CATALYTIC POUR POINT REDUCTION AND VISCOSITY IMPROVEMENT OF LUBRICATING OIL FRACTIONS USING SULFIDED NICKEL-TUNGSTEN CATALYSTS

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ABSTRACT

An investigation was conducted for the process of dewaxing the lubricating oil fraction by catalytic treatment The study conducted to prepare the necessary catalyst needed for the dewaxing, and employing the prepared catalyst in the dewaxing of lubricating oil fractions.

Activity tests of the catalyst was accomplished by experimental trickle bed reactor with operating conditions 548 – 673 K and l– 3 hr–1 LHSV keeping the pressure constant at 35 bar and hydrogen to oil ratio 500 liter/liter. The present investigation shows that the pour point of dewaxed lubricating oil decreases by the temperature increasing and LHSV decreasing, the same effect also appears in viscosity index improvement due to aromatic saturation.

***Keywords**: Catalytic dewaxing , Selective hydrocracking*

INTRODUCTION

High quality lubricating oils are critical for the machinery of modern society. Unfortunately, the supply of natural crude oils having good lubricating properties is not enough to meet the demand (1,2). Numerous processes have been proposed to produce lubricating oils by upgrading the ordinary and low – quality stocks, which ordinarily would be converted into other products (1,2).

Solvent dewaxing is a well – known and effective process but expensive. More recently, catalytic methods for dewaxing have been commercialized. Catalytic dewaxing is a particular hydrocracking process used to improve cold flow properties of middle distillate and lubricants by cracking normal and near normal paraffins. Dewaxing is not always achieved by cracking, this can also be accomplished by isomerization. The properties targeted for improvement are pour point and viscosity of middle distillate and lubricants, cloud point of diesel fuels and freeze point of jet fuel. The properties listed become important especially at low temperature. Due to their high melting points, long chain normal paraffins have the most detrimental effects on the low temperature properties of middle distillates and lube oils. By reducing the amount of chain length of normal and minimally branched paraffins in fuels and lubricants their cold flow properties are improved (3).

Typically, a single stage once through hydrocracking process is used for catalytic dewaxing, with or without hydrotreating depending on sulfur and nitrogen content of the feedstocks. The catalytic process is a trickle flow operation carried out over bifunctional catalyst under hydrogen flow (4).

Little information has been published about the composition of the catalyst used in this process. Although a large number of zeolite materials have been disclosed as employable as catalyst for hydrodewaxing, the use of other crystalline molecular sieve has not received attention. This lack of attention is attributable to the scarcity of molecular sieves other than crystalline aluminosilicates (5).

A problem with the existing art processes for producing high quality lubricating oils is the fact that the dewaxing processes used therein, such as when dewaxing by zeolitic catalyst by means of cracking reactions, and therefore a number of useful products become degraded to lower molecular weight materials. For example, waxy paraffins may be cracked down to butane, propane, ethane and methane and so may the lighter n –paraffins which do not, in any event contribute to the waxy nature of the oil. Because these lighter products are generally of lower value than the higher molecular weight materials, it would obviously be desirable to limit the degree of cracking which taken place during the catalytic dewaxing process.(5 ,6)

The instant investigation provides for catalytic dewaxing of lube oil feedstocks by contacting such with catalyst comprising prepared silicoaluminophosphate molecular sieve The study includes testing the prepared catalyst with the above mentioned lubricating oil fractions in order to reduce its pour point along with other properties.

EXPERIMENTAL WORK

Feedstock

Two oil distillate fractions obtained from vacuum distillation unit of lube oil plant of North Refineries (Baiji site) were used in this investigation. Table (1) shows the properties of these fractions.

Table (1) Properties of Lube Distillate Fractions

Specification	Fraction A	Fraction B
Distillation ASTM D1160	350	400
50 %	396	445
EP	460	500
API	36.2	34.0
Sulfur wt. %	2.26	2.40
Viscosity @ 40°C	18	31
Viscosity @ 100°C	3.6	4.85
Pour Point °C	26	36
Viscosity Index	85	80
Flash Point °C	188	212
Carbon Residue wt%	0.1	0.13
C_7 insoluble	0.01	0.012
(Ni + V + Fe) ppm	3.55	4.2
ASTM color	1.5	2.0

Catalyst Preparation

Equal amount of prepared molecular sieve namely Sieve I and Sieve II were mixed together and crushed in a ball mill and then sieved. The fine product (<65 μm) were gathered and then compressed in a pellet machine designed for make pellet with a well defined dimensions using a high pressure (more than 45 atm) to form a 5 mm diam. x 3 mm height pellet. These pellets then dried at 110 °C overnight and then calcined in stepwise manner by heating from room temperature to 220 °C over one hour period heating at 220 °C for 1.5 hours, heating the catalyst from 220 to 500 °C over one hour period and then heating the pellets at 500 °C for two hours. The schematic diagram for this calcination procedure was shown in Fig.(1)

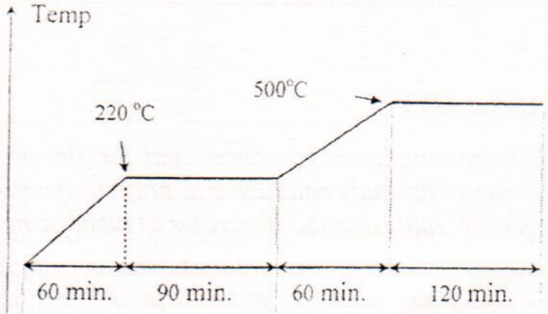

Fig. (1) Calcination sequence of pellets

The catalysts were prepared by impregnation method. Evacuation is applied to remove the air from the pores of the pellets. The impregnation solution is prepared to make a catalyst metal composition 3 wt% NiO, 20wt%WO_3 and balance amount of Sieve I and Sieve II .This wet catalyst then dried at 110 °C for 16 hr and calcined in air using the same above mentioned calcination procedure but at 480 °C instead of 500 °C. Chemical analysis of the prepared are shown in Table (2) .

Table(2) Physical and Chemical Properties of prepared catalyst

Compound	CAT. A
NiO	3 %
WO_3	19 %
Sieve I	39 %
Sieve Ii	39 %
Physical Properties	
Form	Pellet
Mean Particle Diam. (mm)	5
Mean Particle Length (mm)	3
Real Density (kg/m^3)	2.21
Bulk Density (kg/m^3)	0.69
Crushing Strength (N)	33.8

Experiments Conditions

The dewaxing experiments were performed in a laboratory continuous high-pressure unit. This unit consists of feed pump, reactor, pressure separator and cooler with appropriate control system for heating and flow control.

This process employ the activation of NiW/(Sieve I + Sieve II) catalyst by sulfiding process to convert the calcined catalyst into active state.

After the activation is completed the sulfided CAT. A is submitted to dewaxing experiment by applying two feed stocks namely FRAC. A and FRAC. B on this catalyst. The operating conditions are temperature range from 300-400 °C, liquid hourly space velocity range from 1.0 to 3.0 hr^{-1}, pressure 35 bar and hydrogen to hydrocarbon ratio was kept constant at 500 l/l.

Test Methods

For every run accomplished the product gathered and submits to a variety of analysis procedures as follows.

_Gases from each run were analyzed by gas chromatography for C_1 to C_5 analysis as well as the analysis of H_2, H_2S and NH_3

Liquid product first fractionated in a distillation column to separate the light fraction.

The summery of operating conditions of these distillations are:

Fraction	*Temp. range*	*Pressure*	*Reflux ratio*
Gasoline	IBP-150°C	Atmospheric	5:1
Kerosene	150-250°C	5-10 mm Hg	5:1
Gas oil	250-350°C	0.5-5 mm Hg	2:1
Lube fraction	+350°C	0.5-5 mm Hg	2:1

Yield of each run was calculated as the percent of lube oil fraction obtained after separating the light product. Gasoline fraction analyzed in GC for determining the normal to isoparaffins ratio (iso/normal) up to C_8.

Lube oil fractions analyzed for determining the following properties: pour point which is estimated according to ASTM method D97, viscosity at 40°C and at 100°C using U tube viscometer method, viscosity index (ASTM D 2270 and IP 73/53).

RESULTS AND DISCUSSION

Effect of Operating Conditions on Pour Point

The effect of temperature and LHSV on pour point of various lube oil fractions using CAT.A for dewaxing are shown in Fig. (2) and Fig (3).

The pour point decreases as the catalyst bed temperature increases and decreasing the LHSV. These results are in agreement with other studies of pour point reduction (1, 2, 8, 9, 4, 10 and 11).

Pour point reduction at higher temperature can be attributed to two reasons.

At high temperature a high degree of hydrocracking occur and this causes some aromatic rings to decompose and opened resulting a normal or isoparaffin or even isonaphthenic compounds.

At moderate temperature there is a chance for hydroisomerization reaction to occur resulting an isoparaffin formation, which has a low pour point. This conclusion was supported by the iso/normal ratio of produced gasoline which is increased as the catalyst bed temperature increased up to certain level and also by the GC analysis of resulting gases see Table (3)

At the same time, the hydrocracking and hydroisomerization reactions are a function of contact time (reciprocal of LHSV) between reacted feed and the catalyst. Therefore increasing the contact time (low LHSV) leading to increase the rate of pour point reduction reactions as shown from Fig. (4) and Fig.(5).

Table(3) Gases distribution in catalytic dewaxing for FRAC.A and LHSV 1 over CAT.A at various temperature

Component	Vol.%			
	573 K	598 K	648 K	673 K
H_2	73.20	60.47	53.1	39.2
CH_4	4.60	6.7	8.2	10.1
C_2H_6	3.92	4.23	5.58	7.56
C_3H_8	2.95	4.8	5.6	6.2
i- C_4H_{10}	4.5	7.2	7.9	10.63
n -C_4H_{10}	1.5	3.1	4.2	5.6
i-C_5H_{12}	4.1	4.8	5.3	8.6
n-C_5H_{12}	1.71	1.98	2.5	3.0
H_2S	2.74	4.1	4.8	6.1
NH_3	0.78	2.62	2.82	3.01
Total	100	100	100	100

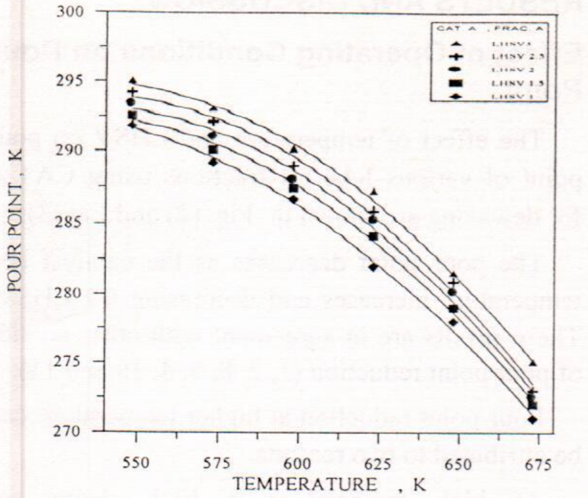

Fig. (2) Effect of temperature on pour point at various LHSV for Frac. A

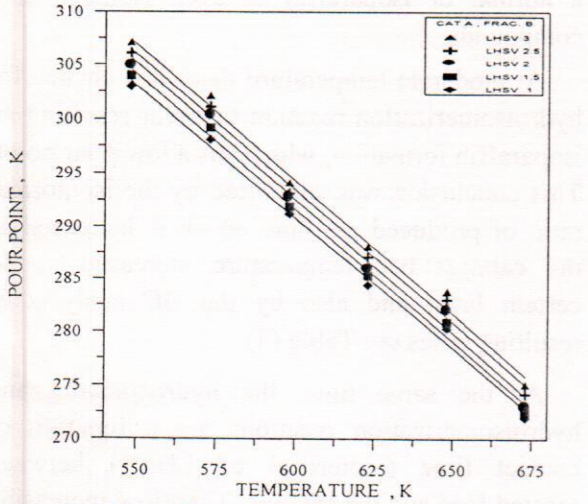

Fig. (3) Effect of temperature on pour point at various LHSV for Frac. B

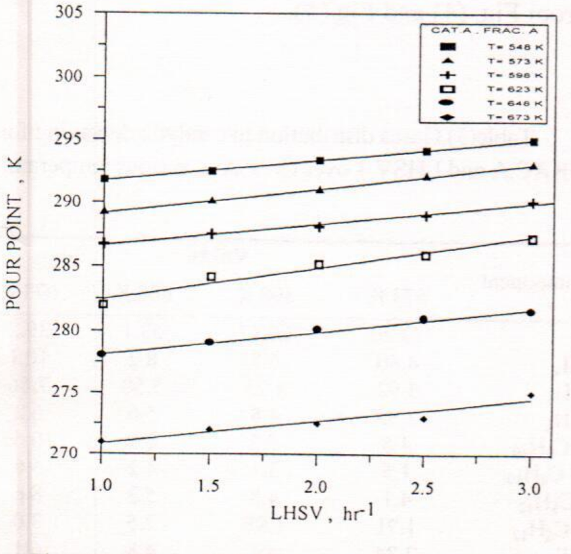

Fig. (4) Effect of LHSV. on pour point at various temperature for Frac. A

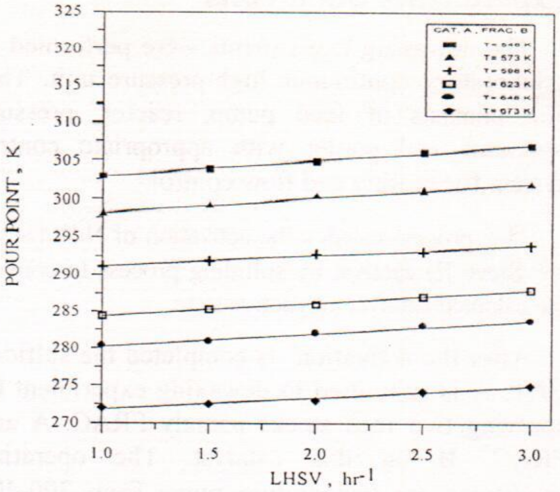

Fig. (5) Effect of LHSV on pour point at various temperature for Frac. B

Effect of operating conditions on Viscosity Index

Viscosity index was one of the most common properties for the lube oil fractions. This property reflects the ability of lube oil viscosity to vary with temperature.

The present study investigates the variation of VI with operating conditions as catalyst bed temperature and LHSV as well as feed type.

It is obvious from Fig. (6) and Fig.(7) that the viscosity index increases monotonically with the catalyst bed temperature increasing and LHSV decreasing, for a given catalyst.

The effect of the feed quality (aromatic and saturated content) also affects VI, and it has a strong relationship with the aromatics and saturates.

The temperature increasing will encourage the saturation of the aromatic species or even decomposes resulting in conversion of aromatics to paraffinic or naphthenic. It was shown also from Fig. (8) to Fig. (11) that temperature has the same effect on the aromatics decreasing and resulting in a high content of saturated compounds and this will improve the viscosity index. This influence was in agreement with the Girgis (12) study which is indicates that the increasing of reaction temperature lead to increase the rate of hydrogenation of aromatic and decrease the equilibrium constant while the LHSV decreasing leads to increase the time of contact and gives the same results.

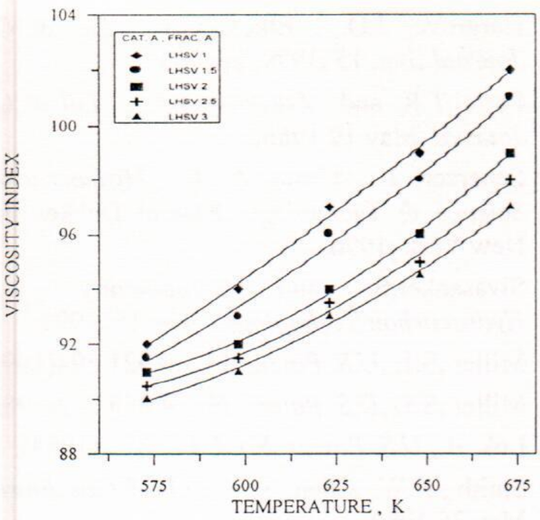

Fig. (6) Effect of temperature on viscosity index at various LHSV for frac. A

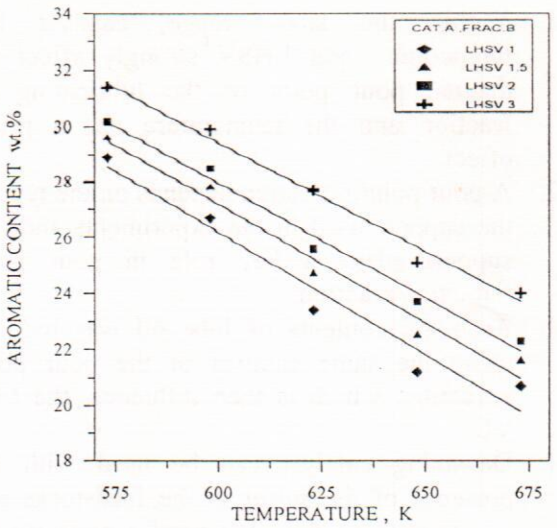

Fig. (8) Effect of temperature on aromatic content of lube oil fraction at various LHSV for frac. B

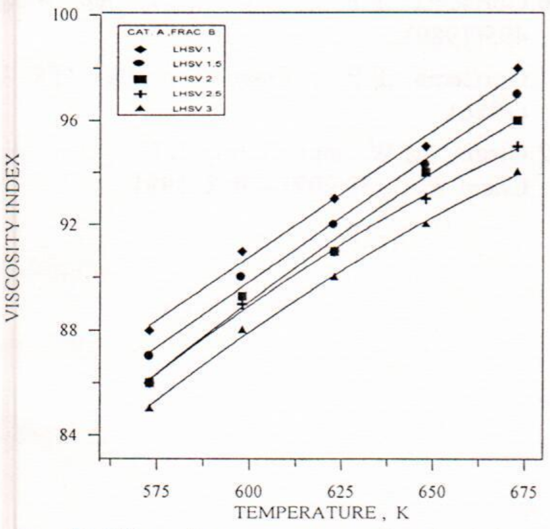

Fig. (7) Effect of temperature on viscosity index at various LHSV for frac. B

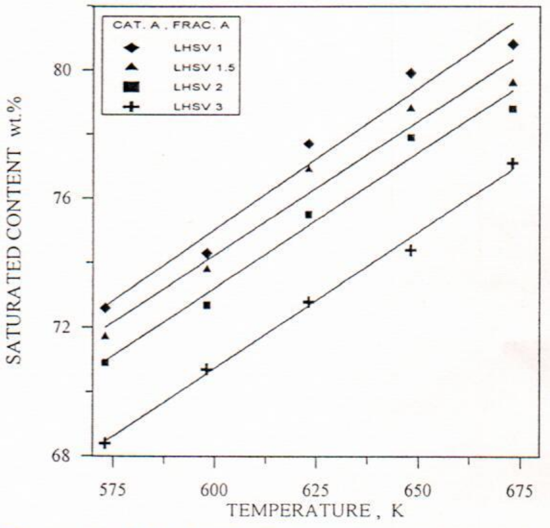

Fig. (9) Effect of temperature on saturated content of lube oil fraction at various LHSV for frac. A

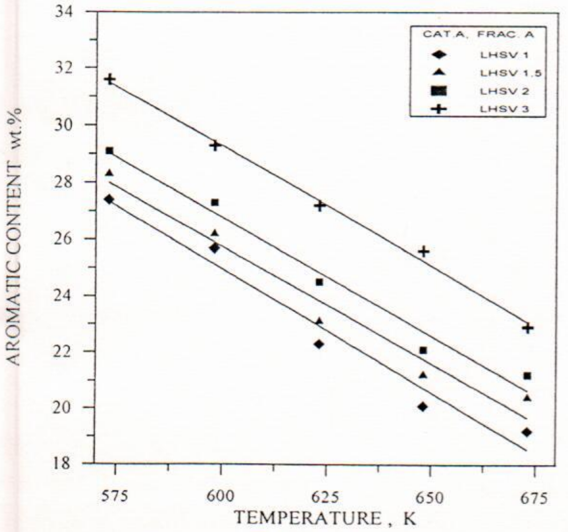

Fig. (8) Effect of temperature on aromatic content of lube oil fraction at various LHSV for frac. A

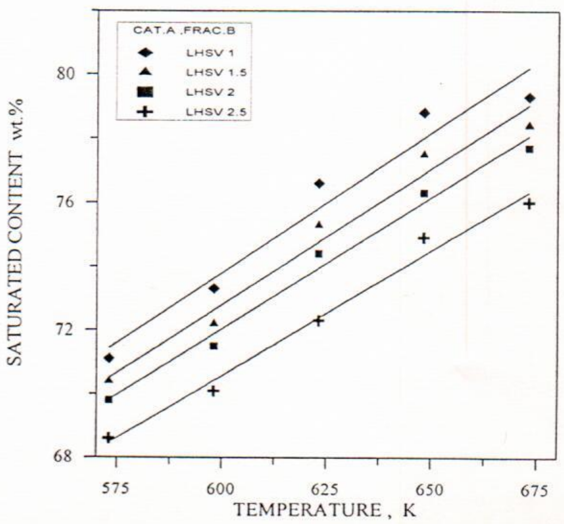

Fig. (10) Effect of temperature on saturated content of lube oil fraction at various LHSV for frac. B

CONCLUSIONS

1. Within the study range, catalyst bed temperature and LHSV strongly affect the desired pour point of the lubricating oil fraction and the temperature has a prime effect.
2. A pour point reduction depends on the type of the support used in the experiments and this support plays a key role in pour point reduction reaction.
3. Aromatic contents of lube oil was reduced using the same catalyst of the pour point reduction, which is then influence, the final VI.
4. Dewaxing catalyst can be used with the presence of the sulfur in the feedstocks and this feedstocks does not need a pretreatment for sulfur removal if the experiments are carried out using metal other than platinum.

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