Biocrude Oil Production from Faecal Sludge and Cow Dung: An Integrated Waste to Green Energy Approach through Hydrothermal Co-liquefaction

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Declaration

This is to confirm that the research work **"Biocrude Oil Production from Faecal Sludge and Cow Dung: An integrated waste to Green Energy Approach through hydrothermal Co-liquefaction"** has been completed by the authors. The research report mentioned above has not been filed anywhere, in its entirety or in any part. This research has been funded by the Directorate of Technical Education, Technical and Madrasah Education Division, Ministry of Education, Bangladesh.

(Raihan Khan Opu)
Signature of Team Leader

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Abstract

The management of faecal sludge collected from septic tanks and cow dung has been a significant problem in developing nations. This issue can be solved by thermochemically converting waste into biofuel. Hydrothermal liquefaction is a thermochemical conversion technology that converts wet waste biomass feedstokes to biocrude. In this study, Faecal sludge (FS) and Cow Dung (CD) were converted to bio-crude oil by co-Liquefation (co-HTL). The co-HTL of FS and CD were evaluated in a 30 cc HTL reactor under 10% solid loading, 320^0C temperature and 60-minute running conditions at different FS to CD ratios (1:0, 3:1, 1:3, 1:1 and 0:1). The individual yield of biocrude was FS (23.71%) and CD (19.82%); however, in the case of co-HTL, the maximum biocrude yield was 19.2% at FS to CD 3:1 ratio, demonstrating an antagonistic effect in terms of biocrude production. The maximum higher heating value (HHV) of 41.70 MJ/Kg of Biocrude was obtained from the co-HTL of FS and CD at a 3:1 ratio, illuminating the synergistic effect in terms of HHV. By elemental analysis, The Co-HTL (3:1, FS:CD) biocrude was found to have 77.1% carbon, 12.1% hydrogen, and 8.95% oxygen, with the potential to resemble petrocrude. The GC-MS fractionation analysis of Co-HTL (3:1, FS:CD) biocrude produced the maximum lighter fraction kerosene-like fuel (70.15%). The findings of this study suggest that the co-HTL of faecal sludge and cow dung at 3:1 ratio could be a comprehensive approach to converting waste to bioenergy products.

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Nomenclature

Every single notation and symbol is explained in the text where it first appears. The meanings of the more popular symbols are provided here for your convenience.

AC	Ash content
ACCE	Applied Chemistry and Chemical Engineering
AP	Aqueous phase
API	American Petroleum Institute
BCSIR	Bangladesh Council of Scientific and industrial Research
CD	Cow Dung
COD	Chemical Oxygen Demand
Co-HTL	Co/Combined hydrothermal liquefaction
DCM	Dichloromethane
EC	Electric Conductivity
ECR	Energy consumption ratio
ER	Energy recovery
FC	Fixed carbon
FS	Faecal sludge
FEC	Faridpur Engineering College
FTIR	Fourier Transform Infrared Spectroscopy
GC-MS	Gas Chromatography-Mass Spectrometry
GHGs	Greenhouse gases
HHV	Higher heating value
HTL	Hydrothermal Liquefaction
IEA	International Energy Agency
JUST	Jashore University of Science and Technology
MC	Moisture content
OSS	On site Sanitation System
VM	Volatile matter

Section 1

1 Introduction

1.1 Background

Energy is a source of economic expansion as well, especially in the nations with the fastest growing economies. One of the biggest shocks to the world's energy markets in decades has been occurring since the first half of 2022. Energy shortages and worries about energy security were made worse by the COVID-19 epidemic and Ukraine war (The World Bank, 2023).

Since ancient times, the world's main source of energy has included fossil fuels, but their use has various adverse effects on environment (Martins et al., 2018). The Intergovernmental Panel on Climate Change (IPCC) claims that emissions from fossil fuels are the primary cause of global warming. In 2018, fossil fuels and industry were responsible for 89% of global CO_2 emissions (Client Earth, 2022). However, using renewable energy sources like solar, wind, water, and biomass can lessen reliance on fossil fuels. Among them all, Biomass stands out as a renewable energy source that is both easily accessible and inexpensive, making it a desirable option for fuel production (Adedeji et al., 2022). The biomass can be divided into a variety of categories, including municipal solid waste (MSW), agricultural crops, crop residues, agricultural waste, wood, animal wastes, aquatic plants, algae, and food processing waste (Sivabalan et al., 2021).

Hydrothermal liquefaction (HTL), a process that turns wet waste biomass into biocrude oil, is one such option for producing biomass energy (Adedeji et al., 2022). The process of hydrothermal liquefaction (HTL) involves the interaction of biomass or organic material with water at hydrothermal conditions, i.e., between 250 and 450 °C and 100 to 350 bar of pressure. Water maintains its liquid or somewhat dense supercritical state under these circumstances. HTL works best with wet feedstocks because it requires a wet reaction environment, minimizing the need for drying. (Castello et al., 2018).

Most developing towns lack the necessary infrastructure to handle and treat the onsite

sanitation facilities, such as pit latrines and septic tanks, that build faecal sludge, described as excreta and blackwater, with or without greywater (Strande & Brdjanovic, 2014). The upshot is that more than 75 percent of faecal sludge is typically not safely treated before being released into urban areas, posing a severe risk to public health and environmental security (C Blackett, 2014). Faecal sludge is currently gaining attention as a potentially valuable resource for the production of biofuel, Biogas and therefore energy (Yin et al., 2016). Studies have shown that FS has the potential to produce biofuel as a replacement for fossil fuel through the thermochemical conversion process (gasification, pyrolysis, and hydrothermal liquefaction) (Hossain et al., 2022).

Dung from herbivorous bovine animals is known as "cow dung" and is the undigested remains of the food that they have devoured (Gupta et al., 2016). The proportion of faeces to urine in it is 3:1. Cow faeces primarily contains lignin, cellulose, and hemicelluloses. The United Nations Food and Agriculture Organisation (FAO) indicates that between 55 and 65 percent of the animal faeces on this planet includes methane, which, when emitted into the atmosphere, can cause global warming at a pace up to 21 times greater than that of CO2 (Lohan et al., 2015). The most abundant alternative and renewable bioresource for producing biofuels and biochemicals in bio-refineries is the lignocellulosic biomass of agricultural wastes (Baruah et al., 2018). Consequently, cow dung ought to be an optimal feedstock for creating biofuel or bio-based chemicals (Khan et al., 2020).

(Opu et al., 2023) explained that biocrude yield and quality significantly improved due to co-HTL of Faecal Sludge with with lignocellulose biomass such as water hyacinth. Co-HTL of sewage sludge with Microalgae showed a synergistic effect (Mishra & Mohanty, 2020).

Despite having abundant biomass for biocrude production, there is a research gap associated with waste management and environmental pollution control issues by using faecal sludge, and cow dung. This study investigated co-HTL of FS with Cow dung. None of the previous co-HTL research had used and FS and Cow dung derived biocrude oil. In this context, this novel approach has been conducted toevaluate the effect of FS and Cow dung for sustainable bioenergy production.

1.2 Objectives of the Study

The specific objectives of the research work are to-

- **a.** investigate the yield and quality of biocrude oil from different Cow dung mixing ratios with faecal sludge.
- **b.** evaluate the petroleum fractions from the biocrude oil.

Section 2

2 Literature Review

2.1 Biomass

Any type of organic substance that originates from animals and plants and currently resides or was recently living is categorized as biomass. Biomass can be found in a variety of places. Some biomass, like poplar and miscanthus, is specifically grown for energy purposes. Biomass waste and residues are produced as byproducts when the preferred raw materials are grown, processed, and consumed (James G et al., 2014). Primary, secondary, and tertiary residues/wastes are the three categories into which biomasses can be classified. Primary residues are produced when food crops and forest products are planted in the ground. Corn leaves, stalks, straws, and stems are a few examples. Wastes left while processing agricultural and food crops into final products, such as woodchips, sawdust, rice husks and hulls, coffee husks, palm kernel cake, sugarcane bagasse, pulp and paper waste, and textiles, are known as secondary biomass residues. After humans or animals have consumed products made from biomass, leading to sludge, tertiary residues are produced (Li et al., 2007; Mahmud et al., 2022). The Biomass sources are shown in figure 2.2

Figure 2.1 Biomass Sources for Energy ; (Raina et al., 2022)

2.2 Biofuel

Any fuel that's produced from biomass, such as plant, algae, or animal waste, is referred to as a biofuel. Unlike fossil fuels like oil, coal, and gas, biofuel is considered a form of renewable energy. Biofuels' energy comes from the biological carbon fixation process, which takes place relatively quickly and involves living things or their products. In contrast to the millions of years it takes for fossil fuels to form. Figure 2.2 is a graphical representation of global biocrude production based on leading countries.

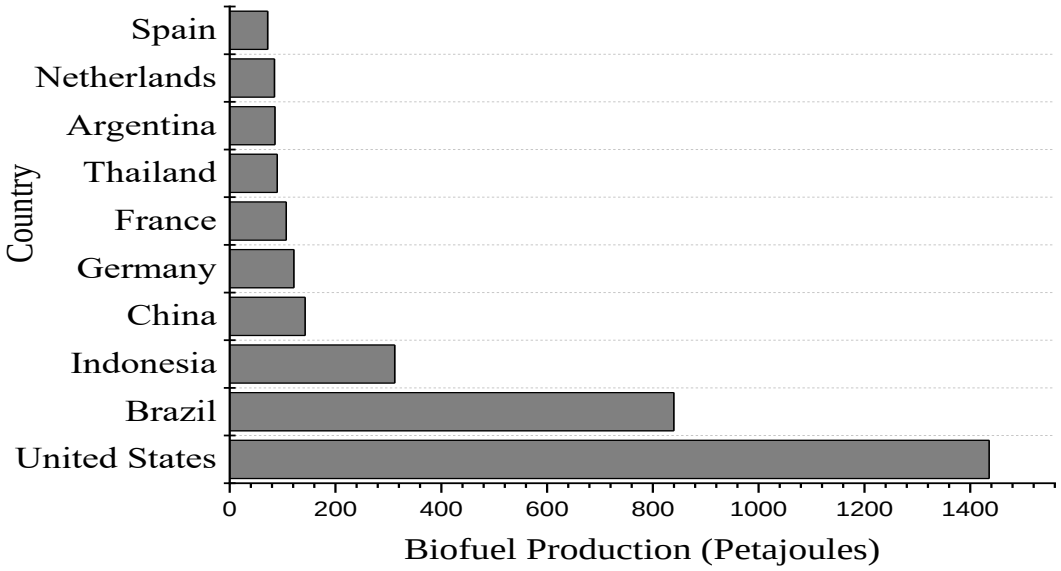

Figure 2.2 : Global Biofuel Production in Petajoules (EIA, 2021)

2.3 Types of Biofuel

Biofuels are classified in the following four categories:

a. **First-generation biofuels**: First-generation biofuels, also known as conventional biofuels derived from various sources such as grains, animal fats, and vegetable oils. These fuels are obtained through traditional production methods. Examples of first-generation biofuels include biodiesel, bio-alcohols, green diesel, biofuel petrol, ethanol, vegetable oil, bio-ethers, biogas, syngas, and solid biofuels. These types of biofuels have been widely utilized in various applications.
b. **Second-generation biofuels**: Second-generation biofuels encompass fuels that can be generated from both plant-based and animal-based biomass. Unlike first-generation

biofuels, the feedstock for second-generation biofuels does not compete with food sources. Notable examples of second-generation biofuels include bio-oil, Fischer-Tropsch (FT) oil, hydrotreating oil, lignocellulosic ethanol, butanol, and mixed alcohols. These advanced biofuels are derived from non-food biomass sources and hold significant potential for sustainable fuel production.

c. **Third-generation biofuels**: Third-generation biofuels are distinguished by their carbon source, which is derived from aquatic autotrophic organisms, particularly algae. These biofuels utilize light, carbon dioxide, and nutrients to produce the feedstock, effectively expanding the available carbon resources for biofuel production. Algae-based biofuels are considered a promising avenue as they offer the potential to efficiently convert these aquatic organisms into renewable and sustainable fuel sources.

d. **Fourth-generation biofuels**: Fourth-generation biofuel production systems consider biomass crops as efficient "carbon capturing" elements that remove carbon dioxide (CO_2) from the atmosphere and store it in their branches, trunks, and leaves. Through second-generation processes, the carbon-rich biomass is subsequently converted into fuels and gases. A crucial aspect of this generation is the capture of carbon dioxide through precombustion, oxyfuel, or postcombustion methods, which occur before, during, or after the bioconversion process. Fourth-generation biofuels encompass biomethane, biohydrogen, and synthetic biofuels. These advanced biofuels leverage biomass crops to sequester CO_2 and employ innovative processes to produce cleaner and more sustainable fuel alternatives. The Figure 2.3 presents the type biofuel

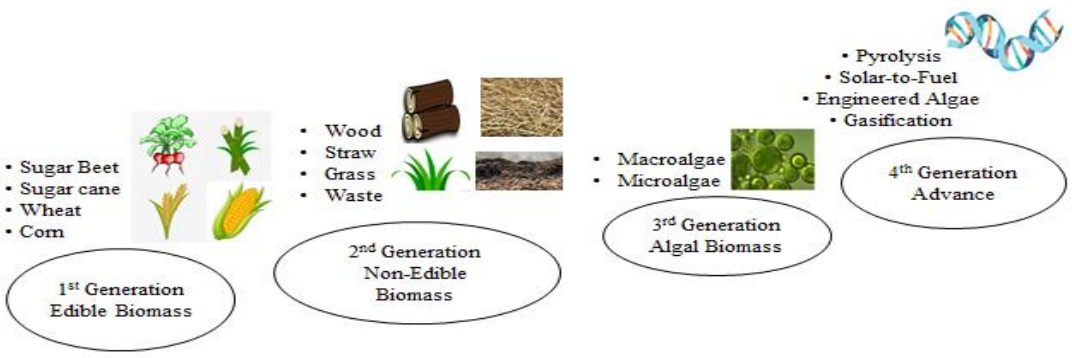

Figure 2.3: Types of Biofuels (Lee & Lavoie, 2013)

First generation biofuel production uses a variety of crops that would otherwise be utilised either for human consumption or indirectly as animal feed. If these crops are converted to biofuels, there may be an increase in the amount of land used for agriculture, the usage of polluting inputs, and the cost of food. Additionally, cellulosic feedstocks may compete for resources (such as land, water, fertiliser, etc.) that would otherwise be used for the production of food. (US EPA, 2014). So as to tackle this issue, second-generation biofuels are produced using non-food crops such as lignocellulosic biomass, municipal and agricultural waste, sludge, manure, etc. Third-generation biofuels related to algal biomass and, to some extent are being utilized globally since second-generation biofuels are not economically viable for commercial application due to technical obstacles (Lee & Lavoie, 2013). However, there are a number of technical difficulties with algal biomass, including dewatering, lipid extraction, clearing away debris during large-scale cultivation, and geographical difficulties like temperatures below 0^0C for the majority of the year, etc.

Therefore, in order to meet increased global demand brought on by the depletion of the world's oil resources, it will be challenging to produce biofuels from single generation biomass rather than a combination of the three generations.

2.3.1 Faecal Sludge (FS) as Biomass:

Faecal sludge, also known as septage, is the mixture of liquid and solid waste that builds up in on-site sanitation systems (OSS), such as septic tanks. In many low-income communities, the bulk of the faecal sludge produced in on-site sanitation techniques like pit latrines and septic tanks is not effectively managed, causing threats to people and the environment. Globally, FS management is a crucial topic. After composting, FS can be controlled by using it as a soil conditioner to produce biogas, charcoal, etc. However, faecal sludge management strategies have increased the use of faecal sludge as a biofuel product because it is a wet-waste-type biomass and is therefore regarded as a second-generation biofuel (Hafford et al., 2018;).

The HHV (10–16 MJ/kg) of the faecal sludge is less than that of typical biomass (18–20 MJ/kg) although it is within the range of previous faecal and sewage sludge data (Phyllis2, 2003). Faecal sludge's HHV value as a fuel is impacted by its high ash content, which decreases the HHV and increases slagging and fouling. It has been hypothesised that faecal sludge's ash content will rise over time due to the organic matter's degradation and gas release

(Still & Foxon, 2012). In table 2.1 the proximate and ultimate compositions of faecal sludge biomass are presented.

Table 2.1: Proximate and Ultimate Analysis Dry of Faecal Sludge

	Coimbatore	Tiruppur
Proximate Analysis	N=2	N=11
Ash (%)	69.3 ± 12.9	39.0 ± 12.8
Volatile Matter (%)	26.5 ± 8.8	47.7 ± 9.9
Fixed Carbon (%)	3.2 ± 3.5	11.4 ± 3.2
HHV (MJ/Kg)	5.4 ± 2.4	13.4 ± 3.2
Sulfer (%)	0.8 ± 0.2	1.1 ± 0.2
	N=2	N=11
Ultimate Analysis		
Carbon as C (%)	16.3 ± 6.7	33.0 ± 7.4
Hydrogen as H (%)	2.4 ± 1.2	4.7 ± 1.0
Nitrogen as N (%)	1.4 ± 0.7	3.1 ± 0.7
Oxygen as O (%)	9.7 ± 4.1	19.2 ± 4.1
Sulfur as S (%)	0.9 ± 0.2	1.1 ± 0.2

N is the number of Samples analysed, Source: (Barani et al., 2020)

2.4 Cow Dung as Biomass:

Cow dung, which is the excrement of cows, is a cheap and widely accessible bioresource on our planet. Additionally, it includes water, microbiota, feed byproducts, and dead skin. In rural areas, cow dung is mainly disposed of in the environment, used as organic fertiliser, or burned as solid fuel. However, the careless disposal and improper elimination of cow dung into the environment has resulted in serious environmental and ecological damage. By thermochemically converting cow dung into biofuel, this worrying issue can be solved. The proximate and Ultimate analysis of Cow Dung are given on Table 2.2

Table 2.2: The proximate and Ultimate composition of Cow Dung

Proximate Analysis	**CD**
Ash (%)	27.72
Volatile Matter (%)	83.91
Fixed Carbon (%)	16.09
HHV (MJ/Kg)	20.08
Sulfer (%)	N/A
Ultimate Analysis	
Carbon as C (%)	49
Hydrogen as H (%)	7
Nitrogen as N (%)	2
Oxygen as O (%)	41
Sulfur as S (%)	1

Source: (Ananno et al., 2021)

2.5 Hydrothermal Liquefaction (HTL)

The thermochemical depolymerization process known as hydrothermal liquefaction (HTL), also known as hydrous pyrolysis, transforms wet biomass into biocrude oil and chemicals at moderate temperatures (usually 200-400°C) and high pressures (typically 10-25 MPa) in an enclosed reactor. Since manure, municipal sludge, and other protein-containing feedstocks frequently have high moisture contents, HTL is a suitable process for them. During HTL, Lipids, proteins, and carbohydrates found in biomass are converted into biocrude/oil, charcoal, aqueous phase, and gaseous phase under high temperature and pressure conditions. The primary fuel products produced during HTL, biocrude and biochar, have larger energy values than raw biomass, indicating that energy is accumulated during the HTL process (Zhang & Chen, 2018). The flow diagram of Hydrothermal liquefaction is shown in figure 2.4

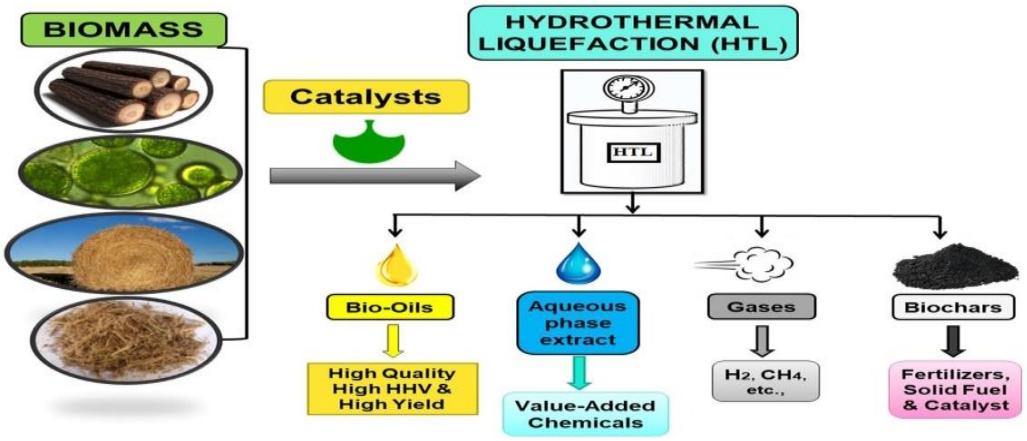

Figure 2.4: Flow diagram of HTL (Nagappan et al., 2021)

2.6 Biocrude Oil

Liquid biofuels such as biocrude/bio-oil, also known as biofuel, are composed of hydrocarbons made from the thermochemical liquefaction of biomass. Bio-crude is a complex mixture of variously sized oxygenated organic molecules. Bio-crude differs from bio-oils or petroleum oil in several ways, including Petroleum is not readily soluble with it, contains 5 to 10% moisture, includes 5 to 15% oxygen, which is more than petroleum but less than bio-oil, denser than petroleum, but significantly less dense than bio-oils. (IEA Bioenergy, Task 34, n.d.). Table 2.3 represents the biocrude properties and the commercial petroleum-crude composition.

Table 2. 3 Comparison of typical properties of biocrude oil and Petro-crude quality

[a]Physical property (biocrude)			**[a]Elemental composition (wt%), biocrude**				**[a]Other properties of biocrude**				
Moisture content (wt%)	pH	Specific gravity	C	H	N	O	Ash	HHV (MJ/kg)	Viscosity (at 50 ºC), cP	Solids (wt%)	Distillation residue (wt%)
15-30	2.5	1.2	54-58	5.5-7.0	0-0.2	35-40	0-0.2	16-19	40-100	0.2-1.0	Up to 50
[b]Petro-crude			**[b]Elemental composition (wt%)**					HHV (MJ/kg)	H/C	O/C	N/C
			83-87	10-14	0.1-0.2	0.05-1.5		42-49	1.5-2.0	<0.02	<0.02

[a] (Banks & Bridgwater, 2016) ,[b](Koley et al., 2018)

Biocrude oil can also be converted into transportation biofuels through the up-gradation/distillation process. Petroleum crude oils are normally classified into lighter to

heavier oil fractions according to petroleum hydrocarbons (i.e., naphtha (C_6-C_{10}), kerosene (C_{10}-C_{16}), diesel (C_{16}-C_{20}), lubricating oil (i.e., lube oil) (C_{20}-C_{30}), and fuel oil (C_{30}-C_{40})) presented in **Fig**ure **2.5**. Gas used for gaseous fuel and making chemicals; gasoline/petrol used for motor car fuel; kerosine used for heating fuel, jet fuel; diesel oil used for lorries, trains, etc. and heating fuel; lube and fuel oil are used for power stations, ships, etc.; finally, bituminous type material used for road construction (GCSE, n.d.).

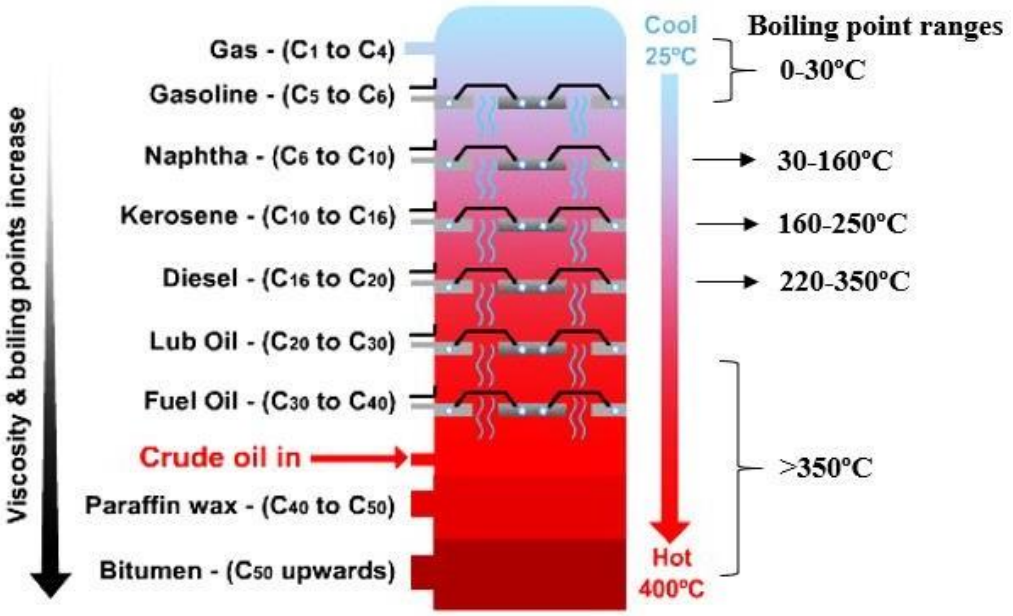

Figure 2.3 General principles of commercial crude oil fractional distillation adoptedfrom (GCSE, n.d.)

Alcohol can totally dissolve biocrude oil, therefore by adding a modest amount of alcohol, fuel characteristics were much improved, viscosity was reduced, and stability was increased. That's why, compared with ethanol, these blended products are more environmentally friendly. On the other hand, Biocrude oil is insolublein diesel, although it could be emulsified by diesel oil. Thus, by adding 10-30% biocrude oil, the viscosity, stability, corrosion preventing ability, and quality of diesel oil become also improved; this kind of diesel oil is similar to pure diesel oil (Zeng et al., 2011). by using catalytic reforming, biocrude oil can be improved.

Section 3

3 Methodology

3.1 Biomass Sample Collection and Preparation:

Faecal sludge (FS) was collected from the drying bed of Faecal Sludge Treatment Plant, Faridpur, Bangladesh. The sample was sieved through a 2 mm mesh to remove the litter and stored at 4 degrees Celsius for the hydrothermal experiment.

Cow dung (CD) biomass was collected from a local cattle farm located at Faridpur, Bangladesh, Near Faridpur engineering college. This two-biomass feedstock will be turned into a raw slurry form. Then the sample was stored at 4˚C prior to hydrothermal experiment.

3.2 Hydrothermal Liquefaction (HTL) Process

A 30 mL stainless steel SS304 customized batch reactor was used for the HTL experiment. With total solid contents of 12.95% (FS) and 14.63% (CD), five different biomass ratios (1:0, 3:1, 1:1, 1:3, 0:1, FS: CD) were employed for HTL. The reactor's actual sample volume was 10 mL. The reactor was filled with 10 mL of the mixed biomass sample, sealed, and put in a muffle furnace. The reaction took place in the reactor for 60 minutes at 320 ^{0}C and 25 MPa pressure (Opu et al., 2023). The reactor was thereafter instantly cooled with tap water for ten minutes. The pressurized gas was released once the reactor head had been carefully opened. Using 25–30 mL of dichloromethane (DCM) as the solvent, the HTL products were collected into a centrifuge tube. To create a consistent combination, the samples were further vortexed for 5 min. To separate the HTL compounds, the materials were centrifuged for 10 min at 4000 rpm. The centrifuge tube has three layers: an aqueous phase at the top, biochar in the middle, and biocrude at the bottom. Using a 3 mm syringe, the aqueous phase and DCM diluted biocrude and biochar were separated. The biochar was then dried at 65 °C for an entire night, and stored in the freezer for later examination. DCM was used to dissolve the biocrude phase, and it was evaporated at room temperature. For a subsequent experiment, the three products were weighed and kept in a refrigerator at 4 ^{0}C. The experimental procedure is outlined at Figure 3.1

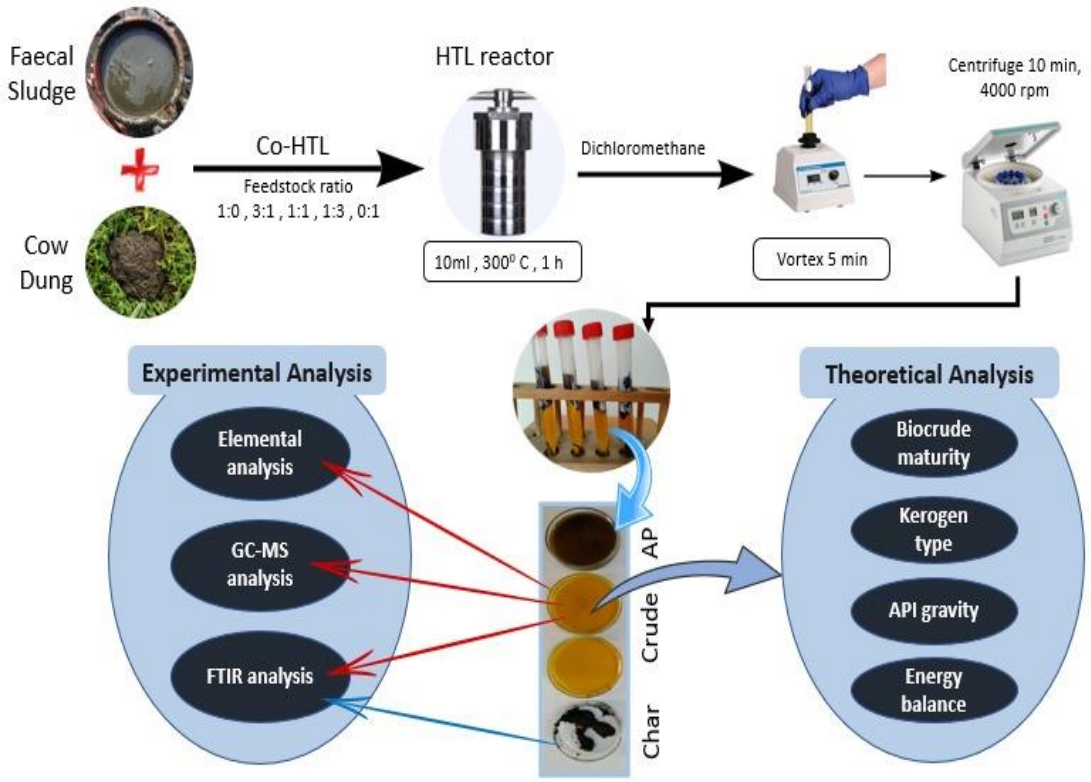

Figure: Experimental flowchart for HTL and co-HTL of Cow Dung and Faecal sludge

3.3 Yield Calculation

The dry basis method was used to determine the amounts of all experimental HTL products (biocrude, biochar, aqueous phase, and gas phase). The following equation (1) to (6) was used to determine the percentage weight yields of each sample for biocrude, biochar, aqueous phase, gas, conversion rate, and Energy Recovery (Hossain et al., 2022). The total dissolved solids of the aqueous phase were considered as water-soluble compounds (WSC) in equation (4).

$$Biocrude\ yield\ (wt\%) = \frac{weight\ of\ biocrude}{weight\ of\ feedstock\ loaded}\ x\ 100\% \quad (1)$$

$$Biochar\ yield\ (wt\%) = \frac{weight\ of\ biochar}{weight\ of\ feedstock\ loaded}\ x\ 100\% \quad (2)$$

$$Aqueous\ yield\ (wt\%) = \frac{weight\ of\ Aqeous\ product}{weight\ of\ feedstock\ loaded}\ x\ 100\% \quad (3)$$

$$Gas\ yield\ (\%) = 100\% - (Y_{biocrude} + Y_{biochar} + WSC) \quad (4)$$

$$Conversion\ rate\ (biomass)\ (wt\%) = 100\% - Y_{biochar} \quad (5)$$

$$Energy\ recovery\ (ER\%) = \frac{HHV biocrude \times Y biocrude}{HHV dry\ biomass)}\ x\ 100\% \quad (6)$$

The HHV was calculated using equations (7) and (8) (Channiwala & Parikh, 2002). Where C, H, O, N and AC were the percentage weight of carbon, hydrogen, oxygen, nitrogen, and ash content, respectively.

$$HHV_{(biocrude)} = 0.3383C + 1.422(H - O/8) \quad (7)$$

$$HHV_{(biomass)} = 0.3491C + 1.1783H - 0.1034O - 0.0151N - 0.021AC \quad (8)$$

3.4 Analytical Analysis

3.4.1 Proximate Analysis

The total solids (TS), moisture content (MC), volatile matter (VM), ash content (AC), and fixed carbon (FC) of FS and CD were determined at Environmental Engineering Laboratory, Faridpur Engineering College, Faridpur according to ASTM D3172-13 standards (ASTM, 2021). The HHV of the biomass samples was calculated using equation (8).

3.4.2 Elemental Analysis

Using an elemental analyzer (Vario Micro Cube, made in Germany), the amounts of carbon (C), hydrogen (H), nitrogen (N), and Sulfur (S) were determined for both biomass and biocrude. Oxygen (O) was determined by difference. This test was performed at BCSIR, Dhaka.

3.4.3 Fourier Transform Infrared Spectroscopy (FTIR) Analysis

FTIR test was conducted at department of ACCE, University of Dhaka. Biocrude and biomass samples from FS and CD were subjected to FTIR analysis to identify the vibrational modes, chemical compositions, and functional groups. (Rizzo & Chiaramonti, 2022). FTIR analyses were conducted using Shimadzu (IRTracer-100) spectrophotometer at room temperature for the spectra ranges 400 cm^{-1} to 4000 cm^{-1} with a resolution of 2 cm^{-1}. The IR data were collected in the transmittance unit (%), which was further analyzed using OriginPro 2018.

3.4.4 Gas chromatography-mass spectrometry Analysis

Gas chromatography-mass spectrometry analysis (GC-MS) was carried out with Clarus®690 gas chromatograph (PerkinElmer, CA, USA) using a column (Elite-35, 30m length, 0.25mm diametre, 0.25µm thickness of film) and it was equipped with Clarus® SQ 8 C mass

spectrophotometre (PerkinElmer, CA, USA). 1µL sample was injected (splitless mode) and pure Helium (99.999%) was used as a carrier gas at a constant flow rate (1mL/min) of 40mins run time. The sample was analyzed in EI (electron ionization) mode at high energy (70eV). Though inlet temperature was constant at 280 ℃, column oven temperature was set at 60 ℃ (for 0min), raised at 5 ℃ per minute to 240 ℃ and hold for 4 mins (Zilani et al., 2021). The sample compounds were identified comparing to the National Institute of Standards and Technology (NIST) database. This test was carried out at JUST, Jashore.

Section 4

4 Results and Discussions

4.1 Biomass Characterization

Proximate, Elemental and Biochemical compositions of FS and CD are presented in table 4.1

Table 4.1: Proximate, Elemental and Biochemical Characteristics of FS and CD

Components	FS	CD
Proximate composition (wt.%)		
Moisture content	**87.05** ± 0.17	**85.37** ± 0.20
Total solids	**12.95** ± 0.17	**14.63** ± 0.20
Volatile matter [a]	**7.49** ± 0.03	**11.49** ± 0.12
Ash content [a]	**5.18** ± 0.05	**2.87** ± 0.14
Fixed carbon [b]	**.28** ± 0.19	**.26** ± 0.11
Elemental composition (wt.%)		
C [a]	**35.49**	**44.3**
H [a]	**5.24**	**5.49**
N [a]	**4.41**	**1.11**
S [a]	**0.48**	**0**
O [b]	**36.38**	**11.5**
Elemental molar ratio		
H/C	**1.79**	**1.48**
N/C	**0.10**	**0.02**
O/C	**0.77**	**0.19**
S/C	0.005	0
H/C_{eff}	0.24	1.09
Chemical formula	$CH_{1.79}O_{0.77}N_{0.1}S_{0.005}$	$CH_{1.51}O_{0.64}N_{0.15}S_0$
HHV (MJ kg^{-1})[a]	12.84	20.75
Biochemical composition (wt.%)		
Lipid	18	12
Protein	27.56	6.94
Carbohydrate	29.18	20.83
Functional groups in biomass		
C=C stretch, (850-930 cm^{-1})	Hemicellulose	Hemicellulose
C-O stretch, (940-1135 cm^{-1})	Carbohydrate	Carbohydrate
C-H bend, (1400-1450 cm^{-1})	Lignin	Lignin
C=O stretch, (1635-1745 cm^{-1})	Protein	Protein
C-H stretch, (2800-3000 cm^{-1})	Lipid	Lipid
[a] Dry basis, [b] by difference. O (wt%) = 100 – sum of (C, H, N, S, ash). Fixed carbon, (%) = 100 – sum of (MC+ VM+ AC), Carbohydrate = 100 – (lipid + protein + ash + moisture).		

The proximate analysis suggested that high organic content (volatile matter) is present in CD (11.49 wt%) compared to FS (7.49 wt%). However, the ash content is higher at FS (5.18 wt%) compared to CD (2.87 wt%). Based on the elemental analysis, the stoichiometric formula of FS and CD were $CH_{1.79}O_{0.77}N_{0.1}S_{0.005}$ and $CH_{1.51}O_{0.64}N_{0.15}S$ respectively. The HHV of CD was found 20.75 MJ/kg higher than FS (12.84 MJ/kg). The HHV of P and FS were comparatively similar to other feedstocks used for HTL purposes in previous studies (Sivabalan et al., 2021).

4.2 Biocrude Yield

The yield of Biocrude from HTL and co-HTL depends on several parameters like temperature, retention time, solid loading, biomass composition etc (Madsen & Glasius, 2019). Recent study (Kabir & Khalekuzzaman, 2022; Madsen & Glasius, 2019) suggested the optimum HTL parameters as the temperature of 320 ºC, TS loading of 8- 10 %, and reaction time of 60 min. Hence, All HTL and co-HTL experiments were conducted on these operating conditions in this study. The product distribution of biocrude, biochar, and the aqueous phase is illustrated in **Figure. 4.1.**

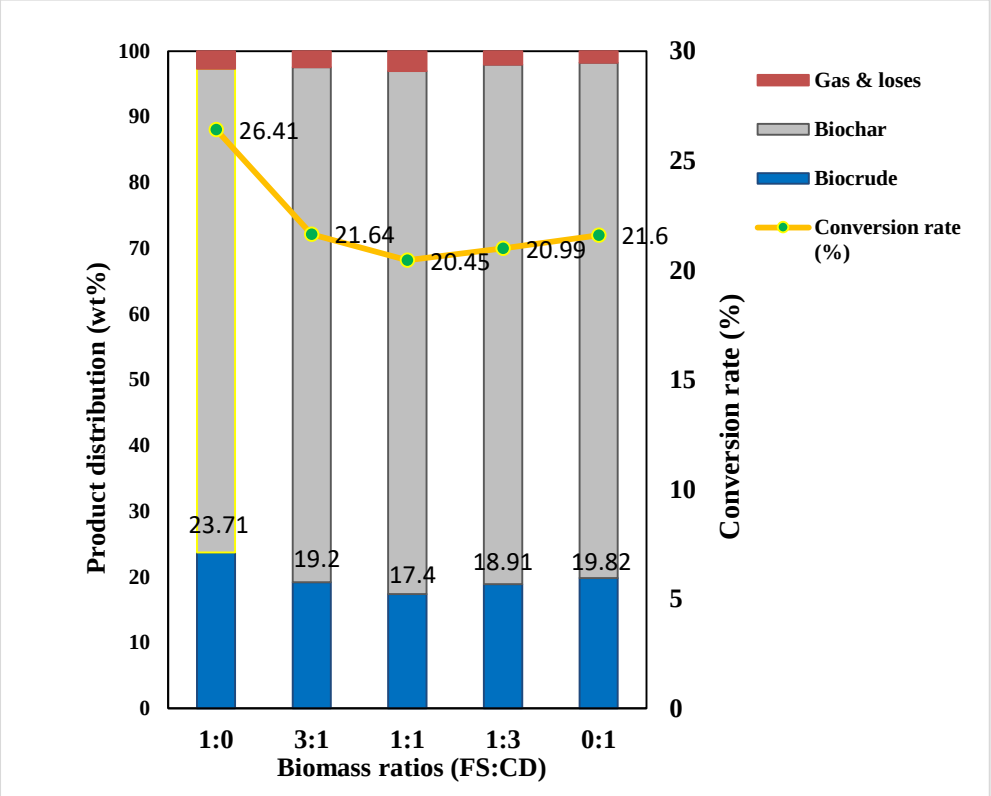

Figure 4.1: co-HTL Product Distribution and Conversion rate due to biomass ratio

4.3 HTL of Faecal Sludge:

The biocrude yield due to HTL of FS was (23.71 wt%). The presence of higher Lipid (18 wt %) and protein (27.56 wt %) content causes higher biocrude yield. Similar findings on HTL of human faeces where human faeces had a lipid content of 14.01 (wt%), protein (34.68 wt%), and a biocrude yield of 34.44 (wt%) was observed (Lu et al., 2017). A study on product yields also suggested that biocrude yield increases with a decrease in biochar yield (Danso-Boateng et al., 2022).

4.3.1 HTL of Cow Dung:

The biocrude yield due to HTL of CD was (19.82 wt%). At same conditions of HTL, the presence of lower Lipid (12 wt %) and protein (6.94 wt %) content causes lower biocrude yield compared to FS. The higher percentage of Biochar (78.4 wt %) causes lower percentage of Biocrude.

4.3.2 Co-HTL of FS and CD

This study focused on analyzing three co-HTL ratios (3:1, 1:3, 1:1; FS: CD) under identical experimental conditions. The results showed that compared to individual HTL of biomass, co-HTL ratios produced smaller amount of biocrude. Among the co-HTL (3:1, FS: CD) sample showed the maximum biocrude yield of 19.2 wt%. The conversion rate at co-HTL is comparatively higher than the HTL of individual biomass CD. According to the findings, the co-HTL of FS and CD at a 3:1 ratio is ideal for creating bio crude employing two biomasses.

4.4 FTIR Analysis of Biomass and Biocrude

Biocrude and biomass (FS and CD) were subjected to FTIR analysis to determine the chemical constituents and functional groups that were present. The FTIR spectrum of the biomass, which includes FS and CD, is shown in Fig. 4.2. Figure 4.2 demonstrates the transmittance peaks associated with the categories of chemical compounds present in FS and CD. The leading bands' interpretation was according to (*IR Spectrum Table*, n.d.; NIU, USA, n.d.). Strong and broader peaks of 3371 cm^{-1} and 3315 cm^{-1} were observed for FS and CD, respectively, within the bands' range of 3200 cm^{-1} to 3550 cm^{-1}, which ensures O-H stretching functional group indicating the presence of phenol and alcohol. The weak broad peak of 2940 cm^{-1} were observed for FS within the bands' range of 2700 cm^{-1} to 3200 cm^{-1} identifies the O-H stretching functional group in alcohol compounds. The C-H bending

functional groups in aromatic compounds were observed in between 1650 cm^{-1} to 2000 cm^{-1} for both FS and CD. Identified peaks at Wavenumbers from 1475 cm^{-1} to 1600 cm^{-1} demonstrate C=C stretching functional group indicating the presence of aromatic compound. The absorption frequency from 1000 cm-1 to 1300 cm-1 relates to C-O functional groups, showing that alcohols, esters, ethers, carboxylic acid phosphorus, and anhydride compounds are present. Bands between 650 cm^{-1} to 1000 cm^{-1} indicate the C=C bending in alkene is present. The appearance of C-Br stretches from 690 to 515 cm-1 band indicates the presence of Alkyl halides.

However, the FTIR spectra to determine the functional groups associated with probable chemical compound at HTL and co-HTL biocrude based is presented at Figure 4.3. For both HTL and co-HTL biocrude, the spectra pattern is identically exhibiting similar chemical compounds present at all biocrude. A strong and broader band of 3350 cm-1 was observed which attributes to the O-H stretching functional group recognizing the presence of alcohol and phenol. A weak band of 2140 cm-1 is attributed to C≡C stretching, indicating the presence of alkyne compound. The absorption band of 1648 cm-1 between the range of 1580 cm-1 to 1650 cm-1 ensures C-N stretching at amine compound. The peak at 1420 cm-1 indicates O-H bending at the alcohol compound. The existence of C-O functional groups was indicated by the absorption frequency in the 1000 cm-1 to 1300 cm-1 region, indicating the presence of alcohols, esters, ethers, carboxylic acid phosphorus, and anhydride compounds. The strong to medium peak at 752 cm-1 was detected which reflects the presence of more aromatic compounds.

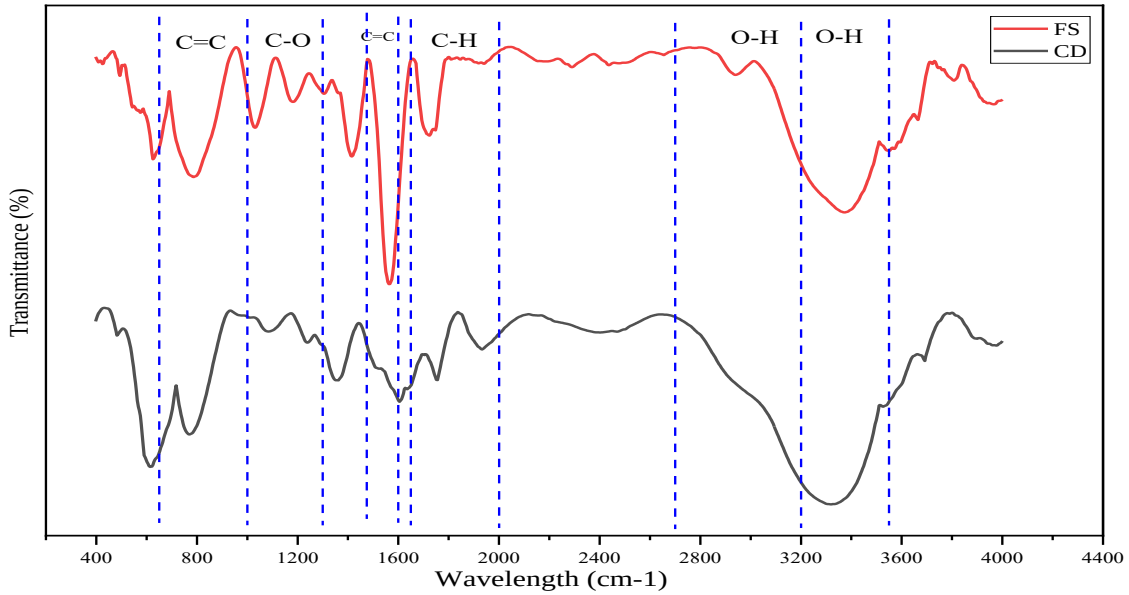

Figure 4.2: FTIR Spectra of FS and CD

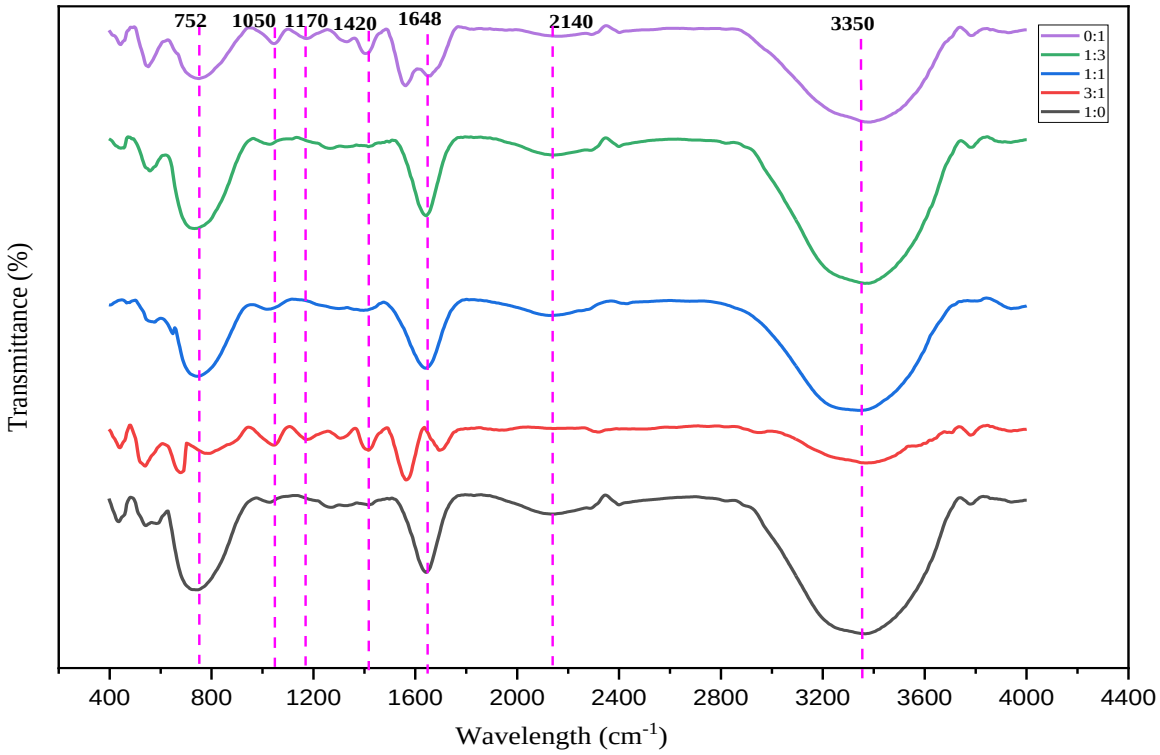

Figure 4.3: FTIR spectra of biocrude samples

4.5 Elemental Analysis of Biocrude:

Biocrude samples had greater carbon and hydrogen contents than biomass samples, determined by elemental analysis, demonstrating energy accumulation during HTL and co-HTL experiments. (Table 4.1 and Table 4.2).

Table 4.2: Elemental Composition of Biocrude Obtained from HTL and co-HTL experiments

[a]Biocrude sample (FS:CD)	Elemental analysis					Atomic ratio		HHV (MJ/kg)	ER (%)	Chemical formula
	C (%)	H (%)	N (%)	S (%)	O[b] (%)	H/C	O/C			$CH_{1.85}O_{0.08}N_{0.002}$
1:0	77.1	11.9	0.23	1.85	8.92	1.85	0.086	41.42	76.47	$CH_{1.88}O_{0.08}N_{0.003}$
3:1	77.1	12.1	0.31	1.54	8.95	1.88	0.087	41.70	54.02	$CH_{1.85}O_{0.21}N_{0.003}$
1:1	68.8	10.6	0.27	0.4	19.93	1.85	0.217	34.81	36.05	$CH_{2.42}O_{1.25}N_{0.003}$
1:3	34.8	7.03	0.13	0.24	57.8	2.42	1.245	11.50	11.57	$CH_{1.83}O_{0.07}N_{0.03}$
0:1	79.1	12.1	0.38	0	8.42	1.83	0.079	42.46	40.56	$CH_{1.85}O_{0.08}N_{0.002}$
[c]Petro-crude	83-87	10-14	0.1-2.0		0.05-1.5	1.5-2.0	<0.02	42-49		

[a]Moisturee free basis
[b]Oxygen contents of biocrude sample was calculated by difference O (%) = 100 – %(C+H+N+S)
[c]Petro-crude elemental analysis was collected from (Koley et al., 2018)

The C and H contents of biocrude samples were higher than those of the equivalent biomass samples, indicating a higher percentage of hydrocarbons than nitrogen and oxygen components. The highest proportion of carbon (>70%) and hydrogen (>10%) were found in co-HTL samples with a (3:1, FS: CD) ratio, indicating a greater rate of energy conversion. The biocrude samples showed lower levels of nitrogen and oxygen compared to the original biomass, which indicates that denitrogenation and deoxygenation occurred during the liquefaction process. All biocrude samples' N/C ratios (0.02) satisfied the petro-crude standard, whereas their O/C ratios (>0.02) did not. (Koley et al., 2018). Table 4.1 and Table 4.2 provide the stoichiometric chemical formulas of biomass and biocrude, respectively, based on their elemental compositions. The HHV of the (1:0, FS:CD) sample was higher than that of the biomass sample, indicating a positive energy outcome from the HTL process. The energy recovery (ER%) of the (1:0, FS:CD) sample was also higher than that of the (0:1, FS:CD) sample. However, the highest ER% was achieved in the co-HTL of

the (3:1, FS:CD) sample, which also had the highest yield and moderate HHV. Therefore, the co-HTL of (3:1, FS:CD) demonstrated a more positive energy outcome.

4.6 Gas chromatography Mass Spectrometry Analysis of Biocrude:

By using GC-MS, the biocrude produced by HTL and co-HTL of various FS and CD biomass ratios were analysed. From GC-MS analysis, it revealed that all biocrude samples had alcohol, ester, fatty acid, hydrocarbon and other compounds as major chemical compounds. Among them the maximum hydrocarbon compound (34.08%) was obtained at (3:1, FS:CD) ratio which is shown in figure 4.4. Based on carbon chain the test result of (1:0, FS:CD) sample stated that the biocrude had a lighter oil fraction (naphtha, kerosene, and diesel) of 54.4 % which was higher than the (0:1, FS: CD) biocrude sample (18.6%). The highest fraction of kerosene was observed for the co-HTL (3:1, FS:CD) sample (70.2%). The results suggested that the lighter fraction biocrude might be obtained using co-HTL of (3:1 FS: CD) sample. The petroleum fractions are shown in Figure 4.5.

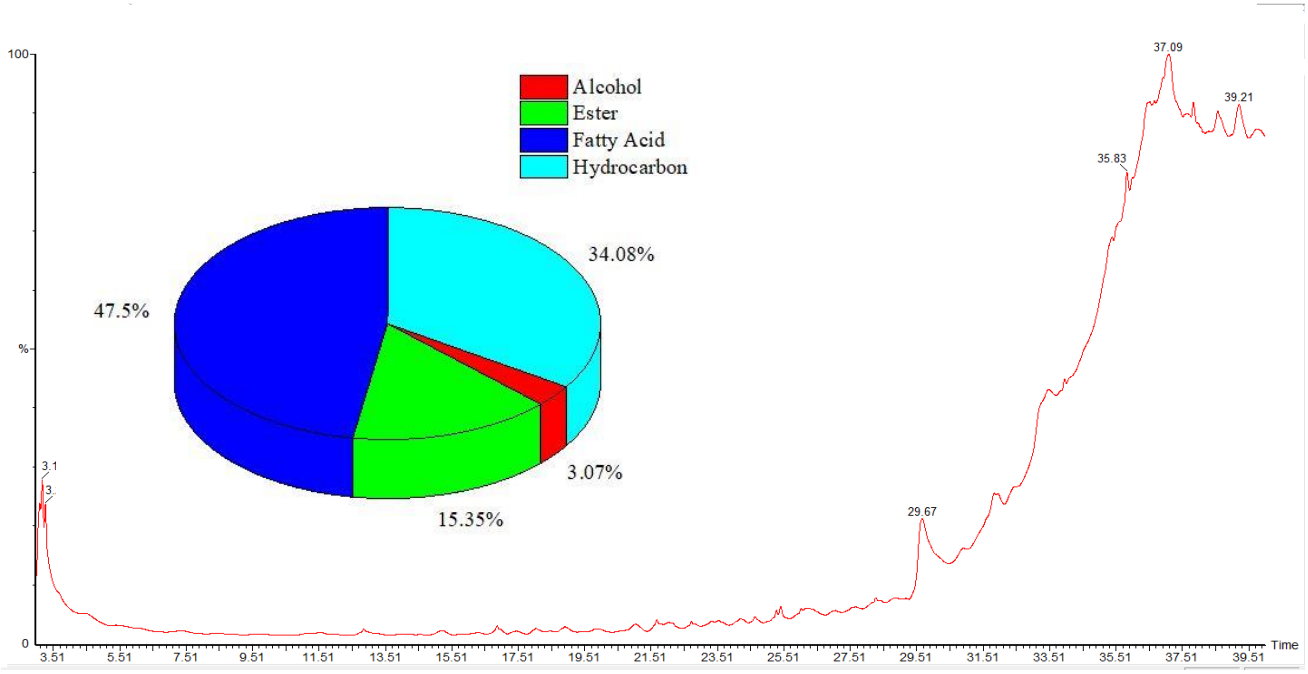

Figure 4.4: GC-MS chromatogram of Biocrude obtained from co-HTL of FS and CD at 3:1 ratio

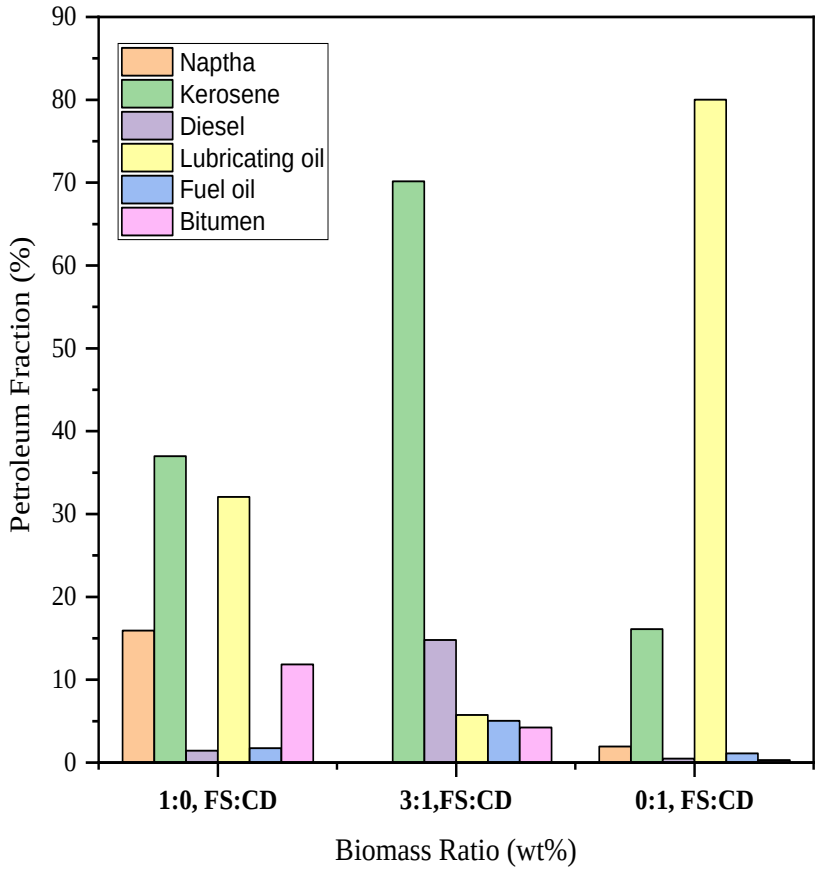

Figure 4.5: Petroleum fractionation of biocrude from HTL and co-HTL of FS and CD

Section 5

5 Conclusions and Recommendations

5.1 Conclusions

In this study, co-HTL was investigated using FS and CD for improved quality biocrude. Faecal sludge, from on-site sanitation system and cow dung from cattle firm were used. These two biomasses co-HTL operation was a novel approach to manage the waste as well as for green biocrude production. Elemental analysis was conducted on biomass and biocrude to find out the energy potentiality and energy recovery from biomass to biocrude. In addition, FTIR analysis was performed for identifying the chemical compositions, functional groups present in biomass and biocrude. GC-MS analysis was examined on biocrude oil to find out the major chemical compounds present in biocrude oil and for petroleum fractionation. The proposed co-HTL assessment on biomass suggested that the overall system was energetically feasible and would be a new direction for sustainable bioenergy production.

The major findings of the current research are the followings:

1. During co-HTL of Faecal sludge (FS) and cow dung, the maximum biocrude yield of 19.2 wt% was reported for a FS to CD ratio of 3:1 with a 21.64 wt% conversion rate. Again, the lower N and O content in (3:1, FS: CD) biocrude resulted in enhanced HHV (i.e., 41.70 MJ/kg). Hence, the biocrude from co-HTL of the (3:1, FS:CD) sample has similarities to petro-crude quality.
2. FTIR analysis confirmed that biocrude samples contain aliphatic hydrocarbons, phenols, and esters.
3. GC-MS analysis revealed that biocrudes have both light and heavy oil fractions. In addition, co-HTL of (3:1, FS:CD) produces maximum lighter fraction fuel (kerosene, 70.15%) which can be used as jet fuel. So that the lighter fraction biofuel can be produced commercially by co-HTL of FS and CD at 3:1 ratio.

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7 Appendices

7.1 Appendix A

Table. A-1: Phytochemical composition of sample (1:0, FS: CD) by GC-MS analysis

Serial No.	Retention Time (RT)	Name of the compounds	Molecular Weight	Molecular Formula	% Area
1	3.17	4-heptanone, 3-methyl-	128	$C_8H_{16}O$	0.03
2	3.27	cyclobutanol, 1-butyl	128	$C_8H_{16}O$	0.08
3	11.57	Hentriacontane	436	$C_{31}H_{64}$	0.88
4	16.86	Triacontane	422	$C_{30}H_{62}$	1.33
5	17.46	Octadecane, 1-chloro	288	$C_{18}H_{37}Cl$	0.60
6	18.90	3,4-dihydroxyphenylglycol, 4tms derivative	458	$C_{20}H_{42}O_4Si_4$	0.47
7	19.80	2-isopropyl-5-methyl-1-heptanol	172	$C_{11}H_{24}O$	0.85
8	21.68	Tetrapentacontane	758	$C_{54}H_{110}$	1.64
9	22.03	Tridecane, 2,2,4,10,12,12-hexamethyl-7-(3,5,5-trimethylhexyl)	394	$C_{28}H_{58}$	1.04
10	22.72	3-methyldotriacontane	464	$C_{33}H_{68}$	0.40
11	24.64	Diethyl phthalate	222	$C_{12}H_{14}O_4$	0.66
12	26.16	Sulfurous acid, butyl octadecyl ester	390	$C_{22}H_{46}O_3S$	2.28
13	29.64	Butoxyacetic acid	132	$C_6H_{12}O_3$	11.69
14	33.46	Hexacontane	842	$C_{60}H_{122}$	7.13
15	36.66	1-bromo-11-iodoundecane	360	$C_{11}H_{22}BrI$	25.89
16	37.11	Ergosta-5,7,9(11),22-tetraen-3-ol, (3.beta.,22e)-	394	$C_{28}H_{42}O$	19.11

Table. A-2: Phytochemical composition of sample (3:1, FS: CD) by GC-MS Analysis

Serial No.	Retention Time (RT)	Name of the compounds	Molecular Weight	Molecular Formula	% Area
1	3.17	3-pentanol, 2,2,4,4-tetramethyl-3-(tetrahydo-2-furyl)-	214	$C_{13}H_{26}O_2$	0.06
2	3.27	Cyclobutanecarboxylic acid, 2-dimethylaminoethyl ester	171	$C_9H_{17}O_2N$	0.08
3	12.86	2-isopropyl-5-methyl-1-heptanol	172	$C_{11}H_{24}O$	0.62
4	16.30	Methyl 2,6-anhydro-.alpha.-d-altroside	176	$C_7H_{12}O_5$	0.21
5	16.86	Hentriacontane	436	$C_{31}H_{64}$	0.54
6	17.45	2,2-dimethylpropanoic acid, 2,6-dimethylnon-1-en-3-yn-5-yl ester	250	$C_{16}H_{26}O_2$	0.25
7	18.05	Octadecane, 2,6,10,14-tetramethyl	310	$C_{22}H_{46}$	0.48
8	18.93	Cyclooctasiloxane, hexadecamethyl-	592	$C_{16}H_{48}O_8Si_8$	0.67
9	21.04	Pentanoic acid, 5-hydroxy-, 2,4-di-t-butylphenyl esters	306	$C_{19}H_{30}O_3$	0.78
10	21.68	Tetrapentacontane	758	$C_{54}H_{110}$	0.73
11	22.72	2-methylhentriacontane	450	$C_{32}H_{66}$	0.33
12	23.54	N-valeric acid cis-3-hexenyl ester	184	$C_{11}H_{20}O_2$	0.37
13	24.19	Terephthalic acid, butyl dec-4-enyl ester	360	$C_{22}H_{32}O_4$	0.51
14	24.64	Diethyl phthalate	222	$C_{12}H_{14}O_4$	0.36
15	25.28	1R,2C,3t,4t-tetramethyl-cyclohexane	140	$C_{10}H_{20}$	0.22
16	25.41	Neophytadiene	278	$C_{20}H_{38}$	0.85
17	28.27	Octadecanoic acid, 11-methyl-, methyl ester	312	$C_{20}H_{40}O_2$	0.69
18	29.67	12-bromododecanoic acid	278	$C_{12}H_{23}O_2Br$	9.59
19	37.84	Cyclononasiloxane, octadecamethyl-	666	$C_{18}H_{54}O_9Si_9$	0.23
20	39.19	Nonadecane, 2,6,10,14,18-pentamethyl-	338	$C_{24}H_{50}$	3.73

Table. A-3: Phytochemical composition of sample (0:1, FS: CD) by GC-MS Analysis

Serial No.	Retention Time (RT)	Name of the compounds	Molecular Weight	Molecular Formula	% Area
1	3.08	2,4,4-trimethyl-1-pentanol	130	$C_8H_{18}O$	0.05
2	5.67	3-hexanol	102	$C_6H_{14}O$	0.76
3	5.89	Acetic acid, 3-methylpentyl ester	144	$C_8H_{16}O_2$	0.62
4	11.58	Hentriacontane	436	$C_{31}H_{64}$	0.22
5	12.85	Carbonic acid, decyl undecyl ester	356	$C_{22}H_{44}O_3$	0.20
6	15.22	Pentasiloxane, dodecamethyl-	384	$C_{12}H_{36}O_4Si_5$	0.68
7	16.86	Heptadecane, 2,6,10,15-tetramethyl-	296	$C_{21}H_{44}$	0.99
8	21.68	Triacontane	422	$C_{30}H_{62}$	1.96
9	24.04	Tritetracontane	604	C43H88	0.23
10	25.27	1r,2c,3t,4t-tetramethyl-cyclohexane	140	$C_{10}H_{20}$	0.66
11	25.40	Neophytadiene	278	$C_{20}H_{38}$	1.51
12	26.01	Phytyl, 2-methylbutanoate	380	$C_{25}H_{48}O_2$	0.83
13	26.38	Phytyl tetradecanoate	506	$C_{34}H_{66}O_2$	0.86
14	28.25	Heptacosanoic acid, 25-methyl-, methyl ester	438	$C_{29}H_{58}O_2$	0.36
15	29.66	12-bromododecanoic acid	278	$C_{12}H_{33}O_2Br$	6.15
16	30.03	D-alanine, n-(2,4,5-trifluoro-3-methoxybenzoyl)-, propyl ester	319	$C_{14}H_{16}O_4NF_3$	4.30
17	31.80	Fumaric acid, 2,4,4-trimethylpentyl hex-4-yn-3-yl ester	308	$C_{18}H_{28}O_4$	0.36
18	33.15	Bis(2-ethylhexyl) phthalate	390	$C_{24}H_{38}O_4$	2.38
19	36.41	13-docosenamide, (z)	337	$C_{22}H_{43}ON$	50.33

Table A-4 Elemental Compsition of Biomass

Biocrude Sample (FS:CD)	C (%)	H (%)	N (%)	S (%)
FS	35.49	5.24	4.41	0.48
CD	44.3	5.49	1.11	0

Table A-5 Elemental Compsition of Biocrude

Biocrude Sample (FS:CD)	C (%)	H (%)	N (%)	S (%)
1:0	77.1	11.9	0.23	1.85
3:1	77.1	12.1	0.31	1.54
1:1	68.8	10.6	0.27	0.4
1:3	34.8	7.03	0.13	0.24
0:1	79.1	12.1	0.38	0

7.2 Appendix B

Photographs Taken during Research Work

Figure B-1: Faecal Sludge Collection from FSTP, Faridpur

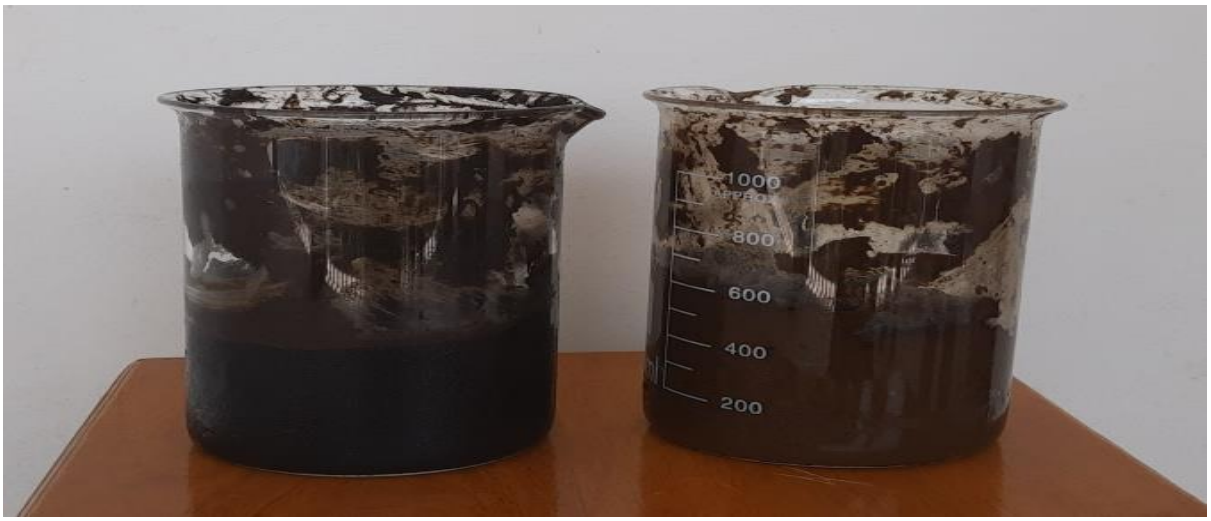

Figure B-2. Prepared Biomass (FS &CD)

Figure B-3: HTL and co-HTL Experiments

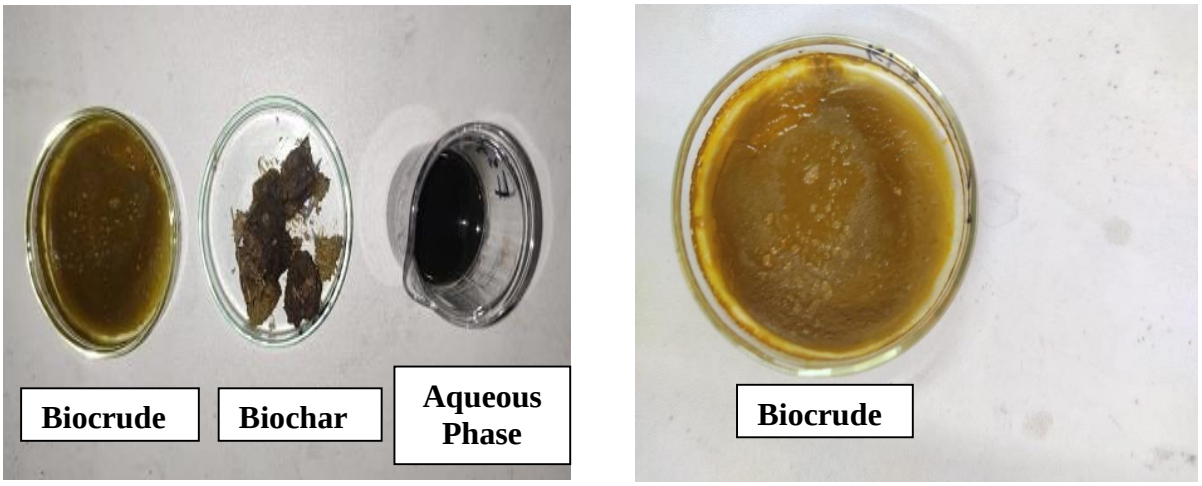

Figure B-4. Biocrude, Biochar and Aqueous Phase

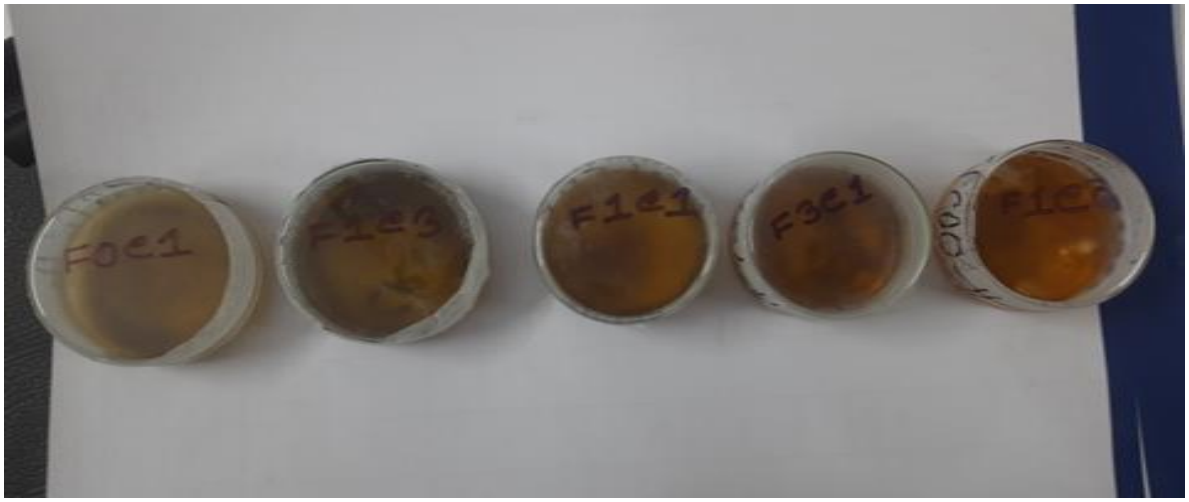

Figure B-5. Biocrude Samples of five ratios