

ENHANCEMENT OF BIOCRUDE QUALITY USING FECAL SLUDGE AND ORGANIC SOLID WASTE THROUGH TWO-STAGE HYDROTHERMAL LIQUEFACTION TECHNIQUE

H M Fairouz Adnan*¹, Md. Atik Fayshal², Dipa Roy Chowdhury³, Tamanna Sharif Jemi³,
Nafis Ahmed Pantho¹, and Md. Khalekuzzaman¹

¹ Department of Civil Engineering, Khulna University of Engineering & Technology, Khulna-9203, Bangladesh,

² Department of Civil, Construction and Environmental Engineering, North Dakota State University, North Dakota-58108, USA,

³ Department of Energy Science and Engineering, Khulna University of Engineering & Technology, Khulna-9203, Bangladesh,

Received: 25 May 2024

Accepted: 20 June 2024

ABSTRACT

The escalating global challenge of managing unmanaged fecal sludge (250-300 million tonnes/year) and organic solid waste (600-700 million tonnes/year) necessitates innovative and sustainable waste-to-energy solutions. Hydrothermal liquefaction (HTL) of FS & OSW to produce biocrude has been seen as a double-edged sword to substitute fossil fuel and address the issues relating to unmanaged waste (GHG emission, global warming, climate change). Through this study, an approach was taken to improve the biocrude production and enhance the biocrude quality by introducing a two-stage heating in HTL of FS and OSW separately. Four different runs were comprised in this study where one run was in conventional one stage, at 320°C for 60 min. In terms of the other three runs, in the first stage, 100, 200, and 300°C were retained for 30 min respectively and the second stage was conducted at 320°C for 30 min. Results indicate a substantial improvement in biocrude yield of 15% & 18% through two-stage heating during HTL (30 min at 200°C, and then 30 min at 320°C) compared to conventional single-stage HTL processes of FS & OSW respectively with a biomass conversion rate of 70%. From the analysis of biocrude maturity & intensity of oil we observe a high potential for crude oil formation being classified as Kerogen type I. GC-FID shows that increasing heat in the first stage tends to produce a lighter fraction (at 300°C in the first stage produces biocrude with a lighter fraction >80% from FS & OSW feedstocks) in biocrude. In addition to improving the overall efficiency of converting organic waste to biocrude, the two-stage system offers a more flexible platform that allows the biofuel composition to be customized to match the needs of individual applications. The results show that a two-stage HTL process is a feasible and effective technique for converting difficult waste streams into biofuels, with implications for both environmental sustainability and energy security.

Keywords: Hydrothermal Liquefaction (HTL), Waste to energy, Fecal sludge, Organic Solid Waste, Two-stage HTL, biocrude.

1. INTRODUCTION

In this modern era of rapid urbanization & development, almost every action requires energy consumption one way or another. About 80% of this energy demand is met by using fossil fuels. This high consumption of fossil fuels causes a detrimental impact on public health and environmental pollution by emitting GHGs. By far, fossil fuels (coal, oil, and gas) are the largest contributor to global climate change, accounting for over 75% of total GHG emissions and nearly 90% of all carbon dioxide emissions (Nations, 2024; Fayshal et al., 2023). Besides, the reserves of fossil fuels are also limited.

Despite the limited reserves, the growing energy demand and global warming issues relating to it have become one of the central problems of the modern-day world. The quest for sustainable energy solutions has gained unprecedented momentum in the face of escalating environmental concerns and the pressing need to transition towards cleaner, renewable resources. In this pursuit, biomass has been considered as a potential alternative solution as a sustainable energy source due to its renewability, huge production, and carbon neutrality. The application of wet waste for bio-energy production works as a two-way solution, mitigating GHG emissions as well as an environmental crisis by managing unmanaged waste and introducing a sustainable path for energy

*Corresponding Author: adnanauntor336@gmail.com

<https://www2.kuet.ac.bd/JES/>

ISSN 2075-4914 (print); ISSN 2706-6835 (online)

generation (Iqbal *et al.*, 2021). Among the myriad approaches, hydrothermal liquefaction (HTL) stands out as a promising technology with the potential to revolutionize the conversion of wet waste into valuable biocrude. A study conducted by Kabir & Khalekuzzaman (2022) introduced a cost-effective way to deal with wet waste through HTL, where no energy consumption is necessary for sample preparation since the moisture acts both as solvent and catalyst for thermochemical reactions (temperature ranges from 200 to 375°C; pressure ranges from 5 to 25MPa). As the world grapples with the challenges of waste management and seeks alternatives to conventional fossil fuels, the optimization of HTL processes becomes paramount. The inherent advantages of HTL include its ability to process a wide array of wet feedstocks, including sewage sludge, algae, and other organic residues, and its potential to produce a versatile range of valuable products such as biocrude, biochar, and nutrient-rich aqueous phases. While the technology has demonstrated considerable potential in transforming wet organic feedstocks, challenges persist in achieving optimal biocrude yields and maintaining process stability (Akhtar & Amin, 2011). Despite the promises, challenges persist in optimizing HTL processes to achieve maximal biocrude yields and ensure the stability of the overall operation. The intricacies lie in understanding the dynamic interplay of temperature, pressure, and residence time during the HTL process, as these factors dictate the complex thermochemical reactions occurring within the reactor. The need for innovative strategies to overcome these challenges is underscored by the urgency to develop efficient and scalable technologies that can be seamlessly integrated into existing waste management and energy production frameworks.

Multiple studies were conducted for the optimization of the HTL process by using different solvents and catalysts. Khalekuzzaman *et al.* (2024) found low phenolic naphtha-rich biocrude by using water-ethanol co-solvent. Kabir *et al.* (2022) worked with temperature variation in the HTL process to get better yield. In hydrothermal liquefaction, the temperature is a crucial factor that dictates biocrude production and properties as well as affects reaction routes, product distributions, and overall process efficiency (Kohansal *et al.*, 2021). Because biomass liquefaction is exothermic at high temperatures but endothermic at low ones, it is thermodynamically unfavorable at low temperatures. The influence of temperature on the yield of liquefaction products seems sequential. Initially, the rise in temperature triggers bio-oil yield. After reaching a maximum yield for the oil yield, a further increase in temperature inhibits biomass liquefaction (Akhtar & Amin, 2011). Several studies have been conducted on different biomass to find optimum temperatures. Studies conducted by Yin *et al.* (2010), Zhang *et al.* (2009), and Zhou *et al.* (2010) show 300–315°C range of temperature was suitable for the efficient production of liquid oils from loosely constructed biomass feedstocks of *Enteromorpha prolifera*, cattle manure, grassland perennials, and eucalyptus. An increasing temperature from 260 to 340°C increased the amount of bio-oil from the liquefaction of manure (Xiu *et al.*, 2010). In case of co-HTL of fecal sludge and organic solid waste, the biocrude yield increases from 38% to 52% with increasing temperature from 280°C to 320°C but decreases while further increasing the temperature to 340°C (Kabir & Khalekuzzaman, 2022). However, in case of liquefied microalgae *Dunaliella tertiolecta* cake 360°C was found as the optimum temperature for yield production (Shuping *et al.*, 2010). So, it can be presumed that the useful temperature range for hydrothermal liquefaction can range from 300 to 350°C, and in addition to that, feedstock types also influence the optimum temperature required for HTL. However, heating rates have a very low impact on the product yield in hydrothermal liquefaction than in pyrolysis. The reason behind this is the better dissolution and stabilization of fragmented species in hot compressed water (solvent) medium (Demirbas, 2011). Residence time has an essential impact on the product quality. Longer residence times suppressed the bio-oil yield except for very high biomass-to-water ratios (Boocock & Sherman, 1985). Kabir & Khalekuzzaman (2022) followed 60 minutes of residence time to ensure biocrude quality and production.

Extensive biomass depolymerization happens when the temperature is high enough to exceed the activation energies for the bond cessation. This raises the likelihood of fragmented species repolymerizing as well as the concentration of free radicals. The interaction of fragmentation, re-polymerization, and hydrolysis reactions determines the temperature's function in pyrolysis (Akhtar & Amin, 2011). Depolymerization of biomass is a dominant reaction during the initial stages. Re-polymerization becomes active at later stages which leads to the formation of char. Intermediate temperature usually yields higher amounts of bio-oil (Collard & Blin, 2014). Different temperature regimes may favor specific reactions and enhance the overall conversion of wet waste into biocrude. However, there are limited studies regarding multi-stage heating. This study appraises to evaluate the effect of two-stage heating on HTL. By carefully designing two distinct temperature stages within the HTL process, we seek to harness synergistic effects that promote the efficient breakdown of complex organic molecules and enhance the yield of biocrude. The first stage (at 100, 200, and 300°C with 30 min retention time) aims to initiate the breakdown of the feedstock into intermediate products, while the second stage (320°C with 30 min retention time) facilitates the conversion of these intermediates into high-quality biocrude. This study comprises to evaluate and quantify the influence of the two-stage heating strategy on biocrude yields, comparing the results with conventional single-stage heating (320°C with 60 min retention time) processes, assess the stability and robustness of the two-stage heating using different feedstocks (FS, OSW) as well as aspires to

make significant contributions to both academic knowledge and practical applications in the realm of hydrothermal liquefaction. The insights gained from this study can inform the design and operation of HTL systems, providing a foundation for the development of more efficient, sustainable, and economically viable processes. Additionally, the potential for enhanced biocrude production through the utilization of two-stage heating holds promise for advancing the integration of bioenergy solutions into mainstream energy production.

2. MATERIALS AND METHODS

2.1 Biomass Characterization

A two-stage HTL technique was employed to create biocrude using FS and OSW. On the residential area of the Khulna University of Engineering & Technology (KUET) campus, FS was taken from the second chamber of the septic tank. The FS sample was then promptly kept for the night at 4°C. To create a uniform combination, the raw FS was lastly mixed and kept for this investigation. The organic solid waste (OSW) includes food scraps, paper, etc. which was gathered from the waste management plant of Khulna University of Engineering & Technology (KUET). It was then sorted, mixed, and screened through a 2-millimeter screen. After being combined to create a homogenous mixture, the sample was lastly kept at 4°C in a lab refrigerator. To understand the characteristics of the biomass, proximate, and ultimate compositions of the two feedstock is illustrated in Table 1.

Table 1: Proximate, and functional group analysis of fecal sludge (FS) and organic solid waste (OSW)

| Parameter | Unit | FS | OSW |
|--------------------------------|------|--------------|--------------|
| <u>Proximate Analysis</u> | | | |
| Total solid (TS) | % | 10.78 ± 0.34 | 13.49 ± 0.58 |
| Moisture content (MC) | % | 89.22 ± 0.59 | 86.51 ± 0.22 |
| Volatile Solids (VS) | % | 5.14 ± 0.66 | 8.76 ± 0.43 |
| Ash | % | 4.77 ± 0.69 | 3.79 ± 0.22 |
| Fixed Carbon (FC) ^c | % | 0.87 ± 0.23 | 0.94 ± 0.19 |
| <u>Biochemical composition</u> | | | |
| Carbohydrate | % | 30.42 | 27.79 |
| Protein | % | 22.19 | 23.67 |
| Lipid | % | 25.39 | 21.44 |

^cFixed carbon, (%) = 100 – sum of (moisture + volatile matter + ash content)

2.2 Hydrothermal Liquefaction (HTL) Process

The Hydrothermal Liquefaction (HTL) experiments were carried out in a specialized stainless steel (SS 304) batch reactor with a 25 mL capacity, containing 10 mL of working volume. Biomass was fed directly into the reactor for each HTL run, and the reactor was hermetically sealed with a carbon and copper gasket. After that, the sealed reactor was put in a furnace to undergo additional processing. Primarily the HTL experiment ran for thirty minutes at 320°C (Haider et al., 2020).

In this experiment, the temperature was controlled with a two-stage hydrothermal liquefaction process. This two-stage heating approach involved a series of batch experiments carried out at three different temperature levels: 100°C, 200°C, and 300°C, each for 30 min, representing the first stage. Subsequently, in the second stage, a hydrothermal liquefaction experiment was conducted at the target temperature of 320°C for 30 minutes within the same reactor. Moreover, a full HTL was conducted for each biomass at 320°C for 60 minutes of reaction time. To sum up, the reaction conditions were set as 100°C-30 min-320°C-30 min, 200°C-30 min-320°C-30 min, and 300°C-30 min-320°C-30 min, labeled as Run 1, Run 2, and Run 3 respectively. Without the first stage HTL, the experiment with a residence time of 60 min at the reaction temperature of 320°C was the blank group (labeled as Run 0). After the completion of the HTL reaction, the reactor was allowed to cool down for 10 minutes, facilitated by tap water circulation. During this cooling phase, any compressed gases within the reactor were vented to ensure safety.

The mixture produced by the reaction, the HTL effluent, was dissolved in a dichloromethane (30 mL) solution (Dandamudi et al., 2020). The combined slurry was then cautiously poured into 15 mL polypropylene centrifuge tubes. The tubes were vortexed for five minutes to allow the organic phase to dissolve in the DCM solvent and to guarantee complete mixing. The subsequent phase comprised separating the HTL products into three separate

layers: the aqueous phase was represented by the top layer, biochar was present in the middle layer, and DCM-dissolved biocrude or oil was present in the bottom layer. A NUVE NF 800/800R multipurpose benchtop centrifuge was employed, running at 4000 rpm for 10 minutes to accomplish this separation (Khalekuzzaman *et al.*, 2021; Adnan *et al.*, 2023). Following that, a 3 mL syringe was used to gently separate the aqueous phase from the biocrude layer that had been dissolved by DCM. The biocrude samples were removed using a rotary evaporator after the DCM, which acted as the organic phase's solvent, evaporated. These biocrude samples were kept for additional examination in a lab refrigerator. Furthermore, the samples of biochar were dried for a whole night in an oven that was preheated to 65°C. The biochar samples were also kept in the freezer after drying, where they remained until further examination. A visual representation of the complete process is given in Figure 1.

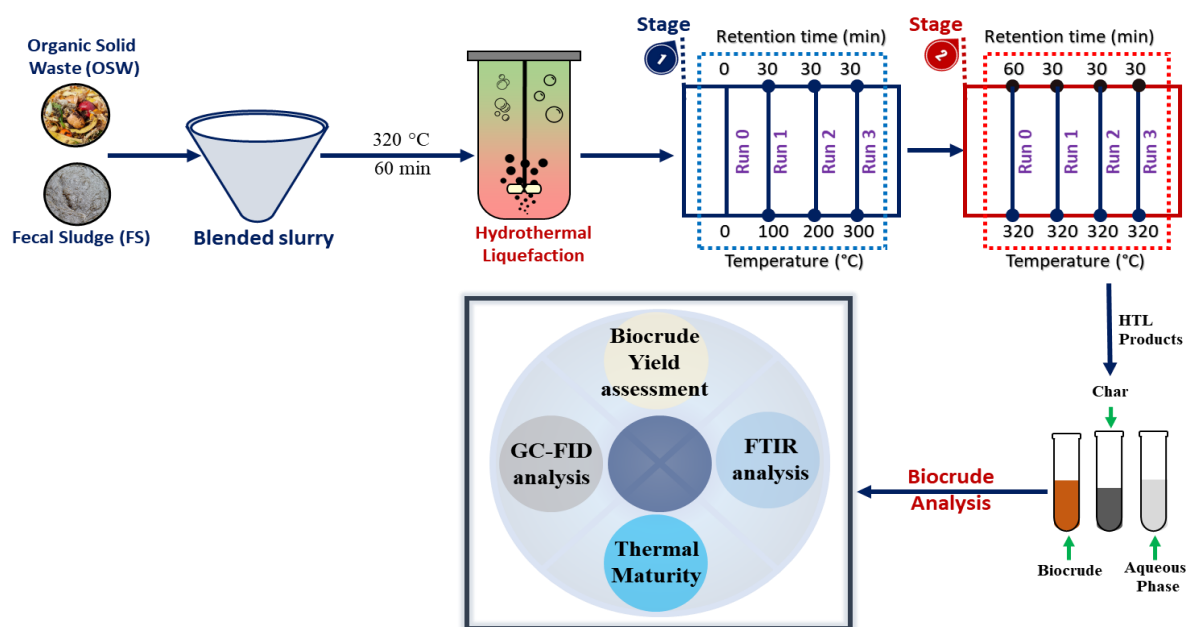


Figure 1: Experimental flow diagram of two-stage hydrothermal liquefaction of fecal sludge and organic solid waste

2.3 Analytical methods

2.3.1 Yield Calculation

Dry basis calculations were used to determine the experimental HTL products (biocrude, biochar, aqueous phase, and gas phase). Using equations (2) to (7), the % weight yields of each sample for gas, aqueous phase, biocrude, and biochar were determined (Chopra *et al.*, 2019; Feng *et al.*, 2020). Water-soluble compounds (WSC) were defined in equation (5) as the total dissolved solids of the aqueous phase.

$$\text{Biocrude yield (\%)} = (\text{mass of biocrude}) / (\text{mass of biomass}) \times 100\% \quad (2)$$

$$\text{Biochar yield (\%)} = (\text{mass of biochar}) / (\text{mass of biomass}) \times 100\% \quad (3)$$

$$\text{Aqueous phase (\%)} = (\text{mass of aqueous phase}) / (\text{mass of biomass}) \times 100\% \quad (4)$$

$$\text{Gas yield (\%)} = 100\% - (Y_{\text{biocrude}} + Y_{\text{biochar}} + \text{WSC}) \quad (5)$$

2.3.2 Fourier transform infrared spectroscopy (FTIR) Analysis

FTIR analyses were performed on the biomass, biocrude, and biochar samples of OSW, and FS to determine the presence of functional groups, chemicals, and vibrations (Hasan *et al.*, 2024). A Shimadzu (IRTracer-100) spectrophotometer was used to perform FTIR analysis at room temperature for spectra with a resolution of 2 cm^{-1} and a range of 800 cm^{-1} to 4000 cm^{-1} (El-Hendawy, 2006). The transmittance device gathered the infrared data, which were subsequently converted into absorbance (%) and analyzed using MS Excel, irAnalyze-RAMalyze (Lab-Cognition GmbH & Co. KG), and OriginPro 2018.

2.3.3 Biocrude Oil Quality and Thermal Property

The A-Factor (aliphatic/aromatic bands) and C-Factor (carbonyl/aromatic bands) of biocrude samples of OSW, P, and FS were assessed using the Ganz and Kalkreuth technique based on FTIR spectra (Ganz & Kalkreuth, 1991). Based on absorbance (%), OriginPro 2018 was used to choose the peak heights of 2930 cm⁻¹, 2860 cm⁻¹, 1705 cm⁻¹, and 1630 cm⁻¹ for this analysis. The A-Factor and C-Factor were determined using equations (6) and (7) (Adedosu & Sonibare, 2005).

$$\text{A-Factor} = (2930+2860) \text{ cm}^{-1} / (2930+2860+1630) \text{ cm}^{-1} \quad (6)$$

$$\text{C-Factor} = 1705 \text{ cm}^{-1} / (1705+1630) \text{ cm}^{-1} \quad (7)$$

A vitrinite reflectance equivalent grid diagram was used to classify the biocrude oil source type, parent kerogen type, and thermal maturity in terms of A-Factor vs. C-Factor (Awadh and Al-Ankaz, 2016). Among the four, type I kerogen is believed to be the most prone to oil buildup. Type II indicates moderately oil-prone crude, type III indicates low oil-prone crude, and type IV indicates no likely presence of petroleum hydrocarbons, according to Awadh and Al-Ankaz (2016). To further classify the biocrude development phases, vitrinite reflectance (VR%) was employed. Based on the thermal maturation criterion (VR%), McNeil et al., (2015) categorized biocrude as immature (biogenic gas zone), premature (heavy oil zone), peak mature (light oil zone), and postmature (thermogenic/dry gas zone). The relationship between biocrude oil maturity and atomic molar ratios (H/C and O/C ratios) was shown by Peters et al., (2019). Peters et al., (2019) demonstrated the connection between biocrude oil maturity and atomic molar ratios (H/C and O/C ratios). An increase in biocrude quality and maturity was linked to a high H/C ratio and a low O/C ratio. Based on VR (%), the paleotemperature (T_{peak} fluids temperature and T_{burial} temperature of biocrude oil) was calculated using equations (8) and (9) (Barker & Pawlewicz, 1994). The estimation of paleotemperature is essential to support the use of biocrude or oil that has been thermally fractured into bitumen.

$$T_{\text{peak fluids}} = [\ln (\text{VR}\%) + 1.19] / 0.00782 \quad (8)$$

$$T_{\text{burial}} = [\ln (\text{VR}\%) + 1.68] / 0.0124 \quad (9)$$

2.4. Gas chromatography-flame ionization detector (GC-FID) analysis

The petroleum fractionation (C6 to C40: naphtha (C6–C10), kerosene (C10–C16), diesel (C16–C20), lube oil (C20–C30), and fuel oil (C30–C40)) was assessed using a GC-FID (Biobase BK-GC112A, China) on the biocrude samples. A capillary column (30 m × 0.320 mm × 0.25 μm) manufactured by DB-5 (Agilent, USA) was installed on the GC and ran at a pressure of 46.6 Kpa and a flow rate of 1.2 mL/min. The GC-FID was initially calibrated using a petroleum hydrocarbon window (C8–C40) defining standard (DRH-008S-R2, AccuStandard, USA) in order to ascertain the retention duration for hydrocarbon ranges C8 to C40. After the sample was dissolved in hexane for each run, it was filtered using a 0.2 μm PTFE filter. The column was then injected with a 1 μL sample. The carrier gas, N₂, flowed at a speed of 0.9 mL/min, whereas the H₂ flow rate was 30.6 mL/min. The FID sensitivity was 10⁹. The detector's temperature was 320°C with a makeup flow of 22 mL/min and a compressed airflow of 332.4 mL/min. The injector temperature was maintained at 280°C at a speed of 24.2 cm/s. The GC was programmed to run at 40°C for two minutes, then ramp up to 320°C at a rate of 15°C per minute, holding that temperature for 30 minutes. The GC data was coordinated using N2000 Chromatography software.

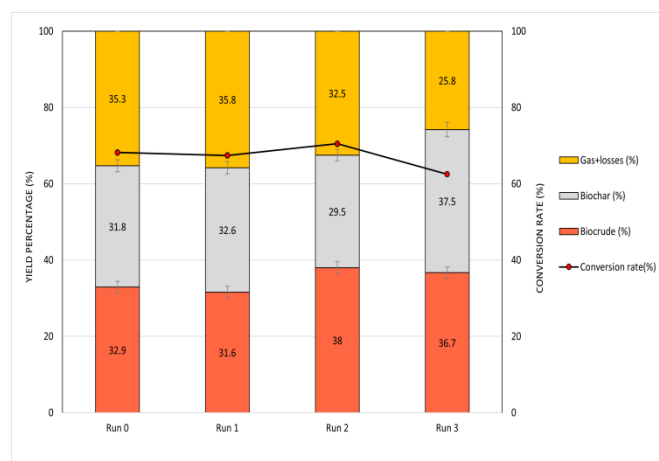
3. RESULTS AND DISCUSSION

3.1 HTL of fecal sludge (FS) & organic solid waste (OSW)

The HTL of FS resulted in biocrude, biochar, gas, and losses as its end products. Figure 2 illustrates the percentage yield of the products and biomass conversion rate. The maximum biocrude output for Run 2 (200°C for 30 minutes and 320°C for 30 minutes) was 38% and 41.2% for FS and OSW, respectively. This was 5.1% and 6.3% greater than when FS and OSW were not preheated (Run 0). Moreover, the yield of biochar was observed to be declining (29.5 % for FS & 31.1 % for OSW during Run 2) while the biocrude yield was increasing. The rate of hydrolysis and solubility of organic substances, such as proteins, carbohydrates, and lipids, from the solid matrix is accelerated in hydrothermal liquefaction when the temperature is raised (Du et al., 2012). As a result, as temperatures increased, less residual solid matter and more biocrude were formed from these compounds. Furthermore, in Run 2, the biomass conversion rate was higher, reaching about 70% for both FS, as shown in Figure 2a, and OSW, as shown in Figure 2b. This indicates that preheating the biomasses had a positive effect. Again, during the preheating phase, Run 2 exhibited minimal gas and losses, while Run 1 experienced maximum gas and losses, mainly because of the increased biomass conversion rate resulting from preheating at 200°C for 30 minutes (Sintamarean et al., 2017). Hence, this study's high biocrude yield suggested

that the FS and OSW feedstocks for HTL with preheating were conducive to a sustainable biocrude production system.

a) FS



b) OSW

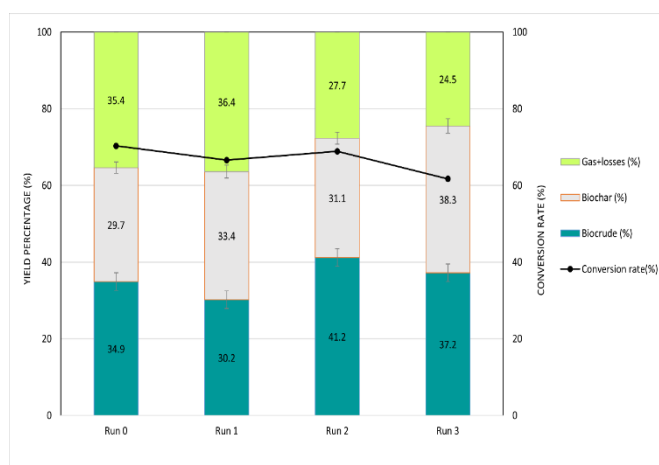
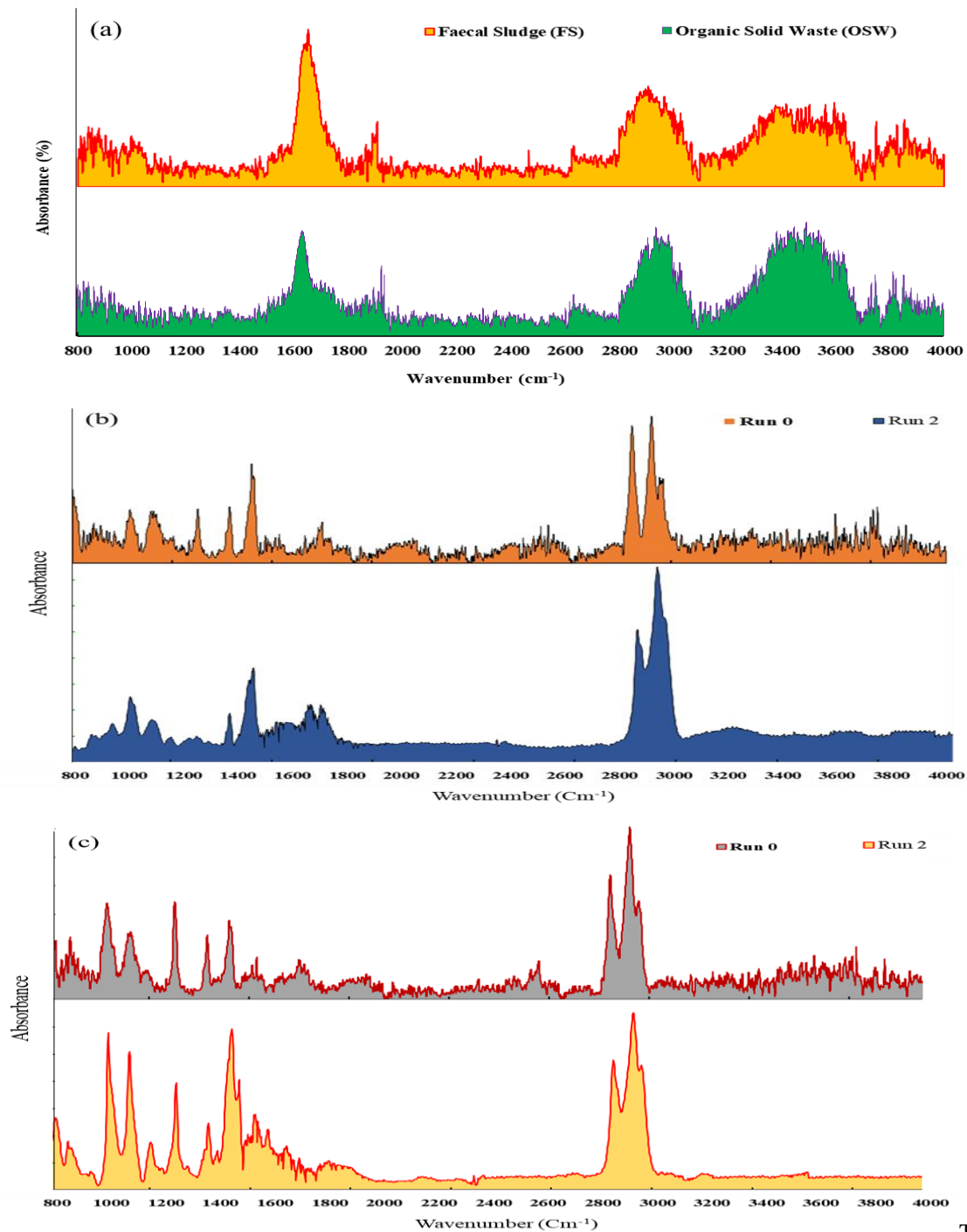


Figure 2: Effects of two-stage thermal variation on HTL Products yield and conversion rate

3.3 FTIR analysis of biocrude

FTIR analysis has been carried out for biomass (FS and OSW) and biocrude. For biocrude FTIR, blank sample (Run 0) and the two-stage optimized sample (Run 2) have been considered for comparison and in-depth discussion. By using FTIR spectroscopy, the presence of functional groups and the mode of vibration of biocrude samples were examined, as presented in Figure 3.

The biocrude samples contained a broad and intense peak in the range of wavelengths $(2800-3000) \text{ cm}^{-1}$ ($-\text{CH}_3$) and $(1350-1460) \text{ cm}^{-1}$ ($-\text{CH}_2$) indicating the existence of long-chain aliphatic hydrocarbons (Li *et al.*, 2018). Additionally, the absorbance peaks in the 1024 cm^{-1} to 1100 cm^{-1} (C-O) range showed the existence of phenolic and alcohol-containing chemicals in biocrude (Ogunkanmi *et al.*, 2018). These are formed as a result of the hydrolysis or depolymerization of the lignin and carbohydrates found in biomass cells (Nandiyanto *et al.*, 2019). Carbonyl functional groups $\text{C}=\text{O}$ ($1650-1750) \text{ cm}^{-1}$, which represented substances like carboxylic acids, ester, and a ketone group, formed as a result of the amino acid deamination, fatty acid hydrolysis, and esterification mechanism (Lu *et al.*, 2018). The spectra range of 1250 cm^{-1} to 1340 cm^{-1} (C-N) revealed the existence of aromatic primary amine (Nandiyanto *et al.*, 2019).



The
Figure 3: (a) Biomass FTIR spectra of fecal sludge (FS) and organic solid waste (OSW) (b) Biocrude FTIR spectra of FS and (c) Biocrude FTIR spectra of OSW on two-stage HTL

3.5 Analysis of biocrude oil maturity and intensity of oil

The thermal maturity of FS and OSW were assessed for two conditions: one without preheating (Run 0) and the other with preheating, which resulted in the highest biocrude yield (Run 2), using the FTIR spectrum data from Table 3. Multiple factors, including the A-Factor, C-Factor, and VR%, affect the maturity of biocrude oil. As shown in Table 4, samples from FS and OSW with an A-Factor of 0.90 or higher indicated high-grade biocrude. On the other hand, as demonstrated in Table 2 and Figure 4, the lower C-Factor of the FS and OSW samples showed a rise in oil maturity (premature) with VR (%) ranges (0.45-0.65) (Glossary, 1998).

The average fluid temperatures (T_{fluid} °C) for biocrude obtained from FS samples were 2.41°C in Run 0 and 17.93°C in Run 2. Additionally, for biocrude derived from OSW samples, the T_{fluid} values were 63.54 °C in Run 0 and 10.40°C in Run 2. Moreover, the average burial temperatures (T_{burial} °C) for FS biocrude were 41.73 °C in

Run 0 and 50.82°C in Run 2, while for OSW biocrude, they were 79.58 °C in Run 0 and 46.08°C in Run 2. These temperature measurements suggest that the biocrude samples are more suitable for conversion into diesel and lubricating oils rather than bitumen (Awadh & Al-Ankaz, 2016). The biocrude sample demonstrated a high potential for crude oil formation rather than gas because of its highly oil-prone character and they are classified as kerogen type I (Figure 4).

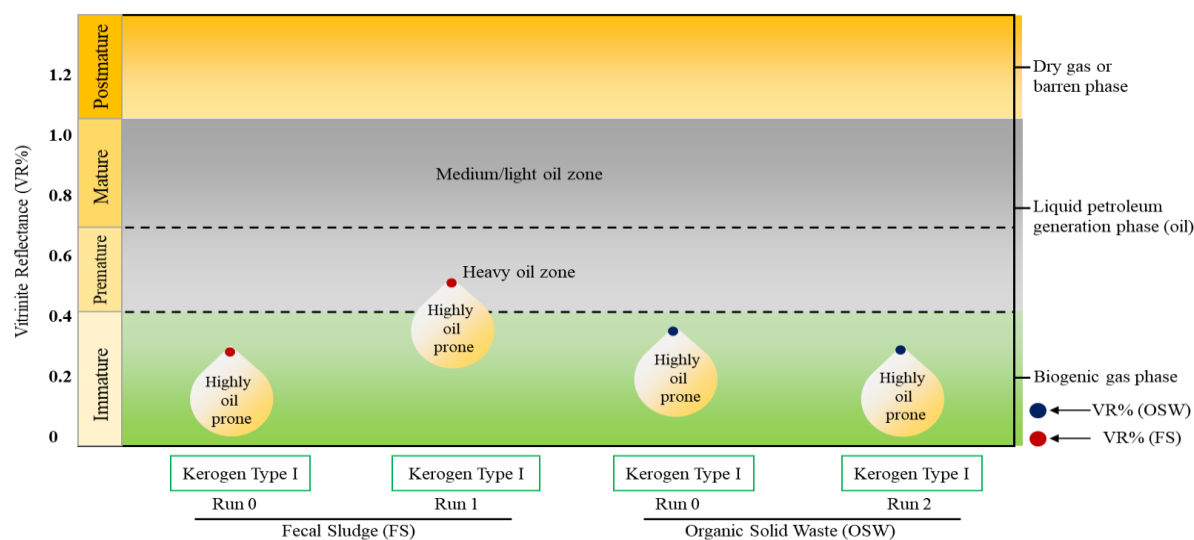


Figure 4: Generation phase of oil, maturity, and kerogen type of biocrude samples using Vitrinite Reflectance (VR %).

Table 2: A-factor, C-factor and Paleotemperature from FTIR spectra of FS and organic OSW

| Sample Type | Sample ID | Peak height (absorbance%) (cm^{-1}) | | | | Parameters | | T_{fluids} | T_{burial} |
|-------------|-----------|--|-------|------|------|------------|----------|---------------------|---------------------|
| | | 2930 | 2860 | 1705 | 1630 | A factor | C factor | | |
| FS | Run 0 | 19.92 | 15.96 | 5.75 | 1.9 | 0.95 | 0.31 | 2.41 | 41.03 |
| | Run 2 | 8.73 | 7.54 | 4.27 | 1.58 | 0.91 | 0.32 | 17.93 | 50.82 |
| OSW | Run 0 | 23.65 | 14.56 | 5.73 | 2.95 | 0.92 | 0.35 | 63.54 | 79.58 |
| | Run 2 | 28.42 | 17.33 | 3.00 | 2.58 | 0.94 | 0.50 | 10.40 | 46.08 |

3.6 Petroleum Fractionation Analysis

As illustrated in Figure 5, GC-FID was used to analyze the biocrude generated by the HTL process with preheating in order to fractionate petroleum hydrocarbons. The biocrude samples are separated into a lighter fraction (naphtha (C6-C10), jet fuel (C10-C16), and diesel (C16-C20)) and a heavier fraction (lubricating oil (C20-C30), fuel oil (C30-C40), and asphaltene (>C40)) based on the findings of the GC-FID analysis (ASTM D-2887-02, 2013). Figure 5(a) clearly illustrates that the most significant increase in the lighter fraction (>80%) in the FS feedstock is achieved in Run 3, where 69% constitutes naphtha. This observation suggests a direct correlation between higher preheating temperatures and an enhanced production of lighter fractions. Whereas for OSW (Figure 5(b)) the lighter fractions are almost the same for both Run 2 and Run 3 (80%>) with 63% and 73% naphtha fraction respectively. In Run 3 for the FS feedstock, the asphaltene content dropped to 9%. Meanwhile, for the OSW feedstocks, Run 2 and Run 3 showed asphaltene contents of 8% and 9%, respectively. Thus, the results indicated that preheating biomass during HTL improves the lighter fraction, lowers the asphaltene concentration of biocrude for both FS and OSW feedstock, and enhances.

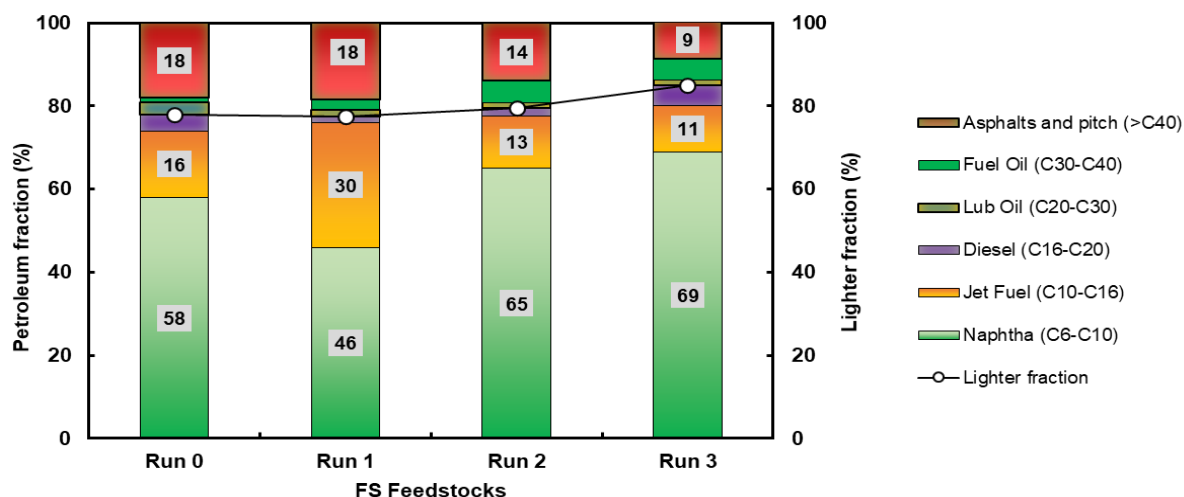


Figure 5: (a) Petroleum fractionation of biocrude/oil derived from HTL of fecal sludge (FS)

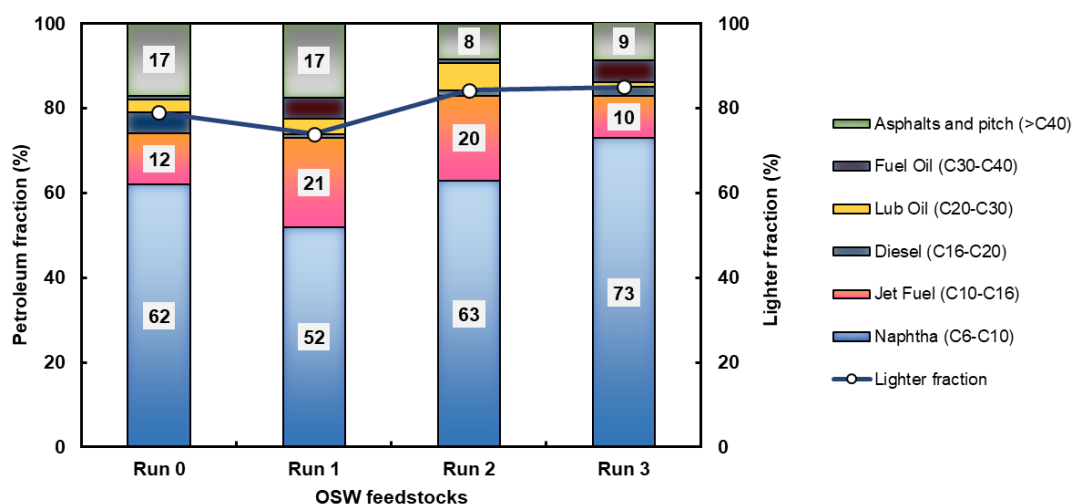


Figure 5: (b) Petroleum fractionation of biocrude derived from HTL of organic solid waste (OSW)

4. CONCLUSION

This study investigates the two-stage HTL method and demonstrates that it is very efficient in converting FS and OSW into biofuels. Optimum biocrude yield (38% and 41.2% for FS and OSW respectively) was observed in the Run where in the first stage feedstock was heated at 200°C for 30 minutes and then in the second stage heated at 320°C for 30 minutes. The yield was 15% and 18% greater than that of conventional one-stage HTL of FS and OSW with high potential oil-prone Kerogen type I crude according to the FTIR analysis. GC-FID analysis revealed that the OSW feedstock being preheated at 200 and 300°C showed higher lighter fractions in biocrude (80%>) with 63% and 73% naphtha fractions respectively, whereas FS feedstock being preheated at 300°C showed lighter fractions in biocrude (80%>) with 69% naphtha fraction. The asphaltene content dropped by 8-9% for both the feedstocks while the sample was preheated at 200 & 300°C which indicates higher biocrude production with improved lighter fraction. Moreover, the biomass conversion rate is high around 70% for both feedstocks during preheating being conducted at 200°C for 30 min implying the positive impact of two-stage heating in HTL of FS & OSW feedstock. The higher output of biofuel not only supports sustainable waste management techniques but also improves waste-to-energy efficiency. The present study offers a significant contribution towards mitigating the urgent problems related to the disposal of organic solid waste and fecal sludge, while also producing a sustainable energy source. Further refinement of the two-stage HTL process and investigation of substitute feedstocks to increase the process's scope are anticipated future directions of this research. Conducting comprehensive techno-economic evaluations and life cycle assessments is necessary to examine the developed process's viability from an economic and environmental standpoint on a broader front. In addition, this technology's potential for decentralized applications and interface with current waste management systems should be taken into account for practical implementation.

REFERENCES

- Adedosu, T. A., & Sonibare, O. O. (2005). Characterization of Niger Delta Crude Oil by Infrared Spectroscopy. *Journal of Applied Sciences*, 5, 906–909. <https://doi.org/10.3923/jas.2005.906.909>
- Adnan, H. M., Khalekuzzaman, M., Fayshal, M., & Hasan, Md. M. (2023). *Separation of Biocrude Produced from Hydrothermal Liquefaction of Faecal Sludge Without Any Solvent*. <https://doi.org/10.6084/m9.figshare.24225589.v1>
- Akhtar, J., & Amin, N. A. S. (2011). A review on process conditions for optimum bio-oil yield in hydrothermal liquefaction of biomass. *Renewable and Sustainable Energy Reviews*, 15(3), 1615–1624. <https://doi.org/10.1016/j.rser.2010.11.054>
- Awadh, S. M., & Al-Ankaz, Z. S. (2016). Inorganic Geochemistry and Origin of Bitumen Intruded in Euphrates and Fatha Formations in Hit Area, Western Iraq. *Iraqi Journal of Science*, 57.
- Barker, C. E., & Pawlewicz, M. J. (1994). Calculation of Vitrinite Reflectance from Thermal Histories and Peak Temperatures. In *Vitrinite Reflectance as a Maturity Parameter* (Vol. 570, pp. 216–229). American Chemical Society. <https://doi.org/10.1021/bk-1994-0570.ch014>
- Boocock, D. G. B., & Sherman, K. M. (1985). Further aspects of powdered poplar wood liquefaction by aqueous pyrolysis. *The Canadian Journal of Chemical Engineering*, 63(4), 627–633. <https://doi.org/10.1002/cjce.5450630415>
- Chopra, J., Mahesh, D., Yerrayya, A., Vinu, R., Kumar, R., & Sen, R. (2019). Performance enhancement of hydrothermal liquefaction for strategic and sustainable valorization of de-oiled yeast biomass into green bio-crude. *Journal of Cleaner Production*, 227, 292–301. <https://doi.org/10.1016/j.jclepro.2019.04.147>
- Collard, F.-X., & Blin, J. (2014). A review on pyrolysis of biomass constituents: Mechanisms and composition of the products obtained from the conversion of cellulose, hemicelluloses and lignin. *Renewable and Sustainable Energy Reviews*, 38, 594–608. <https://doi.org/10.1016/j.rser.2014.06.013>
- Dandamudi, K. P. R., Muhammed Luboowa, K., Laideson, M., Murdock, T., Seger, M., McGowen, J., Lammers, P. J., & Deng, S. (2020). Hydrothermal liquefaction of *Cyanidioschyzon merolae* and *Salicornia bigelovii* Torr.: The interaction effect on product distribution and chemistry. *Fuel*, 277, 118146. <https://doi.org/10.1016/j.fuel.2020.118146>
- Demirbas, A. (2011). Competitive liquid biofuels from biomass. *Applied Energy*, 88(1), 17–28. <https://doi.org/10.1016/j.apenergy.2010.07.016>
- Du, Z., Mohr, M., Ma, X., Cheng, Y., Lin, X., Liu, Y., Zhou, W., Chen, P., & Ruan, R. (2012). Hydrothermal pretreatment of microalgae for production of pyrolytic bio-oil with a low nitrogen content. *Bioresour Technol*, 120, 13–18. <https://doi.org/10.1016/j.biortech.2012.06.007>
- El-Hendawy, A.-N. A. (2006). Variation in the FTIR spectra of a biomass under impregnation, carbonization and oxidation conditions. *Journal of Analytical and Applied Pyrolysis*, 75(2), 159–166. <https://doi.org/10.1016/j.jaap.2005.05.004>
- Fayshal, M., Ullah, M. R., Adnan, H. M. F., Rahman, S. M. A., & Siddique, I. (2023). Evaluating Multidisciplinary Approaches within an Integrated Framework for Human Health Risk Assessment. *Journal of Environmental Engineering and Studies*, 8, 30–41. <https://doi.org/10.46610/JoEES.2023.v08i03.004>
- Feng, A., Zhou, J., Vories, E. D., Sudduth, K. A., & Zhang, M. (2020). Yield estimation in cotton using UAV-based multi-sensor imagery. *Biosystems Engineering*, 193, 101–114. <https://doi.org/10.1016/j.biosystemseng.2020.02.014>
- Ganz, H. H., & Kalkreuth, W. (1991). IR classification of kerogen type, thermal maturation, hydrocarbon potential and lithological characteristics. *Journal of Southeast Asian Earth Sciences*, 5(1), 19–28. [https://doi.org/10.1016/0743-9547\(91\)90007-K](https://doi.org/10.1016/0743-9547(91)90007-K)
- Glossary, Oilfield, 1998. Oil-prone | Oilfield glossary [WWW document], 6.2.21.* <https://glossary.oilfield.slb.com/en/terms/o/oil-prone>.
- Haider, M. S., Castello, D., & Rosendahl, L. A. (2020). Two-stage catalytic hydrotreatment of highly nitrogenous biocrude from continuous hydrothermal liquefaction: A rational design of the stabilization stage. *Biomass and Bioenergy*, 139, 105658. <https://doi.org/10.1016/j.biombioe.2020.105658>
- Hasan, M. R., Abdur, R., Alam, Md. A., Shaikh, Md. A. A., Aziz, S., Sujana, A., Islam, D., Jamal, M. S., & Hossain, M. (2024). Exploring the effects of different parameters on the incorporation of K⁺ ions in eggshell derived CaO reveals highly variable catalytic efficiency for biodiesel conversion. *South African Journal of Chemical Engineering*, 47, 67–74. <https://doi.org/10.1016/j.sajce.2023.10.009>
- Iqbal, W., Tang, Y. M., Lijun, M., Chau, K. Y., Xuan, W., & Fatima, A. (2021). Energy policy paradox on environmental performance: The moderating role of renewable energy patents. *Journal of Environmental Management*, 297, 113230. <https://doi.org/10.1016/j.jenvman.2021.113230>

- Kabir, S. B., & Khalekuzzaman, M. (2022). Co-liquefaction of organic solid waste with fecal sludge for producing petroleum-like biocrude for an integrated waste to energy approach. *Journal of Cleaner Production*, 354, 131718. <https://doi.org/10.1016/j.jclepro.2022.131718>
- Kabir, S. B., Khalekuzzaman, Md., Islam, Md. B., & Hossain, Md. R. (2022). Performance optimization of organic solid waste and peat co-liquefaction mechanism for processing sustainable biocrude. *Fuel Processing Technology*, 231, 107234. <https://doi.org/10.1016/j.fuproc.2022.107234>
- Khalekuzzaman, M., Fayshal, M. A., & Adnan, H. M. F. (2024). Production of low phenolic naphtha-rich biocrude through co-hydrothermal liquefaction of fecal sludge and organic solid waste using water-ethanol co-solvent. *Journal of Cleaner Production*, 140593. <https://doi.org/10.1016/j.jclepro.2024.140593>
- Khalekuzzaman, Md., Kabir, S. B., Islam, Md. B., Datta, P., Alam, Md. A., & Xu, J. (2021). Enhancing microalgal productivity and quality by different colored photobioreactors for biodiesel production using anaerobic reactor effluent. *Biomass Conversion and Biorefinery*, 11(3), 767–779. <https://doi.org/10.1007/s13399-020-00852-5>
- Kohansal, K., Toor, S., Sharma, K., Chand, R., Rosendahl, L., & Pedersen, T. H. (2021). Hydrothermal liquefaction of pre-treated municipal solid waste (biopulp) with recirculation of concentrated aqueous phase. *Biomass and Bioenergy*, 148, 106032. <https://doi.org/10.1016/j.biombioe.2021.106032>
- Li, R., Ma, Z., Yang, T., Li, B., Wei, L., & Sun, Y. (2018). Sub-supercritical liquefaction of municipal wet sewage sludge to produce bio-oil: Effect of different organic–water mixed solvents. *The Journal of Supercritical Fluids*, 138, 115–123. <https://doi.org/10.1016/j.supflu.2018.04.011>
- Lu, J., Watson, J., Zeng, J., Li, H., Zhu, Z., Wang, M., Zhang, Y., & Liu, Z. (2018). Biocrude production and heavy metal migration during hydrothermal liquefaction of swine manure. *Process Safety and Environmental Protection*, 115, 108–115. <https://doi.org/10.1016/j.psep.2017.11.001>
- Nandiyanto, A. B. D., Oktiani, R., & Ragadhita, R. (2019). How to Read and Interpret FTIR Spectroscopy of Organic Material. *Indonesian Journal of Science and Technology*, 4(1), 97. <https://doi.org/10.17509/ijost.v4i1.15806>
- Nations, U. (2024). *Causes and Effects of Climate Change*. United Nations; United Nations. <https://www.un.org/en/climatechange/science/causes-effects-climate-change>
- Ogunkanmi, J. O., Kulla, D. M., Omisanya, N. O., Sumaila, M., Obada, D. O., & Doodoo-Arhin, D. (2018). Extraction of bio-oil during pyrolysis of locally sourced palm kernel shells: Effect of process parameters. *Case Studies in Thermal Engineering*, 12, 711–716. <https://doi.org/10.1016/j.csite.2018.09.003>
- Peters, K. E., Lillis, P. G., Lorenson, T. D., & Zumberge, J. E. (2019). Geochemically distinct oil families in the onshore and offshore Santa Maria basins, California. *AAPG Bulletin*, 103(2), 243–271. <https://doi.org/10.1306/07111818014>
- Shuping, Z., Yulong, W., Mingde, Y., Kaleem, I., Chun, L., & Tong, J. (2010). Production and characterization of bio-oil from hydrothermal liquefaction of microalgae *Dunaliella tertiolecta* cake. *Energy*, 35(12), 5406–5411. <https://doi.org/10.1016/j.energy.2010.07.013>
- Sintamarean, I. M., Grigoros, I. F., Jensen, C. U., Toor, S. S., Pedersen, T. H., & Rosendahl, L. A. (2017). Two-stage alkaline hydrothermal liquefaction of wood to biocrude in a continuous bench-scale system. *Biomass Conversion and Biorefinery*, 7(4), 425–435. <https://doi.org/10.1007/s13399-017-0247-9>
- Xiu, S., Shahbazi, A., Shirley, V., & Cheng, D. (2010). Hydrothermal pyrolysis of swine manure to bio-oil: Effects of operating parameters on products yield and characterization of bio-oil. *Journal of Analytical and Applied Pyrolysis*, 88(1), 73–79. <https://doi.org/10.1016/j.jaap.2010.02.011>
- Yin, S., Dolan, R., Harris, M., & Tan, Z. (2010). Subcritical hydrothermal liquefaction of cattle manure to bio-oil: Effects of conversion parameters on bio-oil yield and characterization of bio-oil. *Bioresource Technology*, 101(10), 3657–3664. <https://doi.org/10.1016/j.biortech.2009.12.058>
- Zhang, B., von Keitz, M., & Valentas, K. (2009). Thermochemical liquefaction of high-diversity grassland perennials. *Journal of Analytical and Applied Pyrolysis*, 84(1), 18–24. <https://doi.org/10.1016/j.jaap.2008.09.005>
- Zhou, D., Zhang, L., Zhang, S., Fu, H., & Chen, J. (2010). Hydrothermal Liquefaction of Macroalgae *Enteromorpha Prolifera* to Bio-oil. *Energy & Fuels*, 24(7), 4054–4061. <https://doi.org/10.1021/ef100151h>