MUNICIPAL WASTEWATER SLUDGE AS A SUSTAINABLE FEEDSTOCK FOR UPGRADEABLE RENEWABLE CRUDE OIL VIA HYDROTHERMAL LIQUEFACTION

Dissertation

Submitted in partial fulfillment of the requirement for the award of degree

of

Master of Technology

in

Chemical Engineering

By

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JUNE 2018

Certificate

This is to certify that the dissertation entitled **"Municipal wastewater sludge as a sustainable feedstock for upgradeable renewable crude oil via hydrothermal liquefaction"** submitted by **Shivangi (Regd. No. 601611002)** in partial fulfilment for the award of degree of Master of Technology in Chemical Engineering from Thapar Institute of Engineering and Technology, Patiala, India has been carried out under my supervision. This work has not been submitted partially or wholly in any other university or institute for the award of this or any other degree or diploma.

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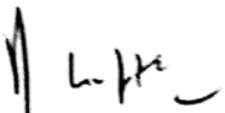

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Declaration

I hereby declare that the work being presented in the dissertation report entitled " **Municipal wastewater sludge as a sustainable feedstock for upgradeable renewable crude oil via hydrothermal liquefaction"** by me in the partial fulfilment of the requirements for the award of degree of Master of Technology in Chemical Engineering from Thapar Institute of Engineering and Technology, Patiala, India, is an authentic record of my work carried under the supervision of **Prof David Lewis**, Professor & Head of School, School of Chemical Engineering, University of Adelaide, Australia and **Prof R. K. Gupta**, Professor & Head, Department of Chemical Engineering, Thapar Institute of Engineering and Technology, Patiala, India. The matter presented in this thesis has not been submitted in any other University/ Institute for the award of any degree / diploma.

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Dated: 30 May 2018

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Acknowledgements

First and foremost, I would like to express my sincere and deepest gratitude to my principal supervisor **Prof David Lewis**, Head of School, University of Adelaide and co-supervisor **Prof Raj Kumar Gupta,** Professor and Head of Department in Chemical Engineering, Thapar Institute of Engineering and Technology, India, for their valuable discussions and suggestions, guidance, strong motivation, and encouragement throughout my M. Tech dissertation journey.

I would like to convey my thanks to **Dr Raj Kumar Arya**, M.Tech Coordinator, for his constant support and valuable suggestions. I express my heartiest gratitude to **Dr Rosemala Lewis**, Adjunct lecturer, school of chemical engineering, University of Adelaide, for her constant support and valuable ideas and advices throughout the period. This thesis would not have been possible without her persistent effort and encouragement.

I am grateful to **Dr Tony Hall, Mr Jasim Mohammed, Mrs Balpreet Kaur** and **Ms Sylvia Editor** for being so cooperative and helped me in my research work whenever i needed. The valuable suggestions and inspiring discussions I had with them has always been proved a driving force in carrying out my research.

I invariably fall short of words to express my heart-felt gratitude and profound thanks to my family for their undying belief in me. Their constant encouragement makes me want to work hard.

Dated: 30-06-2018

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ABSTRACT

Every year billion tonnes of municipal wastes are produced in the world. It is expected that by 2025, the municipal waste produce will rise to approximately 2.2 billion tonnes every year. Due to its nature and dangers associated with it becomes a problem to dispose of the waste product. It also contains various bacteria and virus. Municipal waste obtained after passing through various stages of waste water treatment plat (WWTP) can be put to useful purposes like producing oil. A detailed study on municipal waste is carried out with the purpose of converting it into commercially viable oil. There are many alternatives available like pyrolysis, gasification, transesterification, esterification but hydrothermal liquefaction (HTL) has been considered as the most promising path. During HTL, the water is considered as the reaction medium reducing the requirement to dewater the bio-mass which can be a crucial energy input for bio-fuel yield.

Initially, various parameters like pH, bulk density, ash-free dry weight, moisture content, CHNS, Calorific Value are characterized. High total carbon and oxygen was observed in the municipal waste samples (29-59%). The ash content lies in the range of 32-52%. The sample MW 4 being fibrous in nature has a very low bulk density, almost similar to that of cotton.

The hydrothermal liquefaction of sludge was carried at an elevated temperature (330^0C) and pressure (200 bar) to disintegrate and form bio-mass macromolecule into bio-fuel. It is successfully separated into solid and liquid with visible oil. The highest yield of product obtained is 82.84% of which 50.78% is solid yield and 32.16% is liquid yield. Oil present in liquid can be easily extracted by centrifugation. There is some oil present in solid which is successfully extracted by the methodology developed. After extraction various tests were done like: Rock Analysis of the sample before and after extraction indicating the loss of hydrocarbons which indicates extraction of the oil. The highest yield of oil extracted is from MW1 (36.2%.) which is considered an appreciable percentage (as per literature) keeping in consideration the feedstock is Municipal wastewater.

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ABBREVIATIONS

Abbreviation	Description
HTL	Hydrothermal Liquefaction
WWTP	Waste Water Treatment Plant
GC-MS	Gas chromatography-Mass spectroscopy
GC-FID	Gas Chromatography – Flame Ionization Detector
AFDW	Ash Free Dry Weight
CHNS	Carbon Hydrogen Nitrogen Sulphur
SBL	Symbol Technologies
MW	Melbourne Water
QW	Queensland Water
RAS	Return Activated Sludge
TOC	Total Organic Carbon
SRA	Source Rock Analyzer
FID	Flame Ionisation Detector
S1	The amount of free hydrocarbons in a rock sample
S2	The amount of hydrocarbons generated through thermal cracking of non-volatile organic matter
S3	The amount of carbon dioxide (CO2) produced during pyrolysis of kerogen up to 400^{o}

CHAPTER-1
INTRODUCTION

The fast depleting conventional fossil fuels has raised environmental pollution. Over consumption of fossil fuels and increasing carbon dioxide emissions have put enormous pressure to look or substitute renewable and sustainable sources for fuels [1]. The bio-solids derived from municipal waste could be constructive way to eliminate various different routes are available for the bio-solid processing such as hydrothermal liquefaction, steam reforming, pyrolysis, transesterification, etc. Hydrothermal liquefaction is most widely used technique which involves thermo-chemical depolymerisation process bio mass to convert it sludge into bio crude in an enclosed reactor. The temperature range is moderate (200^0C to 400^0C) while high pressure (10 to 25 MPa) is preferred. The hydrothermal liquefaction (HTL) of wet/dry bio-solids seems to be the promising route, the reason being [2]: i) It accepts all sort of feedstocks like wood, sludge, manure, household and dairy product wastes. ii) The efficiency of HTL is higher compared to other processes so it can be considered as cost-effective. iii) It has a good compatibility with wet feeds. To understand the reaction mechanism of hydrothermal liquefaction we can consider the following pathways:

1. Hydrolysis of bio-mass —› smaller monomer
2. Smaller monomer —› smaller compounds (by cleavage, de-carboxylation).
3. Recombination of smaller fragment —› new compounds (by condensation, polymerisation).

Products obtained after HTL are: Bio-Crude, Solid Residue, gas, aqueous phase.

- Bio-crude obtained is dark and viscous and similar to petroleum crude having high energy density and lower heating value.
- Gaseous phase contains carbon dioxide and hydrocarbon gases (hydrogen, methane, ethane and ethylene).
- Solid Residue consists of carbon, nitrogen, hydrogen and sulphur (in small quantities).
- Aqueous phase contains micronutrients.

There can be many types of bio-solid feedstocks. The feedstock such as manures, food waste, algae etc. We are considering municipal sludge as feedstock in our experiment. Municipal sludge falls under the category of protein –containing feedstock. It contains a high moisture content which makes HTL an appropriate process. In HTL, water is an important reactant. As water reaches its critical point, the properties of water begin changing which

brings out fast, homogenous and efficient reactions [3]. Sludge and bio-solids are difficult to study as [4]:

- It contains many different types of bacteria and virus.
- Metals and organic chemicals can be found in it.
- It's difficult to transfer sludge over a long distance.
- The odour of sludge is intolerable.

Every year, a huge amount of municipal waste is produced in the world. Municipal waste tends to cause a problem for its disposal. Due to its dangers associated with it, it is seldom used for any useful purpose. With hydrothermal liquefaction, it can be converted into oil which can be put to use for commercial purpose. Hence, hydrothermal liquefaction is a promising process. With growing depletion of oil and high demand as compared to supply, it is the need of the hour to find alternative sources of oil.

1.1 ABOUT FEEDSTOCK

The samples taken are either sludge or bio-solids. All the samples taken are from different sources. They are divided in 3 different categories: tertiary sludge, secondary sludge and bio-solids.

1.1.1 SECONDARY SLUDGE

Secondary sludge is a term given to sludge after it is obtained after the secondary treatment of the wastewater in wastewater treatment plant. The various ways of secondary treatment of wastewater are: bio-filtration, aeration, oxidation ponds etc.

QW 4: Calliope WWTP RAS after Clarifier. It was taken after passing through the clarifier.

1.1.2 TERTIARY SLUDGE

Tertiary sludge is the term given to the sludge obtained after the tertiary wastewater treatment. Tertiary waste water treatment is considered as the last step in wastewater treatment. In this step nitrates and phosphates are separated from the water with the help of activated carbon and sand.

QW 1: Gladstone WWTP dry sludge from dry bed**.** Sludge was taken from the dry bed. And can be defined as final sludge (prior to bio-solids).

QW 3: Gladstone WWTP Mt Doom Drying bed fresh digested**.** It was obtained after the digestion.

QW5: Boyne island WWTP Belt pressed + polyelectrolite zetag 8160**.** It is obtained after the belt pressing. It contains polyelectrolyte.

QW 6: Boyne island WWTP Drying pan (no polymer). It was obtained from the drying pan. It does not contain any polyelectrolyte.

QW 7: South trees WWTP Drying pan**.** It was taken from the drying pan.

MW 1: Decanted drying pan**.** It was taken from the drying pan.

1.1.3 BIO-SOLIDS:

Bio-solids are the organic solid by-product obtained after treating the sewage. The have a very low water content.

QW 2: Gladstone WWTP Mt Doom ~ 5 years old.

MW 2: Fresh stockpile obtained from the WWTP (Melbourne Water).

MW 3: 3 years old stockpile obtained from WWTP (Melbourne Water).

1.2 AIMS AND OBJECTIVES OF MY RESEARCH

1.2.1 AIM

The main aim of this research is to investigate the characteristics (parameters) of the feedstock (municipal waste) by suitable methods and perform hydrothermal liquefaction (HTL) followed by extraction of oil and analysis of the product obtained after HTL (Rock analysis, GC-MS)

1.2.2 OBJECTIVES

- To characterise the various properties of feed (municipal waste sludge and bio-solids) like moisture content, bulk density, pH, calorific value, CHNS, Ash-free dry weight.
- To perform the hydrothermal liquefaction of the feedstock.
- Extraction of oil from the product obtained after hydrothermal liquefaction.
- Rock Analysis of the solid obtained.

CHAPTER-2

REVIEW OF LITERATURE

Galadimaa and Muraza [5] stressed on Algae Valorisation via hydrothermal liquefaction to produce liquid fuels. The paper also investigated the role of heterogeneous catalyst in liquefaction process. The Solid catalysts like metals, zeolites and silica-alumina were evaluated by them. It was observed that the catalyst helped in bio-oil and hydrocarbon fuel yields. High quality bio-oils can be derived from biomass by hydrothermal liquefaction.

A study was carried out by Carrisi *et al.* [6] to enquire about the effect of temperature and biomass composition on yield and quality of biomass produced from three different source such as natural hay, oak wood and walnut shell. The experiment was conducted in a micro reactor in a temperature range of 240–320^{0}C and a reaction time of 30 min. The products were analysed by performing an elemental analysis and GC-MS. An observation was made that with increase in lignin content the bio-yield increased too. The minimum bio-oil yield was observed in cellulose while the maximum in walnut shell.

Suda *et al.* [8] revealed the presence of oxygen in combination with nitrogen in heavier compounds thorough Fourier Transform Ion Cyclotron Resonance Mass Spectrometry examination of a bio crude. They found that components of bio-crude were aromatic nitrogen compounds and free fatty acids of lower molecular weight.

Faeth *et al.* [9] showed that high heating rates about (~200°C/min) and at 1-5 min interval of time leads to high yield of bio-oil from algae feedstock. The reaction in the range of 285°C to 350°C are reported being favourable for HTL [10].

Vardon *et al.* [11] conducted a batch experiment where anaerobically digested bio solids were put through a heated at 300°C temperature for a period of 30 minutes. The yield of biocrude was about 9.4% with an HVV of 32 MJ/kg. Neither of the previous studies on sludge and bio solids tested the effect that process conditions had on the yield or composition of the oil [12].

Pienkos and Darzins [13] stated that algal biomass has been extensively researched in the last decade being a promising substitute for production of sustainable fuels because of its to its high photosynthetic efficiency as well as area specific yields. Although Municipal sludge is also favourable feedstock for HTL. The Bio-fuel obtained through HTL comparable to other obtained through animal manure and algae [14]. HTL conversion of sewage slurry can manufacture a biofuel product up to 9500 Btu/lb. That can be utilized in combustion infrastructure, thus saving potential fuels [15].

Yin *et al.* [16] concluded that utilization of air as processing gas in HTL leds to a very low bio-crude oil yield than those that are converted with N_2. Although these Inert gases, like nitrogen, air, and carbon dioxide are used keep reactor headspace pressure and prevents the feedstock from gasifying. He et al. [17] showed that when compressed air is used as the processing gas, it can reach almost similar bio-crude oil yield as those processed with Carbon dioxide and Nitrogen.

Zhang *et al.* [18] did through investigations of swine manure using carbon monoxide as the process gas over several parameters such as reaction temperature, residence time and solid percentage. Heating rate was constant around 5~10°C /min with variable residence time of (5-120) minutes. Different trends in oil yield were obtained depending on the reaction temperature [19]. The highest HHV of 38.5 MJ/kg from crude oil was obtained at from 20% solid at 305°C, 120-minute residence time 20 min. The composition consisted of 77.9% carbon, 9.4% hydrogen, 4.6% nitrogen and 7.0% oxygen [20].

In batch HTL experiments by Suzuki *et al.* [21] on batch HTL digested bio solids in presence of catalyst loading showed that catalyst had no notable effect on yield properties . Yu *et al.* [22] discovered that the carbon recovery of bio-oil is less than 5% at temperatures below 160^0C, and the recovery increases to 43.2% as the temperature increases to 240^0C. However, when the temperature further increases to 300^0C, the carbon recovery remains unchanged. Overall, the C and H content in bio-oil increases with temperature and exceeds the lipid content in the algae feedstock. The oxygen content decreases with temperature.

CHAPTER-3

EXPERIMENTAL METHODS

3.1 Materials

Municipal wastewater is used as the feedstock. Fluidized bed reactor SBL-2D was used in this study for hydrothermal liquefaction.

For drying the samples, TO 300 drying oven was used. Bomb calorimeter AC-350 was used to calculate the calorific value of the samples. Oxygen gas used in bomb calorimeter was provided by Coregas Pty Ltd.

Chemical used were acetone and n-hexane in the ratio of 50:50 for the process of solvent extraction.

3.2 Initial characterisation of the feedstock

Table 3.1 Parameters and equipment used for initial characterization

PARAMETER	**EQUIPMENT**
Moisture content	TO 300 Drying Oven (at 105^0C for an hour until the weight becomes constant)
Bulk Density	By the help of a flask and a weighing machine (BE-20 CLASSIC).
pH	pH Meter (AQUA-Cond/PH)
Calorific Value	Bomb Calorimeter ac-350
CHNS	CHNS Analyser FLASH EA 1112 series
Ash-free dry weight	High Temperature Furnace SCF 1700

3.2.1 Moisture Content

Fig 3.1 Oven for drying

Moisture content determines the amount of water present in the sample. It is important to find out about how much water content was initially present in the sample.

Method to determine moisture content

The samples were dried in an oven (fig 3.1) at a temperature of 110°± 5°C to a constant mass. Then loss of mass due to drying is assumed to be water. The water content was also calculated using the mass of water and the mass of the dry specimen [29].

Steps to determine the moisture content

1. Calculate and record the mass of the clean and dry specimen container (with its lid-optional)
2. Put the moist bio-solids into the container and tighten the lid if used. Determine and record the mass of the container and moist sample using a balance.
3. Remove the lid if used and place samples in a drying oven at 110±5°C until a constant mass is achieved.
4. After getting a constant mass, remove the containers containing the samples from the oven and replace with the lid if used (without a lid-place it in a desiccator). Allow samples and containers to cool down to room temperature before determining the mass of the container and oven-dried samples
5. Compute and analyse results as shown in below:

$$m_w = m_{cws} - m_{cds}$$

$$m_s = m_{cds} - m_c$$

$$w = \frac{m_w}{m_s} x100$$

Where:

w = water content, %

m_{cws} = mass of container and wet sample, g

m_{cds} = mass of container and oven dry sample, g

m_c = mass of container, g

m_w = mass of water, g

m_s = mass of solid particles, g

Significance in my experiment: It will tell about the percentage of water content present in the sample.

3.2.2 Bulk density

Method

1. Determine and record the mass of the clean and dry specimen container (with its lid-optional)
2. Place the bio-solids into the container and tighten the lid if used. Determine and record the mass of the container and sample using a balance
3. Now subtract the mass of the container from total mass and you will get mass for the sample.
4. Calculate the volume of the sample.
5. Compute and analyse results as follows:

$$\text{Bulk density} = \frac{D}{V_o}$$

Where V_o = apparent bulk volume, D = mass of dry samples.

*Significance in my experiment***:** High bulk density is an indicator of low soil porosity and soil compaction. It may cause restrictions to root growth, and poor movement of air and water through the soil.

3.2.3 pH

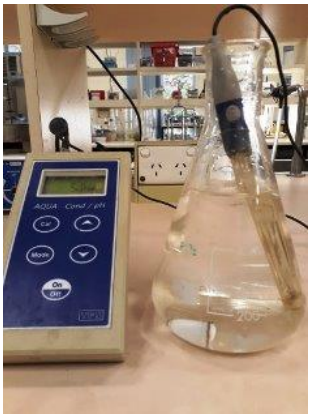

Fig 3.2 pH meter

1. Wash the electrode with distilled water
2. For dried samples of bio-solids, mix samples with distilled water to a known solid concentration, while for wet samples, let it as it is.
3. Run 3 sample tests on buffer solutions of ph 4,7 .
4. Place electrode in the slurry/bio-solids, read and record the measured value.
5. Remove and wash the electrode.

Significance of pH in my experiment: The pH of municipal waste is of much significance while disposing solid waste anaerobically. The pH value of the digester content is an important indicator of the performance and the stability of an anaerobic digester in a well-balanced anaerobic digestion process, almost all products of a metabolic stage are continuously

converted into the next breaking down product without any significant accumulation of intermediary products such as different fatty acids which would cause a pH drop.

3.2.4 Calorific Value

Fig 3.3 Bomb Calorimeter (AC-350)

Calorific value is calculated using the bomb calorimeter. The various steps involved are:

Methods:

1. Crucible Cleaning: Crucible must be cleaned before use
    - Scrub the inside of the crucible with a wire brush.
    - Heat the crucible with a Bunsen burner, or equivalent, to burn off residual matter.
    - Scrub the inside of the crucible with a wire brush again.
    - New crucibles should be heated to 500°C for 5h in a muffle furnace to remove any surface oils.

2. *Sample Preparation*
    - Place the crucible in the centre of the balance and tare the crucible
    - Add sample to the crucible and record the weight of it. Please ensure do not touch the sample with your fingers or hands as you may contaminate the sample.

3. *Combustion Vessel Preparation:*
    - Dry all of the moisture off of the outside of the combustion vessel with a clean, lint free cloth to achieve repeatable results

- Prepare the combustion vessel.
- Remove, rinse, and thoroughly dry combustion vessel cap.
- Remove combustion vessel closure.
- Rinse electrode arms and slide the sleeves up and down until they move freely, dry arms and underside of combustion vessel closure.
- Shake inverted combustion vessel closure to remove water from cavities in the valve assembly and electrode connectors.
- Thoroughly dry topside of combustion vessel closure.
- Dry the sample holder bracket in the combustion vessel cleaning station, Fig 2
- Place the combustion vessel closure in the sample holder bracket, Fig 2.
- Place the crucible containing the sample into the crucible holder, the sample should be in the middle of the crucible to avoid misfire.
- Attach the fuse wire – the length of the fuse wire must be 10 cm long.
- Lift the sleeve on the electrode above the slot in the crucible holder.
- Feed one end of fuse wire into the notch on the electrode arm. Allow approximately 2mm of the fuse to overhang.
- Slide the sleeve firmly over the fuse wire.
- Repeat with the other end of the fuse.
- Bend the fuse wire as shown in Fig 3, to within 0.5 cm of the sample. The top of the fuse wire should be no closer than 7 mm from the top of the sample to prevent misfire.

- Attach the fuse wire – the length of the fuse wire must be 10 cm long.
- Lift the sleeve on the electrode above the slot in the crucible holder.
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- Slide the sleeve firmly over the fuse wire.
- Repeat with the other end of the fuse.
- Bend the fuse wire as shown in Fig. 3, to within 0.5 cm of the sample. The top of the fuse wire should be no closer than 7 mm from the top of the sample to prevent misfire.
- Open the needle valve on the top of the sample holder.
- •Apply thin layer of high vacuum grease to the vessel closer O-ring to ensure it seals combustion vessel well
- Place the combustion vessel closer into the combustion chamber so that the O-ring rests on the chamber, Fig 1.

- Screw the combustion vessel cap clockwise onto the combustion vessel. This will apply even pressure on the vessel allowing it to seat properly without damaging the O-ring.
- Close the needle valve on the vessel by turning it clockwise moderately
- Attach the combustion vessel charger assembly to the combustion vessel and press the Fill switch. The combustion vessel will fill with oxygen until the pressure reaches 420 psi (28.96 bars). The oxygen flow will automatically shut off. To abort filling the combustion vessel, wait five seconds and press the Fill Switch again.
- Remove the combustion vessel charger assembly and prepare the combustion vessel bucket.

4. Combustion Vessel Bucket Preparation

- Thoroughly dry both the inside and the outside of the combustion vessel bucket and remove any fingerprints.
- Position the bucket under the pipette tank.
- Fill the bucket with 2000 mL of water, allowing the water to run down the inside wall of the bucket to reduce the amount of air-bubbles and splashing in the bucket.
- Leave the combustion vessel bucket under the pipette valve for several seconds after the pipette tank has been emptied to allow any remaining drops of water to fall into the bucket.
- Place the bucket in the bucket well, by opening the bucket well lid to the complete vertical position. Carefully place the bucket in the well so no water is spilt onto the insulation and so the indentation on the bottom of the bucket is positioned towards the front of the calorimeter.
- Fold the handle of the bucket towards the back.
- Attach the carrying handle to the combustion vessel by inserting the pins on the end of the handle into the holes on the combustion vessel cap.
- Lower the vessel using the carry handle into the bucket taking care not to disturb the sample.
- Connect the vessel fuse harness to the vessel electrodes before the combustion vessel is fully immersed into the water.
- Centre the vessel over the indentation at the bottom of the bucket.
- Remove the carry handle and shake excess water back into the bucket, making sure not to spill water on the insulation

- Check that no oxygen bubbles are escaping from the vessel. Do not fire the vessel if bubbles are observed. Remove the combustion vessel and correct the problem.
- Close the well lid and push down firmly to latch it.

5. Sample Analysis

Analysis Method:

Before analysing any sample, it is important to develop or select appropriate method to set the analysis parameters. The method chosen will be used in all analyses until a different method is chosen. The most recent calibration will be used for all methods. Up to five methods can be created and stored from the Methods menu.

- Press [4] Setup from the Main menu to develop a method
- From the Setup menu, press [1] Analysis Method. The Analysis Method screen is displayed.
- Press Select to scroll through and select the parameters to edit. Next or Previous may also be used to move the highlight forward or backwards to make a selection.
- Enter the Text or Value from the keyboard or press ←→ to move the cursor to the text or digit to edit. Press Yes or No to select the heat correction mode.
- Press Menu to display the Analysis Method menu. Press [2] Select Method to display the Select Method screen. The highlighted method is the current method in use.
- To select a different method, press the method number, one through five.

3.1.5 Ash Free Dry Weight

Fig 3.4. Muffle furnace

Fig. 3.5 Ash left after heating at 550^{0}C

Sample Preparation:

1. Heat the sample at 40^{0}C for 24 hours.
2. Take it out and keep it in desiccator.

Method

1. Set the program for temperature and time.
2. Start with heating the furnace at 50^{0}C.
3. Wait until it goes up to 250^{0}C.
4. At 250^{0}C, open the muffle furnace (Fig. 3.4) and keep your samples inside.
5. Keep the heating rate to 10^{0}C/min.
6. Let the temperature to reach at 550^{0}C.
7. Let the samples heat at 550^{0}C for one hour.
8. Wait the temperature to come down to 250^{0}C.
9. Now, open the furnace, take out the samples, keep in desiccator and let them cool.
10. Weigh the mass of the sample.
11. Now again put it back to furnace at 250^{0}C
12. Repeat the same procedure until there is constant difference in mass.

CALCULATIONS:

AFDW= [(A-B)/A]* 100

Where,

A = weight of sample before ignition(g)

B = weight of sample after ignition (g)

3.3 HYDROTHERMAL LIQUEFACTION

Hydrothermal liquefaction is a thermal de-polymerization process which converts wet biomass into crude like oil sometimes referred as bio-oil or bio-crude

Fig 3.6 HTL reactor heating inside the fluidized bath.

Fig 3.7 Fluidized bath SBL-2D

Sample Preparation

For hydrothermal liquefactions the samples should be dried at 40^0C for 24 hours in an oven.

3.3.1 Method

For Hydrothermal liquefaction of municipal waste, **30% solid** (sample) and **70% liquid** (water) needs to be taken.

A r**eactor** of **5.5 ml** is used.

Hence solid input is **1.65 ml** and liquid input is **3.85 ml**. The reaction is carried in a **fluidized bed reactor**. Temperature conditions to be taken is **330^{0}C** and pressure of **200 bar**. **Residence time** is **20 mins** after reaching the desired temperature (330^{0}C).

3.3.2 Preparation of samples

1. Grind the bio-solids obtained after heating at 40^{0}C for 24 hours, into fine particles.
2. Zero the balance and weigh a specific amount of solids and water and load it in reactor.

Fig 3.8 oven(40^{0}C) to dry the samples

Loading the reactor

Fig 3.9 5.5 ml reactor for HTL

1. Weigh a small, clean and dry beaker to an accuracy of 0.01g
2. Add the 5.5g of the prepared slurry with known solid concentrations to the beaker. Weigh and record this addition to 3 decimal points.
3. Check that the inside of the reactor tube and its fittings are both dry and clean.
4. Attach the bottom end of the reactor to the reactor tube. Screw the bottom end to the tube so that the fitting is “finger tight”. Further tighten the fitting by clamping the reactor in a vice and

turning the fitting with a wrench (no more than 1/16th of a rotation). Weigh (and record) the reactor with the bottom end attached.

5. Pour the reactant mixture into the reactor tube and then reweigh (and record) either the beaker or the reactor. Make sure that there is at least 2-3cm of headspace in the reactor tube. This will prevent water from rising into the ⅛" tubing and valves.

6. Attach the top end of the reactor to the reactor tube without inverting the reactor. Screw the top end onto the reactor tube in a similar manner to how the bottom was fixed – screw until "finger tight", then tighten with 1/16th rotation with a clamp and vice. Weigh the reactor.

7. Plug in the pressure transducer and reactor thermocouple so that they are connected to the National Instruments data logger.

8. Open the file "multi-channel acquisition 0 – 600bar_10112016" With Lab view 2014. This file is saved in the following location: "Computer > Windows (C:) > hydrothermal processing > Lab view codes".

9. Commence logging reactor temperature and pressure by clicking the white arrow on the control panel. The first readout should appear after approximately 10 seconds.

10. Check that the pressure and temperature readout reflect ambient conditions (~20°C, ~0 bar).

11. Pressure test the reactor:

- Connect the reactor to the nitrogen gas cylinder
- Open the ball valve closest to the nitrogen connection and shut the other ball valve
- Adjust the gas cylinder regulator to 60 bar (6,000kPa)
- Close the ball valve closest to the nitrogen connection
- Monitor the reaction pressure for a few minutes. If the pressure does not decrease with time, then the reactor is properly sealed.
- Gradually release the pressure within the reactor by slowly opening the ball valve furthest from the nitrogen connection. Once all the nitrogen has been released, close the valve.

12. Purge the reactor of oxygen by charging with nitrogen to 3 bar, and then slowly releasing this pressure, as outlined in step 11. Repeat the purge three times.

13. Charge the reactor with nitrogen to the starting pressure of 100 bar. Weigh the reactor to an accuracy of 0.01g (and record).

3.4 EXTRACTION OF OIL

After HTL, we get 2 different products. One is solid and the other is liquid. Liquid might contain some visible oil, but we need to extract oil from solid.

Procedure for extracting oil from solid (Methodology developed):

Fig 3.10 Samples on the shaker

1. Calculate the individual weight of liquid and solid obtained after the hydrothermal liquefaction.
2. Take acetone: n-hexane in ratio 50:50
3. Now, to solid, add the above ratio of acetone: n-hexane 6 times the weight of the solid.
4. Mix it well.
5. Let it rotate for 2 hours in a mixer at 65rpm.
6. Let it settle for 20 minutes.
7. You will observe 2 layers. The above layer is of oil while the lower layer is of solid.
8. Carefully extract the above layer of oil with the help of pipette.
9. After, doing extraction once you can extract the oil for left solids.
10. For that, again take acetone: n-hexane in ratio 50:50
11. Now, to solid, add the above ratio of acetone: n-hexane 4 times the weight of the solid.
12. Mix it well.
13. Let it rotate for 2 hours in a mixer at 65rpm.
14. Let it settle for 20 minutes.
15. You will observe 2 layers. The above layer is of oil while the lower layer is of solid.
16. Again, carefully extract the above layer of oil with the help of pipette.
17. Now evaporate the liquid collected in the environment of nitrogen.
18. The liquid left after the evaporation is the pure oil.

3.5 ROCK ANALYSIS

Method: The rock material is pulverized and passed through a 40-mesh sieve. Approximately 60 - 100 mg of pulverized rock is then accurately weighed into an SRA crucible and placed in the SRA-Agilent auto sampler. The auto sampler transfers the crucible from the auto sampler tray to the SRA pedestal which is raised, putting the sample into the 300C oven. The sample is held isothermal at 300°C for 3 minutes. During this isothermal heating the free hydrocarbons are volatilized and detected by the FID detector where they are quantitatively detected and reported as milligrams (mg) of S**1** per gram of rock. The free CO2 is simultaneously liberated and detected by the IR cell and reported as milligrams (mg) of S3 per gram of rock up to 400°C.

After the isothermal period, the temperature is ramped at 25C/minute to 600C. Between 300C and 600C organic hydrocarbons are generated from the pyrolytic degradation of the kerogen in the rock. This is roughly equivalent to the generative potential of the rock. The hydrocarbons are detected by the FID, labelled as S2, and reported as milligrams (mg) of S2 per gram of rock.

CHAPTER-4

RESULTS AND DISCUSSION

4.1 Physical Characteristics

4.1.1 Gladstone samples

Fig 4.1. Gladstone WWTP dry sludge from dry bed

QW 1: dark brown coloured slurry, large amount of small stones are present most of them are white in colour , grainy solid, becomes lumpy after drying, very unpleasant odour.

Fig. 4.2 Gladstone WWTP Mt Doom ~ 5 years old.

QW2: It is a bio-solid, looks like a dry soil, no water visible, very fine powder like appearance, it is not lumpy.

Fig. 4.3 Gladstone WWTP Mt Doom Drying bed fresh digested

QW3 : dark brown coloured slurry, becomes lumpy on drying, very bad odour.

Fig. 4.4 Calliope WWTP RAS after Clarifier

QW4: very dark brown slurry , becomes very hard on drying, foul odour.

Fig. 4.5 Boyne island WWTP Belt pressed + polyelectrolite zetag 8160

QW5: very dark brown slurry, contains small amount of white fibre like substance, bad odour.

Fig.. 4.6 Boyne island WWTP Drying pan (no polymer)

QW6: looks like dry soil, brown coloured, very hard to break after drying, very bad odour.

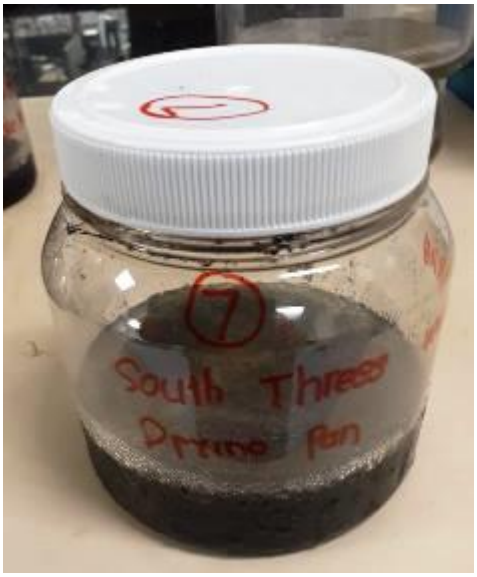


Fig. 4.7 South trees WWTP Drying pan

QW7: Very dark coloured brown slurry, difficult to break after drying, very bad odour.

4.1.2 Melbourne Water Samples

Fig. 4.8 Decanted drying pan

MW1: brown coloured sludge, very obnoxious odour, contains water.

Fig. 4.9 Fresh stockpile

MW2: dark brown coloured bio-solid with bad smell, contains very little amount of water.

Fig. 4.10 3 years old stockpile

MW3: Brown coloured bio-solid, unpleasant smell,very low quantity of water.

Fig. 4.11 Primary Treatment/Screening

MW4: dry fibrous material, no smell.

4.2 MOISTURE CONTENT

4.2.1 (Gladstone samples)

Table 4.1 Moisture content of Gladstone samples

Sample	Initial weight (gm)	Final weight (gm)	Moisture Content (%)
Gladstone wwtp dry sludge from dry bed	7.176	6.908	3.87
Gladstone wwtp mt doom: 5 years	10.734	10.317	4.04
Gladstone wwtp mt doom drying bed fresh digested	1.955	1.829	6.88
Calliope wwtp RAS after clarifier	2.818	2.763	1.99
Boyne island wwtp belt pressed (with polymer)	2.607	2.469	5.58
Boyne island wwtp drying pan (no polymer)	1.193	1.156	3.2
South trees wwtp drying pan	1.16	1.121	3.47

Sample	Initial weight(gm)	Final weight(gm)	Moisture Content (%)
Gladstone wwtp dry sludge from dry bed	6.908	6.894	0.203
Gladstone wwtp mt doom: 5 years	10.317	10.281	0.35
Gladstone wwtp mt doom drying bed fresh digested	1.829	1.827	0.109
Calliope wwtp RAS after clarifier	2.763	2.753	0.363
Boyne island wwtp belt pressed (with polymer)	2.469	2.452	0.693
Boyne island wwtp drying pan (no polymer)	1.156	1.149	0.609
South trees wwtp drying pan	1.121	1.117	0.358

Sample	Initial weight(gm)	Final weight(gm)	Moisture Content (%)
Gladstone wwtp dry sludge from dry bed	6.894	6.876	0.261
Gladstone wwtp mt doom: 5 years	10.281	10.28	0.009
Gladstone wwtp mt doom drying bed fresh digested	1.827	1.819	0.439
Calliope wwtp RAS after clarifier	2.753	2.743	0.364
Boyne island wwtp belt pressed (with polymer)	2.452	2.45	0.081
Boyne island wwtp drying pan (no polymer)	1.149	1.146	0.261
South trees wwtp drying pan	1.117	1.111	0.54

Sample	Initial weight(gm)	Final weight(gm)	Moisture Content (%)
Gladstone wwtp dry sludge from dry bed	6.876	6.862	0.204
Gladstone wwtp mt doom: 5 years	10.28	10.278	0.019
Gladstone wwtp mt doom drying bed fresh digested	1.819	1.824	0.274
Calliope wwtp RAS after clarifier	2.743	2.731	0.439
Boyne island wwtp belt pressed (with polymer)	2.45	2.44	0.409
Boyne island wwtp drying pan (no polymer)	1.146	1.148	0.017
South trees wwtp drying pan	1.111	1.11	0.09

Sample	Initial weight(gm)	Final weight(gm)	Moisture Content (%)
Gladstone wwtp dry sludge from dry bed	6.862	6.871	0.13
Gladstone wwtp mt doom: 5 years	10.278	10.252	0.253
Gladstone wwtp mt doom drying bed fresh digested	1.824	1.818	0.33
Calliope wwtp RAS after clarifier	2.731	2.728	0.109
Boyne island wwtp belt pressed (with polymer)	2.44	2.437	0.123
Boyne island wwtp drying pan (no polymer)	1.148	1.143	0.437
South trees wwtp drying pan	1.11	1.11	0

Sample	Initial weight(gm)	Final weight(gm)	Moisture Content (%)
Gladstone wwtp dry sludge from dry bed	6.871	6.867	0.05
Gladstone wwtp mt doom: 5 years	10.252	10.243	0.08
Gladstone wwtp mt doom drying bed fresh digested	1.818	1.812	0.33
Calliope wwtp RAS after clarifier	2.728	2.724	0.14
Boyne island wwtp belt pressed (with polymer)	2.437	2.432	0.2
Boyne island wwtp drying pan (no polymer)	1.143	1.143	0
South trees wwtp drying pan	1.11	1.109	0.09

MOISTURE CONTENT

4.2.2 (Melbourne Water)

Table 4.2 Moisture content of Melbourne water sample

Sample	Initial weight(gm)	Final weight(gm)	Moisture Content (%)
1	5.066	4.868	4.067
2	7.634	7.328	4.175
3	15.042	14.155	6.266
4	6.083	5.99	1.55

Sample	Initial weight(gm)	Final weight(gm)	Moisture Content (%)
1	4.868	4.825	0.891
2	7.328	7.217	1.538
3	14.155	14.044	0.79
4	5.99	5.977	0.217

Sample	Initial weight(gm)	Final weight(gm)	Moisture Content (%)
1	4.825	4.812	0.27
2	7.217	7.185	0.445
3	14.044	13.986	0.414
4	5.977	5.987	0.167

Sample	Initial weight(gm)	Final weight(gm)	Moisture Content (%)
1	4.812	4.803	0.187
2	7.185	7.18	0.069
3	13.986	13.973	0.093
4	5.987	5.968	0.318

Sample	Initial weight(gm)	Final weight(gm)	Moisture Content (%)
1	4.803	4.802	0.0208
2	7.18	7.179	0.0139
3	13.973	13.979	0.0429
4	5.68	5.971	0.0502

(Gladstone)	
Sample	**Moisture Content %**
QW1	4.306
QW2	4.658
QW3	7.314
QW4	3.913
QW5	6.52
QW6	4.191
QW7	4.31

(Melboune Water)	
Sample	**Moisture Content (%**
MW1	5.211
MW2	5.96
MW3	7.066
MW4	1.841

(Gladstone samples)			
Sample	**%water content dried [40^{0}C]**	**%moisture content obtained**	**%water content dried [105^{0}C]**
QW1	62.976	4.306	67.28
QW2	23.085	4.658	27.74
QW3	86.522	7.314	93.84
QW4	87.429	3.913	91.34
QW5	87.695	6.52	94.21
QW6	90.629	4.191	94.82
QW7	89.662	4.31	93.97

(Melbourne water sample)			
Sample	**% water content dried [40^{0}C]**	**%moisture content obtained**	**% water content dried [105^{0}C]**
MW1	78.72	5.211	83.93
MW2	59.22	5.96	65.18
MW3	16.85	7.066	23.92
MW4	45.6	1.841	47.43

Observation: The moisture content of MW 3 is the lowest as it is a bio-solid. The QW 6 has the highest moisture content. All the bio-solids have very low moisture content as compared to the sludge. QW 5 and QW 6 has almost the same moisture content (highest). The moisture content of all the samples have been observed reducing at the almost same rate. For Gladstone samples, the constant mass was observed after 6 hours while for Melbourne water samples, the constant mass was achieved after 5 hours.

4.3 BULK DENSITY

4.3.1 Gladstone Water

Table 4.3 bulk density of Gladstone water samples

Sample No	Weight (g/cm3)
1	1.3712
2	1.266
3	1.115
4	1.119
5	1.261
6	1.504
7	1.128

4.3.2 Melbourne Water

Table 4.4 Buk density of Melbourne water

Sample No	Weight (gm/cm3)
1	1.291
2	1.342
3	1.191
4	0.002

Observation: Bulk density of all the samples of Gladstone water is almost the same which is also similar to MW1, MW2 and MW3 of Melbourne water. In Melbourne water sample MW4 the bulk density is very small and comes in the range of cotton which can be justified by the fact it contains some light fibrous material.

4.4 pH VALUE

(4.4.1 Gladstone Water)

Table 4.5 pH value of Gladstone sample

Sample	pH
3	6.56
4	6.48
6	6.55
7	5.58

(4.4.2 Melbourne Water)

Table 4.6 pH value of Melbourne Water

Sample	pH
1	6.33

Observation: The pH of only these samples can be recorded as they are slurry. The pH of bio-solids is difficult to record. The pH of the samples are in neutral range except the pH of 7th sample of Gladstone samples. It shows a slight acidic range of pH indicating presence of some acidic substance in the sample.

4.5 CALORIFIC VALUE

4.5.1 (Gladstone water)

Table 4.7 Calorific values of Gladstone sample

Standards:

Standard Number	Weight of std (gm)	Calorific Value (cal/gm)
1	1.0095	6328.8
2	0.9935	6621.6

Gladstone samples:

Samples Number	Weight of samples (gm)	Calorific Value (cal/gm)
1	0.2031	2011.1
2	0.202	693
3	0.2035	2829
4	0.2019	3465.5
5	0.2099	4031.3
6	0.2016	3844.7
7	0.2039	3544

REPEAT (Gladstone samples)

Samples Number	Weight of samples (gm)	Calorific Value (cal/gm)
1	0.209	1906.1
3	0.2016	2819

Observation: The lowest calorific value is of Gladstone wwtp mt doom (Sample 2)~ 5 years old while the highest observed calorific value is of boyne island wwtp belt pressed(with polymer).Sample 4 and 7(i.e calliope wwtp RAS after clarifier and douth trees wwtp drying pan) have almost the same calorific value.

4.5.2 (Melbourne water)

Table 4.8 Calorific value of Melbourne water samples

Standards:

Standard Number	Weight of std (gm)	Calorific Value (cal/gm)
1	0.9972	6155
2	1.0536	6773
3	1.0968	6493.5

(Melbourne water
samples)

Sample Number	Weight of std (gm)	Calorific Value (cal/gm)
1	0.2038	685.8
2	0.2096	3204.6
3	0.2096	3117.9
4	0.2048	3804

REPEAT (Melbourne water samples)

Sample Number	Weight of std (gm)	Calorific Value (cal/gm)
3R	0.2058	3032.8

Observation: The lowest calorific value obtained is of Sample1 i.e. decanted drying pan while highest calorific value is of Sample 4 i.e. primary treatment sludge/screening. The sample 2 and 3 i. e fresh stockpile and 3 years old stockpile has almost similar calorific value.

4.6 CHNS

4.6.1 Gladstone Samples:

Table 4.9 CHNS values for Gladstone sample

CHNSO(%)	Gladstone wwtp dry sludge from dry bed	Gladstone wwtp mt doom: 5 years	Gladstone wwtp mt doom drying bed fresh digested	Calliope wwtp RAS after clarifier	Boyne island wwtp belt pressed (with polymer)	Boyne island wwtp drying pan (no polymer)	South trees wwtp drying pan
Carbon	23.33	13.18	27.21	32.86	37.86	37.05	33.96
Hydrogen	4.97	2.47	4.98	4.97	5.78	5.61	5.48
Nitrogen	3.55	2.02	4.65	5.46	6.55	6.02	5.43
Sulfur	1.53	1.08	1.87	2.15	2.17	2.2	2.39
Oxygen	66.62	81.25	61.29	54.56	47.64	49.12	52.74

Observation: The highest carbon content is observed in Boyne island wwtp belt pressed sample (sample 5) and lowest carbon content is in Gladstone wwtp mt doom~ 5 years old (Sample 2), which can be justified by the fact that it is 5 years old hence less carbon content. Hydrogen content in sample 1 and 4 is exactly the same. Sample 7 has the highest sulphur content.

4.6.2 Melbourne Water Samples

Table 4.10 CHNS values for Melbourne water samples

CHNSO(%)	Decanted drying pan	Fresh Stockpile	3 yrs old stockpile	Screening
Carbon	31.9	28.4	29.53	45.82
Hydrogen	5.56	5.18	5.07	7.03
Nitrogen	5.3	4.49	3.9	2.88
Sulfur	1.97	2.06	1.93	1.47
Oxygen	55.27	59.87	59.57	42.8

Observation: The highest carbon content was observed that of sample 4 i.e primary treatment sludge. The hydrogen content of sample 1,2 and 3 are almost in same range while sample 4 is around 21.5% more than the rest. The sulphur content is almost in same range.

4.7 HYDROTHERMAL LIQUEFACTION

Table 4.11 Solid and liquid yield of Melbourne water samples after HTL

Sample	Bio-solids	Water	(Before HTL) reactor+ bio-solid+water	(Before HTL) reactor+ N2	(After HTL) reactor + N2	(After HTL) reactor - N2	Wt of empty tube for solid	Wt of empty tube for water	(After HTL) Tube+Solid	(After HTL) tube + water	Wt of solid obtained after HTL	Wt of liquid after HTL
MW1a	1.7214	3.7041	1128.34	1129.89	1129.95	1128.25	13.753	13.744	16.482	15.573	2.729	1.829
MW1b	1.7208	3.773	1128.39	1129.75	1129.85	1128.11	13.733	13.132	16.172	15.01	2.439	1.878
MW2a	1.7238	3.772	1128.74	1130.25	1130.16	1128.41	13.142	13.098	16.037	14.309	2.895	1.211
MW2b	1.7381	3.773	1128.54	1130.14	1130.25	1128.38	12.906	12.966	15.0233	14.15	2.1173	1.184
MW3a	1.789	3.725	1128.31	1129.89	1130.03	1128.25	13.422	13.4225	15.992	15.031	5.243	2.8505
MW3b	1.785	3.7289	1128.7	1130.26	1131.12	1129.29			18.665	16.273		
MW4a	1.022	3.837	1106.35	1108.01	1107.77	1105.83	13.17	13.156	14.976	13.763	3.336	1.379
MW4b	1.017	3.831	1105.78	1107.49	1107.37	1105.47			16.506	14.535		

Table 4.12 Solid and liquid yield of Gladstone samples after HTL

Sample	Bio-solids	Water	(Before HTL) reactor+ bio-solid+water	(Before HTL) reactor+ N2	(After HTL) reactor + N2	(After HTL) reactor - N2	Wt of empty tube for solid	Wt of empty tube for water	(After HTL) Tube+Solid	(After HTL) tube + water	Wt of solid obtained after HTL	Wt of liquid after HTL
QW1a	1.7263	3.7864	1107.63	1109.2	1109.37	1107.59	13.128	13.172	16.064	14.643	5.783	3.292
QW1b	1.725	3.7856	1107.74	1109.27	1109.12	1107.41			18.911	16.464		
QW2a	1.7375	3.7772	1107.13	1108.73	1108.97	1107.16	13.139	13.1502	15.943	14.523	5.596	3.5438
QW2b	1.7343	3.7704	1107.43	1109.01	1108.95	1107.29			18.735	16.694		
QW3a	1.6596	3.8724	1107.62	1109.09	1109.16	1107.59	13.154	13.1804	14.081	16.522	2.078	5.8036
QW3b	1.6611	3.8759	1107.43	1108.96	1108.95	1107.42			15.232	18.984		
QW4a	1.6586	3.8502	1108.42	1109.91	1109.9	1108.23	13.779	13.843	16.021	15.544	3.804	3.376
QW4b	1.6522	3.8581	1108.52	1109.99	1109.99	1108.4			17.583	17.219		
QW5a	1.6503	3.8567	1107.87	1109.55	1109.56	1107.82	13.858	13.861	15.656	15.734	2.723	3.297
QW5b	1.5525	3.8539	1108.42	1109.91	1110.75	1109.16			16.581	17.158		
QW6a	1.6519	3.8614	1107.92	1109.92	1108.46	1106.73	13.927	13.793	16.102	14.089	3.911	2.559
QW6b	1.6584	3.8514	1108.36	1109.86	1109.43	1106.71			17.838	16.352		
QW7a	1.655	3.8597	1108.58	1109.97	1110.02	1108.38	13.758	13.919	14.366	17.668	3.239	4.94
QW7b	1.6562	3.8535	1108.71	1110.2	1110.2	1108.51			16.997	18.859		

Table 4.13 Gas yield of Gladstone and Melbourne water samples after HTL

sample names	Temperature (°C)	Residence Time (min)	Mass of Feedstock (g)	Mass of Water (g)	Mass of Reactor with Top + Reactants (g)	Mass of Reactor afte N_2 Addition (g)	Mass of N_2 in Reactor (g)	Mass of Reactor and Reactants after HTL (g)	Mass of Reactor and Reactants after Gas Release (g)	Mass of Gas Released (g)	Gas Yield from HTL (g)	Gas Yield from HTL (%)
MW1a	330	20	1.7214	3.7041	1128.34	1129.89	1.55	1129.95	1128.25	1.7	0.15	8.7
MW1b	330	20	1.7208	3.773	1128.39	1129.75	1.36	1129.85	1128.31	1.54	0.18	10.5
MW2a	330	20	1.7238	3.772	1128.74	1130.25	1.51	1130.16	1128.41	1.75	0.24	13.9
MW2b	330	20	1.7381	3.773	1128.54	1130.14	1.6	1130.25	1128.38	1.87	0.27	15.5
MW3a	330	20	1.789	3.725	1128.31	1129.89	1.58	1130.03	1128.25	1.78	0.2	11.2
MW3b	330	20	1.785	3.7289	1128.7	1130.26	1.56	1131.12	1129.29	1.83	0.27	15.1
MW4a	350	20	1.022	3.837	1106.35	1108.01	1.66	1107.77	1105.83	1.94	0.28	27.4
MW4b	350	20	1.017	3.831	1105.78	1107.49	1.71	1107.37	1105.47	1.9	0.19	18.7
QW1a	330	20	1.7263	3.7864	1107.63	1109.2	1.57	1109.37	1107.59	1.78	0.21	12.2
QW1b	330	20	1.725	3.7856	1107.74	1109.27	1.53	1109.12	1107.41	1.71	0.18	10.4
QW2a	330	20	1.7375	3.7772	1107.13	1108.73	1.6	1108.97	1107.16	1.81	0.21	12.1
QW2b	330	20	1.7343	3.7704	1107.43	1109.01	1.58	1108.95	1107.29	1.66	0.08	4.6
QW3a	330	20	1.6596	3.8724	1107.62	1109.09	1.47	1109.16	1107.59	1.57	0.1	6.0
QW3b	330	20	1.6611	3.8759	1107.51	1108.96	1.45	1108.95	1107.42	1.53	0.08	4.8
QW4a	330	20	1.6586	3.8502	1108.42	1109.91	1.49	1109.9	1108.23	1.67	0.18	10.9
QW4b	330	20	1.6522	3.8581	1108.52	1109.99	1.47	1109.99	1108.4	1.59	0.12	7.3
QW5a	330	20	1.6503	3.8567	1107.87	1109.55	1.68	1109.56	1107.82	1.74	0.06	3.6
QW5b	330	20	1.5525	3.8539	1108.42	1109.91	1.49	1110.75	1109.16	1.59	0.1	6.4
QW6a	330	20	1.6519	3.8614	1107.92	1109.92	2	1108.96	1106.73	2.23	0.23	13.9
QW6B	330	20	1.6584	3.8514	1108.36	1109.86	1.5	1109.43	1107.71	1.72	0.22	13.3
QW7a	330	20	1.655	3.8597	1108.58	1109.97	1.39	1110.02	1108.38	1.64	0.2	15.1
QW7b	330	20	1.6562	3.8535	1108.71	1110.2	1.49	1110.2	1108.5	1.7	0.21	12.7

Table 4.14 Percentage of solid and liquid of Gladstone and Melbourne water samples after HTL

Sample	Percentage of solid obtained	Percentage of liquid obtained
MW1	47.329	33.949
MW2	45.538	21.759
MW3	47.543	25.848
MW4	34.367	14.206
QW1	52.462	29.864
QW2	50.783	32.160
QW3	18.773	52.431
QW4	34.522	30.638
QW5	24.951	30.211
QW6	35.480	23.215
QW7	29.380	44.810

Observation: The highest liquid is obtained in sample QW 3 (52.43%) while it is interesting to note it also has the lowest percentage of solid (18.77%). The lowest percentage of liquid is obtained in MW4 (14.20%). The fibrous nature of sample MW4 makes it difficult to extract liquid. The lowest gas yield is observed in QW5 (9%)while MW4 has the highest percentage of the gas yield.QW5 and QW3 has almost similar percentage of gas yield.

4.8 ASH FREE DRY WEIGHT

Table 4.15 Ash free dry weight of Gladstone and Melbourne water samples

Sample	Wt of crucible	wt of crucible(inclusive of sample)	wt of sample	wt of crucible+ash (after 1 hour)	wt of ash(inorganic)	wt of crucible+ash (after 2 hours)	wt of ash(inorganic)	wt of crucible+ash (after 3 hours)	wt of ash(inorganic)	wt of crucible+ash (after 4 hour)	wt of ash(inorganic)	wt of crucible+ash(after 5 hours)	wt of ash(inorganic)	Percentage of ash content(Inorganic)	Percentage of organic content
MW1	15.99	16.242	0.252	16.078	0.164	15.937	0.141	15.818	0.119	15.718	0.101	15.618	0.1	39.683	60.317
MW2	15.903	16.161	0.258	15.959	0.202	15.79	0.169	15.643	0.147	15.51	0.133	15.376	0.134	51.938	48.062
MW3	8.456	8.714	0.258	8.557	0.157	8.421	0.136	8.321	0.1	8.224	0.097	8.126	0.098	37.984	62.016
MW4	7.238	7.497	0.259	7.31	0.187	7.151	0.159	7.033	0.118	6.95	0.083	6.865	0.085	32.819	67.181
QW1	8.449	8.706	0.257	8.497	0.209	8.316	0.181	8.162	0.154	8.024	0.138	7.886	0.138	53.696	46.304
QW2	11.605	11.861	0.256	11.665	0.196	11.527	0.138	11.405	0.122	11.258	0.147	11.11	0.148	57.813	42.188
QW3	11.606	11.857	0.251	11.656	0.201	11.48	0.176	11.342	0.138	11.217	0.125	11.092	0.125	49.801	50.199
QW4	15.544	15.798	0.254	15.603	0.195	15.435	0.168	15.304	0.131	15.185	0.1189	15.066	0.119	46.850	53.150
QW5	8.655	8.906	0.251	8.719	0.187	8.58	0.139	8.415	0.165	8.313	0.102	8.212	0.101	40.239	59.761
QW6	7.312	7.563	0.251	7.364	0.199	7.191	0.173	7.081	0.11	6.975	0.106	6.868	0.107	42.629	57.371
QW7	8.731	8.989	0.258	8.786	0.203	8.602	0.184	8.489	0.113	8.386	0.103	8.285	0.101	39.147	60.853

Observation: My main area of focus was amount of ash content present in this sample, the ash content in this sample lies in the range of the ash content of the sludge as compared to the literature. QW 2 has the highest percentage of ash content while MW 4 has the lowest percentage of ash content. The ash content range lies in the range of ash content for sludge when compared to the literature. The ash free dry weight yields attained in laboratory are 39-53 % for tertiary sludge, 46% for secondary sludge and 32-57% for bio-solids.

4.9 ROCK ANALYSIS

Rock Analysis before extraction:

Where,

Bext= Before Extraction

Aext= After Extraction

Where TOC is the Total Organic Carbon

S1= Easily extractable material (free hydrocarbon)

S2= Not easily extractable material (can still be converted into oil)

S3= Organic carbon.

Sample Name	TOC (wt %)	S1 (mg HC/g rock)	S2 (mg HC/ g rock)	S3 (mg CO_2/ g rock)
Bext MW1	27.94	42.94	157.13	14.46
Bext MW2	24.4	37.67	126.03	13.7
Bext MW3	24.18	29.33	121.22	14.83
Bext MW4	32.66	29.16	222.72	16.59
Bext QW1	11.32	11.46	46.82	9.89
Bext QW2	8.64	2.35	22.2	7.16
Bext QW3	21.81	39.27	98.51	13.18
Bext QW4	26.16	34.97	124.6	16.25
Bext QW5	29.53	40.13	129.5	18.47
Bext QW6	28.01	34.23	124.95	18.09
Bext QW7	25.72	35.58	122.05	16.47

Rock Analysis after extraction:

Where,

Bext= Before Extraction

Aext= After Extraction

Where TOC is the Total Organic Carbon

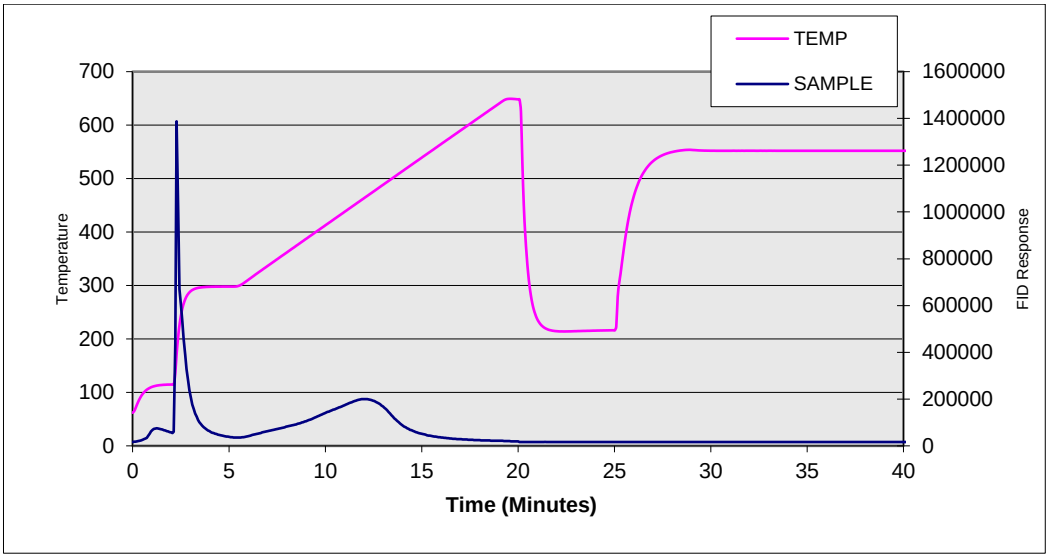
S1= Easily extractable material (free hydrocarbon)

S2= Not easily extractable material (can still be converted into oil)

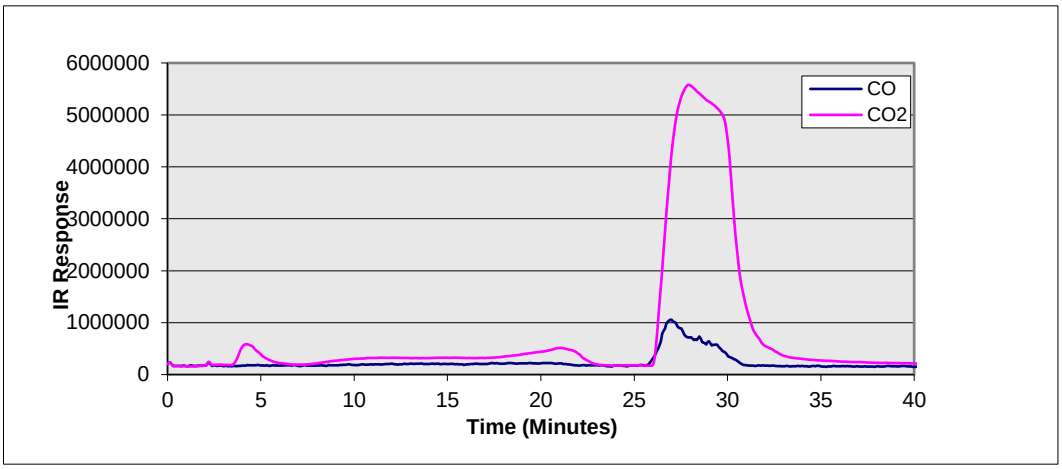
S3= Organic carbon.

Sample Name	TOC (wt %)	S1 (mg HC/g rock)	S2 (mg HC/ g rock)	S3 (mg CO_2/ g rock)
Aext MW1	15.93	30.12	46.12	1.65
Aext MW2a	12.62	31.18	32.35	1.32
Aext MW2b	8.35	21.74	18.45	0.58
Aext MW3	14.66	16.62	39.11	1.33
Aext MW4	23.89	22.08	48.44	0.69
Aext QW1	4.94	4.56	9.57	0.5
Aext QW2	7.96	1.39	9.58	0.43
Aext QW3	17.5	29.37	35.94	1.5
Aext QW4	17.22	35.78	44.71	1.58
Aext QW5	25.34	39.38	75.93	2.21
Aext QW6	17.44	27.78	46.68	1.15
Aext QW7	15.56	43.7	40.95	1.51

The general temperature vs time graph of the sample undergoing rock analysis (Before Extraction):



The Impulse response vs Time graph (After Extraction):



Observation: The Blue line indicates the extractable material. It is observed that before extraction there is a high peak of extractable material while after extraction we observe the decrease in the peak indicating that during the extraction, loosely bound hydrocarbons have been extracted during the extraction. The Total Organic Carbon has been seen to reduce after the extraction.

The Extractable material S1 reduced after the extraction indicating the extraction of loosely bound hydrocarbon during the extraction. It is also noticed that extractable material is more in the Melbourne Water Sample as compared to the Gladstone samples.

4.10 Extraction of Oil

Sample Name	weight of bottle	weight of bottle + oil	weight of oil extracted	%Yield of oil
MW1	3.23	5.221	1.991	36.200
MW2a	3.214	4.917	1.703	30.964
MW2b	3.22	4.293	1.073	19.509
MW3	3.217	4.314	1.097	19.945
MW4	3.224	5.137	1.913	34.782
QW1	3.217	5.001	1.784	32.436
QW2	3.212	3.939	0.727	13.218
QW3	3.23	4.208	0.978	17.782
QW4	3.232	4.642	1.41	25.636
QW5	3.231	5.168	1.937	35.218
QW6	3.22	4.941	1.721	31.291
QW7	3.217	4.955	1.738	31.600

Observation: The highest yield of the oil extracted is from MW1 (36.2%) while the lowest yield of oil extracted is that from QW2 (13.2%). It is interesting to note that the highest percentage of extractable material is of MW1 while the lowest is that of QW2. It proves that the extraction of oil took place as there is also decrease in the percentage of hydrocarbon.MW2a has more yield then MW2b indicating that temperature of 330°C is suitable for HTL.

CHAPTER-5

SUMMARY AND CONCLUSION

In my work, I have tried to solve problem for water industry by managing the wastewater which in turn got utilized to produce the oil. I focused on 2 areas of work i.e wastewater management and energy and tried to bring them together. This thesis inspect municipal wastewater as a potential feedstock for energy recovery via hydrothermal liquefaction. The two main objectives of my research is

1) Management of municipal wastewater

2) Production of energy via municipal wastewater.

Instead of working on one particular sample I worked on 11 different samples from different sources. They are broadly categorized into 3 main categories: tertiary sludge, secondary sludge and bio-solids due to their origin.

I used municipal wastewater as my feedstock and characterized its various properties like CHNS, AFDW, bulk density, pH, Calorific value moisture content. The moisture content of all samples was noticed to be changed by same rate when heated at 105^0C. Being a sludge the highest percentage of moisture content came out to be 94.8 % while the lowest was that of bio-solid, 23.9 % pH of almost all the sample was in neutral range except the sample QW 7 with pH 5.58 which is a slight acidic indicating the presence of any acidic substance in the sludge. . The ash free dry weight yields attained in laboratory are 39-53 % for tertiary sludge, 46% for secondary sludge and 32-57% for bio-solids. The range very well matches with the literature. Being from different origin, the calorific values of all the samples are different from each other. The calorific value of the Gladstone samples varies in the range of 690-4030 cal/gm. While, for Melbourne samples, it varies in the range of 680-3800 cal/gm. The bulk density of all the samples are almost in same range except for sample MW 4 which is fibrous and very light. Its bulk density is similar to the bulk density of cotton.

The municipal wastewater samples were separated into liquid (containing oil) and solid via hydrothermal liquefaction. Elevated temperature (330^0C) and pressure (200 bar) was chosen for the best result. A maximum of 27% gas was lost during the HTL. The highest liquid yield observed was 52.43% while the highest solid yield was 52.46%, they are in same range. Now, both liquid and solid product contains oil. From liquid product, the oil is extracted by

centrifugation and taking out the upper layer, which is oil, with the help of pipette. While taking out oil from solid was challenging but I was successful in extracting it by the methodology developed (mixing it with acetone and n-hexane in 50:50 ratio) and let it mix well in a shaker for 2 hour and after that pipetting out the top layer (usually lighter than the rest). As, by this method, the oil that we extract can be mixed with some amount of water too. So, for obtaining the pure oil, it was evaporated in the presence of nitrogen. Now we are left with pure oil.

The solids left out after extraction is dried at 40^0C for 24 hours so that it can be used for rock analysis. By rock analysis, the percentage of extractable material was known. Melbourne water samples had more extractable material as compared to Queensland water. The percentage of oil obtained was 36.2%. The oil will be tested for GC-MS so as to know which all components are present in the oil.

Looking at the results, municipal wastewater definitely seems to be a promising feedstock for being used as the commercial oil. It is the economics that needs to be worked out, which is possible if one big hydrothermal liquefaction plant will be built to convert large amount of waste into solid and liquid at once. As, the natural reserves of earth are depleting, the municipal wastewater can be a saviour and a sustainable source of energy. A lot of research is already going on to look for alternatives for energy. A lot of work can still be done in this field. This is an upgradable renewable energy and after extracting oil, and the word upgradable suggests that a numerous property of oil can be improved to make it commercially available to be used in vehicles and for other profit-oriented business.

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