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Conversion of Waste Engine Oil (Lubricant) to High Value Products using Ceramic Beads as a Catalyst

Abstract

Lubricating oil is an important resource and a petroleum base product. The high price of lube oil and objective of saving valuable foreign exchange is resulting in efforts for regeneration of used engine oil and/or it's conversion to valuable products. Mismanagement of waste engine oil has a serious worldwide environmental problem, unfortunately, most of used oil is handled improperly, and some is dumped into sewers for going directly into waste water. Some is dumped directly into the ground to kill weeds or is poured into dirty roads or is dumped in deserts, where it could contaminate surface and ground water, in some cases it is used for heating purposes resulting in air pollution. All of these mismanagement and disposal ways are adversely affecting the environment.

Recycling of used oil became the need of hour due to economic, environmental, public health and legal reasons. Using waste engine oil as a source of energy or feedstock for chemical industries is a good option for any country, importantly for India, as it would conserve both the valuable natural resources as well as foreign exchange.

Used automotive engine oil (Lubricant) is cracked at 420^{o}C in presence of ceramic beads, with the intention of assessing the suitability of the process in recovering valuable products from this otherwise difficult to dispose off waste engine oil. The resulting cracked gases condensed into liquid oil, the yield and properties of the recovered products were determined. The recovered cracked liquid and gaseous products can be used as a valuable fuel and/or as an industrial feedstock. The results indicate that cracking of waste engine oil in presence of ceramic beads shows extreme promise as a means for disposing off problematic waste engine oil. The recovery of commercially valuable products from waste engine oil shows advantage over traditional, more destructive disposal methods.

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World lubricant demand increases at 1.6 percent per year to 40.5 million metric tons in 2012. In India the current demand for lube oil is of the order of more than10 lakh tonnes per year. Out of this, almost 60% accounts for automotive and the rest of 40% for industrial lubricants. Indian crude is predominantly waxy, hence, not suitable for lubricating base oil production. In fact, our entire lube oil production is based upon imported lube bearing crude. Huge amount is spent every year towards procurement of lube base stocks and importing the crude oil to meet increasing demand of fuels. More than 75% of total requirement of crude oil is imported from the other countries to meet the rising demand of fuels, lubricants and petrochemicals. (14, 15)

After use, waste engine oils are considered a hazardous waste. After a certain period of useful life, they lose their properties and cannot be used as such in machinery because of their high content of thermal degradation products and combustion products from the fuel and lubricant. (6, 7, 8, 9, 10, 18). Composition of Used Oil Lubricating oil does not wear out during use. It is only the additive part, which gets depleted (18). The oil molecules are not degraded, but because of presence of following contaminants, oil needs replacement:

1. Free and emulsified water.
2. Light hydrocarbons, i.e., gasoline and gas oil.
3. Dust, rust and soot.

4. Metals (iron, copper, zinc, lead, calcium, phosphorus etc.) resulting from engine wear and corrosion.
5. Gasoline/diesel and lube additives.
6. Products of thermal degradation, i.e., carbon, unsaturated hydrocarbons, polymers and asphaltenes.
7. Complex compounds from additive packages. (10, 12, 17)

In our country, re-refined oil is generally termed as spurious. This is the possible reason that is why; the very concept of re-refining could not become successful in our country. In developed countries, re-refined oil is not regarded as spurious. It is rather regarded as an important source of non-conventional energy. There exist well defined guidelines for its (used oil) collection, transportation, processing and re-use (16). As the increased cost of utilizing depleting natural resources is being recognized, the HW (Hazardous waste) Rules 2008 allows for recycling/re-processing of selected group of HW which includes used oil & waste oil. In recent years environmental considerations regarding the conservation of resources have further boosted interest in recycling spent oil which helps in the following ways.

1. Conservation of valuable oil reserves by using the oil again and again.
2. Significant saving of foreign exchange.
3. Checks environmental degradation and saves ecology.
4. Recycling reduces the burden on storage and disposal facilities
5. Recycling also leads to significant reduction of carbon foot print.

The waste engine oils are not toxic, but the contaminants such as additives, degradation products, etc. make them so hazardous. They have high potential to cause damage to the environment by virtue of their persistent nature and potential to spread over large surface areas on land and water. Films of oil prevent light and air from reaching to life forms of all types on land and water, one liter of oil can render one million liters of fresh water unusable. It is also a serious threat to plant and animal life (1,2,3,4,5,13). Marine species can be adversely affected by oil concentrations as low as one ppm. The oil film on water blocks sunlight, making it harder for plants to photosynthesize. Loss of plants and animal life, while tragic, also results in economic loss. When used oil is burnt, the presence of various contaminants and usually high water content, results in the incomplete combustion, thus increasing the air pollution. Hence, re-refining is a much better option. (6,7,8,9,10,11,12,)

For these reasons, most of the countries in the world have classified used oil as hazardous waste and introduced regulations for its collection, handling and disposal. These regulations clearly recommend re-refining of used oils over burning or other means of disposal. (1,2,3,4,5)

Unlike virgin crude oils, re-refined oil is a renewable source of energy. Re-refining or recycling of used oils helps in the following ways:

1. Conservation of valuable oil reserves by using the oil again and again.
2. Saving of huge amount of foreign exchange.
3. Checks environmental degradation and saves ecology. (12).

Sample

In this study, waste engine oil is used as a sample collected from different private two wheeler service stations in Amravati city and mixed together to form a single homogeneous sample. This sample is a typical feedstock for the experiment.

Prior to the runs the oil was filtered to remove solid particle and then heated to 150^{o}C with continuous stirring and maintained for one hour to eliminate water. This filtered and dehydrated waste oil (FDWO) was used as starting material for the experiment.

Thermal cracking, visbreaking, catalytic cracking, fluid catalytic cracking, hydrocracking, and coking are all well-known crude oil refinery processes based on the basic principle of breaking large hydrocarbon molecules into smaller ones thus increasing the production of high value light products from the heavy portion of crude oil as the Lighter fuels are generally more valuable than heavier ones. Gasoline for example, is more valuable than diesel fuel.

Cracking process can be successfully applied for manufacturing distillates from a used oil feedstock. The significant aspect of this technology is its ability to adjust process operating conditions to tailor the desired products. This can be a tremendous advantage in used oil processing due to the variability of the used oil feedstock. It follows that the process parameters can be adjusted to vary the boiling range of product; the process can also be manipulated to maintain a target product quality with feed variability.

Catalytic cracking technology is emerging as the technology of choice for progressive companies as they consider environment friendly technology based choices. Conversion of used oil to gasoil is desirable from an environmental point of view since the product displaces the need to consume a virgin distillates produced from crude oil. This could be a significant benefit to the world environment in aiding to solve the used oil problem. Of all the methods of processing used oil to be consumed for its calorific value, the catalytic conversion to distillates technology is the highest form of processing method available, from an economical and environmental viewpoint.

Waste engine oil (two wheeler petrol engine) is used as a feedstock for cracking. Ceramic beads are used as the catalyst for this process. The used oil is filtered to remove the solid particles and removed moisture by maintaining 150°C temperature for one hour. This filtered dehydrated waste oil (FDWO) is used as the feedstock for the experiment. Basic tests of this sample are done, e.g. Redwood viscosity, pour point, viscosity index and CCR. The results of these tests are shown in Table-

Table-1
Properties of Filtered and Dehydrated Waste Engine Oil

S. N.	Property	Observations
1.	Redwood Viscosity	a) at 40°C--- 424 seconds. b) at 100°C---61 seconds.
2.	Specific Gravity at 29°C	0.8885
3.	API Gravity at 29°C	27.7589°API
4.	Pour Point	-24°C
5.	Flash Point By Clevland Open Cup Method	193°C
6.	Fire Point By Clevland Open Cup Method	252°C
7.	Conradson carbon Residue (wt%)	0.9088%

1200ml (1090.5gms) of feed is cracked in the batch reactor at 420°C in presence of 15% ceramic beads. At 400°C vapors started coming out of the reactor indicating the start of cracking reactions. The temperature of the reactor is immediately raised and maintained at 420°C as closely as possible. As the reaction reached to completion, vapors stopped coming out of the reactor, heating stopped and allowed the reactor to cool. 917.81gms (1032ml) of distillate is collected and 45gms of residue is collected from the reactor. Total material balance on reactor indicates that 127.69gms of feed is gasified.

Liquid products and residue formed in the experiments were measured for the material balance. And the liquid products were subjected to various tests such as ASTM distillation (IP123/93), Redwood viscosity (IP70/62 25th edition), Sp. 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. (19,20)

ASTM distillation characteristics of the product obtained from this experiment shows that around 12%(vol) material falls in the naphtha range (<200°C), 68%(vol) material falls in the gas oil range (200-390°C) and around 20% (vol) material boils in the range of 390°C-415°C. Details of the ASTM distillation characteristics of liquid products obtained are shown in Table-2.

Table-2
ASTM Distillation Characteristics of Distillate Obtained from the Experiment

S.N.	Time (mins.)	Temp.°C	% Volume Distillate	Observations
1.	00	42	---	Heating Started
2.	25	81	---	I.B.P.
3.	44	171	10	Foam Disappeared
4.	52	253	20	
5.	56	300	30	
6.	60	338	40	
7.	62	359	50	
8.	65	374	60	
9.	67	383	70	
10.	70	390	80	
11.	73	406	90	
12.	76	415	98.5	Final Boiling Point

Total Distillate Collected: -- 98.50%, Residue: -- 0.5%, Losses: -- 1.0%

Figure-1: ASTM Distillation Characteristics of Distillate Obtained from the Experiment

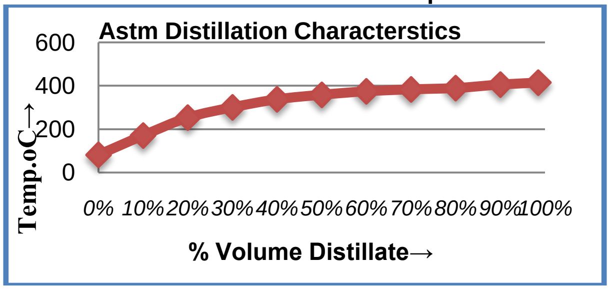

Table-3
Material Balance of an Experimental Run.

S.N.	Cracking Temp.°C→	420
1.	Feed (gms)	1090.50
2.	Liquid product obtained (gms)	917.81
3.	% Liquid product obtained	84.16
4.	Residue formed(gms)	45.00
5.	% Residue formed	04.12
6.	Amount of feed gasified (gms)	127.69
7.	% Amount of feed gasified	11.71
8.	Total Amt. of product formed (liquid+gases) gms	1045.50
9.	% Total conversion	95.87
10.	Time required from 400°C to completion of Cracking (mins)	48
11.	Total time required for cracking (mins)	110

Table-4
Properties of Cracked Liquid Product Obtained

S.N.	Cracking Temp.°C→	430
1.	Redwood viscosity (Sec.) at 40oC	44.00
2.	Specific gravity (at 29°C)	0.8371
3.	API gravity (at 29°C), °API	37.5359
4.	Aniline point (°C)	83.5
5.	Flash & Fire Point by Clevland open cup method, (°C)	48 /60
6.	Conradson carbon residue (wt %)	0.069
7.	Pour point (°C)	-15
8.	Bromine number	6.33
9.	Acid value, mg KOH/gm	2.063

Conclusions

The catalytic cracking of waste engine oil at 420°C yields 11.71% (wt) hydrocarbon gases, 84.16% (wt) liquid products and 4.12% (wt) residue. The viscosity, specific gravity/API gravity, flashpoint 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. So these products forms high value refinery streams which can be further processed with suitable refinery streams. It should be noted that the problems related to used oil treatments by vacuum distillation, such as fouling of heating and distillation equipment can be avoided by catalytic cracking of these oils, even though in presence of simple economical catalyst such as ceramic beads.

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.

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