THE EFFECTS OF A POTASSIUM-MANGANESE CATALYST ON THE ACCELERATION OF WAX OXIDATION BY ATMOSPHERIC OXYGEN

A. A. Perchenko and M. A. Marchenko

In addition to their initiating and inhibiting functions in the liquid-phase oxidation of hydrocarbons by molecular oxygen, the salts of metals having a variable valence also have a controlling action [1-3]. It is considered that the controlling function of a catalyst is not connected with its accelerating action, i.e., its initiating function. The effect of the composition and concentration of catalysts on the composition and quality of the oxidized product has been noted in a number of studies [4-9].

In the present investigation we have studied the effect of the composition of a K-Mn catalyst on the rate of wax oxidation by air, the conversion of intermediate oxidation products (ketones and alcohols), and the formation of acids.

To study the kinetics of wax oxidation and the formation of intermediate products and acids the methods described in [10, 11] were employed.

The properties of the feedstock being oxidized are presented below: wax to GOST 9348-60, melting point 52.4°C, oil content 1.7%, ester value 9.8, hydroxyl value 45.2, iodine value 4.5, carbonyl value 8.5. The initial mixture of wax and unsaponifiables contained 77% hydrocarbons.

Active manganese dioxide of composition (0.4 K₂O·MnO₂·0.9H₂O+0.17K₂O) was used as catalyst, the activity of the manganese dioxide being controlled by adding potassium carbonate.

In the first series of experiments oxidation was carried out in the presence of 0.1% manganese to which 0.025 wt. % potassium (as the metal) has been added; the second series of experiments was conducted in the presence of 0.08% Mn containing 0.005 wt. % potassium. In both series of experiments the oxidation process was carried out under changing temperature conditions (105-120°C). The third series of experiments was conducted at a constant temperature (125°C) and in the absence of a catalyst.

The wax was oxidized in a bubble-type reactor with a charge of 90 kg feedstock. The air feedrate to the oxidation process was 2.1 liter/min·kg. Two parts by weight of unsaponifiables and one part of wax were used in the oxidation process.

Figure 1 shows the change in the functional values of the wax being oxidized. Insufficient catalyst leads to a sharp increase in the content of carbonyls, viz., ketones and keto-acids. The amount of these products increases for the uncatalyzed oxidation. The amount of esters and ester-forming products decreases with an increase in catalyst concentration and a reduction in the oxidation temperature.

Figure 2 shows the kinetic data for wax consumption, and the formation of neutral oxygenated compounds and aliphatic acids. As may be seen, with a decrease in the amount of catalyst (experiments 1, 2) the rate of hydrocarbon conversion increases. Without a catalyst the rate of hydrocarbon conversion is higher at 125°C. In all cases the rate of hydrocarbon conversion is reduced with time, which is caused on the one hand (for experiments at 107-130°C) by a reduction in temperature and a decrease in the hydrocarbon concentration, and on the other hand, by a retardation of the action of the catalyst, particularly when 0.1% Mn is used. The principal role in retarding the oxidation is played by K-Mn soaps, since over the course of the first 3-4 h, as we established previously [9], manganese dioxide is reduced and forms manganese soaps by reacting with fatty acids in the presence of potassium soaps.

In oxidation experiments under the same temperature conditions the equilibrium concentration of neutral oxygenated compounds is higher for a smaller amount of catalyst. In the absence of catalyst the concentration of neutral compounds is higher. Hence, it follows that a potassium-manganese catalyst (and, in the first instance, all-union scientific research institute for synthetic and natural fats. Translated from Khimiya i Tekhnologiya Topliv i Masel, No. 10, pp. 21-26, October, 1968.

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TABLE 1. Wax Oxidation Results

<table>
<thead>
<tr>
<th>Experiments</th>
<th>Oxidation temperature, °C</th>
<th>Catalyst composition</th>
<th>Manganese concentration of catalyst, wt. %</th>
<th>Oxidation composition, wt. %</th>
<th>Properties of oxidate</th>
<th>Yield of oxidate and water soluble acids, % taken on wax oxidation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1–4</td>
<td>120–105</td>
<td>[(MnO₄]₀.₃₃·H₂O + 0.14K) + 0.025K</td>
<td>0.1</td>
<td>21.0, 49.8, 15.8, 34.4</td>
<td>69.1, 44.9, 2.2, 45</td>
<td>99.0, 6.4</td>
</tr>
<tr>
<td>5–8</td>
<td>120–105</td>
<td>[(MnO₄]₀.₃₃·H₂O + 0.14K) + 0.005K</td>
<td>0.08</td>
<td>18.0, 36.6, 25.4, 38.0</td>
<td>70.4, 57.9, 30.7, 240</td>
<td>100.0, 6.4</td>
</tr>
<tr>
<td>9–12</td>
<td>125</td>
<td>No catalyst</td>
<td>-</td>
<td>16.9, 33.3, 27.2, 39.5</td>
<td>65.2, 61.4, 71.3, 240</td>
<td>100.4, 5.8</td>
</tr>
</tbody>
</table>

Fig. 1. Change in the acid, ester, and carbonyl values, and variation in temperature during the oxidation of wax. 1) Containing 0.1% Mn; 2) 0.08% Mn; 3) no catalyst.

Fig. 2. Kinetic curves for the wax consumption a, the formation of neutral oxygenated compounds b, and water-insoluble acids c, during wax oxidation. 1) Containing 0.1% Mn; 2) 0.08% Mn; 3) no catalyst.

Manganese salts of fatty acids) accelerates the oxidation of the alcohols and ketones which comprise the neutral compounds in the acids. This also explains the fact that ketones are formed for an insufficient amount of catalyst, or when it is partially or completely precipitated. Thus, it follows from the kinetic data for the consumption of hydrocarbons and the formation of neutral oxygenated compounds that the controlling function of a manganese catalyst evidently consists of accelerating the oxidation of ketones and alcohols as intermediate products, i.e., it evidently amounts to an initiating function.

On the other hand, in the presence of a larger amount of catalyst oxidation is retarded, particularly by the potassium soaps present in the catalyst. It must be borne in mind here that potassium soaps retard the oxidation at the individual stages of the process. Under these conditions selectivity in the oxidation process is also observed; in the over-all retarding action by potassium soaps, alcohols, and particularly ketones, are oxidized more easily in the presence of a manganese catalyst. For this reason their equilibrium concentration is lower for oxidation using 0.1% Mn than in other experiments when a smaller amount of catalyst or none at all is used.