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OPTIMIZATION OF BIO-CRUDE YIELD FROM FAECAL SLUDGE THROUGH HYDROTHERMAL LIQUEFACTION USING LOCAL CLAYS

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ABSTRACT

Approximately 35,000 metric tons of faecal sludge (FS) are generated daily in Bangladesh and released into the environment without proper treatment, contributing to greenhouse gas (GHG) emissions. A 'waste-to-energy' technique could reduce emissions of greenhouse gases while also providing a sustainable route for energy and resource production. Since FS is a wet waste containing around 90% moisture content, hydrothermal liquefaction (HTL) can be an effective solution for converting it into energy as it operates under wet conditions, using water as a catalyst, removing the requirement for energy-consuming pre-drying. In this study, we took the opportunity to convert FS into bio-crude through HTL and optimized the bio-crude yield using two local clays collected from Khulna and Netrokona districts, as catalysts. Clay-1 obtained a maximum bio-crude yield of 49 wt.% at 300 °C and a retention period of 60 minutes, with a value of heating of 32.6 MJ/kg. The Fourier Transform Infrared Spectroscopy (FTIR) analysis of these clays revealed the presence of SiO_2, Fe2O3, and Al_2O_3 which significantly enhance bio-crude yield due to their catalytic effect. The FTIR study for the bio-crude shows an abundance of C-H stretches between 2855-3000 cm^{-1}, suggesting the presence of long-chain hydrocarbons formed through the decarboxylation of long-chain fatty acids. Additionally, the low APIo gravity value (-28) of the bio-crude using Clay-1, classifies it as extra heavy crude. This particular result shows that using natural clay in the HTL process not just enhances the bio-crude yield but also leads to heavier crude, indicating an increase in asphaltene content. This research underscores the economic and environmental advantages of using local clays in bio-crude production, presenting a hopeful and sustainable alternative to petroleum-based crude, paving the way for a greener future.

Key words: *bio-crude; fecal sludge; hydrothermal liquefaction; clay soils; waste to energy.*

INTRODUCTION

Petroleum-derived crude oils generate severe environmental impacts, such as the emission of GHGs and volatile components that are chemically and toxically hazardous, affecting both the health of pavement workers and the public at large (Ding et al., 2021). In response to these challenges, bio-crude has emerged as a potential sustainable alternative to petroleum-derived oils (Gaudenzi et al., 2023; Aziz et al., 2015). Bio-crude, an organic polymer derived from renewable biomass resources, offers several advantages including lower environmental impact and increased sustainability (Ding et al., 2021; Rouly Sihombing et al., 2019; Williams et al., 2009). It has shown comparable performance to conventional crudes, making it an appealing option as an alternative oil source (Al-Sabaeei et al., 2022).

Approximately 250–300 Mt of moist FS are mishandled annually worldwide, significantly polluting the environment and emitting GHGs (Strande & Brdjanovic, 2014). This issue has gained considerable attention recently, prompting the need for more effective 'waste to resource' approaches that can mitigate GHG emissions and introduce sustainable pathways for energy and resource generation (Sharma et al., 2021). HTL, is an effective thermochemical procedure that turns carbon-based substrates to bio-crude, bio-asphaltene, and other organic products under wet conditions, operating between 250 and 400 °C, at autogenous pressures ranging from 5 and 30 MPa, and for different retention times (Hossain et al., 2022; Leng & Huang, 2018). When compared to alternative thermochemical conversion techniques, HTL has the main advantage of processing wet waste material directly, eliminating the necessity for energy-consuming preliminary drying activities (Posmanik et al., 2017).

To enhance bio-crude yields, researchers have explored the use of different catalysts or solvents (Yan et al., 2018). However, these catalysts or solvents often involve complex and expensive recovery processes unsuitable for large-scale commercial plants. However, natural catalysts provide a more economical and environmentally beneficial substitute, as they can safely return to the environment and typically occur naturally. Metal oxides (e.g., SiO_2, TiO_2, Fe_2O_3) are the primary component of natural clays that act as the catalyst in the HTL process (Mohamed et al., 2022). Clay catalysts, for example, have been shown to facilitate several chemical processes such as dehydration, deoxygenation, denitrogenation, and depolymerization of proteins and carbohydrates, and influence re-polymerization during HTL (Saral & Ranganathan, 2022). Recent studies have demonstrated that natural clay catalysts, such as clay soils can yield asphaltene-rich bio-crude ranging from 38.7% to 58.1% during HTL of high-protein microalgae, indicating their potential for bio-asphaltene production (Cardenas Velandia et al., 2021; Wang et al., 2017).

While very few studies have investigated the production of bio-asphalt using the HTL, none have explored the feasibility of producing asphaltene-rich bio-crude through HTL of FS and comparing it with petroleum-derived crude (Ding et al., 2021; Zhao et al., 2014). Therefore, this study aims to harness the potential of HTL to produce bio-crude from waste sludge in the presence of local clays and to evaluate the catalytic effect on both the yield and quality of the produced bio-crudes.

MATERIALS AND METHODS

Feedstock and Clay Soils

The FS utilized in this research was collected from the second compartment of a septic tank situated at the residential section of Khulna University of Engineering and Technology (KUET), Khulna. To guarantee homogeneity, the obtained materials were well mixed and kept at 4°C in a laboratory freezer until the HTL experiment began. Among the two clay soils, the clay-1 sample was collected from Fulbarigate in Khulna, while the clay-2 sample was taken from Bijoypur in the Netrokona district of Bangladesh. These clay samples underwent preliminary preparation, which involved manually removing grass, roots, and wood residues. Subsequently, the clay samples were oven-dried for one hour at 105°C, followed by sieving using a No. 200 sieve (0.075 mm). The prepared clay samples were then stored in a desiccator for use in the HTL process. Table 1 and Table 2 represent the feedstock and clay soils characterization respectively.

Table 1 Characterization of FS

Components	FS
Proximate composition (wt.%)	
Moisture	89.26 ± 0.40
Total solids	10.1 ± 0.38
Volatile matter	5.89 ± 0.52
Ash content	3.79 ± 0.61
Fixed carbon	1.78 ± 0.51
Elemental composition (dry basis, wt.%)	
C	39.85
H	4.68
N	6.05
O[a]	36.59
S	0.69
Elemental mole ratio	
H/C	1.41
O/C	0.69
N/C	0.13
$H/C_{effective}$	0.03
Molecular formula	$CH_{1.41}O_{0.69}N_{0.13}$
HHV ($MJ\ kg^{-1}$)	14.75

[a] Determined by the difference, O (wt%) = 100-sum of (C, H, N, S, and Ash).

Table 2 Characterization of Clay Soils

	Clay-1	Clay-2
Proximate composition (wt.%)		
Moisture	14.17 ± 1.38	3.15 ± 0.79
Total solids	85.83 ± 1.37	96.35 ± 0.80
Elemental composition (dry base, wt.%)		
C	0.79	0.17
H	0.67	0.81
N	0.34	0.27
S	0.08	0.20

HTL Process and Product Separation

HTL tests were conducted in a 25 mL batch reactor (SS-304), with an operational volume of 10 mL and a headroom of 15 mL. The HTL reactor was sealed with copper gaskets and secured with a steelhead. The temperature of the reactor was maintained constant throughout the experiment using a Boeco Muffle Furnace MF 8/1100. In the HTL process, the FS slurry mixture was heated to 300°C under 10 MPa pressure, with a rate of heating of 66°C/min and a retention time of 60 minutes. Each batch used 10 mL of FS, combined with a 10% clay catalyst based on the feedstock's aggregate solids content (Wang et al., 2017).

During the HTL process, biomass was separated into four phases: syngas, biochar, bio-crude, and an aqueous phase. Throughout per HTL experiment, the reactor was cooled by submerging it in a bath of water set to 25°C, allowing for the safe release of syngas when opened. To extract the HTL products, 30 mL of dichloromethane (DCM) was added to the reactor. The resultant solution was separated into three to four 15-mL centrifuge tubes and carefully mixed with a vortex mixer (VM-10 Witeg, Germany). To separate the phases, the mixes were centrifuged at 4100 rotation per minute for 20 minutes on a NUVE-NF 800/800R multipurpose tabletop centrifuge. The bio-crude layer was carefully extracted with a 5 mL syringe and transferred to pre-weighed Petri dishes, which were stored in a desiccator for several hours to allow the DCM solvent to evaporate. Meanwhile, the biochar phase was dried at 40°C until its weight remained constant. All HTL products were labeled, stored in a laboratory freezer, and set aside for further analysis. Figure 1. provides a schematic flow diagram of the HTL process.

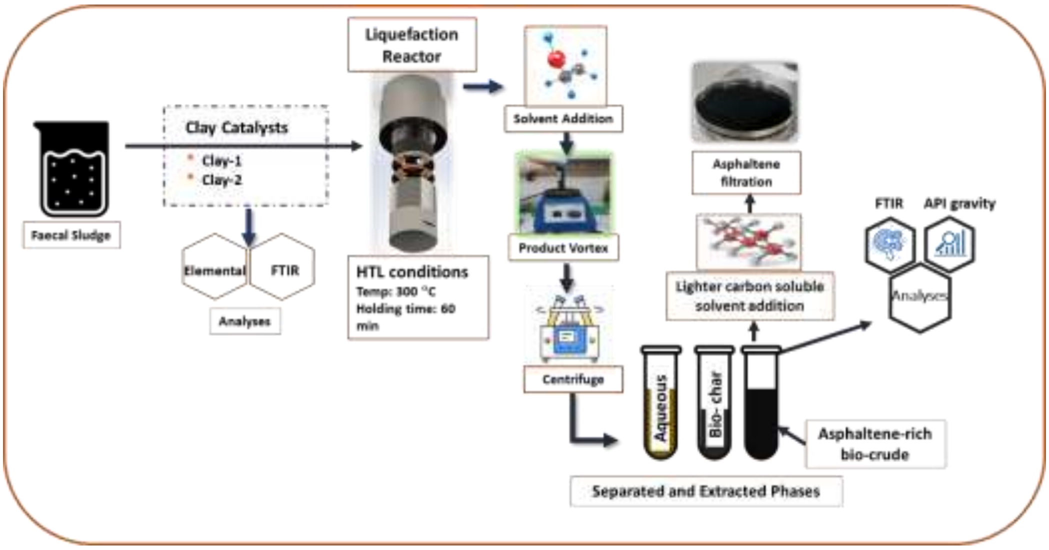

Figure 1 Schematic Flow Diagram of the HTL Process

Analytical Methods

The SM 2540 G method was used to conduct a proximity analysis of the FS feedstocks, which included assessing moisture level, volatile substance, ash content, and fixed carbon. The ash content was determined using ASTM E 1755-01 standard (*Standard Test Method for Ash in Biomass*, 2010). A Shimadzu IRTracer-100 spectrophotometer was used to identify functional groups in clay samples and asphaltene-rich bio-crude. At a spatial resolution of 2 cm^{-1}, the 400–4000 cm^{-1} and 800-4000 cm^{-1} spectral ranges were examined. The collected IR data was analyzed using IR Analyze-RAMalyze (Lab-Cognition GmbH & Co. KG) and the Origin-Pro 2018 program. Lastly, the local clay and asphaltene-rich bio-crude were analyzed using the CE-440 elemental analyzer (Exeter Analytical Inc., USA).

Bio-Asphaltene Precipitation

Around 1-2 g of asphaltene-rich bio-crude was combined with n-hexane at a 1:10 ratio and vortexed for 10 minutes to ensure complete mixing. After that, the resultant mixture was pumped through a 0.22 μm syringe filter. The filters were placed in an oven at 70°C for 24 hours to allow the solvent to evaporate. The bio-asphaltene content was calculated by measuring the weight difference before and after filtration. For each sample, this precipitation procedure was carried out three times, and the average yield was then recorded. The ASTM technique was utilized to measure the bio-asphaltene content (Davarpanah et al., 2015).

Analytical Calculations

The following equations were used to calculate the HTL product yield and other essential parameters. Eq. (1) was used to calculate the higher heating value (HHV) of the feedstock and bio-crude samples (Cheng et al., 2018). To evaluate the potentialities of feedstocks for bio-crude conversion, the effective H/C (H/Ceff) ratio of feedstock was determined, using Eq. (2) (Fan et al., 2021). The asphaltene-rich bio-crude yield was determined by using Eq. 3 (Hassan et al., 2020). The yield of HTL products, comprising biochar, gas phase, aqueous state, and losses, was calculated on dry conditions using Eqs. (4) - (6) (Chopra et al., 2019). To determine the feedstock conversion rate, the production of biochar was subtracted from the overall yield of HTL products, as indicated in Eq. (7). The Asphaltene content was calculated through Eq. (8) (Ahmed Ebrahim et al., 2022).

HHV (MJ kg-1) = $0.3414\,C + 1.4445\left(H - \frac{N+O-1}{8}\right) + 0.093S$ (1)

H/Ceff = $\frac{(H-20)}{C}$ (2)

Bio-crude yield (%) = $\frac{(mass\ of\ biocrude)}{(dry\ mass\ of\ feedstock)}) \times 100\%$ (3)

Bio-char yield (%) = $\frac{(mass\ of\ biochar)}{(dry\ mass\ of\ feedstock)} \times 100\%$ (4)

Aqueous phase (%) = $(\frac{mass\ of\ aqueous\ phase)}{(dry\ mass\ of\ feedstock)} \times 100\%$ (5)

Gas-phase + losses (%) = $100\,\% - (biocrude + biochar + aqueous)$ (%) (6)

Conversion rate (feedstock) (%) = $100\% - biochar\ yield\ \%$ (7)

Asphaltene Yield (asphalt, wt%) = $\frac{(mass\ of\ asphaltene\ (g))}{(mass\ of\ biocrude\ (g)\ )} \times 100\%$ (8)

C, H, and O represent the atomic percentages of carbon, hydrogen, and oxygen, respectively.

RESULTS AND DISCUSSIONS

Identification and analysis of functional groups of clays

FTIR was used to detect the functional groups contained in the local clays. The main bonding types, spectral range, and strength of the spectra are shown in Figure 2. The functional groups (Si-O, Si-O-Al, Al-O-Al, O-C-O, and O-H) were represented by spectra ranging from 500 to 1450 cm^{-1} and 3600 to 3700 cm^{-1} for both clays. For clay-1 peak after 400 cm^{-1} indicates Fe-O (Cottet et al., 2014). The presence of a higher percentage of Al-O-Al in clay-2 resulted in a distinctive sharp peak at 900 cm^{-1} in the FTIR spectrum, representing Al-oxide stretches Similar functional groups have also been identified in the FTIR spectra of other clays by other studies (Cottet et al., 2014; Wang et al., 2017). These functional groups are key factors in the clays that influence the HTL process, as suggested by other researchers (Wang et al., 2017; Zhang et al., 2022).

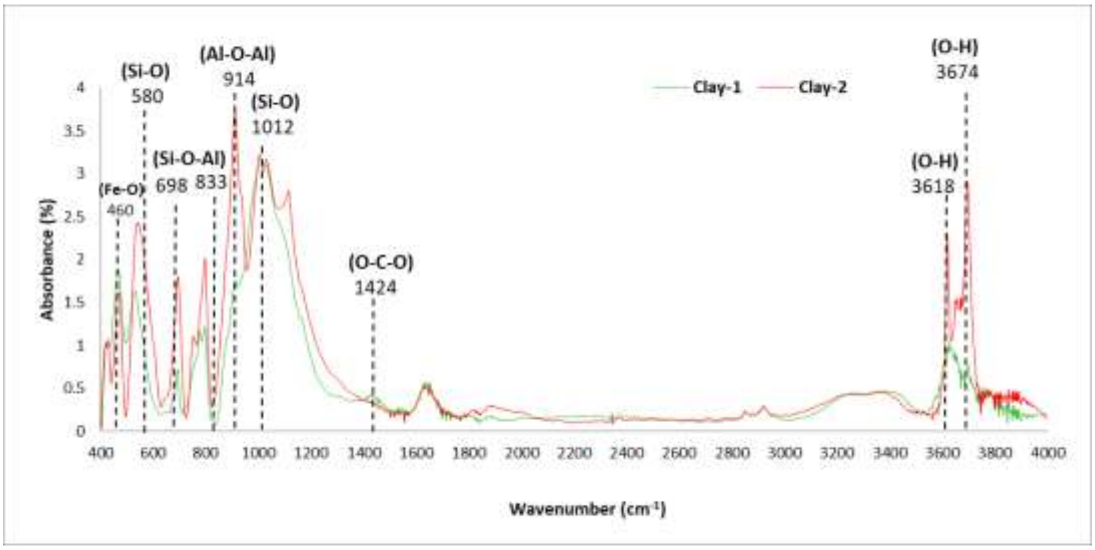

Figure 2 Functional groups in clay soils

Effect of clays on the yield of asphaltene-rich bio-crude

The yield of bio-crude is a crucial factor in determining the financial viability and environmental responsibility of the HTL process. The bio-crude yields from the HTL of FS for two distinct local clays at 300°C and 60 minutes of retention time are demonstrated in Figure 3. The yields of bio-crude range from 33 to 49 wt%, based on the type of clay used. The graph clearly shows that the bio-crude yield was 32.5% without the use of clay, which increased drastically when clays were used. SiO2 and Al2O3 influence the reaction to promote yield in HTL. Specifically, clay-1 showed the highest crude yield of 49 wt%, which might be due to the significant presence of metal oxides, especially iron oxide. Several researchers have also found the best yield and additional catalytic activity where iron metal oxides acted as a catalyst with spirulina (Kandasamy et al., 2019; Saral & Ranganathan, 2022; Wang et al., 2017). Generally, rock and clays act as natural catalysts in natural fossil fuel production at the lithosphere (Sharma et al., 2021).

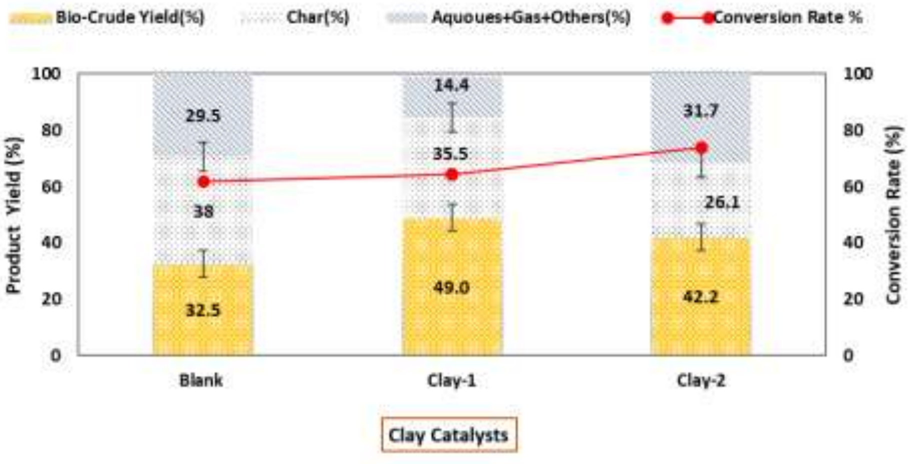

Figure 3 Impacts of clay soils on bio-crude yield

Functional groups of asphaltene-rich bio-crude

The spectrum range and chemical interaction of functional compounds in bio-crude were identified via FTIR testing. The key spectra ranges, corresponding functional groups, and their strengths are depicted in Figure 4. Functional groups such as C-H, N-H, and O-H are linked to phenols, fatty acid amides alcohols, and heterocycles that contain nitrogen, and they are associated with the 1000–1300 cm^{-3} range. These compounds are primarily derived from the Maillard reaction, which involves proteins and carbohydrates, as well as the dehydrating of lignin throughout the HTL process. The C-H stretch, indicative of fatty acid-derived hydrocarbons, was prominently observed between 2855 and 3000 cm^{-1}, highlighting the decarboxylation mechanism of HTL, which facilitates oxygen removal from bio-crude as CO_2 and H_2O. Carbonyl compounds functional groups (C-O) were detected at 1650-1750 cm^{-1}, indicating lipid hydrolysis and amino acid deamination during the HTL process. These functional groups provide insight into the HTL mechanism of the reaction and demonstrate bio-crude's significant commercial potential. In their detailed study, Sun et al. (2017) identified a significant peak around 1735 cm^{-1}, attributed to the C=O stretching vibration during thermal liquefaction. A peak at 1100 cm^{-1}, associated with C-O-C or C-O stretching in bio-oil, indicates that alcohols or ethers were distilled from the feedstock during post-processing.

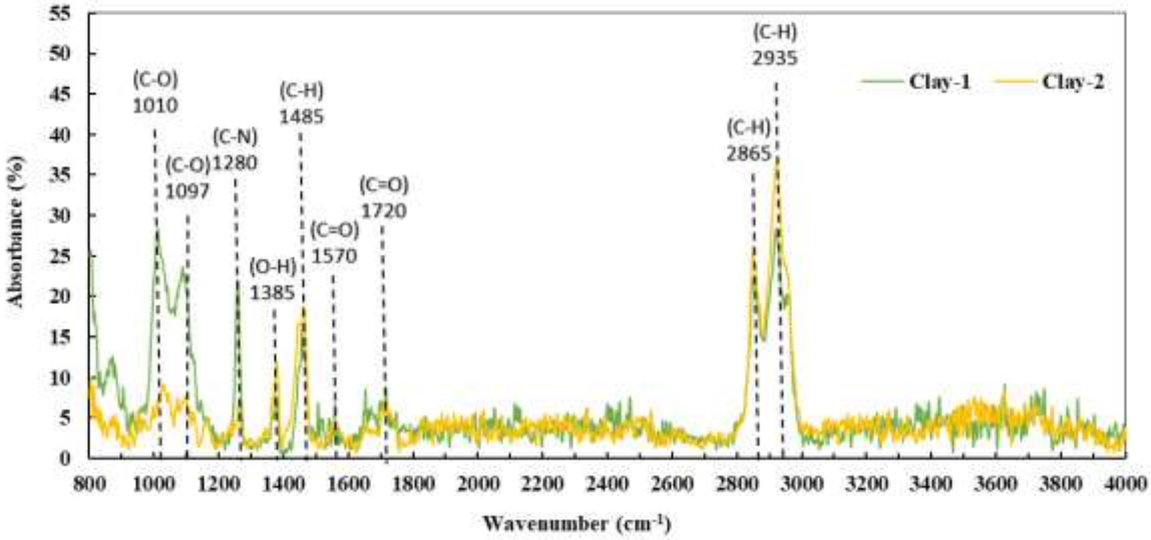

Figure 4 Functional groups assessment of bio-crude using two local clay soils

Bio-asphaltenes yield

The bio-asphaltene yield is presented in Figure 5. This study investigates the impacts of two local clays on the yield of bio-asphaltene through a series of experiments. The results demonstrate that due to the clays incorporation in the reaction mixture induced a significant enhancement in the yield of bio-asphaltene by creating more covalent bonds and re-polymerizing effects; lignin decomposing, deamination, protein, and carbohydrate depolymerizing tendencies also contribute to this process. Specifically, the highest yield of bio-asphaltene achieved in the presence of clay-1 was approximately 48 wt%, which is substantially higher compared to the yield of blank experiments where no catalyst was utilized, resulting in a yield of only 21 wt%. These findings highlight the catalytic potential of clay in the production of bio-asphaltene, which may have practical implications in the field of sustainable resource recovery. Few studies have investigated the production of asphaltene through HTL, as well as the effects of catalysts, process temperature, and retention time on its yield and elemental composition (You et al., 2011). Zhang et al. (2022) revealed that the maximum asphaltene yield was obtained at 300°C during HTL, which decreased slightly at higher temperatures. The use of clays as the catalyst in the HTL of high-protein microscopic algae substantially increased the asphaltene content, bringing it from 27 to 53 wt%. (Wang et al., 2017).

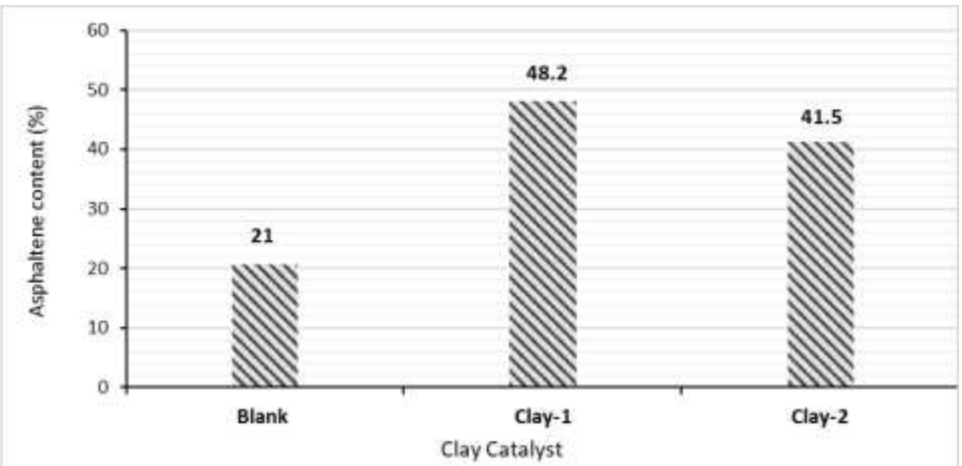

Figure 5 Impact of clay on asphaltene yield using FS

API gravity

The bio-crude samples obtained using clay-1 and clay-2 are presented in Figure 6. The bio-crude samples had specific gravity (SG) values ranging from 1.37 to 1.42. The SG of bio-crude is proportional to its API gravity. Bio-crude with clay-1 and clay-2 possessed ◦API gravity of -28 and -31.7, accordingly, indicating extra heavier bio-crude. In a study, the pyrolysis of 6 distinct biomass sources with ◦API gravity ranging from -5.2 to 2, resulted in the production of extra heavy bio-crude (Mante & Agblevor, 2014). Therefore, the negative ◦API gravity of these two bio-crudes produced using the local clays confirms their classification as extra-heavy crude. Heavy oils with low ◦API gravity are often rich in high molecular weight components, including resins and asphaltenes (Hinkle et al., 2008). This result strongly indicates that the bio-crudes produced using the local clays are rich in asphaltene.

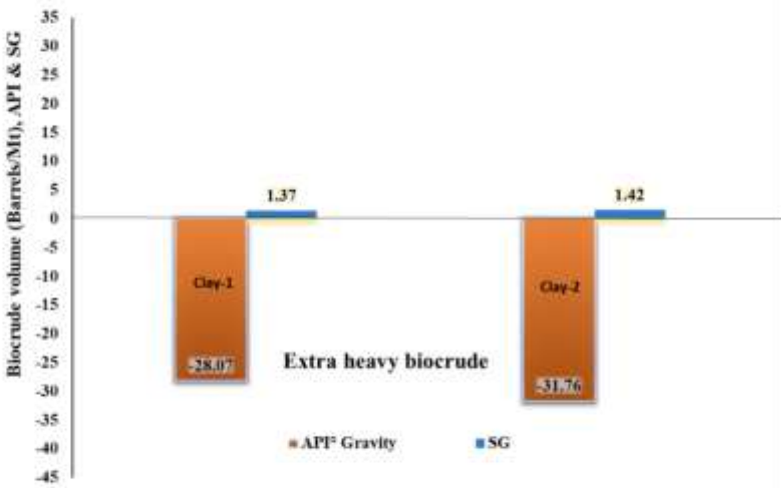

Figure 6 API gravity of asphaltene-rich bio-crudes

CONCLUSION

This study successfully optimized bio-crude yield from FS through HTL using local clays, with clay-1 achieving the maximum bio-crude yield reached 49 wt%, while the bio-asphaltene yield was 48 wt%. Detailed analysis using FTIR and other methods confirmed the presence of functional groups and chemical bonds that enhance HTL reaction mechanisms such as dehydration, deoxygenation, and depolymerization. The significant presence of metal oxides, particularly Si, Fe, and Al oxides, in the clays played a crucial role in boosting catalytic activity and yield. This research underscores the feasibility of using fecal waste sludge as a viable feedstock for producing high-quality bio-crude and bio-asphaltene, supporting waste-to-resource approaches and sustainable energy solutions. The findings indicate the potential of local clays to improve the economic viability and sustainability of HTL processes, providing a viable route for resource recovery and the production of clean energy. Future studies should concentrate on improving HTL parameters and scaling up the process for commercial use.

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