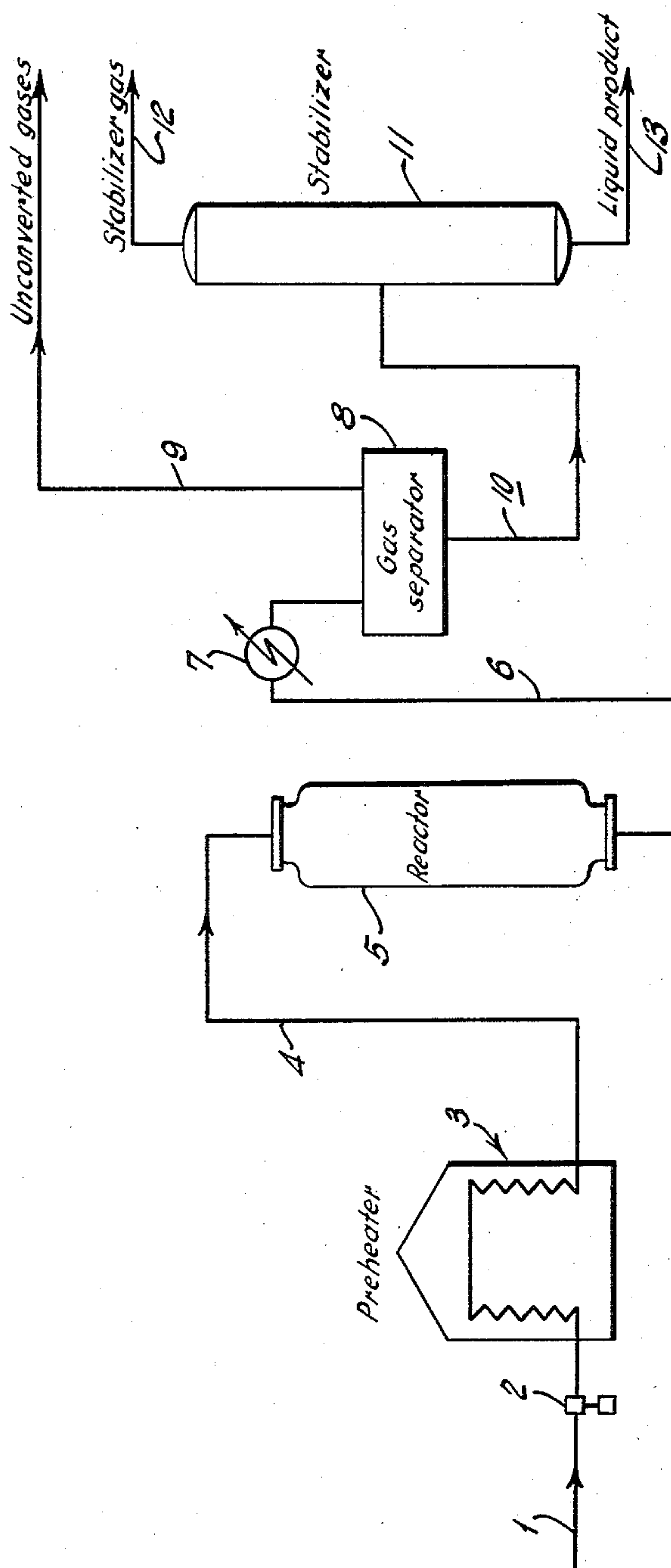


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PRODUCTION OF CYCLIC HYDROCARBONS FROM HYDROCARBON GASES
USING A CATALYST CONTAINING CHROMIA, ALUMINA AND SILICA
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PRODUCTION OF CYCLIC HYDROCARBONS FROM HYDROCARBON GASES USING A CATALYST CONTAINING CHROMIA, ALUMINA AND SILICA

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5 Claims. (Cl. 260-673)

This invention relates to improvements in the conversion of hydrocarbons. More particularly, it relates to a process for the production of cyclic hydrocarbons from olefinic hydrocarbons having two to five carbon atoms. In the process of this invention, olefinic hydrocarbons having two to five carbon atoms are contacted with a cyclopolymerization catalyst comprising a compound of a metal selected from the group consisting of metals of the left hand columns of groups IV, V and VI of the periodic table under cyclopolymerization conditions to form cyclic hydrocarbons having more than five carbon atoms.

In the refining of petroleum, large quantities of low boiling hydrocarbons are produced which are unsuitable for inclusion in motor fuel. Some of these low boiling hydrocarbons may be further processed to convert them to higher boiling hydrocarbons suitable for inclusion in motor fuel. For example, olefins may be polymerized in the presence of a phosphoric acid catalyst to produce higher molecular weight, higher boiling polymers. In the petroleum refining industry, polymerization of olefins is effected at temperatures of about 350 to 475° F. and at a pressure ranging from 150 to 1200 p. s. i. g. The higher boiling polymers produced by this process are entirely unsaturated aliphatic hydrocarbons. Olefins, such as, butylenes and pentylenes may be alkylated with iso-butane or iso-pentane to form high octane number alkylates. These alkylates consist entirely of saturated aliphatic hydrocarbons. Low boiling hydrocarbons which are not converted to higher boiling hydrocarbons suitable for inclusion in motor fuels are generally discarded to fuel gas where their value is determined by the cost of fuel for heating purposes. Such value is considerably below the equivalent value of motor fuel.

We have now found that low boiling olefinic hydrocarbons may be converted to cyclic hydrocarbons by the process of cyclopolymerization. The cyclic hydrocarbons produced comprise both aromatic and naphthene hydrocarbons and we have found that conditions may be selected to produce greater or lesser proportions of naphthene and aromatic hydrocarbons as may be desired. The naphthene hydrocarbons produced may be useful as high octane motor fuels, as chemical intermediates, or may be further processed to produce aromatic hydrocarbons. The aromatic hydrocarbons are useful as high octane number motor fuel blending stocks and for chemical purposes.

The production of cyclic hydrocarbons from hydrocarbons having from two to five carbon atoms requires effecting both polymerization and cyclization reactions. Compounds of metals of the left hand columns of groups IV, V and VI of the periodic table are known to be active catalysts for the cyclization of hydrocarbons having

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more than six carbon atoms. These compounds have not been considered to be active catalysts for the polymerization of low molecular weight olefinic hydrocarbons. We have found that unsaturated low molecular weight olefinic hydrocarbons may be polymerized and cyclized in the presence of catalysts comprising compounds of metals of the left hand columns of group IV, V and VI of the periodic table.

The cyclopolymerization of low molecular weight hydrocarbons may be conducted at a temperature in the range of about 500 to 900° F. However, we prefer to employ a temperature in the range of about 750 to 850° F. Pressures in the range of about 500 to 5000 p. s. i. g. may be employed although higher pressures favor cyclopolymerization and pressures over 1000 p. s. i. g. are preferred.

Ethylene, propylene and butylene are preferred feed stocks for the process of this invention.

As stated, heretofore, compounds of metals selected from the left hand columns of groups IV, V and VI of the periodic table are active catalysts for cyclopolymerization. These compounds may be, for example, the oxides, sulfides, halides, chromates, chromites, manganates, molybdates, phosphates, selenides, tellurides, tungstates, etc. or mixtures thereof. These metals are usually used, however, in the form of their oxides. It may also be desirable to composite the active cyclopolymerization catalyst with a carrier or support which alone is substantially inactive as a cyclopolymerization catalyst. Alumina, magnesia, and silica, among others, are suitable supports.

An advantage of this process is that low boiling hydrocarbons may be converted to higher boiling high octane number hydrocarbons suitable for inclusion in premium quality motor fuel.

Another advantage of the process of this invention is that low boiling aliphatic hydrocarbons may be converted to aromatic and naphthene hydrocarbons which are useful as chemicals.

The accompanying drawing diagrammatically illustrates the process of this invention. Although the drawing illustrates one arrangement of apparatus in which the process of this invention may be practiced, it is not intended to limit the invention to the particular apparatus or material described.

Propylene from an external source not shown is admitted through line 1. Charge pump 2 increases the pressure of the propylene to about 3500 p. s. i. g. Liquid propylene is introduced into preheater 3 where the temperature is raised to 800° F. Propylene vapor flows through transfer line 4 to reactor 5 which contains a catalyst comprising chromic oxide deposited on alumina. The propylene is passed through the reactor at a rate of 0.12 weight of oil per hour per weight of catalyst. The reactor effluent is discharged through line 6, cooled in exchanger 7 and discharged into gas separator 8. Unconverted propylene and gases produced in the process are withdrawn through line 9. Liquid from gas separator 8 is withdrawn through line 10 and passed to stabilizer 11. Stabilizer 11 is a fractional distillation means which is employed to separate dissolved gaseous hydrocarbons from the liquid product. Stabilizer gas is withdrawn through line 12 and stabilized liquid product is withdrawn from the stabilizer through line 13. Means not shown may be provided to recycle unconverted gas from the separator and gas from the stabilizer to increase the yield of liquid products.

The process of this invention is illustrated in the following examples:

| Examples | A | B | C | D | E | F | G |
|---|-------|-------|-------|-------|-------|-------|-------|
| Charge stock, weight percent: | | | | | | | |
| Ethylene | 13.6 | | | | | | 15.7 |
| Propylene | | 95 | 95 | 95 | 95 | 95 | 40.0 |
| Propane | 86.4 | 5 | 5 | 5 | 5 | 5 | 44.3 |
| Catalyst | I | III | I | IV | V | II | II |
| Operating conditions: | | | | | | | |
| Temperature, ° F. | 700 | 751 | 709 | 725 | 725 | 800 | 800 |
| Pressure, p. s. i. g. | 2,700 | 3,469 | 3,500 | 3,500 | 3,000 | 3,500 | 3,500 |
| Weight hourly space velocity, oil to catalyst | 0.4 | 0.09 | 0.04 | 0.04 | 0.04 | 0.12 | 0.12 |
| Yields, weight percent olefin charge: | | | | | | | |
| Total liquid | 78 | 81.0 | 78.7 | 63.1 | 35.3 | 79.5 | 88.1 |
| Aromatics | 6.4 | 13.0 | 10.2 | | 6.7 | 8.7 | 15.9 |
| Naphthenes | 28.1 | 1.6 | 25.2 | | .7 | 31.8 | 21.2 |
| Total cyclics | 34.5 | 14.6 | 35.4 | 18.9 | 7.4 | 40.5 | 37.1 |

¹ Boiling below 401° F.

Catalyst compositions

Catalyst I.—11.0 weight percent Cr₂O₃ composited on silica-alumina base (6.2 weight percent SiO₂, 82.8 weight percent Al₂O₃).

Catalyst II.—11.3 weight percent Cr₂O₃ composited on alumina base.

Catalyst III.—21.7 weight percent Cr₂O₃ composited on alumina base.

Catalyst IV.—10.82 weight percent Cr₂O₃, 0.34 weight percent CrF₃·H₂O composited on alumina-aluminum fluoride base (85.90 weight percent Al₂O₃, 2.94 weight percent AlF₃·½H₂O).

Catalyst V.—11.1 weight percent MoO₃ composited with silica alumina base (2.5 weight percent silica; 86.4 weight percent Al₂O₃ by difference).

Example A shows that ethylene is converted to cyclic hydrocarbons by the process of this invention. Examples B, C, D and F show the conversion of propylene to cyclic hydrocarbons and Example G shows the conversion of a feed stock comprising ethylene and propylene to cyclic hydrocarbons. The examples show that chromia is an active cyclopolymerization catalyst and may be advantageously supported on various carriers, for example,

alumina or a composite of silica and alumina. Molybdena on silica alumina is also shown to be an active cyclopolymerization catalyst. The examples show that both aromatic and naphthene hydrocarbons may be produced by cyclopolymerization of ethylene and propylene by the process of this invention.

Obviously many modifications and variations of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof and only such limitations should be imposed as are indicated in the appended claims.

We claim:

1. A process for the production of cyclic hydrocarbons which comprises contacting a normally gaseous olefin with a chromia-alumina catalyst containing a minor amount of silica at a temperature of about 700° F. and a pressure between about 2700 to 3500 p. s. i. g.

2. A process for the production of cyclic hydrocarbons which comprises contacting an olefin selected from the group consisting of ethylene and propylene with a chromia-alumina catalyst containing about 6 percent silica by weight at a temperature of about 700° F. and a pressure between about 2700 and 3500 p. s. i. g.

3. The process of claim 2 in which the olefin is ethylene.

4. The process of claim 2 in which the olefin is propylene.

5. A process for the production of cyclic hydrocarbons which comprises contacting an olefin selected from the group consisting of ethylene and propylene with a catalyst containing about 11 weight percent Cr₂O₃ composited on a silica-alumina base, said base containing about 6 weight percent SiO₂ and about 82 weight percent Al₂O₃ based on the total composite weight at a temperature of about 700° F. and at a pressure between about 2700 and 3500 p. s. i. g.

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