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Study of Thermal Cracking of Used Lubricating Oil to Produce Gasoline

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Abstract

Used lube oil (ULO) was thermally cracked under different parametric conditions such as molar ratio of used lube oil to diesel; cracking temperature and cracking time to optimize the yield of the final product. The cracked product was increased gradually with the increase in temperature and time. After a certain time and temperature, no significant increase in yield was observed. Thermo gravimetric analysis (TGA) of cracked product was done to observe the volatility of its constituents. Then the cracked oil was fractionated by atmospheric distillation unit. Products obtained from different experiments under different conditions showed almost similar physico-chemical properties. So, optimization was done on the basis of yield (% wt).The optimum yield of cracked distillate (%wt) was obtained under the following experimental conditions: molar ration of used lube oil (ULO) to diesel = 95: 05, cracking temperature 450 ^{0}C, and cracking time 30 minutes. Cracked distillate properties such as density, water content, ash content, pour point, flash point, viscosity, sulfur content, carbon residue, octane number etc. were found similar to that of commercial gasoline.

Keywords: Used Lube Oil, Thermal Cracking, Yields, Characterization.

1. Introduction

Lube oil is used for lubrication of various internal combustion engines. While the main function is to lubricate moving parts as well as to inhibit corrosion, improve sealing and cool the engine by carrying heat away from moving parts. When properties of lube oil such as viscosity index, density and color wear out, it then becomes out of use for motor vehicles, industry's equipment for lubricating purpose. From heavy industry, a mammoth volume of used lube oil can be collected, which is usually dumped into soil, sea water or open ground. But an interesting matter is that, by reclaiming this used lube oil , a small fraction of world fuel demand can be mitigated as well as a great extent of environmental pollution can be reduced [1, 2]. The dumping of used lube oil may have adverse effects on the environment. Just one gallon of used lube oil can make a million gallons of fresh water undrinkable. A film of oil on a water surface prevents oxygen from entering the water and blocks sunlight. This film makes O_2 absorption difficult for plants to grow, thus reducing the animal and plant life in body of water [3, 4]. On an average 100,000 metric tons of lube oil is used in Bangladesh every year, of which 70,000 metric tons is used for diesel engine oil, gasoline engine oil, automotive gear oil, motor cycle engine oil and rest 30,000 metric tons is used as industrial oil and marine engine oil [5]. Lubricating oil goes through normal degradation while being used about 50% of its consumed in the process. The rest of the oil picks up number of contaminants from the working environment, such as residual components of engine fuels, solids from wear processes along with corrosion products and dirt, soot, combustion products etc. [6, 7]. Solving the problem of ULO is undoubtedly a major challenge being faced in all the countries of the world. From several alternatives, recycling is the best technique to mitigate the problem because it is the most environment friendly solution [8, 9] Thermal cracking, as a recycling technique produce several value added products from waste ULO [10]. More than half of the waste ULO can be converted into lighter usable cracked product by this method. Cracked product thus obtained can be separated into various fractions according to boiling range. Distilled product then, can be used as a substitute for fossil fuels to generate heat energy [11, 12]. Furthermore, there is a wide range of chemicals that can be extracted or derived from the distilled cracked ULO [13]. Cracking residue is a significant co-product of the cracking process. It is a granular sticky solid with properties similar to coal and therefore it simply can be added to the coal feedstock [14, 15].

3. Materials and Methods

3.1 Raw materials: Used lube oil (ULO) was collected from some petrol pumps and motor servicing stations around Dhaka city, Bangladesh. Collected ULO was sieved with a 200 mesh sieving cloth. Moisture of ULO was removed by heating at 105^{0}C for 2 hrs. Various characteristics of ULO such as pour point, ash content, carbon residue, TGA, water content, density, viscosity were carried out. The values obtained are shown in table 1.

Table 1: Characteristics of used lube oil

Characteristics	Methods	Value
Density at 15^{0}C, Kg/L	IP-160/57	0.906296 g/cm^3.
Ash Content, %Mass	ASTM D 482-63	0.526107%
Carbon Residue, %mass	ASTM D189-65	4.786
Pour Point, ^{0}C	ASTM D 97	-7 ^{0}C
Flash Point, ^{0}C	ASTM D 93	170 ^{0}C
Kinematic Viscosity at 38^{0}C, cst	ASTM D 445	Max. 16
Acid Value	ASTM D 473	8.19 mg KOH/gm
Water content, %Vol	IP-74/57	0.0958
Sulfur, %Mass	ASTM D 1552/ ASTM D 4294	0.715%

3.2 Methods

Pre treated ULO was thermally cracked in a Parr 4843 Model thermal cracker (Parr Instrument Company, USA). Moisture free ULO was taken into the cracking reactor. The reactor was electrically heated between 350°C - 500°C for several experiments. Cracked product came out through the outlet line and condensed in a cooling condenser. Condensed cracked product was collected from the condenser and distilled in atmospheric distillation unit. Cracked distillate was collected with in a boiling range 38°C- 180°C. Multifarious characteristics of the distillate were analyzed by ASTM, IP methods. The characteristics were then compared with commercial gasoline. The properties of the obtained distillate were found very much similar to the commercial gasoline. The schematic representation of the ULO cracking process is shown in figure 1.

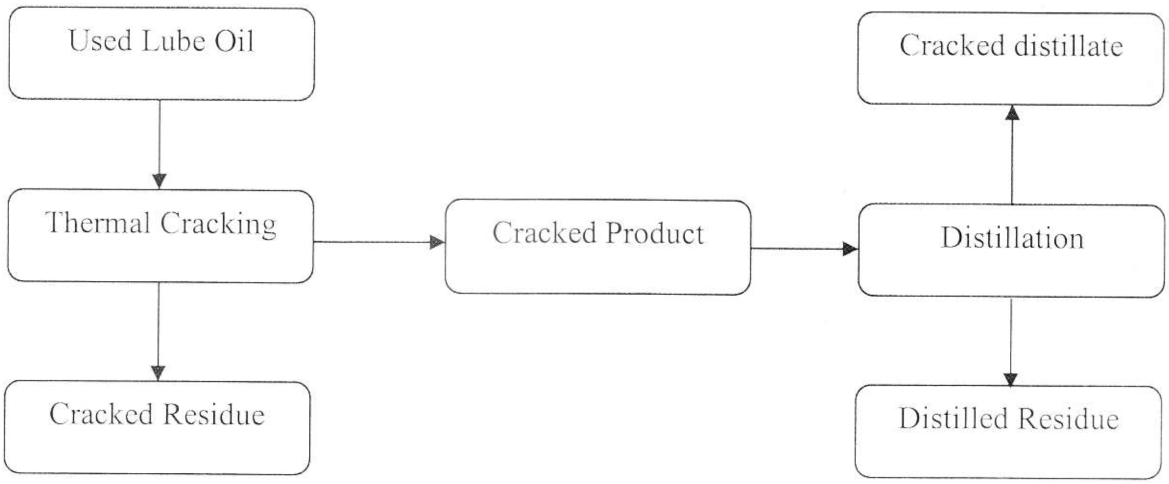

Fig. 1: Schematic representation of cracked distillate production from ULO cracking.

4. Results and Discussion

4.1 Optimization of ULO cracking :

Temperature, time and molar ratio of ULO to diesel for ULO cracking was optimized. Cracking temperature was varied from 350°C-480°C.Cracked product increased with increase in temperature, but above 450°C the product was not significantly increased. Variations of cracked product with temperature are shown in table 2.

Table 2: Experimental Result preview for cracking temp optimization

Exp no.	Cracking time	Cracking temp°C	Cracked product(%)
1	30 minutes	350	2.70
2		375	9.45
3		400	37.30
4		425	41.43
5		450	55.16
6		475	57.40
7		500	58.90

Diesel addition to ULO was observed for enhancing cracked yield. Little amount of diesel addition increased cracked product significantly. Variations of Molar ratio of ULO to diesel on product yields are shown in table 3.

Table 2: Experimental result previews for molar ratio optimization.

Exp no.	Cracking temp	Molar Ratio (ULO to diesel)	Cracked Product (%)
1	450°C	100:0	49.48
2		95:05	55.16
3		90:10	47.95
4		85:15	41.50
5		80:20	40.34

From the above figure, the yield (% wt) is increased with increasing of cracking time. The increment in yield is very significant up to 30 minutes. After that period the increment of the yield is not so significant. Moreover, the more is the time required for cracking, the more fuel amount is required for burning. Hence to make the process more economical, the optimum cracking time was chosen to be 30 minutes.

Table 3: Experimental Result preview for cracking time optimization

SL no	Cracking temp	Cracking Time	Cracked Product(%)
1	450°C	20	21.01
2		25	42.84
3		30	55.16
4		35	55.95
5		40	56.67
6		45	57.34

4.2 Distillation

Cracked product was distilled in distillation unit and 38°C-180°C fraction was taken. About 80 % of cracked distillate was obtained from ULO in this boiling range. Beyond this fraction the rest was collected as distilled residue.

4.3 Characterizations: Various fuel characteristics of the obtained cracked distillate as well as commercial gasoline were analyzed by several IP, ASTM methods. The properties of cracked distillate were then compared with the commercial gasoline (shown in table 4). From this comparison it is evident that the properties of cracked distillate are similar to commercial gasoline. Hence, cracked distillate may be used as commercial gasoline.

Table 4: Comparison of properties of cracked distillate with commercial gasoline

Name of the analysis	Method	Cracked distillate of ULO	Commercial gasoline
Density at 15°C, g/cc	IP -160/57	0.7865	Around 0.7423
Kinematic viscosity,40°C cst	ASTMD445-65	0.5683	Appx. 0.5253
Pour point, °C	ASTMD 97-57	-20	< -20
Flash point,°C	ASTMD 93-62	-32	< -46
Calorific value, MJ/kg	Bomb calorimeter	40.16	45
Acid value, mg KOH/g	IP – 1/58	0.01	0.09
Octane Rating	ASTMD 2700	75.6	77
Sulfur content, %mass	ASTMD 129-64	0.271	0.455
Water content, %	IP -74/57	Nil	0
Corrosion	ASTMD 130-65	Zero	Zero
Carbon residue, %	ASTMD 189-65	0.06294	1.50
Ash content, %	ASTMD 482-63	untraceable	Zero

4.4 Thermo Gravimetric Analyzer (TGA) Thermo gravimetric analysis is a good technique to know the volatility of a solid/liquid at different temperature. It gives the relation between temperatures vs. weight loss measurement (fig. 2). The temperature at which a large peak obtained indicated that component having boiling point at those temperatures dominates in the constituents.

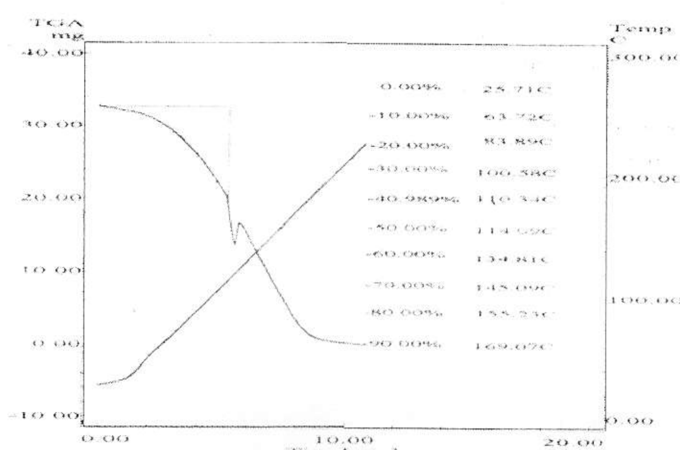

Fig. 2: TGA graph of cracked product

4.5 ICP-OES of cracked distillate

Heavy metal contents of the cracked distillate, cracked residue and distilled residue were analyzed by ICP-OES. The value obtained are shown table 5.

Table 5: Heavy Metal contents by ICP- OES

Name of Heavy Metals	Distilled Products (ppm)	Distilled Residue (ppm)	Cracked Residue (ppm)
Arsenic (As)	n.d	2.0	0.95
Barium(Ba)	.05	0.65	0.2
Cadmium(Cd)	n.d	n.d	n.d
Chromium(Cr)	2.0	0.5	0.25
Mercury(Hg)	n.d	n.d	n.d
Lead(Pb)	2.0	7.0	4.35
Antimony(Sb)	0.2	2.5	n.d
Selenium(Se)	n.d	7.0	1.5

4.6 FTIR analysis of cracked distillate :

The presence of C-C, C-H and C=C group in the FTIR analyzed chart it is evident that the composition is homologous group of alkane and alkene. It is quite similar to that of commercial gasoline. Table 6 represents the comparative details of functional group compositional analysis.

Table 6: FTIR analysis of cracked distillate of ULO.

Frequency range (cm^{-1})	Group	Class of compound
3600-3200	O-H	In H-bonded ROH
3000-2800	C-H	In alkanes
1750-1690	C=O	Aldehydes, Ketones, Esters& Carboxylic acids.
1680-1620	C-C	Alkanes
1600-1450	C=C	Aromatic rings
1475-1315	C-H	In Alkanes
1400-1050	C-O	In Ethers, Alcohols, Esters.

5. Conclusion:

The optimum temp, time and molar ratio (ULO: diesel) of ULO cracking was 450^{0}C, 30 mins and 95:05. The cracked products yield about 70% of 38-180^{0}C boiling range cracked distillate. The physico- chemical properties of obtained cracked distillate were found similar to commercial gasoline. The ICP-OES analysis of cracked distillate indicates that, the heavy metal contents are within acceptable limits. Hazardous component sulphur was totally absent in the product. Therefore, this cracked distillate could be used as gasoline for automobile and power plant. By this way, we can convert waste into valuable fuel. Consequently, our environment is protected from pollution and certain extent of energy demand may be satisfied.

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7. Nomenclature

ULO: Used Lubricating Oil

TGA: Thermo gravimetric analysis/analyzer

ASTM: American Society for Testing Materials

IP: Institute of Petroleum

n.d.: Not detectable

ppm: Parts per million

ICP-OES: Inductively Coupled Plasma- Optical Emission Spectrophotometer FTIR: Fourier Transform Infra-Red.

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