REFORMING OF TUIMAZIN GASOLINE IN CONTACT WITH TROSHKOV KAOLIN

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We have studied the catalytic properties of Troshkov kaolin under the conditions applying in the refining of the middle fraction (170-300°) from the primary tar of Budagov sapropelites [1], in the desulfurizing of various gasolines [2], and in the transformations of individual hydrocarbons of various classes [3-5]. It was shown in these investigations that Troshkov kaolin has many valuable catalytic properties: ability to bring about the cracking, isomerization, alkylation, and dehydrocyclization of hydrocarbons, disproportionation of hydrogen, and also desulfurization.

In the present investigation our object was to explore the possibility of effecting a substantial increase in the octane number of Tuimazin gasoline by bringing it into contact with activated Troshkov clay at atmospheric pressure. As the result of experiments on the reforming of the whole gasoline in contact with the clay, and also of the same gasoline after the separation of detonating centers (n-alkanes), we succeeded in finding conditions under which the octane rating of the gasoline was considerably increased — up to 72.0 and 76.8 in presence of 1.5 ml of ethyl fluid (TEL, i.e. tetraethyllead).

EXPERIMENTAL

The experiments on the reforming of gasoline were carried out in the usual flow-type apparatus at 500° at a space velocity of 0.3 hr⁻¹. The contents of sulfonatable compounds were determined by treating the original gasoline and the catalyzates with 2% oleum; their iodine numbers were determined by the Margosches method [6]; sulfur contents by the lamp method [6], and octane numbers by the motor method. The composition of the kaolin is given in one of our previous papers [1]. The clay was activated with sulfuric acid.

The properties of the original Tuimazin gasoline are given in Table 2.

Catalytic Treatment of Tuimazin Gasoline in presence of Activated Troshkov Clay

A head fraction boiling up to 66° (18% by weight) was separated from the original gasoline by fractionation through a 20-plate column. The gasoline, freed from the head fraction, was subjected to reforming in contact with activated Troshkov clay [100 ml (73.0 g) of catalyst, layer 360 mm in length catalyst tube diameter 18 mm] at 500° at a space velocity of 0.3 hr⁻¹. Altogether, 1200 ml (887 g) of gasoline was passed over the catalyst (without its being regenerated). After the catalyst had been regenerated, 300 ml (196 g) of the head fraction of the gasoline was passed over the catalyst at 400° and at the same space velocity. From 100 ml of gasoline 3.27 liters of gas was obtained, and this contained 22.9% of unsaturated hydrocarbons, 12.3% of hydrogen, and 64.8% of alkanes. Table 1 gives the properties of the original head fraction and gasoline freed from head fraction, and also of the catalyzates derived from these.

The catalyzates from the two gasoline fractions were mixed in the appropriate proportions. The properties of the gasoline so obtained are given in Table 2.

Thus, as the result of the catalytic treatment of Tuimazin gasoline in presence of activated Troshkov clay, the sulfur content is reduced by a factor of 18.5 and the fractional composition is improved. The octane number of gasoline with 1.5 ml of TEL is increased by 19.5. The group composition of the gasoline is changed: the content of aromatic hydrocarbons is increased by 11%, the content of cyclohexane hydrocarbons is reduced by one-half, the content of cyclopentane hydrocarbons is increased somewhat, and the content of alkanes is reduced.

Reforming of Tuimazin Gasoline in Contact with Activated Troshkov Clay after Prior Removal of Detonating Centers

The whole gasoline was distilled through a 20-plate column and 6° fractions containing n-alkanes were separated. From 6544.8 g of gasoline we obtained:
1) Fractions containing n-alkanes ........................................ 1486.2 g
   including:
   Hexane fraction 66.0 - 72.0° .................................... 268.4 g
   Heptane 95.0 - 101.0° ............................................. 402.9 g
   Octane 122.5 - 128.5° ............................................. 341.3 g
   Nonane 148.0 - 154.0° ............................................. 300.0 g
   Decane 171.0 - 178.0° ............................................. 173.6 g

2) Gasoline without detonating centers ............................ 4956.4 g
   including the head fraction .................................... 699.1 g

3) Losses ............................................................... 102.0 g

From the fractions containing n-alkanes, aromatic hydrocarbons and sulfur compounds were separated by adsorption on silica gel. These fractions were then fractionated through a 70-plate column. The properties of the n-alkane concentrates then obtained are given in Table 3.

The data in Table 3 show that the properties of the n-alkane concentrates obtained from the gasoline are fairly close to those of the corresponding pure hydrocarbons.

**TABLE 1**

Properties of Distillates from the Original Gasoline and their Catalyzates

<table>
<thead>
<tr>
<th></th>
<th>$\rho_D$</th>
<th>$\rho_{20}$</th>
<th>Sulfur content (%)</th>
<th>Sulfonatable hydrocarbons (% by vol.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gasoline</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Original gasoline freed</td>
<td>1.4193</td>
<td>0.7491</td>
<td>0.141</td>
<td>12.0</td>
</tr>
<tr>
<td>from head fraction</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Its catalyzate</td>
<td>1.4230</td>
<td>0.7519</td>
<td>0.009</td>
<td>22.5</td>
</tr>
<tr>
<td>Head fraction</td>
<td>1.3710</td>
<td>0.6537</td>
<td>0.121</td>
<td>—</td>
</tr>
<tr>
<td>Its catalyzate</td>
<td>1.3720</td>
<td>0.6446</td>
<td>0.011</td>
<td>—</td>
</tr>
</tbody>
</table>

The gasoline without the n-alkanes and the head fraction was subjected to reforming in contact with activated Troshkov clay at 500° at a space velocity of 0.3 hr⁻¹. Over 100 ml of catalyst, 944 ml (698.6 g) of gasoline was passed; the catalyst was not regenerated. The head fraction was treated separately at 400° at the same velocity. The catalyzates were mixed to give the gasoline whose properties are presented in Table 2. Thus, as a result of the refining of the gasoline by this method its octane number was increased by 18.7 units in absence of TEL and by 24.3 units in presence of 1.5 ml of TEL. The amount of aromatic hydrocarbons was increased by 13% by volume, the sulfur content suffered a sevenfold reduction, and the content of low-boiling fractions was increased. There can be no doubt that, if required, n-alkanes could be prepared from Tuimazin gasoline in a higher degree of purity.

**Effect of Thermal Treatment on the Properties of Tuimazin Gasoline**

In order to determine the effect of a purely thermal treatment on the properties of the gasoline, 500 ml of the whole Tuimazin gasoline was passed at 500° and at the same velocity as in the catalytic reforming experiments through the catalyssis tube filled with glass wool. The resulting gasoline, obtained in 89.0% yield, had $\rho_D$ 1.4144 and $\rho_{20}$ 0.7403, contained 0.09% of sulfur and 13.5% of sulfonatables, and had an iodine number of 8.2 and an octane number of 62.0 in presence of 1.5 ml of TEL. Thus, one thermal treatment on Tuimazin gasoline has a lower refining effect than contact with Troshkov kaolin under the same conditions.