THERMAL CRACKING OF PARAFFINS TO OBTAIN α-OLEFINS

Z. V. Gerasicheva, Ya. A. Botnikov,
and E. V. Osipova

A considerable amount of normal α-olefins with various molecular weights is used for obtaining alcohols, surfactants, additives for motor oils, synthetic lubricants and other products. Thermal cracking of paraffins is the chief method for obtaining α-olefins [1]. Many reports have been published on thermal cracking of synthetic and petroleum paraffins, and gatch. Some of these deal with the low-temperature range [2, 3]. Information on high-temperature cracking [4-8], which is of maximum interest in view of recent developments, is somewhat inadequate; in particular, some of these reports contain little information on the effect of the crude's quality on the chemical composition and structure of the unsaturated hydrocarbons in the cracking products.

For several years VNII NP and KNII NP [9] have been studying high-temperature cracking of different sorts of paraffin crude, with the aim of developing a continuous industrial process. Our reports [10, 11] have dealt with the production of crude for obtaining wetting agents and alcohols by cracking paraffin.

The present paper deals with the study and production of α-olefins with different molecular weights and 6-18 carbon atoms, with the aim of their all-purpose utilization in petrochemical synthesis. In the processing of different sorts of paraffin crude we studied the following cracking products:

1) the 40-140°C fraction (crude for obtaining alcohols by oxosynthesis);
2) the 140-180°C fraction (crude for alkylation to obtain motor oil additives; when mixed with the 240-320° C fraction, this fraction can be used for obtaining secondary alkyl sulfates—the wetting agent "Tipol");
3) the 180-240°C fraction (crude for making sodium alkylbenzoyl sulfonate—NP-3 sulfonol);
4) the 240-320°C fraction (crude for making motor oil additives).

These fractions can also be used in different combinations to make other products, particularly synthetic oils etc.

Table 1 gives the characteristics of the crude subjected to cracking. All the specimens were obtained by deparaffinization of distillates of mixtures of Eastern sulfur oils.

The experiments were performed in a pilot plant with a coil reactor [10].

Cracking was performed at atmospheric pressure, the temperature at the inlet of the reaction coil being ~500° C, and at the outlet 550° C; in some cases a one-way process was used, in others recirculation. Steam was not fed to the system because it was found that it has no effect on the yield and quality of the products during high-temperature cracking at atmospheric pressure. In plants where the excess pressure reaches 3-5 atm, to retain the same yields and qualities of the products as those obtained at atmospheric pressure a steam feed (5-10 % of the furnace charge) is necessary. The effect of steam and pressure will be discussed more fully in a separate paper.

To change the degree of conversion we varied the volumetric flow rate of the crude from 0.9 through 12.0 h⁻¹ for solid paraffins of gatch, and from 0.8 through 4.8 h⁻¹ for liquid paraffins. The mass balance and product quality were determined for each degree of conversion. In addition to overall analysis of the liquid cracking products we studied the group hydrocarbon composition; for the 40-140° C fraction we used mass spectrometry, for the higher boiling fraction a combination of the sulfuric acid and selective hydrogenation methods [12, 13]. The structures of the unsaturated hydrocarbons were established by the infrared absorption spectrum. The relative content of diene hydrocarbons with a conjugated bond was characterized by the maleic anhydride number (determined by reacting with maleic anhydride for 1 h). The hydrocarbon composition of the gas was determined by chromatography.

Figure 1 plots the degree of conversion in the one-way cracking process versus the yields of monoolefin hydrocarbons (for the 40-140° C fraction) and unsaturated open-chain hydrocarbons (for the higher boiling fraction;
TABLE I. Characteristics of Cracking Crude

<table>
<thead>
<tr>
<th>Crude</th>
<th>Density $\rho^{20}$</th>
<th>Melting point, °C</th>
<th>Mol. wt.</th>
<th>Content of oils, wt. %</th>
<th>Kinematic viscosity at 80°C, cSt</th>
<th>Elemental composition, wt. %</th>
<th>Formula (from analysis data)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid paraffin (260-370°C fraction)</td>
<td>0.7942</td>
<td>-</td>
<td>255</td>
<td>-</td>
<td>at 50°</td>
<td>84.80 15.10 0.10</td>
<td>$C_{18}H_{38}$·$S_{0.008}$</td>
</tr>
<tr>
<td>Solid paraffin (400-500°C)</td>
<td>0.8287</td>
<td>62.2</td>
<td>468</td>
<td>1.7</td>
<td>7.7</td>
<td>85.18 14.72 0.10</td>
<td>$C_{33}H_{68}SO.016$</td>
</tr>
<tr>
<td>Solid paraffin (ibp 450°C)</td>
<td>0.8336</td>
<td>64.0</td>
<td>535</td>
<td>2.7</td>
<td>11.4</td>
<td>85.31 14.51 0.13</td>
<td>$C_{39}H_{77}SO.022$</td>
</tr>
<tr>
<td>Gatch</td>
<td>0.8331</td>
<td>51.0</td>
<td>428</td>
<td>11.0</td>
<td>6.5</td>
<td>85.30 14.56 0.19</td>
<td>$C_{30}H_{62}SO.025$</td>
</tr>
</tbody>
</table>

Note. The liquid paraffin has pour point 23°C and contains 4.5 wt. % aromatic hydrocarbons.

Fig. 1. Content of monoolefin hydrocarbons and unsaturated open-chain hydrocarbons versus the depth of cracking: 1) monoolefin hydrocarbons in the 40-140°C fraction from liquid paraffin; 2) ditto from solid paraffin; 3) ditto from gatch; 4) unsaturated hydrocarbons in the 150-300°C fraction from solid paraffin; 5) ditto in the 180-240°C fraction from gatch; 6) ditto in the 240-320°C fraction from gatch.

Fig. 2. Content of aromatic hydrocarbons versus the depth of cracking: 1) 40-140°C fraction from liquid paraffin; 2) ditto from solid paraffin; 3) 180-240°C fraction from gatch; 4) 240-320°C fraction from gatch.

Fig. 3. Maleic anhydride numbers of the 40-140°C fraction, plotted versus the depth of cracking: 1) liquid paraffin; 2) solid paraffin (400-500°C fraction); 3) gatch.