DEHYDROGENATION OF ISOPENTENES BY IODINE

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Experiments on the dehydrogenation of isopentenes by iodine have been carried out in a quartz flow reactor packed with a solid soda acceptor (Na₂O/Al₂O₃),* using the method described in [1].

The feedstock was an isopentene fraction of the following composition (in wt. %):

- butenes ................. 0.57
- n-pentane ................ 3.11
- n-pentenes ............... 9.90
- isopentane .............. 5.15
- isopentenes ............. 80.00
- isoprene ............... 1.07

The ratio 2-methylbutene-2 : 2-methylbutene-1 : 3-methylbutene-1 in the feedstock was 18.1 : 10.3 : 1.

As in the case of the dehydrogenation of isopentane [2, 3], the present work was carried out in the presence of large amounts of oxygen and water vapor. The earlier investigations of the oxidative dehydrogenation of isopentenes by iodine were carried out in a reactor filled with a quartz packing [4].

Preliminary experiments showed that the process goes extremely efficiently even when the iodine content is 0.05 mole per mole of isopentenes; this ratio was therefore chosen for the whole series of experiments.

The following factors affecting the process were studied.

Effect of Added Oxygen. This was investigated at 520°C at a space velocity of 0.11 h⁻¹, with the molar ratios iodine : water vapor : isopentenes equal to 0.05 : 8.1 : 1 (Fig. 1).

An experiment carried out in the absence of oxygen was characterized by a low isopentene conversion and isoprene yield (20 and 8%, respectively) at a low process selectivity (40%). The addition of oxygen significantly increased the conversion, isoprene yield, and selectivity; the latter reached 93% at a molar ratio of oxygen : isopentenes = 1 : 1 and then decreased slightly.

On adding oxygen the yield of decomposition products is reduced, reaching a minimum (about 1%) when oxygen : isopentenes = 1.0-1.25; the amounts of products resulting from extensive oxidation are very small, but are increased significantly when the oxygen content is greater than 1 mole/mole.

*Acceptor not iodinated.

TABLE 1. Effect of Diluting the Feedstock with Water Vapor on the Oxidative Dehydrogenation of Isopentenes with Iodine at a Constant Contact Time (1.3 sec)

<table>
<thead>
<tr>
<th>Indicators</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water vapor: isopentenes, mole/mole</td>
<td>0.0, 4.5, 12.4</td>
</tr>
<tr>
<td>Isopentene conversion, wt. %</td>
<td>61.5, 70.5, 80.0</td>
</tr>
<tr>
<td>Isoprene yield, wt. % based on isopentenes</td>
<td>33.8, 55.7, 75.5</td>
</tr>
<tr>
<td>Selectivity, wt. %</td>
<td>64.5, 81.0, 94.2</td>
</tr>
</tbody>
</table>


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Fig. 1. Effect of oxygen concentration on the dehydrogenation of isopentanes: 1) C₁⁻C₄; 2) CO₂; 3) CO; 4) conversion of isopentenes; 5) isoprene yield based on isopentenes passed; 6) selectivity for isoprene; 7) oxygen conversion.

Fig. 2. Effect of feedstock dilution with water vapor on the dehydrogenation of isopentenes: 1) C₁⁻C₄; 2) CO₂; 3) CO; 4) selectivity for isoprene; 5) isopentene conversion; 6) isoprene yield based on isopentenes passed.

Effect of Dilution. It has been shown [4, 5] that, in a reactor filled with quartz packing, dilution of the feedstock with water vapor leads to reduced isopentane conversion and increased isopentene conversion. The isoprene yield and the selectivity increase with dilution in both the dehydrogenation of isopentane and the dehydrogenation of isopentenes with iodine. We have found similar behavior for the isopentenes using a reactor packed with the solid acceptor at 520°, space velocity 0.11 h⁻¹, and iodine : oxygen : isopentenes = 0.05 : 1 : 1 (Fig. 2).

As the dilution is increased, the yield of decomposition products is reduced very little, but there is a large decrease in the yield of products resulting from extensive oxidation.

In the experiments included in Fig. 2 the space velocity of the feedstock was kept constant, so that in addition to dilution there was a change in the contact time; this could have an effect on the experimental results. Therefore, a further series of experiments was carried out at 520° with molar ratios of components iodine : oxygen : isopentenes = 0.05 : 1 : 1, in which the contact time was constant for various dilutions (Table 1). The results in Table 1 indicate that the maintenance of a constant contact time has no significant effect on the behavior observed.

Effect of Space Velocity. This was studied at 520° with iodine : oxygen : water vapor : isopentenes = 0.05 : 1 : 12.4 : 1 (molar ratios). Kinetic curves for the dehydrogenation of isopentenes by iodine are shown in Fig. 3, where the nominal contact time (inverse of the space velocity) is plotted on the abscissa.