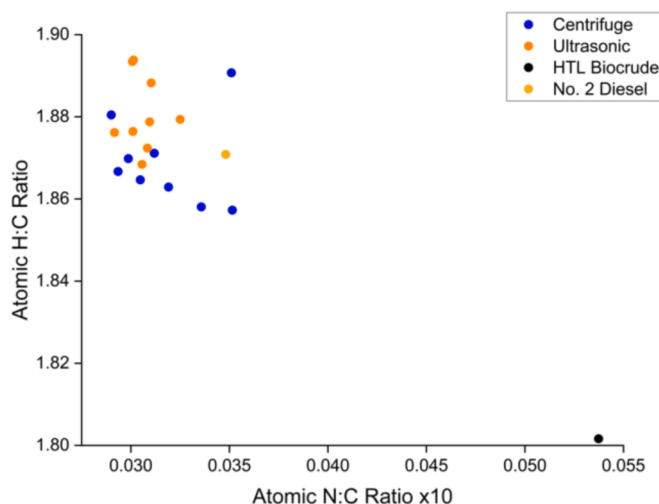


Fig. 14. Van Krevelen diagram of atomic H:C vs. N:C x10 ratios.

Depicted in the Van Krevelen diagram in Fig. 13, emulsification led to a significantly decreased O:C ratio despite minor changes in H:C values. The O:C ratios of the emulsions ranged from 0.0046 to 0.05, compared to 0.12 for HTL biocrude and 0.0003 for No. 2 Diesel. Both the H:C and O:C ratios of the emulsions were closer in value to No. 2 diesel than the HTL biocrude oil. The H:C ratios of the emulsion samples were 1.8573–1.8938. The H:C ratio of the HTL biocrude was 1.80 and No. 2 diesel was 1.87. Given the high H:C and low O:C atomic ratios in the emulsified fuels, the emulsions may contain high amounts of aliphatic chains and relatively low amounts of hetero and polyaromatic compounds [50]. In Fig. 14, it can also be seen that emulsification led to a decreased N:C ratio. The N:C ratio of HTL biocrude was relatively low at 0.05, but still higher than diesel which was 0.03. The N:C ratios of the emulsions were 0.03–0.04, with values lower than the HTL biocrude and most of them similar or better than diesel. It is clear that emulsification of HTL biocrude oil with diesel improved fuel characteristics through decreased oxygen and nitrogen content.

3.3.5. Energy return ratio and yield

The energy return ratio was higher for ultrasonic compared to centrifuge for all cases (Fig. 15) and the calculated values can be found in Supplementary Table S6. The energy return ratios for centrifuge emulsions ranged from 0.28 to 0.57, while for ultrasonic they were

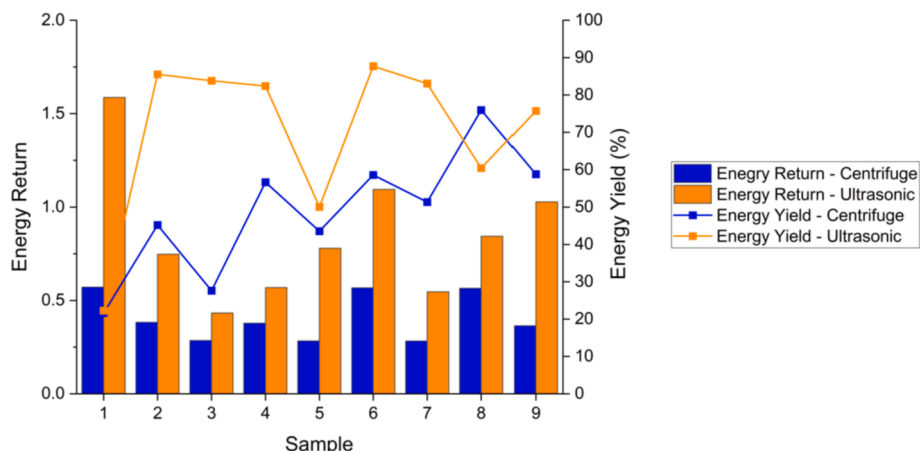


Fig. 15. Energy return ratio and energy yield of the centrifuge and ultrasonic emulsion samples.

Table 6

Fuel property comparisons of the emulsions, base fuels, and ASTM fuel specifications for whole biocrude (B100) and biodiesel blends (B6-B20).

Property	No. 2 Diesel	HTL Biocrude	C8	U7	B100	B6-B20
Viscosity (mm ² /s)	0.43 ± 0.03	122.60 ± 2.80	8.53 ± 0.40	9.31 ± 0.23	1.9–6.0	1.9–4.1
Density (g/mL)	0.832	0.847	0.844	0.839	–	–
TAN (mg KOH/g)	0.43 ± 0.03	184.08 ± 2.15	40.65 ± 1.63	50.31 ± 2.10	0.50	0.30
C (wt%)	86.18 ± 0.08	75.77 ± 0.06	84.24 ± 0.29	84.14 ± 0.06	–	–
H (wt%)	13.44 ± 0.04	11.38 ± 0.01	13.20 ± 0.00	13.10 ± 0.07	–	–
N (wt%)	0.35 ± 0.03	0.48 ± 0.02	0.29 ± 0.02	0.30 ± 0.00	–	–
O (wt%)	0.04 ± 0.01	12.39 ± 0.08	2.28 ± 0.31	2.47 ± 0.01	–	–
HHV	45.93 ± 0.01	38.52 ± 0.02	44.72 ± 0.14	44.55 ± 0.06	–	–
Water content (%), max	0.00 ± 0.00	1.19 ± 0.04	0.07 ± 0.00	0.13 ± 0.01	0.05	0.05
T ₉₀ (°C), max	219.41	431.97	257.30	269.57	360	343
CCI, min	25.70	63.51	27.13	30.28	47	40
CFP (°C), min	15.62	76.40	23.70	19.53	93	52

0.43–1.59. Several samples had notably high energy returns or yields. The highest energy return stands out at 1.59 for sample U1. In this sample, the ultrasonic instrument was operated for the shortest time (20 min) at 20 °C, requiring no heating.

The HTL biocrude and surfactant fractions were also at their lowest levels, so the resulting HHV of the emulsion was higher compared to emulsion samples with higher fractions of biocrude due to the higher HHV of No. 2 diesel. Therefore, the low energy requirement to create the emulsion and high HHV led to a greater energy return ratio. The energy yield was also higher for emulsification by ultrasonic than centrifuge for all cases except Case U8. The highest energy yield for an emulsion produced by centrifugation was 75.98% (sample C8). The higher energy yields in the ultrasonic sample may be due to their higher biocrude solubility compared to centrifugation, which leads to an improved energy yield according to Eq. (3). Considering energy efficiency of the emulsion process, ultrasonic treatment is superior. However, further study may be needed as the energy efficiency could be changed when the process is scaled up.

3.3.6. Fuel specification analysis of base fuels and emulsions

Several physicochemical and thermal properties of No. 2 diesel, HTL biocrude, C8 and U7 emulsion samples were compared to the ASTM D6751 and D7467 fuel specifications for B100 and B6-B20 biodiesel blends, respectively, and listed in Table 6. It was found that while the emulsions had significantly lower viscosities compared to HTL biocrude, they were still too high to meet the B100 or B6-B20 specifications. In comparison to the density of diesel (0.832 g/mL), both emulsions had densities more like HTL biocrude (0.847 g/mL), at 0.844 and 0.839 g/mL for C8 and U7, respectively. This is mainly attributed to heavier weight compounds from HTL biocrude that were able to be dissolved in the emulsions due to increased solubility from addition of the surfactant. The TAN of the emulsions reflected a 72.67–77.92% decrease in acid number in comparison to HTL biocrude but was higher than the B100 and B6-B20 ASTM standards. As discussed in section 3.3.4, emulsification produced biodiesel blends with elemental properties and calorific values similar to diesel. Notably, their carbon and hydrogen content were higher than HTL biocrude while their nitrogen and oxygen content was lower. This resulted in a 15.65–16.10% increase in HHV compared to the biocrude, pointing to the improved energy properties resulting from emulsified biocrude and diesel. With water contents of 0.07 and 0.13% for C8 and U7, respectively, the emulsions were just above the ASTM specification of 0.05%. The high water content was attributed to the moisture in HTL biocrude (1.19%), suggesting that further dewatering take place prior to emulsification. Water removal methods such as gravitational separation or distillation may be employed. The distillation temperature for 90% recovery was 257.30 and 269.57 °C for C8 and U7, respectively. This was a decrease from HTL biocrude which had a T₉₀ of 431.97 °C. Therefore, emulsification and addition of the block copolymer surfactant effectively improved the boiling point distribution of the biodiesel blends, with both 90% recovery temperatures below the ASTM maximum of 360 °C. It was found that the CCI and HTL biocrude (63.51) was already above the minimum ASTM specification for B100 (47). However, diesel had a much lower CCI of 25.70 and the resulting emulsions had CCI values of 27.13 and 30.28 for C8 and U7, respectively. Therefore, the emulsions did not meet the B6-B20 specification but did reflect improved auto-ignition characteristic with respect to diesel. A similar pattern was seen in the CFP of the base fuels and emulsions. The CFP of both HTL biocrude and diesel, 76.40 and 15.62 °C, respectively, were below the minimum B100 specification of 93 °C. The higher CFP of biocrude compared to diesel may be due to the presence of heavier weight components in the HTL biocrude. Accordingly, the CFP of the emulsified fuels fell in between these two values, with CFPs of 23.70 and 19.53 °C for C8 and U7, respectively. Therefore, it was seen that emulsification aided in increasing the CFP compared to diesel. While emulsification greatly improved the physicochemical and thermal properties of the fuels in comparison to HTL biocrude, the

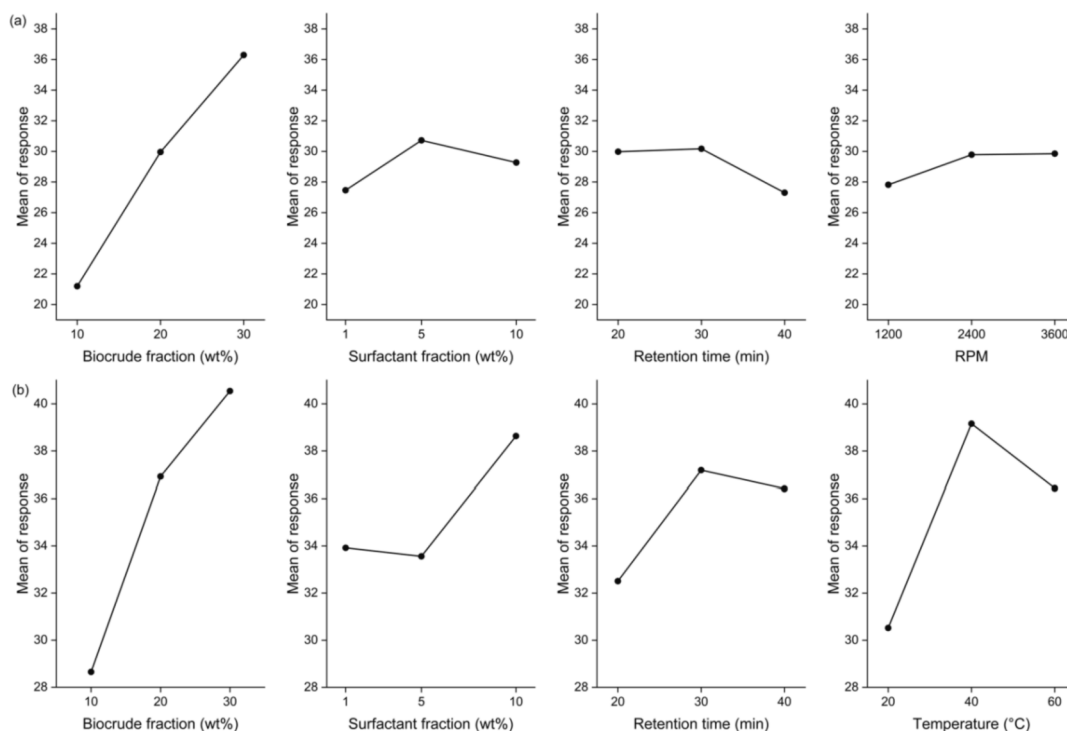


Fig. 16. Main effects plots for the overall mean of response for (a) centrifuge emulsions and (b) ultrasonic emulsions.

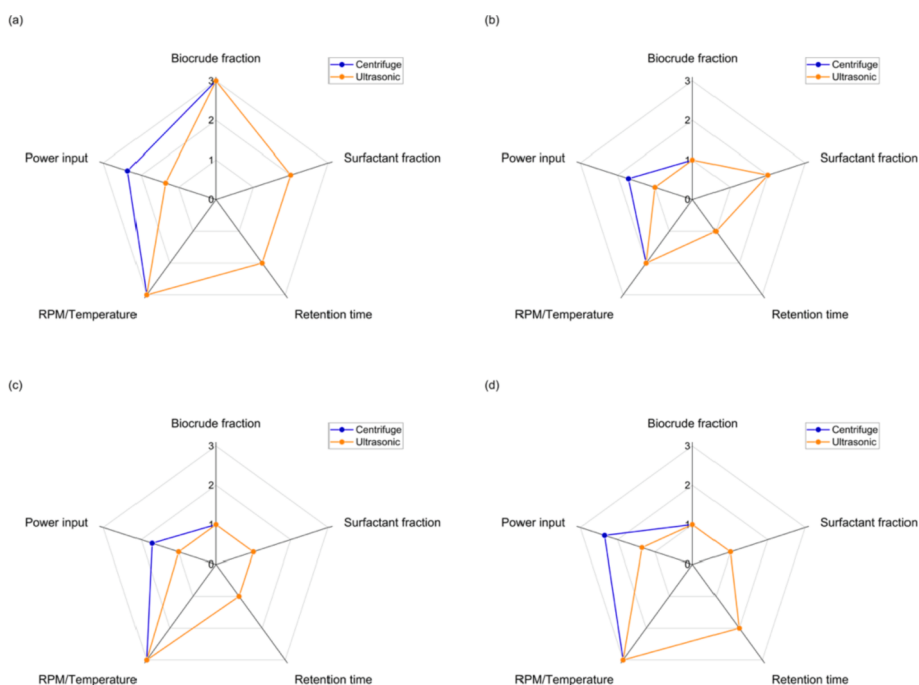


Fig. 17. Optimal emulsion treatment parameter levels to maximize the response variables (a) biocrude solubility and (b) HHV and minimize the response variables (c) viscosity and (d) TAN.

properties were close but still outside of ASTM requirements. This indicated that these emulsions are not yet suitable for direct use as a transportation fuel. Therefore, further upgrading of the HTL biocrude in addition to emulsification is desirable in order to improve the fuel properties and meet ASTM standards. Otherwise, emulsification may not be suitable as the sole upgrading method for this specific HTL biocrude oil. Other methods, such as hydrotreating/cracking, distillation, or esterification, should be used in combination with emulsification.

3.4. Sensitivity of treatment variables

The main effects of each emulsification treatment variable were determined for the centrifuge and ultrasonic processes. The tabulated averages of all response variables (solubility, HHV, viscosity, and TAN) at each level can be found in Supplementary Table S7. Biocrude fraction was ranked highest for both methods, indicating that the emulsion properties and fuel qualities were most sensitive to changes in the

amount of biocrude. From most to least influential: biocrude fraction, surfactant fraction, retention time, and lastly RPM affected the centrifuge emulsions. Meanwhile for ultrasonic, it was biocrude fraction, temperature, surfactant fraction, and then retention time. These responses were plotted as a main effects plot in Fig. 16, where the effect of biocrude fraction is seen to be much greater with its steep slope and larger range compared to the other treatment variables.

Averages were also determined for each response variable individually and used to select the ideal levels of each treatment variable based on a maximum or minimum response. The results are plotted in the Fig. 17 radar diagrams. It is shown that ideal levels of treatment variables are the same for centrifuge and ultrasonic methods, except for the process power input. Since the centrifuge and ultrasonic instruments had different power requirements, their power input levels were plotted relative to the range of their lowest and highest power. In each case, the emulsions produced by ultrasonification had lower power input. Therefore, using an ultrasonic to emulsify biocrude with diesel can lower energy requirements and these levels could be recommended to optimize specific physicochemical properties of an emulsion.

4. Conclusion

Emulsification of HTL biocrude from food waste and diesel with the aid of Atlox 4912 surfactant by centrifugation and ultrasonification was an effective and economical approach to produce diesel blends. The use of a block copolymer surfactant led to increased biocrude solubility in the emulsions, producing a fuel blend with calorific value, viscosity, and TAN close in value to diesel quality. The boiling point distribution of the emulsion samples showed that lighter components in HTL biocrude dissolve more easily into diesel, leading to diesel blends with viscosities lower than the predicted values, and much lower than HTL biocrude oil. Emulsification proved to reduce the nitrogen and oxygen content of fuel in comparison to HTL biocrude. However, pretreatment of the HTL biocrude, such as hydrotreating or esterification, is recommended prior to emulsification since multiple physicochemical and thermal properties of the emulsion fuels did not yet meet ASTM biodiesel fuel specifications. Biocrude fraction was identified as the most significant emulsification treatment variable, and emulsions with 10–30 wt% biocrude fraction, 1–5 wt% surfactant fraction, 30–40 min retention time, and 2400–3600 RPM or 40–60 °C were recommended as optimal levels for centrifuge or ultrasonic methods, respectively. At this scale, the ultrasonic method demonstrated better energy yield and energy return ratio than the centrifuge method.

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.fuel.2022.124817>.

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