Pyrolysis of Oil Refinery Sludge: A Thermo Kinetic Study

By

Rizwan Aslam

School of Chemical and Materials Engineering

National University of Science and Technology

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Name: Rizwan Aslam

Reg. No: 00000171925

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Supervisor Name: Dr. Salman Raza Naqvi

School of Chemical and Materials Engineering (SCME)

National University of Sciences and Technology (NUST)

H-12 Islamabad, Pakistan

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Dedication

I dedicate this work to my parents, whose unwavering support and confidence in my abilities has made this work much easier

Acknowledgment

All praise belongs to Allah Almighty, the Most Benevolent, the Most Merciful, who has granted me the strength, courage, and willpower to complete my work, and to overcome all the impediments that come in my way. I consider myself, highly fortunate to be able to complete this work in the time allotted to me.

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Abstract

Petroleum refineries are producing an enormous amount of oil sludge and declared as "Hazardous Waste" under schedule waste 2. This sludge is a mixture of oxy-hydrocarbon, traces of heavy elements, oil and water. If this oily sludge dispose of in an environment prior to treatment, then it will cause a great threat to both marine and land environment. Therefore, research is being underway to find the most optimized process of its treatment and disposal into environment. Combustion, gasification, anaerobic digestion, pyrolysis and few other methods are most commonly employing and currently under research for oily sludge disposal. In above mention process pyrolysis is considered to be the most suitable candidate. The current research emphasis on the pyrolysis process of oily sludge to study the thermal degradation behavior through thermo gravimetric analysis and by using lab scale reactor (autoclave pyrolysis unit) to obtain useful products. Elemental composition of oily Sludge is determined by ultimate and proximate analysis. The Effect of heating rate (5°C/min, 20°C/min and 40°C/min) on thermal degradation behavior is studied by TGA-DTA technique in Nitrogen atmosphere and found the main degradation phase between 200-600°C which is further divided into two phases one from 200-400°C and 400-600°C for the thermal disintegration of different components. The kinetic and thermodynamic parameters are calculated by model free kinetics such as Friedman, KAS and OFW is done to describe pyrolysis behavior of refinery sludge by using TGA-DTA data. The effect of temperature (350°C, 400°C and 450°C) is studied through autoclave pyrolysis unit by keep feedstock, pressure, and agitation conditions constant. In lab scale pyrolysis process, highest bio-oil yield was achieved at 450°C. The products such as dry sludge and gasses are further analyzed by proximate, ultimate and TGA analysis. These all results are in complete agreement with the research already conducted by researcher all around the world. Our thermodynamics parameters and model free kinetics will provide basis for future researcher to design equations of simulation base study of oil refinery sludge and predicts the gaseous products and volume of residual produced from oily sludge sample.

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List of acronym

PAHs	Polycyclic Aromatic Hydrocarbon
DRS	Dry refinery sludge
ER	Equivalent ratio
C	Carbon
H	Hydrogen
N	Nitrogen
S	Sulphur
O	Oxygen
TGA	Thermo gravimetric analysis
Wt.%	Weight percentage
w.r.t	With respect to

Chapter 1

Introduction

1.1 Background

The escalation of demand in energy rise too many fold in 20th century due to rapid industrialization and urbanization all around the world. In this scenario fossil fuels became the first and only source of fuel that provide 10100 kcal/kg (Min) of energy. So, this immense amount of energy easily accessible because of excessive exploration of oil and gas reservoirs all around the world. At last, this constraint of energy is being boosted by using alternative way because of speedy intensification in worth and exhaustion of fossil fuels beyond the limits. By employing fossil fuels, in every industry, consequently enhanced the volume of carbon dioxide in the troposphere and contribute in enormous GHG emissions and result in rise of overall temperature of atmosphere [1]. Other than this reason that these fuels have restricted reserves, crude oil when explored from underground reserves undergo refinery operation and converted into variety of products. In refining operations variety of waste generated from different hydrocarbon products and called refinery sludge[2]. This refinery sludge containing enormous weight percentage of hazardous components and its disposal is hot topic of discussion between environmentalists. Most proficient methods of disposals are combustion, pyrolysis and gasification of refinery sludge result in the availability of excess energy that can be utilized in different process. The release of surplus energy also compensated in balancing the energy requirement of refinery. In this sense, anaerobic treatment of refinery sludge would be the most optimum method of disposal [3].

Refinery sludge can be a potential source of energy and fuel by thermochemical conversion so this is reflected as most promising alternate technology to lessen the volume of waste and harmful environmental impact [4].

1.2 Production of refinery sludge

Generally, a rough estimates suggests that a refinery with production capability of 106,576 drums per day will produce 49-55 tons of refinery sludge per year. Sludge stayed at the base of storage tanks, in oil separation tanks, in floatation pool, and in other storage facilities. The basic components of refinery sludge include simultaneous solids with oil ratio varies from 11-56% and water composition about 45 to 92%. Further components are: hydrocarbons, asphalt, benzene, pyrene, paraffin wax, moisture contents, and traces of inorganic components, iron oxides, iron sulphide, heavy metals such as cadmium, mercury and even traces of radioactive elements as well [5-7].

Table 1: Concentration of heavy metals in refinery sludge[7]

Serial No.	Heavy Metals	Concentration in refinery sludge
1.	Zinc Zn	1300 mg/kg
2.	Iron Fe	61,000 mg/kg
3.	Copper Cu	510 mg/kg
4.	Chromium Cr	485 mg/kg
5.	Nickel Ni	489 mg/kg
6.	Lead Pb	570 mg/kg

1.3 Methods of treatment of refinery sludge

The inappropriate disposal of refinery sludge to the environment create havoc to land and water bodies. In addition, it leads to substantial alternation in chemical and physical characteristics of surrounding soil, lakes, streams and water bodies. In soil if untreated sludge buried, resulted in deficiency of nutrient and stunned growth in vegetation, high viscosity of sludge also entrapped in soil pores and prevent entry of air and water to roots, decline in moisture content of soil and hydraulic conductivity of soil. Furthermore, development of hydrophobic crust also prevent the access of water and water- air exchange into soil. The presence of petroleum hydrocarbons (PHC) are Genotoxic to human health [8-10].

Therefore, improper management of refinery sludge also received significant attention from environmentalist. Lots of approaches have been prepared to reduce hazardous contaminant in refinery sludge in order to heal environment & protect masses from harmful effects of untreated oily sludge. The following are the approaches mostly employed but not restricted to it:

- Land farming/landfilling
- Photo-catalysis

- Incineration
- Solidification/stabilization
- Solvent extraction
- Pyrolysis
- Chemical handling
- Gasification[11, 12]

From above mentioned procedures of treatment of refinery sludge a few methods are practically utilized for refinery sludge disposal and it depends on following factors: nature of hazardous component in refinery sludge, environment regulation and cost of treatment. In addition, general treatment methods for oily sludge are divided into three stages, i.e.:

- By employing optimized treatment method to reduce petroleum sludge production
- Recovery of oil from oily sludge
- Disposal of unrecoverable petroleum sludge

1.4 Refinery sludge as a source of fuel

With this huge production of refinery sludge per day from oil refineries provide us a reasonable source of gases that can be utilized in infinite chemical processes. From incineration the organic constituent converted into carbon dioxide and water. From microbial treatment of sludge released of combustible gases such as methane CH_4 utilized in combustion and as a fuel in power generation units. By buried under soil generally called landfill result in percolation and leaching of hazardous liquids in adjacent formation and soil if not buried properly. Therefore, the most suitable technique of treating refinery sludge is pyrolysis. Extensive research have been performed by researchers in pyrolysis of oily sludge[13]. Key noncombustible gasses evolved during pyrolysis of refinery sludge are mentioned in Table 2:

Table 2: weight percentages of gases gained during pyrolysis of refinery sludge

Serial No.	Gases or products	Weight percentage (wt. %)
1.	Carbon dioxide CO_2	51
2.	Hydrocarbons HCs	25
3.	Water H_2O	18

4.	Carbon monoxide	6.5
5.	Paraffin and olefin (C1-C2)	52% of HCs

The heating value of liquid product is approximately 46,322 kJ/kg.

1.5 Pyrolysis of refinery sludge

Pyrolysis is defined as thermal decomposition of organic matter at high temperature of 525-1254 ^{0}C in an inert environment[14] It result in the production of less molecular weight hydrocarbon either in condensable liquid or non-condensable gases. Final product of pyrolysis is mostly char, liquids and gases rely on the temperature, pressure, availability of catalyst. In literature it was studied that the pyrolysis of oil refinery sludge resulted in released of oil at high temperature up to an optimum temperature of 530 ^{0}C. Further increased of temperature above 530 ^{0}C record a decline of yield of oil refinery sludge. Optimum temperature range 330-455 ^{0}C would convert approximately 80% of oily sludge into usable hydrocarbon. The measurable released of oil from oily sludge happened at 465-655 ^{0}C & almost 71-81% of oil got separated form sludge. However, optimum rate of conversion of oil from oily sludge at temperature 444 ^{0}C. Conversion of products start appearing at low temperature of 355 ^{0}C and majority of products achieved at 500 ^{0}C[15, 16].

In pyrolysis the products are obtained in the form of liquids that's why there storage, transportation and handling of recovered oily products is easy. The recovered oil have similar properties with the oil obtained from low distillates from refinery operations. Therefore, it can be employed as fuel in diesel engine. There are few factors that restrict the pyrolysis procedure, i.e. suitable temperature, heating rate, properties of sludge, chemical additives, and cost. The gases obtained after the pyrolysis of refinery sludge contained PAH, so it should be purify from these contaminants before storage[17]. Oxidizing condition of a reactor can be measured by stoichiometric index (λ), elaborated as ratio b/w actual air flow and stoichiometric air flow compulsory for complete combustion, measured by following equation:

$$\lambda = \frac{(m_{O_2})_{actual}}{(m_{O_2})_{stoic}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(1)}$$

$$= \frac{m_{air}.23}{\left(\frac{m_{sample}v}{L}\right)\left(\left(\%\frac{C}{12}\right)+\left(\%\frac{H}{4}\right)+\left(\%\frac{S}{32}\right)+\left(\%\frac{O}{32}\right)\right).32} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(2)}$$

Where %C, %O, %H and %S are wt. % of carbon, oxygen, hydrogen & sulphur respectively in sludge; m_{air} is mass of air flow rate in kg/s; m_{sample} weight of sludge kg, and L length of tube filled with sample (m); ν linear velocity of introduction of tube (m/s). If $\lambda<1$ combustion is produced in sub-stoichiometric conditions, whereas $\lambda>1$ present air is in excess. In pyrolysis most common reaction products formed are as follow:

$$C + CO_2 \longleftrightarrow 2CO + 165\ \text{kJ/kmol} \qquad (1)$$

$$C + H_2O \longleftrightarrow CO + H_2O + 123\ \text{kJ/kmol} \qquad (2)$$

$$CO + H_2 \longleftrightarrow CO + H_2O + 44\ \text{kJ/kmol} \qquad (3)$$

$$C + 2H_2 \longleftrightarrow CH_4 + 79\ \text{kJ/Kmol} \qquad (4)$$

$$CO + 3H_2 \longleftrightarrow CH_4 + H_2O - 206\ \text{kJ/Kmol} \qquad (5)$$

$$C + CO_2 + H_2O \longleftrightarrow 2H_2 - 42\ \text{kJ/Kmol} \qquad (6)$$

The reaction became satisfactory through enhancing gas distribution around particles[13]. It's further noted by researchers that if the heating temperature is high and also keeps increasing heating rate, it results in speedy released of volatile components and generate a absorbent char. This producing char also lead to increase ultimate transformation of biomass & increase reaction rate in steam gasification. The detailed schematic diagram of pyrolysis of refinery sludge is shown in figure 1.

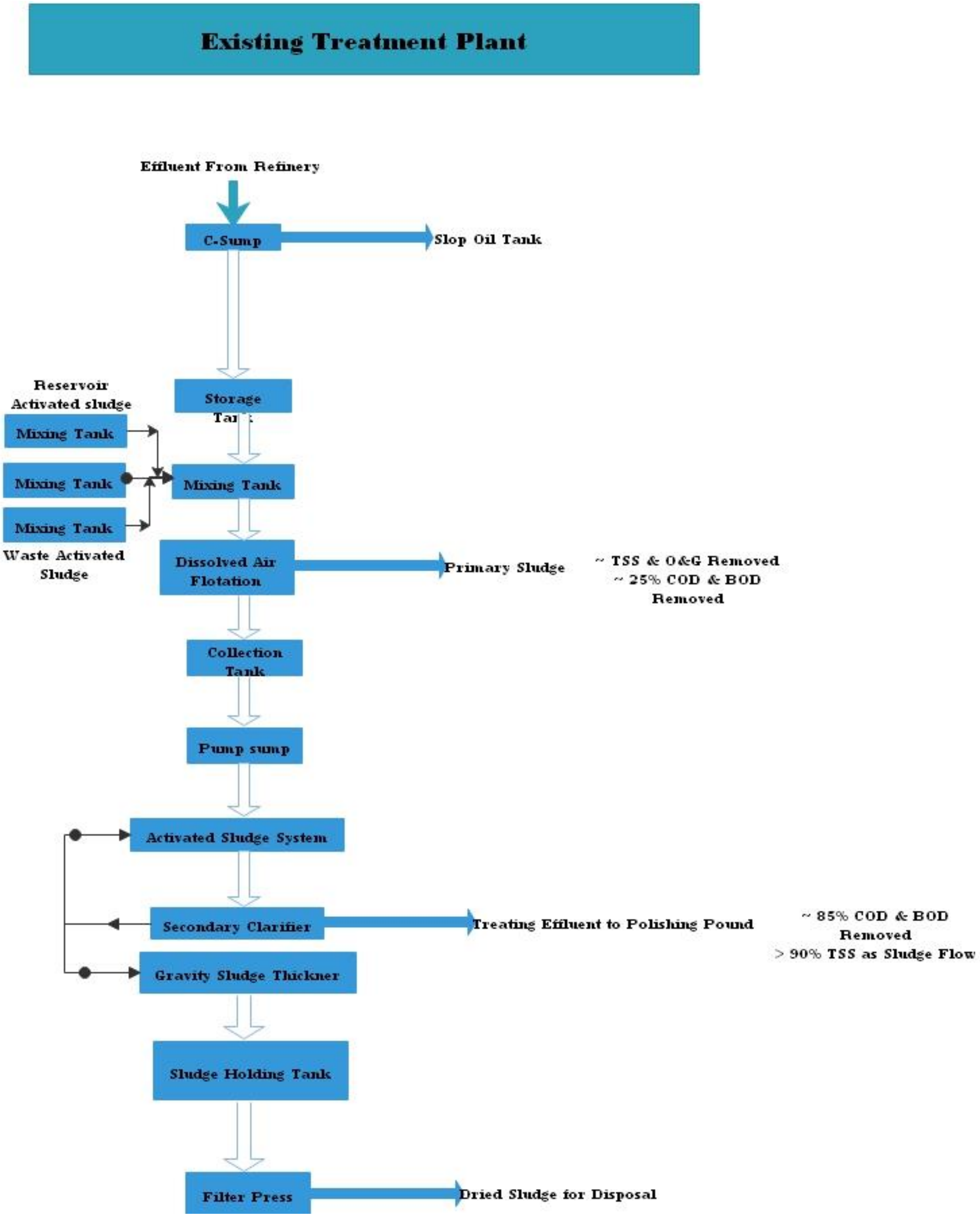

Figure 1: Flow sheet of refinery sludge production

1.6 Analytical approach of pyrolysis

Analytical pyrolysis is to study the pyrolysis behavior by using different analytical tools like thermo gravimetric analyzer TGA, differential gravimetric analyzer DTA and gas chromatography online attached with mass spectrometry GC-MS. These analytical pyrolysis techniques are usually used to find out the thermal degradation behavior during pyrolysis and configuration of non-condensable gases. In all analytical pyrolysis, usually mass loss happens in three steps, positioned about 350°C, 450°C or 549°C, by generating large amount of pyrolysis products.

TGA is to a thermo gravimetric analysis technique whose working principle is a controlled temperature program used to measure the weight of a sample continuously. The physical and chemical properties of sample centered on deviation of sample weight w.r.t time and temperature can be obtained by using the differential thermo gravimetric (DTG) curve resulted from differential of TGA curve. The usage of thermo gravimetric analyzer has a lot of advantages like it requires minimum amount of feedstock, due to programed based technique its operation is easy, accurate and precise record of temperature and percentage of weight loss. TGA system can be helpful in defining proximate analysis of refinery sludge and to figure out the thermal physiognomies like ignition and exhaustion points and chemical kinetics of oil refinery sludge by using different techniques like combustion, Torre faction, pyrolysis, gasification.

Presently, TGA, DTA and DSC techniques are able to give thermal degradation and kinetic evaluation of solid fuel. These evaluations become very essential to find out reactivity and thermal ability of burning material. These techniques can be employed to evaluate kinetic parameters under isothermal and non-isothermal conditions. TGA can be able to suggest the thermal deprivation outlines of oil refinery sludge and char obtained from either hydro treatment or bio treatment underneath air or inert atmosphere for subsequent kinetic investigation. Configurations explain the consequence of heating rate, properties of sludge, stability & compatibility of oil refinery sludge to progression. Several types of kinetic methods exist that are based on thermal statistics for assessment & development. The foremost guidelines of these kinetic evaluations for thermal investigation are boundaries and analytical records. They are mutually obtained from analogous experiment and conducted in very limited time.

1.7 Problem statement

Oil refinery sludge is an abundant source of providing oil, carbon monoxide, hydrogen and methane. Furthermore, its disposal without proper treatment becomes a reason of several hazardous threat to environment. Therefore, it’s necessary to treat it prior to disposal. Pyrolysis, gasification, combustion and few more processes hence employed for oil refinery sludge disposal. In all of above mention method pyrolysis received more consideration to be used for treatment of oil refinery sludge. This task included pyrolysis of oil refinery sludge and it was analyzed on the basis of thermodynamics and kinetic parameters. Later on, these parameters will provide the basis for designing of any simulation base program for study the behavior of pyrolysis of oil refinery sludge. So, before this study, no such parameters were established that provide the basis for simulation base study.

1.8 Research objective

To report the current challenges in oil refinery sludge pyrolysis, this thesis work inspects the analytical and non-catalytic pyrolysis of dried oil refinery sludge for production of CO, H_2 and CH_4. The inclusive research objective is to produce and characterize the released gases from oil refinery sludge pyrolysis and performance evaluation of pyrolysis process by different kinetic models. The following assessable objectives are undertaken in the present study.

- To collect and characterize the oil refinery sludge to explore the physiochemical properties
- To study the influence of pyrolysis temperature of oil refinery sludge using indigenously fabricate reactor and characterize the products
- To investigate the oil refinery sludge pyrolysis behavior using thermo gravimetric analysis
- To determine kinetic parameters and thermodynamic parameter of refinery sludge pyrolysis process using model-free method.

1.9 Scope of study

The research work primarily emphases on the study of analytical pyrolysis of dried oil refinery sludge for oil production, and gas product. For understanding the thermal degradation behavior thermo gravimetric analysis technique is employed.

Oil refinery sludge was collected from a Attock Refinery Morgah, Rawalpindi and size reduction was occurred by using ball mill. To comprehend the properties of the refinery sludge, proximate and ultimate analysis were performed to achieve the essential knowledge about the physicochemical properties of refinery sludge.

Powdered form dried refinery sludge is experimented to explore behavior of pyrolysis process of refinery sludge in autoclave pyrolysis unit to produced bio-oil.

Characterization techniques such as proximate analysis, ultimate analysis & TGA were carried out to find out the composition and characterization of products.

This study presents the kinetic study on analytical pyrolysis of dried refinery sludge. Model free method such as Friedman, KAS, & OFW method were employed to construe thermo gravimetric data attained through pyrolysis process.

1.10 Chapter Summary

This manuscript contains of five sections. The contacts of each section are specified in the following passages.

- **Chapter 1** delivers need of proposed topic, contextual and existing issues related to the topic. It also clarifies the definite terms, process, problem statement, objectives and scope of the strategic research work.
- **Chapter 2** will draft the literature survey accomplished to describe preceding efforts done on thermal breakdown of oil refinery sludge obtained from Attock Refinery Morgah, Rawalpindi. It also comprises surveys based on source and properties of oil refinery sludge and various pyrolysis techniques.
- **Chapter 3** contains the methodology associated to the sample preparation and characterization, pyrolysis inquiry work and kinetic and thermodynamic analysis. It will also provide the related information about procedure and apparatus contributing in the experimental investigations.
- **Chapter 4** delivers results and discussions. The material characterization, experimental, kinetic, and thermodynamic modeling consequences are existed and explained based on various point of view.

- **Chapter 5** contains all the findings and conclusions in the existing learning and delivers the upcoming endorsements for the related work.

Chapter 2

Literature review

2.1 Introduction

This section narrates source, chemical composition, elemental analysis, percentage of dissolved gases and quantitates analysis of refinery sludge through thermo-gravimetric data. Furthermore, detailed statistical study also presented in this section of pyrolysis of refinery sludge: and qualitatively as well as quantitatively thermodynamic and kinetic study of refinery sludge also explained. Literature related to practical applications for refinery sludge also mentioned in this chapter.

2.2 Characteristics and sources of refinery sludge

The refinery sludge also named petroleum refinery product an oily matter classified as "Hazardous Waste" under schedule waste 2. Petroleum sludge mostly generated from the base of oil storage tanks, oil-water separators, from the base of process equipment in refineries and in oil spill sites in both crude processing and drilling sites[18]. The sludge composition depends on the storage and its sources. Normally it contains: 11-30 wt. % hydrocarbons and oxy-hydrocarbons, 5-24 wt. % solids such as heavy metals Cu, Cd, Zn, Ni, Mn and Pb and 50-80 wt. % water[19, 20].

2.3 Processing of refinery sludge

Several conventional and unconventional techniques have been devised for treatment of refinery sludge. In the next few paragraph some conventional methods for the treatment of sludge will be explained.

Landfilling of sludge became a practice for many years and it caused serious health and environmental hazards. Contamination of ground water, diffusion of volatile organic chemicals into atmosphere result in air pollution, presence of bad odor in air, fire threats and adverse health problems[6, 7].

Combustion of refinery sludge consequently emits greenhouse gases and increased carbon dioxide content in the atmosphere. Although it supply surplus amount of energy for the power generation units[21]. Incineration also a reliable method for disposal of refinery sludge. In this technique sludge undergo entire ignition in presence of air and auxiliary fuel. This combustion takes place in rotary kiln and fluidized bed reactor. Temperature range of 979-1200 ^{0}C for rotary kiln with approximately 30 minutes of residence time. On contrary temperature range of 729-759 ^{0}C with residence time measured in days in fluidized bed reactor[22]. Stabilization/solidification of refinery sludge waste was treated with a binder to prevent any leaching into soil and by chemical or physical means convert the refinery sludge into eco-friendly waste substance. This waste substance can also be utilized either in construction industry as well as landfill disposal. The conversion of refinery sludge into useful constructing material can be done by following ways:

1. First of all, chemical interaction has to be developed between the cement and chemical components of sludge.
2. The encapsulation of contaminated waste in the cementing material [23-25].

One more way of treating refinery sludge is to introduce oxidative chemical into sludge that convert organic compound carbon and hydrogen of oily sludge into carbon dioxide and water and non-hazardous waste material[26]. List of oxidation reagent are as follow: hypochlorite, ozone (O_3), ultrasonic irradiation and Fenton’s reagent. Mater et al. found that by treating oily sludge with Fenton’s reagent can minimize the weight percentage of PAHs, phenols and other perilous contaminants that are not harmful for soil disposal. In reasonably short duration this oxidizing agent can breakdown refinery sludge into environmentally friendly components and the end products are also biodegradable. But if scale up this process it would be costly because of frequent use of expensive chemicals, large equipment, and energy intensive and high cost of operation[11, 27]. By the use of microorganism and converting refinery sludge into less toxic substance is called bioremediation. This process can be done by three different ways i.e. land farming, bio/pile composting and bio-slurry treatment.

In land farming treatment refinery sludge was mixed with soil and degraded biologically, chemically, and physically. This is the most feasible method of treating sludge because of low utilization of energy, cost effective, and accommodate large volume of sludge in simple operating procedure[28]. Martin et al. narrated the removal of PHCs from sludge with a time duration of 11 month by land farming treatment in semi-arid climate[29]. In treatment of refinery sludge by shaping into piles and treating with indigenous and extraneous micro-organism is called bio pile composing. Wang et al. described the increasing microbial activity by incorporating cotton stalk in treating with oily sludge. This technique is an environment friendly and need smaller area for the consumption of sludge[30].

Reem Ahmed et al. studied the gasification of refinery sludge in updraft reactor. In this experiment temperature profile within reactor were focused in place of several equivalent ratios. In addition, change in temperature with operation time also discussed. The dynamic result revealed with the varying ER from 0.196-0.245 modifies combustion zone peak temperature from 860C-989C. This displacement in combustion zone peak temperature induces turbulence in reduction zone behavior. Additionally, the optimal gasification process run at ER of 0.195 & axial gasifier temperature operating time of 37 minutes[4].

Reem Ahmed et al. conducted analysis on gasification of refinery sludge under adiabatic updraft gasifier and derived some conclusion on the basis of energy and exergy values. The values of chemical energy (6.8-10.1 times) and chemical exergy (2.3-5.7 times) obtained of producing gas after gasification of refinery sludge exceed corresponding physical values. The ultimate analysis indicated the more wt. % C & H_2 content in dry refinery sludge. The efficiencies of cold gas, energy and exergy of DRS is mention in Table 3.

Table 3: DRS energy, exergy, and cold gas efficiencies

Cold gas	22.98-56%
Energy efficiencies of DRS	44-73%
Exergy efficiencies of DRS	32-51%

During the gasification process a maximum rise in these values seen at ER of 0.195 then decline in these values observed with further increased of ER values. As the increased in ER results observed it is related to increase in supply of oxygen that intensifies the oxidation process and finally lead the rise in gasification temperature. As the oxidation processes increased the gasification no longer remain feasible to achieve the required targets. Because drop in gas properties, energy & exergy observed. If additional equivalent ration rises nitrogen also inject with the injected air that deteriorate the gas quality. The optimum quality of produced gas achieved when primary to secondary air ratio is 0.5, this not only result in better gas quality as well as higher energy efficiencies[31, 32].

Juan A Consea ET, al. studied the pyrolysis of oil refinery sludge in pilot plant equipment in variety of range of temperatures. In addition, quantification and analysis of gases evolved also studied. Elemental analysis of oil refinery sludge indicated, and it contained 34% of carbon and 23% of oxygen. This pyrolysis of oil refinery was performed at temperature range of 340-535 ^{0}C in pilot plant. In this case at low temperature no fraction of sludge decomposed, and with increased of temperature liquid fraction enhances. Gases released from pyrolysis of this sample includes CH_4, C_2H_6, C_2H_2, C_3H_8, and C_3H_4. Liquid portion includes light hydrocarbon and aromatic compounds and their yields increase and decreased respectively with rise in temperature[33].

Hanzhong Jia ET, al. did research on low temperature pyrolysis of oil refinery sludge by introducing Fe/Al-pillared bentonite as catalyst. With the introduction of this catalysts increased the yield of oil from sludge from 29% to 54% as compared to sample without the introduction of catalyst. This all because of peculiar characteristics of Fe/Al pillaring in bentonite which generates porosity and enhancement of surface area in a material. This also help in decomposing of sludge into oily products and increases the yield of oil. However, catalyst reduced the yield of char and stimulate the release of methane and carbon dioxide and also improves the quality of oil produces from pyrolysis of refinery sludge. Oil recovered in this process has large percentage of aliphatic hydrocarbon of carbon chain range C13-C19 and less concentration of hetro-chain compounds due to presence of catalysts. Finally, presence of Fe/Al pillared bentonite is most promising candidate as catalyst in pyrolysis of oil refinery sludge[34].

2.4 Oil refinery sludge analysis by TGA

The performance of the thermal deprivation conducts for oil refinery sludge Investigated by inspecting pyrolysis conduct by assistance of TGA. For example, as for temperature and time and to analyze the warm disintegration conduct amid pyrolysis. It is additionally useful in concentrate the energy of debasement of natural material amid pyrolysis process[35, 36]. Warm debasement is enter component in planning of maintainable pyrolysis and co-pyrolysis processes[37, 38].

DTG is a straightforward investigative instrument to discover the measure of mass misfortune or mass pick up of a solid as a component with temperature. It could assist to discover active constraints (actuation vitality, pre-exponential factor, request response) through various natural resources at isothermal and non-isothermal circumstances. Because of littler trial period and necessity of a lesser amount of trial information, procedure has vital significance. By looking at DTG bends, temperature by the side of which most extreme rate mass misfortune show up, can be dictated by the position of the crests[39]. The thermo gravimetric investigation system necessitates insignificant amount of feedstock, exact regulator and simple in work[40].

Table 4: Literature Review

Year	**Sample**	**Process And temperature range**	**Kinetic model**	**Type**	**Activation Energy**	**Pre-exponential factor**	**Ref**
2020	oily sludge	Combustion 160-380°C 400-720°C	Coats and Redfern model	-	18.19-20.25 31.01-34.07 KJ/mole	1.83-3.04 27.75-60.80 min^{-1}	[41]
2018	Oil Sludge	Pyrolysis 500-900K	Arrhenius equation	Starink and Friedman Method	<85-105> kJ/mole	-	[42]
2017	Wet Oily sludge	Pyrolysis 400–740 K.	Model free approach	Flynn–Wall–Ozawa analysis	Average 35.21 kJ mol^{-1}	-	[43]
2009	Wet Oil sludge	Pyrolysis 450-900K	Model free method	Direct numerical integration	46-111kJ /mole	-	[9]

2007	Waste petroleum refinery sludge	Pyrolysis 100-500°C	Model fitting approach	One and two reaction model	88.28KJ oml^{-1} 64, 112kJmol^{-1}	12.2*10^{7} min^{-1} 2.97*10^{5}-1.4*10^{10} min^{-1}	[44]
2000	Dry Oily sludge	Pyrolysis 450–800 K	Arrhenius equation	One two and three reaction	78.22 kJ mol^{-1}	9.48 × 105 min^{-1}	[45]

Chapter 3

Materials and Methodology

2.1 Raw material

Refinery sludge was obtained from Attock Refinery, Morgah Rawalpindi. Obtained sample was primarily air desiccated for a week to remove the surface moisture, then the sample was dried in an electric oven for a day at 104±5°C until constant weight was obtained to remove the inbound moisture contents. Drying is an essential part before the start of characterization because it can highly affect the calorific value. The refinery sludge sample was crushed with mortar and pestle. Then crushed sample was further grind into fine powder which was sieved through 1000µm screen & stored into airtight bags before further analysis.

2.2 Thermal degradation behavior of oil refinery sludge through TGA

The thermal degradation behavior of oil refinery sludge was measured by thermo gravimetric analyzer in the absence of N_2 environment. Flow of N_2 was maintained as 60ml/min having temperature range of 24-900°C. Quantitative analysis of oily sludge sample was first performed and 0±3mg of sample was used for this purpose. Heating rate was 5, 20 and 40°C/min at which the mass loss and rate of mass plots was determined with respect to temperature and time. The slow heating rate was chosen to overlook the heat transfer restrictions. To achieve the maximum accuracy and least error experiment was repeat at least three times. Data obtained from TGA and DTA both helped to understand the thermal decomposition behavior during pyrolysis process and also in estimation of kinetics and thermodynamic parameters of oil refinery sludge pyrolysis.

Thermo gravimetric analyzer consists of a pan positioned in a programmable incinerator. This pan is braced by a delicate precision balance. The sludge is placed onto the pan with a predefined heating rate and a temperature range at which changes is in sample is to be detected is given to the incinerator. The incinerator is heated from a lower temperature and reaches the maximum temperature and then it is cooled. The mass loss is observed during the entire process. The atmosphere of the incinerator is controlled by an inert gas such as nitrogen or helium. The data obtained from TG analysis of the refinery sludge permits the interpretation of loss of volatile components in sludge, its thermal steadiness, and disintegration. The data attained is graphed among temperature range on x-axis and percentage mass loss on y-axis[46].

2.3 Characterization of oil refinery sludge

2.3.1 Proximate analysis of oil refinery sludge

Proximate analysis was performed in electric oven and muffle furnace according to ASTM Standards method to determine the percentage of M, VM, FC and ash. For weight percentage of different contents, initially 5g of oil refinery sludge is used to burn at specific conditions until the weight became constant according to ASTM 3173-11 standard method[47]. The percentage of different elements was calculated by using the following equation.

$$percentage\ of\ element = \frac{m_i - m_f}{m_i} x100 \ldots\ldots\ldots\ldots\ldots\ldots \text{(3)}$$

Where m_i initial weight placed of sample placed in oven, m_f weight of oil refinery sludge after drying from oven at 105 ^{0}C.

Table 5: Specification of equipment and condition for proximate analysis of oil refinery sludge

Components	**Instruments**	**Temperature and time**
Moisture removal	Electric oven	105 ^{0}C for 24 hours
Volatile matters	Muffle furnace	700 ^{0}C for 7 min
Ash sample	Muffle furnace	900 ^{0}C for 3hours
Fixed carbon	= (100-(M% + VM% +Ash %))	

2.3.2 Ultimate analysis of oil refinery sludge

Ultimate analysis was achieved through CHNS elementary analyzer (PerkinElmer 2400II, USA) to obtain the percentage of C, N, H, N and O was determined by ASTM standard D 3172-07a. Bomb calorimeter was used to determine high calorific value according to given ASTM standards D 5373 and D 4239[47].

The High Heating Value (HHV) designates the amount of energy to be progressed from the oil refinery sludge sample. Salam et al. told in his study that the tentative measures to determine the HHV contain significant flaws so numerous correlation model equations were established to measure the HHV[48].

2.4 Thermodynamic parameter calculations

The changes in enthalpy ΔH, Gibbs free energy ΔG, and entropy (ΔS) also can be determined with the help of activation energy E_a and pre-exponential factor A by using these given equations.

$\Delta H = E_a - RT$……………. (4)

$\Delta G = E_a + RT_m \left(\frac{K_b.T_m}{h.A}\right)$…… (5)

$\Delta S = \frac{\Delta H - \Delta G}{T_m}$………. (6)

Where K_b represents Boltzmann constant whose value is 1.381×10-23 J K-1, h represents Plank constant whose value is 6.626×10-34 J s and Tm the DTG peak temperature.

2.5 Kinetic analysis

Kinetic analysis of oily sludge was determined by model free methods and set of equations govern for this methods are as follow:

Friedman equations: $\ln \left(\frac{d\alpha}{dt}\right)_{\alpha i} = const \frac{-E_a}{RT_{\alpha i}}$ …………………. (7)

Kas equation; $\ln \left(\frac{\beta_i}{T_{\alpha i}^2}\right) = \text{const} \frac{-E_a}{RT_{\alpha i}}$ ……………………… (8)

OFW equation: $ln\beta = const - 1.052 \frac{E_a}{RT_{\alpha i}}$……………………….. (9)

ASTM E1641-16 (ASTM International, 2016a) using OFW for a non-isothermal thermo gravimetric conversion is used to estimate pre-exponential coefficient (A) considering 1st order decomposition

$A = -\frac{\beta' R}{E_a}[\ln(1-\alpha)]10^a$……………… (10)

Chapter 4

Results and Discussion

4.1 Characterization of oil refinery sludge

4.1.1 Proximate analysis of oil refinery sludge

Figure 4.1 depicts the proximate analysis of oil refinery sludge sample which illustrates the organic matter content of sample. The oil refinery sludge sample contained higher percentage of moisture content 39.16% and volatile matters 24.4% on dry basis but it has slightly lower percentage of ash 21.77% from volatile matter and significant percentage of fixed carbon 17.30% on dry basis. Despite of higher moisture content in oil sludge, dried oil refinery sludge has high heating value (HHV)[49]. These proportions of HHV may be related to high fixed carbon value and coincidently this sludge sample has encompassed considerable percentage of it. Higher percentage of volatile matter in sample is on indication of less aromatic structure and more functional group. Ash contain a certain amount of Fe, Ca, Mg and K which can be used activated catalyst for the pyrolysis reaction and also high percentage of ash effect on HHV of sludge as well[50, 51].

Table 6: weight percentage of elements in oil refinery sludge sample

Serial No.	Elements wt. % on dry basis	Wt.%	Elements wt. % on wet basis	Wt. %
1.	Carbon C	33.19	Carbon C	25.96
2.	Hydrogen H	4.61	Hydrogen H	7.26
3.	Nitrogen N	0.0	Nitrogen N	0.0
4.	Sulphur S	1.56	Sulphur S	0.72
5.	Oxygen O	60.64	Oxygen O	66.06

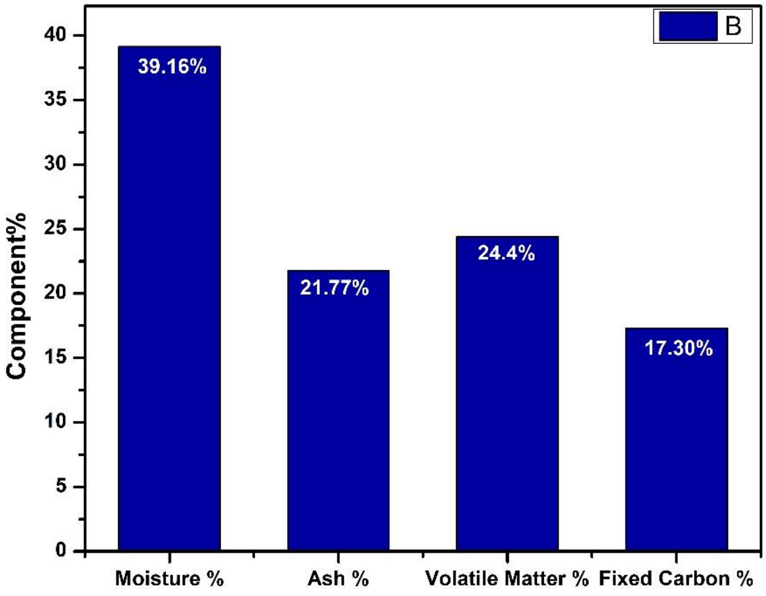

Figure 4.1: Proximate Analysis of oil refinery sludge

4.1.2 Ultimate analysis of oil refinery sludge

Figure 4.2 depicts the ultimate analysis of refinery sludge sample that illustrated the chemical composition of sample. The refinery sludge sample has higher percentage of oxygen contents (O) 60.64% and carbon content (C) 33.19% on dry basis but it contained lower percentage of hydrogen (H) and sulphur (S), 4.61% and 1.56%, respectively. Nitrogen (N) is completely absent in this sludge sample. Oil refinery sludge sample with low ash contents with low sulphur, an absence of nitrogen results in low NOX and SO_2 emissions[51, 52].

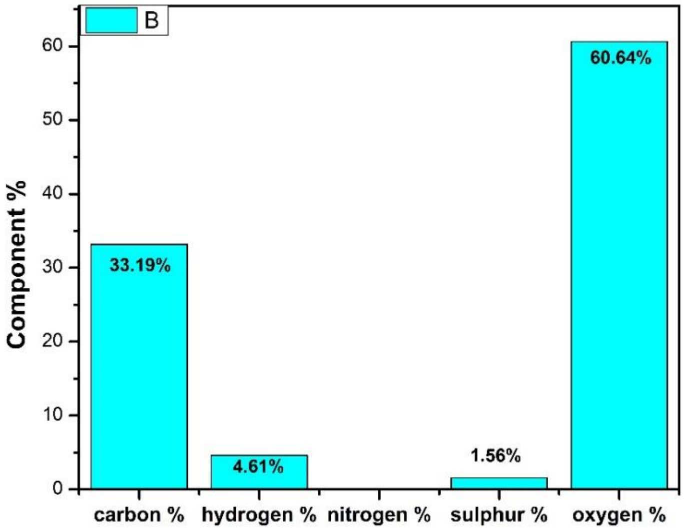

Figure 4.2: Ultimate analysis of oil refinery sludge

4.2 Thermal degradation behavior of oil refinery sludge

Three mass loss curves w.r.t temperature at three different heating rates 5, 20 and 40°C/min are represented in Figure 1. These three curves were primarily distributed into three stages. Stage one involved removal of inbound moisture at 25-200°C. Second stage involved the disintegration of decomposable organic matter for example proteinases, carboxylic acids, cellulosic compounds) and the breakdown of non-convertible `carbon-based substance like aromatics, saturated aliphatic, and long chain aliphatic amides, nitriles at 200-600°C. Second range was the focal part of thermal degradation of oily sludge because main disintegration occurs in this range. So, this range was further alienated into two ranges one is 200-400°C and other is 400-600°C.

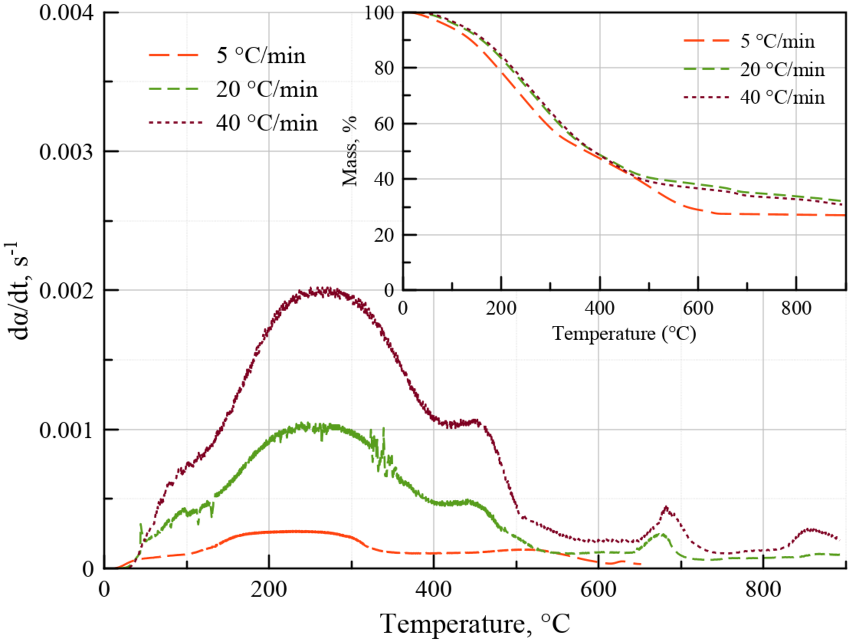

Figure 4.3: TG and DTG curves of oil sludge at 5, 20 and 40 ℃·min^{-1}

The TG and DTG curves of wet oily sludge was showed in figure 2(a)at 20°C/min which provided characteristic temperature and percentage mass loss. It delivers data about heat loss or gain during decomposition process & specified about reaction endo-thermicity or exo-thermicity. It even predicted temperature at which the maximum mass loss occurs. Moreover, it narrates about percentage mass loss as each stage. As stated above, key thermal degradation range was 200°C to 600°C which was further alienated into two ranges. In 1st range, maximum peak temperature Tp observed at 235°C for 20°C/min with 50 % mass loss and 310°C for 20°C/min at initial temperature (Ti) 137°C to final temperature (Tf)717°.

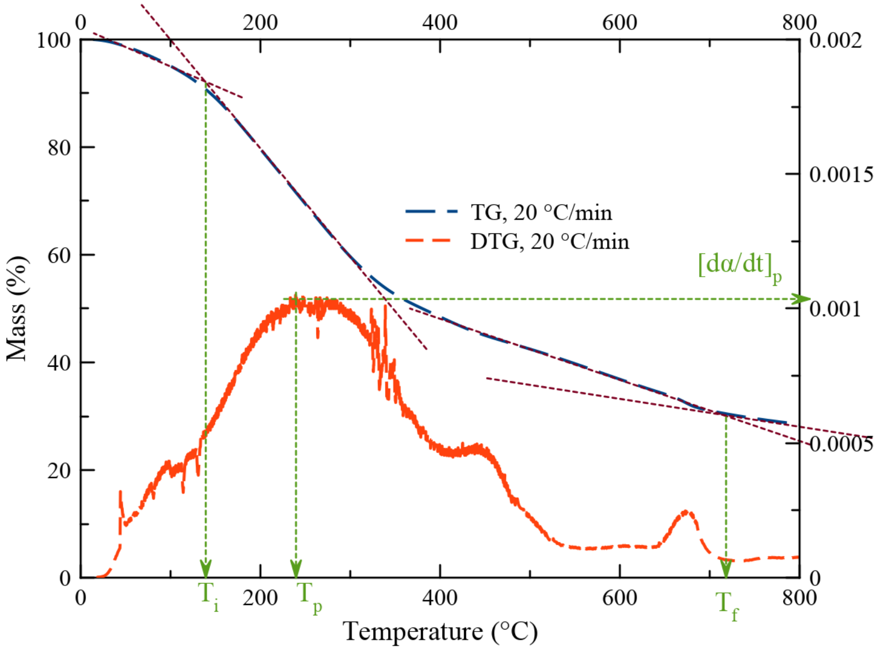

Figure 4.4: (D)TG characteristics parameters at 20 °C/min

In Figure 4.4 shows assessment of characteristics parameters & peak degradation rate at different heating rates, where Ti is the degradation starting temperature, Tf is the degradation terminating temperature, and Tp as peak maximum temperatures. The degradation starting and degradation terminating temperature are almost similar for all the three heating rates while the peak maximum temperature of two heating rates (20°C/min and 40°C/min) are similar & slight greater than maximum temperature for 05°C/min. The increase of heating rates promotes the slowing of thermal degradation of wet oily sludge at higher temperatures. This fact can be seen that the higher heating rate of oily sludge w.r.t given temperature with fast heating rate will increase the thermal delay[53, 54]. Additionally, the quantity of volatiles also reduces with increase of heating rates. Also, the reduction of heating rates not only relocates the temperature ranges but also changes the disintegration of oily sludge.

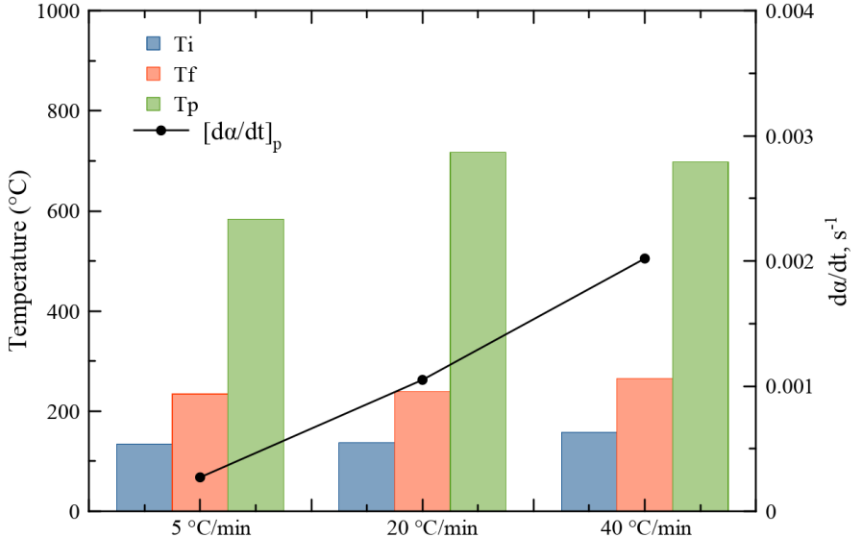

Figure 4.5: Comparison of characteristics parameters and peak degradation rate at different heating rates, where Ti is the degradation starting temperature, Tf is the degradation terminating temperature, and Tp as peak maximum temperatures

Table 7: (D)TG characteristics parameters

$\boldsymbol{\beta}$, ℃/**min**	$\mathbf{T_i}$, ℃	$\mathbf{T_p}$, ℃	$\mathbf{T_f}$, ℃	$\left(\frac{\mathbf{d\alpha}}{\mathbf{dt}}\right)_{\mathbf{max}}, \mathbf{s^{-1}}$
5	134	234	584	0.000271
20	137	239	717	0.00105
40	158	265	698	0.00202

4.3 Isoconversional methods

4.3.1 Kinetic Parameters through Friedman, KAS, and OFW Method:

Activation energies and pre-exponential factor are kinetic parameters of wet oily sludge pyrolysis, which were obtained by applying model free kinetics such as KAS, OFW, Friedman and method. This research includes, connection between E_a and conversion percentage, model free kinetics were used. In Friedman method E_a can be evaluated by using equation, which provides slopes by linear graph between 1/T and $ln\ (d\alpha dt)$ at progressive conversion degrees depicted in figure 4.6.

Friedman: $\ln(\frac{d\alpha}{dt})_{\alpha i} = const - \frac{E_\alpha}{RT_{\alpha i}}$ ……………… (07)

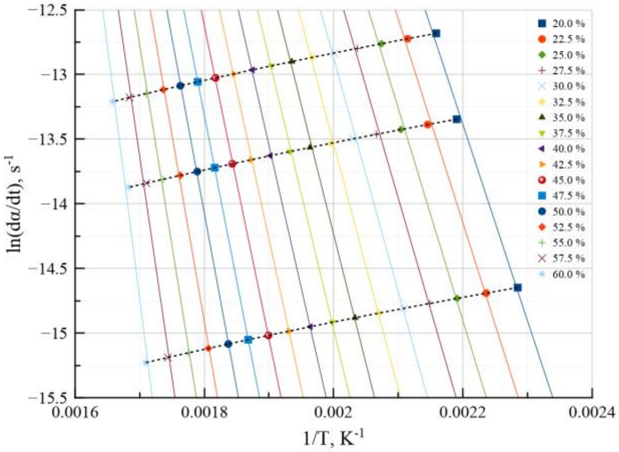

Figure 4.6: Arrhenius plots of Friedman

Kas: $\ln\left(\frac{\beta_i}{T_{\alpha i}^2}\right) = const - \frac{E_\alpha}{RT_{\alpha i}}$……………. (08)

Where, Ea can be determined by drawing a plot of inverse of temperature and ln (β/T²). Slopes obtained from linear plot between 1/T and ln (β/T²) give −Ea/R at regularly growing conversion degrees.

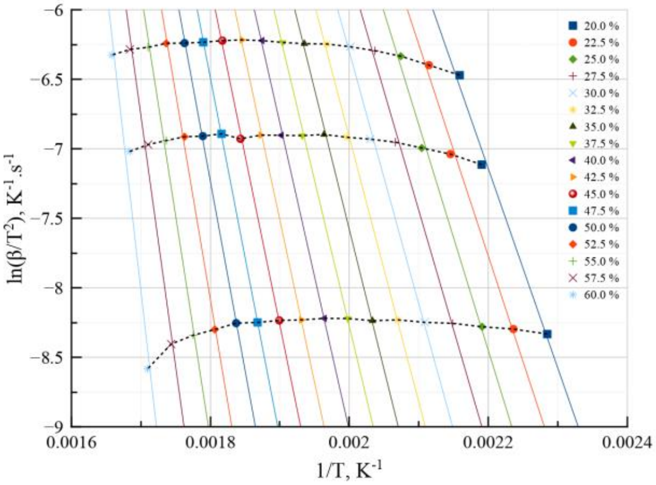

Figure 4.7: Arrhenius plots of KAS method

OFW method was employed to calculate E_a by following Equation.

$ln\beta = const - 1.052\frac{E_\alpha}{RT_{\alpha i}}$…………………….. (09)

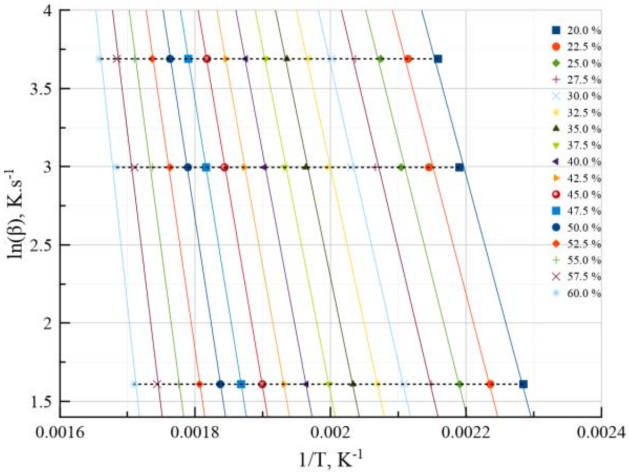

Figure 4.8: Arrhenius plots of OFW method at various conversions

The Figure 4.8 illustrates slopes through linear plot between 1/T and logβ which give −0.453 (Ea/R) at progressing conversion degrees. Damartzis et al. predicted that conversion degrees below 2% and above 95% does not included in calculation because of short correlation values[55].Pre-exponential factor (A) can be measured by employing intercept obtained from figure 4.9 for all three methods. The calculated figures of E_a, pre-exponential factor and linear regression of Friedman, KAS, and OFW methods are listed in Table 8. The Values calculated from Friedman, KAS, and OFW methods were in a virtuous contract with a standard error below 15%. This agreement authenticates the consistency of calculations and established the analytical power of Friedman, KAS, and OFW methods[56].

ASTM E1641-16 (ASTM International, 2016a)using OFW for a non-isothermal thermo-gravimetric conversion is used to estimate pre-exponential coefficient (A) considering 1st order decomposition.

$A = \frac{\beta R'}{E_\alpha}[\ln(1-\alpha)]10^{\alpha}$ ……………… (11)

where α is conversion, $\beta'$is nearest to the midpoint heating rate, R is universal gas constant, $E_a$is effective activation energy and a is Doyle approximation factor.

Table 8: Ea obtained from Friedman, KAS and OFW methods and pre-exponential coefficient estimated from ASTM E1641-16 method considering 1st order reaction mechanism at 20C/min

Conversion (%)	$\mathbf{E_a}\left(\frac{\mathbf{kJ}}{\mathbf{mol}}\right)$ **Friedman**	$\mathbf{R^2}$	$\mathbf{E_a}\left(\frac{\mathbf{kJ}}{\mathbf{mol}}\right)$ **KAS**	$\mathbf{R^2}$	$\mathbf{E_a}\left(\frac{\mathbf{kJ}}{\mathbf{mol}}\right)$ **OFW**	$\mathbf{R^2}$	$\mathbf{A\ (s^{-1})}$
20.0	119.35	0.99	126.24	0.99	127.15	0.99	16766934.19
22.5	126.57	0.99	131.08	0.99	131.90	0.99	18985124.73
25.0	135.00	0.99	136.62	0.99	137.32	0.99	22934120.88
27.5	142.62	0.99	143.29	0.99	143.81	0.99	33087817.51
30.0	150.94	0.99	150.25	0.99	150.57	1.00	47186138.21
32.5	158.44	1.00	157.93	1.00	158.01	1.00	64499895.40
35.0	167.62	1.00	166.14	1.00	165.95	1.00	83307956.98
37.5	174.52	1.00	174.32	1.00	173.86	1.00	107869631.11
40.0	184.23	1.00	183.28	1.00	182.51	1.00	142074328.12
42.5	194.53	1.00	192.25	1.00	191.18	1.00	175404646.87
45.0	202.91	1.00	201.45	1.00	200.06	1.00	208763129.10
47.5	215.22	1.00	212.56	1.00	210.77	1.00	272033150.11
50.0	226.76	1.00	224.65	1.00	222.40	1.00	349268571.37
52.5	246.93	1.00	239.63	1.00	236.79	1.00	450750398.99
55.0	267.50	0.99	258.53	0.99	254.91	0.99	571179746.17
57.5	300.10	0.98	284.31	0.98	279.59	0.99	793167244.03

60.0	364.41	0.95	325.60	0.96	319.02	0.96	1028720967.59

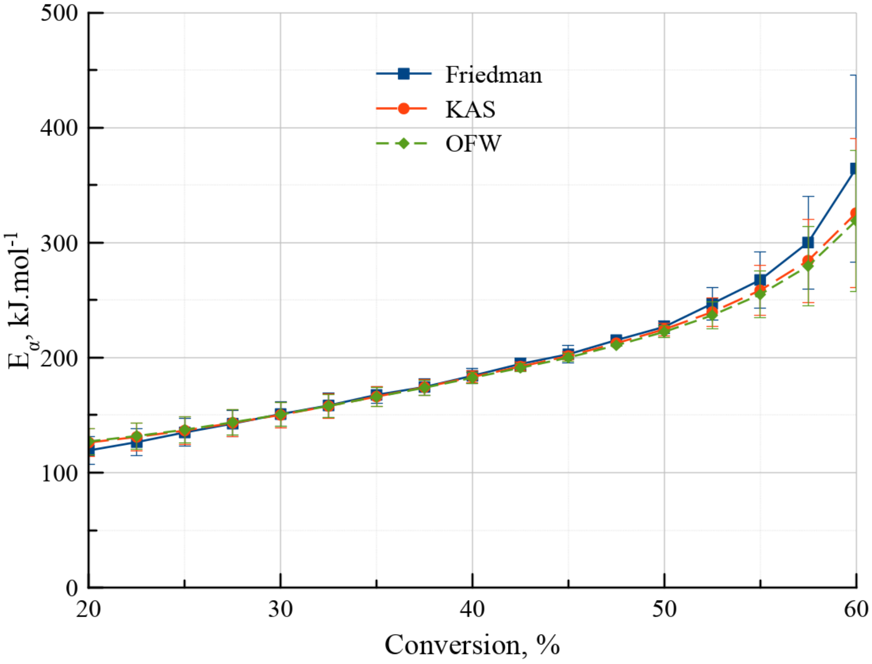

Figure 4.9: Activation energies w.r.t conversion

Finally, it is observed in kinetic analysis of refinery sludge that.

- Thermo gravimetric analysis-based pyrolysis has positive activation energy

- Pyrolysis process depends on heating rate and temperature zones

- In majorly of model, E_a declined at higher temperature zone which means that reaction rate continually improved and speed-up the reactions occurring during pyrolysis process.

Linear regression values show that the above models are appropriate mechanism.

4.4 Thermodynamic Parameters through Friedman, KAS, and OFW Method

Thermodynamic parameters involved Enthalpy ΔH, Gibbs free energy ΔG and entropy ΔS. These thermodynamic parameters would be calculated for maximum peak temperature Tm acquired through DTG curve of wet oily sludge pyrolysis[57]. Enthalpies ΔH explain the reaction state either endothermic or exothermic with help of negative or positive sign and explain the heat exchange profile. Gibbs free energy ΔG is important thermodynamic potential and express as net quantity of energy required for reaction to reach the equilibrium situation. Entropy ΔS is disintegration of arranged structure of material or distortedness of material in thermodynamic system[58, 59]. Entropy can be either negative or positive. All three thermodynamic parameters for Friedman, OFW, and KAS method at different conversion are given in table 9.

The changes in enthalpy ΔH, Gibbs free energy ΔG, and entropy (ΔS) also evaluated with the help of activation energy E_a & pre-exponential factor A by employing these given equations:

$$\Delta H = E_\alpha - RT \text{………………} (12)$$

$$\Delta G = E_\alpha + RT_m\left(\frac{E_\alpha T_m}{h.A}\right) \text{……………..} (13)$$

$$\Delta S = \frac{\Delta H - \Delta G}{T_m} \text{………………} (14)$$

Where, K_B represents Boltzmann constant whose value is 1.381×10^{-23} J K^{-1}, h represents Plank constant whose value is 6.626×10^{-34} J s and Tm the DTG peak temperature.

Table 9: Thermodynamic parameters of wet oily sludge obtained from Friedman, KAS and OFW methodsestimated from ASTM E1641-16 method considering 1st order reaction mechanism at 20C/min

Conversion (%)	$\Delta H\left(\frac{kJ}{mol}\right)$ **Friedman**	$\Delta G\left(\frac{kJ}{mol}\right)$ **Friedman**	$\Delta S\left(\frac{kJ}{mol}\right)$ **Friedman**	$\Delta H\left(\frac{kJ}{mol}\right)$ **KAS**	$\Delta G\left(\frac{kJ}{mol}\right)$ **KAS**	$\Delta S\left(\frac{kJ}{mol}\right)$ **KAS**	$\Delta H\left(\frac{kJ}{mol}\right)$ **OFW**	$\Delta G\left(\frac{kJ}{mol}\right)$ **OFW**	$\Delta S\left(\frac{kJ}{mol}\right)$ **OFW**
20.0	113.52	176.14	-0.1222	120.41	183.03	-0.1222	121.32	183.94	-0.1222
22.5	120.74	182.83	-0.1212	125.25	187.34	-0.1212	126.07	188.16	-0.1212
25.0	129.17	190.46	-0.1196	130.79	192.08	-0.1196	131.49	192.78	-0.1196
27.5	136.79	196.52	-0.1166	137.46	197.19	-0.1166	137.98	197.71	-0.1166
30.0	145.11	203.33	-0.1137	144.42	202.64	-0.1137	144.74	202.96	-0.1137
32.5	152.61	209.50	-0.1111	152.10	208.99	-0.1111	152.18	209.07	-0.1111
35.0	161.79	217.59	-0.1089	160.31	216.11	-0.1089	160.12	215.92	-0.1089
37.5	168.69	223.40	-0.1068	168.49	223.20	-0.1068	168.03	222.74	-0.1068
40.0	178.40	231.94	-0.1045	177.45	230.99	-0.1045	176.68	230.22	-0.1045
42.5	188.70	241.34	-0.1028	186.42	239.06	-0.1028	185.35	237.99	-0.1028
45.0	197.08	248.98	-0.1013	195.62	247.52	-0.1013	194.23	246.13	-0.1013
47.5	209.39	260.17	-0.0991	206.73	257.51	-0.0991	204.94	255.72	-0.0991
50.0	220.93	270.64	-0.0970	218.82	268.53	-0.0970	216.57	266.28	-0.0970

52.5	241.10	289.73	-0.0949	233.80	282.43	-0.0949	230.96	279.59	-0.0949
55.0	261.67	309.29	-0.0930	252.70	300.32	-0.0930	249.08	296.70	-0.0930
57.5	294.27	340.50	-0.0902	278.48	324.71	-0.0902	273.76	319.99	-0.0902
60.0	358.58	403.70	-0.0881	319.77	364.89	-0.0881	313.19	358.31	-0.0881

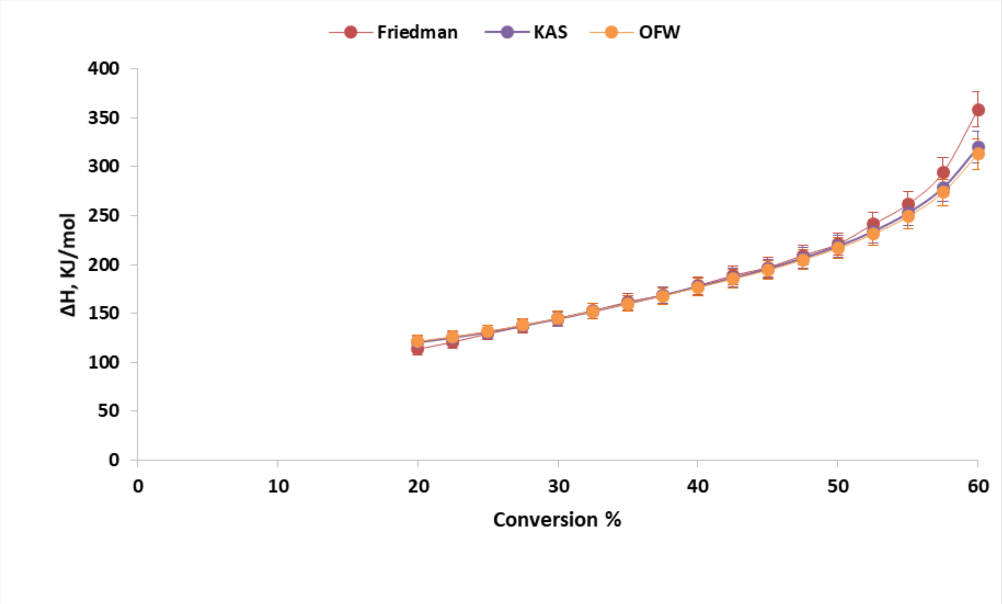

Figure 4.10: Change in Enthalpies w.r.t conversion % for wet oily sludge

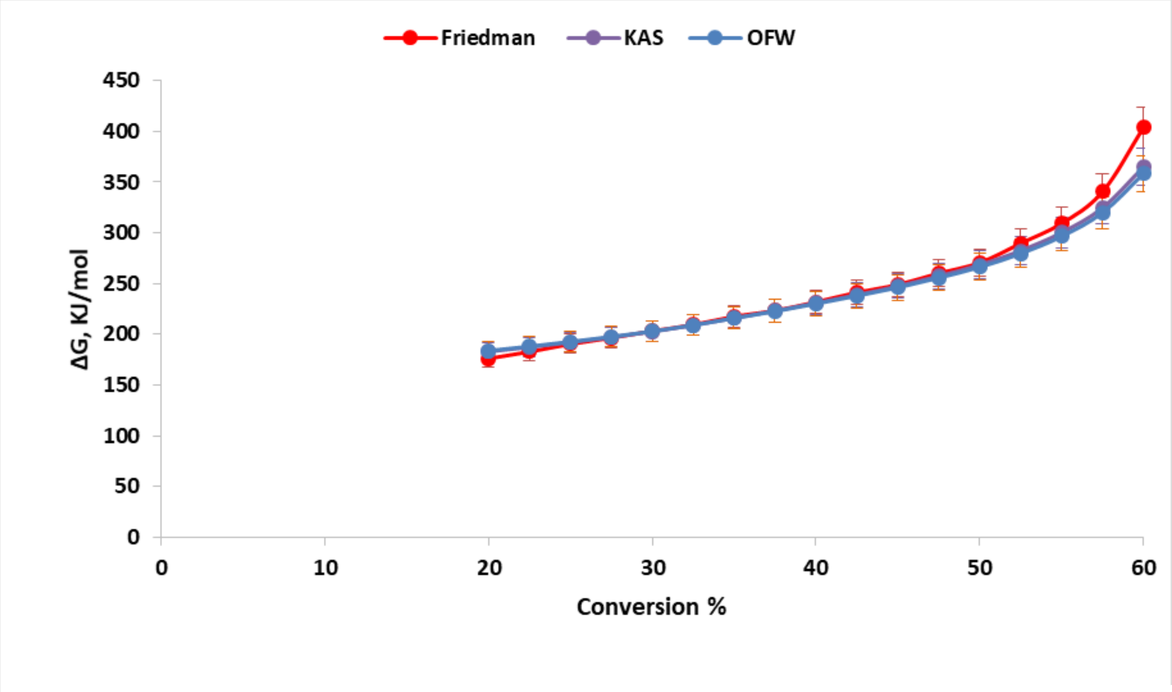

Figure 4.11: Change in Gibbs free energies w.r.t conversion % for wet oily sludge

The table 9 illustrates that in all three methods the enthalpy is positive at each conversion which shows that at these conversions endothermic reaction occurs during pyrolysis process. The values of Gibbs free energy are also positive for all three methods. It is distinct from table that entropy is negative throughout the conversion levels. Negative entropy enlightens that the breakdown in stimulated condition has well regimented assembly than before the thermal breakdown and pyrolysis process involved disordered to well organize structure.

4.5 Testing for evaluating organic or inorganic content

A test also conducted for evaluating the percentage of organic and inorganic contents in oil refinery sludge sample. Results of test revealed organic content of 91.33 wt. % and inorganic content of 8.67 wt. %. The results are tabulated as shown below in table 10.

Table 10: wt. % of organic and inorganic matter in oil refinery sludge

Serial No.	Component	Weight percentage
1.	Organic matter	91.33%
2.	Inorganic matter	8.67%

Conclusion and Future Recommendations

Thermal degradation behavior in pyrolysis process of oil refinery sludge was carried out by using a lab scale autoclave pyrolysis unit and thermo gravimetric analysis. Oil refinery sludge sample in dried and powdered form was used for all treatments. Thermodynamic and kinetic parameters through model free were also analyzed in this research.

The oil refinery sludge sample contained higher percentage of volatile matters 24.40%, ash 21.78%, carbon 33.19% and oxygen 60.64% on dry basis. These proportions of volatiles in sample favors for thermal degradation processes because desirable products could be obtained by utilizing such material.

Model free method for kinetic and thermodynamic parameters calculation were investigated in this study by using thermo gravimetric data to analyze the nature of reaction characteristics of oil refinery sludge pyrolysis. TGA and DTA curves of oil refinery sludge pyrolysis were analyzed, and two phases were identified: phase 1 from 200 to 400 °C and phase 2 from 400 – 600°C. In model free kinetics, for all calculated values from Friedman, KAS, and OFW method, activation energy Ea rises in the range of 2.5% to 60% conversions and decreases in the range of 60% to 95% conversion. For Friedman method activation energy abruptly raises after conversion of 50% and in all three methods the enthalpy is positive at each conversion which shows that at these conversions endothermic reaction occurs during pyrolysis process. The values of Gibbs free energy and entropy are positive and negative respectively for all three methods.

The influence of the reaction temperature (350 –450°C) on products yield and characteristics in lab scale pyrolysis process was considered. The highest bio-oil yield of 39 weight % can be attained at the pyrolysis temperature of 450°C. Biochar and gaseous product yield showed declining profile with increment of pyrolysis temperature as concluded from TGA data.

Future Recommendation

Based on the above results, for more exploring in pyrolysis process, the following future work is recommended:

- The design amendment in pyrolysis unit in terms of high production liquid fuel could be prolonged by providing new techniques and optimum process condition such as temperature, nature of feedstock and residence time.
- A computational model should be established to enhance the physical, chemical and reaction parameters which will help to design the process.
- Different kinetic model should be established to investigate the best functioning condition to design the pyrolysis process to obtain the maximum yield with lower investment.
- It should be developed on commercial scale because oil refinery sludge can process and yield more barrels of oil and gaseous products. Among different gaseous products methane is one of the most useful by-product we obtained. This methane would be utilized in different energy processes as a source of fuel.

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