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Catalytic cracking reaction of used lubricating oil to liquid fuels catalyzed by sulfated zirconia

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Abstract−The conversion of used lubricating oil to transport fuel by direct cracking is a suitable way to dispose of waste oil. The aim of this research was to study the catalytic cracking of used lubricating oil, and thus change its classification from a waste produce to a liquid fuel as a new alternative for the replacement of petroleum fuels. The experiments were carried out in a 70-cm^3 batch microreactor at a temperature of 648-698 K, initial hydrogen pressure of 1-4 MPa, and reaction time of 10-90 min over sulfated zirconia as a catalyst. The conditions that gave the highest conversion of naphtha (~20.60%) were a temperature of 698 K, a hydrogen pressure of 2 MPa, and a reaction time of 60 min, whereas, under the same conditions, kerosene, light gas oil, gas oil, long residues, hydrocarbon gases, and a small amounts of solids were present (~9.04%, 15.61%, 5.00%, 23.30%, 25.58%, and 0.87%, respectively). The liquid product consisted of C_7-C_{15} of n-paraffins, C_7-C_9 of branched chain paraffin and aromatic compounds such as toluene, ethylbenzene and xylene. The kinetic study reveals that the catalytic cracking of waste lubricating oil follows a second order reaction, and the kinetic model is defined as $k(s^{-1})=2.88\times10^4\exp[-(103.68\ \mathrm{kJmol^{-1}})/(RT)]$.

Key words: Used Lube Oil, Liquid Fuels, Sulfated Zirconia, Cracking, Kinetic

INTRODUCTION

Alternative energy resources are becoming more imperative because there is an increasing demand for clean transport fuels. Many researchers are concentrating on developing alternative and renewable sources of liquid fuels, which are new energy resources to replace commercial petroleum products for the future. Large and increasing volumes of used lubricating oil are produced each year that, after use, are considered hazardous wastes. This is so because waste oils typically consist of a mixture of undegraded base oil and additives which high concentrations of metals, varnish, gums, and other asphaltic compounds coming from overlay on bearing surfaces and degradation of the fresh lubricant component [Rincon et al., 2005; Wills, 1990]. The used oil is disposed in many ways including incineration, landspreading, and dumping on the ground and into water. All used oil eventually creates environmental hazards. However, combustion and incineration of wastes is often difficult and cleaning of flue gases is complex and expensive because they contain important quantities of contaminants. As a solution to this problem of disposal, waste lubricating oil could be collected and processed via a re-refining process to become “re-refined lubricating oil” with an equivalent quality to new lubricating oil [Linnard et al., 1979] or via direct upgrade from thermal cracking or catalytic cracking. In thermal cracking, hydrocarbons with higher molecular weight in lubricating oils can be transformed to lighter hydrocarbon products by thermolysis at higher temperature, which is accompanied with the formation of coke; large amounts of gas and naphtha with lower quality are produced due to overcracking. Moliner et al. [1997] reported a higher yield in volatile gases when the temperature was increased (35-60% from 873 K to 973 K). Methane, light olefins, and benzene, toluene, and xylene (BTX) were the most abundant byproducts. Kim et al. [2000] studied batch low temperature pyrolysis of waste oils (693-713 K) with a high holding time of the residue (5-50 min), in order to elucidate the cracking reaction kinetics of the paraffins at low temperature to obtain naphtha. Kim et al. [2005] investigated the pyrolysis of a mixture of waste ship lubricating oil (WSLO) and waste fishing rope (WFR) in the temperature range of 573-723 K; the fraction of light hydrocarbons below C_{15} in the pyrolyzed oil of the WSLO/WFR mixture was higher than that of the WSLO or WFR alone. These lubricating oils are long-chain hydrocarbon molecules, which can be converted to light hydrocarbons, by using many types of catalysts. HZSM-5 was determined to be most efficient in the oil cracking processes of organic liquid fuel production that give mainly aromatic hydrocarbons [Prasad et al., 1986]. In addition, sulfated zirconia, as a member of the sulfated metal oxide, was first reported by Hino et al. [1979] as a solid superacid catalyst for the isomerization of n-butane at room temperature. It has also been shown to be active in several other reactions, including cracking, alkylation, and esterification [Hino et al., 1979; Kazushi, 1990; Satterfield, 1980]. Sulfated zirconia uses a stronger acid catalyst and is more reactive as a cracking catalyst for long-chain hydrocarbons, under mill conditions. It has been termed as a strong solid acid and is effective for hydro-isomerization and hydrocracking of long-chain paraffins [Katada et al., 2000; Yadav et al., 1999; Zhou et al., 2003]. The higher acidity of sulfated zirconia shows an increase in the frequency of hydride abstractions, which can be derived from the cracking mechanism [Yadav et al., 1999; Zhou et al., 2003]. In this study, sulfated zirconia was applied to the catalytic cracking of used lubricating oil to become liquid fuel, and the effects of temperature, initial pressure, reaction time, and kinetic model were investigated.

EXPERIMENT

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Table 1. Properties of treated lubricating oil

Properties	Results
Physical properties	
Dynamic viscosity (cSt)	18.24
Density (g/cm^3)	0.89
Ultimate analysis	
C (wt%)	84.52
H (wt%)	13.45
N (wt%)	0.49
S (wt%)	0.35
O by diff (wt%)	1.19
SIMDIST distillation fractions	
Naphtha (wt%)	0.00
Kerosene (wt%)	0.50
Light gas oil (wt%)	3.77
Gas oil (wt%)	8.48
Long residue (wt%)	87.25

1. Raw Material and Chemicals

Used lubricating oil that was used in all the experimental runs was supplied by Bangsue Train Station, Bangkok, Thailand. Prior to the runs the oil was filtered to remove solid particle and then treated in a rotary evaporator at 333 K under vacuum (80 kPa) to eliminate water. Then, the contaminant agent which is suspended in waste lubricating oil was separated by solvent extraction technique [Alves dos Reis, 1991]. Mixtures of used oil and 2-propanol in weight proportion of 10/1 solvent/oil were poured into glass centrifugal tubes that were later introduced in the support of a centrifuge. After centrifugation at 500 rpm for 10 min, a sludge phase (additive, impurities and carbonaceous particle) was segregated from the mixture of solvent and oil. The solvent was separated from the solvent/oil mixture by distillation in a rotary evaporator, and the recovered oil was obtained and used as starting material in all experimental runs. Used oil properties after this treatment are shown in Table 1.

Hydrogen gas (99.5% purity; Enviromate Co., Ltd. Bangkok, Thailand) was used to trace the effect of the initial hydrogen gas pressure. A commercial-grade (minimum of 80% purification) 2-propanol (from S.R.Lab Co. Ltd, Bangkok, Thailand) was used without further purification.

2. Catalyst Preparation and Characterization

Sulfated zirconia was prepared according to the method described by Charusiri et al. [2005]. Zirconium oxynitrate ($ZrO(NO_3)_2$) was dissolved in a nitric acid solution, and aqueous ammonium was slowly added under stirring to precipitate zirconium hydroxide until pH 11 was attained. The obtained solid was washed with water and calcined to prepare zirconia at 573 K for 4 h under atmospheric conditions. Sulfate was loaded by using an impregnation method, and 5 g of zirconia was suspended in aqueous solutions containing various amount of sulfuric acid with a constant volume of 100 cm^3, followed by drying on a hotplate. After drying for 2 h, the obtained solid was calcined at 923 K for 4 h under atmospheric conditions. The N_2 adsorption-desorption isotherms were measured at 77 K under 30.39 kPa of nitrogen (P/P^o=0.3) on a Quantachrome Autosorb 1 instrument by using standard adsorption techniques. The surface area of 133 m^2/g was obtained by application of the BET procedures.

3. Apparatus and Procedure

A quantity (20 g) of used lubricating oil was poured in a 316 SS stainless-steel cylindrical microreactor that had a volume of 70 cm^3. Sulfated zirconia (1 wt% based on weight of used oil) was added and hydrogen gas was supplied from a hydrogen tank to fill the reactor. The reactor was constructed to reaction unit specifications, with an injection heater and insulator. The reactor was heated from ambient room temperature to the desired temperature and maintained at the desired temperature for any reaction times. The reaction was controlled by a programmable temperature controller with a K-type thermocouple used as a temperature detector. A control speed motor controlled the shaking of the micro-reactor. After the reaction was finished, the reactor was cooled down to room temperature. The liquid product was collected by vacuum filtration to separate the liquid oil products from solids. Liquid yield was calculated as (weight of oil)×100/(weight of feed), while solid yield was defined as (weight of solid)×100/(weight of feed). Gas yield was defined as (100-liquid yield-solid yield).

4. Liquid Product Analyses

The boiling range distribution of oil products were analyzed by a Simulated Distillation Analyzer following the ASTM method D2887. The system consisted of Varian CP-3800 gas chromatograph equipped with an automatic sampler and a flame ionization detector (FID). Capillary column (15 m×0.25 mm, i.d. 0.25 μm film thickness) CP-SIL 5CB was employed with a programmed temperature from 303 K to 593 K. The gas chromatography was calibrated by analyzing a mixture of normal paraffins with known boiling points and samples were injected in the CS_2 solution. Naphtha, kerosene, light gas oil, gas oil and long residue fractions in product oils were referred to by boiling point in each fraction as follows: under 473 K (naphtha), 473-523 K (kerosene), 523-623 K (light gas oil), 623-643 K (gas oil) and over 643 K (long residue).

Information on molecular structures of oil products obtained was only available in terms of analyses in the GC-MS. A SHIMADZU GC-MS QP2010 equipped with DB-1 capillary column (30 m×0.25 mm, i.d. 0.25 μm film thickness), and a 1 : 30 split ratio was used. The GC column was ramped at 293 Kmin^{-1} from 313 K (hold 2 min) to 593 K. Helium gas was used as the carrier gas with a flow rate 1.5 ml/min. Sample were injected into a CS_2 solution.

RESULTS AND DISCUSSION

1. Effect of Reaction Temperature

The effect of reaction temperatures on the conversion of waste lubricating oil with sulfated zirconia catalyst was examined. Product distribution as a function of reaction temperature is shown in Fig. 1. The liquid yield was decreased with increasing temperature, whereas the yield of naphtha fraction increased from 5.61% at 648 K to 20.60% at 698 K with increasing temperature. Further increases in the reaction temperature resulted in markedly increased gas yield. A possible reason for this behavior is that the higher temperature accelerated the thermal decomposition and, hence, changed the long-chain hydrocarbon molecule from thermal cracking to a middle hydrocarbon molecule. Thereafter, gas oil and light oil were catalytically cracked at the surface of the sulfated zirconia, converting them to gases and a light hydrocarbon fraction and gases [Yadav et al., 1999; Zhou et al., 2003].

This process can be identified as deoxygenation cracking with

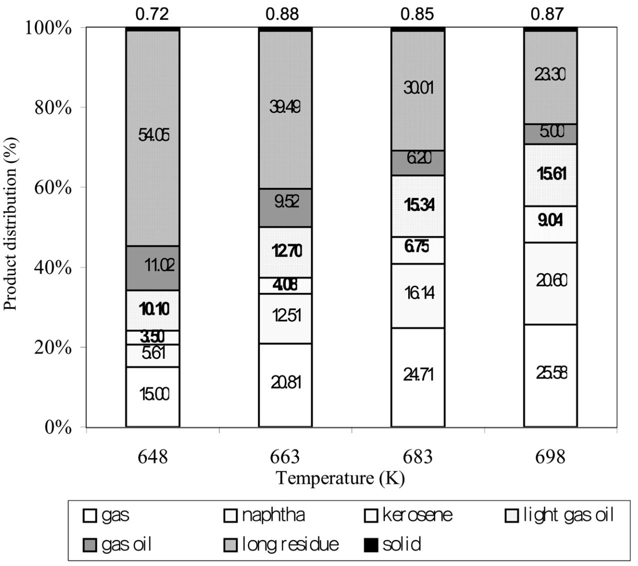

Fig. 1. Effect of reaction temperature on the product distribution at an initial pressure of 2 MPa reaction time of 60 min over sulfated zirconia catalyst.

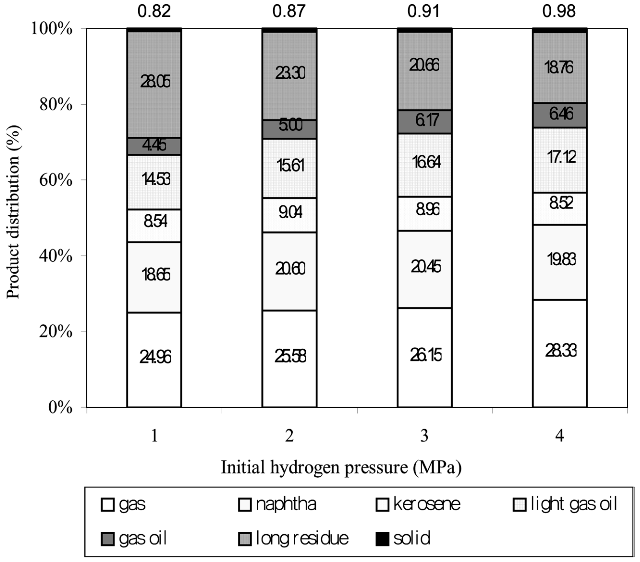

Fig. 2. Effect of initial hydrogen pressure on the product distribution at a temperature of 698 K and a reaction time of 60 min over sulfated zirconia catalyst.

hydrogen transfer from the properties of the metal support catalyst over sulfated zirconia in catalytic cracking processes [Yadav et al., 1999]. Subsequent reactions such as isomerization, cyclization, and hydrogen transfer lead to the formation of aromatic hydrocarbon [Zhou et al., 2003]. At a temperature of 698 K, a large amount of gaseous products were observed. It seemed that when a higher temperature was used, light hydrocarbons could be cracked continually. The result of this effect showed that a temperature of 698 K, an initial hydrogen pressure of 2 MPa and a reaction time of 60 min gave the appropriate fraction of naphtha. The product yield consisted of 25.58 wt% gases and 0.87 wt% solid. In addition, a balance of 73.55 wt% liquid product was obtained (20.60 wt% naphtha, 9.04 wt% kerosene, 15.61 wt%, light gas oil 5.00 wt% gas oil, and 23.30 wt% long residue).

2. Effect of Pressure

The initial hydrogen pressure was responsible for the catalytic cracking step, and hydrogenation and hydrocracking was possible for the cracking and rearrangement of light hydrocarbon molecules. The effect of varying the hydrogen pressure over a range from 1 MPa to 4 MPa, relative to the product distribution, remained almost unchanged, shown by the product distribution (see Fig. 2). Thus, yield of liquids varied insignificantly with pressure, whereas the yield of gas and solid also increased with increasing pressure. The increasing of hydrogen pressure from 1 MPa to 2 MPa increased yield of naphtha from 18.65 wt% to 20.60 wt%. It can be described as that an increase in amount of hydrogen helps to stimulate cracking reaction and causes higher catalytic cracking reaction. This is confirmed in the theory of spill-over of hydrogen on catalyst during the reaction--some hydrogen at the surface of catalyst was consumed--so the higher the pressure of hydrogen, the more mass transfer from gas phase to solid phase of catalyst. Therefore, it causes high conversion and more quantity of recovery product. However, the yield of naphtha and kerosene also decreased slightly with the hydrogen pressure in the range of 3-4 MPa. Because of too high severity in the reaction causing violent cracking and followed by coking, the reaction could not continue at so high pressure. An initial hydrogen pressure of 2 MPa was high enough to give a naphtha fraction amounting to 20.60 wt% naphtha, 9.04 wt% kerosene, 15.61 wt% light gas oil, 5.00 wt% gas oil, and 23.30 wt% of long residue.

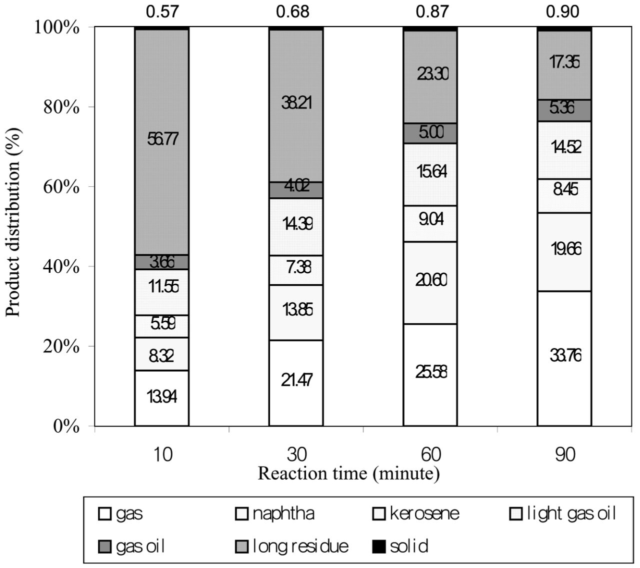

Fig. 3. Effect of reaction time on the product distribution at a temperature of 698 K and an initial hydrogen pressure of 2 MPa over sulfated zirconia catalyst.

3. Effect of Reaction Time

The reaction time contributed mainly to the liquid yield and product distribution; the yield of liquid was decreased from 85.89 wt% to 65.34 wt%; in the meantime gas yield increased from 13.54 wt% to 33.76 wt%. The yield of naphtha, kerosene and light gas oil also increased with the reaction time in the range of 10-60 min and decreased slightly with reaction time in the range of 60-90 min (see

Fig. 3). The results show that used lubricating oil begins to crack and undergoes more cracking when the reaction time is longer. Therefore, the light hydrocarbon molecules were produced from the effect of thermal cracking. When the time of reaction was continued, the liquid yield consisted of a fraction of light hydrocarbons, which continued cracking until it became a gaseous product. In contrast, results confirmed that the amount of gases that were produced dramatically increased as the reaction time increased. The effect of reaction time on the product distribution indicated that temperature was also a main significant factor affecting the conversion of long-chain hydrocarbon molecules to light molecules, and continued cracking led to light hydrocarbon gases by increasing the reaction time. Nevertheless, with the solid yield increasing with increase reaction time implied that the surface of catalyst was contaminated with coking or poisoning from impurities presented in the waste lubricating oil. For this reason, the activity of the catalyst was lost and a decreasing of naphtha, kerosene and light gas oil yield at higher reaction time may have occurred. These results show that, in terms of optimum yield and product distribution, at a reaction time of 60 min, at temperature of 698 K, and an initial hydrogen pressure of 2 MPa over 1 wt% sulfated zirconia produced a higher naphtha fraction than lower reaction times.

4. Product Analysis by GC-MS

Oil products from the cracking of waste lubricating oil at optimum condition were determined the chemical components by GC-MS. Table 2 shows hydrocarbon compounds in oil products.

Table 2. Components detected in liquid product from cracking of waste lubricating oil over sulfated zirconia catalyst

No.	Compound	Formula	Classification
1.	n-Heptane	C_7H_{16}	Alkane C_7
2.	3-Methyl hexane	C_7H_{16}	Alkane C_7
3.	2,4-Dimethyl hexane	C_8H_{18}	Alkane C_8
4.	Toluene	C_7H_8	Alkyl-benzene
5.	n-Octane	C_8H_{18}	Alkane C_8
6.	Ethylbenzene	C_8H_{10}	Alkyl-benzene
7.	1,3-Dimethyl benzene	C_8H_{10}	Alkyl-benzene
8.	o-Xylene	C_8H_{10}	Alkyl-benzene
9.	n-Nonane	C_9H_{20}	Alkane C_9
10.	2,3,4-Trimethyl hexane	C_9H_{20}	Alkane C_9
11.	2,4-Dimethyl heptane	C_9H_{20}	Alkane C_9
12.	1-Ethyl-3-methyl benzene	C_9H_{12}	Alkyl-benzene
13.	1,2,3-Trimethyl benzene	C_9H_{12}	Alkyl-benzene
14.	n-Decane	$C_{10}H_{22}$	Alkane C_{10}
15.	1,2,4-Trimethyl benzene	C_9H_{12}	Alkyl-benzene
16.	4-Ethyl-1,2-dimethyl benzene	$C_{10}H_{14}$	Alkyl-benzene
17.	n-Undecane	$C_{11}H_{24}$	Alkane C_{11}
18.	1-Phenyl-1-butene	$C_{10}H_{12}$	Alkyl-benzene
19.	Naphthalene	$C_{10}H_8$	Naphthalene
20.	1-Ethyl-2,4,5-trimethyl benzene	$C_{11}H_{16}$	Alkyl-benzene
21.	Dodecane	$C_{12}H_{26}$	Alkane C_{12}
22.	Tridecane	$C_{13}H_{28}$	Alkane C_{13}
23.	1-Methyl naphthalene	$C_{11}H_{10}$	Alkyl-naphthalene
24.	2-Methyl naphthalene	$C_{11}H_{10}$	Alkyl-naphthalene
25.	Tetradecane	$C_{14}H_{30}$	Alkane C_{14}
26.	Pentadecane	$C_{15}H_{32}$	Alkane C_{15}

Product oil from the cracking of waste lubricating oil by sulfated zirconia catalyst was mainly composed of n-paraffin, branch chain paraffin and aromatics (1-ring and 2-rings), none of 3-rings aromatic. It can be observed that n-paraffin in liquid product from catalytic cracking has carbon atoms in the range from naphtha to light gas oil, namely 7 to 15 atoms.

The liquid products also consisted of 1-ring aromatic compounds. The 1-ring aromatic hydrocarbons may have been formed first by thermal cracking or catalytic cracking of the waste lubricating oil fed followed by aromatization of some of the cracked molecules (mainly olefins) via cyclization and hydride transfer reactions. The major compounds were toluene, ethyl benzene, o-xylene, and substituted benzene.

5. Kinetic Study

This experiment aimed to investigate the kinetic of catalytic cracking reaction of used lubricating oil over sulfated zirconia catalyst. Order of reaction and activation energy were determined from this study. Kinetic experiments were carried out at reaction times of 10-90 minutes and reaction temperature of 663, 683 and 698 K under initial hydrogen pressure of 2 MPa with 1 wt% of sulfated zirconia catalyst.

A kinetic study for each experiment was performed in a batch reactor [Billaud et al., 2003]. Furthermore, the following assumptions are accepted, in regard to the kinetic model: (i) the reactant feed is constant; (ii) the reactor is isothermal at the desired temperature T, under a hydrogen gas pressure of 2 MPa (loss of changes negligible); and (iii) the conversion for each desired temperature can be calculated from the analysis of the long residue fraction.

Determination of reaction order was obtained from the relationship between the reaction rate ($-r_A$) and the concentration of long residue consisting in the liquid product (C_A), which can be written as follows:

$$-r_A = -\frac{dC_A}{dt} = k_n C_A^n \qquad (1)$$

If a first-order reaction is obtained by the relationship between $-r_A$ and C_A (from Eq. (1)), the following is obtained:

$$-\frac{dC_A}{dt} = k_1 C_A \qquad (2)$$

Which $C_A = C_{Ao}(1-X)$, where X is the fractional conversion of long residue. The conversion of long residue at any time could be represented by

$$X = \frac{C_{Ao} - C_A}{C_{Ao}} \qquad (3)$$

Where C_{Ao} and C_A refer to the long residue fraction at time t=0 and t, respectively.

Integration of Eq. (2) between t=0 and t, the first order kinetic equation in terms of fractional conversion of long residue is the following:

$$\ln\left(\frac{1}{1-X}\right) = k_1 t \qquad (4)$$

A plot of $\ln[1/(1-X)]$ versus t gives a straight line with a slope equal to k_1.

If a second-order reaction is obtained by the relationship between $-r_A$ and C_A (from Eq. (1)), then the following is obtained:

$$-\frac{dC_A}{dt}=k_2C_A^2=k_2C_{Ao}^2(1-X)^2 \tag{5}$$

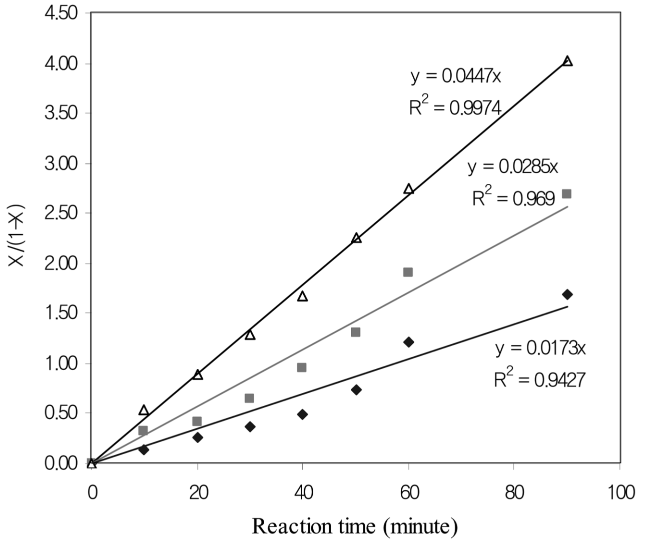

Fig. 4. Plot of conversion (X) versus time of reaction for various temperature; (◆) 663 K, (■) 683 K, and (△) 698 K. The order of the hypothesis is equal to 2.

Integration of Eq. (5) and rearranging, the second order kinetic equation in terms of fractional conversion of long residue is the following:

$$\frac{X}{1-X}=k_2C_{Ao}t \tag{6}$$

Plotting between X/(1−X) and t, k_2 was obtained from slope of straight line.

Fig. 4 allows us to determine the reaction order of the catalytic cracking of used lubricating oil over sulfated zirconia at various temperatures of 663, 683 and 698 K. The plotting of eight points of the graph, from a reaction time of 0 min to a reaction time of 90 min (data are listed in Table 3), gives a correct straight line with a better regression constant ($R^2 \approx 1.00$) than that of the first-order reaction; thus, the conversion of long residue of the used lubricating oil to liquid fuels is a second-order reaction.

Consider a constant rate at the various temperatures. The correlation between $\ln(k_2)$ and 1/T, from the Arrhenius equation is given as

$$k_2=A\exp\left(-\frac{E}{RT}\right) \tag{7}$$

Table 3. Analysis of product distribution from the cracking of used lubricating oil over Sulfated zirconia catalyst

Time (min)	Composition (%)							Conversion, X
	Gas	Naphtha	Kerosene	Light gas oil	Gas oil	Long residue	Solid	
				Temperature=663 K				
0	0.00	0.00	0.50	3.77	8.48	87.25	0.00	0.0000
10	11.65	1.56	1.35	4.45	4.27	76.17	0.55	0.1270
20	12.98	3.68	1.94	6.23	5.35	69.21	0.61	0.2068
30	14.69	4.84	2.21	7.48	6.29	63.82	0.67	0.2685
40	16.24	6.32	2.65	8.39	7.32	58.34	0.74	0.3313
50	18.25	8.51	3.28	10.24	8.59	50.32	0.81	0.4233
60	20.81	12.51	4.08	12.70	9.52	39.49	0.88	0.5474
90	23.36	13.85	5.02	13.64	10.73	32.51	0.89	0.6274
				Temperature=683 K				
0	0.00	0.00	0.50	3.77	8.48	87.25	0.00	0.0000
10	10.89	4.99	3.43	9.88	4.29	65.96	0.56	0.2440
20	11.32	6.87	4.51	10.25	4.65	61.77	0.63	0.2920
30	13.81	10.65	5.19	11.54	5.01	53.13	0.67	0.3911
40	16.89	13.95	5.49	12.63	5.55	44.80	0.69	0.4865
50	19.35	15.84	6.23	13.98	5.97	37.85	0.78	0.5662
60	24.71	16.14	6.75	15.34	6.20	30.01	0.85	0.6560
90	26.74	17.63	7.25	17.22	6.57	23.68	0.91	0.7286
				Temperature=698 K				
0	0.00	0.00	0.50	3.77	8.48	87.25	0.00	0.0000
10	13.54	8.32	5.59	11.55	3.66	56.77	0.57	0.3493
20	17.85	12.12	6.04	13.26	3.87	46.25	0.61	0.4699
30	21.47	13.85	7.38	14.39	4.02	38.21	0.68	0.5621
40	23.02	15.84	8.31	14.98	4.25	32.85	0.75	0.6235
50	24.55	19.36	8.83	15.26	4.39	26.76	0.85	0.6933
60	25.58	20.60	9.04	15.61	5.00	23.30	0.87	0.7330
90	33.76	19.66	8.45	14.52	5.36	17.35	0.90	0.8011

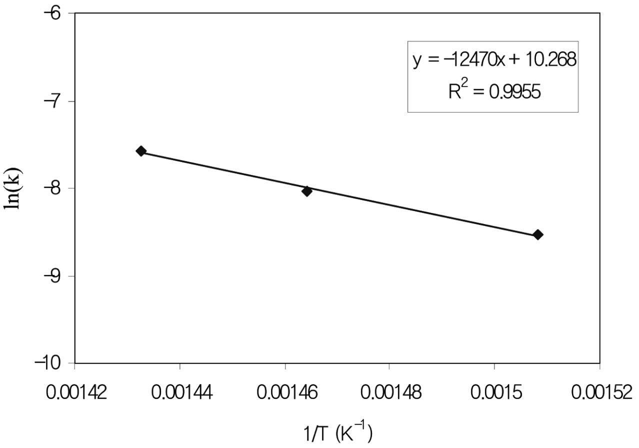

Fig. 5. Plot of the logarithm of the specific reaction rate (ln(k)) versus the reciprocal of reaction temperature (1/T).

The equation can be expressed logarithmically, as follows:

$$\ln(k_2)=\ln(A)-\frac{E}{RT} \tag{8}$$

The activation energy (E) was obtained from the plotted slope of $\ln(k_2)$ vs 1/T, as shown in Fig. 5, which gave a straight line with a slope of −E/R and an intercept of ln(A). Over the temperature range of 663-698 K, the value of E is estimated to be 103.68 $kJmol^{-1}$ and the value of A is estimated to be 2.88×10^4 s^{-1}. According to the earlier reported work on thermal cracking, the activation energy of the thermal cracking reactions lies between 133 and 268 $kJmol^{-1}$ [Del Bianco et al., 1993; Kim et al., 2004b, 2005; Krishna et al., 1998; Singh et al., 2004; Xiao et al., 2002]. The activation energy of catalytic cracking reaction was less than that of thermal cracking. It can be concluded that catalytic cracking was a suitable process for converting waste lubricating oil to liquid fuels when compared with thermal cracking.

CONCLUSION

Used lubricating oil can be a raw material for converting to liquid fuels such as naphtha, kerosene and light gas oil by using sulfated zirconia as a catalyst. The experiment was performed with temperature changing from 648 K to 698 K, initial hydrogen pressure of 1-4 MPa, and reaction time of 10-90 min. The highest yield of naphtha-20.60 wt%-was obtained at a temperature of 698 K, an initial hydrogen pressure of 2 MPa, and a reaction time of 60 min, whereas under the same conditions, the quantities of kerosene, light gas oil, gas oil, long residues, gaseous products that consisted of small hydrocarbon molecules, and solids were 9.04%, 15.61%, 5.00%, 23.30%, 25.58%, and 0.87%, respectively. Liquid product essentially consisted of fuel range hydrocarbons and chemicals such as C_7-C_{15} of n-paraffins, C_7-C_9 of branched chain paraffin and aromatic compounds. The kinetic study was defined to determine the reaction order and the kinetic parameters E (the activation energy) and A (the pre-exponential factor), which indicate that the catalytic cracking of used lubricating oil over sulfated zirconia is a second-order reaction and the kinetic model is described as $k(s^{-1})=2.88\times10^4\exp[-(103.68\ kJmol^{-1})/(RT)]$.

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NOMENCLATURE

A : pre-exponential factor [s^{-1}]
C_A : long residue fraction at time t [g]
C_{AO} : long residue fraction at time t=0 [g]
E : activation energy [$kJmol^{-1}$]
k : reaction rate constant [s^{-1}]
n : reaction order
R : gas constant=8.314 $Jmol^{-1}K^{-1}$
t : reaction time [s]
T : reaction temperature [K]
X : fraction conversion of long residue

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