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# Fractionation and catalytic upgradation of crude tall oil into sustainable transportation fuels via blending and co-refining†

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The integration of biogenic non-edible oils into conventional fuels is a lucrative pathway to lower the carbon intensity of the transportation industry. This study investigates the emerging co-refining potential of tall oil fatty acids when blended with conventional oil refinery streams before hydrotreatment and distillation to produce high-quality low-carbon transport fuels. Among refinery integration points, the strong miscibility of tall oil fatty acids with unifiner hot feed highlights the feasibility of seamless tall oil fatty acid integration into existing infrastructure. Hydrotreatment using NiMo and CoMo catalysts effectively upgraded the tall oil fatty acid–unifiner hot feed blends, increasing heating values by up to 9.4% from the original blend and achieving high values (45.4–47.9 MJ kg<sup>−1</sup>), while significantly reducing oxygen content from 12.2 wt% in tall oil fatty acid to 0.2 wt% in the final NiMo-treated diesel fraction. Both catalysts were effective, with NiMo exhibiting higher deoxygenation activity, while CoMo had higher selectivity for lower volatility fuel products. The resulting distillate fractions exhibited improvements in deoxygenation, viscosity, density, and total acid number (TAN), with kerosene fractions demonstrating particularly desirable fuel properties when compared to ASTM and European fuel standards. However, the TAN, viscosity, density, and sulphur content of select gasoline and diesel fractions presented a challenge, necessitating adjustment of these property deviations through further development of this refinement pathway to meet increasingly stringent specifications. Overall, the measured behaviour and microscopic imaging showed that the fuel products of this study were comparable to those available commercially. Advancing the utilization of bio-derived feedstocks like TOFA can contribute to reducing dependence on fossil fuels and achieving long-term net-zero emissions goals for Canada.

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## 1. Introduction

Approaches to improve sustainability in the dynamic environment of transportation are needed to transition away from the vast negative impacts of fossil fuel overuse.<sup>1</sup> As a massive and necessary industry for connecting the world, 37% of global CO<sub>2</sub> emissions stem from transportation, while concerningly maintaining the highest reliance on oil products at 91% of its total energy output.<sup>2</sup> Among policy-compliant methods to increase sustainability, the co-refining of fossil fuels with renewable tall oil fatty acids offers an innovative approach to produce lower-carbon intensity transportation fuels efficiently and cost-effectively using existing oil & gas refinery infrastructure. As a byproduct of the global pulp and paper industry, tall oil has a global production of nearly 2 million metric tonnes and offers an advanced renewable feedstock with properties suitable for

integration into existing oil refining processes, while avoiding competition with vital supply chains of food-based oils.<sup>3</sup> With paper and pulp mills having established infrastructure and consistent production to yield 30–50 kg of tall oil per tonne of pulp, tall oil offers lucrative convenience for biofuel production.<sup>4</sup> Crude tall oil (CTO) contains a significant fraction of tall oil fatty acids (TOFA) (17–86 wt%), typically 16 to 22 carbons in length, ideal for fuel usage if the acidic and less-energy dense monocarboxylic group is deoxygenated to a hydrocarbon.<sup>4</sup> As depicted in Fig. 1, common tall oil fatty acids include linoleic, oleic, stearic, and palmitic acids, which naturally occur as free accessible acids, unlike nutritious triglyceride-based fatty acids that are found in vegetable oils.<sup>5</sup>

Hydrotreatment is an established process of oil refineries, utilized to remove heteroatoms like sulphur, nitrogen, and oxygen, improve fuel properties, and achieve compliance with increasingly stringent environmental regulations; it was selected as the operation of choice in this study for upgrading TOFA blends. Sulphided NiMo (nickel–molybdenum) and sulphided CoMo (cobalt–molybdenum) supported on alumina are crucial commercial catalysts used in the hydrotreatment process due to their high efficiency, low cost, and longevity in

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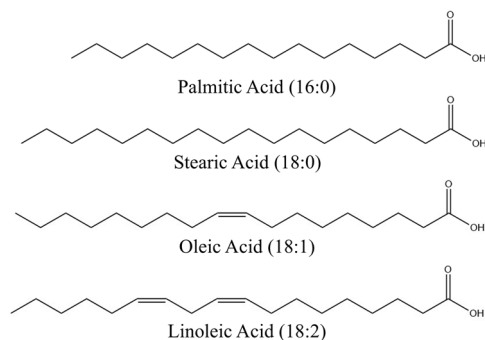


Fig. 1 Common fatty acids in tall oils.

removing sulphur, nitrogen, and oxygen compounds, reducing average molecular weight, and saturating double bonds in hydrocarbons for enhanced fuel quality.<sup>6</sup> Molybdenum is catalytically active and selective for key hydrogenation and heteroatom-removal reactions to hydrocarbons, while transition metals like cobalt and nickel as well as sulphur possess structural and electronic properties to promote molybdenum's activity with the support of acidic, robust, and porous alumina. Proven effective in the oil refinement industry, these bimetallic catalysts can play a vital role in facilitating the conversion of bio-derived feedstocks like TOFA into cleaner low-carbon fuels, as demonstrated in limited studies with other biogenic oils.<sup>7–9</sup>

As an established industry, crude oil refinement is a complex and optimized process with several streams, process units, and recycles. Among the several methods, many initial units include catalytic crackers, hydrotreaters (also known as a unifiner), and distillation columns. These units contain multiple potential entry points to introduce co-refining with biogenic feeds, highlighting the streams evaluated in this study in red in Fig. 2. With these multiple potential refinery entry-points to help transition fossil fuel production to lower carbon-footprints, it is important to compare the co-refining suitability of these entry-points, despite it being a method sometimes overlooked in the co-refining literature.<sup>4,10</sup> Some studies have also elected for individual upgrading of biogenic oils, successfully deoxygenating fatty acids similar to those in tall oil.<sup>11,12</sup> However, the prospect of co-refining biogenic oils like tall oil with existing infrastructure and refinery streams is particularly lucrative

economically, working with the oil & gas industry to accelerate renewability, instead of competing. There are also potential synergies identified with co-processing biogenic oils and refinery intermediates as it facilitates higher hydrogen transfer from hydrogen-rich petroleum fractions to hydrogen-deficient biogenic oils, when compared to stand-alone processing.<sup>13</sup>

Unlike many industrial processes that have developed from promising experimental work in academia, the use of tall oil in fuel production has recently gained desirability and been implemented by some European companies such as UPM (United Paper Mills Ltd) of Finland & SunPine of Sweden, with scarce scientific studies highlighting this valuable and green application.<sup>14,15</sup> This work presents a detailed investigation of the fractionation of CTO followed by the blending of tall oil fatty acids (TOFA) with conventional refinery streams before common hydrotreatment and distillation refinery operations to convert a select blend into high-quality lower-carbon intensity transport fuel. Considering increasingly stringent fuel regulations, CTO, TOFA, TOFA blends, and the produced hydrotreated fuel fractions underwent detailed physiochemical characterization with direct comparison to North American and European fuel standards. The future commercial relevance and current industrial applications of this study's tall oil feedstock, liquid hydrocarbon products, and residue by-products were also highlighted. Exploring and demonstrating the viability of this integrated tall oil-to-fuel approach lays the necessary foundation for further commercializing the transition to a decarbonized transportation sector while meeting international, Canadian federal, and Canadian provincial low-carbon fuel standard mandates.

## 2. Experimental

### 2.1. Feedstock and chemicals

The CTO and refinery fractions (Unifiner Hot feed (UH), Unifiner Cold feed (UC), Fluid Catalytic Cracking feed (FCC), and crude oil) used in this study were collected from a pulp plant and local oil refinery in British Columbia, Canada. Although every crude oil refinery differs in its methods, the refinery fractions originate from a similar setup to that depicted in Fig. 2. The TOFA was produced from CTO under vacuum distillation (10 torr) from 180–222 °C, corresponding to an atmospheric temperature of 320–375 °C. Besides producing TOFA, the distillation also produced lighter components like tall oil heads and heavier compounds like rosin acid residue. The study used commercial catalysts, *i.e.*, unsulphided NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The catalysts were sulphided with a butanethiol solution and then used for the hydrotreatment of the blended fuel. Butanethiol for catalyst sulphidation was purchased from Sigma-Aldrich, Oakville, Canada. Furthermore, all other chemicals were purchased from the University of Saskatchewan Chemistry Store, Canada.

### 2.2. Sulphidation of catalysts

The sulphidation of the catalysts was carried out using a catalyst basket, arranged in a column between a top and bottom layer of

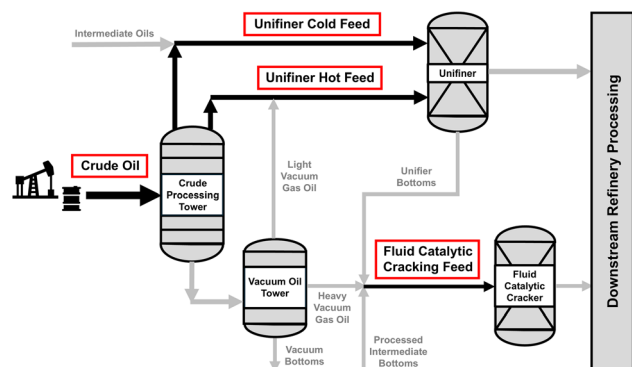


Fig. 2 Simplified refinery flow diagram with the streams evaluated in this work, highlighted in red.



**Table 1** Mass balance of UHF and final distillation products of hydrotreated UHF as well as 6 wt% TOFA-UHF blends (@10 torr vacuum)

| Products | Temperature (°C) | UHF (wt%) | CoMo treated (wt%) |       | NiMo treated (wt%) |       |
|----------|------------------|-----------|--------------------|-------|--------------------|-------|
|          |                  |           | UHF                | Blend | UHF                | Blend |
| Gasoline | 0–55             | 18.2      | 19.0               | 18.6  | 18.7               | 18.3  |
| Kerosene | 55–138           | 38.7      | 42.0               | 43.9  | 38.8               | 45.8  |
| Diesel   | 138–205          | 30.1      | 28.9               | 24.9  | 31.6               | 19.9  |
| Residue  | >205             | 13.0      | 10.1               | 12.6  | 10.9               | 16.0  |

glass beads, in the order of 10 mm glass beads at the top and the bottom, and 0.5 g of catalyst between the layers of glass beads.<sup>16</sup> The glass beads in the system help provide a higher surface area for activation and help regulate the temperature to avoid any damage to the catalysts due to high heating conditions. The sulfidation was carried out by immersing the catalyst basket in a 250 ml solution of butanethiol (2.9 vol%) and straight-run gas oil in a hydrotreater, over two stages for a total of 8 hours, with 4 hours of residence time at each stage.<sup>17</sup> Stage 1 operated at 193 °C at an average ramping rate of 2.5 °C min<sup>−1</sup>, followed by the 2nd stage at 343 °C at the same ramping rate. The initial pressure of the system was 90 bar with a stirring rate of 400 rpm, followed by cooling before collection.

### 2.3. Blending and hydrotreatment

A blend of TOFA (6 wt%) and unifiner hot feed (UHF) refinery fraction was prepared for co-refining in a Parr batch reactor–hydrotreating unit. The blend was added to the reactor with 5 wt% catalyst and flushed with H<sub>2</sub> gas to remove traces of other gases within the system. The temperature was set at a ramping rate of 2.5 °C min<sup>−1</sup> and an initial pressure of 30 bar, which gradually reached a pressure reading of 50 bar. Upon achieving the desired temperature and pressure conditions, the hydrotreatment was then conducted at 300 °C, 50 bar H<sub>2</sub> pressure, and 500 rpm stirring rate over 3 hours. The presence of H<sub>2</sub> gas supplied and sulphur in the feedstock leads to the production of H<sub>2</sub>S gas within the system; thus the collected product was flushed with excess N<sub>2</sub> gas to remove the H<sub>2</sub>S.

### 2.4. Distillation of hydrotreated products

The final hydrotreatment product was taken into a vacuum distillation unit for segregation of different hydrocarbon components. The final distillation was carried out at a vacuum pressure of 0.013 bar (10 torr), and relative temperature ranges of 0–55 °C, 55–138 °C, and 138–205 °C, for gasoline, kerosene, and diesel fractions, respectively. Table 1 shows the mass balance of different petroleum products extracted after the vacuum distillation of hydrotreated UHF as well as the hydrotreated TOFA-UHF blend.

### 2.5. Physical and chemical characterization of CTO, TOFA, and distilled products

The derived distillate products, feedstocks (TOFA and UHF) and hydrotreated intermediate products were analysed for their physical and chemical properties through varying methods, discussed below.

**2.5.1 Ultimate analysis of feedstocks, intermediates and products.** The elemental composition (C, H, N, and S) of the feedstocks, hydrotreated intermediate products, UHF, final distilled products, and the residue, was determined by a Vario EL III CHNS elemental analyzer (Elementar Americas, Inc., Ronkonkoma, NY, USA). The concentration of oxygen was calculated by mass difference, following eqn (1).

$$O \text{ (wt\%)} = 100 - [C \text{ (wt\%)} + H \text{ (wt\%)} + N \text{ (wt\%)} + S \text{ (wt\%)}] \quad (1)$$

**2.5.2 High heating value (HHV) test.** To avoid the use of erroneous empirical formulae for HHV based on elemental content, an oxygen bomb calorimeter (Parr 6400 Calorimeter, IL, USA) was used. The instrument was calibrated according to the ASTM D5865 standards.<sup>18</sup>

**2.5.3 Gas chromatography-mass spectrometry (GC-MS) analysis.** The chemical composition of the feedstocks, hydrotreated samples, and final distilled products was analyzed by GC-MS, using a trace 1310 gas chromatograph and a TSQ duo mass 19 Spectrometer (Thermo Fisher Scientific, Waltham, MA, USA). GC-MS samples were prepared through 10× dilution with carbon disulphide. 1 µL of the sample was injected at 250 °C with a split-flow of 60 mL min<sup>−1</sup> and a split ratio of 50 : 1, while the source temperature was set at 250 °C with a helium purge flow rate of 3.0 mL min<sup>−1</sup>. The oven temperature was first set at 40 °C with a 1-minute hold period, then raised to 150 °C at 5 °C min<sup>−1</sup>, and finally raised to 330 °C at 7 °C min<sup>−1</sup>, which was maintained for 10 minutes. The mass spectrum data for the analyzed samples were acquired between 50 and 650 *m/z*, and the peaks were identified after comparing them with the standard NIST (National Institute of Standards and Technology) library following Chromeleon™ 7.2 chromatography data system (CDS) software.

**2.5.4 Density.** The density of the samples was measured *via* mass and volume at a controlled temperature of 20 °C in the lab. 10 mL of each sample was filled and weighed in a 50 mL volumetric flask to calculate the density of the sample.

**2.5.5 Viscosity.** The viscosity of the samples was analyzed using a Brookfield RVDV-II/pro viscometer (AMETEK Brookfield, Middleboro, MA, USA) at a temperature of 40 °C *via* a circulating water bath, following the ASTM D2270 standards.<sup>19</sup> The observation cycles were repeated in triplicates to consider an average value and reduce possible error.

**2.5.6 Total acid number (TAN).** Biocrude acidity was measured by volumetric KOH base titration using isopropyl alcohol, following ASTM D664 standards.<sup>20</sup> Each sample was analyzed three times to obtain an average value of TAN, minimizing errors.



**2.5.7 Visual miscibility test.** Visual imaging of the original blends, derived products, and commercially available fuels was carried out through microscopic imaging of the products. The microscope used for this analysis was a Leica Galen III microscope equipped with a 10× Lecia lens. The microscope consisted of an Omax A35100U camera, and the images were viewed using Omax-ToupView 3.7 software. Commercially purchased fuels were also imaged using the same setup to determine the extent of the miscibility by microscopic observation.

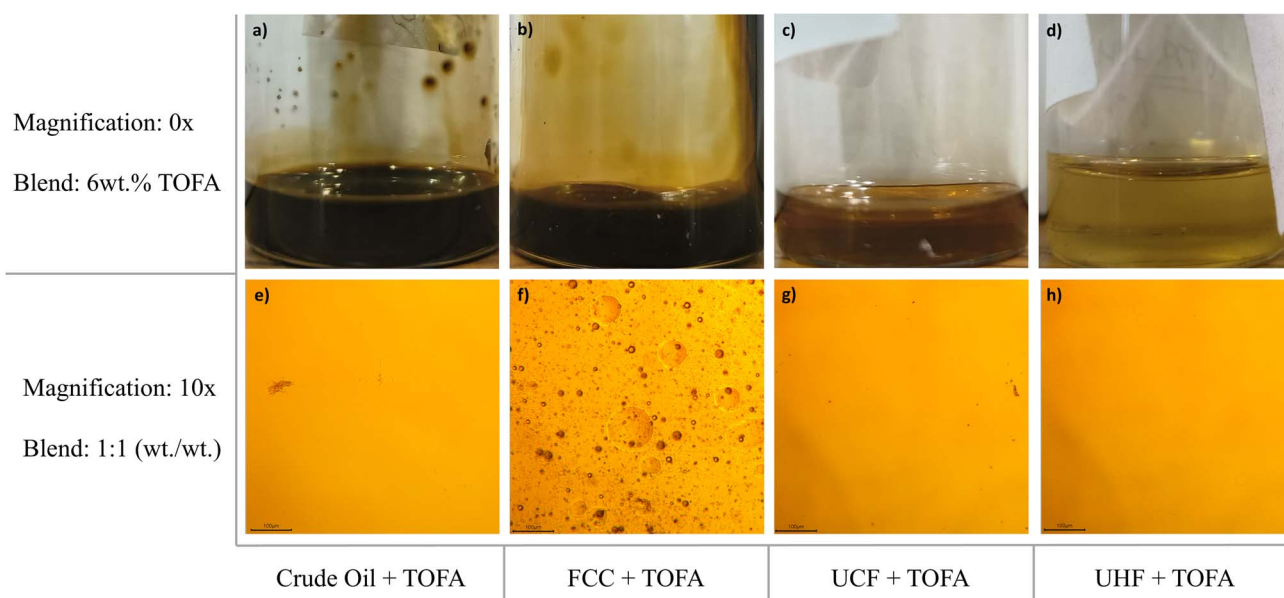
**2.5.8 Simulated distillation (SimDis) measurements.** The boiling point distribution of liquid fuel products were then compared to commercially available fuel, using simulated distillation. Samples were also compared to simulated distillation standards to determine carbon distribution. The samples were examined using a Varian CP-3800 gas chromatograph (Varian, Inc., Walnut Creek, CA, USA). Simulated distillations were planned after the ASTM method, D2887, where the samples were dispersed in CS<sub>2</sub> (Fisher Scientific, Canada) to prepare the SimDis analysis sample.<sup>21</sup>

### 3. Results and discussion

#### 3.1. Evaluating TOFA blending with refinery streams

Miscibility is critical for the effective upgradation of TOFA with unrefined streams in a refinery, eliminating handling challenges, mass-transfer limitations, and improving interactions between the co-processed feeds.<sup>22</sup> Four common refinery feed streams were selected for blending with TOFA. Possible refinery entry points include unrefined crude oil, FCC bottoms from vacuum distillation, UCF from the tops of atmospheric crude distillation, and UHF from a blend of atmospheric and vacuum distillation products. Microscopic analysis is a practical method consistent with studies evaluating the homogeneity of biogenic

oil blends with various refinery feeds, including those by Manara *et al.*,<sup>10</sup> who observed blending with pyrolysis bio-oil, and Bhat *et al.*<sup>23</sup> who investigated hydrothermal liquefaction bio-crude. All samples appeared soluble without magnification, as shown in Fig. 3a, c and d, except for the FCC blend that had the poorest miscibility by a wide margin and it formed a partially miscible layer with TOFA above the darker insoluble contents (Fig. 3b). Qualitatively observing the blends as shown in Fig. 3 under 10× magnification revealed some differences in the blends (Fig. 3e–h). It was apparent that TOFA in combination with UHF (Fig. 3h) exhibited the highest degree of miscibility among blends, fully homogeneous at a 1 : 1 volume ratio and lacking agglomerates. Although a smaller, more practical ratio of TOFA to refinery samples was used to upgrade the blend (6 wt% TOFA), this promising miscibility of TOFA/UHF at a high 1 : 1 ratio ensures uniformity for co-processing. Although 6 wt% TOFA blending was selected based on the much larger availability of refinery intermediates compared to TOFA, future studies could implement a blending-ratio analysis for optimal production and to meet case-by-case logistical needs of refineries. As UHF contains distilled intermediates from the lighter end of crude oil-derived hydrocarbons, it is consistent that this fraction is miscible with TOFA due to a lack of high-molecular-weight components and non-hydrocarbon contaminants that can be seen excessively in the FCC blend (Fig. 3f).<sup>24</sup> Although there is a lack of extensive studies investigating TOFA miscibility in refinery fractions, this observed homogeneity between fatty acids and hydrocarbons is reported in the literature.<sup>25</sup> The long hydrocarbon tails of the fatty acids have similar carbon chain lengths and therefore similar hydrophobicity and miscibility with the UHF hydrocarbons, overcoming the intermolecular hydrogen bonding of the TOFA carboxylic groups. The properties of CTO, TOFA, UHF, and the TOFA-UHF blend are



**Fig. 3** Unmagnified 6 wt% blends (a–d) as well as 10× magnification of 1 : 1 volume blends (e–h) of TOFA with refinery streams: crude oil, fluid catalytic cracking (FCC), unifiner cold feed (UCF) and hot feed (UHF).





**Table 2** Properties of crude tall oil (CTO), tall oil fatty acids (TOFA), unfiner hot feed (UHF), 6 wt% blend of TOFA in UHF, and nitrogen treated HDO products

| Sample name   | HHV<br>(MJ kg <sup>-1</sup> ) | TAN<br>(mg KOH per g) | Density<br>(kg m <sup>-3</sup> @20 °C) | Kinematic viscosity<br>(cSt @40 °C) | C<br>(wt%) | H<br>(wt%) | N<br>(wt%) | S<br>(wt%) | O<br>(wt%) |
|---------------|-------------------------------|-----------------------|----------------------------------------|-------------------------------------|------------|------------|------------|------------|------------|
| CTO           | 38.7                          | 137.2                 | 937.6                                  | —                                   | 76.7       | 10.7       | 0.1        | 0.3        | 12.2       |
| TOFA          | 39.7                          | 169.6                 | 845.2                                  | 29.6                                | 79.6       | 11.3       | 0.1        | 0.0        | 9.0        |
| UHF           | 44.3                          | 1.0                   | 743.6                                  | 1.7                                 | 85.7       | 14.0       | 0.1        | 0.3        | 0.0        |
| TOFA-UHF      | 43.8                          | 12.7                  | 748.0                                  | 1.9                                 | 83.2       | 13.7       | 0.1        | 0.3        | 2.8        |
| NiMo-UHF      | 44.8                          | 0.4                   | 757.1                                  | 1.7                                 | 85.6       | 14.2       | 0.0        | 0.2        | 0.0        |
| CoMo-UHF      | 45.0                          | 0.6                   | 749.1                                  | 1.5                                 | 85.8       | 14.0       | 0.0        | 0.2        | 0.0        |
| NiMo-TOFA-UHF | 44.6                          | 10.8                  | 818.5                                  | 1.4                                 | 85.2       | 13.9       | 0.1        | 0.2        | 0.6        |
| CoMo-TOFA-UHF | 45.1                          | 12.4                  | 791.0                                  | 1.3                                 | 84.5       | 13.7       | 0.1        | 0.4        | 1.3        |

highlighted in Table 2. The properties of miscible TOFA and UHF show some differences, indicating that the immiscible components of crude oil, FCC, and UCF likely fall outside the density (743.6–845.2 kg m<sup>-3</sup>) and viscosity (1.7–29.6 cSt) ranges. CTO maintains high viscosity (beyond viscometer limits) and density compared to its distilled TOFA component, primarily due to the presence of bulky carbon-ring containing resin acids.<sup>4</sup> Further highlighting the need to distill CTO into TOFA, the undesirable sulphur content in CTO is also notably higher than in TOFA due to the presence of volatile sulphur compounds, present in turpentine compounds.<sup>26</sup> The TOFA–UHF blend showed only a minor decrease in the HHV percentage (1.1%) as well as a minor increase in viscosity (11.7%) and density (0.6%) compared to UHF alone. However, due to the acidic nature of the carboxylic groups in TOFA, the TAN and oxygen content increased prominently in the blend compared to UHF and are the key properties targeted for improvement through hydrotreatment in this study. The miscibility results justify the selection of a TOFA and UHF blend for further hydrotreatment with commercial catalysts, mimicking the downstream refinement process that UHF undergoes to produce gasoline, kerosene, and diesel hydrocarbons.

Upon further observation of Fig. 3, FCC exhibited limited miscibility with TOFA (Fig. 3b and f) due to its higher molecular weight (heavy) components with differing flow properties, making FCC dark in colour and solid at room temperature compared to the clear liquid TOFA with tails that are 18 to 23 carbons in length, as confirmed by GC-MS in the ESI data.†(ref. 4) Although these blends were mixed at room temperature without any additional emulsifiers, the use of emulsions and/or solvents could be considered for improving the FCC–TOFA blend.<sup>23</sup> Crude oil (Fig. 3a and e) and UCF (Fig. 3c and g) both appeared primarily soluble, containing only small amounts of agglomerates that differed too much in properties from TOFA to become dispersed homogeneously. Crude oil is the most unrefined feed and therefore contains a wider range of hydrocarbon components as well as more likely contaminants such as metals and sediments, causing less than ideal heterogeneity in blends with refined components like TOFA.<sup>27</sup> Furthermore, UCF (Fig. 3c and g) was nearly homogeneous and well dispersed when blended with TOFA; however, a few agglomerates were

present, indicating that some components were not soluble. UCF and UHF (Fig. 3d and h) having similarly strong miscibility is consistent as both leave the light ends of distillation units and have a similar position in the refinery scheme of Fig. 2, while UCF's incomplete homogeneity likely arises from its partial recycled composition of intermediate oil components which are absent in UHF. Although no screening of tall oil blends with refinery fractions could be observed in the literature, these blending results are consistent with the results reported by Manara *et al.*,<sup>10</sup> indicating that more refined streams such as light cycle oil (similar to UCF & UHF) have higher homogeneity with pyrolysis bio-oil, while more dense and viscous streams like gas oil and heavy cycle oil (similar to FCC) are heterogeneous.

Ideally, refinery feeds and streams are non-acidic with a TAN of <0.5 mg KOH per g to avoid corrosion concerns; however, reported literature reports indicate that some refineries regularly handle higher acidity values similar to the TOFA–UHF blend of this study. For example, crude oil samples with a TAN as high as 9.8 mg KOH per g and refined vacuum gas oil samples up to 14.7 mg KOH per g were reported by Chakravarthy *et al.*,<sup>28</sup> where naphthenic acid compounds (also containing carboxylic acids like TOFA) are present and managed within the refinery. Elevated TAN values in refinery streams can be managed through cost-effective adjustment of the corrosion environment (such as process parameters) as well as by adding corrosion inhibitors, before considering costly retrofitting of refinery infrastructure.<sup>29</sup> The miscibility results justify the selection of a TOFA and UHF blend for further hydrotreatment with the commercial catalysts, mimicking the refinement process UHF undertakes downstream to produce gasoline, kerosene, and diesel hydrocarbons.

### 3.2. Catalytic hydrotreating of TOFA and UHF

Catalytic hydrotreatment of UHF and the TOFA–UHF blend results in significant alterations to their properties. Depending on the catalyst used for HDO, the samples were segregated into two types, NiMo samples and CoMo samples. HDO was carried out to decrease the level of contaminating compounds in the TOFA–UHF blend and stabilize the oxygenated compounds to ensure the production of a homogenous hydrocarbon mixture. However, the presence of sulphur compounds on the catalyst



surface produces  $\text{H}_2\text{S}$  as a byproduct during HDO. Thus, to remove  $\text{H}_2\text{S}$ , the sample was treated with  $\text{N}_2$  gas and then analysed as the intermediate product for its physicochemical properties. The samples were labelled NiMo-TOFA-UHF and CoMo-TOFA-UHF and studied for properties like CHNSO, HHV, density, viscosity, and TAN. Table 2 lists the properties of the hydrotreated samples.

There are some differences in mass balance between the hydrotreated UHF and hydrotreated blend (TOFA-UHF) fuel cuts shown in Table 1. Significant fractions of all fuel ranges were observed ( $>18.3$  wt% gasoline,  $>38.8$  wt% kerosene, and  $>19.9$  wt% diesel), while the residue fraction was consistently the lowest (10.1–16.0 wt%). The yield of gasoline fractions showed insignificant differences between NiMo and CoMo catalysts as well as between UHF and the blend (18.3–19.0 wt%), suggesting that the catalyst nor the TOFA content impacted the yield of gasoline content. Hydrotreatment of the TOFA-UHF blend with NiMo and CoMo showed an increase in both kerosene and residue fractions compared to hydrotreatment of UHF alone, while diesel content was reduced. One explanation for this trend could be the deoxygenation of TOFA during hydrotreatment, which further contributed to hydrocarbons in the kerosene phase. At the same time, TOFA's high oxygen content may have also led to increased repolymerization, coking, *etc.*, to increase the residue phase over the diesel phase.<sup>30</sup> The larger increase in the kerosene fraction (7.0 wt%) and the residue fraction (5.1 wt%) for the NiMo-hydrotreated blend compared to CoMo may indicate higher catalytic activity for deoxygenation, but also polymerization in the presence of NiMo.

**3.2.1 Improvement of key properties.** Analysis showed a significant reduction in the oxygen content of the HDO intermediates compared to the feedstocks (TOFA and the TOFA-UHF blend). NiMo exhibited higher catalytic activity for deoxygenation, reducing oxygen by 93 wt% compared to the original TOFA sample and 80 wt% compared to the TOFA-UHF blend, while CoMo reduced oxygen by 86 wt% and 55 wt%, respectively. The results also showed a considerable increase in the carbon content of the HDO intermediates, compared to TOFA carbon content, *i.e.*, 5.6 wt% for NiMo-TOFA-UHF and 4.9 wt% for CoMo-TOFA-UHF, respectively. The reduction in oxygen content enhanced the heating value of the intermediate products, which increased by  $1.3 \text{ MJ kg}^{-1}$  to  $45.1 \text{ MJ kg}^{-1}$  for CoMo-TOFA-UHF and by  $0.8 \text{ MJ kg}^{-1}$  to  $44.6 \text{ MJ kg}^{-1}$  for NiMo-TOFA-UHF, comparable to fuel fractions. However, a marginal difference in TAN was observed in the intermediate products across both catalysts. Key properties like sulphur (0.2–0.4 wt%) and HHV ( $44.6$ – $45.1 \text{ MJ kg}^{-1}$ ) were comparable between the hydrotreated blend and hydrotreated UHF products for both catalysts. However, the TAN remained undesirably high (10.8–12.4 mg KOH per g) in the NiMo- and CoMo-hydrotreated blends compared to their hydrotreated UHF counterparts (0.4–0.6 mg KOH per g), indicating that TOFA significantly contributed to acidic components even after hydrotreatment. Section 3.3 Further discusses the improvement of these key properties in the hydrotreated TOFA-UHF blends' distillates.

**3.2.2 GC-MS analysis of the blend, intermediates, and final products.** A comparison of the GC/MS data for the TOFA-UHF

blend and hydrotreatment products shown in Fig. 4 highlights the transformation of oxygenated fatty acids into fuel-range hydrocarbons. The TOFA-UHF blend features a mix of hydrocarbons and fatty acids, including methyl-cyclohexane (5.6%), undecane (4.9%), *p*-xylene (4.8%), nonane (4.7%), and oleic acid (4.2%). The significant presence of oleic acid despite TOFA's small blend ratio can be explained by the dominant presence of oleic acid in the TOFA samples at 47.4%, followed by linoleic acid (12.5%), and stearic acid (10.5%), all requiring deoxygenation to yield hydrocarbons with improved HHV.<sup>4</sup> The data collected from the hydrotreatment intermediates suggest an effective reduction of oxygenated compounds, producing lighter hydrocarbons. The CoMo-TOFA-UHF product increased in methyl-cyclohexane up to 7.8%, along with light to moderate alkanes like undecane ( $\text{C}_{11}$ , 6.5%), tetradecane ( $\text{C}_{14}$ , 6.3%), and hexadecane ( $\text{C}_{16}$ , 6.6%), indicating effective cracking and saturation of larger molecules in the untreated blend. In the NiMo-TOFA-UHF sample, methyl-cyclohexane increased to 10.6%, with significant amounts of undecane (8.5%), nonane (8.1%), and toluene (8.0%). This shift towards lighter hydrocarbons indicates that the catalytic process effectively breaks down larger molecules (including TOFA) into smaller fuel-range alkanes and aromatic hydrocarbons. This catalytic breakdown of the TOFA-UHF blend into lighter hydrocarbons confirms the effectiveness of the hydrotreatment process, enhancing energy content and stability of the final products for fuel applications. Overall, these transformations underscore the efficacy of CoMo and NiMo catalysts in producing fuel-range hydrocarbons.

Vacuum distillation of the CoMo and NiMo hydrotreated blends into fuel-range hydrocarbons yielded significant fuel fractions: 18.6 & 18.3 wt% gasoline ( $<172^\circ\text{C}$ ), 43.9 & 45.8 wt% kerosene ( $172$ – $275^\circ\text{C}$ ), and 24.9 & 19.9 wt% diesel ( $275$ – $355^\circ\text{C}$ ); the residue was the lowest for both fractions at 12.6 & 16.0 wt%, respectively. Although the distillation residues are less desirable and solid at room temperature for both catalysts, this by-product likely contains many high-carbon number hydrocarbons ( $>\text{C}_{27}$ ) that can be further processed for petroleum or binder applications, further discussed in Section 3.4.3.<sup>22</sup> Table 3 outlines the physicochemical analysis of the produced fuel in comparison to ASTM standards utilized across North America and EN standards across Europe. The effect of CoMo and NiMo was similar during hydrotreatment, with both catalysts upgrading the quality of the TOFA-UHF blend with nearly identical acidity, viscosity, and density among fuel fractions. NiMo had a slight advantage in increasing HHV, reducing sulphur, and reducing oxygen, indicating potentially improved desulphurization, deoxygenation, and hydrocarbon-saturating reactions that improve process efficiency and desirability of the fuels.<sup>31</sup> These findings agree with previous biogenic oil hydrotreatment, which reported similar improvements but with sulphided NiMo exhibiting more useful surface geometries ( $\text{Ni}_3\text{S}_2$  crystallites, Ni atoms, and Ni cations in octa- or tetrahedrals) over CoMo, leading to higher catalytic activity, selectivity to hydrogenation, and less coke/solid residual formation.<sup>9,22,32</sup>



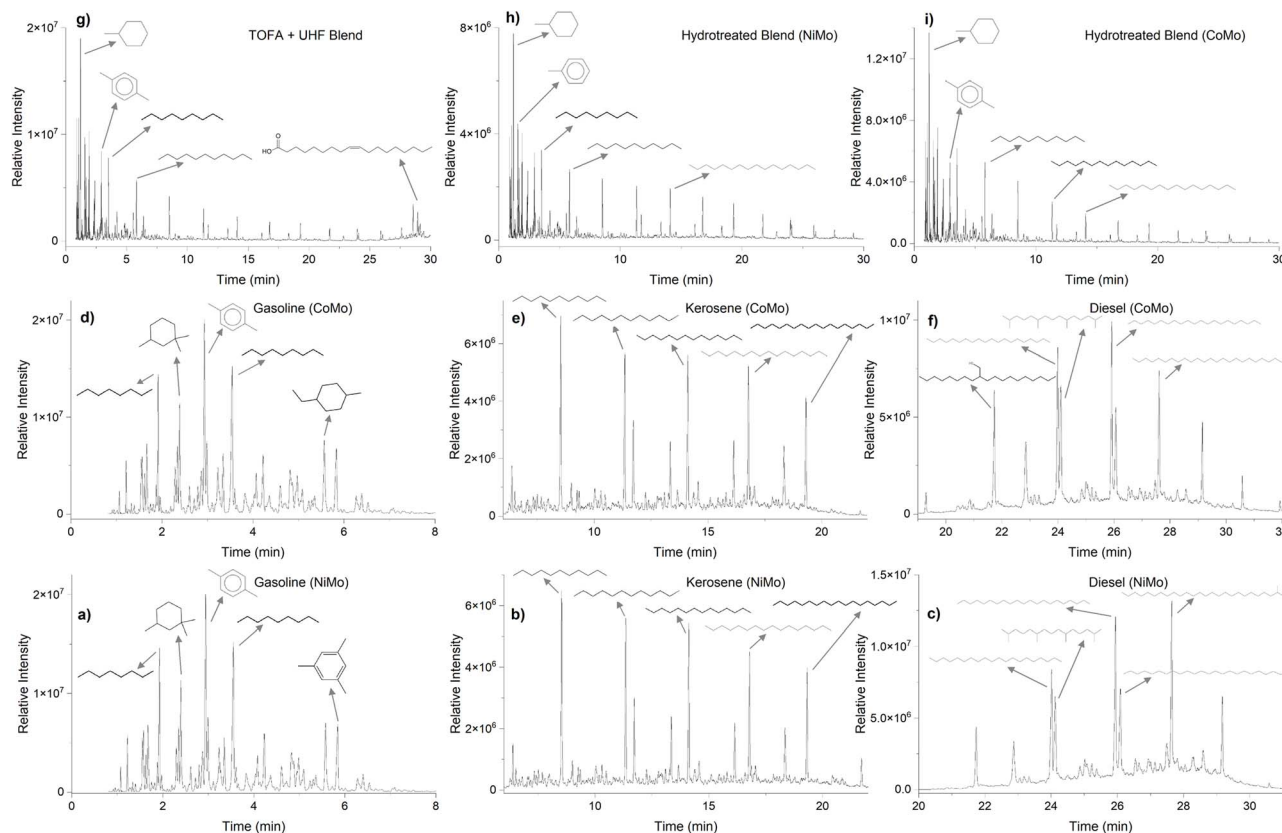


Fig. 4 GC/MS results of the initial TOFA–UHF blend (g), hydrotreated products (h and i), and distilled fuel-range products from NiMo (a–c) and CoMo (d–f), with significant compounds labelled.

### 3.3. Assessing the physiochemical properties of final fuel distillates

**3.3.1 Notable fuel specifications.** Comparing the hydro-treated TOFA–UHF blend distillates to ASTM and EN standards in Table 3, it is apparent that some base properties (including HHV, TAN, density, viscosity, CHNO, *etc.*) are not reported in many ASTM and EN fuel guidelines as these properties are of minimal concern in conventional crude oil refinement.<sup>33–39</sup> The HHV of all fuel samples was desirably high and consistent with expectations for fuel products from previous literature ( $>40$  MJ  $\text{kg}^{-1}$ ), suggesting a lack of contaminating heteroatom bonds that produce much less energy than hydrocarbons.<sup>4</sup> The HHV of the hydrotreated blend fuel distillates were also desirably similar to that of the hydrotreated UHF fuel distillates, with kerosene and diesel fractions within  $0.7$  MJ  $\text{kg}^{-1}$ , while gasoline fractions derived from the blend exceeded those of UHF counterparts. Density, viscosity, carbon, and hydrogen also did not vary significantly between fuel distillates from the TOFA–UHF blend and their UHF counterparts, indicating that the addition of TOFA to the hydrotreatment process does not notably impact these fuel properties. Oxygen content was not detected in UHF or its hydrotreated fuel distillates, indicating that the small oxygen content in the fuel distillates from hydrotreating the blend is derived solely from TOFA. Oxygen content and the TAN (as a result of the oxygenated compounds) were the most

notably differing properties between fuel distillates derived from hydrotreating UHF and the TOFA–UHF blend.

Although acidity was relatively high after hydrotreatment for the intermediate products shown in Table 2 ( $10.8$ – $12.4$  mgKOH  $\text{g}^{-1}$ ), this acidity was not reflected in the final fuel distillate fractions of gasoline, kerosene and diesel. Most of the acidic components were separated from the lighter oil fuel fractions *via* the residue of the final distillates. Nonetheless, the reduction of TAN to  $0.9$ – $6.5$  mg KOH per g in the fuel fractions remains elevated compared to UHF and other refinery intermediates before and after hydrotreatment ( $<1.1$  mg KOH per g). This acidity from TOFA–UHF co-processing would need to be managed in a refinery setting as described in Section 3.1. Furthermore, the TAN values are acceptable for gasoline and kerosene fuel fractions as products; however, the more acidic diesel fractions ( $4.9$  &  $6.5$  mg KOH per g) exceed specifications for use in diesel engines. This higher acidity can be neutralized through additives or remedied through further purification processing to remove acidic heteroatoms (primarily oxygen) and metal content (such as molecular sieves or, in some cases, further hydrotreatment).<sup>29,40</sup>

Among ASTM and EN limits, gasoline and diesel are particularly high in sulphur and would potentially benefit from reducing catalyst sulphiding during hydrotreatment. Interestingly, the sulphur content between hydrotreated UHF fuel fractions and hydrotreated blend fractions is comparable,





Table 3 Properties of fuel product-range fractions from TOFA–UHF hydrotreatment, arranged by catalyst treatment and ASTM specifications

| Properties                               | Gasoline                |                      | Kerosene                    |                             |                             |                             |                         |                      |                             |                             | Jet fuel                    |                             | Diesel                  |                        |                     |                             |                             |                             |                             |
|------------------------------------------|-------------------------|----------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-------------------------|----------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-------------------------|------------------------|---------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
|                                          | ASTM D8275<br>(ref. 31) | EN 228<br>(ref. 36)  | NiMo                        |                             | CoMo                        |                             | ASTM D3699<br>(ref. 30) | BS 2869<br>(ref. 34) | NiMo                        |                             | CoMo                        |                             | ASTM D6615<br>(ref. 33) | ASTM D975<br>(ref. 32) | EN 590<br>(ref. 35) | NiMo                        |                             | CoMo                        |                             |
|                                          |                         |                      | UHF                         | Blend                       | UHF                         | Blend                       |                         |                      | UHF                         | Blend                       | UHF                         | Blend                       |                         |                        |                     | UHF                         | Blend                       | UHF                         | Blend                       |
| HHV (MJ kg <sup>-1</sup> )               | —                       | —                    | 46.1                        | 47.9                        | 44.5                        | 45.5                        | —                       | >42.8                | 46.3                        | 46.0                        | 46.3                        | 45.9                        | >42.8                   | —                      | ~45.4               | 46.2                        | 45.5                        | 46.1                        | 45.4                        |
| TAN (mgKOH g <sup>-1</sup> )             | —                       | —                    | 1.0                         | 1.7                         | 1.1                         | 1.7                         | —                       | —                    | 0.7                         | 1.0                         | 0.7                         | 0.9                         | <0.1                    | <0.1                   | ~0                  | 0.8                         | 4.9                         | 0.6                         | 6.5                         |
| Density<br>(kg m <sup>-3</sup> @20 °C)   | 720–750                 | 720–775 <sup>a</sup> | 749                         | 709                         | 757                         | 702                         | —                       | 775–840 <sup>a</sup> | 761                         | 737                         | 763                         | 733                         | 751–802                 | —                      | <820 <sup>a</sup>   | 785                         | 773                         | 793                         | 772                         |
| Kinematic<br>viscosity<br>(cSt@40 °C)    | —                       | —                    | 0.7                         | 0.8                         | 0.6                         | 0.8                         | 0.9–1.9                 | 1.0–2.0              | 1.3                         | 1.7                         | 1.4                         | 1.5                         | <12                     | 1.7–4.1                | 2.0–4.5             | 4.7                         | 5.0                         | 5.0                         | 5.5                         |
| C (wt%)                                  | —                       | —                    | 85.4                        | 85.4                        | 85.2                        | 84.9                        | —                       | —                    | 85.7                        | 84.7                        | 85.6                        | 83.3                        | —                       | —                      | ~87                 | 85.8                        | 85.6                        | 85.8                        | 85.6                        |
| H (wt%)                                  | —                       | —                    | 14.4                        | 14.5                        | 14.5                        | 14.0                        | —                       | —                    | 14.2                        | 14.0                        | 14.3                        | 13.6                        | —                       | —                      | ~12.75              | 13.9                        | 13.9                        | 13.8                        | 13.6                        |
| N (wt%)                                  | —                       | —                    | 0.0                         | 0.0                         | 0.0                         | 0.1                         | —                       | —                    | 0.1                         | 0.1                         | 0.1                         | 0.1                         | —                       | —                      | <0.05               | 0.0                         | 0.0                         | 0.1                         | 0.1                         |
| S (wt%)                                  | <0.001                  | <0.001               | 0.1                         | 0.1                         | 0.2                         | 0.2                         | <0.3                    | <0.1                 | 0.1                         | 0.1                         | 0.0                         | 0.1                         | <0.3                    | <0.0015–0.5            | <0.002              | 0.3                         | 0.3                         | 0.3                         | 0.4                         |
| O (wt%)                                  | —                       | <2.7                 | 0.0                         | 0.0                         | 0.0                         | 0.8                         | —                       | —                    | 0.0                         | 1.1                         | 0.0                         | 2.9                         | —                       | —                      | —                   | 0.0                         | 0.2                         | 0.0                         | 0.3                         |
| Lead, Pb (mg L <sup>-1</sup> )           | <13                     | <5                   | 0.6                         | 0.6                         | 0.7                         | 0.5                         | —                       | —                    | 0.4                         | 0.6                         | 0.3                         | 0.1                         | —                       | —                      | —                   | 0.9                         | 0.9                         | 0.3                         | 0.0                         |
| Manganese,<br>Mn (mg L <sup>-1</sup> )   | <0.25                   | —                    | 0.0                         | 0.0                         | 0.0                         | 0.0                         | —                       | —                    | 0.0                         | 0.0                         | 0.0                         | 0.0                         | —                       | —                      | —                   | 0.0                         | 0.0                         | 0.0                         | 0.0                         |
| Distillation °C<br>(final boiling point) | 360                     | 210                  | 176                         | 184                         | 194                         | 199                         | 300                     | 300                  | 269                         | 288                         | 274                         | 275                         | —                       | —                      | —                   | 375                         | 373                         | 383                         | 380                         |
| Distillation °C<br>(90 vol%)             | —                       | —                    | <sup>b</sup> <sub>163</sub> | <sup>b</sup> <sub>169</sub> | <sup>b</sup> <sub>164</sub> | <sup>b</sup> <sub>170</sub> | —                       | 210                  | <sup>b</sup> <sub>252</sub> | <sup>b</sup> <sub>272</sub> | <sup>b</sup> <sub>262</sub> | <sup>b</sup> <sub>264</sub> | 245                     | 282–338                | 350 (85 vol%)       | <sup>b</sup> <sub>351</sub> | <sup>b</sup> <sub>331</sub> | <sup>b</sup> <sub>355</sub> | <sup>b</sup> <sub>344</sub> |

<sup>a</sup> Density measurement @15 °C. <sup>b</sup> Distillation °C @90 wt%.



within 0.1 wt% or less across each sample, indicating that desulphurization was not significantly inhibited by the addition of TOFA. The maximum sulphur content varies among ASTM diesel grades. The diesel fractions produced in this study, containing 0.3–0.4 wt% (3000–4000 ppm) sulphur, are only suitable for grades no. 1-D S5000 (special-purpose) & 2-D S5000 (general-purpose).<sup>35</sup> These special- and general-purpose grades are primarily used for off-road, rail, industrial, and marine applications often due to a combination of less accessibility, lower regulation, or older engines that rely on higher sulphur content for lubrication.<sup>41</sup> Grade nos. 1-D S15, 2-D S15, 1-D S500, and 2-D S500 have more stringent sulphur limits between 0.0015 wt% (15 ppm) and 0.05 wt% (500 ppm) to meet emission controls and are therefore not compatible with the diesel fractions produced in this study, unless further refining is conducted. Both NiMo & CoMo kerosene fuel fractions were within kerosene's British standard sulphur limit of 0.1 wt% (1000 ppm). Gasoline has a stricter standard for sulphur, driven in recent decades by environmental emission regulations, with both ASTM & EN standards specifying 10 ppm or less (<0.001 wt%). A significant reduction in sulphur is therefore needed for gasoline products with recycling, reprocessing, and adjustment of process parameters being common techniques for mitigating high sulphur content in refinery settings; likewise, viscosity and density can be modified using additives.<sup>42,43</sup> As kerosene is not used for transport but rather for domestic heating, its standard is less restrictive, particularly with sulphur and oxygen limits, while concerns over transport-related SO<sub>x</sub> emissions have long driven low gasoline and diesel limits.<sup>34,35</sup>

The density and viscosity of various gasoline, kerosene, and diesel standards are within or near their specification ranges.

Specifically, the gasoline products are only 1.5% and 2.5% below the lower density threshold of ASTM and EN standards (720 kg m<sup>-3</sup>). In comparison, the kerosene fractions met viscosity requirements but had lower densities—4.9% and 5.4% below the British standard threshold (775 kg m<sup>-3</sup>) for the NiMo and CoMo products, respectively. It should also be noted that the kerosene density difference is partially explained by the British standard density specification reported at 15 °C, whereas this study conducted density measurements at 20 °C to align with ASTM fuel standards.<sup>34,35</sup> Density was within acceptable limits for the diesel products, but viscosity exceeded the EN standards by 11.1% and 22.2% for NiMo and CoMo diesel fuel products, respectively. Ultimately, the differences in density and viscosity from standards were relatively small. To address this, property adjustments are a familiar practice in the petroleum refining industry through implementation of different distillation fractionation temperatures, different hydrotreatment conditions, product reprocessing, and blending with other refinery streams or additives.<sup>42,43</sup> This flexibility in troubleshooting and adjusting stream properties to meet specifications has become more common and straightforward with the continuous monitoring of product properties in modern refineries.<sup>44</sup>

With jet fuel typically derived from kerosene-range hydrocarbons, all requirements were met except for acidity, stemming from minor heteroatom content. Nonetheless, kerosene

hydrocarbons typically undergo further processing like isomerization for improved cold-flow properties. The oxygen content of the fuel products was elevated in kerosene cuts, indicating that some oxygenated compounds (1.1–2.9 wt%) are prevalent in the intermediate boiling point range of kerosene (172–275 °C), while the less-volatile diesel fraction has minimal oxygen (<0.3 wt%) as did the more-volatile gasoline fraction (<0.9 wt%). Due to the combustive nature of gasoline-powered engines, the oxygen content in gasoline products is of minimal concern aside from potential acidity, as oxygenates like ethanol are added to improve combustion efficiency as well as emission control of harmful products like carbon monoxide.<sup>45</sup> Metal contents of lead and manganese are outlined in the gasoline ASTM standard, known for pollution and health concerns; however, no metals are of concern in the kerosene and diesel standards.<sup>34</sup> Even so, all NiMo and CoMo fuel products in this work had minimal metal content, well below the allowable limit of the fuel standard (<5 mg L<sup>-1</sup>) at 0.9 mg L<sup>-1</sup> or less. The metal content of hydrotreated UHF fuel distillates was notably similar to that of the hydrotreated blend fuel distillates, with lead content within 0.3 mg L<sup>-1</sup> and no detectable manganese. This similarity of low metal content across samples, regardless of TOFA content, suggests that there are no metal contamination concerns when implementing TOFA for co-processing.

Despite the lack of studies or patents to directly compare the promising properties of the hydrotreated TOFA–UHF blend distillate, there is limited tall oil co-processing research that this research draws parallels to or exceeds. Löfstedt *et al.*<sup>46</sup> successfully co-hydrotreated up to 70 wt% Scandinavian TOFA/kraft lignin with refinery light gas oil over a sulphided NiMo catalyst, only reporting distillation, density, and composition specifications of EN590 (road diesel) fulfilled by the produced hydrocarbons. Mikulec *et al.*<sup>47</sup> catalytically co-hydrotreated 20–30 wt% depitched CTO with different Ni catalysts, reporting hydrocarbons that complied with EN diesel standards except for high sulphur content due to resistant sulphur compounds, like the diesel products reported in this study. Lastly, Janosik *et al.*<sup>48</sup> used TOFA as a 17 wt% blending agent for the co-hydrotreatment of pyrolysis bio-oil with light gas oil over a sulphided NiMo catalyst, reporting successful desulphurization but inability in denitrification, lacking comparison and compliance with fuel standards. These experimental studies also differed from the current study's batch reactor setup, utilizing continuous fixed-bed reactors that more closely align with large-scale hydrotreaters extensively used in the petroleum refining industry.<sup>49</sup> As batch reactors provide more flexibility and ease of analysis, this method was well-suited for the small-scale hydrotreatment development in this study. Due to differences in scale and setup, continuous reactors tend to experience higher mass-transfer limitations, leading to lower catalytic activity and reduced product quality in direct comparison to batch setups (H/C ratio, heteroatom content, and viscosity).<sup>50</sup> Yin *et al.*<sup>50</sup> compared batch and continuous hydrotreatment, confirming the industrial relevance of fixed-bed reactors, while describing their mass-transfer limitations that differ from batch reactors and can lead to lower catalytic activity. Building on the promising results of this batch study, future work will consider



continuous fixed-bed reactor studies, with parameter optimization and durability testing for the catalysts.

Overall, there are mostly minimal deviations in the fuel distillates produced in this study from North American and European standards, showing promise in sustainable fuel development. With property concerns such as sulphur content in the produced products, further optimization and development of the hydrotreatment process is suggested. Techniques such as employing hydrotreatment additives, adjusting process parameters, and developing novel catalysts are future research directions.<sup>6</sup> In particular, one innovative method developed by the authors' research group involves utilizing functionalized polymers to remove undesired heteroatoms (such as high sulphur content) from fuel samples under ambient conditions.<sup>51</sup> This method applies to the improvement of these sulphur-challenged fuel samples in future research.

**3.3.2 Comparative magnified imaging with commercial fuels.** Under magnification in Fig. 5, hydrotreated samples exhibited a visual appearance strikingly similar to commercial fuels (g–i), observing minimal contaminants, complete homogeneity, and indicating effective upgradation of TOFA–UHF, regardless of NiMo (d–f) or CoMo (a–c). The lack of any major contaminants across the samples is desirable as it reduces incomplete combustion and particulate buildup that can increase maintenance and reduce efficiency in combustion engines.<sup>52</sup> Many visible contaminants were faint in appearance indicating the likely formation of similar components that have a higher affinity for each other than with the rest of the fuel mixture; however, the commercial kerosene sample notably had a few dark contaminants that may be of more concern as they could contribute to unwanted soot formation and incomplete combustion emissions like CO when burned.<sup>52</sup> In this case, the NiMo (e) and CoMo (b) kerosene fractions shown in Fig. 5 had fewer contaminants and were notably more homogeneous than

their commercial equivalent (h). However, these particulates may have resulted from less-stringent storage and handling of the commercial kerosene, rather than from formation during production, as the commercial kerosene was marketed for personal heating/cooking instead of highly regulated transport. Observing Table 3 and Fig. 5, minor deviations in some properties/appearance suggest that further optimization of hydrotreatment and sulphiding may be required to fully align with fuel benchmarks, outside of kerosene.

**3.3.3 Comparative SimDis with commercial fuels.** Simulated distillation (SimDis) was conducted on the distilled fuel products and directly compared to commercial gasoline, kerosene, and diesel, as illustrated in Fig. 6. The NiMo and CoMo UHF as well as blend products were relatively similar, showing comparable effects of the catalysts on boiling point distribution of the products. The kerosene fractions (b) were nearly identical between CoMo and NiMo blend products, while both gasoline (c) and diesel (a) fractions exhibited the presence of less volatile components under CoMo compared to NiMo. Indicated by an elevated tail-end of the CoMo boiling point distributions, the presence of less volatile and therefore higher carbon number products is consistent with the findings from GC–MS in Section 3.2.2., highlighting NiMo's influence on the formation of lower carbon number products over CoMo. These results are consistent with studies such as Priharto *et al.*<sup>53</sup> and Horáček *et al.*<sup>54</sup> that compare the hydrotreatment of biological oils with sulphided NiMo and CoMo catalysts, noting NiMo's higher deoxygenation activity while CoMo has higher selectivity for lower volatility.

NiMo and CoMo gasoline fractions were nearly indistinguishable from the commercial gasoline product as shown in Fig. 6c, with the commercial gasoline having slightly lower volatility. Kerosene fractions (b; boiling point range: 150–275 °C) showed the highest deviation from their commercial fuel counterparts among tested fuels, owing to the higher volatile

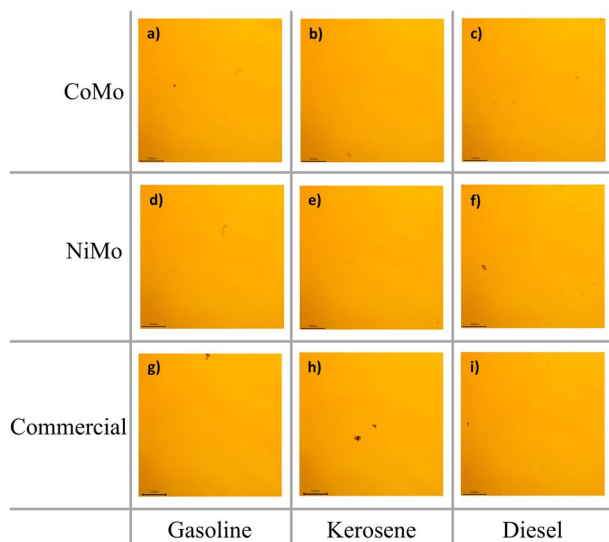


Fig. 5 10× Magnification of fuel-range fractions from the distillates of hydrotreated TOFA–UHF blends with CoMo (a–c) & NiMo (d–f) catalysts compared to commercial fuels (g–i).

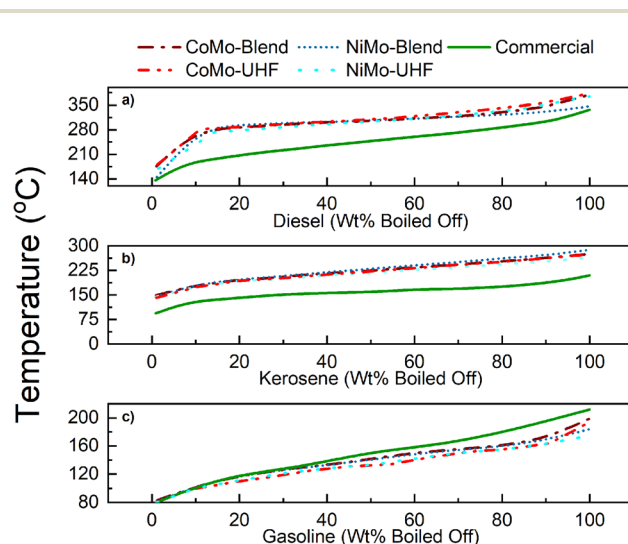


Fig. 6 Boiling point distribution of diesel (a), kerosene (b), and gasoline (c) fuel products compared to commercially available equivalents via SimDis.



nature of the kerosene (boiling point range: 90–210 °C). Given that store-bought kerosene is less regulated than commercial gasoline and diesel while also being marketed for heating and cooking applications in outdoor Canadian winter conditions, its preference for higher volatility and hence lower hydrocarbon freezing temperatures is consistent. Both NiMo and CoMo fractions exhibit some deviation from commercial diesel during the initial boil-off as the commercial fraction has higher volatility; however, as the temperature rises, all diesel range products (a) settle at a similar final boiling point of ~350 °C. The convergence of the diesel products to a similar end boiling point is desirable, as the diesel standard in Table 3 (ASTM D6615) emphasizes that 90 vol% should distill between 282 and 338 °C to ensure uniform handling and combustion performance.<sup>35</sup> One rationale for the moderate deviations between the commercial products and those from this study is that conventional refineries typically vary product boiling points under several conditions to meet the changing output demands of the complex refining process.<sup>43</sup> Due to the diligent distillation of the final fuel products in this work, the final fuel distillates from CoMo and NiMo catalysts exhibit volatility distributions largely within the intended ranges (gasoline: >172 °C, kerosene: 172–275 °C, diesel: 275–355 °C). Given the commercial variability of fossil fuels' boiling point distribution, the SimDis profiles of CoMo and NiMo distillates confirm that they are reasonably volatile for their applications in comparison to the commercially available liquid fuel products.

Further analysis of the SimDis boiling point curves in Fig. 6a–c, it is apparent that the fuel distillates derived solely from UHF hydrotreatment are similar to their hydrotreated blend fuel distillate counterparts, following the same previously discussed trends of volatility. The lack of deviation in the boiling point distribution between hydrotreatment fuel distillates from UHF and the TOFA–UHF blend suggests that the addition of TOFA does not significantly impact boiling point distribution. The minimal change in SimDis results is beneficial, as it indicates that co-processing does not significantly disrupt expected boiling points, avoiding potential costly adjustments in refinery operations.<sup>43</sup> These boiling point

distribution results are further supported by the distillation characteristics provided in Table 3, where the 90 wt% and final boiling points differ by less than 20 °C between hydrotreated UHF and hydrotreated blends.

**3.3.4 Carbon number distribution of distillate products and commercial fuels.** Analysis of the carbon number distribution of the final distillate products showed results (Table 4) that were consistent with the SimDis analysis in Section 3.3.2. Comparing the fuel distillates from hydrotreating with CoMo and NiMo catalysts, the similarity in carbon number distribution across all fuel cuts confirms comparable catalytic activity between these commercial catalysts. Gasoline fractions from the blend differed by <0.2 wt% across each carbon # range, with a distribution from <C<sub>6</sub> to C<sub>10</sub> that aligns with the typical range of gasoline (C<sub>5–12</sub>) and commercial gasoline.<sup>55</sup> Kerosene fractions from the blend differed by a maximum of only 3.4 wt% between carbon # ranges with both distillates spanning C<sub>9</sub> to C<sub>16</sub>, matching the predominant commercial range of petroleum refineries.<sup>56</sup> Comparing diesel fractions from the blend hydrotreated with NiMo and CoMo catalysts, the largest difference in carbon # ranges among the three distillates was observed, although still relatively small at <5.8 wt%. The diesel ranges did show a slight difference in distribution, with NiMo-catalyzed hydrotreatment distillates having a smaller carbon range of C<sub>15</sub> to C<sub>20</sub>, while CoMo-catalyzed had a small portion of C<sub>13–14</sub> (3.7 wt%) with a wider range from C<sub>13</sub> to C<sub>20</sub>. This difference in the carbon distribution range of diesel samples could simply arise from the inevitable small difference in the distillation runs. Ultimately, the similar effectiveness observed between these commercial catalysts in carbon number distribution when deoxygenating biological oils is consistent with previous findings by Borugadda *et al.*,<sup>17</sup> who reported comparable catalytic impact when hydrotreating biocrude–refinery distillate blends.

The carbon number distribution of fuel cuts from the hydrotreated TOFA–UHF blend did have some differences from the hydrotreated UHF fuel fractions. Most fuel fractions derived from the hydrotreatment of UHF had a preference for lighter carbon numbers. The gasoline fuel fractions for both NiMo and

**Table 4** Carbon number distribution of produced fuel distillates using NiMo (A) & CoMo catalysts (B) in comparison to commercial samples (Com)

| Carbon # ranges    | Weight (%) |      |       |      |      |          |      |       |      |      |        |      |       |      |      |
|--------------------|------------|------|-------|------|------|----------|------|-------|------|------|--------|------|-------|------|------|
|                    | Gasoline   |      |       |      |      | Kerosene |      |       |      |      | Diesel |      |       |      |      |
|                    | UHF        |      | Blend |      |      | UHF      |      | Blend |      |      | UHF    |      | Blend |      |      |
|                    | Com        | NiMo | CoMo  | NiMo | CoMo | Com      | NiMo | CoMo  | NiMo | CoMo | Com    | NiMo | CoMo  | NiMo | CoMo |
| <C <sub>6</sub>    | 72.3       | 13.0 | 14.6  | 8.4  | 8.2  | 1.2      | —    | —     | —    | —    | —      | —    | —     | —    | —    |
| C <sub>7–8</sub>   | 13.2       | 69.4 | 69.6  | 67.8 | 67.9 | 37.3     | 2.5  | 3.5   | 1.0  | 0.5  | —      | —    | —     | —    | —    |
| C <sub>9–10</sub>  | 8.9        | 14.1 | 12.9  | 19.2 | 19.2 | 57.9     | 30.9 | 28.8  | 28.3 | 30.2 | 35.1   | —    | —     | —    | —    |
| C <sub>11–12</sub> | 1.0        | —    | —     | —    | —    | 0.7      | 42.1 | 38.8  | 35.8 | 38.4 | 30.7   | —    | —     | —    | —    |
| C <sub>13–14</sub> | —          | —    | —     | —    | —    | —        | 20.3 | 23.7  | 25.6 | 25.1 | 14.6   | 18.3 | 5.0   | —    | 3.7  |
| C <sub>15–16</sub> | —          | —    | —     | —    | —    | —        | —    | 0.6   | 2.8  | 0.5  | 7.4    | 40.0 | 42.9  | 48.6 | 52.0 |
| C <sub>17–18</sub> | —          | —    | —     | —    | —    | —        | —    | —     | —    | —    | 1.9    | 26.6 | 32.4  | 36.7 | 30.9 |
| C <sub>19–20</sub> | —          | —    | —     | —    | —    | —        | —    | —     | —    | —    | —      | 5.4  | 10.7  | 4.4  | 4.4  |



CoMo hydrotreated UHF had low molecular weight hydrocarbons ( $<C_6$ ) of 13.0 & 14.6 wt%, nearly double the amount in the NiMo and CoMo hydrotreated blends, at 8.4 and 8.2 wt%, respectively. Similarly, the kerosene and diesel fractions from the hydrotreatment of UHF had larger amounts of lower carbon number constituents ( $C_{7-8}$  for kerosene &  $C_{13-14}$  for diesel) compared to the hydrotreated blends. The prevalence of lower carbon numbers in the UHF hydrotreated fuel fractions, regardless of the catalyst, may indicate more extensive hydrocracking compared to the hydrotreatment of the TOFA-UHF blend, due to the lack of competing hydrodeoxygenation reactions without TOFA's presence. Aside from the lighter carbon numbers, one of the largest differences between hydrotreated UHF and hydrotreated blend carbon distributions is the significant increase in the  $C_{15-16}$  blend fractions for both NiMo and CoMo, at 8.6 wt% and 9.1 wt%. This increase in the  $C_{15-16}$  content (and  $C_{17-18}$  for the NiMo hydrotreated blend) likely results from the intended hydrodeoxygenation of TOFA into desirable kerosene- and diesel-range hydrocarbons, supporting the successful co-processing of UHF and TOFA demonstrated in this study.

The comparison of carbon distribution between the fuel distillates (blend as well as UHF) and commercial samples confirms a similar trend to the SimDis findings discussed in Section 3.3.2. All commercially purchased fuels exhibit carbon distribution favouring lower carbon numbers and therefore higher volatility, compared to the produced distillates of this study. Due to the harsh winter temperatures of Saskatoon, Canada, where these fuels were purchased, it is consistent that the commercial fuels are on the lighter end of carbon distributions, resulting in lower freezing points. Commercial gasoline's largest fraction was in the smallest hydrocarbon range  $<C_6$  at 72.3 wt%, while NiMo and CoMo were both slightly less volatile with the majority of their carbon distribution in the  $C_{7-8}$  range at 67.8 & 67.9 wt%, respectively. Both NiMo and CoMo-hydrotreated kerosene distillates of this study had their largest fraction in  $C_{11-12}$  at 35.8 & 38.4 wt%, respectively, while more volatile commercial kerosene had its largest fraction of 57.9 wt% at  $C_{9-10}$ . Commercial diesel's primary fraction ( $C_{9-10}$ : 35.1 wt%) was multiple carbon fractions lower than the NiMo and CoMo-catalyzed diesel fractions at  $C_{15-16}$  with 48.6 wt% and 52.0 wt%, respectively. The commercial sample and distillates of this study are both valid, as diesel typically spans a wide range at  $C_{10-20}$ , with differences in carbon distribution depending on the demands of the refinery and regional specifications needed for the fuel.<sup>55</sup> The commercial fraction being on the lighter-end of the carbon distribution aligns with the need for lower freezing point fuels in Northern USA as well as Canada, especially for the least-volatile diesel fuel fraction, while the diesel distillates produced in this work are more suitable for warmer climates.<sup>35</sup>

### 3.4. Relevant commercial applications

**3.4.1 Commercial TOFA applications.** Tall oil fatty acids (TOFA), derived from crude tall oil (CTO), are globally produced and serve as precursors to a wide array of value-added chemicals

used in coatings, resins, polymers, lubricants, cosmetics, and adhesives, owing to their long carbon chains and reactive carboxylic acid groups.<sup>4,57-61</sup> Despite this versatility, TOFA accounts for only about 5% of the global fatty acid market demand.<sup>62</sup> Crude tall oil, containing TOFA, also has many applications in simpler, lower-value uses such as fuel for lime kilns or additives in soaps, rubbers, insecticides, and foams.<sup>63-67</sup> However, the growing interest in converting TOFA into sustainable fuels offers a significant opportunity to increase its commercial value, particularly for the pulp and paper industry.<sup>4</sup> The relevance of upgrading tall oil components to sustainable fuels has become lucrative commercially over the past decade with several companies such as UPM Kymmene Oy (Finland), SunPine AB (Sweden), and UOP LLC (USA) all filing for relevant patents on deoxygenating production methods from CTO feeds.<sup>68-71</sup> However, it should be noted that these companies have mostly focused on the approach of stand-alone processing of tall oil, differing from the integrated blending and co-upgradation of TOFA investigated in this research work.

**3.4.2 Commercial application of fuel-range hydrocarbons derived from distilled TOFA & UHF blends.** The distillation of hydrotreated blends from TOFA and UHF yields fuel-range hydrocarbons with promising commercial applications, largely determined by their elemental composition and physical properties. The resulting gasoline, kerosene, and diesel fractions produced using NiMo and CoMo catalysts exhibit high heating values and carbon content, making them suitable candidates for lower-carbon-intensity energy applications. The kerosene fraction shows potential for further processing into jet fuel applications, with GC-MS analysis indicating a predominance of lighter hydrocarbons, enhancing fuel desirability.<sup>4,72</sup> While limitations such as elevated oxygen and acidity in gasoline as well as high sulphur and viscosity in diesel may constrain direct use in some transportation applications, these partially biogenic hydrocarbons can serve in power generation, heating, and as feedstocks for chemicals, lubricants, and polymers beyond transportation.<sup>73</sup> Adoption of such bio-derived fuels is growing globally, with countries like the USA, Canada, and Brazil pioneering industrial use.<sup>74-76</sup> Overall, the commercial applications of biogenic-derived fuels are related to the general distinctions of transportation fuels, non-transportation energy, and chemical/material production.

**3.4.3 Commercial applications of distillation residues pre- and post-hydrotreatment of TOFA blends.** The distillation residues from both pre- and post-hydrotreatment of TOFA-UHF blends were found to be dense, highly viscous, and solid at room temperature, exhibiting high heating values (NiMo: 44.2 MJ kg<sup>-1</sup>; CoMo: 44.6 MJ kg<sup>-1</sup>) and elevated acidity (NiMo: 40.9 mgKOH g<sup>-1</sup> & CoMo: 44.9 mgKOH g<sup>-1</sup>). These properties suggest potential for use in industrial applications such as asphalt modification, where heavy carbon-rich compounds can be blended with synthetic rubbers to replace or enhance conventional asphalt.<sup>77</sup> While additives like tall oil and vacuum gas oil are currently used sporadically in U.S. asphalt production, the consistency and sustainability of TOFA-derived residues present an opportunity to develop more reliable bio-based alternatives for the pavement industry.<sup>78</sup>





Comparable to bitumen, these distillation residues show promise in a range of applications, including adhesives, sealants, coatings, soaps, waxes, and even energy-dense binders for solid biofuels.<sup>79–82</sup> The CoMo and NiMo hydrotreatment of the TOFA-UHF blend produced significant amounts of residue (12.6 wt% and 16.0 wt%, respectively), highlighting their commercial relevance. Furthermore, the adhesive properties and chemical similarity of unblended tall oil distillation residues to petroleum-derived residues make them suitable for use as environmentally degradable adhesives, demonstrated in studies using terpene-based polymers.<sup>83,84</sup> Overall, the valorisation of TOFA-UHF residues could provide a sustainable pathway to displace fossil-derived materials in construction, manufacturing, and energy sectors.

## 4. Conclusions

In conclusion, this study presents a novel approach for producing lower-carbon intensity TOFA-derived transportation fuels through CTO distillation, blending TOFA with UHF collected from conventional refineries, and catalytic co-hydrotreatment and vacuum distillation of the blend. The promising miscibility of TOFA with refinery streams, particularly with UHF, underscores its potential for integration into existing oil refinery infrastructure. Both NiMo and CoMo catalysts effectively upgraded the TOFA-UHF blends, yielding gasoline, kerosene and diesel fractions with high heating values (HHV) ranging from 45.4 to 47.9 MJ kg<sup>−1</sup>. The hydrotreated samples of TOFA and UHF blend also showed a significant drop in oxygen concentration and a noticeable rise in carbon concentration. The final distilled products derived from the hydrotreated samples also show promising outcomes in terms of deoxygenation, viscosity reduction, density improvement, and total acid number (TAN) decline. The diesel fractions of both samples showed desirable HC compound readings and density correction. The oxygen content improved significantly, reducing from 12.2 wt% in CTO to 0.2 wt% in the final NiMo diesel fraction, indicating effective hydrodeoxygenation. However, the presence of sulphur in gasoline and diesel fractions remains a concern due to stringent transportation regulations, necessitating further refinement considerations. Additional reprocessing and process optimization are established methods in the petroleum refining industry for adjusting fuel product properties (such as TAN, viscosity, and density) that deviated from fuel specifications, as observed for select fuels in this study.

The high content of unsaturated fatty acids in TOFA complicates fuel production, requiring efficient catalysts to break down complex compounds. Process intensification such as multi-stage upgradation or functionalized polymer treatment of the TOFA and UHF blends is a helpful novel consideration for meeting the fuel standards. Future work should focus on continuous fixed-bed hydrotreatment, catalyst reusability, durability, and sustainability assessments, including techno-economic and life cycle analyses. Unlike competing renewable fuel strategies, such as stand-alone biofuel production, this successful co-refining approach leverages existing

infrastructure to accelerate the transition to sustainable fuel production. Developing methods to reuse agricultural residues in a similar way to TOFA in this study can help replace fossil fuels and achieve net-zero goals, leading to a more sustainable and protected environment.

## Data availability

The data supporting this article have been included as part of the ESI.†

## Author contributions

John Churchill: conceptualization, data curation, formal analysis, investigation, methodology, validation, visualization, writing – original draft, writing – review & editing. Gourav Rath: conceptualization, formal analysis, investigation, methodology, validation, writing – original draft, writing – review & editing. Venu Borugadda: conceptualization, methodology, writing – review & editing, supervision. Ajay Dalai: conceptualization, funding acquisition, project administration, writing – review & editing, supervision.

## Conflicts of interest

The authors declare that no conflicts, personal or financial, appear to influence this work.

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