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A Comparative Study of Thermal and Thermo-Catalytic Treatment of Used Lubricating Oil Using Cobalt Oxalate as Catalyst

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Abstract

This paper presents a comprehensive comparative analysis of two prominent methods, Thermal and Thermo-Catalytic treatment by using cobalt oxalate as a catalyst (1.0% by wt.) for conversion of used lubricating oil into desirable high value lighter petroleum fractions. The comparison focuses on the utilization of cobalt oxalate as a catalyst in Thermo-catalytic treatment. Through experimentation and analysis, the efficiency, the product yield, quality of products formed and environmental impact of both treatment techniques are evaluated and compared. The experimental results indicate that Thermo-Catalytic treatment with cobalt oxalate as a catalyst exhibits superior performance in terms of higher conversion of used lubricating oil into desirable high value lighter petroleum products and reduced environmental footprints compared to Thermal treatment. The finding of this study provides valuable insights for the development of sustainable used lubricating oil management strategy and the optimization of thermo-catalytic treatment for industrial applications for disposal of hazardous used lubricating oil in environment friendly way generating high value source of energy. It is observed that the yield of high value hydrocarbon fraction obtained from thermo-catalytic treatment is more as compared to thermal treatment.

Keywords: Used Engine Oil, Thermal Treatment, Thermo-Catalytic Treatment, Cobalt Oxalate, Catalyst, ASTM, API

Introduction

The quest for efficient and sustainable methods of hydrocarbon conversion has been a corner stone of chemical engineering and industrial processes. Among all the methodologies, thermal and thermo-catalytic treatment stood out as a fundamental technique for transformation of heavy hydrocarbons to valuable lighter products. The recycling of spent engine oil and reusing it has gained attention from researchers in recent years. The majority of lubricating oil is typically derived from petroleum resources. Fuel or Lube oil base stock (LOBS) can be produced by re-refining and treating waste or used lubricating oil. On the other hand, the used lubricating oil constitutes metallic particles and other contaminates which can cause environment hazards. The high-volume used lubricating oil that was having hydrocarbon with bulk can be turned into desirable high value lighter petroleum fraction by treatments i.e., thermal and thermo-catalytic treatment. In thermal treatment spitting of larger hydrocarbon molecule into smaller molecule is carried out with formation of little amount of residuum where all the impurities including metallic are concentrated so that liquid fraction remains free of such hazardous impurities that have been accumulated in the lubricants over the prolonged use in engines. In thermal treatment the product obtained is moreover heavy gas oil fraction. Hence thermo-catalytic treatment is done. Thermo- Catalytic treatment is the process that can apply variety of feedstock ranging from gas oil to heavy crude oil and residuum. The concept of Thermo-catalytic treatment is same that of thermal treatment but it differs by the use of catalyst that was not in the earlier process and it is one of several practical application in refinery that employ the catalyst to improve process efficiency, product quality and quantity. In India the diesel consumption is more therefore to get more of valuable diesel range fraction from waste engine oil by using 1.0% cobalt oxalate is the objective. And simultaneous study of a thermal and thermos-catalytic treatment is carried out to understand the desirable yield pattern of diesel range fractions obtained and at the same time compare the thermal and thermos-catalytic treatment. This work is carried out with the aim to address the gap by conducting the systematic and comparative analysis of thermal and thermo-catalytic treatment methodologies, elucidating the mechanism efficiency and product distribution. The focus was on the utilization of cobalt oxalate as a catalyst through the comparative study and valuable insights into the advantages and limitations of each approach will be gleaned, paving the way for optimizing hydrocarbon transformation process and contributing to the advancement sustainable chemical engineering processes.

Experimental Procedure

In the study, used lubricating oil sample is collected from various private two-wheeler service station from Amaravati city and mixed together in such way that it from homogenous mixture. Firstly, the used lubricating oil was filtered to remove suspended particles and then heated to 150^{0}C with continuous stirring for 60 min to remove the water content in it. The filtered and dehydrated used lubricating oil was used as a feed for experiments. Various tests of feed are carried out to know characteristics of sample feed i.e., Density, Specific Gravity, API Gravity, Saybolt viscosity, Viscosity Index, CCR and Flash & Fire Point. The experimental results and tests are shown below

Table-1: Properties of Filtered and Dehydrated Used Engine Oil

Sr. No.	Test on Product Fractions	Results
1	Density (gm/ml), at 34^{0}C	0.8491
2	Specific Gravity, at 34^{0}C	0.8551
3	API Gravity (^{0}API), at 34^{0}C	33.9770
4	Viscosity, at 34^{0}C (Saybolt sec)	210
5	Viscosity Index	176.34
6	Conradson Carbon Residue, (wt. %)	1.664
7	Flash Point (Cleveland Open Cup), ^{0}C	215
8	Fire Point (Cleveland Open Cup), ^{0}C	225

Experimental setup

The experiments were carried out in continuous pipe reactor which is made up of stainless steel (SS304) having dimensions 600mm length, 56mm inner diameter (ID), 60mm outer diameter (OD), and flanges of 160mm. Heating coils were wrapped on the reactor covering 400mm length of the reactor using mica sheet for insulation. The reactor was insulated in order to avoid any heat losses from outer side. The reactor was provided with thermowell to measure temperature of the reactor. The digital thermometer was used to measure the temperature having platinum resistance thermocouple, the heating coil were wrapped on the reactor such that the complete area of the reactor is covered. The heating rate was controlled by two dimmerstat each of 1kw. Ceramic packings were used to provide the reaction zone within the reactor. The reactor outlet was connected to the two necks round bottom flask in order to collect the cracked vapors coming out of the reactor which are high value fraction and this round bottom flask is placed in the chilled water bath so it helps in condensing the cracked vapours coming out of the reactor. One end of the two-neck flask was connected to the condenser through which cold water is circulated to avoid the vapour losses of condensable hydrocarbons.

Thermal Treatment

In this experiment, 1000ml (885gm) of feed is cracked by thermal treatment having flowrate of 6.5ml/min, by maintaining the continuous pipe type reactor at 390 ± 10^{0}C. The liquid fractions obtained from the reactor were condensed and collected in the round bottom flask. The high value liquid fractions are obtained in which the liquid product obtained is 695gm, residuum obtained is 10gm and 180gm of feed is gasified. The liquid product obtained from this experiment are subjected to various tests for its characterization purpose.

Thermo-Catalytic Treatment

For this experiment, 1000ml (885gm) of feed is taken in which 1.0 wt.% cobalt oxalate (8.85gm) is used as a catalyst. The feed and catalyst were mixed thoroughly for thermo- catalytic treatment and the feed flowrate was maintained at 6.5ml/min at 390 ± 10^{o}C reaction temperature. The total feed 893.85gm feed is used for this experiment. After attaining the temperature, the charging of feed was started and the vapours started coming out of the reactor indicating start of the reaction. The temperature of the reactor is constantly maintained at 390 ± 10^{o}C. The vapours coming out of the reactor were condensed and collected in the two-neck round bottom flask and the product obtained is subjected to various tests for characterization.

Liquid product and residuum obtained formed Thermal and Thermo-Catalytic treatment inthese experiments were measured for material balance. In thermal treatment, the liquidproduct obtained is 695gm, 10gm of residuum is obtained and 180gm of feed was gasified.Similarly In thermo-catalytic treatment the liquid product obtained is 745gm, 17gm of residuum is obtained with traces of catalyst and 131.85gm of feed was gasified.

Table 2: Material Balance of An Experimental Run

Sr. No.		Product by Thermal Treatment	Product by Thermo-Catalytic Treatment
1	Flow R ate (ml/min)	6.5	6.5
2	Cracking temperature, ^{o}C	390±10	390±10
3	Feed, gm	885	885
4	Catalyst (gms), 1% by wt.	NIL	8.85
5	Total Feed, gm	885	893.85
6	Liquid products obtained, gm	695	745
7	Liquid products obtained, % (wt.)	78.53	84.18
8	Gaseous products obtained, gm	180	131.85
9	Gaseous products obtained, % (wt.)	20.34	14.82
10	Residue obtained, gm	10	8.85
11	Residue obtained, % (wt.)	1.13	1.0
12	Total amount of Product Formed (liquid + gases), gm	875	876.85
13	Conversion, % (wt.) = Liquid product, %(wt.) + gases formed, % (wt.)	98.87	99

The liquid fraction obtained from Thermal and Thermo-Catalytic treatment in presence of cobalt oxalate (1% by wt.) as a catalyst were subjected to detailed analysis & various tests such as ASTM distillation (IP123/93), Sayboult viscosity (IP71/73 3rd edition), Specific Gravity, Aniline Point (IP2/91,ASTM D611-87, ISO 2977:1989(E)), Conradson Carbon Residue (CCR) (IP13/82,ASTM D189-88, BS:2000 Part 13:1993), Pour Point (IP15/67,ASTM D97-87, BS:2000:Part 15:1993), Flash and Fire Point by Clevland Open Cup Method (IP 36/84(1989), ASTM D92-90)), Total Acidity (IP 1/74 (1990), BS 2000: Part 1:1993)) Bromine Number (IP129/93, BS2000 :Part 129:1993) etc.

Table 3: Properties of Thermal & Thermo-Catalytically Treated Liquid Products

Sr. No.	Products Tests / Properties	Product by Thermal Treatment	Product by Thermo-Catalytic Treatment
1	Density (gm/ml), at 34^{0}C	0.8433	0.850
2	Specific Gravity, at 34^{0}C	0.8349	0.8415
3	API Gravity (^{0}API), at 34^{0}C	37.9813	36.6521
4	Viscosity, at 34^{0}C (Saybolt sec)	56	101
5	Kinematic Viscosity, (m^2/sec)	9.90	20.88
6	Conradson Carbon Residue, (wt. %)	0.110	0.6609
7	Flash Point (Cleveland Open Cup), ^{0}C	75	135
8	Fire Point (Cleveland Open Cup), ^{0}C	85	183
9	Aniline Point, ^{0}C	106	56
10	Pour Point, ^{0}C	- 9	Less than -10
11	Bromine Number	3.0730	2.5885
12	Acid Value, mg KOH/gm	1.01	0.523

ASTM Distillation characteristics of product obtained from the Thermal and Thermo- Catalytic Treatment in presence of cobalt oxalate (1.0% by wt.) as a catalyst shows that in thermal treatment 5.0% (vol.) material falls in the naphtha range fraction (<200°C), 25% (vol.) material falls in light gas oil range fractions (200-350°C) suitable for blending in refinery diesel fraction and around 65% of fractions falls in heavier gas oil range fraction where material boils in the range of 350 to 380°C and this fraction is also suitable for blending in the refinery diesel stream. In thermos-catalytic treatment 4.5% (vol.) material falls in the naphtha range fraction (<200°C), 45% (vol.) material falls in light diesel range fractions (200-350°C) suitable for diesel steam blending in the refinery and around 45% of fractions in the heavier gas oil range fraction that boils in the range of 350 to 370°C and again this fraction is also suitable for the diesel stream blending in the refinery. Details of ASTM characteristics of liquid products obtained from thermal as well as thermo-catalytic treatment are shown in the following Table-4.

Table 4: ASTM Distillation of Product Obtained by Thermal Treatment

Sr. No.	Time (min)	Temp (^{o}C)	% Distillate	Observations
1	00	30.4	---	Heating Started
2	28	44.8	---	Foaming Started
3	62	94.4	---	Foaming Disappeared
4	91	121.9	---	IBP Observed
5	115	307.1	10	
6	124	329.4	20	
7	130	338.0	30	
8	134	346.5	40	
9	138	350.5	50	
10	142	355.6	60	
11	147	356.9	70	
12	150	363.8	80	
13	152	365.5	90	
14	155	368.4	94.5	FBP Observed

Total Distillate Collected = 190ml = 95%, Residuum = 7.5ml = 3.75%,Losses = 2.5ml = 1.25%

Table 4: ASTM Distillation of Product Obtained by Thermo-Catalytic Treatment

Sr. No.	Time (min)	Temp (^{o}C)	% Distillate	Observations
1	00	32.5	---	Heating Started
2	65	55.7	---	Foaming Started
3	85	104.6	---	Foaming Disappeared
4	88	130.0	---	IBP Observed
5	128	265.8	10	
6	132	318.7	20	
7	147	358.0	30	
8	151	367.6	40	
9	164	369.2	50	
10	172	370.2	60	
11	185	375.4	70	
12	191	376.4	80	
13	209	377.4	90	
14	213	378.6	95	FBP Observed

Total Distillate Collected = 189ml = 94.5%, Residuum = 8ml = 4%Losses = 3ml = 1.5%

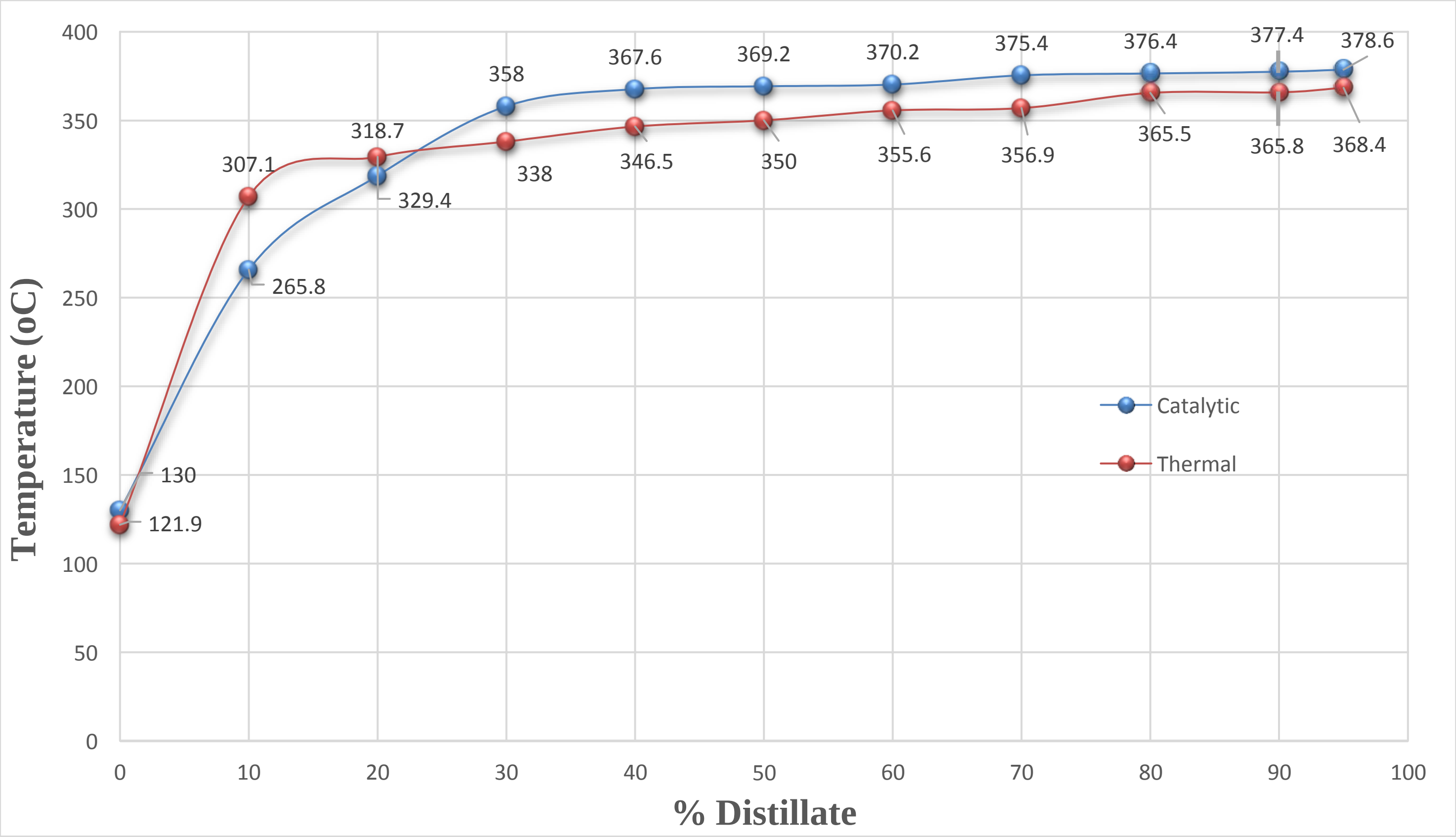

Figure 1: ASTM Distillation Characteristics of Distillate Obtained from Thermaland Thermo-Catalytic Treatment

Energy Consumption

Treatments		Energy Generated (Kcal.)	Energy Consumed (Kcal.)
Thermal	For Gaseous obtained	2142	4299.226
	For Liquid boiling below 200°C	3822.5	
	For Liquid boiling range in between 200-350°C	1859.125	
	For Liquid boiling above 350°C	4219.625	
	For Residue obtained	42	
Total Energy for Thermal Treatment		**12085.25**	**4299.226**
Thermo-Catalytic	For Gaseous obtained	1588.65	4299.226
	For Liquid boiling below 200°C	3687.75	
	For Liquid boiling range in between 200-350°C	3587.068	
	For Liquid boiling above 350°C	3184.78	
	For Residue obtained	27.3	
Total Energy for Thermo-Catalytic Treatment		**12075.54**	**4299.226**

Conclusion

In conclusion, this comparison strictly sheds light on the efficiency of thermal and thermo- catalytic treatment process in the conversion of used lubricating oil into desirable high value petroleum fraction. Both methods have dominated their potential in enhancing product yields and quality. The Thermal and Thermo-Catalytic Treatment of used lubricating oil using cobalt oxalate as a catalyst was conducted at a constant temperature of 390±10°C and a constant feed rate of 6.5 ml/min. The results of the thermal treatment process were 20.34% (wt.) hydrocarbon gases, 78.53% (wt.) liquid products, and 1.13%(wt.) residuum. In the thermo-catalytic treatment of used lubricating oil at 390±10°C with (1.0% by wt.) cobalt oxalate was present. Thus, result obtained was 1.0%(wt.) residuum, 84.18% (wt.) liquid products, and 14.82% (wt.) hydrocarbon gases. It is evident from a number of tests including Viscosity, Conradson Carbon Residue (CCR), Flash Point, and Fire Point, that temperature and catalyst cobalt oxalate (1.0% by wt.) had an impact on the degree of cracking. It is possible to observe Differences in the product's characteristics from both cracking processes. Because of the catalyst and constant high temperature, there were no contaminants in the product formed as all the contaminants were concentrated in the residue. The catalyst can be recycled and reused after regeneration. The capacity to modify process operating parameters to customize the desired result was a major feature of the thermal treatment and thermo-catalytic treatment processes. Operating parameters in this process may be changed to change the product's boiling range as a result, the process can also be changed to maintain a target product quality even in the event of feed quality fluctuation. These products therefore comprise high-value refinery product streams, which may be processed further along with the corresponding refinery streams. The liquid and gaseous fractions obtained are free of any pollutants since contaminates were build up in residuum. Consequently, these products create high value refinery streams. It should be noted that the problems related to the used lubricating oil treatment by vacuum distillation, such as fouling of heating and distillation equation can be avoided by thermal and thermos-catalytic treatment of used lubricating oil by using cobalt oxalate as a catalyst (1.0% by wt.). This may be one of the best methods of preserving the precious oil and slowing down the rate at which the crude oil is being depleted. This way used lubricating oil can be used as a best source of fuel. Recycling not only generate energy but also lowers air, water and land pollution, also slows down the depletion of most valuable resource. An important environmental issue is improper handling of used lubricating oil. Nearly every kind of used lubricating oil has the potential to be recycled safely, reducing environmental pollution and preserving a valuable non-renewable resource. Having negative environmental impact, used lubricating oil can save lots of money & energy on a new crude oil if it is properly recycled & reused. Disposal of used lubricating oil into the ecosystem creates environmental hazards. Several regulations are being passed globally about the disposal of spent petroleum fractions, and every sincere attempt ought to be made to reuse them. In order to meet changing energy market demands while minimizing environmental effects, a comprehensive strategy that incorporates the advantages of both thermo-catalytic and thermal treatments, as well as innovations in catalyst design, process optimization, and integration with renewable feedstocks, appears highly promising.

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