Experimental Investigation of Refinery Waste Cake for its Potential use as Biofuel Source

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ABSTRACT

Biofuel is a type of oil which is formed through anaerobic digestion process. It is frequently used as a transformation of biomasses into useful energy product. Thermal degradation is an effective technique for the characterization of waste cake for biofuel production. This research work was focused on the characterization of waste cake collected from oil refinery. The sample was analyzed for its calorific value, proximate value and elemental analysis. The results reflected that HHV of dry waste cake was higher (22.5MJ/kg) than wet waste cake (20.5MJkg) and commonly used sugar can bagasse (17.88MJ/kg).

The percentage composition of carbon (49.8 percent, 40.8), hydrogen (7.9 percent, 6.0 percent), nitro gen (2.8 percent, 1.9 percent), sulphur (1.9 percent, 0.5 percent), and oxygen content (37.6 percent, 4 0.4 percent) were shown in the elemental analysis of dry waste cake versus moist cake. When it come s to the thermal degradation behaviour of dry and wet cake in TGA, wet cake has greater moisture co ntents (68.50 percent) than dry cake (40.1 percent).

Wet cake has a low volatile matter (30.9%) and a high volatile matter (30.9%). (14.3 percent). Simila rly, the percentage of ash in dry cake (17.3 percent) increases while it decreases in moist cake (5.11 p ercent). In contrast to the foregoing, the percent fraction of carbon in wet cake increased (12.09%) w hereas it decreased in dry cake (11.7 percent).

Keywords: Thermal Degradation, Biofuel, Waste Cake, Characterization, Thermo-gravimetric analysis.

INTRODUCTION

Due to significant population increase and industrial development, the need for energy is growing eve ry year. The Renewable Energy Directive (RED) estimates that biomass will supply half of the EU's r enewable energy requirements (EU,2009).

Every manufacturing, transportation, production, and consumer activity requires energy as a primary input (Afgan et al., 1998). Wastewater is a semi-solid by-product created during the treatment of oil refinery waste water. During the treatment, a thicker sludge with a solid content of 3-5 percent forms, which is centrifuged to remove the water. The dewatered product is a dry cake with a solid content of 30% (by weight), which is obtained at the centrifuge's output with the dewatering polyelectrolyte dosage. Depending on the type of industry, the final product may include innocuous water, bio-solids, oils and mud, as well as other detritus. During the oil refinery process, three types of sludge are formed: oily sludge, chemical sludge, and bio sludge. Cleaning oil tanks usually results in the formation of oily sludge. Oily sludge is formed during the crude oil refining process and contains oil, phenols, benzenes, and other toxic and aromatic materials (Richard L. Skaggsa, André M. Colemana, 2018). Variations in chemical and physical characteristics of substances are regulated as a function of a constant rate of heating, or as a time function with infinite temperature or constant mass loss (Cleverson Vittorio, et al, 2007).Many thermal actions like desorption, absorption, oxidation, sublimation, reduction, decomposition and vaporization change the sample mass when exposed to temperature change. Gaseous products are generally absorbed by elastomers, fibres, thermoplastics, composites, and paints throughout the process (Cleverson Vittorio, et al, 2007). Figure 1 depicts global biofuel output in recent years.

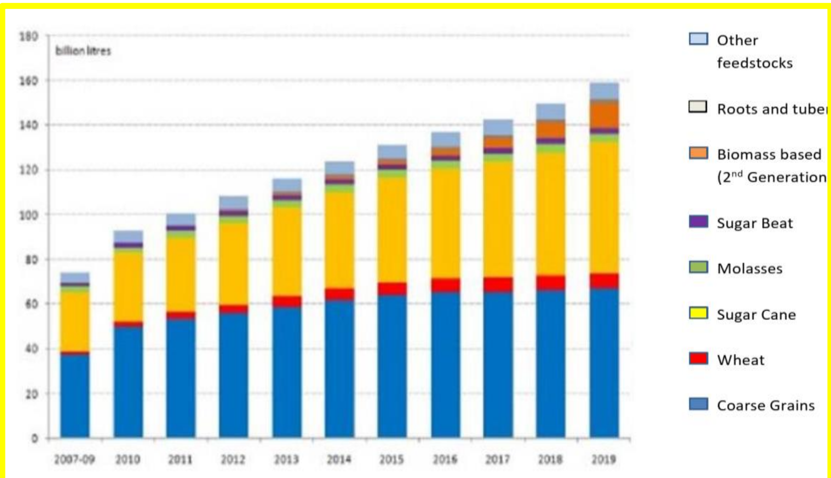

Figure 1: Worldwide Biofuel production

Nevertheless, studies cited in literature are usually related to biofuel applications. For instance (Ning SK, et.al., 2013), analyzed the burning of biofuels is clean compared to fossil fuels. They do not generate sulfur or aromatics that is why there is no unpleasant fragrance by burning of biofuels. The emission of carbon dioxide is at lower level. According to National Renewable Energy Laboratory (NREL) report, biodiesel emit 78.5% less carbon dioxide than petroleum diesel. Recently (Abu Bakr et.al.,2018), In a Spanish oil refinery, the biological sludge and physio-chemical sludge were determined by running at varied rates of heating at 4 and 10 K/s, with varying gas interaction times. Similarly, TGA was used to examine the influence of operational factors such as heating rate of different biomass (S. Hussain et al., 2014). At a constant heating rate of 200°C/min, the activation energy (Ea) values for coal-biomass combination (91/9) were 26.75, 24.98, and 25.64 kJ/mole for ER values 0.25, 0.30, and 0.35, respectively. The influence of operational conditions on the thermal deterioration of low-grade coal, bagasse, and their mixes is critical. Similarly, (Hou B, et al., 2002) refineries create enormous amounts of oily sludge during the crude oil refining process.

For sewage sludge, (Antonio et.al., 2017) to explain its pyrolysis process the kinetic parameters were used. The sludge has same proportion of heterogeneous composition.

(Muhammad Usman., 2018) investigated that yielding of oil from wastewater sewage treatment is remarkably much prominent to alternative sources such as microbiological, soybean and the rate of lipid extraction from wastewater treatment is about 0.03$ per gallon which is very low than other feedstock for production of biodiesel.

Types of sludge

Large quantity of water is consumed at different phases of petroleum processing process such as thermal cracking, distillation catalytic cracking and desalting. During these phases, large volumes of wastewater are produced. Petroleum refining processes produces 1.6 times of total wastewater compared to the total volume of crude oil processed (Coelho A, et.al., 2006). Oil refineries generate three types of sludge, namely oily sludge, chemical sludge and bio sludge shown in figure 2.

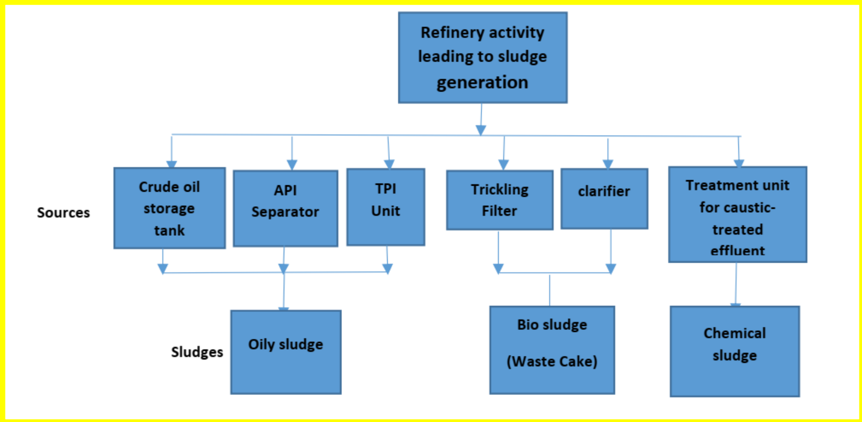

Figure 2: Sources of sludge from refinery (Noorhaza, et.al, 2015),

Oily sludge

Oily sludge is typically formed through cleaning processes of Crude oil tanks. In the refining process of crude oil, large amount of sludge called oily sludge is formed containing oil, phenols benzenes and various toxic and aromatic materials. These materials are considered as harmful wastes. But oily sludge has rich number of hydrocarbons which have average calorific value of 3900 kcal/kg. This shows that Oily sludge has higher potential of energy (Richard L. Skaggsa, André M. Colemana, 2018).

Chemical sludge

The caustic treatment of effluents with polyelectrolyte and $FeCl_3$ produces chemical sludge. The quantity of sludge formed during caustic treatment depends on many factors such as: structures of crude oil, effluent and waste treatment processes etc. It comprises of consumed caustic, spent acids and waste amines (Coelho A, et.al., 2006).

Biological sludge

Biological sludge is produced by biological treatment of wastewater of oil refinery. It is found in clarifier unit and trickling filter of wastewater treatment plants. The hydrocarbon products contain sulphide, phenolic and other acidic compounds the solution of sodium hydroxide is used to eliminate these dissolved substances. Bio-sludge is collected from drying beds. The drying beds uses sands and gravels as filter medium. Dehydrated bio sludge is also useful in agricultural land and gardens to exploit its fertilizer potential. However, the sludge contains heavy metals that is a major restriction for its use as a fertilizer (Coelho A, et. Al., 2006).

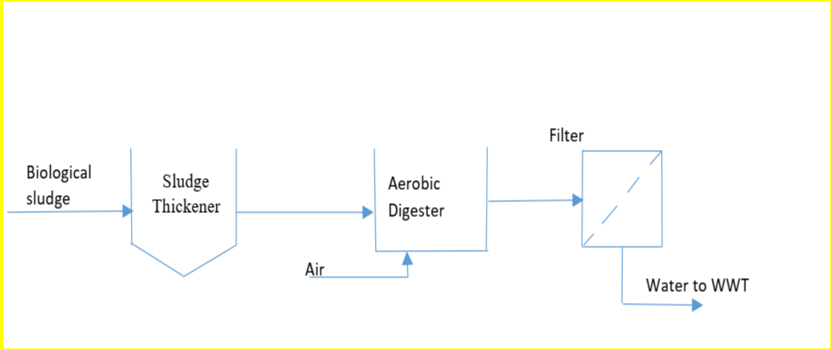

Figure3: Biological sludge treatment

The paper was focused on the refinery waste cake used for biofuel potential. Therefore, none has attempted to perform detailed thermogravimetric analysis for its use as biofuel. It is worth noted that Pakistan is considered to be major oil producing regions all over the world. The identification of the characteristics of waste cake was the prime objective of present study. For this TG analysis was used to investigate the thermal degradation behavior of waste cake. Moreover, ultimate analysis was also used to detect the elemental composition (carbon, hydrogen, nitrogen, oxygen and Sulphur). Lastly, the calorific value of waste cake is calculated.

Sludge generation from Oil Refinery

All oily wastewater streams from the refinery are pumped to API Oil/Water Separation Basin for removal and recovery of oil and sludge. The two-gravity type API Oil/Water separators have a design capacity of 170m^3/hr. Each API separator is fitted with chain driven scrapper and rotary drum skimmer, the scrapper rakes the oily sludge to sludge storing section whereas rotary drum skimmer collects floating oil and drains the skimmed oil to skimmed oil sump. The effluent water from API Oil/Water Separation Basin is pumped to the Equalization Tank to maintain constant feed quality and quantity. This Tank is provided with the air compressor that maintains the homogeneity of the tank.

The Flash Mixing Basin (FMB) receives its feed from Equalization Tank (ET) at the rate of 192m^3/hr. The pH is maintained either by dosing 25Be caustic soda and 98wt% sulfuric acid in FMB. Ferric Chloride and DAF Polymer is also dosed to facilitate the growth of macro-flocs. The flocculated effluent flows to the Dissolved Air Floatation (DAF) which removes flocculated suspended solids and floating oil. The DAF is provided with DAF Recycle water pressure vessel. A portion of treated water resulting from DAF process is pumped into DAF Recycle Water Pressure Vessels. The water in each vessel becomes saturated with air and is then injected into inlet of DAF Basin. On injection into each Basin, the dissolved air is released as millions of fine air bubbles that attach the particles dispersed in wastewater and floats the floc particles to the surface which is later on skimmed into DAF Scum Sump.

The effluent of DAF is fed into two Biological Aeration Basin (BAB) where the biological oxygen demand is reduced to the prescribed acceptable limits (2ppm) through the infusion of oxygen into the water. Ammonium Phosphate is dosed into the inlet of BAB is to supply nutrients to the bacteria necessary for the activation of biological process. After aeration, the next treatment process is clarification. The two clarifiers separate the biological solids formed in BAB effluent. Each Clarifier has a sludge scrapper mechanism which draws off the bottom of the clarifier. Some of the clarifier bottom sludge is recycled back by the clarifier sludge recycle pump to the BAB to maintain concentration of mixed liquor suspended solids in BAB. The skimmer arm skims any scum floating in the surface of the clarifier into Clarifier Skimming Tank which is transferred to Aerobic Digester as shown in Figure 4.

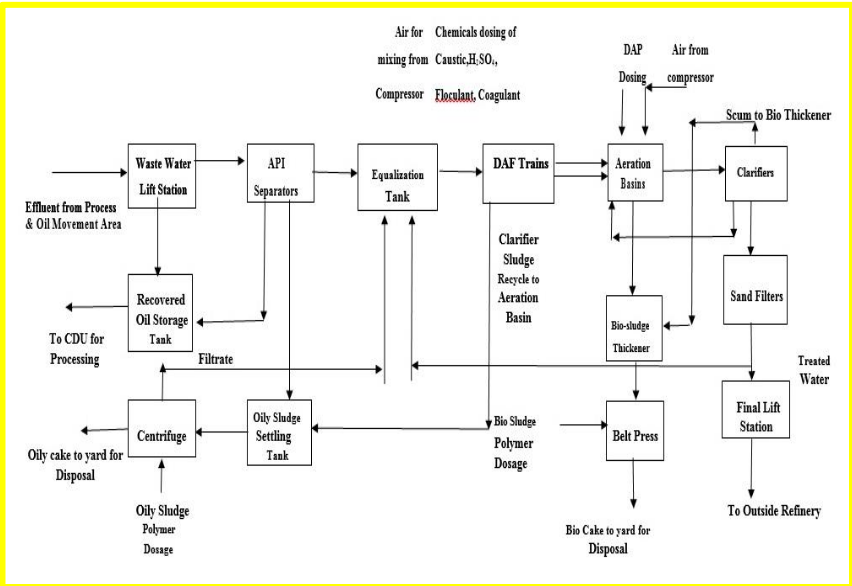

Figure 4: Effluent treatment Plant flow Diagram

The clarified water from Clarifiers flows to four rapid gravity type sand filters each of which is designed to have capacity of 50% of the maximum dWaesign flow. The sand filter media comprises of anthracite (top layer), sand (middle layer) and graduated support gravel (bottom layer). The filter back washing is automatic and normally time based. The back wash sequence consists of air scrubbing through 470Nm^3/hr air blower and water flow washing. The wash water will be returned to Equalization Tank. The Filtered water is pumped to Final Lift Station for dispose of into Saim Nalla.

Bio-Sludge handling system will be provided to produce bio-sludge cake with 17% dry solids from bio-sludge feed with 1% dry oil solids by using thickening and belt drying. The bio-sludge from biological treatment plant and sanitary waste treatment plant will be continuously disposed off at the rate of 2.2m^3/hr on a continuous basis of aerobic digester with a nominal capacity of 175 m^3. This system operates for 8 hours per day, 5 days per week. Bio-sludge polymer dozing system is provided to facilitate the growth of macro flocs.

Waste Cake Treatment

Due to the presence of pathogen contents and decomposable nature, raw waste cake is hazardous to health and environment. Now a day many treatment processes are being used to treat waste cake to reduce its hazardous contents and increase its solids particles. Some processes are used for stabilizing and reducing pathogens in waste cake (Cleverson Vittorio, et. al., 2007). By analysis of metals, it was found high amount of Fe (1,850 ppm) and noteworthy quantity of Zn, Na, Al and Mg which classify the waste sludge as schedule waste (Mokhtar, et.al, 2011). During the disposal of sludge, care should be taken during discharge of heavy metals into ground water and gasification as exhaust gas (Julia, et.al, 2013). This study revealed the different properties of sludge and their amount. The main object was to ease the sludge dewatering difficulty. The benefits and drawbacks of different techniques were defined and the domination of one over the others was discussed with respect to energy condition and environmental effects. Some recommendations were also made for optimum use of each method (Mowla.D a. et.al, 2013).

Thickening

Thickening is the basic step in treatment process of waste cake as it is not feasible to treat very thin sludge in form of a slurry which floats in water. A gravity thickener is used for thickening of slurry. The overall volume of waste cake is reduced to half the original volume of sludge in thickening process. A dissolved-air flotation is used as alternative to gravity thickening. In this process, a layer of thickened waste cake is produced as air bubbles take the solids to the surface (Cleverson Vittorio, et.al., 2007).

Digestion

Digestion of waste cake is a process of splitting up some organic solids into stable particles. In digestion process, the overall mass of solids is decreased, pathogens are abolished and made it very easy to dry or dewater the waste cake. The digested waste cake is not harmful, and it has the properties of a rich potting soil.

In a waste water treatment plant, a digestion system of two stage digestion is used in which organic substances are digested without oxygen by bacteria. Firstly, the thickened waste cake is converted to about 5 percent dry solids particles. Then it is mixed and heated in a tank for a few days. The waste cake flows into another tank in which the bacteria convert the mixed matter into a mixture of carbon dioxide (CO_2) and methane (CH_4), called biogas. Methane is used for heating the first digestion tank and to produce electricity for treatment plant (Cleverson Vittorio, et.al., 2007).

MATERIALS AND METHODS

SAMPLE PREPARATION

To perform experimental work, the source of the waste cake was from waste water treatment plant from oil refinery. It comprises of high moisture content and in slurry form. The last line of waste water treatment plant was elected to obtain the waste cake. Collected waste cake samples were prepared, processed and investigated in the Coal Research Laboratory of NFC-IET. To make sure that there is no degradation of the quality or thermal characteristics of the waste, all the waste cake samples were refrigerated. The dewatered sample was subsequently oven dried at 105°C for two hours. After drying, all samples were manually pulverized in a steel ring and sieved to meshing sieve size of 60μm to obtain a uniform particle size.

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Figure 5: Waste cake sample

PROXIMATE ANALYSIS

Proximate analysis reports moisture, volatile matter, ash and fixed carbon content of a fuel by percentage weight, as defined by ASTM D 5142.In this method a specific amount of finely powdered waste cake sample (0.7 - 1.2 g) was taken in crucible and heated at 25°C to 107°C in the presence of nitrogen gas, here moisture is removed. After that, sample is heated at 107°C to 950°C where volatile matter is removed. Now the lid is opened and furnace is cooled to 600°C and then starts heating at 600°C to 750°C in the presence of oxygen and combustion of sample starts. The weight of the incinerated residue is the ash content. The fixed carbon is obtained by subtracting the weights of moisture, volatile matter and ash content from 100.

Figure 6: Thermo-gravimetric Analyzer

ULTIMATE ANALYSIS

The ultimate analysis was carried out by LECO Tru-Spec CHN-S Analyzer. The sample was weighed and put in special tin made sample holder, which was later folded to form capsule. Approximately 0.100gm of sample was used. The capsule was fed to CHN-S analyzer using sample feeder cartridge and combusted at 1300°C using pure oxygen where the conditions were static. In order to make sure that all inorganic and organic substances present in the sample have been completely combusted a dynamic burst of oxygen is added Numerous gases such as Carbon Dioxide (CO_2), Water (H_2O), Nitrogen (N_2) and oxide of Nitrogen are generated when combusted products pass through specialized reagents Unwanted gases such as Halogen, Sulphur and Phosphorous can also be removed by using these reagents. Oxides of Nitrogen are reduced to Elemental Nitrogen, excess oxygen is scrubbed once the gases are passed over copper A mixing volume chamber is operated at constant temperature and pressure in order to make sure that a homogenous mixture is formed.

Figure 7: LECO Truspec CHN-S Analyzer

CALORIFIC VALUE

The calorimeter was used to measures the combustion heat given out by the burning of sample in presence of oxygen. The heat capability of sample and increase in temperature difference between maximum and minimum were used to find out the higher heating value of sample. An Auto Bomb Calorimeter LECO AC-500 was used to conduct present research.

The heating energy of a fuel sample can be measured through calorimetry where the sample is burned under stable temperature The fuel sample whose value needs to be determined should be solid or liquid but not gas The procedure is simple in which weighed sample in a crucible is placed inside a container which is made of stainless steel also known as bomb vessel. The pressure inside the bomb vessel is 30 bars of pure oxygen. The weight of the sample is approximately 1 gram.

The reading has to be taken under control environment without external influence. For this, the bomb vessel is sealed and isolated from outside environment while filled bomb vessel is placed inside water container making sure the lid is closed. The capacity of container is 2 Liter. The sample will then be ignited after making sure that the temperature of bomb vessel has stabilized.

Figure 8: Auto Bomb Calorimeter LECO AC-500

Thermochemical conversion of biomass for production of bio-fuel.

A series of Chemical Processes such as combustion, liquefaction gasification and pyrolysis can be employed for Thermochemical conversion of biomass. Combustion is an oxidation reaction between oxygen and fuel. Carbon dioxide, water and heat is released during this process (Badrul Islam, 2015).

Gasification is the process of conversion of biomass to renewable fuels. In gasification process, the biomass reacts with steam or oxygen producing a gaseous combination of H_2 and CO with different amount of CH_4, CO_2, N_2 and some other gases for different temperatures depending upon the fraction of gaseous components called syngas and producer gas (Lee, et. al., 2007).

Liquefaction of biomass is done in the presence of propanol, alkalis, butanol and glycerin solutions or directly liquefaction process (Badrul Islam, 2015). In this process, the oil produced is water insoluble and has very high viscosity by using solvents for lessening gases such as H_2 and CO. The catalyst is also added to biomass (Rowlands, et.al., 2008).

RESULTS AND DISCUSSION

CHARACTERIZATION OF WASTE CAKE SAMPLE

In present study Thermo-gravimetric Analysis (TGA) was used to study the thermal degradation of waste cake The results showed that 92% weight loss occurred. Furthermore, Thermogravimetric curve (TG) revealed that moisture was evaporated between 32 and 107^{O}C. The three zones of waste cake degradation were shown in TG Profile. These include drying zone ranging in which the temperature range is from 32-107^{O}C, the devolatilization zone (107-950^{O}C) and the last one is char formation zone (600-750^{O}C). In zone: 1, the moisture in the waste cake was removed and sample was dried at 107 ºC. In zone: 2, devolatilization of waste cake started. The volatile matter in the sample was removed at 950 °C. In char formation zone, the waste cake was heated from 600°C to 750°C. At this stage the waste cake sample was converted to char. At temperature around 107^{O}C, it was observed that moisture contents were reduced and lower molecular weight compounds occurred up. In the second zone of temperature 107 °C to 950 °C, maximum decomposition was observed. Decomposition was observed to occur between 150ºC and 450ºC, as seen in the gradual decrease in the TG curve.

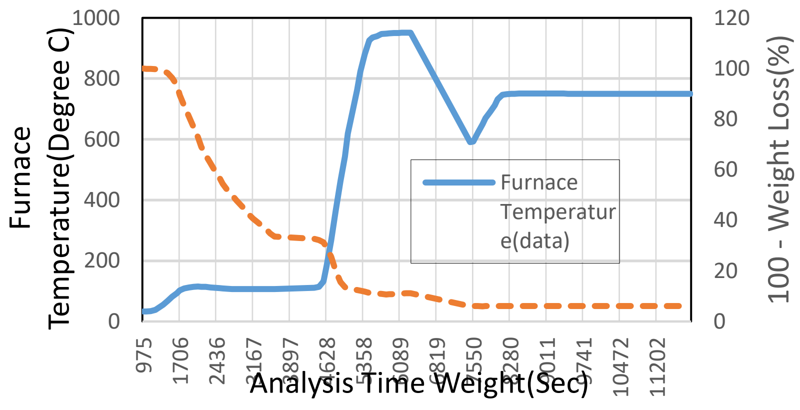

Figure 9: TGA Curve for waste cake

There was a sharp peak at around 100^{O}C was observed in DTG. This could be because a large volume of moisture was present in the sample. However, the reduction in weight loss was observed between 100^{O}C and 150^{O}C in comparison to earlier stages. The sharp fall in the DTG curve also confirms the presence of such region. This region is also reflected in the DTG curve with a sharp fall. This change can be explained through the fact that small quantity of low temperature hydrocarbons that are present in the sample, their moisture is evaporated, and volatilization occurs. The slight fall and rise in DTG curve was due to the difference in boiling points and concentrations in the waste cake. This explains the variation in weight loss with respect to temperature. Figure 10 shows TG and DTG curve for waste cake.

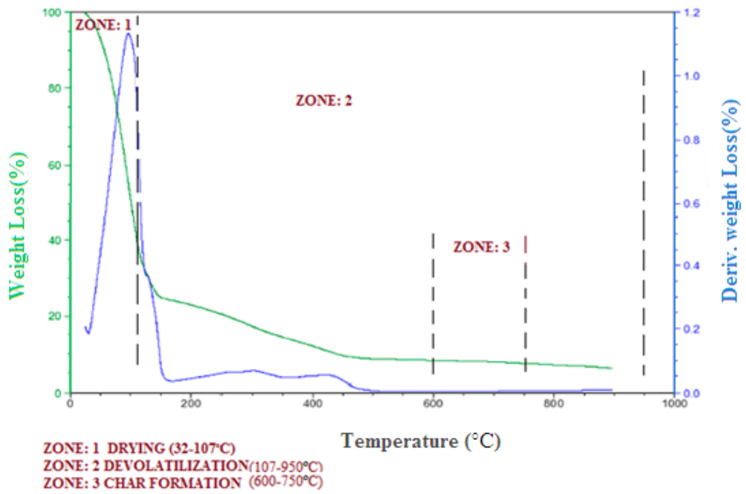

Figure 10: TG and DTG Curve for Waste cake

PROXIMATE ANALYSIS OF WASTE CAKE

Table 1 depicts the proximate analysis of wet waste cake, oily sludge and dry waste cake. It has been observed that volatile matter which is 30.9% and ash which is 17.3% is relatively higher in dry waste cake. Higher concentration of microbes in dry waste cake is the reason for higher volatile matter. Small decrease in fixed carbon of DWC (11.7%)as compared to WWC (12.09%). Table 1 represents the comparison of proximate analysis through TGA.

Table 1: Comparison of Proximate Analysis of Different Biomass

Samples	**Moisture Content (Wt. %)**	**Volatile Matter (Wt. %)**	**Fixed Carbon (Wt. %)**	**Ash (Wt. %)**
Wet waste cake	68.50	14.30	12.09	5.11
Dried waste cake	40.1	30.9	11.7	17.3
Oily Sludge *	78.9	5.5	10.1	5.06
Sugar Cane Bagasse (dry sample)	1.03	81.33	12.28	5.35

ULTIMATE ANALYSIS OF WASTE CAKE

Table-2 represents the ultimate analysis of wet waste cake, oily sludge and dry waste cake. The dry waste cake contains higher percentage of carbon (49.8%) and oxygen (37.6%). The rate of combustion reaction depends on the content of oxygen present in the sample, higher the oxygen content higher will be the combustion reaction rate. The high carbon content related to good fuel properties. The hydrocarbon elements (hydrogen and carbon) and oxygen constitute about 95.3%, while nitrogen and sulfur account for 4.7%. There is high Oxygen content in the sample when compared to oily sludge and less than sugarcane bagasse. The oxygen content in sample will help combustion reaction. The combine values of nitrogen and sulfur is lower when compare to values reported by literature (Abu Bakar, 2018). During combustion the formation of poisonous gasers such as NO_x and So_x is due to the Prescence nitrogen and sulphur. In order to stop the formation of these gases product gas cooling and thermal decomposition needs to be properly controlled. Table 2 depicts the comparison of ultimate analysis through elemental Analyzer.

Table 2: Assessment of Ultimate Analysis of Different Biomass

Samples	**C (wt. %)**	**H (wt. %)**	**N (wt. %)**	**S (wt. %)**	**O (wt. %)**
Waste cake	49.8	7.9	2.8	1.9	37.6
Oily Sludge	51.4	7.3	3.3	2.2	35.8
Sugar Cane Bagasse	43.07	6.6	1.41	0.16	43.41

CALORIFIC VALUE OF WASTE CAKE

The heating value (HHV) of oily sludge and sugar cane bagasse was 22.5 MJ/kg, which is greater tha n the value of oily sludge and sugar cane bagasse. The high HHV value observed might be attributed to the waste cake's high fixed carbon and low ash content. Figure 8 shows a comparison of HHV in s everal samples.

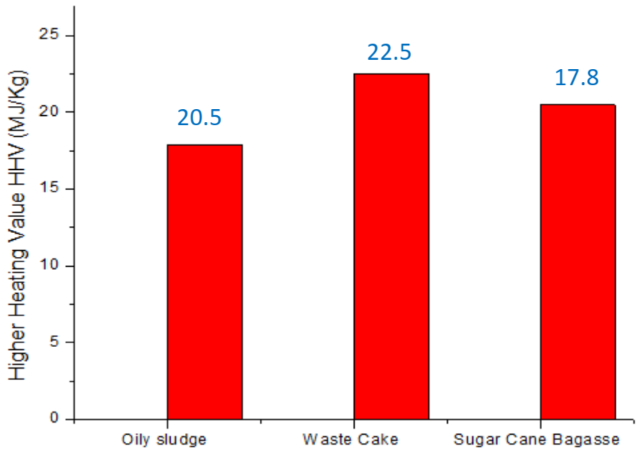

Figure 11: Comparison of HHV of Different samples

Direct correlation was detected between higher heating value (HHV) and content of volatile matter which noticeably shows the major involvement of the volatile matter content of the biomass to its total calorific value.

COMPARISON OF DIFFERENT BIOMASSES FOR BIOFUEL POTENTIAL

Waste cake has the potential to be used in the creation of biofuels. When waste cake was compared to other biomass sources, it was discovered that waste cake contains biofuel. It contains 50% biofuel by weight, which is somewhat lower than Corn cob, Switch grass, and Corn Stover. Table 3 compares the biofuel output and calorific value of different biomasses. Biofuel may be made from a variety of biomasses using a variety of ways. Biofuel was made from dry waste cake using the trans-esterification method, and the resulting biofuel was biodiesel. Biodiesel is a popular and commonly utilised biofuel.

Table 3: Comparison of different biomass for biofuel potential

Biomass Source	**Biofuel Yield (Wt. %)**	**Calorific Value(MJ/Kg)**
Waste cake	50	22.5
Sawdust of mixture of wood	33-45	10.3
Corn cob	56.7	15.8
Switchgrass	60.7	16.02
Corn stover	61.6	22.1

CONCLUSION

The waste cake comprises 40.1 percent moisture, 17.3 percent ash, 30.9 percent volatile matter, and 11.7 percent fixed carbon, according to the characterization. Despite its high moisture content, the waste cake has a greater heating value (HHV) of 22.5 MJ/kg. This HHV might be linked to a lot of fixed carbon, a lot of volatile stuff, and a lot of ash. The waste cake contains a high oxygen concentration and volatile materials, indicating that it has an excellent combustion reaction capacity. Because the levels of nitrogen and Sulphur are modest, current technologies can readily accomplish their emission effects. The higher the heating value, the more accessible energy that can be collected. The purpose of this experiment is to investigate the thermal behaviour of a waste case that has been exposed to controlled heating and cooling within a TGA furnace. When a sample dehydrates, the curve deviation begins at a specific point. The calorific value, volatile matter, and organic content of the waste cake sample utilised in this investigation are comparable to biomass with biofuel production potential. Biofuel manufacturing from waste cake is also a possibility Biofuel manufacturing from waste cake is also a possibility. When comparing the biofuel content of waste cake to that of other biomass sources, it was discovered that it has a 50 percent biofuel content by weight, which is higher than some other biomass sources for biofuel generation.

REFERENCES

1. **A. A. Boateng, D. E. Daugaard, N. M. Goldberg, and K. B. Hicks,** "Bench-scale fluidized-bed pyrolysis of switchgrass for bio-oil production," Industrial and Engineering Chemistry Research, vol. 46, no. 7, pp. 1891–1897, 2007.
2. **Abubakar M. Ali, Mohd A. Abu-Hassan,R.K. Ibrahim** ",Characterization of Petroleum Sludge from Refinery Industry Biological Wastewater Treatment Unit" 2018.
3. **Aneta Magdziarz, Sebastian Werle** ", Analysis of the combustion and pyrolysis of dried sewage sludge by TGA and MS" Waste Management 34 (2014) 174–179.
4. **Antonio Soria-Verdugo, Elke Goos, Andrés Morato-Godino,** "Pyrolysis of biofuels of the future: Sewage sludge and microalgae –Thermogravimetric analysis and modelling of the pyrolysis under different temperature conditions", Energy Conversion and Management, Elsevier: 2017.
5. **Balasubramanian.S, R.D. Tyagi** ", Value-Added Bio-products from Sewage Sludge''. Current Developments in Biotechnology and Bioengineering: Solid Waste Managementhttp://dx.doi.org/10.1016/B978-0-444-63664-5.00002-2.
6. **B. J. He, Y. Zhang, T. L. Funk, G. L. Riskowski, and Y. Yin,** "Thermochemical conversion of swine mamure: an alternative process for waste treatment and renewable energy production," Transactions of the American Society of Agricultural Engineers, vol. 43, no. 6, pp. 1827–1833, 2000.
7. **Badrul Islam ",** Petroleum sludge, its treatment and disposal: A review" Int. J. Chem. Sci.: 13(4), 2015, 1584-1602 ISSN 0972-768X.

8. **C. A.Mullen, A. A. Boateng, N. M. Goldberg, I. M. Lima, D. A. Laird, and K. B. Hicks,** "Bio-oil and bio-char production from corn cobs and stover by fast pyrolysis," Biomass and Bioenergy, vol. 34, no. 1, pp. 67–74, 2010.
9. **Cleverson Vittorio, Marcos Vonsperling and Fernando Fernandes ",** Sludge treatment and disposal'' Volume VI, 2007, ISBN: 1 84339 166 X.
10. **Coelho, A.; Castro, A. V.; Dezotti, M.; Sant'Anna, G. L.,''** Treatment of petroleum refinery sourcewater by advanced oxidation processes''. Journal of hazardous materials 2006, 137 (1), 178-184.
11. **Demirbas, M.F.,"**Current technologies for biomass conversion into chemicals and fuels"*Energy Source, 2006, 28:1181-1188.*
12. **Daming. Huang, Haining Zhou, Lin Lin** ", Biodiesel: an Alternative to Conventional Fuel'' 2012 International Conference on Future Energy, Environment, and Materials.
13. **Hou.B, S. X. Xie, M. Chen, Y. Jin, D. Hao, and R. S. Wang,** "The Treatment of Refinery Heavy Oil Sludge" Petroleum Science and Technology.2002.
14. **Julia Moltó, Agustín G. Barneto, José Ariza,** ",Gas production during the pyrolysis and gasification of biological andphysico-chemical sludges from oil refinery" *Journal of Analytical and Applied Pyrolysis 103 (2013) 167–172*
15. **Lee, J.G Speight, S.K. Loyalka**,"Handbook of alternative fuel technologies." 2007, CRC, Taylor and Francis Group USA. ISBN 9780824740696.
16. **Muhammad Usman.** "Production of Biodiesel from Wastewater Sludge Treatment by Direct Lipids Extraction", Journal of renewable energy,2018.
17. **Mokhtar.N.M, R.Omar, M.A Mohammad Salleh,** "Characterization of Sludge from the Wastewater-Treatment Plant of A Refinery", *International Journal of Engineering and Technology, Vol. 8, No.2, 2011, pp. 48-56* .
18. **Mowla.D a, H.N. Tran b, D. Grant Allen ",** A review of the properties of biosludge and its relevance to enhanced dewatering processes" *biomass and bio energy, 2 0 1 3, 3 6 5-3 7 8.*
19. **Ning SK, Hung MC, Chang YH, Wan HP, Lee HT, Shih RF."** Benefit assessment of cost, energy, and environment for biomass pyrolysis oil". J Clean Prod 2013; 59:141–9.
20. **Noorhaza Binti Aliasa, Norazana Ibrahima, Mohd. Kamaruddin Abd,** "Investigation of oil palm wastes' pyrolysis by thermogravimetric analyzer for potential biofuel production", The 7th International Conference on Applied Energy – ICAE2015.
21. **Richard L.Skaggsa, André M. Colemana** "Waste-to-Energy biofuel production potential for selected feedstocks in the conterminous United States", Renewable and Sustainable Energy Reviews 82 (2018) 2640–2651.
22. **Rowlands, W .N. A. Masters and T. Maschmeyer."** The biorefinery challenges, opportunities and an Ausstralian Perspective" Bull.Sci.Technol.Soc.2008, 28:149-158.
23. **S. Hussain1, K. Shahzad, K.S. Akthar, N.A. Akhthar, A. Chughtai,** "Investigations of thermal conversion and kinetics of low-grade coal and bagasse using thermogravemetric technique.", Journal of Faculty of Engineering & Technology, JFET 21(2) (2014) 105-117. Fundamentals of Renewable Energy.