

A step change towards sustainable aviation fuel from sewage sludge

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ARTICLE INFO

Keywords:

Biofuels

Waste

TCR

Hydrodeoxygenation

Hydrocracking

Jet Fuel

ABSTRACT

Sewage sludge, an abundant and problematic organic waste, was successfully converted into sustainable jet fuel range hydrocarbons (C₈-C₁₆). Sewage sludge was pre-conditioned and processed through a Thermo-Catalytic Reforming (TCR) system (2 Kg/h) at 450 °C pyrolysis and 700 °C post-reforming temperature to produce a biocrude oil. The bio-crude oil was subsequently conditioned and upgraded via consecutive two-step hydro-processing, comprising hydrodeoxygenation and hydrocracking as two separate unit operations. The two-step hydroprocessing was carried out in a bench-scale batch high-pressure reactor (autoclave). The process parameters such as temperature, feed volume, catalyst loading, and batch time were held constant, whilst the H₂ pressure was varied. The effect of H₂ pressure across 30 – 60 bar on the quality of the hydroprocessed oil was evaluated in terms of elemental composition, chemical compound distribution, and fuel properties. Hydro-processing at 60 bar H₂ resulted in better fuel properties compared to hydroprocessing at 30 bar H₂. Hence, approximately 25% by weight jet fuel fraction, including normal, cyclo and iso-paraffins and aromatics in the C₈-C₁₆ range, was recovered via atmospheric distillation of the hydroprocessed oil at 60 bar H₂. Sewage sludge derived jet fuel range fraction met the majority of the jet fuel specifications for calorific value, viscosity, density, and freeze point under the ASTM D7566 standard. Some parameters such as smoke, flash point and total acid number slightly fell out of specifications. The process also produced green naphtha and diesel as by-products. In addition, the process was further tested for catalyst reusability and regeneration potential that showed promising results for future research.

1. Introduction

In recent times, climate change has immensely accelerated due to increased greenhouse gas emissions, and CO₂ is a major greenhouse gas contributor. Two main contributors to CO₂ emissions are power generation and transportation. The two sectors combined accounts for 64% of total CO₂ emissions worldwide [1]. CO₂ emissions from the transport sector have been estimated to increase by 80% by 2030 [2]. This will only become more prevalent as other sectors begin to decarbonise. The transport sector uses fossil-petroleum derived liquid fuels, which are the primary source of energy to date. In addition, the demand for these fossil fuels is also increasing proportionally to the increasing demand for more

transport of cargo and people [2,3].

The aviation industry is an integral part of the transport sector [2] and consumes annually approximately 1.5–1.7 billion barrels of petroleum jet fuel. Out of every barrel of crude oil, 4 gallons of kerosene are produced [4]. In 2007, the EU parliament legislated for the addition of the aviation sector to their greenhouse gas (GHG) emission trading system. This legislation has taken effect from 2012 that obliges all airlines operating within Europe to cut down their CO₂ emissions by 10% or buy CO₂ allowances. Furthermore, fuel consumption is also a high cost for the aviation industry that constitutes 10 – 15% of the total operating cost of an airline [5].

Jet fuel for use in aircraft gas turbine engines is mostly petroleum-

Abbreviations: SAF, Sustainable aviation fuel; IATA, International Air Transport Association; SPK, Synthetic paraffinic kerosene; HRJ, Hydroprocessed renewable jet; HEFA, Hydroprocessed esters and fatty acids; FT-BTL, Fischer-Tropsch – Biomass to Liquid; TCR, Thermo-Catalytic Reforming; HDO, Hydrodeoxygenation; HC, Hydrocracking; MAH, Monocyclic aromatic hydrocarbons; BAH, Bicyclic aromatic hydrocarbons; DoD, Degree of deoxygenation.

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<https://doi.org/10.1016/j.jaap.2022.105498>

Received 6 September 2021; Received in revised form 7 March 2022; Accepted 9 March 2022

Available online 12 March 2022

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derived [6]. The most common aviation fuels consumed by commercial and military aircraft are Jet A, Jet A-1 and JP-8 that are produced from petroleum refining [7,8]. It has been estimated that between 2% and 6% of all global carbon emissions come from the aviation industry. It is perceived that sustainable aviation fuels (SAF) can potentially substitute petroleum-derived jet fuels in the short term as blend components and can significantly reduce GHG emissions [4]. SAF, derived from organic waste biomass resources, can significantly contribute to carbon savings when compared to its fossil fuel equivalents. This is because a proportion of the CO₂ emitted upon its combustion is considered to be carbon neutral, consequently producing less net CO₂. SAF can also contain very little sulphur, which leads to a reduction in SO_x emissions.

The utilisation of SAF in the aviation industry has been recognised by the International Air Transport Association (IATA) as the most promising way to reduce air emissions and dependence on fossil jet fuels [1]. Accordingly, IATA aims to add 30% SAF as a fuel blend in conventional jet fuel by 2030 [2].

Hence, increased CO₂ emissions, rise in fuel demand, price, and strict environmental legislations have led the aviation industry to adopt renewable and sustainable fuels, which may provide a long-term solution [7,8]. SAF fuel, and more specifically in this context known as synthetic paraffinic kerosene (SPK), is composed of renewable hydrocarbons in the same carbon range as fossil kerosene. SPK has a similar composition to fossil jet fuel that gives it almost the same or, in some cases, superior characteristics as fossil jet fuel. However, some properties, such as the aromatic content in SPK, may be more variable and is highly influenced by the processing route as well as biomass feedstock being processed [1].

There are very few technologies available that can convert biomass feedstock into SAF, and only a minority of these processes are currently ASTM approved routes and commercially available to enter the jet pool, whilst other technologies are still either in demonstration stages or in early research and development [4]. SAF fuels derived from second generation biomass feedstock (camelina, jatropha, and algae) have been successfully tested in commercial flights with an 80% reduction in carbon footprint relative to fossil jet fuel [5].

The existing SAF production pathways can largely be categorised into hydroprocessing, thermo-chemical processing, and biochemical processing. The aviation fuel derived from hydroprocessing is called hydroprocessed renewable jet (HRJ) or sometimes hydroprocessed esters and fatty acids (HEFA). HRJ technology is commercially available HRJ fuels that fall within specification with ASTM D7566 can be used up to a maximum blend ratio of 50% with fossil jet fuel without requiring any engine modifications or further approvals [9]. The Ecofining™ process, developed by Honeywell UOP in collaboration with ENI, is the first technology under the hydroprocessing route to produce SAF from biomass resources [1].

Thermochemical pathways, also called biomass to liquid (BTL) processes convert biomass into liquid fuel via three possible routes – gasification, pyrolysis and hydro-thermal upgrading [1,10,11]. Gasification followed by Fischer-Tropsch (FT) synthesis is considered to be one of the alternative production routes for SAF fuel [1,12,13]. Fischer-Tropsch – Biomass to Liquid (FT-BTL) via gasification is also an ASTM D7566 certified technology to produce renewable jet fuel. It is approved for a 50% blend with fossil kerosene (Jet A-1) [6,8].

Alcohol to Jet (ATJ) and catalytic upgrading of sugars to hydrocarbons, also known as Aqueous Phase Reforming (APR), are the two main processes which exist under the biochemical conversion route [4,9]. LenzaTech's ethanol to Jet technology has recently been certified in ASTM D7566 under the Annex A5 ATJ route for production and blending with fossil jet from 30% to 50% [4,5].

There are a number of stringent quality specifications that SAF must meet to be accepted within the jet pool [8]. ASTM D7566 is the certifying standard for the new SAF that defines its production route and quality specifications [4]. Previously, other renewable alternatives such as synthetic alcohols (bio-ethanol and bio-methanol), fatty acid methyl

esters (FAME), sugar derived hydrocarbons, dimethyl ether (DME), and hydrogen were also considered to be used in jet gas turbine engines; however, stringent and high quality performance criteria for commercial jet fuel limits their application without engine modifications or disruption to the current fuel distribution infrastructure [5].

Conventional jet fuel is a mixture of alkanes, cyclic alkanes and aromatics. However, the SPKs derived from the catalytic hydro-treatment of triglycerides and FT process lack sufficient cyclic alkanes and aromatics levels which are required for the adequate function of aircraft seals and valves and must be present within the fuel up to 25%; hence, they are blended with fossil kerosene jet fuel to bring this level up [8]. The pyrolytic conversion of lignocellulosic biomass to liquid hydrocarbon drop in transport fuels is usually performed by fast pyrolysis. This is extremely challenging due to the fact that fast pyrolysis bio-oil has undesirable fuel properties such as high acidity, high viscosity, poor stability, and low calorific value. These unwanted properties make fast pyrolysis derived bio-oil unsuitable for engine applications. The catalytic upgrading of fast pyrolysis bio-oil over zeolites or other catalysts have been demonstrated; however, the bio-oil composition is still not sufficient to be upgraded into SAF [14,15]. There are also concerns raised over catalyst deactivation and poisoning.

Hence, new and improved methods and systems are needed to rise to the challenges associated with SAF production [6]. Sewage sludge, the solid by-product of municipal and industrial wastewater treatment plants [16], is a negative cost lipid-rich feedstock [17]. Due to containing a significant proportion of lipids, sewage sludge has been proposed as a potential feedstock for biodiesel production [18]. The lipids content in sewage sludge materials varies between 2.9% and 12.3% [19]. Thermo-chemical processing (combustion, gasification, and pyrolysis) are some of the most promising routes to convert sewage sludge into biofuels and energy [20]. Intermediate pyrolysis with catalytic reforming has the advantage of producing liquid fuels with less tar formation and is preferred over other processing routes. It is perceived as a promising pathway to valorise biomass wastes into transport fuels and chemicals [20–22].

Thermo-Catalytic Reforming (TCR) Technology, an advanced intermediate pyrolysis-based technology, can process a wide range of waste biomass into energy vectors. Previous TCR studies [23–27] have successfully converted various organic wastes into crude bio-oils with enhanced physiochemical properties suitable for upgrading into drop-in fuels.

Previously, a few studies have been conducted for the pyrolytic conversion of biomass into jet fuel at lab scale. Zhang et al. [6] studied the novel transformation of sawdust (lignocellulosic biomass) into sustainable jet fuel range hydrocarbons using catalytic fast pyrolysis technology. As a result, it was found that the production of the preferred C₈–C₁₅ aromatics with the maximum selectivity of 92.4% was reached by low-temperature alkylation reactions using an ionic liquid. Wang et al. [8] investigated a new conversion of bio-oil from fast pyrolysis of straw stalk (lignocellulosic biomass) into bio-jet fuel. Accordingly, it was concluded that the production of C₈–C₁₅ aromatics (selectivity of 88.4%) was achieved by the alkylation reactions using an ionic liquid. Furthermore, a new pathway was studied to form bio-jet fuel range paraffins and aromatics through catalytic microwave-induced pyrolysis of intact biomass which was integrated with the hydrotreating upgrading process, achieving the highest yield (12.6%) of sustainable jet fuel range cycloalkanes [28]. Lately, Tomasek et al. [1] investigated bio-jet fuel production from cracked fractions of waste polyethylene and polypropylene plastics on commercial NiMo/Al₂O₃/P catalyst. As a result, it was concluded that olefins affect the hydro-de-aromatisation and hydrosulphurisation at 240 °C and 220 °C, respectively.

This work presents novelty is to produce SAF from sewage sludge via TCR technology followed by hydroprocessing of TCR crude oil which has not been previously reported in the literature. Production of SAF from hazardous and regulated waste, such as sewage sludge, has not been previously investigated, whilst recent lab-scale studies utilised

lignocellulosic biomass and plastics and mainly targeted a specific type of jet fuel hydrocarbons [1,6,8,28]. This work aims to achieve a SAF with conventional jet fuel paraffins (e.g., normal, cyclo, and iso) and aromatics using established hydroprocessing techniques that are commercially practised in crude oil refining. With the ambition of future integration as a SAF blend component with conventional jet fuels. The TCR-SAF product was characterised for its major fuel properties and compared with ASTM D7566.

With the global pandemic outbreak (COVID-19), the aviation industry has been severely hit with a drop in air travel and subsequent lower aviation fuel consumption. Still, the aviation sector is an essential part of the global economy. In terms of future assessment, the aviation sector will recover as travel restrictions are eased; however, it may be slow. As a result, there will be a lower demand for massive aircraft and a possible return to smaller and single-aisle aircraft, which in turn have lower fuel demands [29,30]. However, with regards to commercial-scale production of SAF, recently, there has been a surge of research and development projects and initiatives. The main challenges in the large scale production of SAF are the cost of jet fuel and its composition. The UK department for transport has recently launched a competition, 'Green Fuels Green Skies' for large scale process development for SAF [31]. Some major players, including LanzaTech, develop technologies to produce SAF from waste biomass [31,32]. However, this work has been carried out as part of the GreenFlexJET project, which aims to design and build a precommercial demonstration plant to produce SAF. Through an innovative technology which is not yet commercially available.

2. Materials and methods

2.1. Raw material

Sewage Sludge was sourced from SABESP, Brazil – a water and waste management company. The sewage sludge contained an initial moisture content of 80 wt%, which was reduced to approximately 20 wt% through natural open-air drying in Brazil. Post-drying, the sewage sludge was pelletised at the University of Birmingham UK using DORN-TEC PTE 50 pelletiser. The final pellets were approximately 1.5 cm long and 0.7 cm in mean diameter.

2.2. Experimental set-up

2.2.1. Thermo-catalytic reforming (TCR) system

The experiment was carried out in a 2 kg/h pilot-scale TCR unit located at the University of Birmingham (Fig. 1). The TCR run was carried out under fixed optimum process conditions (constant pyrolysis and reforming temperatures). The main components of the TCR rig and the process are described as follows:

I. Hopper/Feed Tank

The sealed hopper had a batch feed capacity of 7 Kg. Before feeding the tank, the whole system was purged with nitrogen to create an oxygen-free atmosphere. The tank was charged with 5 Kg of dried sewage sludge feedstock pellets.

II. Pyrolysis Reactor

The first reactor was an intermediate pyrolysis screw (auger) reactor, and the temperature was at 450 °C, producing pyrolysis gas and char.

III. Reforming Reactor

The second reactor (post reformer) was a fixed bed reforming reactor. In this section, the pyrolysis gas and char from the pyrolysis reactor undergo reforming at 700 °C. The reforming temperatures and increased gas/solid residence time serve to produce H₂ rich syngas and a reformed lower molecular weight condensable organic fraction.

IV. Cooling System

The condensable and incondensable fractions from the reforming reactor were cooled in a U-tube shell and tube condenser. The condenser contained a water/glycol mixture as a service fluid at a temperature of – 5 °C to ensure complete condensation of the organic vapours. The condensable fraction was recovered as condensate, while the remaining permanent syngas fraction passed through an ice-bath cooler. The second stage ice-bath cooling ensured the maximum recovery of condensable vapours, which might have escaped the first stage cooling.

V. Cleaning System

The permanent gas containing aerosols and impurities is passed through a cleaning system. Wash bottles containing aqueous phases were used to capture aerosols, while a bottle filled with a fibrous filter

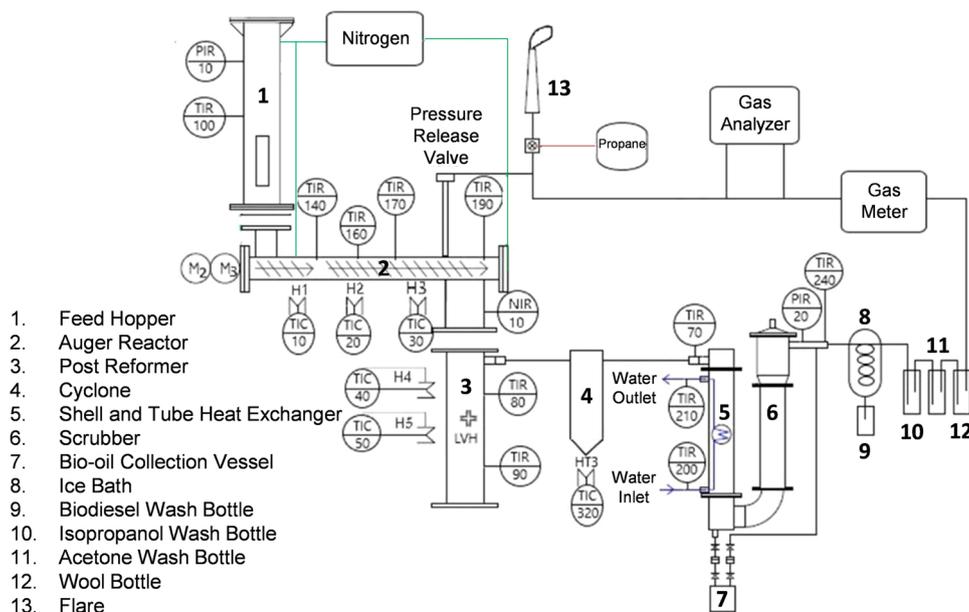


Fig. 1. Process schematic diagram of the TCR (2 kg/h) technology. Reproduced with permission from ref. [21], Copyright © 2020, Elsevier.

removed particles from the gas. Post-cleaning, the gas was routed to the Pollutek 3100 P gas analyser for detection and then on to the flare, where it was combusted using a propane support fuel.

2.2.2. Hydroprocessing experiments

The hydroprocessing of the TCR crude oil was carried out in two steps; the TCR crude oil was first hydrodeoxygenated (HDO) in the presence of a catalyst which was followed by hydrocracking (HC) using a different catalyst. Commercial catalysts from HALDOR TOPSOE were used for hydroprocessing. NiMo catalyst supported on alumina (NiMo/ γ -Al₂O₃) was used for HDO, whilst (HC) utilised NiW catalyst supported on silica-alumina (NiW/SiO₂-Al₂O₃) under the same process parameters. The TCR crude oil was hydrodeoxygenated and hydrocracked in a mini-bench top high-pressure batch reactor system from Parr autoclave series 4560. The autoclave used was a 300 ml pressure vessel manufactured in T316 stainless steel and fitted with high torque sealed magnetic stirrer drive unit in T316SS. The vessel was a fixed head style with a PTFE flat gasket and C-clamp closure. The working pressure and temperature limits for the pressure vessel were 200 bar and 350 °C. The internal diameter and depth of the vessel were 6.5 cm and 10 cm, respectively. In addition, the vessel head was fitted with a pressure gauge (0–200 bar), gas inlet, vent needle valves, safety rupture disk, and a J-type thermocouple. Before each HDO and HC run, the autoclave was purged with nitrogen to remove oxygen from the system. The system was pressurised with hydrogen to desired initial pressures (30–60 bar) and heated to a set point temperature (350 °C). For the hydroprocessing and hydrocracking steps, the amount of catalyst was adjusted to keep the catalyst to oil ratio constant (1 g catalyst/10 ml TCR oil). In this study, the HDO-30 and HDO-60 denote oils produced from hydrodeoxygenation at 30 and 60 bar H₂, respectively, whilst HC-30 and HC-60 represent oils from hydrocracking at 30 and 60 bar H₂, respectively.

2.2.3. Catalyst activation and reusability

Both hydrodeoxygenation and hydrocracking catalysts were activated in-situ before each hydroprocessing experiment. Dimethyl disulphide (99% purity, Alfa Aesar) as sulphiding agent was used to activate the catalysts at 350 °C under 20 bar H₂ for 4 h. Both hydrodeoxygenation and hydrocracking spent catalysts were also tested to determine their reusability potential. The spent catalysts were reused with and without regeneration. Prior to regeneration, the spent catalysts from the previous experiments were washed using hexane to remove organic species (contaminants) adsorbed on the catalyst surface and later dried at 110 °C for 24 h. The catalyst calcination was done in an oxidising atmosphere in a convective oven at 450 °C. The heating rate was approximately 3 °C/min, while the regeneration time was kept 4 h (the same as activation). For the reusability tests without catalyst regeneration, no calcination was performed, whilst the spent catalysts were washed and dried only. In this study, the HPWR denote hydroprocessed oil over spent catalysts (without regeneration), whilst HPR-1 and HPR-2 represent hydroprocessed oils produced (with first and second regeneration, respectively). Also, the HPF denotes hydroprocessed oil produced over the fresh catalyst. Table 1 shows the summary of the hydroprocessing parameters:

Table 1
Process parameters for two-step hydroprocessing (HDO and HC).

	Unit	Value
Batch time	h	4
Temperature	°C	350
Pressure	bar	30–60
Catalyst Loading	g catalyst/ml TCR oil	1/10
Catalyst Activation Time	h	4
Catalyst Activation Temperature	°C	350
Catalyst Regeneration Temperature	°C	450
Catalyst Regeneration Time	h	4

2.2.4. Fractionation

Fractional distillation is one of the most important unit operations of a crude oil refinery which physically separates petroleum products into valuable fractions. The separation takes place due to differences in the boiling points of the components. After hydroprocessing, the fuel was distilled using a lab-scale distillation kit. The distillation apparatus comprised a heating mantle, round bottom flask, a fractionating column containing rasching rings, a thermometer, a condenser with cold water flow, and a distillate receiving flask. The fractionation was carried out up to 285 °C under atmospheric pressure to separate three fractions – naphtha, kerosene and diesel. Naphtha was collected at 140 °C; the second cut collected at 235 °C which separated the kerosene range; while from 235 °C to 285 °C, a green diesel fraction was recovered.

2.3. Analytical methods and measurements

Ultimate analysis was performed by an external company Medac Ltd. The ultimate analysis was performed on a dry basis using the FlashEA®112 analyser that works on the quantitative dynamic flash combustion method. During ultimate analysis, the calorific value was also measured. Before hydroprocessing, the TCR crude oil was filtered to remove entrained fine char particles. This was done using a 20–25 μ Whatman™ filter paper from which the bio-oil was passed under gravity. In addition to solid filtration, the crude oil for any potential miscible water was also separated using a Thermo-Scientific CL31R Multispeed centrifuge. The centrifugation was carried out at 3000 RPM for 15 min. The same settings were used for the separation of water after the hydrodeoxygenation of TCR crude oil.

GC-MS analyses were carried out in Green Fuels Research, Berkeley, UK. Approximately 10 μ L of the sample was dissolved in 1000 μ L of hexane as solvent. The mixture was further stabilised in the GC-MS vials using a vortex mixer. An Agilent 8890 GC system linked to Q-TOF MS operating in EI mode with a scan range between 50 and 600 *m/z* was used for GC-MS analyses. A DB5 MS column (30 m, 250 μ m, 0.25 μ m) was used for GC with a gas flow of He (1 ml/min) under 50 °C holdup for 1 min and then 5 °C/min ramp up to 300 °C. The chemical compounds were identified using the NIST library. The mass spectra evaluation was calculated in terms of peak area relative abundance (the percentage is the individual peak area as a proportion to the total).

The biocrude oil and hydroprocessed fuels were measured for acid number by manual titration, which was carried out in line with ASTM method D974 [21]. The unit of measurement is mg KOH/g. The water content of the bio-oil was determined using Karl Fisher (KF) volumetric auto-titrator as per ASTM D1744 [27]. The Karl Fisher method is based on the oxidation of SO₂ by Iodine in a methanol hydroxide solution. The unit of measurement is % (w/w). All samples were measured by Houillon viscometer at a fixed temperature of 40 °C for kinematic viscosity. This was performed in line with ASTM method D445 [27]. The viscosity for the kerosene fraction was also measured at – 20 °C with respect to ASTM D445 [27]. The unit of measurement is cSt. A sample of each oil was analysed in line with ASTM method D4052 by using an Anton-Paar DMA 35 Digital density metre. The unit of measurement is g/ml [21]. The freezing point was tested with a HUBER refrigeration bath system with a controlled freezing temperature up to – 50 °C following the ASTM D2386 test method for the freezing point of aviation fuels [33,34]. Flash point was tested using the IP523 method [35], for which the unit of measurement is degree Celsius. The smoke point was made in line with ASTM 1332 [36]. The unit of measurement is mm.

3. Results and discussion

3.1. Sewage sludge TCR crude oil

Pelletised sewage sludge was processed through the TCR system. The mass balance revealed 6 wt% of the dried sewage sludge converted to phase-separated TCR crude oil, 25.4 wt% converted to syngas composed

of CO, CO₂, CH₄, H₂ and C_xH_y, and 48.5 wt% converted to char, and the remaining 20.1 wt% converted into water effluent. Table 2 contains elemental composition, calorific value, and fuel characteristic data of sewage sludge derived TCR crude oil. The TCR crude oil was rich in hydrocarbons with 78.9 wt% carbon and 10.3 wt% hydrogen content with calorific value of 39.4 MJ/kg.

The nitrogen content was slightly high, which is not desirable due to potential NO_x emissions. The nitrogen content in the bio-oil is attributed to the presence of protein in sewage sludge [37,38]. Due to low oxygen content, the TCR crude oil also showed excellent fuel heating properties comparable to biodiesel. The oil was characterised as lower in density (0.97 g/cm³), and viscosity (7.2 cSt). Low viscosity is desirable for good flow properties as high viscosity can cause serious pumping issues. The oil was also found to be lean in acidity (5.7 mg KOH/g), which is essential to avoid corrosion in the pipelines and engines [37]. Furthermore, the oil was not miscible in water and contained a total water content (3.0 wt%).

Fig. S1 shows the gas chromatograms of the TCR crude oil. The compounds identified in the TCR crude oil were largely mono-aromatic hydrocarbons (ethylbenzene, p-Xylene, o-Xylene, styrene, benzene, 1-propynyl-); polycyclic aromatic hydrocarbons (naphthalene, 1-methyl, naphthalene, 2-methyl, azulene, biphenyl); free fatty acids methyl esters (hexadecanoic acid, methyl ester, 9, 12-octadecadienoic acid, methyl ester, 9-octadecenoic acid (Z)-, methyl ester); and N-heterocyclic compounds (benzotrile, 1 H-indole, 4-methyl-).

3.2. Physicochemical characteristics of hydroprocessed oils

The sewage sludge derived TCR crude oil was further processed and converted into synthetic paraffinic kerosene. The purpose of hydroprocessing is to remove heteroatoms from the bio-oil; saturate unsaturated hydrocarbons; and decrease O/C and increase H/C ratios. This was achieved via two-step catalytic hydrotreating under fixed process parameters, except H₂ pressure which was varied between 30 and 60 bar. The comparative chemical composition, calorific values, H/C ratios, degree of deoxygenation (DoD) achieved during HDO step and the major fuel properties of the hydroprocessed oils across 30–60 bar H₂ pressure are tabulated in Table 2. The elemental composition of the TCR crude oil was greatly enhanced during each hydrodeoxygenation and hydrocracking step as more and more hydrogenation removed heteroatoms

Table 2
Physicochemical characteristics of oils in two-step hydroprocessing.

Analyses	TCR Crude Oil	(HDO and HC) @ 30 Bar H ₂		(HDO and HC) @ 60 Bar H ₂	
		HDO-30 Oil	HC-30 Oil	HDO-60 Oil	HC-60 Oil
Ultimate analysis					
C (wt%)	78.9	84.3	86.4	86.3	88.0
H (wt%)	10.3	10.4	11.0	11.0	11.5
N (wt%)	4.5	2.8	1.8	2.0	0.5
S (wt%)	2.1	< 0.10	< 0.10	< 0.10	< 0.10
O (wt%)	4.2	2.5	0.8	0.7	0
Molar H/C	1.56	1.48	1.52	1.53	1.56
DoD (%)	–	40	81	83	100
Fuel properties					
HHV (MJ/kg)	39.4	40.5	42.1	42.1	43.4
Ash (wt%)	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Water (wt%)	3.0	1.7	0.3	1.6	0
Density (g/cm ³)	0.97	0.90	0.87	0.86	0.84
TAN (mg KOH/g)	5.7	1.6	0.8	0.7	0.6
Viscosity at 40 °C (cSt)	7.2	3.9	2.5	2.3	1.6

O = calculated by the difference; DoD = degree of deoxygenation.

from the TCR crude oil. The O and N content decreased whilst C and H content increased as a function of H₂ pressure.

A noticeable degree of deoxygenation and denitrogenation was observed in both HDO and HC steps. The highest deoxygenation (100%) and denitrogenation (89%) were observed in HDO and HC at 60 bar H₂, indicating that HDO/HC catalysts had significant catalytic effects and were not deactivated. The molar H/C ratio and the gross calorific value for the HC-60 oil reached 1.56 and 43.4 MJ/Kg, respectively. With the upgrade of the elemental content of the oil, other properties such as density, TAN (total acid number), water and viscosity are also enhanced in parallel. Under the hydroprocessing at 60 bar H₂, an upgraded oil with zero water content, lower viscosity (1.6 cSt) and lean in acidity (0.6 mg KOH/g) was produced.

3.3. Two-step hydroprocessing

The first step, known as HDO, involved the catalytic conversion of oxygenated organic (TCR crude oil) compounds to saturated hydrocarbons (alkanes) by removing oxygen. Besides hydrodeoxygenation, other reactions such as hydrodesulphurisation (HDS) and hydrodenitrogenation (HDN) also take place, which results in sulphur and nitrogen removal, respectively. The second step, known as HC, dealt with the catalytic conversion of long-chain paraffins (alkanes) from the HDO process into small chain paraffins corresponding to the jet fuel range (C₈-C₁₆). Besides cracking, isomerisation and hydrodealkylation reactions also take place. However, the range and extent of reactions are highly influenced by the initial composition of the feed and process parameters.

The hydrogen pressure is one of the key parameters in hydroprocessing that affects product distribution. In order to effectively understand the effect of H₂ pressure on the distribution of chemical compounds, the hydroprocessed oils have been compared for their relative distribution of components in HDO and HC processes as a function of pressure. For comparison, only chemical compounds appeared with consistency and identified with more than 80% match with the NIST library have been presented. Furthermore, the chemical compound in the hydroprocessed oils found were distributed across several organic groups. Hence for the purpose of discussion, the GC-MS results (Fig. S1) has been arranged on the basis of their organic classification and their corresponding carbon number (Table S1).

3.3.1. Distribution of monocyclic and bicyclic aromatic hydrocarbons (MAH and BAH)

Figs. 2 and 3 show the distribution of monocyclic and bicyclic aromatic hydrocarbons (MAH and BAH, respectively) of hydroprocessed oils. In HDO of the sewage sludge oil, the C₈-C₉ monocyclic (Fig. 2a) and C₁₀-C₁₂ bicyclic (Fig. 2b) aromatics constituted the majority of the aromatics detected in the hydroprocessed oils. The C₈-C₉ monocyclic aromatics detected were essentially the isomers of benzene and its substituted derivatives, whilst the C₁₀-C₁₂ bicyclic aromatics were naphthalene and its derivatives.

Increasing H₂ pressure in the HDO process favoured the formation of C₈-C₁₃ monocyclic with greater selectivity towards C₈ (Fig. 2a). The relative abundance of C₈ increased from 22.5% to 26.1% by increasing pressure from 30 to 60 bar H₂. The monocyclic aromatics across C₉-C₁₃ also showed a minor increase. On the other hand, increasing H₂ pressure to 60 bar in the HDO step curtailed the formation of C₁₀-C₁₂ bicyclic aromatics, indicating that some simultaneous cracking of the heavy aromatics occurred in the HDO step. The relative content of the bicyclic aromatics in the HDO-60 oil reduced to 8.9% compared to 12.7% in HDO-30 oil (Fig. 2b).

Increasing H₂ pressure to 60 bar in the HC step influenced the oil composition by cracking light and heavy aromatics (Fig. 3). Monocyclic aromatics' relative abundances significantly decreased in the HC-60 oil across the entire carbon range compared to HC-30 oil (Fig. 3a). The relative areas of C₈-C₉ combined reduced from 36.1% to 18.8%, with

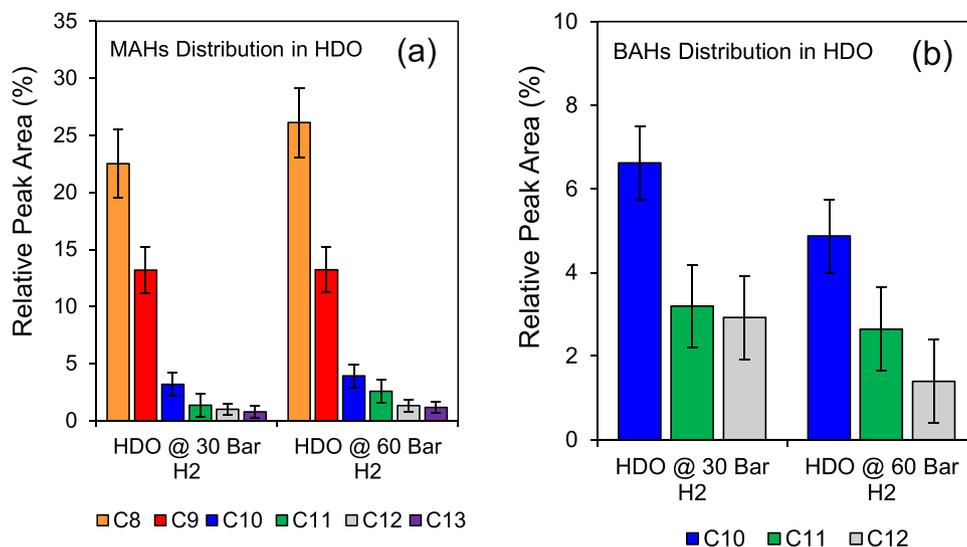


Fig. 2. The product distribution in HDO oil at different H₂ pressures for (a) MAHs and (b) BAHs.

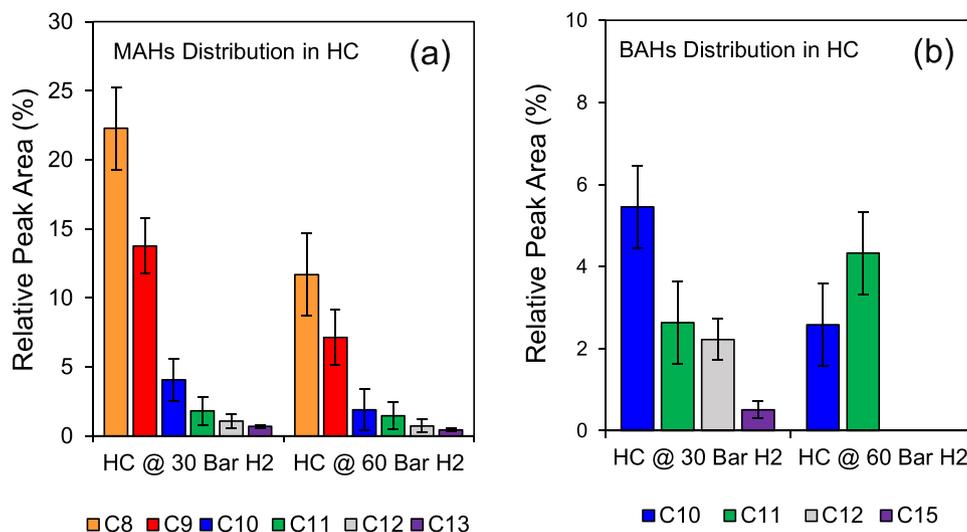


Fig. 3. The product distribution in HC oil at different H₂ pressures for (a) MAHs and (b) BAHs.

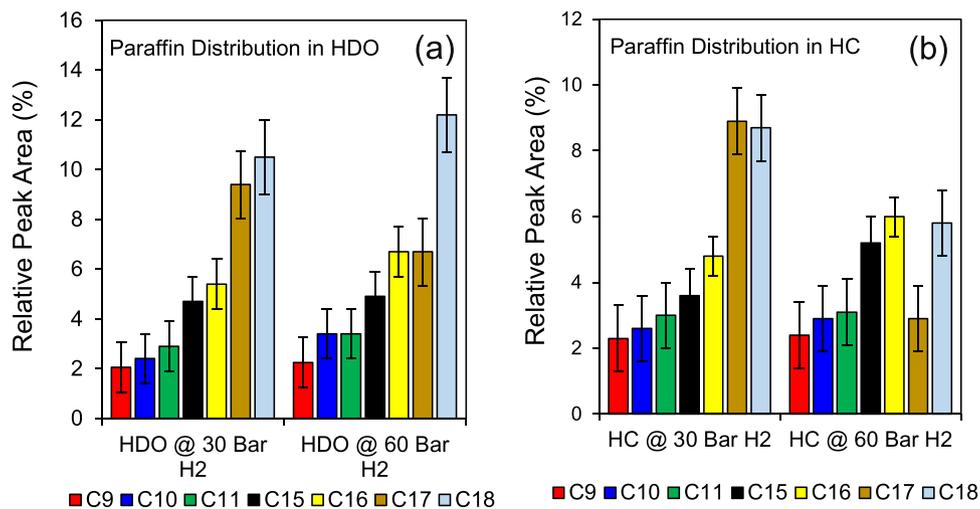


Fig. 4. Distribution of paraffin at different H₂ pressures for (a) HDO oil and (b) HC oil.

also more than 50% reduction across C₁₀-C₁₃ monocyclic aromatics. The relative abundances of bicyclic aromatics changed considerably across the entire carbon range (Fig. 3b). The C₁₀ bicyclic aromatics dropped from 5.5% to 2.6% by increasing HC pressure from 30 to 60 bar. However, the C₁₁ bicyclic aromatics escalated from 2.6 to 4.3 by increasing pressure. The C₁₅ bicyclic aromatic compound emerged in the HC-30 oil, possibly due to oligomerisation reactions of lighter aromatics [8].

3.3.2. Distribution of paraffins

Paraffins were the second most abundant chemical compounds in terms of relative abundance on the GC spectrum of the hydroprocessed oils. The paraffins were distributed across cyclo-alkanes, n-alkanes, and iso-alkanes. However, only n-alkanes were detected and identified in the hydro-treated oils with consistency. The n-alkanes detected and identified by the NIST library were n-C₉-C₁₁ and n-C₁₅-C₁₈ (Fig. 4).

In the HDO step at 30 bar H₂ pressure, the relative area distribution of the fuel range C₉-C₁₁ and C₁₅-C₁₈ was 7.3% and 30%, respectively. On the other hand, applying 60 bar H₂ pressure in HDO influenced all the carbon numbers by increasing the n-C₉-C₁₁ to 10% and the n-C₁₅-C₁₈ to 30.5% (Fig. 4a). This suggests that some cracking and isomerisation of the n-alkanes also took place in the hydrodeoxygenation at 60 bar H₂. However, the n-C₁₈ emerged with a greater relative area under 60 bar than 30 bar H₂ pressure that can be associated with the relatively greater conversion of FAME in the feed to n-C₁₈ due to higher hydrogenation saturation pressure [39].

Applying 60 bar H₂ pressure in hydrocracking influenced the entire spectrum of n-alkanes across n-C₉-C₁₈ with enhanced cracking and isomerisation of n-C₁₇-C₁₈ (Fig. 4b). In hydrocracking, cracking and isomerisation reactions are competitive reactions that can occur either simultaneously or sequentially [40,41]. Although a range of cyclic-paraffin was present and identified, only cyclohexane was detected in the hydroprocessed oils (Table S1). The relative content of cyclohexane increased with the hydrogen pressure and reached 4.8% at 60 bar H₂.

3.3.3. Oxygenates and N-heterocyclic

The only oxygenated compound detected in hydrotreated oils were phenols and nitrile (Table S1). At 30 bar HDO, phenols were detected with the relative area which was reduced in the HC step, showing little conversion. At 60 bar H₂, the phenols appeared to have completely hydrogenated and hydrocracked into cyclohexane. Indole, a nitrile compound, was the only N-heterocyclic compound identified in the hydroprocessed oils. The relative content of indole decreased in both HDO and HC reactions. At 30 bar H₂, it was detected with the relative area of 2.5% in the HDO-30 oil and was reduced to 1.4% in HC-30 oil. Increasing pressure to 60 bar H₂ in the HDO step reduced indole further to 1.1%, and further cracking at 60 bar enhanced the removal. Indole was not detected post hydrocracking at 60 bar H₂.

3.3.4. Possible reaction mechanisms in hydroprocessing of sewage sludge TCR crude oil

3.3.4.1. Hydrodeoxygenation of FAME. The FAME during HDO was converted to paraffins (n-alkanes). Unsaturated FAME under hydrogenation gets converted into saturated FAME. Then, the saturated FAME is decomposed into one less carbon through a hydrogenolysis reaction. The formed carboxylic acid further undergoes decarboxylation, decarbonylation and HDO reactions to form paraffins. Finally, cracking and isomerisation reactions convert longer-chain alkanes into shorter-chain alkanes [42].

3.3.4.2. Hydrocracking of n-paraffins. The HDO of FAME resulted in the formation of n-paraffins across the n-C₉-C₁₈ carbon range. During hydrocracking, the n-C₁₇-C₁₈ paraffins, in particular, underwent cracking and isomerisation to yield more n-C₉-C₁₅ range to produce lighter and

branched/cyclic paraffins in order to meet essential jet fuel characteristics. In hydrocracking, n-paraffins crack and self-isomerise between temperature 310 °C-350 °C where longer chain n-paraffins such as n-C₁₆-C₁₈ have been reported to exhibit enhanced transformation in comparison to shorter chain n-paraffins (< n-C₁₆) where the temperature is a key factor [41]. In HC, cracking and isomerisation reactions are competitive reactions that can occur either simultaneously or sequentially [41,43].

3.3.4.3. Conversion of phenols to cyclo-paraffin. In the HDO/HC, the phenols were converted into cyclohexane (C₆H₁₂). The phenols conversion into cyclohexane during hydroprocessing fall under three possible reaction pathways as follows: First, direct deoxygenation breaks the C-O bond in the aromatic chain to produce benzene, followed by cyclohexene and cyclohexane. Second, the phenol aromatic ring on hydrogenation forms cyclohexanol. The intermediate cyclohexanol undergoes deoxygenation to produce cyclohexene and cyclohexane. The third pathway is the combination of simultaneous hydrogenation and HDO that results in cyclohexanol as an intermediate. Further hydrogenation yields cyclohexene and cyclohexane [42]. It is worth mentioning that isomerisation can also convert cyclohexane to methylpentane [42]. Operating parameters such as temperature, pressure, type of catalyst, and support influence the above pathways, leading to the formation of different intermediates and products.

3.3.4.4. Hydrogenation of naphthalene. In the HDO reaction, naphthalene was converted into tetralin (detected as naphthalene, 1,2,3,4-tetrahydro-) and its substituted derivative (naphthalene, 1,2,3,4-tetrahydro-6-methyl-) in the hydroprocessed oils. Naphthalene is hydrogenated to produce tetralin, and tetralin, on further hydrogenation, converts into decalin [44]. Hydrogenation of naphthalene to tetralin is easier than decalin due to the high rate of reaction, which has been reported to be 30 times higher than decalin [44].

3.3.4.5. Hydrocracking of tetralin to monoaromatic hydrocarbons. Tetralin, the hydrogenated derivative of naphthalene, under high pressure of H₂ can undergo simultaneous hydrogenation, dehydrogenation, ring contraction, ring-opening, and cracking to produce light monoaromatic (< C₁₀). The high yield of monoaromatic hydrocarbons has been reported at 350 °C and 60 bar H₂ [45].

3.3.4.6. Hydrodenitrogenation of indole. Indole on hydrogenation converts into 2,3-dihydroindole. Further hydrogenation of 2,3-dihydroindole can transform it into octahydroindole as an intermediate compound. The octahydroindole further converts into ethylcyclohexane and ethylcyclohexene as the final compounds. Besides, the octahydroindole can further convert to intermediate o-ethylaniline through ring-opening and subsequently to ethylbenzene. Denitrogenation is rather difficult compared to desulphurisation [46] because H₂ saturation of aromatic ring is an essential reaction step in denitrogenation, whilst it is not needed in sulphur removal [47].

To sum up Section 3.3, monocyclic and bicyclic aromatic hydrocarbons (MAH and BAH, respectively) were the main compounds of hydroprocessed TCR oils. However, other products of the hydroprocessing reactions were mainly water, carbon monoxide, carbon dioxide, methane and ethane [40]. The carbon balance of these compounds will be studied as a future work.

Table 3

The product distribution from sewage sludge hydroprocessed oil at 60 bar H₂.

Fraction	Mass Yield (%)	Volumetric Yield (%)
Kerosene	25	25.5
Gasoline (Naphtha)	18	20.5
Diesel	25.5	29

3.4. Distillation Yields

Table 3 shows the percentage mass and volumetric yields of the products recovered from sewage sludge, the most hydroprocessed oil at 60 bar H₂ after distillation. Naphtha and diesel were recovered as by-products. The kerosene fraction was 25 wt%, but naphtha and diesel were 18 wt% and 25.5 wt%, respectively.

3.5. GC-relative distribution of kerosene

The GC-MS data (Fig. S2) of the jet fuel (C₈-C₁₆) range fraction, including chemical compounds, retention times and their relative peak areas, are shown in Table S2. The chemical compounds detected in the jet fuel range can be classed as MAHs, BAHs, n-paraffins, cyclo-paraffins, iso-paraffins and traces of esters, phenols and ketones. The overall distribution of aromatics was across C₈-C₁₃, which is in line with the aromatics carbon range (C₈-C₁₅) mainly found in jet fuel. The aromatics are vital for elastomer swelling, lubricity and material compatibility [48].

Fig. 5 shows the relative area of kerosene compounds. The C₈-C₁₃ monocyclic aromatics were detected as relatively the most abundant chemical compounds with approximately 60% relative combined relative area on the GC spectrum. The C₈-C₁₀ aromatics detected in the jet fuel range were mainly alkylbenzenes such as ethylbenzene, benzene, 1, 2, 3-trimethyl-, benzene, propyl-, benzene, 1-ethyl-4-methyl- etc. which are considered as desirable aromatics in jet fuel as they tend to produce less soot on combustion compared to other aromatics [49]. Further, they produce less NO_x in combustion due to methyl radicals which act as sinks for O radicals [49].

The bicyclic aromatics (C₁₀-C₁₂) detected were essentially naphthalene and its isomers. They are undesirable in fuels as they are known to produce high smoke and soot. Moreover, they are considered toxic and environmentally hazardous [50]. JP-8 jet fuel has been reported to contain 0.26–1% naphthalene as an aromatic compound [51]. However, naphthalene in jet fuels has also been reported to cause greater swelling in elastomers [52] which is essential to avoid leakage in aircraft components. In addition, tetra-hydro-naphthalene (tetralin), a derivative of naphthalene hydrogenation, was also present in the fuel, which is known to negatively affect the oxidative stability of jet fuels by producing peroxides [53,54].

Paraffins were the second most abundant compounds in the hydroprocessed oil, with approximately 27% combined relative abundance in gas chromatography. Paraffins were mainly distributed across n-paraffin with a considerable presence of cyclo-paraffin. A high concentration of n-paraffin results in a higher H/C ratio but relatively increases the freezing point. A couple of iso-paraffins were also detected in the fuel.

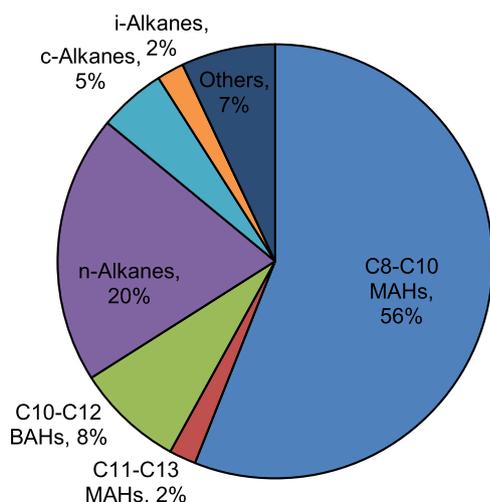


Fig. 5. Gas chromatogram relative area percentage of compounds in kerosene.

Cyclo-paraffin gives lower H/C [55] but produce less soot and are considered to be thermally more stable than iso-paraffin and aromatics. Due to higher density, the cyclo-paraffin also give shorter ignition time and faster flame speed [49]. The paraffin distribution into straight, cyclic and branched alkanes varies and depends on the composition of crude oil used in the refining process [55].

Hetero-atoms (others) such as ketones were also detected, which possibly formed due to initial oxidation of jet fuel which can lead to deposit precursors [53,54].

3.6. Fuel properties of sewage sludge derived jet fuel

There are a number of strict specifications that jet fuels are required to meet in order to be approved as jet fuel. The ASTM D7566 (an expansion of D1655) is a certifying standard that defines the SPK fuel performance criteria to control the production and quality of bio-jet fuel. Table 4 summarises some essential fuel characteristic data of previously commercially produced SPKs through FT and HRJ technology and the sewage sludge jet fuel produced in this work against the ASTM D7566 standard. In addition, Table 4 provides a comparison of sewage sludge derived Jet fuel produced in this work with commercial/military jet fuels.

The sewage sludge derived jet fuel range met the majority of the ASTM fuel specification such as acceptable minimum heating value (42.8 MJ/Kg), maximum freeze point (−47 °C), maximum allowable viscosity (8 cSt at −20 °C) and sulphur content (0.3 wt%). The sewage sludge TCR jet fuel showed high net energy content (43.4 MJ/Kg). The sewage sludge TCR jet fuel exhibited excellent low-temperature properties such as freezing point (−50 °C) and viscosity at −20 °C (3.2 cSt), which is essential for the aircraft to fly at high altitude [4]. Likewise, the high viscosity of jet fuel can cause pumping problems, poor atomisation and incomplete combustion [52]. These excellent low-temperature characteristics can be attributed to a large number of cyclo-paraffins [55] which were detected at several retention times in the sewage sludge TCR jet fuel during GC-MS. The amount of sulphur (<0.10) detected was well within the ASTM limit. The sulphur is present in jet fuels in the form of mercaptans, sulphides, thiosulphides or other sulphur containing compounds [55].

However, the flash and smoke points for the sewage sludge TCR jet fell below the minimum allowable limit due to higher aromatics [56]. Which suggests the fuel may be suitable as a blend component only. The quantification of the aromatics was not done; however, higher flash and the smoke points are an indication that the aromatics present in the sewage sludge TCR jet fuel are above the ASTM limit (25 vol%). Reducing the number of bicyclic aromatics (C₁₀-C₁₂) will increase the flash point and smoke point of the fuel, which can be done by greater hydrogenation/cracking of bicyclic aromatics. Furthermore, blending with a low aromatic jet fuel such as HRJ-SPK and FT-SPK will help the sewage sludge TCR jet fuel be in specification. Similarly, the TAN (0.6 mg KOH/g), generally associated with naphthenic and cresylic acids, can be reduced in many ways, such as casting washing, blending with non-acidic crude [57]. As a future work, optimising the hydro-processing conditions of TCR jet fuel will be investigated to bring all properties within the ASTM range.

3.7. Catalyst reusability and regeneration

The catalyst reusability and regeneration tests were carried out under the same process parameters used for the production of the jet fuel range (Fig. S3). The gas chromatogram relative area distribution of chemical compounds in catalyst reusability tests is shown in Table S3. The catalytic performance has been evaluated by comparing the physicochemical properties of the hydroprocessed oils from spent and regenerated catalysts with the hydroprocessed oils from the fresh catalytic test.

The elemental composition, degree of deoxygenation and the fuel

Table 4

Fuel Properties of sewage sludge derived kerosene fraction.

Specification	ASTM D7566	TCR Jet Fuel	JP-8	Shell FT	Sasol FT	R8-HRJ	Camelina HRJ
HHV (MJ/Kg)	Min 42.8	43.4		44.1	44.2	44.1	44.1
S (wt%)	Max 0.3	< 0.1	43	< 0.001	< 0.001	< 0.001	< 0.0003
Freezing Point (°C)	Max - 47	-50	0.064	-55	-77	-49	-77
Density, 15 °C (g/cm ³)	0.75–0.84	0.84	-49	0.73	0.76	0.76	0.75
TAN (mg KOH/g)	Max 0.1	0.6	0.79	0.002	0.002	0.002	0.002
Viscosity, - 20 °C (cSt)	Max 8	3.2	0.03	2.6	3.8	5.5	5.3
Smoke Point (mm)	Min 25	13	22	40	> 40	> 40	> 40
Flash Point (°C)	Min 38	< 38	48	44	44	48	43

Min = minimum; Max = maximum.

properties of the hydroprocessed oil for without regeneration (HPWR) and regenerated catalysts (HPR-1, HPR-2) have been compared to the hydroprocessed oil produced over the fresh catalysts (HPF) in Table 5. It can be seen that the highlighting difference in the elemental composition is the higher oxygen content of the HPWR oil compared to the rest of the oils. The spent HDO catalyst without regeneration exhibited poor deoxygenation efficacy, dropping to 33% compared to 83% in the HPF oil. This is likely due to the deposition of coke on the catalyst active sites. It is well known that the formation of coke and coke-like polymers is the root reason for catalyst deactivation during the bio-oil HDO process [58].

Coking is associated with the thermal instability and re-polymerisation of phenolic compounds in HDO [59]. However, the following HC step compensated for the poor deoxygenation by removing 66% of the oxygen content. The fuel properties of all the hydroprocessed oils were also comparable. The poor deoxygenation in HPWR oil is also reflected in its fuel properties with relative higher TAN, water, density and viscosity.

Fig. 6 shows the total relative aromatics and paraffin content in hydrodeoxygenation and hydrocracking reactions over the fresh catalysts (HPF), spent catalysts without regeneration (HPWR) and regenerated catalysts. (HPR-1 and HPR-2).

In the HDO reaction, the relative aromatics distribution of the HPR-1 (52.9%) and HPR-2 (52%) oils were comparable to the HPF oil (57.1%). The relative paraffin distribution of HDO oils was also similar across the HPR-1, HPR-2 and HPF oils with relative content of 40.3%, 40.2%, and

45.5%, respectively. However, a significant decline in the aromatics and paraffins in the HPWR oil is associated with poor hydrodeoxygenation (DoD, 33%) over the spent catalyst without regeneration. The main difference was observed across C₈–C₉ MAHs and C₉–C₁₈ n-paraffins (Table S3), for which the relative content declined by approximately 50% compared to HPF, HPR-1 and HPR-2 oils. In addition, phenols were also detected with higher relative content in the HPWR oil, indicating lower conversion of phenols in the HDO step due to coking.

In the HC reaction, the aromatics and paraffins' relative content was moderately similar across all the hydroprocessed oils (HPF, HPR-1, HPR-2 and HPWR), indicating that the HC catalyst without regeneration did have a significant catalytic effect and was not deactivated.

4. Conclusion

Sewage sludge was converted to crude oil through the TCR system and was successfully upgraded to sustainable aviation fuel within the hydrocarbon range. The TCR crude oil had a low oxygen content (<5 wt %) content due to which the oil was conveniently deoxygenated in the hydroprocessing step requiring less hydrogen partial pressure. Both hydroprocessing steps showed high catalytic activity at 60 bar H₂. It was found that both hydrodeoxygenation and hydrocracking steps resulted in oxygen and nitrogen removal, which will be an important consideration from the process design point of view in the scale-up of the process. The yield of the jet fuel fraction can be optimised by running the hydrocracker at a higher H₂ pressure which will increase the jet fuel range

Table 5

Physicochemical characteristics of hydroprocessed oils in catalyst reusability and regeneration tests.

Physicochemical Properties	HPF Oil		HPWR Oil		HPR-1 Oil		HPR-2 Oil	
	(As Reference)		(without Regeneration)		(First Regeneration)		(Second Regeneration)	
	HDO	HC	HDO	HC	HDO	HC	HDO	HC
Ultimate analysis								
C (wt%)	86.3	88.0	83.7	86.2	86.1	86.7	86.2	87
H (wt%)	11.0	11.5	11.3	11.5	11.2	12.2	11.0	11.0
N (wt%)	2.0	0.5	2.2	0.9	1.5	0.3	2.0	0.6
S (wt%)	< 0.10	< 0.10	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
O (wt%)	0.7	0	2.8	1.4	1.2	0.8	0.8	1.4
Molar H/C	1.53	1.56	1.62	1.60	1.56	1.68	1.53	1.52
DoD (%)	83	100	33	66	71	80	80	66
Fuel properties								
HHV (MJ/Kg)	42.1	43.4	42.2	43.5	43.1	44.5	43.0	43.2
Ash (wt%)	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Water (wt%)	1.6	0	1.8	0.3	1.6	0	1.6	0
Density (g/cm ³)	0.86	0.84	0.87	0.85	0.86	0.83	0.87	0.83
TAN (mg KOH/g)	0.7	0.6	1.6	0.9	0.6	0.6	0.8	0.5
Viscosity (cSt)	2.3	1.6	2.8	1.9	2.3	1.6	2.6	2.0

O = calculated by difference; DoD = degree of deoxygenation.

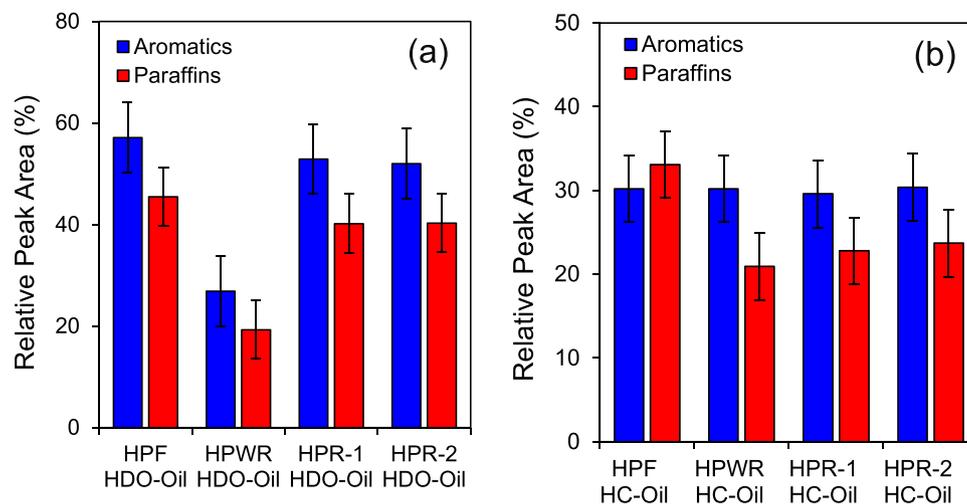


Fig. 6. Total relative aromatics and paraffin content in a) hydrodeoxygenation, and b) hydrocracking.

paraffins at the expense of C_{17+} paraffins separated as a diesel fraction. The jet fuel fraction for the majority of its fuel characteristics fell within the ASTM D7566 specification standard. The quality parameters such as total acid number, smoke point and flash point can be certainly be improved through additional treatment and process optimisation. Upon testing the process for catalyst reusability and regeneration potential, it was observed that the efficiency of the spent NiMo/ γ - Al_2O_3 catalyst (without regeneration) in the HDO process had significantly declined, possibly due to coking. However, both HDO and HC spent catalysts were successfully regenerated, showing similar catalytic activities as the fresh catalysts during hydrotreatment. The potential of catalyst regeneration is also of considerable importance in the scale-up of the process. As a result, the TCR conversion of sewage sludge can be a sustainable pathway for jet fuel production and promising valorisation route for sewage sludge.

CRedit authorship contribution statement

Muhammad Asif Bashir: Conceptualisation, Data curation, Formal analysis, Investigation, Methodology, Project administration, Resources, Software, Validation, Visualization, Writing – original draft, Writing – review & editing. **Sergio Lima:** Conceptualisation, Data curation, Formal analysis, Investigation, Methodology, Project administration, Resources, Software, Validation, Visualization, Writing – original draft, Writing – review & editing. **Hessam Jahangiri:** Conceptualisation, Data curation, Formal analysis, Funding acquisition, Supervision, Investigation, Methodology, Project administration, Resources, Software, Validation, Visualization, Writing – original draft, Writing – review & editing. **Artur J. Majewski:** Conceptualisation, Data curation, Formal analysis, Investigation, Methodology, Project administration, Resources, Software, Validation, Visualization, Writing – original draft, Writing – review & editing. **Martin Hofmann:** Conceptualisation, Data curation, Formal analysis, Investigation, Methodology, Project administration, Resources, Software, Validation, Visualization, Writing – original draft, Writing – review & editing. **Andreas Hornung:** Conceptualisation, Data curation, Formal analysis, Funding acquisition, Supervision, Investigation, Methodology, Project administration, Resources, Software, Validation, Visualization, Writing – original draft, Writing – review & editing. **Miloud Ouadi:** Conceptualisation, Data curation, Formal analysis, Funding acquisition, Supervision, Investigation, Methodology, Project administration, Resources, Software, Validation, Visualization, Writing – original draft, Writing – review & editing.

Declaration of Competing Interest

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

Acknowledgements

The authors would like to acknowledge the European Union's Horizon 2020, GreenFlexJET project (Reference Number: 792216) and To-Syn-Fuel project (Reference Number: 745749) for financial support.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jaap.2022.105498](https://doi.org/10.1016/j.jaap.2022.105498).

REFERENCES

- [1] S. Tomasek, Z. Varga, J. Hancsók, *Fuel Process. Technol.* 197 (2020), 106197.
- [2] N. Yilmaz, A. Atmanli, *Energy* 140 (2017) 1378.
- [3] H. Jahangiri, J. Santos, A. Hornung, M. Ouadi, in: K.K. Pant, S.K. Gupta, E. Ahmad (Eds.), *Catalysis for Clean Energy and Environmental Sustainability: Biomass Conversion and Green Chemistry - Volume 1*, Springer International Publishing, Cham, 2021, p. 1.
- [4] W.-C. Wang, L. Tao, *Renew. Sustain. Energy Rev.* 53 (2016) 801.
- [5] G. Liu, B. Yan, G. Chen, *Renew. Sustain. Energy Rev.* 25 (2013) 59.
- [6] Y. Zhang, P. Bi, J. Wang, P. Jiang, X. Wu, H. Xue, J. Liu, X. Zhou, Q. Li, *Appl. Energy* 150 (2015) 128.
- [7] S.K. Kim, J.Y. Han, H.-s Lee, T. Yum, Y. Kim, J. Kim, *Appl. Energy* 116 (2014) 199.
- [8] J. Wang, P. Bi, Y. Zhang, H. Xue, P. Jiang, X. Wu, J. Liu, T. Wang, Q. Li, *Energy* 86 (2015) 488.
- [9] T. Kandaramath Hari, Z. Yaakob, N.N. Biniha, *Renew. Sustain. Energy Rev.* 42 (2015) 1234.
- [10] M. Klaas, C. Greenhalf, M. Ouadi, H. Jahangiri, A. Hornung, C. Briens, F. Berruti, *Results Eng.* 7 (2020), 100165.
- [11] M. Ouadi, A. Fivga, H. Jahangiri, M. Saghri, A. Hornung, *Ind. Eng. Chem. Res.* 58 (2019) 15914.
- [12] H. Jahangiri, A. Osatiashiani, O. Doustdar, N. Akbari, J. Wood, A. Tsolakis, M. L. Wyszynski, *Fuel Process. Technol.* 208 (2020), 106477.
- [13] H. Jahangiri, J. Bennett, P. Mahjoubi, K. Wilson, S. Gu, *Catal. Sci. Technol.* 4 (2014) 2210.
- [14] H. Jahangiri, A. Osatiashiani, M. Ouadi, A. Hornung, A.F. Lee, K. Wilson, *Catalysts* 9 (2019) 841.
- [15] H. Jahangiri, A. Osatiashiani, J.A. Bennett, M.A. Isaacs, S. Gu, A.F. Lee, K. Wilson, *Catal. Sci. Technol.* 8 (2018) 1134.
- [16] D. Barry, C. Barbiero, C. Briens, F. Berruti, *Biomass - Bioenergy* 122 (2019) 472.
- [17] C. Kech, A. Galloy, C. Fripiat, A. Piel, D. Garot, *Fuel* 212 (2018) 132.
- [18] X. Zhang, S. Yan, R.D. Tyagi, R.Y. Surampalli, *Renew. Energy* 55 (2013) 392.
- [19] F. Zhu, X. Wu, L. Zhao, X. Liu, J. Qi, X. Wang, J. Wang, *Water Res.* 116 (2017) 149.
- [20] G. Gerasimov, V. Khaskhachikh, O. Potapov, G. Dvoskin, V. Kornileva, L. Dudkina, *Waste Manag.* 87 (2019) 218.

- [21] A. Fivga, H. Jahangiri, M.A. Bashir, A.J. Majewski, A. Hornung, M. Ouadi, *J. Anal. Appl. Pyrolysis* 146 (2020), 104773.
- [22] J. Santos, M. Ouadi, H. Jahangiri, A. Hornung, *Food Bioprod. Process.* 114 (2019) 23.
- [23] M.A. Bashir, H. Jahangiri, A. Hornung, M. Ouadi, *Chem. Eng. Technol.* 44 (2021) 194.
- [24] Jo Santos, H. Jahangiri, M.A. Bashir, A. Hornung, M. Ouadi, *ACS Sustain. Chem. Eng.* 8 (2020) 18420.
- [25] J. Santos, M. Ouadi, H. Jahangiri, A. Hornung, *Journal of the Energy Institute*, 1960 93 (2020).
- [26] J. Santos, M. Ouadi, H. Jahangiri, A. Hornung, *Fuel Process. Technol.* 203 (2020), 106402.
- [27] M. Ouadi, M.A. Bashir, L.G. Speranza, H. Jahangiri, A. Hornung, *Energy Fuels* 33 (2019) 9843.
- [28] X. Zhang, H. Lei, L. Zhu, Y. Wei, Y. Liu, G. Yadavalli, D. Yan, J. Wu, S. Chen, *Fuel* 160 (2015) 375.
- [29] K. Dube, G. Nhamo, D. Chikodzi, *J. Air Transp. Manag.* 92 (2021), 102022.
- [30] I. Moerland-Masic, F. Reimer, T.-M. Bock, F. Meller, *Post-pandemic Flight: Establishing the Mission of the Aircraft Cabin of the Future from a Passenger's Point of View*, : *Adv. Hum. Asp. Transp.*, Cham (2021) 573.
- [31] DepartmentForTransport, in, *Energy and Environment* <https://ee.ricardo.com/gfqs> (accessed November 2021), 2021.
- [32] K.S. Ng, D. Farooq, A. Yang, *Renew. Sustain. Energy Rev.* 150 (2021), 111502.
- [33] M. Lapuerta, L. Canoira, in: C.J. Chuck (Ed.), *Biofuels for Aviation*, Academic Press, 2016, p. 47.
- [34] A. INTERNATIONAL, in.
- [35] D. Capuano, M. Costa, S. Di Fraia, N. Massarotti, L. Vanoli, *Renew. Sustain. Energy Rev.* 69 (2017) 759.
- [36] A. INTERNATIONAL, in.
- [37] R.O. Arazo, D.A.D. Genuino, M.D.G. de Luna, S.C. Capareda, *Sustain. Environ. Res.* 27 (2017) 7.
- [38] A. Hornung, M. Artmann, M. Ouadi, H. Jahangiri, R. Daschner, D. Liefertink, S. Capaccioli, A. Contini, S. Righi, D. Marazza, F. Baioli, I. Rapone, J. Zhou, M. Langley, C. Tuck, A. Claret and A. Grassi, in *European Biomass Conference and Exhibition Proceedings, 2021*, p. 8.
- [39] Q. Ouyang, J. Yao, N. Yang, Y. Wang, M. Yao, X. Liu, *Catal. Commun.* 120 (2019) 46.
- [40] Y.-K. Chen, C.-H. Lin, W.-C. Wang, *Energy* 201 (2020), 117655.
- [41] G. Xing, S. Liu, Q. Guan, W. Li, *Catal. Today* 330 (2019) 109.
- [42] M. Patel, A. Kumar, *Renew. Sustain. Energy Rev.* 58 (2016) 1293.
- [43] Y.-K. Chen, C.-H. Hsieh, W.-C. Wang, *Renew. Energy* 157 (2020) 731.
- [44] T. He, Y. Wang, P. Miao, J. Li, J. Wu, Y. Fang, *Fuel* 106 (2013) 365.
- [45] D.P. Upare, S. Park, M.S. Kim, Y.P. Jeon, J. Kim, D. Lee, J. Lee, H. Chang, S. Choi, W. Choi, Y.K. Park, C.W. Lee, *J. Ind. Eng. Chem.* 46 (2017) 356.
- [46] S. Izhar, S. Uehara, N. Yoshida, Y. Yamamoto, T. Morioka, M. Nagai, *Fuel Process. Technol.* 101 (2012) 10.
- [47] G.H.C. Prado, Y. Rao, A. de Klerk, *Energy Fuels* 31 (2017) 14.
- [48] S. Guo, Y. Wu, T. Jin, H. Wang, C. Dong, J. Zhang, M. Ding, *Fuel* 275 (2020), 117890.
- [49] F. Cheng, C.E. Brewer, *Renew. Sustain. Energy Rev.* 72 (2017) 673.
- [50] M. Bernabei, R. Reda, R. Galiero, G. Bocchinfuso, *J. Chromatogr. A* 985 (2003) 197.
- [51] P.P. Egeghy, L. Hauf-Cabalo, R. Gibson, S.M. Rappaport, *Occup. Environ. Med.* 60 (2003) 969.
- [52] I.A. Al-Nuaimi, M. Bohra, M. Selam, H.A. Choudhury, M.M. El-Halwagi, N. O. Elbashir 39 (2016) 2217.
- [53] T. Jia, S. Gong, L. Pan, C. Deng, J.-J. Zou, X. Zhang, *Fuel* 264 (2020), 116843.
- [54] M. Raza, Y. Qian, S. Wang, Y. Mao, J. Zhu, X. Lu, *Fuel* 266 (2020), 117081.
- [55] S. Blakey, L. Rye, C.W. Wilson, *Proc. Combust. Inst.* 33 (2011) 2863.
- [56] J. Yang, Z. Xin, Q. He, K. Corscadden, H. Niu, *Fuel* 237 (2019) 916.
- [57] A. Donkor, S. Nyarko, K.O. Asemanni, J.-C. Bonzongo, K. Kyeremeh, C. Ziwu, *Egypt. J. Pet.* 25 (2016) 473.
- [58] X. Zhang, W. Tang, Q. Zhang, Y. Li, L. Chen, Y. Xu, C. Wang, L. Ma, *Fuel* 215 (2018) 825.
- [59] T. Cordero-Lanzac, R. Palos, I. Hita, J.M. Arandes, J. Rodríguez-Mirasol, T. Cordero, J. Bilbao and P. Castaño, *Appl. Catal. B: Environ.* 239 (2018) 513.