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PROCESS FOR CRACKING DICYCLOPENTADIENE

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PROCESS FOR CRACKING DICYCLO-PENTADIENE

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This invention relates to an improved process for obtaining high purity cyclopentadiene and/or methyl cyclopentadiene from crude concentrates of their dimers and/or codimers by the vapor phase cracking of these materials. More particularly, this invention relates to incorporating with the feed 0.1—5 wt. percent of a refractory heavy oil to reduce coke and resin deposition in the unit and thus give smoother operations with longer onstream periods. Most particularly, this invention relates to cracking high purity, above 90 wt. percent, cyclopentadiene in the presence of said 0.1—5 wt. percent of diluent oil under severe conditions to obtain high throughputs along with high yields and selectivities.

The vapor phase cracking of cyclodienes dimers gives higher conversions to monomers as compared to liquid phase cracking. However, a serious problem associated with vapor phase cracking is the coking of the cracking tube. This coking, of course, results in short onstream periods along with losses in yield of high purity monomers. In the past a number of proposed solutions have been suggested for dealing with this coking problem. Thus, it has been suggested to merely use large amounts of gaseous diluents. Alternatively, schemes for obtaining vaporization of the monomer from large amounts of a high boiling oil or counter-current washing of the cracking zone with a liquid superheated oil have been suggested. Now it has been surprisingly found, contrary to all of these elaborate suggestions, that an extremely economical solution to this problem can be obtained by merely adding an extremely small amount of a high boiling diluent oil directly to the feed, in the range of 0.1—5 wt. percent, preferably 0.5—1.5 wt. percent. Further, it has been found that by this expedient an extremely efficient cracking of high purity dimer under severe conditions can be obtained. Thus, in this particular process high throughputs combined with long onstream periods are obtained.

According to the present invention suitable diluent oils are generally any relatively thermally stable (to cracking) petroleum oils having very low volatility so as to be liquid under the cracking conditions. A convenient measure of this volatility for most oils is in terms of TAG Open Cup Flash. Thus, the oils should have Flash inspections of above 250°C, preferably above 300°C. Suitable oils are certain Bright Stocks, cycle oils from thermal or catalytic cracking, and other petroleum oils which are thermally stable under the dimer cracking conditions used. A preferred diluent is a heavy oil which previously has been processed under severe conditions and thus is quite refractory. Obviously, oils which are both cheap and readily available are preferred since recycle would complicate the process.

According to the present invention the dimer materials are cracked at temperatures of 180 to 400°C, pressures of atmospheric to 100 psig and with feed rates of 0.1 to 5 v. liquid/v. reactor/hour. Preferred conditions, particularly with respect to cracking high purity dimers, are temperatures of 350 to 400°C, pressures of atmospheric to 15 psig and feed rates of 0.5 to 2 v. liquid/v. reactor/hour. Further preferred reaction conditions, in this case particularly with respect to cracking lower purity dimers, are temperatures of 220 to 300°C, pressures of atmospheric to 15 psig and feed rates of 0.1 to 0.5 v. liquid/v. reactor/hour. It should be noted that in all cases reactor surface temperatures are much higher than the reaction temperatures disclosed above. Thus, for example, for this latter range of conditions skin temperatures may be about 600°C. With respect to the cracking of the high purity feeds (cracked at the severe conditions above described) it should be noted that very high throughputs are obtained.

In general, the crude feeds which may be processed according to the process of the present invention may be, for example, those containing more than about 40 wt. percent cyclopentadiene (or methyl cyclopentadiene dimer or codimers of cyclopentadiene and methyl cyclopentadiene) in a petroleum fraction boiling in the range of 110—260°C. This petroleum fraction is, of course, obtained usually from thermal or steam cracking processes. Particularly, pure dimer concentrates containing more than 90 wt. percent, preferably 95 wt. percent, cyclopentadiene (or methyl cyclopentadiene dimer) are preferred feed stocks. Additionaly, mixtures of dimers of cyclopentadiene and dimers of methyl cyclopentadiene, and codimers of cyclopentadiene and methyl cyclopenta
diene, may be cracked together and separation obtained on the effluent stream as described in U.S. 2,801,270. Thus, with respect to this latter embodiment, a mixture containing about 35—45 wt. percent of cyclopentadiene dimer along with 30—35 wt. percent methyl cyclopenta
diene dimer in a stream having an equivalent atmospheric pressure boiling range of 185—230°C may be cracked. It should be noted that throughout in this description of the invention the term cyclopentadiene material refers to cyclopentadiene, methyl cyclopentadiene, or to mixtures of these materials.

The invention will be further described with reference to the drawing, wherein is shown a flow diagram of a preferred process. Crude dimer, for example dicyclo
pentadiene, is passed from tank 1 through valued line 2 to feed drum 3. Small amounts of heavy oil are supplied from heavy oil tank 4 through valued line 5, also to feed drum 3. From this feed drum the combined feed is passed through line 6, pump 7 and through line 8 to preheater-cracker furnace 9. A recycle fraction of high boiling cyclopentadiene dimer may also be supplied to preheater 9 through line 10. However, it should be noted that by the present invention substantially complete cracking can be obtained. Preheater-cracker 9 may be operated with an outlet temperature of 180—400°C and with pressures of about 0—100 psig. In this preheater the liquid feed is almost completely vaporized. The combined stream from preheater 9 passes to knock-out drum 11 where high boiling unvaporized dimer is separated and is passed on through line 14 to the cracking furnace 15. Here temperatures are raised to full cracking temperatures and cracking is conducted to obtain essentially complete recovery of monomer available in the feed.

Generally in the preheater and cracker the liquid di-
cyclopentadiene or other dimer oil containing the diluent oil is sprayed into a vapor chamber, heated externally by conventional heaters such as, for example, gas heaters to bring certain areas of the surface to a dull red heat, thus maintaining temperatures in the vapor space at the preferred cracking conditions described above. Baffling is utilized in the preheater and cracking chambers to provide the desired amount of contacting time with reduced backmixing and the vapors are then passed through line 16 to heat exchanger 17 where the vaporous material is rapidly quenched to a temperature of about 50 to 100° C. and the effluent is supplied through line 18 to a small fractionation tower 19. In this tower monomer is separated overhead through line 20 and any unconverted dimer is taken off the bottom of the column and may be recycled through valve line 21 back to pump 13 and line 10 to the process. If desired, a purge stream may be also removed through line 22 to remove any portion of the bottoms from column 19 heavier boiling than the dimer which it is not desired to recycle to the process. Tower 19 also has a conventional reboiler system 23 and overhead condenser and reflux system 24. The condensed reflux monomer stream not recycled is passed through line 25 to a gas vent separator 26 where light ends are removed overhead through line 27 and then the remaining relatively pure monomer is passed to monomer storage through line 28 to monomer storage tank 29. This tank is maintained at a low temperature of down to about —80° C. in order to prevent redimerization of the monomer.

The following examples present data obtained in the laboratory and commercially in the cracking of dicyclopentadiene, both with and without the addition of small amounts of high boiling diluent oil.

**Example 1**

A sample of pure (95%) dicyclopentadiene analyzing as follows:

- DCPD .................................. wt. percent 96.0
- Methyl cyclopentadiene in dimers ........ 2.5
- Acyclic dienes ........................................... 1.5
- Higher dienes (C7-dimers) .............. 0.0
- Flash (T.O.C.) (i.e. Tag Open Cup) .... 45° F.
- Inhibitor (p.p.m.) .................. 150
- Color Gardner ........................................ 1.0
- Peroxides (p.p.m. active oxygen) ...... 1.0

was cracked from a 230–260° C. glass surface. It was found that after cracking a hard brittle residue remained on the glass. Another sample of the same dicyclopentadiene was cracked from the same glass surface with additionally 1 wt. % of a Bright stock (i.e. a high viscosity lubricating oil refined to produce a clean product of good color) added. This Bright stock analyzed:

- API gravity (0.9159 specific gravity) ........ 23.0°
- ASTM color ......................................... 4½
- Flash TAG open cup, ° F. ............... 565
- Conradson carbon residue ................. 1.09

In this case the residue after cracking remained a fluid and no solid precipitated from the fluid even upon cooling.

**Example 2**

The same concentrate of dicyclopentadiene containing about 95 wt. % percent dicyclopentadiene described in Example 1 was cracked in a small commercially operated system as disclosed in FIGURE 1 and described above. The 95 wt. % dicyclopentadiene was sprayed as a liquid into the preheating-cracking chamber 9 in which certain areas of the surface were heated to a dull red heat while vapor phase temperatures as measured by thermocouple probes were kept in the range of 230 to 260° C. The material from this chamber then was passed through a knock-out chamber 11, and thence to the baffled cracking section 15 which was similarly heated. Cracking conditions here were vapor phase temperatures of 230–260° C., pressures of 5–10 p.s.i.g. and contact times of about one minute. Cracked product was then passed to the short bubble cap column 19 where the monomeric cyclopentadiene was taken off under reflux. When one batch of the regular supply of this dicyclopentadiene material was passed through the system operation was halted in each of several attempts to crack this material after as little as three hours due to plugging not only in the cracking furnace baffle section but also in the bubble cap distillation column. When the unit was opened it was found that a coarse brittle powder had formed which plugged up not only the horizontal cracking section but also in the preheater-cracker 9 and cracking furnace 15 but also the bubble caps in the distillation column. After these failures the present invention process improvement was applied. Thus, 1 wt. % percent based on feed of the Bright stock described in Example 1 was added and the combined stream was cracked. Where the addition of this material was utilized on-stream periods of 3–4 months were obtained and smooth operations were achieved. It is not known whether the oil keeps the carbonaceous residue from actually forming or whether it only fluxes or dissolves whatever material has formed after it, but it has a combination of both of these phenomena. Regardless of which factor is involved important improvements are obtained at very small expense. Additionally, it was noted that the added oil did not contaminate the cyclopentadiene monomer and was found to be generally stable under these conditions.

Although it is not intended to limit this invention by any explanation of the mechanism by which these large improvements are achieved it is speculated that perhaps the oil produces a film on the heated surface of the reactor which not only gives improved heat transfer but also keeps the concentration of lower cracked dicyclopentadiene at the high temperature walls high, relative to that in the vapor phase. This would of course not only improve yields but also actually speed up the cracking operation.

It is to be understood that this invention is not limited to the specific examples, which have been offered merely as illustrations, and that modifications may be made without departing from the spirit of this invention.

**What is claimed is:**

1. An improved process for obtaining a high purity cyclopentadiene material with a minimum formation of byproducts and coke which comprises continuously passing a mixture consisting of vapors of a petroleum feed stream boiling in the range of 110–260° C. containing more than 40 wt. % percent of dimers of said cyclopentadiene material thoroughly mixed with about 0.1 wt. % percent of heavy petroleum oil having a TAG Open Cup Flash Point above about 250° C., through a cracking zone maintained at a temperature in the range of 180–400° C. and recovering a cyclopentadiene material from said zone.

2. The process of claim 1 in which the cyclopentadiene material is cyclopentadiene.

3. The process of claim 1 in which the cyclopentadiene material is methyl cyclopentadiene.

4. The process of claim 1 in which the cyclopentadiene material is a mixture of cyclopentadiene and methyl cyclopentadiene.

5. The process of claim 1 in which the amount of the heavy petroleum oil is in the range of 0.5–1.5 wt. %.

6. The process of claim 1 in which the heavy petroleum oil is a virgin petroleum oil having a TAG Flash Point above about 300° C.

7. The process of claim 1 in which the heavy petroleum oil is a cycle stock from thermal cracking.

8. The process of claim 1 in which the dimers of the cyclopentadiene material comprise more than 90 wt. % of the total feed stream to the cracking zone and in which cracking is conducted at temperatures of 350–400° C.
C., pressures of atmospheric to 15 p.s.i.g. and feed rates of 0.1–2 v. liquid/v. reactor/hour.

9. The process of claim 1 in which cracking is conducted at temperatures of 220–300° C., pressures of atmospheric to 15 p.s.i.g. and feed rates of 0.1–0.5 v. liquid/v. reactor/hour.

10. The process of claim 1 in which the said mixture is preheated to reaction temperatures separately in a preheat zone.

11. An improved process for obtaining high purity cyclopentadiene with a minimum formation of byproducts and coke which comprises continuously passing a mixture consisting of vapors containing above 95 wt. percent di-
cyclopentadiene thoroughly mixed with 0.5–1.5 wt. percent, based on total feed, of a lubricating oil having a TAG Open Cup Flash Point of about 300° C. through a cracking zone maintained at temperatures in the range of 350–400° C., pressures of atmospheric to 15 p.s.i.g. and feed rates of 0.5–2 v. liquid/v. reactor/hour.

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