

## Remediation of Guwahati Refinery Waste Sludge By Pyrolysis

R. C. Borah

School of Engineering and Technology  
The Assam Kaziranga University  
Jorhat, Assam, India

### ABSTRACT:

Refineries in the North Eastern Region of India processing local crude have a large quantity of deposits of oil sludge, collected over a number of years. Guwahati Refinery alone has more than  $16 \times 10^6$  Kgs of accumulated sludge; kept in lagoons. The major sources of refinery sludge include the oil storage tank sludge, the biological sludge, the dissolved air floatation (DAF) scum, The American Petroleum Institute (API) separator sludge and the chemical sludge. For both economic and environmental reasons, it has become important to transform the oil sludge to useful energy sources. Guwahati refinery waste sludge contains a large quantity of water and has been found to behave like complex water-in-oil-in-water, emulsion system. Pyrolysis of sludge in the inert atmosphere at a very low heating rate has been found to be conducive in separation of water and oil and recovering lower molecular weight hydrocarbons from Guwahati refinery waste sludge as distillate. Also the pyrolysis residue contains about 60% carbon. Separation and recovery of water was complete at a temperature of 473K. Yield of oil is consistent at 70 % of the oil content.

**KEYWORDS:** Waste sludge, water-in-oil-in-water emulsion, pyrolysis, lower heating rate, remediation.

### 1. INTRODUCTION:

Waste oily sludge of a petroleum refinery contains a large amount of combustibles with high heating values. Therefore, waste sludge is a useful recycling resource and the conversion of waste sludge into fuels has been recognized as an alternative approach. Refineries in the North Eastern Region of India processing local crude have a large quantity of deposits of oil sludge, collected over a number of years. Guwahati Refinery alone has more than  $16 \times 10^6$  Kgs of accumulated sludge; kept in lagoons. The waste sludge in Guwahati Refinery contains approx. 30% of oil after recovery by steam heating [1]. The sludge amount collected over the years has become enormously large, and it is creating great problems from the point of view of environment pollution, specifically during the rainy season. The refinery has to create new areas for dumping, and it has to protect the sludge from seepage to nearby areas. For both economic and environmental reasons, it has become important to transform the oil sludge to useful energy sources. This waste is hazardous in nature, because many of the constituents of oily sludge are carcinogenic and potent immunotoxicants [2-3] and the sludge's containing poly aromatic hydrocarbons are genotoxic in nature and the exposure to these may pose a potential genotoxic risk to human beings [4]. Hence their disposal or resource recovery is an important global issue [5-7]. Effort on conversion of waste sludge to useful resources such as lower molecular weight organic compounds and high heating value residue by low temperature thermal treatment is reported in literature [8]. The conversion of refinery sludge into lower molecular mass hydrocarbon by pyrolysis not only solves the disposal problem, but also has the appeal of resource utilization [9-11].

Various options namely, the followings are identified as long term viable solution. There are existing methods for incineration of sludge such as Fluidized bed combustion; Circulating fluidized bed combustion, Rotary kilns, Rack and Step type furnaces, etc. at a temperature of 1073-1173K [12]. Because of excessive temperature requirement, frequent clinker formation, high flue gas temperature, high pressure drop, etc. emission of poly aromatic hydrocarbons (PAHs), Phenanthrene (phA) fluoranthane (fluA) and pyrene (pyr) have put the incineration process to be inconvenient.

Land farming with microbial treatment is an existing method to convert the hydrocarbons of the waste sludge [12]. The difficulty in this process is that if stabilization of oil sludge is not complete, then there can be risk of pollution. It can pollute ground water and cause health problem. Moreover, large land surface areas are needed. It takes long time to complete the reaction. In addition it can cause air pollution. Organic compounds of oil sludge such as aromatics, PAHs are carcinogenic.

The electrically heated drying of waste sludge such as Mx-2500 is a method to minimize the waste volume and oil recovery [12]. It is a low temperature thermal treatment process. It provides waste minimization of up to 40% in volume. Decrease of volume of the waste sludge and increase of the quality of oil is the advantage of the process.

Pyrolysis is a process where depolymerization and thermal decomposition of the functional group go alongside to each other. Pyrolysis of petroleum sludge can be used to produce valuable low boiling products such as liquid hydrocarbons. Z Wang et al [13] reported that pyrolysis reaction occurs in the temperature range 373-773K, however maximum evolution rate i.e. the peak temperature has been observed in the temperature range of 673-773K. Choudhury et al [1] has reported that pyrolysis reaction is significant in the temperature range of 473-623K. A two reaction model is found to fit the experimental results. J-L Shie et al [14] reported a one reaction model of order 2.92 with activation energy of 78.22 kJmol<sup>-1</sup> and frequency factor of 9.48×10<sup>5</sup> min<sup>-1</sup>. Choudhury et al [1] has reported a two reaction model for the pyrolysis reaction and activation energy, reaction order and frequency factor of 64 KJmol<sup>-1</sup>, 2.08, 2.97×10<sup>5</sup> and 112 KJmol<sup>-1</sup>, 2.98 and 1.498×10<sup>10</sup> respectively for the two reactions. All the above mentioned work has been reported for oven dried sludge. Drying of a complex sludge such as that of Guwahati Refinery is a difficult one. Also there are no report has been made on the effect of rate of heating on the drying and pyrolysis of sludge till now. Knowledge of pyrolysis kinetics and product distribution is of very much importance in case of combustion and gasification of petroleum sludge as rapid pyrolysis is the first step in combustion. It is also necessary to get useful information to get product distribution of solid, liquid and gas. Treatment of waste sludge by catalytic cracking has some advantages over thermal degradation [15], such as shorten cracking time, lower the required temperature, increase the cracking ability of wastes, reduce the proportion of solid residue, and narrow the product distribution.

The aim of the present work is to develop an economic and environment friendly process for removal of water and recovery of oil from the oily waste sludge of Guwahati Refinery. Pyrolysis of sludge has been chosen to be the method of separation and recovery of oil.

## **2. EXPERIMENTAL SECTION:**

### **2.1 MATERIALS:**

The refinery waste sludge in this study was collected from the common storage pit from Guwahati Refinery of Indian Oil Corporation Limited, which is situated in the North East Region of India. The major sources of refinery sludge include the oil storage tank sludge, the biological sludge, the dissolved air floatation (DAF) scum, The American Petroleum Institute (API) separator sludge and the chemical sludge. The sludge is extremely heterogeneous and greasy in nature. The physico-chemical characteristics of the waste sludge such as total solid residue, moisture content, volatile organic content, and fixed residue and oil contents are determined by the method given in literature [16]. The components extractable by chloroform are herein referred to as 'oil' content in the sludge. The method is elaborated in literature [16]. In this method oil was extracted from about 10 gm of vacuum dried sludge with 50 ml of chloroform in each extraction. The procedure was repeated till maximum amount of oil is extracted. The chloroform extracts were dried over anhydrous sodium sulphate, filtered and then the solvent was removed. The weight of the residual oil was measured. Brief characterization of the sludge is given in Table 1.

The concentrations of all the constituents are expressed in terms of mass % of the raw sludge. Inorganic ingredients in terms of elements, such as Fe, Mg, Ni, Co, Pb, Na and K present in the fixed residue is determined by Atomic Absorption Spectrometer(AAS, Model: Perkin Elmer 2380, USA). The fixed residue is defined by the amount of solid remaining after ignition and expressed as percentage weight of wet sludge [16]. The hydrocarbon content in the oil was analyzed by GC-MS (Model: HP5181-7487). The results of characterization are given in Table1.

## 2.2 EXPERIMENTS ON SEPARATION OF WATER AND OIL FROM SLUDGE:

The sludge was dried in an air oven at a temperature of 378K for 48 h until it attains a constant weight and the dried sludge sample was used for degradation analysis by TG/DTG. The TG/DTG of sludge sample was carried out in nitrogen gas (purity 99.99% and moisture free) at a flow rate of 100 ml min<sup>-1</sup> in DTA-TG equipment (SDT-2960, M/S TA Corporation, USA). Approximately, 0.02 g of sample mass was taken in a platinum crucible.  $\alpha$ -Aluminium oxide is used as a reference material. Three chemicals are selected and tested as additives from literature which reported to give higher yield [17] and directly added without further treatment into the platinum crucible with oven dried sludge after thorough mixing. The chemicals are: (1) Sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>), (2) Iron Oxide (Fe<sub>2</sub>O<sub>3</sub>) and Potassium carbonate (K<sub>2</sub>CO<sub>3</sub>). Amount of additives used: with 1 g of sludge 0.1–0.2g of additives was used as reported in literature [17]. The experiments were carried out at three different heating rates 3, 6 and 9Kmin<sup>-1</sup> to study the effect of heating rate on the yield of pyrolysis.

## 2.3 APPARATUS AND PROCEDURE FOR PYROLYSIS OF SLUDGE:

The experimental setup consists of a horizontal furnace for pyrolysis, inert gas cylinder, flow meter, condenser and gas collector. The horizontal furnace consists of a cylindrical tube made of sillimanite having 50 mm internal diameter and 600 mm length. The total resistance of the heating element [made: Kanthal (UK)] was 55 $\Omega$ , which delivered a maximum of 1 kW power. The furnace had to provision for heating up to 1273K. A Digital temperature controller [made: Max-Thermo (Taiwan)] was used for heating and maintaining the temperature of the furnace. Nitrogen gas was supplied to the system directly from the gas cylinder. The flow rates of the gases were measured by a rotameter. A chromel-alumel thermocouple was put horizontally into the top section of the horizontal furnace to measure the furnace temperature. The linking glass tube between the pyrolysis furnace and condensing trap was wrapped with asbestos rope insulating material so that oil vapor does not condense in the tube. The sludge sample under investigation was taken in a quartz boat of 12 mm wide and 50 mm length and 7mm depth. The boat was put inside the horizontal furnace with the help of a pusher rod. Initially, the power input to the electric coil was started with simultaneous purging of the nitrogen gas at a rate of 500ml min<sup>-1</sup>. Rate of heating was regulated at a rate of 1.5K min<sup>-1</sup> (based on DTA/TGA results) until the temperature of 473K, and then it is kept at that temperature for 30 minutes, so that release of water from sludge and its evaporation is complete. The gas coming out of the furnace is passed through two numbers of traps where the gas temperature comes down to 298K and the condensate collected. The condensate collected up to 473K is primarily water. Then the furnace is again heated until it attains the temperature of 773K. The condensates collected between 473–773K are kept separately, which is the product oil from pyrolysis of sludge. Then the furnace is allowed to cool down to room temperature; the quartz boat was taken out and weighed. The char remains of the pyrolysis of sludge are collected by scraping the boat.

The mass of oil sludge used for the experiments on the pyrolysis were 0.032-0.042 Kg. Similar furnaces with higher mass handling capacity has also been used for pyrolysis(0.272-0.577Kg). The products of pyrolysis of oil sludge were divided into solid residues, liquid oils (condensable liquid, 298K), and non-condensable gases (298K) which were vented to a fume hood. The programmed rise of the temperature of the furnace was set to stop at 773K. It has been found from thermo gravimetric degradation study that there is no further reaction after 773K. The condensates collected in the range of 473-773 K were the liquid oils.

## 3. RESULTS AND DISCUSSION:

An emulsion is a thermodynamically unstable system consisting of at least two immiscible liquid phases one of which is dispersed as globules in the other liquid phase stabilized by a third substance called emulsifying agent. The droplet phase is called the dispersed phase or internal phase and the liquid in which droplets are dispersed is called the external (continuous phase). In case of oil water emulsion the easy and quick method of determining the type of emulsion is to measure its solubility in water and in oil.

If the emulsion is found to dissolve readily in both n-hexane and toluene but not in water, which means that the oil is the continuous phase and the water is the dispersed phase, then the emulsion is of the type of water in oil (w/o) emulsion. When Oil droplets are dispersed in a continuous aqueous phase, then it is oil in water (o/w) emulsion. These are macro emulsion. When the water content is high i.e. water is the continuous phase, dispersed oil droplets contains some water droplets. Oil phase (hydrophobic) separates the internal and external aqueous phases. This type of emulsion is water-in-oil-in-water type. This type of emulsion has been reported as double emulsion [18] or multiple emulsions [19]. These type emulsions are sometimes developed with a view to delay the release of an active ingredient. It has three phases. Generally this type of emulsion is unstable and it needed stabilization. Guwahati Refinery sludge sample is of similar type. It is a stable emulsion as all those efforts stated above could not separate oil, water and residual matter completely. Probably the sludge has become a stable emulsion when a portion of oil was recovered by steam heating before putting it to the waste pond. When it is kept in oven for about 48 hrs at 378K only external water is evaporated. The water droplets trapped inside the oil droplets are released completely only at 473K. Hence our sludge is of water-in-oil-in –water type of emulsion.

DTA and TGA of the oven dried sludge and its mixture with three additives, particularly sodium carbonate, potassium carbonate and iron oxide, in two proportion 10, 20% by weight, has been completed in a DTA-TGA apparatus (SDT-2960 of Thermal analysis, USA make) in an inert atmosphere of nitrogen. DTA-TGA of oven dried sludge has been at different heating rate have been shown in Fig.1. It can be seen that as heating rate increases the peak temperature of DTG shifts towards right. It can also be seen that the yield decreases with rate of heating. Overall results of effect of additives are shown in Fig.2. From Fig.2 it can be seen that additives used in the degradation process of the sludge did not increase the yield as in the case reported in the literature [17], rather the yield is smaller than pyrolysis yield of the raw oven dried sludge. The reason may be that the water is still entrapped inside the oven dried sludge sample for which the additives have shown no influence. In above comparison blank run for each catalyst has been considered. It has also been observed that as the rate of heating increases the yield decreases. This signifies that the degradation process is favorable to the lower rate of heating. Hence pyrolysis experiments at lower heating rate have been done in details.

Pyrolysis of raw sludge has been completed at a heating rate of 1.5K min<sup>-1</sup>. The average yield of oil is 68.66% (with respect to oil content of the sludge). The average yield of the char is 14.45% with respect to raw sludge. Average water recovered is 60% [Table2-3]. Characteristics of the recovered oil are determined and given in Tables 4-5. From this it can be observed that in the recovered oil hydrocarbons from C<sub>12</sub>to C<sub>37</sub> are present. This can be added to cracker feedstock for further cracking. The byproduct residue is an important product as it contains 58% carbon (Table 6), which will produce heat on burning. Table 7 gives the analysis of the flue gas. From the Table 7 it can be observed that flue gas generated are rich in hydrocarbons. It can be used as a resource for heat energy.

#### **4. CONCLUSION:**

Extensive experimental work to study remediation of Guwahati Refinery waste sludge has been done. It has been concluded that the Guwahati Refinery waste sludge is a complex oil-in-water-oil emulsion. Furthermore, it has been concluded that pyrolysis is the effective method for recovery of oil from the sludge. The process generates two byproducts namely char and flue gas, which can be utilized as a source of heat energy. Electrical power consumption per 100grams has been measured. Consumption of power is low. However further study in a large capacity pyrolyzer is necessary to acquire knowledge on power consumption and recirculation of the inert gas.

#### **5. ACKNOWLEDGEMENT:**

Author is grateful to the Ministry of environment & Forest, New Delhi for providing necessary funds to carry out the experimental work. The work has been done in CSIR-NEIST Jorhat (2008-2011).

## REFERENCES:

1. D. Choudhury, R.C. Borah, R.L. Goswamee, H.P. Sarmah and P.G Rao, Journal of Thermal Analysis and Calorimetry vol.89,pp965-970, July2007.
2. S.Mishra, J. Jyot, R. C. Kuhad, and B. Lal, "Evaluation of inoculum addition to stimulate in situ bioremediation of oily sludge-contaminated soil", Appl. Environ. Microbiol. Vol.67, pp1675-1681, April 2001.
3. T. L. Propst, R. L. Lochmiller, C. W. Qualis, Jr., and K. McBee. "In situ (mesocosm) assessment of immunotoxicity risks to small mammals inhabiting petrochemical waste sites", Chemosphere, vol. 38, pp1049-1067, Feb 1999.
4. K. Krishnamurthi, S. Saravana Devi and T. Chakrabarti, "The Genotoxicity of Priority Polycyclic Aromatic Hydrocarbons (PAHs) Containing Sludge Samples", Toxicology Mechanisms and Methods, Vol. 17, pp 1-12, January 2007,.
5. A. P Kuriakose, Manjooran and S. Kochu Baby, Utilization of Refinery Sludge for Lighter Oils and Industrial Bitumen, Energy & Fuels, vol.8, pp 788-792, May1994.
6. B. J. Milne, H. R Baheri, and G. A Hill, Composting of a heavy oil refinery sludge, Environmental Progress, vol.17, pp 24-27, January1998.
7. I.H. IBagouri, A.S ElNawawy, M. Abdal, R. Al-Daher, and M.S. Khalafawi, Mobility of oil and other sludge constituents during oily sludge treatment by landfarming, Resources, Conservation and Recycling, vol.11, pp 93-100, June1994.
8. R. J. Ayen, and C.P. Swanstrom, Low temperature thermal treatment for petroleum refinery waste sludges, EnvironEnvironmental Progress, vol.11, pp 127-33, May 1992.
9. W. Kaminsky, Pyrolyse von Biomasse. Chemie Ingenieur Technik, vol.61, pp775-782, October,1989.
10. W Kaminsky, A. B.Kummer, Fluidized bed pyrolysis of digested sewage sludg Journal of Analytical and Applied Pyrolysis, vol.16, pp27-35, May,1989.
11. M.R Stammbach, B Kraaz, R Hagenbucher, and W. Richarz, Pyrolysis of sewage sludge in a fluidized bed ,Energy & Fuels, vol.3,pp 255-259, March 1989.
12. N.J. Saikia, P. Sengupta, P.K. Gogoi and P.C. Barthakur, Thermo gravimetric combustion kinetics of petroleum effluent treatment plant sludge, J. of Thermal Analysis and Calorimetry, vol.79, pp 653-662, February,2005.
13. Z. Wang, Q. Guo, X. Liu and C. Cao , "Low temperature pyrolysis characteristics of oil sludge under various heating conditions", Energy Fuels, vol.21,pp 957-962, March,2007.
14. J-L Shie, C-Y Chang, J-P Lin, C.H. Wu and D-J Lee, "Resource recovery of oil sludge by pyrolysis: Kinetic study", Journal of Chemical Technology and Bio technology, vol. 75, pp 443-450, June,2000.
15. S. J. Chiu, W. H. Cheng, Thermal degradation and catalytic cracking of poly(ethylene terephthalate), Stability, vol.63,pp 407- Polymer Degradation and 412, January,1999.
16. S.K Wahi, A.K Agnihotri and J.S. Sarma, "Environment Management in Petroleum Industry", Wiley Eastern Limited, New Delhi 1993.
17. Je-Lueng Shie, Jyh-Ping Lin, Ching-Yuan Chang, Duu-Jong Lee and Chao-Hsiung Wu, "Pyrolysis of oil sludge with additives of sodium and potassium compounds" , Resources, Conservation and Recycling, Vol.39, pp 51-64 , August 2003,.
18. Characterization of a Double Emulsion System (oil-in-water-in-oil emulsion) with Low Solid Fats: Microstructure, JAOCS, Vol. 80, January,2003.
19. A. Aserin, Multiple Emulsion: Technology and Applications, ISBN: 978-0-470-17093-9,326 pages,November 2007

**Table 1**  
**Compositions and constituents of the refinery sludge:**

	Mass/Mass%	Hydrocarbon distribution in the oil	Mass %
Total solid residue	44.55	Heptadecane	2.10
Moisture	55.11	Dodecane	1.90
Organic content	39.26	Eicosane	1.70
Inorganic content	5.68	Tridecane	0.93
Oil content	28.07	Penta decane	0.89
(Chloroform extractable)		Undecane	0.83
		Nonadecane	0.81
Elements	(ppm)	Decane	0.75
		Dodecane-2,6,11-trimethyl	0.56
Fe	107.670	Decane-2,5,9-trimethyl	0.26
Mg	5.570	Nonadecane-3-methyl	0.24
Ni	0.230	Benzene-1-ethyl-3-methyl	0.21
Co	0.065	Others	0.59
Pb	0.010		
Na	0.472		
K	6.350		

**Table 2**  
**Experimental Results of pyrolysis of raw sludge (Quartz boat):**

Room Temperature K	Duration Heating minutes	of in Raw in gm	Amount of Sludge	Amount of Product oil in gm
301	420	35		7
303	445	32		8
303	410	42		7
303	690	36		9

**Table 3**  
**Experimental Results pyrolysis of raw sludge:**

Sludge weight in gm	Oil in gm	Water ml	Residue in gm	Oil yield (%)	Water yield (%)	Char yield (%)
577	80	90	21	13.87	15.60	3.64
272	97	90	38	35.66	33.09	13.97
427	118	164	54	27.64	38.41	12.65
265	56	86	88	21.17	32.51	33.27
283	66	112	37	23.32	39.58	12.97
332	70	106	73	21.08	31.93	21.99
305	68	80	45	22.30	26.23	14.75

**Table 4**  
**Characteristics of product oil recovered from sludge:**

Pour point = 27<sup>0</sup>C  
 Flash point=92<sup>0</sup>C  
 Fire point=140<sup>0</sup>C  
 Distillation Pattern  
 Weight of the material =96gms  
 Volume of the material=100ml  
 IBP=95<sup>0</sup>C  
 Distillation Characteristics

Volume	Temperature <sup>0</sup> C
5	260
10	290
15	295
20	300
25	310
30	320
35	325
40	330
45	336
50	342
59	350

Weight of the distillate=56gms  
 Volume of the distillate=59ml  
 Weight of the residue=36gms  
 Volume of the residue=39ml

**Table 5**  
**Hydrocarbon constituents in the recovered oil [GC Model C-1000 with FID detector of make Chemito Instruments Pvt. Ltd. (India):**

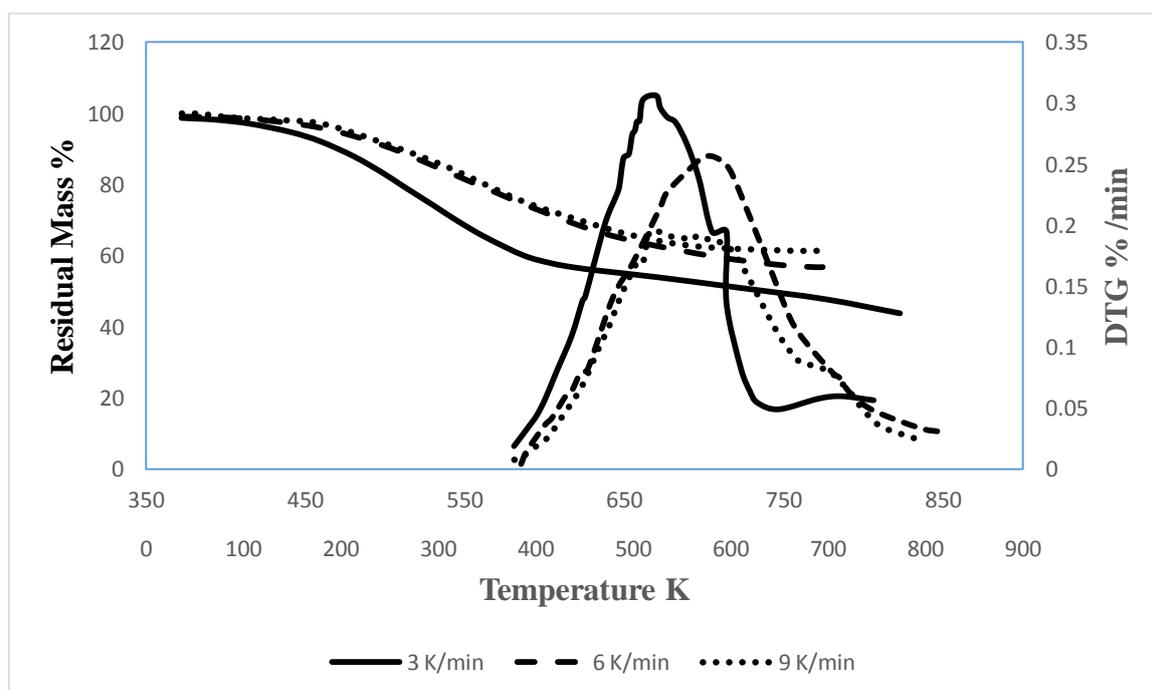
Hydrocarbon	%	Hydrocarbon	%
Dodecane	0.276	Pentacosane	3.51
Tridecane	0.530	Hexacosane	6.689
Tetradecane	1.089	Heptacosane	7.243
Pentadecane	2.966	Octacosane	3.033
Hexadecane	3.035	Nonacosane	5.557
Heptadecane	12.833	Hexamethyltetracosane	3.120
Octadecane	5.057	Hentriacontane	2.148
Nonadecane	7.192	Dotriacontane	1.489
Eicosane	6.097	Tritriacontane	1.739
Henicosane	7.141	Tetratriacontane	1.548
Docosane	5.960	Pentatriacontane	0.278
Tricosane	5.797	Hexatriacontane	0.891
Tetracosane	3.631	Heptatriacontane	1.151
		Total	100.00

**Table 6**  
**Carbon, hydrogen and nitrogen analysis of Char [CHN-Perkin Elmer (USA) Model PE2400 Series II]:**

Elements	%
Carbon	57.65
Hydrogen	2.33
Nitrogen	0.45

**Table 7**  
**Flue gas analysis (99% Nitrogen; 1% flue gas) [GC Model C-1000 with FID detector of make Chemito Instruments Pvt. Ltd. (India)]:**

Hydrocarbons	%
C <sub>1</sub>	37.3
C <sub>2</sub>	15.3
C <sub>3</sub>	13.6
C <sub>4</sub>	5.9
C <sub>5</sub>	4.0
C <sub>6</sub>	6.3
Other gas	
CO <sub>2</sub>	17.6
Total	100.0



**Fig.1. Residual mass and DTG%/min vs. Temperature of oven dried sludge**

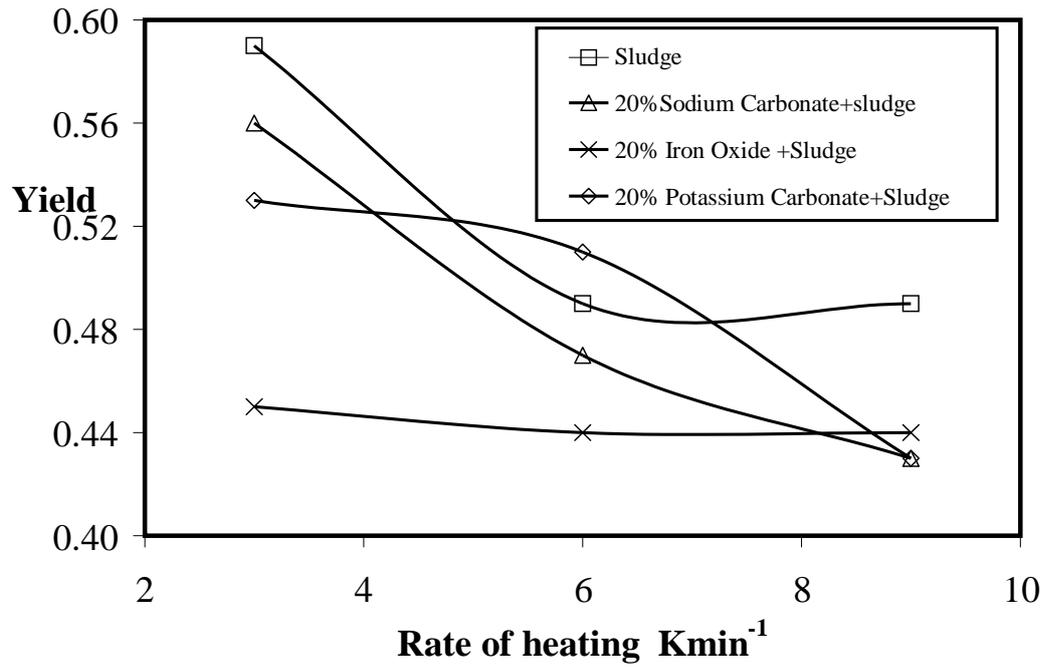


Fig.2. Yield of oven dried sludge with or without additives at different heating rates