Catalytic dewaxing of an inter neutral raffinate over Ni-impregnated HZSM-5

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Dewaxing of an inter neutral raffinate has been studied over HZSM-5 (SiO₂/Al₂O₃ ratio 80) impregnated with nickel in a high pressure, fixed bed reactor under varying conditions of temperature, pressure and feed flow rate. The zeolite is bound in an alumina matrix (zeolite to alumina ratio 65:35 w/w). The feed, which has a pour point of 313K, shows a vast improvement in fluidity characteristics after dewaxing. The pour point is found to be dependent on the reaction temperature and decreases to 249 K with reaction temperature increasing to 596 K.

Dewaxing is a process for the removal of waxy substances from a petroleum crude for improving the fluidity characteristics at low temperature. Solvent dewaxing uses a suitable solvent for bringing the oil into solution while the wax separates out as crystals with lowering of the temperature1. The operating cost of this process is very high and the desired pour point of the dewaxed oil has to be compromised with the enormous cost of refrigeration to low temperature2. The present trend is, therefore, to substitute solvent dewaxing with catalytic dewaxing3,4.

The straight chain or the slightly-branched chain paraffins are selectively removed in the catalytic dewaxing process. The olefin-rich products of dewaxing are simultaneously hydrogenated for maintaining product quality. For this purpose, a bifunctional catalyst is normally used. A shape-selective catalyst like the ZSM-5 zeolite serves as the most versatile dewaxing component5,6 while a Group VI or Group VIII metal usually functions as the hydrogenation component. The influence of the zeolite parameter variation such as crystalline size, SiO₂/Al₂O₃ ratio and isomorphous substitution on catalytic dewaxing has already been reported7-10. The zeolite to be an effective catalyst, must be able to convert high pour point normal alkanes selectively, and at the same time, must restrict the size of the transition state complexes for preventing deposition of bulky coke precursors inside the pores. Coke deposition will reduce the effective life of the catalyst.

The pore dimensions11 of ZSM-5 are such that aromatics, naphthenes and highly branched paraffins can pass through the channels unchanged while the normal paraffins and the slightly-branched paraffins are cracked inside the pores to low molecular weight hydrocarbons. The present study reports on the dewaxing of an inter neutral raffinate over Ni-impregnated HZSM-5 at different temperatures, pressures and feed rates.

Experimental Procedure

The zeolite ZSM-5 was synthesized with a SiO₂/Al₂O₃ ratio of 80 by a well-known hydrothermal technique12. The ZSM-5 structure was confirmed by XRD.

The catalyst for dewaxing was prepared13 by mixing the zeolite with alumina (ZSM-5 to Al₂O₃ ratio 65:35 w/w) and dilute acetic acid, and was extruded. The extrudates were calcined at 811 K for 3 h in flowing nitrogen, cooled and contacted with a 1M ammonium nitrate solution for 1 h at room temperature. The exchange was carried on till the sodium level was less than 0.05 wt%. The extrudates were dried and treated with an aqueous solution of 1.5% nickel nitrate. The volume of the solution was just enough to cover the extrudates completely. The mixture was heated in a water bath at 353 K with gentle stirring till all the water evaporated. The extrudates were then washed and dried at 383 K for 12 h and calcined at 811 K for 6 h in a flowing mixture of nitrogen and air in the ratio of 9:1. The catalyst was found to contain 1.5% NiO. The extrudates were broken into size 1.5 mm × 3.0 mm and 60.0g of it was loaded into the reactor.

A high pressure, fixed bed down-flow stainless
steel (SS 316) reactor (Catatest model B, Geomechanique, France) was used in this work. The tubular reactor had a total volume of 220 mL, length 88.5 cm and i.d. 1.9 cm. A thermowell of o.d. 6 mm in the centre of the reactor contained four thermocouples for measuring the temperature of the reactor at four different zones along the entire length. The temperature of each zone can be controlled independently with a set of controllers. Hydrogen gas could be introduced to the reactor from the top through a mass flow controller while the feed was introduced also through the top with a micro feed pump.

The catalyst after being loaded into the reactor was dried by passing air (100 mL/min) for 2 h at 573 K and then for 5 h at 773 K. It was then purged with nitrogen and cooled to 373 K. The catalyst temperature was then raised and maintained at 623 K for 12 h during which hydrogen was introduced. The reactor was pressurised to the required extent by adjusting hydrogen flow rate and the feed was introduced at a pre-determined rate. The reactor temperature was simultaneously adjusted to the desired temperature.

An inter neutral raffinate of middle east origin was used as a feed. It had an initial boiling point (IBP) of 625 K, pour point of 313 K and distillation characteristics of 5 and 95% at 669 and 817 K, respectively.

The reaction products, both liquid and gaseous, were collected periodically and were analysed by a combination of techniques including gas chromatography (Hewlett Packard Model 5880A) and ASTM methods14,15 for distillation and pour point measurement. Multi-refrigerated baths were used in the determination of pour points.

Results and Discussion

Typical gas chromatograms, before and after dewaxing of the raffinate are shown in Fig. 1. The dewaxing was studied at five different temperatures in the range of 556 to 569 K at 10° intervals at a constant pressure of 3.1 MPa and WHSV of 1 h⁻¹. The product distribution is given in Table 1. The gaseous products were mostly C₃ and C₄ hydrocarbons both of which steadily increased with rising reaction temperature. Consequently, the amount of dewaxed oil (DWO) showed some decrease. The pour point of the feed, which was only 313 K, improved from 259 to 249 K in the range of reaction temperature used. C₁ also showed a perceptible increase in yield with temperature which was likely to be due to enhanced cracking of higher hydrocarbons as the temperature went up. Yield of C₂ indicated some abnormalities at 566 and 576 K, this might be due to some unknown reason or experimental deficiency. C₅₊ hydrocarbons showed an increase between 556 and 566 K, and then the yield remained almost constant. It is likely that the yield of these hydrocarbons was balanced by their removal through cracking at high temperature.

The inter-relationships among the yield of DWO, pour point and temperature of dewaxing are shown in Fig. 2. A decrease in pour point is achieved through the removal of normal and slightly-branched alkanes and hence, an improvement in pour point results in some sacrifice in the yield of DWO. When the pressure was increased from 2.1 to 3.6 MPa with the reaction being carried out at 596 K and WHSV 1 h⁻¹, the pour point showed very little change (Table 2). The product distribution changed considerably when the pressure changed from 2.1 to 3.1 MPa, though the distribution was not much affected between 3.1 and 3.6 MPa pressure. Both C₁ and C₂ exhibited an increasing yield with rise in pressure while C₄ and C₅₊ recorded a decline. The yield of C₃ increased between 2.1 and 3.1 MPa pressure, and then decreased with further increase in pressure. These results may be explained on the basis of increased cracking activity of higher hydrocarbons with rise in pressure.

Influence of feed flow rate was studied by carrying out the dewaxing at WHSV of 0.5, 1.0 and 1.5 h⁻¹ at a constant reaction temperature and pressure of 576 K and 3.1 MPa respectively. The results are shown in Table 3. It is seen that the
Table 1—Influence of temperature on product distribution in dewaxing of an inter neutral raffinate at 3.1 MPa pressure, 1 h⁻¹ WHSV, \( \text{H}_2/\text{oil ratio} \) 415 v/v

<table>
<thead>
<tr>
<th>Temperature K</th>
<th>( C_1 )</th>
<th>( C_2 )</th>
<th>( C_3 )</th>
<th>( C_4 )</th>
<th>( C_{5+} ) to IBP</th>
<th>DWO</th>
<th>Pour point of DWO, K</th>
</tr>
</thead>
<tbody>
<tr>
<td>556</td>
<td>0.0666</td>
<td>0.1321</td>
<td>5.5254</td>
<td>4.6987</td>
<td>1.3871</td>
<td>88.19</td>
<td>259</td>
</tr>
<tr>
<td>566</td>
<td>0.0880</td>
<td>0.6737</td>
<td>5.9921</td>
<td>4.9564</td>
<td>1.6193</td>
<td>86.67</td>
<td>256</td>
</tr>
<tr>
<td>576</td>
<td>0.1098</td>
<td>0.2695</td>
<td>8.4766</td>
<td>5.6657</td>
<td>1.6164</td>
<td>83.86</td>
<td>253</td>
</tr>
<tr>
<td>586</td>
<td>0.1703</td>
<td>0.4042</td>
<td>10.6400</td>
<td>6.0821</td>
<td>1.6183</td>
<td>81.08</td>
<td>251</td>
</tr>
<tr>
<td>596</td>
<td>0.2198</td>
<td>0.5273</td>
<td>11.5029</td>
<td>5.9435</td>
<td>1.5662</td>
<td>80.24</td>
<td>249</td>
</tr>
</tbody>
</table>

Table 2—Influence of pressure on product distribution for dewaxing of the inter neutral raffinate at 596 WHSV 1 h⁻¹ and \( \text{H}_2/\text{oil ratio} \) 415 v/v

<table>
<thead>
<tr>
<th>Pressure MPa</th>
<th>( C_1 )</th>
<th>( C_2 )</th>
<th>( C_3 )</th>
<th>( C_4 )</th>
<th>( C_{5+} ) to IBP</th>
<th>DWO</th>
<th>Pour point of DWO, K</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>0.1345</td>
<td>0.3529</td>
<td>9.8521</td>
<td>6.3687</td>
<td>2.1308</td>
<td>81.14</td>
<td>249</td>
</tr>
<tr>
<td>3.1</td>
<td>0.2198</td>
<td>0.5273</td>
<td>11.5029</td>
<td>5.9429</td>
<td>1.5662</td>
<td>80.24</td>
<td>249</td>
</tr>
<tr>
<td>3.6</td>
<td>0.2625</td>
<td>0.5603</td>
<td>11.2850</td>
<td>5.2108</td>
<td>1.2800</td>
<td>81.40</td>
<td>250</td>
</tr>
</tbody>
</table>

Table 3—Effect of feed flow rate on product distribution in dewaxing of an inter neutral raffinate at 576 K and 3.1 MPa pressure, with \( \text{H}_2/\text{oil ratio} \) 415 v/v

<table>
<thead>
<tr>
<th>WHSV h⁻¹</th>
<th>( C_1 )</th>
<th>( C_2 )</th>
<th>( C_3 )</th>
<th>( C_4 )</th>
<th>( C_{5+} ) to IBP</th>
<th>DWO</th>
<th>Pour point of DWO, K</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.1611</td>
<td>0.3760</td>
<td>10.7296</td>
<td>6.2497</td>
<td>1.7479</td>
<td>80.74</td>
<td>251</td>
</tr>
<tr>
<td>1.0</td>
<td>0.1098</td>
<td>0.2695</td>
<td>8.4766</td>
<td>5.6657</td>
<td>1.6164</td>
<td>83.86</td>
<td>253</td>
</tr>
<tr>
<td>1.5</td>
<td>0.0667</td>
<td>0.1618</td>
<td>5.6206</td>
<td>4.3807</td>
<td>1.3807</td>
<td>88.39</td>
<td>263</td>
</tr>
</tbody>
</table>

Fig. 2—The relations between DWO yield, pour point and temperature of dewaxing at a pressure of 3.1 MPa, WHSV of 1 h⁻¹ and hydrogen/oil ratio of 415 v/v
fluidity of the DWO deteriorated with increasing WHSV. The increase in pour point and consequently the increase in the amount of DWO yield were more pronounced when the WHSV was changed from 1.0 to 1.5 h⁻¹. An increase in space velocity resulted in more DWO indicating in actual terms a decrease in the extent of cracking of alkanes. This is also evident from the yields of C₁⁻C₅ hydrocarbons, all of which registered decrease with increasing space velocity, i.e., with decreasing contact time between the feed and the catalyst.

Ni-HZSM-5 can, therefore, be used as an efficient dewaxing catalyst under suitable conditions. The presence of two intersecting channels in ZSM-5, both formed by 10-membered oxygen rings, but differing slightly in their pore size, plays an important role in spacio-specific cracking of paraffins in the dewaxing reaction. The reactant and the product molecules in dewaxing reactions are small enough to diffuse through the channels, but the reaction intermediates are larger than either the reactants or the products and are spatially constrained. This hinders the formation of reaction intermediates of branched chain alkanes present in the raffinate, and, therefore, the cracking is limited only to straight chain and slightly-branched chain alkanes. This also ensures formation of little or no coke deposits inside the pores such that the active sites for dewaxing remain exposed and the deactivation of the catalyst is considerably slowed down. The catalyst in this work was used for many runs without much evidence of deactivation.

The mechanism of dewaxing essentially consists of two main steps:

(i) n-alkanes and slightly-branched alkanes

\[ \text{cracking} \]

olefinic products

(ii) olefinic products + H₂ → lower alkanes + DWO

The dewaxing proceeds via a carbenium ion mechanism and the relatively high yield of C₅ alkanes in the final product distribution may be explained on the basis of β-scission of secondary carbenium ions, being the favoured way of cracking. With increase in reaction temperature, the rate and extent of cracking also increase, and consequently C₁ to C₅ recorded a net increase while the DWO yield decreased. Enhanced cracking at high temperature helps in the removal of the waxy substances from the raffinate resulting in the improvement of its fluidity, i.e., a decrease in the pour point.

Conclusion

Using HZSM-5 with 1.5% NiO, it is shown that an inter neutral raffinate could be successfully dewaxed with a decrease in pour point up to 249 K at a reaction temperature of 596 K which is well below the IBP of the feed. High temperature and low space velocity favour the dewaxing process, while pressure does not have a pronounced affect.

Acknowledgement

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References