# Cracking of Waste Engine Oil in Presence of Cobalt Oxalate

**A. L. Rathod**
Assistant Professor,
Deptt.of Chemical Technology,
Sant Gadge Baba Amravati
University,
Amravati

## Abstract

Nowadays, demand for lube oil is increasing because of increased use of vehicles. This increased use of lube oil is generating almost 60% of waste engine oil. It is estimated that worldwide over 25 million tons waste engine oil is generated annually worldwide. Waste lube oil consists of various organic compounds other than hydrocarbons; it contains solvent, heavy metals, combustion products etc.If not disposed off carefully these components harm the environment and are very difficult to get rid of these components (e.g. soot, Poly-cyclic aromatic hydrocarbons (PAHs). Generally, to get rid of waste oil, simple methods of Incineration and Combustion for Energy Recovery and Vacuum Distillation and Hydro-Treatment for Re-Refining are practised. However, these methods can only get rid of the chemical value of waste and they become increasingly impracticable because of concerns over environmental pollution due to combustion products. These processes even involved difficulties and additional costs of sludge disposal, recognized due to the undesirable contaminants present in waste oil. Catalytic Cracking is the unique environment friendly technique to get rid of waste lube oil. Temperature, pressure, reactor type, type of material is having direct effect on catalytic cracking which results differently to form hydrocarbon oils, gases and coke. Oil and gas are the end products having high calorific value. Advantage of catalytic cracking process is gaining 86% oil, 10% gas, rest is residue.The study of catalytic cracking technique is done to explore yield (product quantity, qualification of catalytic cracking of oil, especially Hydrocarbon composition using cobalt oxalate as a catalyst) to the benefits of society and industry. Indeed, this technique can reduce costs from imported technology and produce alternative choice of energy from wastelube oil and thereby reduce the imports of crude oil.

**Keywords:** Waste Engine Oil, Cracking, Combustion Products, Degradation Products, Petrochemicals, ASTM, $^{O}$API, Waste to Energy, Recycling Waste, Cracking.

## Introduction

The study of catalytic cracking of waste engine oil is done to explore yield of valuable products (product quantity,qualification of catalytic cracking of oil, especially Hydrocarbon composition using cobalt oxalate as a catalyst) to the benefits of society and industry.

Objective of this work is conservation of precious resource and environment protection. Little reduction in imports of high value oil can result in saving valuable foreign exchange.Efforts for regeneration or converting this waste/used oil to valuable petroleum products can result in making it a highly valuable resource.

Therefore it can be said that, used oil, a valuable resource, is wasted if improperly disposed off.Conserving and utilizing it more effectively means directly boosting country’s energy resources.Immediate effect of such conservation can be small but effective reduction in energy imports as our country is almost totally dependent on crude oil / lube base oil imports.All these efforts can result in saving of huge amount of foreign exchange and utilizing better the countries financial resources.

When used oil is dumped, it is capable of seeping into ground and surface water.Just one liter of used oil can render one million liters of water undrinkable.It is also a serious threat to plant and animal life.Marine species can be adversely affected by oil concentrations as low as one ppm. Loss of plants and animal life, while tragic, also results in economic loss.When used oil is burnt, it results in the incomplete combustion, thus increasing the air pollution. Hence, re-refining or converting used oil to other valuable products is much better option over burning or other means of disposal or re-use. And thus checks environmental degradation and saves ecology.

**Experimental Procedure**

In this study, waste engine oil was collected from different private two wheeler service stations in Amravati city and mixed together to form a single homogeneous sample.

**Table-1**
**Properties of Filtered and Dehydrated Waste Oil**

| S.N. | Property | Observations |
|---|---|---|
| 1. | Redwood Viscosity | a) at 40 $^{o}$C - 424 seconds.<br>b) at 100 $^{o}$C -61 seconds. |
| 2. | Specific Gravity at 29 $^{o}$C | 0.8885 |
| 3. | API Gravity at 29 $^{o}$C | 27.7589 $^{o}$API |
| 4. | Pour Point | -24 $^{o}$C |
| 5. | Flash Point (Clevland Open Cup method) | 193 $^{o}$C |
| 6. | Fire Point (Clevland Open Cup method) | 252 $^{o}$C |
| 7. | Conradson Carbon Residue (wt %) | 0.9088% |

Cobalt-based catalysts are important in reactions involving carbon monoxide; steam reforming also uses cobalt oxide-base catalysts. Use of cobalt oxalate in gasification of hydrocarbon stocks is well established. Cobalt is also a catalyst in the Fischer Tropsch process. The hydrodesulphurization of petroleum uses a catalyst derived from cobalt and molybdenum. The hydroformylation of alkenes often rely on cobalt octa-carbonyl as the catalyst, although such processes have been partially displaced by more efficient iridium- and rhodium-based catalysts. Therefore cobalt based catalysts i.e. Cobalt Oxalate **[**$CoC_2O_4$] is considered for the cracking of waste engine oil.

A 3 liters batch reactor prepared for this purpose is used to perform the experiment, which is of 90 mm height and 206 mm diameter.

1200ml (1090.5gms) of feed is cracked in the batch reactor at 420$^{0}$C in presence of 1.0% cobalt oxalate. At 394$^{0}$C vapors starts coming out of the reactor indicating the start of cracking reactions. The temperature of the reactor is immediately raised and maintained at 420$^{0}$C as closely as possible. 939.7gms of distillate (cracked product) is collected and 40.89gms of residue is obtained from the experiment. Total material balance on reactor indicates that 109.92gms of feed is gasified; 939.7gms of liquid products are obtained while 40.89gms of residue is formed.

**Table-2**
**Material Balance**

| S. N. | Products | Products Obtained, Gms | % Products Obtained |
|---|---|---|---|
| 1. | Liquid product obtained, (gms) | 939.7 | 86.17 |
| 2. | Residue formed, (gms) | 40.89 | 03.75 |
| 3. | Feed gasified, (gms) | 109.92 | 10.08 |
| 4. | Total amount of product formed (liquid+gases), gms | 1049.62 | 96.25 |
| 5. | Time required to start liquid collection, (mins) | 43 | ----- |
| 6. | Time required from 400$^{o}$C to completion of cracking, (mins) | 49.00 | ----- |
| 7. | Total time required for cracking, (mins) | 93 | ----- |

**Table-3**
**Properties of Products Obtained**

| S.N. | Properties | Observations |
|---|---|---|
| 1. | Redwood viscosity, seconds, at 40$^{0}$C | 43 |
| 2. | Specific gravity,at 29$^{o}$C | 0.8409 |
| 3. | API Gravity, $^{o}$API at 29$^{o}$C | 36.7721 |
| 4. | Aniline point,$^{o}$C | 77.5 |
| 5. | Flash point (Clevland open cup method),$^{o}$C | 39 |
| 6. | Fire point (Clevland open cup method), $^{o}$C | 56 |
| 7. | Conradson carbon residue, wt% | 0.0195 |
| 8. | Pour point, $^{o}$C | -13 |
| 9. | Bromine number | 3.83 |
| 10. | Acid value, mg KOH/gm | 0.5991 |

Liquid products obtained are subjected to various tests such as Distillation characteristics (IP123/93), Redwood viscosity (IP70/62 25th edition), Specific gravity (API 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 D 97-87, 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. (19,20)

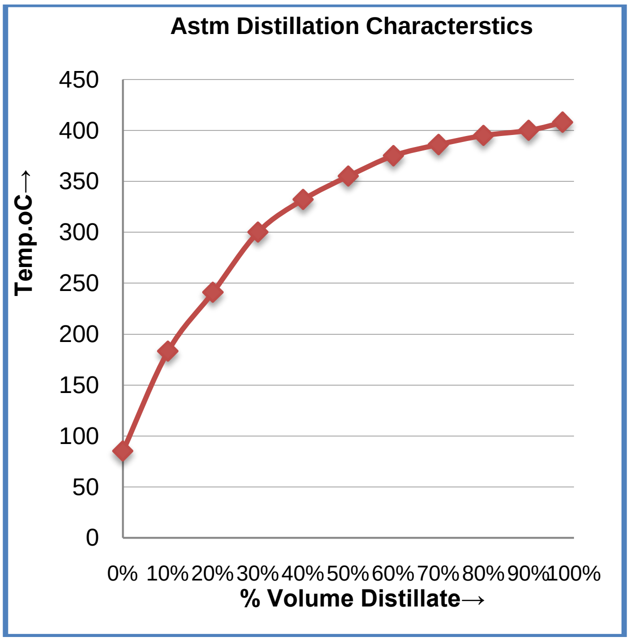
The gaseous products obtained can be a very good feedstock for petrochemicals or can be used as a fuel in the industry. ASTM distillation characteristics of the product obtained from this experiment shows that around 12.5%(vol.) material falls in the gasoline range (<200$^{o}$C), 62.5%(vol.) material falls in the gas oil range (200-390$^{o}$C) i.e. dieseland around 22.5% (vol.) material boils in the range of 390$^{o}$C-408$^{o}$C. While 0.75% residue collected from distillation flask; 1.75% vapor losses occurred during the distillation. Details of the ASTM distillation characteristics of liquid products obtained are shown in Table-4.

**Table-4**
**ASTM Distillation Characteristics of Distillate Obtained**

| S.N. | Time (mins.) | Temp. °C | % Volume Distillate | Observations |
|---|---|---|---|---|
| 1. | 00 | 40 | --- | Heating Started |
| 2. | 25 | 85 | --- | I.B.P. |
| 3. | 55 | 183 | 10 | Foaming Observed |
| 4. | 65 | 241 | 20 | |
| 5. | 72 | 300 | 30 | |
| 6. | 74 | 332 | 40 | |
| 7. | 76.5 | 355 | 50 | |
| 8. | 79 | 375 | 60 | |
| 9. | 81 | 386 | 70 | |
| 10. | 83 | 395 | 80 | |
| 11. | 85 | 400 | 90 | |
| 12. | 88 | 408 | 97.5 | Final Boiling Point |

**Total Distillate Collected**: -- 97.50%, Residue: -- 0.75%, Losses: -- 1.75%.

**Figure-1**
**ASTM Distillation Characteristics of Distillate Obtained**



**Aim of the Study**

Objective of this work is conservation of precious energy resource and environment protection.

**Conclusion**

The catalytic cracking of waste engine oil at 420°C in presence of 1.0% cobalt oxalate yields 10.08% (wt) hydrocarbon gases, 86.17% (wt) liquid products and 3.75% (wt) residue. The viscosity, specific gravity/API gravity, flash point and fire point of products indicates the extent of cracking occurred. As all the contaminants accumulate in residue, the liquid and gaseous products obtained are free from all type of contaminants that makes these products as clean as virgin fractions obtained in the refinery. So these products forms high value refinery streams, 62.5% products can be blended with diesel fraction and 12.5% products are suitable to blend in gasoline range product.

It should be noted that the problems related to used oil treatments either by vacuum distillation (such as fouling of heating and distillation equipment), or by using it as a fuel in cement kilns, furnaces etc. which have potential to cause serious harms to the environmentcan be avoided by catalytic cracking of these oils in presence of cobalt oxalate.

This can be one of the ways to conserve the valuable oil and reducing the rate of depletion of crude oil. So used lubricating oil may again be a source of fuels. Recycling doesn't just slow the depletion of number one resource; it also saves energy and reduces the pollutions of land, water and air. Mismanagement of waste lube oil is a serious environmental as well as economical problem. Almost all types of waste oil have the potential to be recycled safely, saving a precious non-renewable source and at the same time minimizing environmental pollution. Besides its great adverse impact on the environment, if used oil is properly recycled and/or reused, it could have significant savings on fresh crude oil. Disposal of used lubricating oil into the eco-system creates environmental hazards. Tough laws are being enacted throughout the world for the disposal of waste petroleum products and every genuine effort should be made for its re-use.

**References**

1. G. Warmate, T. J. K. Ideriah, I. T. Tamunobereton A. R. I., U. E. UdonamInyang and T. Ibaraye, Concentrations of heavy metals in soil and water receiving used engine oil in Port Harcourt, Nigeria, Journal of Ecology and the Natural Environment Vol. 3(2), pp. 54-57, February 2011.
2. Odjegba V J, Atebe J O, The effect of used engine oil on carbohydrate, mineral content and nitrate reductase activity of leafy vegetable (AmaranthushybridusL.), J. Appl. Sci. Environ. Manage. June, 2007, Vol. 11 (2) 191 – 196.
3. Fidelis I Achuba, Spent Engine Oil Mediated Oxidative Stress In Cowpea (Vignaunguiculata) Seedlings, Electronic Journal Of Environmental, Agricultural and Food Chemistry, 9 (5), 2010. [910-917].
4. J. Kayode, A.A. Oyedeji, and O. Olowoyo, Evaluation of the Effects of Pollution with Spent Lubricating Oil on the Physical and Chemical Properties of Soil, The Pacific Journal of Science and Technology, Volume 10. Number 1. May 2009 (Spring) (387-390).
5. Okonokhua B O, Ikhajiagbe B, Anoliefo G O, Emede T O, The Effects of Spent Engine Oil on Soil Properties and Growth of Maize (Zea mays L.),J. Appl. Sci. Environ. Manage. September, 2007 Vol. 11 (3) 147 – 152.
6. Thallada Bhaskar, MdAzhar Uddinb, Akinori Muto, Yusaku Sakata,Yoji Omura, Kenji Kimura, Yasuhisa Kawakami, Recycling of waste lubricant oil into chemical feedstock or fuel oil over supported iron oxide catalysts, Fuel 83 (2004) 9–15, Elsevier Ltd. (Available on Science Direct).
7. Jesusa Rincon, Pablo Canizares, Maria Teresa Garcia, Regeneration of used lubricant oil by ethane extraction, J. of Supercritical Fluids 39

(2007) 315–322, Elsevier B.V. (Available on Science Direct).
8. Su Shiung Lam, AlanD.Russell, Howard A.Chase, Microwave pyrolysis, a novel process for recycling waste automotive engine oil, Energy 35(2010)2985-2991, Elsevier Ltd. (Available on Science Direct).
9. M. M. Rahman, T. A. Siddiquee, S. Samdani and K. B. Kabir, Effect Of Operating Variables On Regeneration Of Base-Oil From Waste Oil By Conventional Acid-Clay Method, Chemical Engineering Research Bulletin 12 (2008) 24-27.
10. H. Bridjanian, M. Sattarin, Modern Recovery Methods In Used Oil Re-Refining, Petroleum & Coal 48 (1), 40-43, 2006.
11. Amnat Permsubscul, Tharapong Vitidsant and SomsakDamronglerd, Catalytic cracking reaction of used lubricating oil to liquid fuels catalyzed by sulfated zirconia, Korean J. Chem. Eng., 24(1), 37-43 (2007).
12. Mithilesh Kumar Jha, Re-refining of Used Lube Oils: An Intelligent and Eco-friendly Option, CHEMCON 2003(209-211), at Bhubaneswar.
13. Steve Boyde, Green Lubricants. Environmental benefits and impacts of lubrication, The Royal Society of Chemistry 2002, Green Chemistry, 2002, 4, 293-307.
14. Basic Statistics on Indian Petroleum & Natural Gas Ministry of Petroleum & Natural Gas Government of India New Delhi (Economic Division) http: // petroleum .nic.in/petstat.pdf
15. M K Chaudhari Fuel Efficiency Policies for HDVs– Indian Perspective http ://www.iea. org / work /2007/vehicle/Chaudhari.pdf.
16. Jhanani. S 1, Kurian Joseph, Used oil generation and management in the automotive industries, International journal of applied engineering research, Dindigul, Volume 2, No 1, 2011.
17. Joel Ogbonna F and Ovuru Samuel E, Comparative study of different media in reduction of pollutants in used lubricating oil, Nigeria- A case study, ARPN Journal of Engineering and Applied Sciences, Vol. 4, No. 8, October 2009.
18. Latif H. Ali and Khalid A. Al-Ghannam, Studies on reclaiming spent lubricating oils, FUEL, 1980, Vol 59, October.
19. Institute of Petroleum London, Standard methods for analysis and testing of petroleum and related products, Volume I, Published on behalf of the Institute of Petroleum, London by J. Wiley, 1993, page 1.1-1.2, 2.1-2.6, 13.1-13.4, 15.1-15.3, 16.1-16.3, 36.1-36.3, 123.1-123.14, 129.1-129.3,.
20. Institute of Petroleum London, Standard methods for analysis and testing of petroleum and related products, Volume II, Published on behalf of the Institute of Petroleum, London by J. Wiley, 1993.