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Research Article

Treatment and Refining of Used Lubricating Oil by Clay with Polymeric Surfactants

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Abstract: The aim of this research was studying the hydro treatment of extracted used oil from clay by phase transfer catalyst. The used oil was pretreated with local clay and then treated with isopropanol, butanol and potassium hydroxide solution. The treated oil was distilled and fractionated to obtain 400–550 °C fraction. The fraction was hydro-treated using commercial clay supported by an adsorbed phase-transfer catalyst. The effects of the reaction temperature, liquid hour space velocity and total hydrogen pressure on the oil fraction properties were investigated. The basic properties of oil such as colour and viscosity index improved. Thus, it can be suggested the addition of a polymeric sulfonate with a catalyst described occurs viahere, here is a novel mechanism. The results were compared with those obtained using catalyst without any additive.

Keywords: Hydrofinishing, lube oil, phase-transfer catalyst, surfactants

INTRODUCTION

Hydrofinishing of lubricating oil has been carried out using hydrogen over a suitable catalyst. Many investigators have studied the chemical changes in lubricating oil upon hydrotreatmenting (Jones, 1954; Jazl *et al*., 1958).

Hydrotreating catalysts consist of critical metals such as Mo, Co and Ni as active metals and are generally supported by alumina or silica alumina and are usually used in the hydrotreatment of petroleum. Although these catalysts deactivate with time, their partial or complete regeneration can be carried out (Marafi *et al*., 2009).

Different types of clay can be used for regeneration, depending on the technical feasibility and economic considerations (Marafi and Stanislaus, 2007). The increased usage of additives in oil and regeneration processes is based on different steps such. The increase using of additive in oil and regeneration processes based on different step as solvent extraction and clay treatment (Short *et al*., 1987).

Typical waste lubricating oil comprises stable dispersion additives and base oil with a high concentration of metals, gums and polymerized additives such as naphthalene, additives, wax, cross-linked olefin and other asphaltic compounds (Rincón *et al*., 2007). To reduce waste creation and protect the environment from its harmful effects, recycling and re-refining of waste into lubricating oil is a suitable method. A catalyst used in a hydrogenation processes must be able to convert the hydrocarbons present in the feed to those with better viscosity properties and other property indexes. An ideal example of such a catalyst is the Zeolite, used in isomerisation and hydrogenation reactions by zeolite catalyst.

This study describes the recycling of waste lubricating oil by using a laboratory-prepared Ni/clay catalyst, which is a phase-transfer catalyst.

MATERIALS AND METHODS

Catalyst preparation and treatment of waste lubricating oil: The Ni/clay catalyst is comprised a of kaolinite clay powder (100 mesh in size), which was purified using the flotation processes described by Omar (1989). It was then subjected to impregnation using a nickel nitrate solution containing 0.5 wt% Ni in the presence of benzyltriethylammonium bromide as a phase-transfer catalyst. Next, it was dried after which, it agglomerates as billets. The catalyst was calcined at 500°C for 3 h. Then, the temperature was lowered to 400°C in a hydrogen gas stream for 4 h.

The waste lubricating oil was treated subjected to solvent extraction using 20 wt% isopropanol/potassium hydroxide solution and was freed from the sludge by centrifugation.

The treated oil was vacuum distilled at 0.1 mm Hg. The physicochemical characteristics of the treated oil are listed in Table 1.

The hydrotreatment of oil was carried out in a continuous high-oil-pressure autoclave. The oil was hydrotreated using the catalyst under the following conditions: pressure, 20 atm; temperature range, 300-450°C; liquid hourly space velocity, 0.5-1 LHSV h^{-1}; and H_2/oil ratio, 400 L L^{-1}.

Table 1: Physicochemical characteristics of the treated oil after vacuum distillation

Analysis test	Result
Specific gravity 60 °F/60 °F	0.8721
Sulphur content, wt%	1.41
Nitrogen, ppm	430
Total acid number, mg KOH g^{-1} oil	0.34
Carbon residue, wt%	1.7
Ash content, wt%	1.1
Colour ASTM	Opaque
Pour point	-3
Kinematic viscosity, cSt	
100 °C	12.1
40 °C	82
Viscosity index	86
Flash point	235
Metal concentration, ppm	
Ca	800
Zn	600
Co	74
Mo	40
V	30
Pb	34
Hydrocarbon content, wt%	
%C A	8.74
%C N	29.92
%C R	37.65
%C P	64.31
Ring analysis	
R A	0.34
R N	1.68
R T	2.12

Table 2: Chemical analysis of raw clay, wt%

Test	Result
SiO_2	58.1
Al_2O_3	24.51
Fe_2O_3	0.75
TiO_2	2.4
CaO	0.56
MgO	0.51
Na_2O	1.5
Ignition loss	11

RESULTS AND DISCUSSION

The Kaolinite clay was purified using the flotation process described by Omar (1989) and by using an impregnated with Ni cation with in the presence of the phase-transfer catalyst, benzyltrimethylammonium bromide. As a phase transfer catalyst. The chemical analysis results of raw kaolinite are given in Table 2.

The Ni/clay catalyst with the a surface area of 38.5 $m^2\ g^{-1}$ and an average size dimension of 18 Å has been was studied by differential thermal analysis. The results show two peaks appearing at 140°C and 560°C. The first peak shows water adsorption in clay and the other peak represents destruction of the clay lattice of clay destruction. This result confirms that hydrofinishing must be carried out below 560°C. The polymeric sodium salt of phenol paraformaldehyde sulfonate with an average molecular weight of 4000 g, synthesized using the methodology of Nabih *et al*. (2003), was used as an activator with the Ni/clay catalyst.

Hydrofinishing changes the oil composition. The pour point of the feed decreases as the temperature is increased (Fig. 1). An increase in the hydrogen pressure from 20 to 30 bar changes the temperature and hence, also changes the pour point. Both densities and refractive indices change with an increase in the reaction temperature. The effect of adding 1% polymeric sulfonate on the activity of Ni/clay is shown in Table 3.

The results shown in Table 3 depict the effect of reaction temperature on hydrofinished-product composition in the presence of a catalyst and polymeric sulfonate. It is clear that the sulphur and nitrogen contents are reduced with increasing temperatures. The group analysis also confirms increasing percentages of paraffinic carbon and decreasing percentages of aromatic and naphthenic carbons, as the reaction temperature increases. The results can be discussed

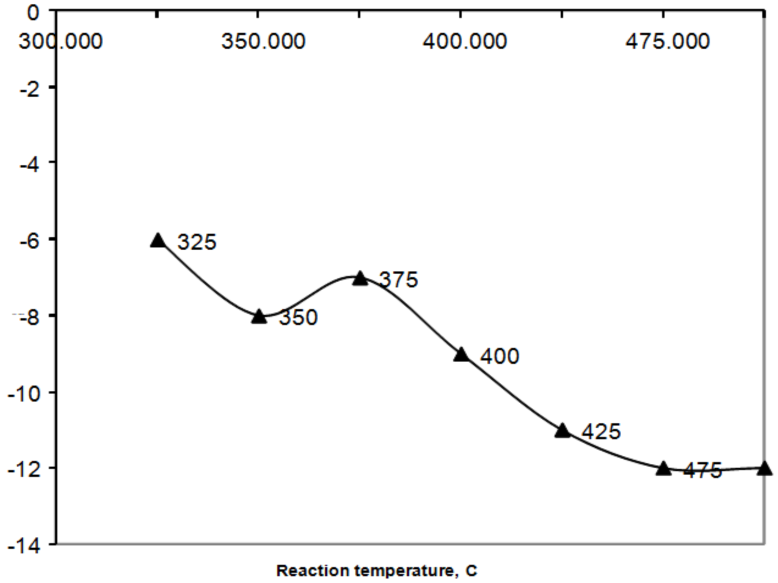

Fig. 1: Effect of reaction temperature on pour point of the product

Table 3: Effect of adding additive, on the yield and physical properties

Characteristics		Reaction temperature (°C)				
Yield, wt%	Feed	375	400	425	450	475
	100	96	87	86	83	82
Refractive index, 70°C	1.4673	1.4656	1.4643	1.4621	1.4619	1.4615
Molecular weight	390	395	396	410	420	415
Density, g cm^{-3}	0.861	0.8451	0.8441	0.8438	0.8378	0.8367
Sulphur content, wt%	0.86	0.66	0.57	0.34	0.25	0.14
Nitrogen content, ppm	437	421	290	188	160	134
Pour point, C	-5	-4	-3	-2	-4	-7
Group analysis						
%C A	8.74	7.31	7.11	6.56	6.55	6.47
%C N	29.92	28.46	28.21	28.29	28.30	26
%C R	37.65	37.77	37.33	33.85	33.55	33.1
%C P	64.31	63.23	64.67	66.15	66.45	66.1
Ring analysis						
R A	0.34	0.30	0.28	0.27	0.26	0.25
R N	1.68	1.50	1.45	1.46	1.45	1.42
R T	2.12	1.95	1.90	1.90	1.80	1.75

Table 4: Reaction rate constant, K s^{-1}, for oil

		Temperature, °C									
		375		400		425		450		475	
Feed	Contact time (min)	Yield%	K, s^{-1}	Yield%	K, s^{-1}	Yield%	K, s^{-1}	Yield%	K, s^{-1}	Yield%	K, s^{-1}
	5	56.6	1.5×10^{-4}	60.5	1.7×10^{-4}	70	1.7×10^{-4}	76	1.8×10^{-4}	81	1.9×10^{-4}
	10	76	1.2×10^{-4}	77.5	1.4×10^{-4}	80	1.4×10^{-4}	84	1.6×10^{-4}	88	1.7×10^{-4}
	15	81	0.8×10^{-4}	83	0.85×10^{-4}	85	0.85×10^{-4}	90	0.9×10^{-4}	93	1.1×10^{-4}
	20	90	0.6×10^{-4}	90	0.7×10^{-4}	93	0.7×10^{-4}	95	0.8×10^{-4}	97	0.95×10^{-4}

based on the hydrogenation of the poly-aromatic ring. The polymeric sulfonate additive promotes the initiation reaction, resulting in reactions with activation energies lower than those occurring in the absence of the additive, as reported by Nabih *et al*. (2003).

Hydrofinishing is a first-order reaction that depends only on the residence time and the heating temperature. Thus, the applied kinetic rate equation can be described as follows:

$$\text{Log } C^1/c = Kt/2.3$$
$$\text{Log } C^1/C(1-X) = Kt/23$$
$$\text{Log } 1/(1-x) = Kt/2.3$$
$$K = K^0.e^{-E/Rt}$$

where, k is the specific rate constant, s^{-1}; K^0 and E are constants; T is the reaction temperature; R is the universal gas constant; X is the yield; and T is the reaction time, s.

The K values for the yield at various operating conditions in the presence of polymeric sulfonates are given in Table 4. It is clear that K values increase as the temperature increases for the same residence time and temperature.

The additive effect of the polymeric sulfonate is compatible to act according to the mechanism discussed by Nabih *et al*. (2003).

CONCLUSION

It can be concluded that the Ni/Clay catalyst is effective in hydrofinishing used lube oil. The catalyst efficiency increases by using a polymeric sulfonate additive. These results are confirmed by kinetic studies.

REFERENCES

Jazl, J.A., A.P. Stuart and A. Schneider, 1958. Ind. Eng. Chem. Proc. DD., 50: 947.

Jones, W.A., 1954. Hydrofining improves low-cost lube quality. Oil Gas J., 53(26): 81-84.

Marafi, M. and A. Stanislaus, 2007. Studies on recycling and utilization of spent catalysts: Preparation of active hydrodemetallization catalyst compositions from spent residue hydroprocessing catalysts. Appl. Catal. B-Environ., 71(3-4): 199-206.

Marafi, M., H. Al-Sheeha, S. Al-Omani and A. Al-Barood, 2009. Activity of hydroprocessing catalysts prepared by reprocessing spent catalysts. Fuel Process. Technol., 90(2): 264-269.

Nabih, H.I., A.M.A. Omar and R.M. Habib, 2003. Visbreaking of a heavy gas oil fraction promoted by phenol formaldehyde sulphonate polymer. Afinidad-Barcelona, 60(505): 289-294.

Omar, A.M.A., 1989. M.Sc. Thesis, Ain Shams University, Cairo, Egypt.

Rincón, J., P. Cañizares and M.T. García, 2007. Regeneration of used lubricant oil by ethane extraction. J. Supercrit. Fluid., 39(3): 315-322.

Short, H., D. Hunter and G. Parkinson, 1987. Three re-refining methods for waste lube oils. Chem. Eng., 20: 21-23.