



## Research article

# Biocrude from hydrothermal liquefaction of indigenous municipal solid waste for green energy generation and contribution towards circular economy: A case study of urban Pakistan

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## ABSTRACT

In this study, biocrude was successfully produced by the hydrothermal liquefaction of municipal solid waste collected from the landfill site of Lahore, the capital of Punjab, Pakistan, boasting a population of 12 million and an annual waste collection of 10 million tons. The hydrothermal liquefaction process was performed at reaction parameters of 350 °C and 165 bars with 15 min of residence time. The solid waste was found to have 78 % dry matter, 22 % moisture contents, 22.2 % ash, 22.69 MJ/kg higher heating value, 52.062 % C, 8.007 % H, 0.764 % N, and 39.164 % O. Non-catalytic process only produced 10.57 % oil, however when using the catalytic process, the biocrude yield improved to 17.61 %, with 22.61 % energy recovery for biocrude and 12.14 % for solids, when using 2 g dose of K<sub>2</sub>CO<sub>3</sub>. The resultant biocrude has a 28.61 MJ/kg higher heating value, having 60.28 % C and 9.28 % H. In contrast, the aqueous phase generated had 4.43 pH, 71.5 g/L TOC, and 1.35 g/L Total Nitrogen. TGA indicated that biocrude contains approximately

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80 % of volatile fractions of different fuels. The organic compounds having the six highest peak areas in GC-MS were Ethyl ether 25.74 %, 2-pentanone, 4-hydroxy-4-methyl 9.08 %, 2-propanone, 1,1-dimethoxy 5.62 %, Silane, dimethyl (docosyloxy) butoxy 5.08 %, 1-Hexanol, 2-ethyl 4.53 %, and. Phenol 4.07 %. This work makes the first-ever successful use of indigenous solid waste from a landfill dumping site in Lahore to successfully produce useful biocrude with aims of waste reduction and management, circular economy, and energy recovery.

## 1. Introduction

Climate change is resulting in the gradual rise of the temperature of our planet, and greenhouse gases (GHGs) are believed to be primarily responsible for this phenomenon [1]. One of the reasons for this is excessive resource consumption; if our current consumption patterns continue, we will need more than the equivalent of two Earths' worth of natural resources by 2030 and three planets' worth by 2050 [2]. Increased resource consumption is primarily caused by increase in the population, urban development and industrialisation, which consequently causes an increase in municipal waste and industrial waste generation, improper management of which may adversely impact human and environmental health [3]. As per the World Bank, municipal waste will increase to 3.4 billion tons by 2050 [4]. Considering the world, 70 % of solid waste is disposed of in landfills, 11 % is used for waste to energy, and 19 % is recycled [5]. It is pertinent to mention that out of the worldwide population of 7.6 billion, waste management facilities are not available for 3.5 billion people [6]. By 2050, around 5.6 billion population will be without waste management services [7]. Meanwhile, efforts have been taken to improve the waste management sector, which involves source segregation, where recyclable materials, organics, and non-recyclable items are sorted at the original source. This reduces the amount of waste going to landfills and allows for properly treating each waste stream [8].

Almost every country is trying to reduce GHG emissions to comply with the requirements of the United Nations Framework Convention on Climate Change (UNFCCC) [9]. Most landfill sites worldwide are not designed correctly, so these cannot minimise contamination. These landfills are the sources of land, water and air pollution [10]. Municipal Solid Waste (MSW) in landfills is arguably a very, if not the most, important origin of fine particulate matter known as PM<sub>2.5</sub>, which is the main reason due to which smog badly influences the air quality, and it also serves as a cause for a variety of heavy metals that degrade the probable risks for public health [11]. MSW comprises of organic and inorganic components. Inorganic fractions primarily consist of metals, paper, textiles, wood and plastic, whereas organic waste consists of biodegradable waste, which is more than 50 % of total waste [12]. The MSW composition is different worldwide, but for the most part it is biodegradable primarily, and non-biodegradable parts include kitchen glass, electronics, metal, and other materials [13].

Lahore City is one of Pakistan's oldest cities and the capital of the Punjab province, which covers an area of 1,772 square kilometres. The population is about 12.642 million, the second largest in the country, and the population growth rate in 2020 was 3.73 % [14]. Thirty years of land use change classification maps from 1990 to 2020 have shown a significant increase in built-up area and decreased open area and vegetation land in Lahore [15]. Based on the population and average household waste production (0.65 kg/person/day), the daily amount of household waste is estimated at 7,150 tons per day [16]. Lahore faces environmental issues, including solid waste and air pollution [17]. Currently, a total of 40,948 tons of CO<sub>2</sub>, 9855.7 tons of CH<sub>4</sub> and 0.2693 tons of NO<sub>2</sub> are released to the environment, combined with a Global Warming Potential (GWP) of approximately 248,000 tons for MSW management in Lahore City [18]. The MSW is collected in Lahore by Lahore Waste Management Company (LWMC) and transported to the Lakhodair landfill site having location coordinates 31.626647° N, 74.419218° E, situated in Lahore, Punjab, Pakistan. Solid waste and its

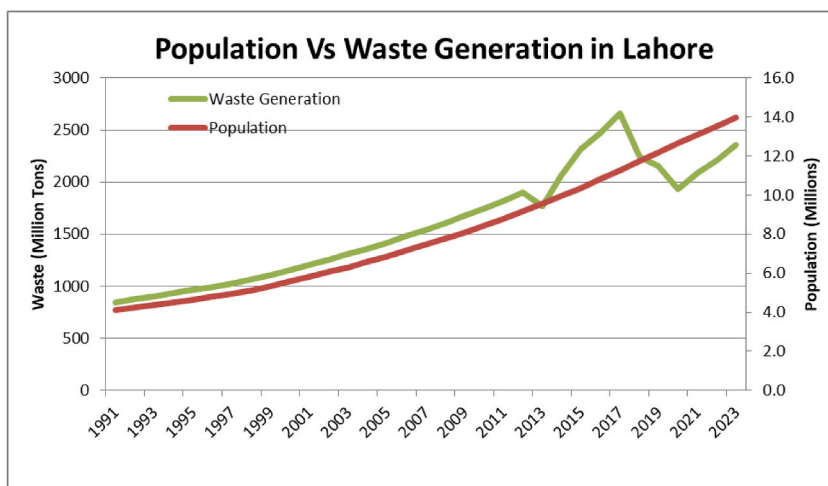


Fig. 1. Annual population and waste collection in Lahore, Punjab, Pakistan.

management are the main issues among the other problems in Lahore and Pakistan [19]. The waste management facilities are not well managed in Pakistan, which is also causing an increase in multiple diseases and environmental pollution [20]. Fig. 1 compares population growth and waste collection in Lahore district from 1991 to 2021. Lahore's population has continuously increased to 13.1 million in 2021 from 4.1 million in 1991, displaying a growth of 3.2 times. The waste collection increased continuously from 1991 to 2012. Then, it decreased in 2012 and 2013 because, at that time, the Lahore Waste Management Company (LWMC), the first waste collection company in Pakistan, was barely established. From 2013 to 2018, the waste collection increased, and after 2018, the LWMC stopped collecting construction and demolition waste due to high costs, and waste collection decreased. After 2020, waste collection increased again due to the restructuring of LWMC.

As the MSW in landfills is a significant source of GHGs, different waste reduction policies are implemented worldwide to cut these emissions [21]. Various waste minimization methods practised worldwide have their strengths and weaknesses. Harnessing energy from waste by incineration has the advantages of combined power and heat, a small footprint with low noise and odour generation, continuous supply, high yield, and system installation within city limits, thus significantly reducing transportation costs and the amount of waste going to landfills [22]. However, it also has certain drawbacks, such as potentially high concentrations of metals in the ash, maintenance requirements, increased operations, and particulate emissions [23]. Pyrolysis leads to the generation of gaseous or liquid fuels and its significant advantages are reduced flue gas treatment, production of higher quality fuels (coal, bio-oil, syngas), low NO<sub>x</sub> and SO<sub>x</sub> emissions, up to 80 % energy recovery, high-quality solid residue removal from syngas, high calorific value product (38 MJ/kg), and convenient transportation [13,24]. The principal negatives are coke generation from liquid products due to water, the high pyrolytic viscosity, the high cost of working capital, and increased fuel maintenance and water contents [25]. Gasification's benefits include fuel gas production, easy scalability, tailoring to any garbage, and removing up to 90 % of waste volume [26]. The disadvantages include high operating and investment costs, tar generation, immature and rigid technology, a significant failure risk, and corrosion of metal pipelines during intense reactions [13]. Anaerobic digestion is mainly suitable for biomass that contains a lot of water, produces more methane (CH<sub>4</sub>) and much less carbon dioxide (CO<sub>2</sub>), and is ideal for the production of organic materials and fertilisers [9,20]. The chief disadvantage is the slow degradation of lignin for a very long time, making it unsuitable for garbage containing little organic content [27].

In this article, Hydrothermal Liquefaction (HTL) has been selected for treating MSW and producing biocrude from it. The significant advantages of HTL are its suitability for wet biomass with low and high cell density and reduced water and oxygen contents of the final product, compared to that obtained from pyrolysis [28]. For wet feedstocks, the HTL process is considered as a favorable option because it reduces the requirement of fresh water for the process. However, the releasing of water i.e., organic loading water termed as aqueous phase is also a challenge that needs to be treated accordingly. Previously, the authors reported the utilization of aqueous phase for recycling within the process and consequently obtained the higher yield [29,30]. The latest work in HTL explores the use of different and innovative catalysts, promotion of continuous process, recycling of aqueous phase, introduction of machine learning, and upgrading the product fuels; nevertheless understanding and researching the changed feedstock remains one the most important aspect of HTL [31]. Samples of unsegregated MSW were collected from the actual Landfill site of the Metropolitan City of Lahore to get bio-crude and solid residue at optimised parameters of the HTL process. Furthermore, Acetone is used as a co-solvent to prevent the re-polymerisation of broken down compounds and monomers in MSW and for bettering the yield and quality of biocrude obtained from HTL. To the authors' best of the knowledge, this is the first-ever study performed to produce HTL biocrude from the Municipal Solid waste (MSW) of Lakhodair Landfill site, Lahore which is considered as metropolitan city (about 11 million populations). It is pertinent to mention that the daily generation capacity of MSW is more than 5500 tons/day in Lahore, and the disposal of MSW is core issue for Lahore Waste Management Company. Till to date, number of biomass materials have been used for the conversion to advanced biofuels via HTL process route. Lignocellulosic biomass, algae, and dry as well as wet feedstocks are used for said process. In light of that, our study – Conversion of indigenous MSW to biocrude through HTL process may play an important role for academia and stakeholders to put this renewable approach for waste minimization as well as energy recovery. This work can also be considered a parametric study to gain the baseline data for the transformation of MSW into oil or for energy recovery before the commissioning of a plant at the pilot scale, thus contributing towards the initial stages of such processes."

## 2. Materials and methods

### 2.1. MSW collection and pretreatment

The MSW samples were obtained from the dumping site at location coordinates 31.626647° N and 74.419218° E in Lahore, a metropolitan city of Punjab, Pakistan. LWMC is the government-owned organisation that manages this dumpsite. The samples of MSW employed in this investigation for HTL were collected from the above-mentioned LWMC dumping site using a simple random sampling technique. Solid waste of selected sites was mixed thoroughly from different time periods. The sample size (quantity) of solid waste was 1 kg. This collected sample was sealed in plastic packing and was kept at room temperature for lab analysis [32,33].

Most of the bio-organics, especially large sized, were separated through size-based separation from the other portion i.e., bio-inorganic, of the MSW [34]. Visual inspection showed that this MSW has noteworthy quantities of plastic packaging waste, garden waste, fabric remnants, inorganic materials (such as glass), and inert materials (such as stones and construction debris). The MSW was sieved so that the ash contents and inorganic matter were reduced to minimum possible levels. Thereafter, it underwent shredding into smaller pieces in the 4.75 mm–1.5 mm size range.

## 2.2. MSW characterization

MSW's CHNS contents were analysed using a Thermo-Flash 2000 elemental analyser. The proximate analysis of MSW was performed in an automatic multi-sampler Thermogravimetric Analyzer (TGA-2000A, Navas Instruments) by drawing 0.8 g as sample, according to ASTM E1131-08 method (ASTM 2021). The mass loss profiles for MSW and the HTL bio-crude were attained using an SDTQ-600 TGA (TA Instruments) at a heating rate of  $10\text{ }^{\circ}\text{C min}^{-1}$  in inert ( $\text{N}_2$ ) ambience ( $100\text{ mL min}^{-1}$ ). IKA C2000 bomb calorimeter was used for determining the higher heating value (HHV) of MSW.

## 2.3. Solvents and chemicals

Distilled water and water with other co-solvents, such as glycerol and tetralin, have been used as solvents in this study. All chemicals were of analytical grades obtained from Sigma Aldrich.

## 2.4. Experimental setup

All experiments and sample analysis for MSW and HTL biocrude were performed by the authors during the research AAU. Energy Laboratory, Aalborg University Denmark. The HTL experimentation was done using four exactly similar high-pressure cylindrical autoclaves operating in batch mode [33]. The picture of the experimental setup for the HTL process is given in Fig. 2. Each device had been designed at reaction pressure and temperature of 220 bar and  $400\text{ }^{\circ}\text{C}$ , respectively. All cylinders were designed at interval volumes of 200 mL, and were fabricated from stainless steel (SS-304). Each cylinder's main body was firmly closed, sealed and covered using a bolted steel flange. Full details of the HTL experimental setup can be found in another of our published works [35].

## 2.5. Experimental procedures

Hydrothermal liquefaction (HTL) of municipal solid waste (MSW) was conducted at  $350\text{ }^{\circ}\text{C}$  and at approximately 165 bar pressure. The holding time, excluding heating process, lasted 15 min, and it was chosen to meet specific experimental objectives. Typically, lignocellulosic feedstocks are processed under subcritical ( $350\text{ }^{\circ}\text{C}$ ) and supercritical ( $400\text{ }^{\circ}\text{C}$ ) conditions, with intermediate

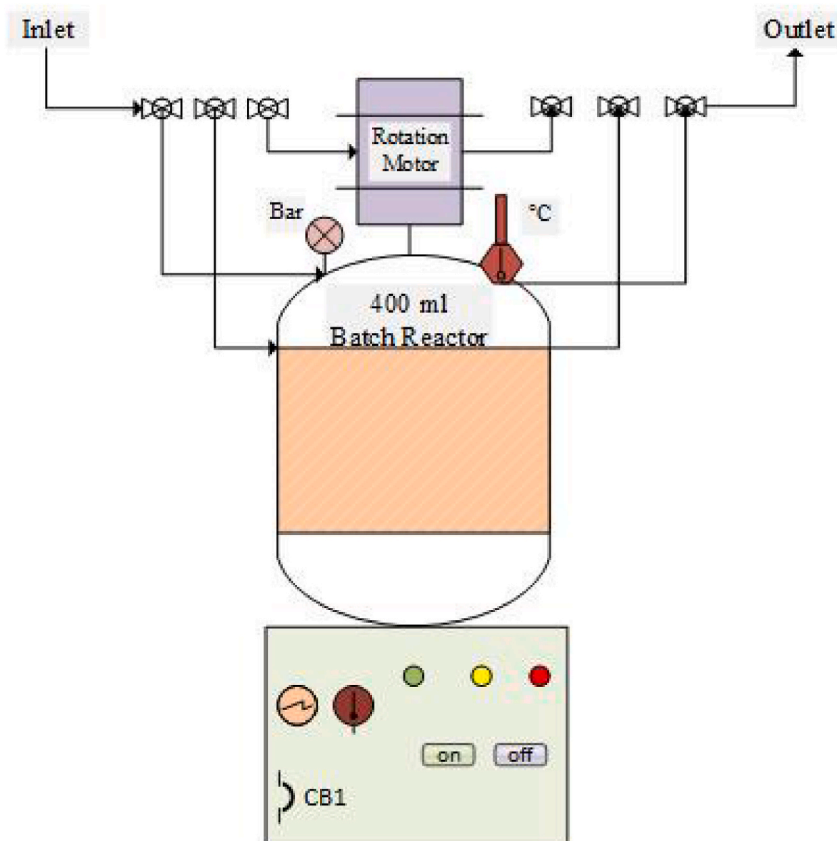


Fig. 2. Experimental setup for the HTL process.

temperatures generally yielding higher biocrude yields [30,33,36].

However, at higher temperatures such as under supercritical conditions, increased depolymerization occurs due to higher reaction rates. This enhanced depolymerization results in higher quality biocrude characterized by higher heating values, lower oxygen content, and reduced viscosity. A 400 mL autoclave was loaded with 100 g of feed consisting of 25.65 g dry biomass and 74.35 g distilled water.  $K_2CO_3$  was chosen as the catalyst for this experimental study. In HTL processes, two main categories of catalysts have been extensively studied: homogeneous and heterogeneous. Homogeneous catalysts, including alkali salts like  $K_2CO_3$ ,  $NaCO_3$ , and potassium bicarbonate, significantly enhance biocrude yield by favourably accelerating the water-gas shift reaction. Moreover, these catalysts are considered environmental friendly and economically viable. Literature indicates that during HTL,  $K_2CO_3$  reacts with water to form bicarbonate and hydroxide, which in turn enhances the biocrude yield. Potassium salts also promote biocrude repolymerization, thereby increasing its non-polarity and facilitating separation from water. Additionally,  $K_2CO_3$  does not cause corrosion and is suitable for commercial-scale HTL plants, especially considering its widespread availability.

It has been reported that  $K_2CO_3$  catalysts contribute to higher product yields and improved biofuel quality during rapid hydrothermal liquefaction, particularly in processes involving  $CO_2$ -tolerant microalgae [37]. Examples include the conversion of phycocyanin to biocrude through integrated isothermal/fast HTL and aqueous phase recirculation [38], as well as the efficient and fast HTL of microalgae and sludge with waste aqueous phase recycling for microalgal growth [39].

After the reaction, the relevant separation methods, as shown in Fig. 3 were used to recover the bio-crude, solid, gas, and residual aqueous phases. Specifically, During the HTL experiment procedure, acetone was used to rinse the reactor for the collection and separation of the products by adopting the methodology mentioned by researchers [29,40,41].

The collected mixture was filtered and then processed by drying the solids in an oven at 105 °C until constant weight was achieved for mass balance determination. Subsequently, acetone was removed via vacuum evaporation using a rotary evaporator. Dichloromethane was added to the remaining mixture to extract the biocrude, which was then evaporated to yield the final product, i.e., biocrude. The weight of the biocrude was measured to calculate the yield. Gas and water phases were collected for further analysis, and for complete mass balance closure. Throughout the reaction, main operational parameters of temperature and pressure were closely examined. After the completion of HTL process, the autoclave was cooled down to achieve room temperature.

This study investigates the impact of catalyst specifically alkali catalyst on the conversion of indigenous municipal solid waste biomass to biocrude by using HTL process. Use of alkali catalyst results in enhancing biocrude yield in terms of lignocellulosic feedstocks, however, the evaluation of reaction environment in case of mixture of Municipal solid waste in presence and absence of alkali catalyst is objective of this study [29,30,32,42–48].

## 2.6. Products analysis

GCMS of make Shimadzu, model Tracera GC – 2010 Plus, was used to determine gas phase composition. In which, the GC had a micro-packed column of make having length 2.0 m and ID 0.53 mm using a BID (barrier discharge ionisation) detector. The temperature in oven was maintained at 85 °C. The total flow of solvent is 803 mL min<sup>-1</sup>, with 1: 200 as the split ratio, and the pressure was set as flow control mode (400 kPa). The injection volume was 0.1 mL. Total organic carbon (TOC) measurements and total nitrogen (TN) analysis in the aqueous phase were determined using appropriate kits and a spectrophotometer of make Hach & Lange, model

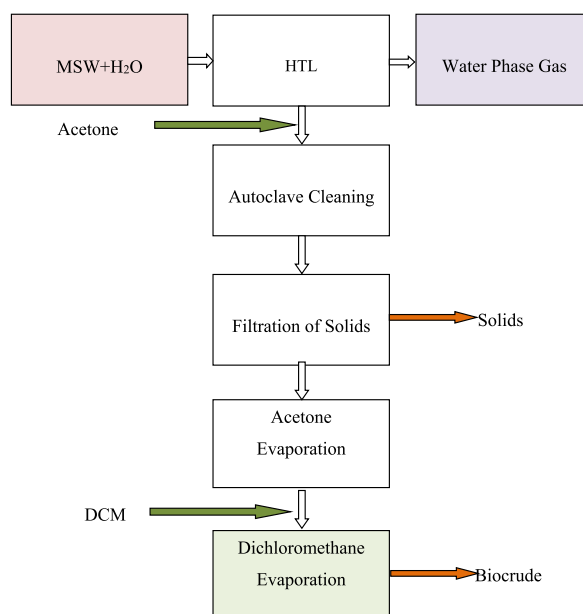


Fig. 3. Steps involved in products recovery from solid waste.

DR3900. Elemental compositions of solids and biocrude were determined using an elemental analyser (PerkinElmer, 2400 Series II CHNS/O). Gas chromatography-mass spectrometry (GC-MS) also qualitatively characterised several solids and crudes. Analyses were measured on a Thermo-Scientific gas chromatograph (trace 1300) that had been equipped with a capillary column of make Agilent Technologies, 30 m length, 0.25 mm ID, and 0.25  $\mu\text{m}$  film thickness, and connected to a mass spectrometer (ISQ QD). TA Discovery TGA was used to determine the oil samples' degradation extent. To check degradation, the oil samples at room temperature were heated to 775  $^{\circ}\text{C}$  at a heating rate of 10  $^{\circ}\text{C min}^{-1}$ .

### 3. Results and discussion

#### 3.1. MSW characterization

MSW obtained from the Lahore dump site was used as raw material in this work. After preliminary screening, the proportion of the sand and dirt particles was around 5 %, the plastic part (mainly polyethene bags, LDPE) around 25.85 %, and the textile part (especially cotton cloth) was 7.63 %. In contrast, the major proportion of biodegradable material (paper, garden waste, fruit and vegetable residues) was 61.52 %. The source material was crushed and shredded into smaller pieces, as visible in Fig. 4, and then comminuted into slurries. The general composition of biomass such as Dry matter, Moisture content, Ash, and Higher Heating Value are considered as the primary indicators generally used for Biomass when performing HTL process [42,43,45]. However, the organic composition of biocrude has been highlighted in Table 6 and the characterization of bio-oil is also reflected by TGA analysis reported in Fig. 6. The proximate analysis, i.e., moisture and ash content and HHV of MSW determined using oven, furnace and bomb calorimeter, respectively, are given in Table 1. Additionally, the ultimate or elemental analysis of the MSW in terms of percentages of Carbon, Hydrogen, Nitrogen and Oxygen is shown in Table 2.

#### 3.2. HTL of Lahore municipal solid waste

The potential and analysis of biocrude are dependent on the type of solid waste utilised [49]. Fig. 5 shows the yield of crude and solid after the HTL process at 350  $^{\circ}\text{C}$ . Oil and solid results differ for non-catalytic (NC) and catalytic (CAT) processes, while using  $\text{K}_2\text{CO}_3$  of 2 g dose for 100 g slurry. It can be seen from Fig. 5, that the solid yields for NC and CAT are 54.17 %, and 37.80 %, respectively. On the other hand, the oil yields for NC and CAT are 10.52 %, and 17.6 %, respectively. It has been observed that solid yield decreased from 54.17 % to 37.80 % with CAT, and oil yield increased from 10.52 % to 17.61 % with CAT. The yields and corresponding Standard Deviations are summarised in Table 3. So, the Lahore MSW has the potential of 18 % biocrude, which is well within the range of yields found in literature for MSW, i.e., 15–24 % [31]. As reported in section 3.2, Fig. 5. And Table 3, the oil yield reported as (10.572%- without Cat) and (17.615%-with Cat). That seems that alkali catalyst enhances the biocrude yield and reduce solid yield [30,50–52].

However, overall low yield may be due to high ash containing available in biomass that was 22.20 % reported in Table 1. Another probable reason that may have decreased the biocrude yield is the incidence of the condensation reaction in the solid phase of residue, that enhanced overall solid concentration and declined biocrude oil yield, as well as the presence of inorganics or trace materials that may act as barrier for migration of carbon content resulting in low biocrude yield. Furthermore, It may also be indicating a higher degree of repolymerization, so that we get more solids at product stream. Wang et al. also reported that maximum quantities of solid were formed in deoxyliquefaction during the conversion of biomass to biocrude via HTL process [53].



Fig. 4. MSW Feedstock before (left side) and after (right side) crushing for slurry.

**Table 1**  
Proximate analysis and HHV of MSW.

Parameter	Value
Dry matter (%)	78.00
Moisture content (%)	22.00
Ash (%)	22.20
Higher heating value (MJ/KG)	22.69

**Table 2**  
Elemental analysis of municipal solid waste.

Elemental analysis in Percent %	Value
Carbon (C)	52.062
Hydrogen (H)	8.007
Nitrogen (N)	0.764
Oxygen (O)	39.164

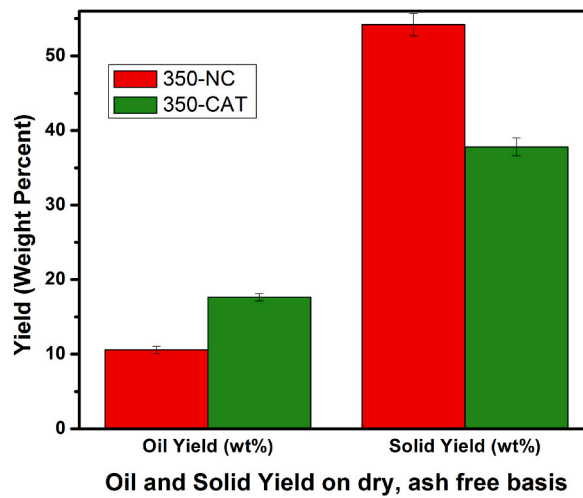


Fig. 5. Oil and solid yield on a dry, ash-free basis for 350-NC and 350-CAT processes.

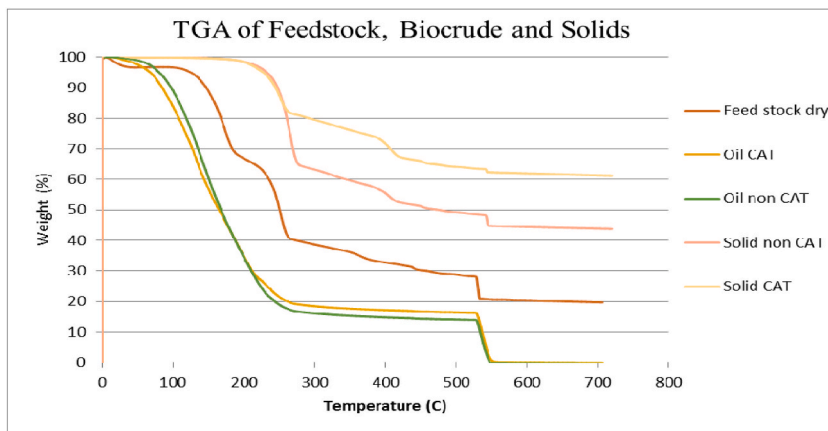


Fig. 6. TGA curves of the feedstock, and H.T.L. biocrudes and solids.

**Table 3**  
Product yield of oil and solids in HTL.

Title	350 without CAT.	350-CAT
Average Oil Yield (wt.%)	10.572	17.615
Average Solid Yield (wt.%)	54.175	37.804
SD. Oil	1.846	2.138
SD. Solid	1.025	1.498

### 3.3. Elemental composition of biocrude and solids

The elemental composition, atomic ratios, and higher heating values of biocrude and solids obtained at both catalytic and non-catalytic are mentioned in Table 4. It was observed that the carbon content in biocrude, as well as solids, was increased in the case of the non-catalytic condition. In connection with that, the oxygen percentage was found to be slightly higher with the addition of a catalyst. However, recovery of energy in the CAT biocrude was higher than the biocrude produced without catalyst. It was concluded that the presence of a catalyst could enhance the overall energy recovery in the biocrude [54]. The maximum energy recovery in the biocrude in case of the addition of catalyst was also reported by other researchers by converting the different feedstocks through HTL, for example, higher energy recovery (77.7 %) in biocrude at 350 °C catalytic condition is noted as compared to non-catalytic condition (74.3 %) at same process temperature during the HTL of sewage sludges [43,46]. In connection with that, energy recovery in the biocrude can also be increased by utilising the organic-rich water (aqueous phase) within the process during the HTL of bio-pulp [55], or performing Co-HTL of wet feedstocks at different mixture ratios [56].

### 3.4. Characterisation of aqueous phase

The hydrothermal liquefaction process famously utilizes water as a reaction medium, yielding an aqueous phase downstream [57]. This aqueous phase is recognized as an additional energy source due to its content of total organic carbon (TOC), total nitrogen (TN), and other nutrients, which require efficient treatment. Analysis of the aqueous phase from both HTL conditions included pH, TOC, and TN measurements, detailed in Table 5. The pH of the aqueous phase exhibited significant variation, consistently showing an acidic nature under both conditions. This acidity likely stems from the hydrolysis of sugar compounds during the process, leading to the production of monomeric sugars that subsequently decompose into organic acids. Variations in pH are also influenced by operating conditions and the composition of the feedstock used in the process [58,59]. It was observed that the loss of TOC was higher (71.5 g/L) in the case of a catalyst's addition, which may be due to the shifting of more carbon in the presence of a catalyst [29,60,61]. Pedersen et al. also reported a higher value of TOC in the aqueous phase by the co-HTL of lignocellulosic biomass [62]. At the other end, TN in the aqueous phase was found between 1.35 and 2.78 g/L. That may be because, in actuality, the feedstock used in this study, i.e., MSW, has low nitrogen content, as mentioned in Table 2. Low TN is favorable in the aqueous phase so that organic-rich water can be recirculated. For the scale-up of the HTL plant, a detailed study is recommended to investigate the effect of aqueous phase recirculation by using MSW so that organic-rich water can be utilised efficiently and reduce the demand for freshwater consumption. Other researchers have also suggested using HTL's aqueous phase for recirculation to enhance the process efficiency [63].

### 3.5. TGA of MSW solid waste feedstock and products

TGA was used to analyse the weight loss and estimate the quantity of organic matter that was to be converted into biocrude. The thermogravimetric curves of MSW feedstock and biocrudes obtained are illustrated in Fig. 6. It was observed from these curves that the MSW used in this study contains about 20–30 % carbon along with 70–80 % volatile matter, which reflects the presence of organic matter, which will be transformed into biocrude and other products. This indicates the opportunity for processing MSW to produce biocrude via the HTL route. TGA revealed that biocrude obtained at both catalytic and non-catalytic conditions contains approximately 80–82 % of volatile fractions of different fuel cuts comprising gasoline, jet fuel, diesel, and maritime fuel. The reductions are based on the volatility and temperature co-relation reflected during the TGA. Volatile fraction below 180 °C shows the proportion of gasoline fuel, and 180–260 °C indicates the jet fuel fraction. However, obtained volatile fractions at 260–350 °C reflect the identification of

**Table 4**  
Elemental composition, heating values and energy recovery of H.T.L. products.

Sample	C (%)	H (%)	N (%)	O (%)	H/C	O/C	HHV (MJ/kg)	ER (%)
C.A.T. Biocrude	60.28	9.20	3.36	27.17	0.34	1.83	28.61	22.21
NON-CAT Biocrude	62.82	9.39	2.94	24.86	0.30	1.79	30.15	14.05
MSW CAT Solid	31.03	4.24	1.38	63.36	1.64	1.54	6.46	12.14
MSW NC Solid	43.12	6.21	1.10	49.57	1.73	0.86	15.49	20.45



**Table 5**  
Characterisation of hydrothermal liquefaction-aqueous phase.

	NC.	C.A.T.
pH	3.85	4.43
Total organic carbon (g/l)	36.8	71.5
Total nitrogen (g/l)	2.78	1.35

diesel fuel. After 350–575 °C, the curve shows maritime fuel fractions.

Additionally, after 575 °C, the remaining fractions are considered as properties of asphalt, residue, etc. A similar identification of fuel cuts using TGA technique can be found elsewhere in the literature [64,65]. Furthermore, a large amount of heavy residue, asphalt, was noticed by analysing the curves of solids at both conditions. The amount of this heavy residue can be minimised by improving the quality of HTL biocrude by applying the upgrading stage.

### 3.6. Analysis of oil by GCMS

The presence of organic compounds in obtained biocrudes was identified using the GCMS technique at boiling point under 300 °C. The comprehensive information regarding the produced compounds' names, retention times (RT), and peak area contributions of biocrude samples under both conditions is provided in Table 6. The compounds were classified into six classes namely ketones, aldehydes, oxygen aromatics, alkanes, alcohols, and nitrogen containing compounds. The feedstock i.e., MSW used in this study contains higher amount of oxygen (39.164 %), which may be the one of reasons having higher number of ketones and oxygen aromatics [66]. It was also evident that the peak area of ketones at 350 °C is boosted by addition of catalyst. Among ketones, 2-Propanone, 1, 1-dimethoxy and 2-Cyclopenten-1-one, 3,4,4-trimethyl covered the higher area. The feedstock (MSW) is a mixture containing variable materials, which may also contain carbohydrates that start to degrade and turn into acetic acid and other different acids, visible in biocrude through GCMS data [67]. GCMS did not detect carboxylic acid and ester after adding catalyst. However, phenol and p-Cresol were found in comparatively higher concentrations among phenolic compounds. The GCMS results showed that the biocrudes at both conditions have low nitrogen-containing compound concentrations. The reason may be a lower percentage of nitrogen (0.764 %) in the feedstock. The nitrogenous compound 9-Octadecenamide was only found in biocrude at non-catalytic conditions. The decreased concentration of N-containing compounds reflects one of the excellent quality aspects of HTL biocrude. The higher concentration of nitrogen-containing compounds is unfavourable because, at one side, it contaminates the atmosphere through the emissions of nitrogenous gasses during biocrude combustion. On the other side, it leads to increase in viscosity, creating instability of HTL biocrude [68]. Therefore, upgrading HTL biocrude reduces the concentration of heteroatoms and transforms the biocrude into a drop-in fuel.

## 4. Conclusions

This study investigates the hydrothermal liquefaction (HTL) of indigenous municipal solid waste (MSW) as a promising method for biofuel production and waste management. The experimentation was conducted at 350 °C and 165 bar with a residence time of 15 min. When experimenting without a catalyst, biocrude yield and energy recovery were suboptimal. However, the addition of 2 g K<sub>2</sub>CO<sub>3</sub> as a catalyst dramatically enhanced the biocrude yield to 17.61 %, with energy recovery reaching 22.61 % for biocrude and 12.14 % for solids. The resultant biocrude exhibited a higher heating value of 28.61 MJ/kg, and consisted 60.28 % carbon and 9.28 % hydrogen. Moreover, the aqueous phase produced had a pH of 4.43 and total organic carbon (TOC) concentration of 71.5 g/L. The biocrude contained approximately 80–82 % volatile fractions akin to conventional fuels like gasoline and kerosene, underscoring its potential as a viable alternative. The study also highlighted the effectiveness of aqueous phase recirculation in boosting biocrude yield while reducing freshwater consumption, thereby enhancing the overall process efficiency and economic viability of continuous HTL plants. Critical operational parameters including temperature, catalyst presence, retention time, and composition significantly influenced process performance in terms of biocrude quality and yield.

Challenges such as the pumpability of the dry lignocellulosic feedstock and management of chlorine to mitigate reactor slugging were identified for future investigation. Additionally, the necessity for post-HTL treatments like hydrotreating to further enhance biocrude quality was emphasized. The research proposes a dual benefit: addressing waste management issues and contributing to renewable biofuel production. It suggests potential economic benefits for stakeholders, particularly in urban sectors of developing countries like Pakistan, where MSW management remains a pressing concern. Future research directions include exploring aqueous phase recirculation and co-HTL of MSW to optimize biocrude production in terms of yield, quality, and energy recovery. Ultimately, this technology aligns with Sustainable Development Goals (SDGs), particularly SDG 7 (Affordable and Clean Energy) and SDG 12 (Responsible Consumption and Production), by converting waste into energy and reducing reliance on imported crude oil, thus fostering a circular economy approach to resource utilization. This study lays the groundwork for scaling up HTL processes and warrants detailed techno-economic evaluations to facilitate broader implementation and impact assessment.

### CRedit authorship contribution statement

**Syed Imran Hussain Shah:** Formal analysis. **Tahir Hussain Seehar:** Formal analysis. **Muhammad Raashid:** Investigation. **Rab Nawaz:** Supervision. **Zafar Masood:** Writing – review & editing. **Sara Mukhtar:** Validation. **Thamer Abdulhameed Al Johani:**

**Table 6**  
Main organic compounds detected in the biocrude, as identified by GC-MS.

No	RT (min)	Compounds Name	Peak area %	
			350 non-CAT	350 CAT
<b>Ketones Aldehydes</b>				
1	2.07	2-Propanone, 1,1-dimethoxy	5.45	5.62
2	8.92	2-Cyclopenten-1-one, 2-methyl	ND	2.17
3	9.59	Cyclopentanone, 2-ethyl	ND	1.24
4	10.12	2-Cyclopenten-1-one, 3-methyl	ND	1.37
5	10.65	2-Cyclopenten-1-one, 3,4-dimethyl	ND	1.26
6	10.74	2-Cyclopenten-1-one, 2,3-dimethyl	1.62	3.29
7	11.49	2-Cyclopenten-1-one, 2,3-dimethyl	1.94	ND
8	11.50	2-Cyclopenten-1-one, 2,3-dimethyl	ND	3.76
9	11.91	2-Cyclopenten-1-one, 2,3,4-trimethyl	ND	1.16
10	12.35	5-Ethyl-2-furaldehyde	2.69	ND
11	12.37	2-Cyclopenten-1-one, 3,4,4-trimethyl	ND	3.97
12	13.07	2-Cyclopenten-1-one, 3-(1-methylethyl)-	ND	1.22
13	14.00	2-Cyclopenten-1-one, 2,3,4,5-tetramethyl	2.36	ND
14	14.01	2-Cyclopenten-1-one, 2,3,4,5-tetramethyl	ND	2.84
15	16.11	1(2H)-Naphthalenone	ND	1.09
16	20.48	2-Nonadecanone	1.64	ND
17	22.05	2-Pentadecanone, 6,10,14-trimethyl	1.77	ND
18	22.63	2-Heptadecanone	2.31	ND
19	29.52	4,11-Dispiro(2'-cyclobutanone) tricyclo, hexamethyl	1.73	ND
<b>Carboxylic acid, Ester</b>				
20	22.85	Hexadecanoic acid, methyl ester	1.38	ND
21	23.23	n-Hexadecanoic acid	6.82	ND
22	24.96	trans-13-Octadecenoic acid	3.67	ND
23	26.27	cyclic butylboronate	2.04	ND
<b>Aromatics</b>				
24	10.45	Phenol	2.71	ND
25	10.47	Phenol	ND	4.07
26	11.75	Phenol, 2-methyl	1.49	ND
27	11.77	Phenol, 2-methyl	ND	1.47
28	12.09	Phenol, 4-methyl	2.46	ND
29	12.11	p-Cresol	ND	2.48
30	13.14	Phenol, 2-ethyl	ND	1.07
31	13.57	Phenol, 2-ethyl	3.11	ND
32	13.58	Phenol, 4-ethyl	ND	2.51
33	14.49	Phenol, 4-(1-methylethyl)-	1.59	1.54
34	16.74	Benzoic acid, pentadecyl ester/1,3-Benzenediol, 4-ethyl	1.31	ND
35	16.81	1H-Indole, 6-methyl	1.38	ND
36	16.82	1H-Indole, 3-methyl	ND	1.63
37	18.05	Benzonitrile, 2,4,6-trimethyl	ND	1.23
38	18.17	1H-Indole, 2,3-dimethyl	1.87	ND
39	18.18	1H-Indole, 2,3-dimethyl	ND	1.74
40	18.34	Phenol, 2,4-bis(1,1-dimethylethyl)-	ND	1.13
41	26.15	cyclic phenylboronate	7.31	ND
<b>Alkanes</b>				
42	2.18	Ethyl ether	24.44	25.74
43	27.10	Heptacosane	2.46	ND
44	27.90	Octacosane	1.7	ND
45	28.67	Heptacosane	2.45	ND
46	29.38	Silane, dimethyl(docosyloxy)butoxy	ND	2.4
47	29.42	Hentriacontane	1.98	ND
48	29.44	Silane, dimethyl(docosyloxy)butoxy	ND	5.08
<b>Alcohols</b>				
49	7.53	2-Pentanone, 4-hydroxy-4-methyl	ND	9.08
50	11.28	2-Ethyl-1-hexanol	3.1	ND
51	11.29	1-Hexanol, 2-ethyl	ND	4.53
52	22.06	1-Dodecanol, 3,7,11-trimethyl	ND	1.17
<b>Nitrogen containing compounds</b>				
53	17.56	Bicyclo [2.2.2]oct-5-ene-2-carbonitrile	ND	1.66
54	25.31	Hexadecanamide, Dodecanamide	1.32	ND
55	26.89	9-Octadecenamide, (Z)-	3.87	2.47

Project administration. **Anthony Doyle:** Methodology. **Muhammad Nasir Bashir:** Funding acquisition. **Muhammad Mahmood Ali:** Validation. **M.A. Kalam:** Methodology.

### Declaration of competing interest

I have attached the manuscript entitled: Biocrude from Hydrothermal Liquefaction of Indigenous Municipal Solid Waste for Green Energy generation and contribution towards Circular Economy: A Case Study of Urban Pakistan. Imran Naqvi(PhD), Tahir Hussain Seehar(PhD), Muhammad Raashid(PhD), Rab Nawaz(PhD), Zafar Masood(PhD), Sara Mukhtar(MSc), Thamer Abdulhameed Al Johanif(BSc), Anthony Doyle(MSc), Muhammad Nasir Bashir(PhD), Muhammad Mahmood Ali(PhD), M.A. Kalam(PhD), have submitted a research paper for possible publication in Journal of Fuel have no conflict of interest. All the authors who contributed to the work have been mentioned, and they reviewed the manuscript. The work is the author's work and has not been submitted to any journal. Moreover, there is no ethical issue with the manuscript.

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### References

- [1] S.I.H. Shah, et al., Sustainability assessment of modern urban transport and its role in the reduction of greenhouse gas emissions: a case study of Metro Bus System (MBS), Lahore, Kuwait journal of science 47 (2) (2020).
- [2] M. Esposito, T. Tse, K. Soufani, Is the circular economy a new fast-expanding market? Thunderbird Int. Bus. Rev. 59 (1) (2017) 9–14.
- [3] S. Khan, et al., Technologies for municipal solid waste management: current status, challenges, and future perspectives, Chemosphere 288 (2022) 132403.
- [4] S.J. Klees, J. Samoff, N.P. Stromquist, The World Bank and Education: Critiques and Alternatives, vol. 14, Springer Science & Business Media, 2012.
- [5] J.M. Twenge, C. McAllister, T.E. Joiner, Anxiety and depressive symptoms in US Census Bureau assessments of adults: trends from 2019 to fall 2020 across demographic groups, J. Anxiety Disord. 83 (2021) 102455.
- [6] T.W. Bank, International Debt Statistics 2022, World Bank Publications, 2021.
- [7] M.P. Choudhary, V. Garg., Causes, consequences and control of air pollution, in: All India Seminar on Methodologies for Air Pollution Control, Held at MNIT, 2013.
- [8] A. Majeed, S.A. Batool, M.N. Chaudhry, Environmental quantification of the existing waste management system in a developing world municipality using EaseTech: the case of Bahawalpur, Pakistan, Sustainability 10 (7) (2018) 2424.
- [9] M.J.S. Zuberi, S.F. Ali, Greenhouse effect reduction by recovering energy from waste landfills in Pakistan, Renew. Sustain. Energy Rev. 44 (2015) 117–131.
- [10] S. Mukherjee, et al., Contemporary environmental issues of landfill leachate: assessment and remedies, Crit. Rev. Environ. Sci. Technol. 45 (5) (2015) 472–590.
- [11] A.B. Attiq, et al., Urban air quality nexus: PM<sub>2.5</sub> bound-heavy metals and their alarming implication for incremental lifetime cancer risk, Pollution 10 (1) (2024) 580–594.
- [12] O. Romero-Hernández, S. Romero, Maximizing the value of waste: from waste management to the circular economy, Thunderbird Int. Bus. Rev. 60 (5) (2018) 757–764.
- [13] S. Nanda, F. Berruti, A technical review of bioenergy and resource recovery from municipal solid waste, J. Hazard Mater. 403 (2021) 123970.
- [14] M. Nasar-u-Minallah, et al., Spatio-temporal analysis of urban expansion and future growth patterns of Lahore, Pakistan, Geography, Environment, Sustainability 14 (3) (2021) 41–53.
- [15] S. Shah, A. Ahmed, R. Nawaz, Analysis of land use change and population growth using geo-spatial techniques in Lahore-Pakistan, Pakistan J. Sci. (2) (2021) 490.
- [16] M. Azam, et al., Status, characterization, and potential utilization of municipal solid waste as renewable energy source: Lahore case study in Pakistan, Environ. Int. 134 (2020) 105291.
- [17] H.M. Malhi, et al., Monitoring of ambient air pollution in Lahore city, Pakistan Journal of Emerging Science and Technologies (PJEST) 4 (3) (2023) 1–9.
- [18] I. Amir, et al., Catalytic Ozonation for the Treatment of Municipal Wastewater by Iron Loaded Zeolite A, vol. 152, 2019, pp. 108–115.
- [19] M.S. Korai, et al., Comparison of MSW management practices in Pakistan and China, J. Mater. Cycles Waste Manag. 22 (2020) 443–453.
- [20] M.S. Korai, R.B. Mahar, M.A. Uqaili, The feasibility of municipal solid waste for energy generation and its existing management practices in Pakistan, Renew. Sustain. Energy Rev. 72 (2017) 338–353.
- [21] C. Yaman, I. Anil, O. Alagha, Potential for greenhouse gas reduction and energy recovery from MSW through different waste management technologies, J. Clean. Prod. 264 (2020) 121432.
- [22] M. Möslinger, G. Ulpiani, N. Vetter, Circular economy and waste management to empower a climate-neutral urban future, J. Clean. Prod. 421 (2023) 138454.
- [23] Y. Xue, X. Liu, Detoxification, solidification and recycling of municipal solid waste incineration fly ash: a review, Chem. Eng. J. 420 (2021) 130349.
- [24] Y. Zhang, et al., Investigation of the evolved pyrolytic products and energy potential of Bagasse: experimental, kinetic, thermodynamic and boosted regression trees analysis, Bioresour. Technol. 394 (2024) 130295.
- [25] R. Saengsuriwong, et al., Biocrude oil production via hydrothermal liquefaction of food waste in a simplified high-throughput reactor, Bioresour. Technol. 341 (2021) 125750.
- [26] D. Yu, et al., Biofuel production by hydro-thermal liquefaction of municipal solid waste: process characterization and optimization, Chemosphere 328 (2023) 138606.
- [27] S. Sethupathy, et al., Lignin valorization: status, challenges and opportunities, Bioresour. Technol. 347 (2022) 126696.
- [28] H. Shahbeik, et al., Biomass to biofuels using hydrothermal liquefaction: a comprehensive review, Renew. Sustain. Energy Rev. 189 (2024) 113976.
- [29] A.A. Shah, et al., Bio-crude production through aqueous phase recycling of hydrothermal liquefaction of sewage sludge, Energies 13 (2) (2020) 493.
- [30] T.H. Seehar, et al., Biocrude production from wheat straw at sub and supercritical hydrothermal liquefaction, Energies 13 (12) (2020) 3114.
- [31] M. Usman, et al., From biomass to biocrude: innovations in hydrothermal liquefaction and upgrading, Energy Convers. Manag. 302 (2024) 118093.
- [32] K. Kohansal, et al., Hydrothermal liquefaction of pre-treated municipal solid waste (biopulp) with recirculation of concentrated aqueous phase, Biomass Bioenergy 148 (2021) 106032.
- [33] A.A. Shah, et al., Hydrothermal liquefaction of high ash containing sewage sludge at sub and supercritical conditions, Biomass Bioenergy 135 (2020) 105504.
- [34] D. Mahesh, et al., Hydrothermal liquefaction of municipal solid wastes for high quality bio-crude production using glycerol as co-solvent, Bioresour. Technol. 339 (2021) 125537.
- [35] R. Saengsuriwong, et al., Conversion of tobacco processing waste to biocrude oil via hydrothermal liquefaction in a multiple batch reactor, Clean Technol. Environ. Policy 25 (2) (2023) 397–407.

- [36] J. Akhtar, N.A.S. Amin, A review on process conditions for optimum bio-oil yield in hydrothermal liquefaction of biomass, *Renew. Sustain. Energy Rev.* 15 (3) (2011) 1615–1624.
- [37] B. Cao, et al., Response surface optimization of product yields and biofuel quality during fast hydrothermal liquefaction of a highly CO<sub>2</sub>-tolerant microalgae, *Sci. Total Environ.* 860 (2023) 160541.
- [38] L. Qian, et al., Phycocyanin to biocrude via the integration of isothermal/fast hydrothermal liquefaction and aqueous phase recirculation: reaction products and process analyses, *Fuel* 332 (2023) 126226.
- [39] C. Yuan, et al., Integrated route of fast hydrothermal liquefaction of microalgae and sludge by recycling the waste aqueous phase for microalgal growth, *Fuel* 334 (2023) 126488.
- [40] T.H. Pedersen, L.A. Rosendahl, Production of fuel range oxygenates by supercritical hydrothermal liquefaction of lignocellulosic model systems, *Biomass Bioenergy* 83 (2015) 206–215.
- [41] F. Conti, et al., Biocrude production and nutrients recovery through hydrothermal liquefaction of wastewater irrigated willow, *Biomass Bioenergy* 118 (2018) 24–31.
- [42] K. Sharma, et al., Co-hydrothermal liquefaction of lignocellulosic biomass in supercritical water, *Energies* 14 (6) (2021) 1708.
- [43] F. Conti, et al., Valorization of animal and human wastes through hydrothermal liquefaction for biocrude production and simultaneous recovery of nutrients, *Energy Convers. Manag.* 216 (2020) 112925.
- [44] T.H. Seehar, et al., Catalytic hydrothermal liquefaction of contaminated construction wood waste for biocrude production and investigation of fate of heavy metals, *Fuel Process. Technol.* 212 (2021) 106621.
- [45] T.H. Seehar, et al., Influence of process conditions on hydrothermal liquefaction of eucalyptus biomass for biocrude production and investigation of the inorganics distribution, *Sustain. Energy Fuels* 5 (5) (2021) 1477–1487.
- [46] S.S. Toor, et al., Bio-crude production from protein-extracted grass residue through hydrothermal liquefaction, *Energies* 15 (1) (2022) 364.
- [47] A.A. Shah, et al., Sub-supercritical hydrothermal liquefaction of lignocellulose and protein-containing biomass, *Fuel* 5 (1) (2024) 75–89.
- [48] S. Bhatwadekar, et al., Co-liquefaction of sewage sludge with wheat straw in supercritical water—potential for integrating hydrothermal liquefaction with wastewater treatment plants, *Sustain. Energy Fuels* 6 (5) (2022) 1269–1280.
- [49] C. Barrère-Mangote, et al., Study of biocrudes obtained via hydrothermal liquefaction (HTL) of wild alga consortium under different conditions, *Processes* 9 (2021), <https://doi.org/10.3390/pr9091494>.
- [50] P. Biller, et al., Effect of hydrothermal liquefaction aqueous phase recycling on bio-crude yields and composition, *Bioresour. Technol.* 220 (2016) 190–199.
- [51] H. Hwang, et al., Comprehensive characterization of hydrothermal liquefaction products obtained from woody biomass under various alkali catalyst concentrations, *Environ. Technol.* 40 (13) (2019) 1657–1667.
- [52] H.-M. Liu, M.-F. Li, R.-C. Sun, Hydrothermal liquefaction of cornstalk: 7-lump distribution and characterization of products, *Bioresour. Technol.* 128 (2013) 58–64.
- [53] Y. Wang, et al., Investigating the influence of extractives on the oil yield and alkane production obtained from three kinds of biomass via deoxy-liquefaction, *Bioresour. Technol.* 102 (14) (2011) 7190–7195.
- [54] B. Hao, et al., Catalytic hydrothermal liquefaction of municipal sludge for biocrude production over non-noble bimetallic catalyst in ethanol solvent, *Fuel* 331 (2023) 125812.
- [55] K. Kohansal, et al., Bio-crude production improvement during hydrothermal liquefaction of biopulp by simultaneous application of alkali catalysts and aqueous phase recirculation, *Energies* 14 (15) (2021) 4492.
- [56] H. Liu, et al., Incorporating hydrothermal liquefaction into wastewater treatment—Part I: process optimization for energy recovery and evaluation of product distribution, *Chem. Eng. J.* 449 (2022) 137838.
- [57] C. Yang, et al., Hydrothermal liquefaction and gasification of biomass and model compounds: a review, *Green Chem.* 22 (23) (2020) 8210–8232.
- [58] B. Maddi, et al., Quantitative characterization of aqueous byproducts from hydrothermal liquefaction of municipal wastes, food industry wastes, and biomass grown on waste, *ACS Sustain. Chem. Eng.* 5 (3) (2017) 2205–2214.
- [59] L. Huang, M. Gu, Effects of biochar on container substrate properties and growth of plants—a review, *Horticultrae* 5 (1) (2019) 14.
- [60] Y. Sugimura, Y. Suzuki, A high-temperature catalytic oxidation method for the determination of non-volatile dissolved organic carbon in seawater by direct injection of a liquid sample, *Mar. Chem.* 24 (2) (1988) 105–131.
- [61] C. Xu, T. Etchevery, Hydro-liquefaction of woody biomass in sub-and super-critical ethanol with iron-based catalysts, *Fuel* 87 (3) (2008) 335–345.
- [62] W. Ge, et al., DOSY NMR: a versatile analytical chromatographic tool for lignocellulosic biomass conversion, *ACS Sustain. Chem. Eng.* 4 (3) (2016) 1193–1200.
- [63] I.J. Tews, et al., Biomass Direct Liquefaction Options. Technoeconomic and Life Cycle Assessment, Pacific Northwest National Lab.(PNNL), Richland, WA (United States), 2014.
- [64] T.H. Seehar, Hydrothermal Liquefaction of Waste Lignocellulosic Feedstocks from Agricultural, Urban, and Forest Waste Streams for the Production of Biofuels, 2021.
- [65] O. Okoligwe, et al., Characterization of municipal solid waste residues for hydrothermal liquefaction into liquid transportation fuels, *Waste Manag.* 140 (2022) 133–142.
- [66] V. Patil, et al., Applicability of ketone-gasoline blended fuels for spark ignition engine through energy-exergy analyses, *Fuel* 339 (2023) 127416.
- [67] D.J. Nowakowski, et al., Potassium catalysis in the pyrolysis behaviour of short rotation willow coppice, *Fuel* 86 (15) (2007) 2389–2402.
- [68] J. Zimmermann, K. Raffelt, N. Dahmen, Sequential hydrothermal processing of sewage sludge to produce low nitrogen biocrude, *Processes* 9 (3) (2021) 491.