



# Design of catalyst and process for the dewaxing of petroleum oils

S. Sivasanker, A.V. Ramaswamy<sup>\*</sup>, P. Ratnasamy

*National Chemical Laboratory, Pune 411 008, India*

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## Abstract

The influence of zeolite characteristics, feed properties and process parameters on the dewaxing of petroleum oils are reported. Specifically, the influence of the zeolite properties and process parameters on the quality and yield of the dewaxed products and the deactivation rate of the catalyst are discussed. A typical example of upgrading a paraffinic feedstock into a refrigeration grade oil is presented.

*Keywords:* Dewaxing; ZSM-5 Dewaxing of oils over; Lubricating oils, production of; Dewaxing of petroleum oils; ZSM-5, catalytic properties of

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## 1. Introduction

Catalytic dewaxing based on ZSM-5 zeolites is used commercially in the dewaxing of diesel and lubricating oil base stocks [1–4]. Catalytic dewaxing involves the selective cracking of the high melting, waxy, n-paraffinic components in the oil. It is an excellent example of shape selective catalysis by zeolites [5]. The design of a dewaxing catalyst, therefore, involves primarily, the optimization of the shape selective properties of the zeolite. As the reaction is carried out in hydrogen, the addition of a metallic component improves the life and regenerability of the catalyst. The process parameters of the reaction are, to a large extent, determined by the feed quality and product specifications. In this article, we discuss the parameters that influence the design of zeolite catalysts

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<sup>\*</sup> Corresponding author. Fax. (+91-212) 334761.

and processes for the dewaxing and upgrading of different feedstocks originating from both naphthenic and paraffinic crudes.

## 2. Experimental

ZSM-5 samples with different  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios and crystallite sizes were prepared following established procedures [6–8]. The H-forms of the samples were blended with alumina monohydrate (Catapal-B, Vista Chemical Co., USA), peptised with acetic acid and extruded (1.5 mm dia.). The extrudates were dried at 383 K (6 h) and calcined at 753 K (6 h). The extrudates contained 65 wt.-% H-ZSM-5 on dry basis. These extrudates were loaded with the required metal salts and calcined (753 K, 6 h) and used in the studies.

The feed stocks used were different VGO fractions obtained from a naphthenic Persian Gulf crude. A VGO fraction of a paraffinic Indian (Assam) crude was also used in some studies. The characteristics of the feeds are presented in Table 1. All the feeds except the VGO fraction (AS) were raffinates obtained after extraction of the aromatics using furfural.

The dewaxing reactions were carried out in a high pressure, fixed bed, down flow reactor (Catatest Model B, Geomecanique, France). Usually, 60 g of the catalyst (crushed into 1–2 mm particles) were used. The catalyst was dried in-situ inside the reactor at 773 K in nitrogen and reduced in hydrogen at 723 K (6 h). The temperature was adjusted to the reaction temperature before pressurizing with hydrogen and injection of the feed. Mass balances based on the feed and product weights and inlet and outlet gas volumes and composition were carried out for all the runs. The products were analyzed by a combination of techniques including gas-chromatography (Hewlett–Packard, 5880 A) and ASTM procedures (distillation, pour point and viscosity measurements). The gas chromatographic analysis included: (1) the analysis of the gaseous fraction using a commercial Refinery Gas Analyser (HP 5880 A; 18900C Option 816) and (2) the analysis of the  $\text{C}_{5+}$  fraction by a simulated distillation procedure (HP 5880 A; 18900C Option 840).

Table 1  
Characteristics of the feeds used

Name	Code	Distillation (wt.-%)		pp (K)	S (wt.-%)
		5 (K)	95 (K)		
Spindle Raffinate	SP	598	692	290	0.22
Light Neutral Raffinate	LN	660	752	309	0.50
Inter Neutral Raffinate	IN	698	802	321	0.81
Heavy Neutral Raffinate	HN	756	859	331	1.10
Bright Stock	BS	756	1028	333	–
VGO Fraction (Assam)	AS	605	753	294	0.98

### 3. Results and discussion

Zeolites and molecular sieves possessing 8 to 10 membered ring (MR) openings have been used in many shape selective reactions. For example, erionite (8 MR) and ZSM-5 (10 MR) have been used in octane boosting processes such as Selectoforming [9] and M-forming [10]. Mordenite (12 MR) has been used as a catalyst in the dewaxing process offered by BP [11], while similar processes offered by Mobil [2–4] and Chevron [12] use ZSM-5 zeolites. The major advantages of ZSM-5 are its optimum pore size, the 3-dimensional pore characteristics, resistance to coking, poor H-transfer characteristics and high thermal stability. Zeolites with unidimensional pore systems such as erionite and mordenite deactivate rapidly. They are always used in conjunction with a hydrogenation component, such as Ni or Pt, in order to reduce the deactivation rate. ZSM-5 on the other hand, has a very low deactivation rate and can be often reactivated by simple hydrogen treatment due to the 'soft' nature (higher H/C ratio) of the coke formed over it [13]. A small amount of a metal component is often added to the ZSM-5 to enhance its catalytic activity and reduce the deactivation rate further. The added metal imparts bifunctional characteristics to the catalyst and often enhances the cracking rate. The design of a catalyst for a shape selective cracking reaction involves not only the optimization of the shape selective properties of the zeolite, but also the choice of the most suitable metal component. We will now discuss the design rationale adopted by us.

#### 3.1. Optimization of the zeolite component

Zeolites are acid catalysts and owe their acidities to the  $H^+$  ions present to compensate the negative charge created due to the presence of  $Al^{3+}$  ions in the silicate lattice. As a result, the number of acid sites present (and acid-catalytic activity) is a function of the  $Al^{3+}$  content of the zeolite. For example, Haag et al. [14] have found that the n-hexane cracking rate is directly proportional to the Al-content of H-ZSM-5. However, when diffusion effects are present, the observed rates may not be a linear function of the  $Al^{3+}$  content. The results of dewaxing a heavy neutral raffinate over Ni/H-ZSM-5 with  $SiO_2/Al_2O_3$  ratios of 32, 84 and 347 are presented in Table 2 (A). The shape selective cracking activities of the catalysts are reported in terms of the pour point (pp) of the product, the lower the pp, the greater the selective removal of the waxy components (normal paraffins). As expected, the catalyst with the highest  $SiO_2/Al_2O_3$  ratio (347) is the least active (pp = 279 K) and also deactivates faster, necessitating an increase in temperature of 75 K in 33 h to maintain the same pp. The catalysts with  $SiO_2/Al_2O_3$  ratios of 32 and 84 have higher activities and lower deactivation rates. Interestingly, the performance of both the latter samples are similar, suggesting that, beyond a certain limit, higher

Table 2  
Influence of  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio and crystallite size on catalytic dewaxing

$\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio	Crystallite size ( $\mu\text{m}$ )	TOS <sup>a</sup> (h)	T (K)	pp (K)
(A)				
32	0.5	76	563	265
32	0.5	208	573	271
84	0.5	76	562	266
84	0.5	208	569	271
347	0.5	13	596	279
347	0.5	46	671	279
(B)				
80	0.1	49	552	280
80	0.1	145	557	280
80	6.0	66	595	282
80	6.0	145	613	283

<sup>a</sup> TOS = Time on stream (h).

Conditions:

(A) Feed: HN; catalyst = Ni(2 wt.-%)-ZSM-5;  $P = 3.0$  MPa;  $\text{H}_2/\text{Oil}$  (v/v) = 400; WHSV =  $0.8 \text{ h}^{-1}$ .

(B) Feed: LN; catalyst = Pd(0.3 wt.-%)/Zn(1.0 wt.-%)-ZSM-5;  $P = 4.0$  MPa;  $\text{H}_2/\text{Oil}$  (v/v) = 300; WHSV =  $1.2 \text{ h}^{-1}$ .

Al-contents do not further improve dewaxing rates presumably due to diffusion limitations.

The pore dimensions of ZSM-5 (5.4–5.7 Å) are just adequate for the entry of the normal and slightly branched alkanes. In the cracking of hexane isomers over ZSM-5 crystallites of 1.35  $\mu\text{m}$  dia., while the intracrystalline diffusion of n-hexane and 3-methylpentane were not rate limiting, the diffusion of 2,2-dimethylbutane was found to be the rate limiting step [15]. However, in the case of heavy feedstocks ( $\text{C}_{20}$ – $\text{C}_{60}$ ), such as those used in the dewaxing of lube base stocks, the diffusion of even the normal and mildly branched molecules is expected to be rate limiting. As a result, one would expect smaller crystallites possessing shorter diffusion paths to perform better than larger crystallites. The results of the influence of crystallite size on the temperature required to obtain the same pp ( $\pm 2$  K) during the dewaxing of an inter neutral feed are presented in Table 2 (B). Smaller crystallites (0.1  $\mu\text{m}$ ) are able to achieve the same pp reduction ( $\Delta\text{pp} = 40$ ) at a lower operating temperature (552 K) than larger crystallites, the  $\Delta T$  required to maintain the same pp being 5 K in the case of the 0.1  $\mu\text{m}$  crystallites and 18 K in the case of the 6  $\mu\text{m}$  crystallites. Another disadvantage of larger crystallites is that, due to the higher temperatures of operation and the longer residence of the primary cracked products inside the pores, the yield of light gases arising by secondary cracking reactions tends to be higher. For example, the temperature required to dewax an inter neutral feed (pp = 321 K) to a pp of 263 K was 619 and 602 K when the crystallites were 5 and 0.5  $\mu\text{m}$  in size, respectively and the  $\text{C}_1$ – $\text{C}_4$  gas yield over the two catalysts were 14.2 and 10.1 wt.-%, respectively.

Table 3  
Influence of crystallite size and surface pacification

Crystallite size ( $\mu\text{m}$ )	$T$ of reaction (K)	Product distribution (wt.-%) <sup>b</sup>			Viscosity index of DWO <sup>c</sup>
		$C_1-C_4$	$C_5- < \text{DWO}$	DWO	
0.2	581	8.8	7.4	83.2	90.3
0.2 (s) <sup>a</sup>	578	8.1	7.2	84.7	92.0
2.0	603	11.5	5.0	84.4	91.9

Conditions: Feed: BS;  $P = 4.5 \text{ MPa}$ ;  $\text{WHSV} = 0.8 \text{ h}^{-1}$ ;  $\text{H}_2/\text{Oil} (\text{v/v}) = 400$ ; DWO pp = 267 K.

<sup>a</sup> External surface pacified by depositing 15%  $\text{SiO}_2$  by adsorbing di-trimethylsilylamine from an hexane solution and decomposing at 773 K.

<sup>b</sup> Deviations in mass balance from 100% are due to errors in estimation of lighter fractions. The DWO yields are accurate to  $\pm 0.2 \text{ wt.-%}$ .

<sup>c</sup> Values accurate to  $\pm 0.4$  units.

Small crystallites, however, expose a larger external surface area and are less shape selective than larger crystallites. They also catalyse unwanted reactions (of the branched paraffins, for example) at the external surface leading to lower yields of dewaxed oil [16]. Besides, they also destroy more naphthenic components which generally possess higher viscosity indices (VI) than the other components, leading to a lower VI value for the product. However, if the external surface of the small particles is passivated (by silicifying, for example), then the dewaxed oil yields are higher since branched paraffins are not cracked on the passivated external surface (Table 3). Passivation is also found to increase the viscosity index (VI) of the dewaxed oil (Table 3).

### 3.2. Choice of the metal component

Very often, the addition of a metallic component to an acid catalyst enhances its activity, reduces deactivation and improves its regenerability. The influence of added metallic component [17] on the activity of H-ZSM-5 in the cracking of

Table 4  
Influence of metal component on hydrocracking

Catalyst	Metal content <sup>a</sup>	Feed		
		n-hexadecane Conversion (wt.-%)	n-hexadecane + 0.2% S	Heavy neutral $T$ (C) for DWO of pp = 273 K
H-ZSM-5	0.0	33.5	54.0	295
Pd-ZSM-5	0.2	99.0	52.5	310
Pd/Zn-ZSM-5	0.3/1.0	60.2	39.2	315
Ni-ZSM-5	2.0	46.4	53.5	298

Conditions: n-hexadecane:  $P = 0.1 \text{ MPa}$ ;  $T = 593 \text{ K}$ ;  $\text{WHSV} = 3 \text{ h}^{-1}$ ;  $\text{H}_2/\text{Oil} (\text{v/v}) = 400$ . Heavy neutral:  $P = 3 \text{ MPa}$ ;  $\text{WHSV} = 0.65 \text{ h}^{-1}$ ;  $\text{H}_2/\text{Oil} (\text{v/v}) = 400$ .

<sup>a</sup> The metal components were incorporated using salts by wet impregnation, drying (383 K) and calcination (773 K).

n-hexadecane in the presence and absence of S is presented in Table 4. In the absence of sulfur, Pd and Ni increase the rate of cracking of n-hexadecane with Pd being more effective than Ni. This enhancement is mainly due to the hydrogenolysis activity of the metals. On the other hand, in the presence of 0.2 wt.-% S in the feed, the activities of all the catalysts even out to nearly similar levels due to the suppression of the metallic function. The reason for the enhancement of the activities of H-ZSM-5 and Ni-ZSM-5 by feed S is not clear, though it could be due to the creation of more acidic –SH groups. The influence of the metal on the temperature required to dewax heavy neutral raffinate to a pp of 273 K is also presented in Table 4. The addition of a metal component does not appear to enhance the catalytic activity of H-ZSM-5 in the case of the above feed (1.1 wt.-% S). This is similar to the results obtained while hydrocracking n-hexadecane containing S.

### 3.3. Influence of process parameters

An increase in temperature or a decrease in space velocity (WHSV) increases the conversion of the waxy molecules and lowers the pp of the dewaxed oil (DWO) (Figs. 1 and 2). In dewaxing operations, the temperature and feed rates are fixed based on the pp desired for the product oil. The influence of process parameters on the relationship between temperature and WHSV to maintain a constant pp of the product are presented in Table 5. A proper combination of temperature and WHSV leads to maximum yields of the DWO and minimum yields of the least desired C<sub>1</sub>–C<sub>2</sub> gases. The other process parameters, viz., pressure and H<sub>2</sub>/Oil ratios also influence the DWO yield and product distribution (Table 6). Lower pressures increase DWO yields while the influence of

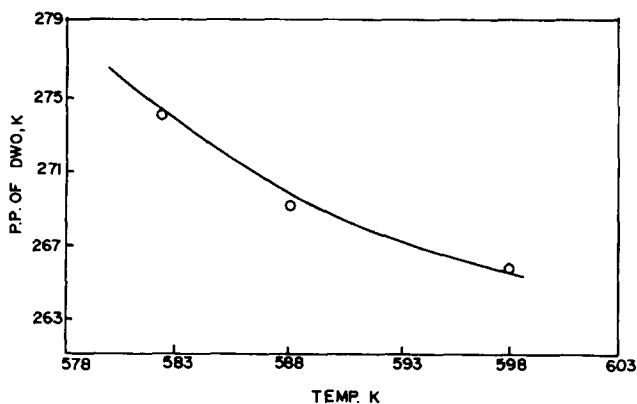


Fig. 1. Influence of temperature on pour point of dewaxed oil. Feed: BS; catalyst = Ni(2 wt.-%)-ZSM-5;  $P = 4.5$  MPa,  $WHSV = 0.6$  h<sup>-1</sup>; H<sub>2</sub>/Oil (v/v) = 600.

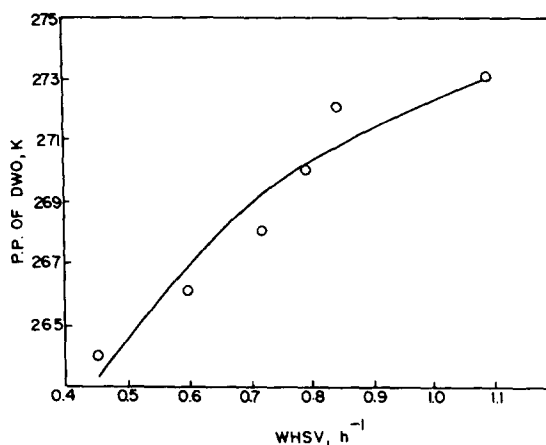


Fig. 2. Influence of WHSV on pour point of dewaxed oil. Feed: BS; catalyst = Ni(2 wt.-%)-ZSM-5;  $P = 4.5$  MPa;  $T = 593$  K;  $H_2/Oil = (v/v) = 600$ .

variation in  $H_2/Oil$  (in the range studied; Table 6) is not significant. However, lower pressures and  $H_2/Oil$  ratios cause more rapid deactivation (Fig. 3).

### 3.4. Influence of feed characteristics

For a desired product pp, the yield of the dewaxed oil is related to its wax content. In Table 7, the n-paraffin contents of a number of oils belonging to the

Table 5  
Influence of temperature and WHSV<sup>a</sup>

T (K)	WHSV (h <sup>-1</sup> )	Product distribution (wt.-%)			
		C <sub>1</sub> + C <sub>2</sub>	C <sub>3</sub> + C <sub>4</sub>	C <sub>5+</sub> - < DWO	DWO
576	0.45	0.6	8.7	8.9	81.7
582	0.65	0.4	8.6	8.9	81.7
592	0.77	0.3	8.7	8.4	82.6
598	0.83	0.5	8.4	8.7	82.3

<sup>a</sup> Catalyst = Ni(2 wt.-%)/H-ZSM-5; Feed: HN;  $P = 4.5$  MPa;  $H_2/Oil (v/v) = 510$ .

Table 6  
Influence of pressure and  $H_2/Oil$  ratio<sup>a</sup>

P (MPa)	$H_2/Oil (v/v)$	Product distribution (wt.-%)			
		C <sub>1</sub> + C <sub>2</sub>	C <sub>3</sub> + C <sub>4</sub>	C <sub>5+</sub> - < DWO	DWO
3.5	500	0.3	7.7	8.0	84.0
4.5	510	0.5	8.4	8.7	82.3
5.0	520	0.6	9.0	8.3	82.1
5.5	510	0.6	9.2	8.9	81.4
4.5	330	0.4	7.9	9.1	82.6
4.5	680	0.6	8.7	8.6	82.2

<sup>a</sup> Catalyst = Ni(2 wt.-%)/H-ZSM-5; Feed: HN; WHSV = 0.86 h<sup>-1</sup>;  $T = 597$  K.

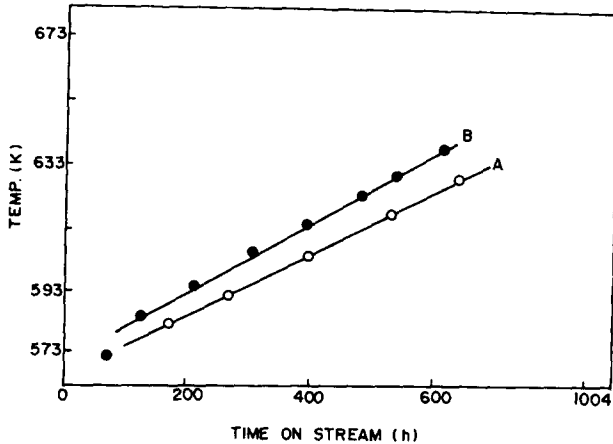


Fig. 3. Influence of process parameters on deactivation rate. Feed: BS; catalyst = Ni(2 wt.-%)-ZSM-5; (A)  $P = 4.5$  MPa,  $WHSV = 0.9$   $h^{-1}$ ;  $H_2/Oil$  (v/v) = 600; (B)  $P = 3.0$  MPa;  $WHSV = 0.6$   $h^{-1}$ ;  $H_2/Oil$  (v/v) = 400.

same crude are presented along with the yields of DWO and the product pps. The yield of DWO is inversely related to the n-paraffin content of the oil (Table 7). The n-paraffin content of the oil itself decreases as the feed becomes heavier (Spindle Oil to Bright Stock). It is, therefore, surprising that a pp reduction of 60 K is achieved in the case of Bright Stock even when negligible n-paraffins are present in it. It is probable that, n-paraffin removal mostly contributes to pp reduction in the case of the lighter feedstocks and cracking of the paraffinic side chains in poly condensed molecules contributes to pp reduction in the case of the heavier feeds [3]. The yield of DWO is also a function of its pp (Fig. 4). For a given feed, products with different pps can be obtained by changing the WHSV, keeping other process parameters the same.

### 3.5. Processing of paraffinic oils

Usually, lubricating oil base stocks, are processed from naphthenic crudes which contain less paraffins (wax) and aromatics. The choice of the right crude

Table 7  
Influence of feed paraffin content on DWO yield

Feed	n-paraffins (wt.-%)	DWO (pp, K)	$\Delta pp$ . <sup>a</sup> (K)	DWO yield (wt.-%)
SP	16	263	27	72.5
LN	12	263	46	75.0
IN	8	267	54	79.0
HN	4	273	58	83.3
BS	–	273	60	86.9

Conditions:  $P = 4.0$  MPa;  $H_2/Oil$  (v/v) = 400;  $T$  and  $WHSV$  varied to get desired pp of DWO.

<sup>a</sup>  $\Delta pp = \text{Feed pp} - \text{DWO pp}$ .



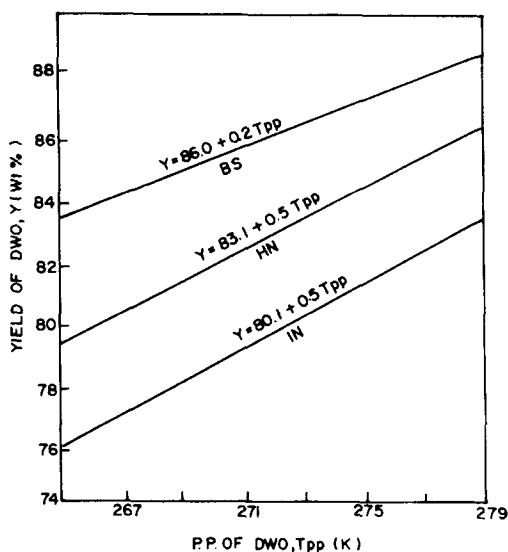


Fig. 4. Yield vs. pour point relationships for different feedstocks [18]. Yield and pour point of product fitted into linear equations; catalyst = Ni(2 wt.-%)-ZSM-5;  $P = 4.5$  MPa;  $T$  and WHSV varied for the different feeds to get products with different pps.

becomes even more important when producing speciality oils such as those used in refrigeration machinery and transformer oils, as these oils have to possess, in addition to low pps, high aniline points, good thermal stability and desired electrical properties. The production of such oils is, therefore, restricted to naphthenic crudes. We now report our attempt to convert a fraction from a paraffinic (and aromatic-rich) crude oil obtained from Assam, India, into a low pour (243 K) refrigeration/transformer oil.  $^{13}\text{C}$ -NMR data reveal that the aromatics constitute 33.5% (on C-basis) of the feed. Two options are available for upgrading this oil; the aromatics could be extracted with a solvent (say furfural) or hydrogenated prior to dewaxing. Solvent extraction of this feed will, however, lead to a loss of product yield by about 40%. Hence, the hydrogenation option was selected. The important product specifications were: pp = 243 K, aniline point = 353 K and viscosity of 100 Cst at 313 K. Though the desired viscosity could be realised by adjusting the feed cut points, the other properties had to be realized by optimising the process parameters.

The optimized process conditions and the feed and product characteristics are presented in Table 8. An increase in aniline point from 338 to 350 K (decrease in aromatics) was observed after step 1. However, the pp did not change suggesting that the pp of the oil was determined mainly by its paraffinic component. After step 2 (dewaxing), the pp decreased to 243 K, a drop of 51 degrees. But then, the aniline point decreased to 334 K due to an increase in concentration of the aromatics in the fraction remaining after the removal of the paraffinic materials by dewaxing. In step 3, further hydrogenation of the

Table 8  
Process optimisation for upgrading a lube cut from Assam crude

	pp (K)	Aniline point (K)	Viscosity (Cst), 313 K
Feed	294	338	–
<i>Product</i>			
After step 1	294	350	–
After step 2	243	334	–
After step 3	243	353	98

Step 1: *Hydrogenation of aromatics*: catalyst <sup>a</sup> = Ni/Mo-Al<sub>2</sub>O<sub>3</sub>; *P* = 10 MPa; *T* = 573 K; WHSV = 0.25 h<sup>-1</sup>.

Step 2: *Hydrodewaxing*: catalyst = Ni(2 wt.-%)/H-ZSM-5; *P* = 4.5 MPa; *T* = 573 K; WHSV = 1.0 h<sup>-1</sup>.

Step 3: *Hydrofinishing*: catalyst <sup>a</sup> = Ni/Mo-Al<sub>2</sub>O<sub>3</sub>; *P* = 13 MPa; *T* = 573 K; WHSV = 0.25 h<sup>-1</sup>.

<sup>a</sup> Commercial catalyst: NiO = 4 wt.-%, MoO<sub>3</sub> = 13 wt.-%.

aromatics occurred and the aniline point increased significantly to the desired value, 353 K meeting the product specification.

#### 4. Conclusions

Small particles (ca. 0.1 μm) of ZSM-5 are more active and deactivate less than large particles (6 μm) during the dewaxing of heavy petroleum fractions. Similarly, intermediate SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios (around 80) appear to be more suitable. Further improvement of the catalyst performance is possible by pacifying the external surface of the small particle zeolites with SiO<sub>2</sub>. Optimization of the feed rate and temperature of dewaxing leads to maximum yields of the desired products, while pressure and hydrogen partial pressure influence deactivation rate. By suitable design of an integrated process scheme, even paraffinic, aromatic rich feedstocks — such as those from Assam, India — can be converted into valuable low pour lube stocks for the production of refrigeration and transformer oils.

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