CARBON DISULFIDE

Emphasis in raw materials shifts further from charcoal to methane, but impact of new processes using coke or liquid petroleum fractions remains to be seen

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A variety of reactions are available for making carbon disulfide, but only two have become important commercially; one is from carbon and sulfur and the other from methane and sulfur. The classic method uses charcoal and sulfur—heat is applied with carbon electrodes to a hearth or to retorts directly fired by natural gas, producer gas, or other fuels. Recently, however, especially in the United States, production from methane and sulfur has become more common.

Considerable data on carbon disulfide are available in the literature, including a description of both routes of manufacture (6). An excellent thermodynamic analysis of both the methane and charcoal routes is given (7) and, for the methane route, thermodynamic and kinetic data are available (2, 8) as well as kinetic data for plant design (1, 3). Thermodynamic properties of sulfur (11), carbon disulfide (5), and hydrogen sulfide (10) are tabulated in the literature.

REACTIONS FOR MAKING CARBON DISULFIDE (4)

\[ \text{CH}_4 + \frac{4}{n}\text{S}_n = \text{CS}_2 + 2\text{H}_2\text{S} \]

\[ 2\text{CO} + \frac{2}{n}\text{S}_n = 2\text{COS} = \text{CS}_2 + \text{CO}_2 \]

\[ \text{C} + 2\text{H}_2\text{S} = \text{CS}_2 + 2\text{H}_2 \]

\[ 3\text{C} + 2\text{SO}_2 = \text{CS}_2 + 4\text{CO} \]

The last three methods are not important commercially.

Methane Route—Process Technology

To obtain satisfactory reaction rates, most plants use temperatures above 1000° F., although stoichiometric conversion is theoretically possible at temperatures as low as 600° F. Pressures are 20 to 30 p.s.i.g. Saturated sulfur vapor at 1180° F. contains 21% diatomic, 58% hexatomic, and 21% octatomic molecules (9). However, available kinetic data are correlated satisfactorily by assuming a second order reaction between methane and diatomic sulfur which is probably the true reactant.

Activation energies of 61,920 and 68,940 B.t.u. per pound-mole have been reported. At space velocities of 600 standard cubic feet per cubic foot per hour, catalytic reactors generate 35 pounds of carbon disulfide per hour per cubic foot of catalyst. Some plants are designed to operate on the exothermic and some on the endothermic side of the adiabatic reaction temperature of about 1200° F. Heating the reactants (neglecting heat losses) requires about 1650 to 1750 B.t.u. per pound of carbon disulfide product.

Carbon disulfide can be made from methane and sulfur by either a high or low pressure purification process (Figure 1). In either case, the methane should contain less than 1% propane and heavier hydrocarbons and no more than 2% ethane. The high pressure process is especially applicable for small plants where recovery of hydrogen sulfide is uneconomical and where the hydrogen sulfide may be used elsewhere as a reactant.

Coils in the sulfur vaporizer are of high-chrome steel, and the reactor also is preferably of this material. Distillation towers in the purification section can be of carbon steel.

New Methods

Although the methane route has many advantages over the charcoal method, incentives to develop new processes still exist, particularly for foreign areas where low cost methane is unavailable. An inventor of the original methane process, Carlisle M. Thacker, is work-
However, this production picture may be affected by an impending merger. Regenerated cellulose consumes about 80% of the total carbon disulfide output; this is a big factor in the planned acquisition by FMC Corp. of American Viscose, a leading rayon manufacturer which has also one fourth of the nation's cellophane capacity. FMC may have a better chance than Stauffer Chemical which was thwarted by the Justice Department last year from acquiring American Viscose. If FMC is successful, considerable plant expansion may result.

**TABLE 1. CARBON DISULFIDE PLANTS**

<table>
<thead>
<tr>
<th>Company</th>
<th>Raw Material</th>
<th>Capacity, a Million Lb./Yr.</th>
</tr>
</thead>
<tbody>
<tr>
<td>J. T. Baker Chemical</td>
<td>Charcoal</td>
<td>&lt;20</td>
</tr>
<tr>
<td>Penn Yan, N. Y.</td>
<td>Methane</td>
<td>100</td>
</tr>
<tr>
<td>FMC Corp. &amp; Allied Chemical</td>
<td>Charcoal</td>
<td>Captive</td>
</tr>
<tr>
<td>So. Charleston, W. Va.</td>
<td>Carbon</td>
<td>Captive</td>
</tr>
<tr>
<td>Old Hickory Chemical</td>
<td>Methane</td>
<td>&lt;10</td>
</tr>
<tr>
<td>Old Hickory, Tenn. Richmond, Va.</td>
<td>Methane</td>
<td>50</td>
</tr>
<tr>
<td>Pennsalt Chemical</td>
<td>Methane</td>
<td>10</td>
</tr>
<tr>
<td>Houston, Tex.</td>
<td>Methane</td>
<td>340-360</td>
</tr>
<tr>
<td>Pittsburgh Plate Glass</td>
<td>Methane</td>
<td>600-620</td>
</tr>
<tr>
<td>Natron, W. Va.</td>
<td>Methane</td>
<td>50</td>
</tr>
<tr>
<td>So. Charleston, W. Va.</td>
<td>Methane</td>
<td>10</td>
</tr>
<tr>
<td>Stauffer Chemical</td>
<td>Methane</td>
<td>340-360</td>
</tr>
<tr>
<td>Delaware City, Del. Lowland, Tenn.</td>
<td>Charcoal</td>
<td>600-620</td>
</tr>
</tbody>
</table>

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**CARBON DISULFIDE**

Figure 1. Sulfur vapors pass through the catalyst chamber at 1200° to 1300° F. and a space velocity of 500 to 6000 standard cubic feet per cubic foot per hour. Carbon disulfide is formed according to the reaction $\text{CH}_4 + 4/3 \text{S}_2 \rightarrow \text{CS}_2 + 2\text{H}_2\text{S}$. Most plants use 5 to 10% excess sulfur. The product is caustic-washed before going to storage. In the high pressure process, the area circled above is replaced by the section in color at left.
Although prices have remained firm for many years, carbon disulfide growth rates have lagged behind those of carbon tetrachloride (Figure 2). Two main factors are responsible: demand for the tetrachloride in making fluorocarbons is strong, and carbon disulfide’s rayon markets are barely holding their own against major inroads by nylon tire cord.

For carbon tetrachloride, capacity is equally difficult to estimate, because of the variable output obtainable from methane chlorination. Trade estimates now are as high as 570 million pounds per year, but previous figures were about 400 million. Annual production increases of 6% are predicted for the next five years, even though carbon tetrachloride seems destined to remain a one-product commodity (fluorocarbons). That about 35% of total output is derived from carbon disulfide is reasonably safe to assume: Diamond Alkali operates a 60-million-pound-per-year plant; FMC Corp., a 50-million; and Stauffer, now operating a 100-million-pound plant, plans to put on stream in 1964 a 70-million-pound plant.

Despite the declining tire cord production, however, rayon output is moving upward (Figure 3). But its future is difficult to predict. Since Du Pont dropped out, only four producers are left: American Enka, American Viscose, Beaunit Mills, and Industrial Rayon.

This year marks the end of an era for Du Pont, which entered the rayon business 33 years ago at Buffalo. The company now has a “radically” new nylon which it claims reduces “significantly” flat spotting in tires. If this is so, nylon may be headed for the original automotive equipment market—the last stronghold for rayon tire cord. Du Pont estimates that nylon cord is now used for about 70% of the replacement tires on automobiles and trucks, 40% of original equipment truck tires, and 100% of airplane and off-the-road tires.

Producers of rayon for uses other than tire cords include Celanese, Courtaulds (Ala.), Fair Haven Mills, Hartford Rayon, and Mohasco Industries.

Meanwhile, cellophane continues to consume more carbon disulfide. Recent predictions indicate a probable output of 500 million pounds during 1967. At present, three manufacturers have an estimated capacity of 540 to 580 million pounds per year: American Viscose, 150 million; Du Pont, 320 to 350 million; and Olin Mathieson, 70 to 80 million.

Worldwide, demand for carbon disulfide continues upward but the United States exports very little—less than 1.3 million pounds in 1961. Of this, 672,000 pounds went to Canada, 445,000 to Colombia, and the balance was distributed among 12 other countries.

SUGGESTED READING
(2) Folkins, H. O., Miller, E., Hennig, H., Ibid., 42, 2202-7 (November 1950).
(8) Thacker, C. M., Miller, E., Ibid., 36, 182-4 (February 1944).