

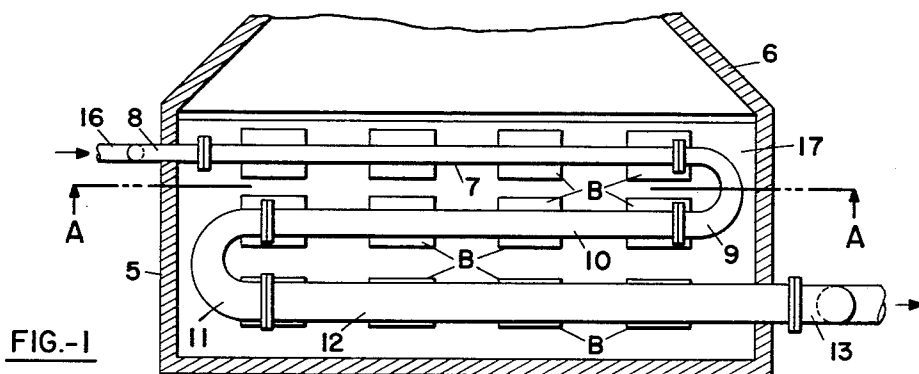
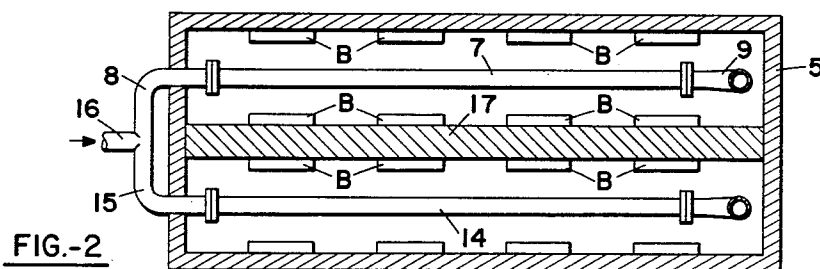
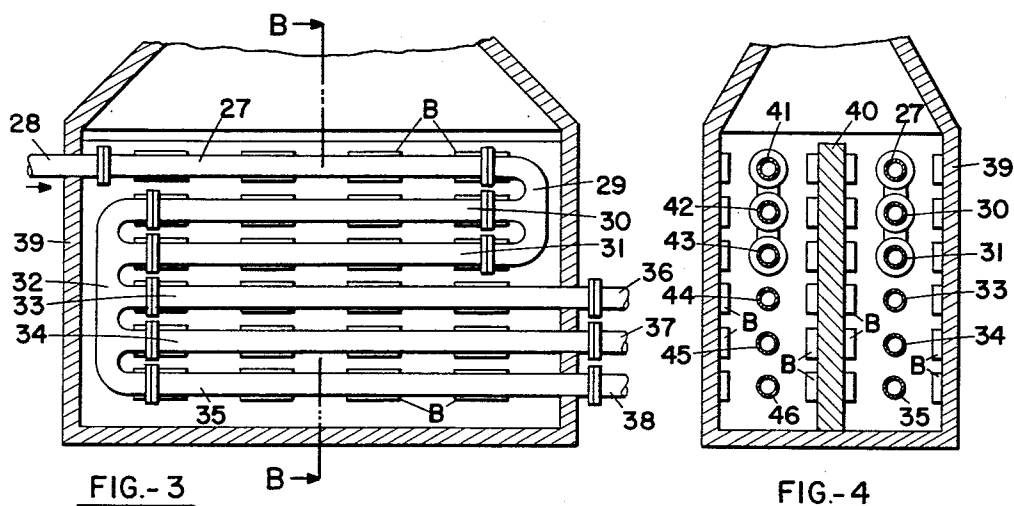
Aug. 1, 1961

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2,994,724

CYCLODIENE DIMER VAPOR PHASE CRACKING METHOD AND FURNACE

Filed Aug. 14, 1958



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2,994,724

CYCLODIENE DIMER VAPOR PHASE CRACKING METHOD AND FURNACE

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Filed Aug. 14, 1958, Ser. No. 754,954
2 Claims. (Cl. 260-666)

This invention relates to a method for vapor-phase cracking dimers of cyclopentadiene and methylcyclopentadiene present in high purity concentrates of their dimers or in crude concentrates of their dimers, codimers, trimers, and cotrimers with other hydrocarbons, e.g. having 7 to 9 carbon atoms per molecule.

It relates to the vapor-phase cracking of these materials under controlled conditions for obtaining the C_5-C_6 cyclo-diene monomers with low coke formation by the use of a furnace constructed to obtain uniform heating and mini-mized pressure build-up within the cracking tubes.

In the U.S. Patent No. 2,801,270 of J. F. Nelson et al. is described a process for recovering the cyclo-diene monomers involving a vapor-phase cracking for which the present invention provides an improved cracking tech-nique and furnace. The present invention is also related and useful in connection with the vapor-phase cracking process described in U.S. application Serial No. 597,662 of G. O. Hillard, Jr., et al., filed July 13, 1956, now U.S. Patent 2,913,504, patented November 17, 1959.

In accordance with the present invention, the cracking tubes through which the C_5-C_6 cyclo-diene dimer vapors are passed and heated to a suitable vapor-phase cracking temperature are constructed to give the vapor stream or streams of the dimers undergoing cracking an overall consecutively increased cross-sectional area as the crack-ing progresses. By increasing the cross-sectional area of the stream or streams progressively, as by increasing the size of the tubes or the number of tube branches in the direction of flow, the pressure build-up is minimized and the deleterious effects of back pressure can be substan-tially overcome.

Experimental operations proved that in vapor-phase cracking of the concentrates containing dimers of the C_5-C_6 cyclo-dienes, successful operation is favored by the use of reduced pressures with low pressure drop as well as by uniform heating temperatures.

In earlier operations conducted with cracking tubes hav-ing an constant internal diameter so that the vapor stream of dimers and their cracked products passing through such tubes could not expand progressively, it was found diffi-cult to prevent the build-up of back pressure. This build-up of back pressure was found to become augmented as the cracking tubes were used for an extended period of time and the build-up of pressure was accompanied by increased formation of coke in the tubes which then be-came fouled with especially heavy coking toward the outlet. Fouling of the tubes means that the cracking ap-paratus has to be shut down and the coke has to be removed. The removal of the coke is difficult and time consuming.

While some success has been attained in lowering coke formation in the vapor-phase cracking of the dimer con-centrates passed through two or more separate tubes with controlled heating, a more effective control was found necessary with respect to the difficulty of preventing an increase in pressure build-up. Using the tubes mounted in 6 rows and all having the same internal diameter, the vapor pressure build-up toward the inlet of these tubes was found to increase from 40 to 60 lbs. per square inch (p.s.i.) after a few hours of operation and then to increase even to as high as 100 lbs. per square inch. In other

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words, the vapor stream cross sectional area through the series of tubes was gradually decreased by coke forma-tion and starting with a pressure of 10 pounds per square inch gage (p.s.i.g.) for both the inlet and outlet of the tubes, the inlet pressure gradually builds up in the tubes to above 50 p.s.i.g. With the build-up of back pressure the operation became more erratic so that at times the back pressure would rise to as high as 90 p.s.i.g. and with such a build-up of back pressure coking of the tubes took place rapidly. The furnace and tube construction was redesigned to obtain improved operation by having the initial tubes of relatively low internal diameter followed by tubes of increasing internal diameter (I.D.), e.g., a first row of 1.5 inch I.D. joined to a second row of 2.0 inch I.D., then a third connected row of 2.5 inch I.D. to reduce the pressure drop to less than 20 p.s.i.

The furnace construction and method of operation for reducing the pressure drop or minimizing back pressure in accordance with the present invention will be described with reference to the schematic drawing.

FIG. 1 of the drawing is a side elevation sectional view of a cyclo-diene dimer cracking furnace in which the crack-ing tubes connected in coil form have progressively en-larged internal diameters from inlet to outlet.

FIG. 2 shows a horizontal cross-section along the plane of the line A—A to show a first row of two parallel pass tubes through which the dimer vapors are passed before they enter a second row of parallel tubes having increased bore.

FIG. 3 shows a side elevation sectional view of an alternative furnace and tube construction in which an initial cracking tube is connected to a branched pair of cracking tubes having substantially the same internal diameter as the first tube and the second set or pair of tubes is connected to a branch of three tubes in parallel having the same diameter as the first tube, the increasing number of tubes for each of said succeeding sets or branches furnishing the overall increased cross-section or enlargement of vapor space for the vapor streams being passed continuously from an inlet to outlets of the final set of tubes.

FIG. 4 is a vertical cross-sectional view for a multipass furnace taken along a plane B—B in FIG. 3 to illustrate how the sets of tubes are arranged in the furnace with relation to radiant heating burners of the pre-mix, short flame type.

Referring to FIG. 1, the interconnected cracking tubes of different internal diameters form one complete cracking coil arranged within the furnace surrounded by the fur-nace walls 5 of refractory material, e.g. fire brick. At the upper part of the furnace is a roof structure 6 acting as a duct for leading flue gases to a furnace stack. An initial tubular section 7 of the cracking coil receives at its inlet 8 dimer vapors or liquid to be cracked in vapor-phase. The initial tube 7 is connected through a U-shaped tube 9 to a second segment of the coil having a larger internal diameter, this segment being shown as tube 10. Similarly, the tube section 10 is connected through a U-shaped bend connection 11 to the still larger bore segment of the coil in the form of tube 12. Additional segments of the coil may be thus added, if desired. The final tube segment has a discharge outlet 13 from which the cracked vapors are passed to a heat exchange cooler to a monomer recovery system, including fractionating columns. The discharge ends of the coils may be interconnected to form a single combined stream which is cooled and fractionated.

In FIG. 2 is shown an arrangement of parallel coils in the furnace, the parallel coils having top tube seg-ments 7 and 14 with their respective inlets 8 and 15 joined to a common inlet 16. In the furnace walls are arranged short-flame pre-mix burners B. Similar burners are arranged in the center or dividing baffle wall 17.

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These burners are spaced and aligned to supply largely radiant heat uniformly distributed over each of the tubes in order to maintain substantially uniform temperatures throughout the length of each tube and throughout the coil, the tubes being located equidistant from each of the radiant heat burners. A number of the spaced burners, e.g. eight or more per coil, may be used. Preferably for each horizontal tube there is a tier of burners.

In the alternative construction shown in FIG. 3 the initial coil segment tube 27 has an inlet 28. It is joined by a header or bend 29 to the set of two tubes 30 and 31 as branches to accomplish the increase of cross-sectional area. The tubes 30 and 31 are joined by a header band 32 to a set of three parallel tubes 33, 34 and 35 which have discharge outlets 36, 37 and 38. The final discharge outlets may be joined for forming a combined single stream which is passed to a cooler and fractionation recovery system. With the arrangement shown in FIG. 3 all of the tubes may have the same internal diameter, and the progressively increased number of tubes allow for expansion in volume for minimizing back pressure. The tubes in successive branches may, also, have increasing internal diameters.

In FIG. 4 it is shown how the tubes are arranged within the furnace walls 39 with respect to a plurality of short flame burners to supply uniform radiant heat to all the tubes, the burners being arranged along the level of each of the tubes as indicated in FIG. 2 and at suitable vertical levels for each of the tubes as shown in FIG. 4. The tubes are spaced equidistant from the burners both in the peripheral walls 39 and in a partitioning wall 40. As indicated with reference to FIG. 2, the tubes may be used for parallel passes of divided streams from a common inlet, the initial tube for one pass being 27 and the initial tube for a second pass being 41.

Starting with the upper tube 41 there is a connected set of parallel tubes 42 and 43, which are joined to a set of parallel tubes 44, 45 and 46. The furnace may be constructed to use additional banks of tubes having a similar arrangement.

In the operation of the furnace, the cyclodiene dimer concentrate to be fed into the initial part of the coil or initial tube may be preheated, vaporized or partially vaporized. Generally, the preheating temperature is in the range of 150° to 500° F. The temperatures in the cracking tubes are maintained in a narrow range, and preferably in the range of 500° to 575° F. The pressures in the tubes are maintained preferably below 50 p.s.i.g. and may be subatmospheric pressure with a pressure drop of less than 20 p.s.i. With the increased velocity, i.e., for increasing capacity or throughput, the pressure drop tends to increase, but with applicants' method of increasing the cross-sectional areas of the streams, the pressure drop is decreased.

For practical purposes, the increase of the cross-sectional areas of the streams from inlet to outlet amounts to a two-fold to four-fold increase.

What are called dimer concentrates of the C₅-C₆ cyclodienes as feeds to the furnace may include dimers, codimers, trimers and cotrimers of these cyclodienes with C₆ and higher impurities and also heavier polymers, but the better quality feeds will contain mainly the dimers, codimers, trimers, and cotrimers of the C₅-C₆ cyclodienes, e.g., at least 70 weight percent thereof.

While in using relatively low temperatures and low feed rates, a cracking coil of uniform cross-sectional area gave fairly good results in avoiding coking for a period in the range of 300 to 500 hours, the outlet temperature had to be kept relatively low, i.e., below 530° F. On raising the temperature to 550° F. with such a furnace the back-pressure increased and there was excessive coke formation.

The present invention is illustrated by the following example on a pilot plant scale operation.

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EXAMPLE

For a feed having a 70 weight percent content of dimeric and trimeric C₅-C₆ cyclodienes the feed rate to the inlet of an initial tube section is at the rate of 4.4 gallons per minute, this initial tube section having an internal diameter of 1.5 inches. The temperature in the initial tube section is 500° F. at the outlet. The internal diameter of the second tube section through which the vapors of the feed are passed has an internal diameter of 2 inches and in this second tube section uniformly heated by radiant heat the temperature is maintained at 500° to 550° F. The totally vaporized product stream from the second tube section is then passed through a third tube section having an internal diameter of 2.5 inches. At the outlet of the third tube section the temperature is 550° F. The inlet pressure of the first tube section is 19.4 pounds per square inch absolute (p.s.i.a.). The outlet pressure of the third tube section is 17.45 p.s.i.a., making the pressure drop only 1.89 p.s.i. The total residence time of the streams in the coil was 100 seconds, of which 1.2 seconds was at cracking temperature of 550° F. By increasing the outlet temperature by 20° F. with the lowered pressure in this manner, the cracking rate of the dimer concentrate is increased by nearly 50% and the period of operating of the coil without removal of coke is also increased by nearly 50% as compared to an operation in which the coil has a uniform internal diameter. In other words, the rate of monomer recovery obtained by operating with outlet temperatures of 550° to 575° F. is 70 to 80% compared to a higher pressure operation which requires outlet temperatures usually well below 550° F. to prevent fast coking.

As indicated in the foregoing example, the vapor stream undergoing cracking should be permitted to expand a two-fold to four-fold extent in flowing from the inlet to the outlet of the interconnected tubes or coil. The pressures in the tubes should be maintained close to atmospheric or at subatmospheric pressures with a low pressure drop or back pressure amounting to less than 20 p.s.i., preferably less than 10 p.s.i.

Data on respective conditions of operation are summarized in the following table:

Table

RELATIVE MEASUREMENTS FOR FURNACE TUBES
BASED ON FEED RATE OF 2.2 GALLONS/MINUTE
[½ total feed rate to two series of tubes in furnace]

	Pipe Section			Total
	1.5 inch	2.0 inch	2.5 inch	
Heat Input, B.t.u./Hr.	37,000	23,400	75,000	468,000
Fluid Velocity, Ft./Sec.	0.6	51	44	
Length of Tubes, Ft.	60	20	52	132
Pressure Drop, p.s.i.	0.87	0.47	0.55	1.89
Residence Time, sec.	98	0.5	1.2	100
Temperature Section Range (° F.)	300 to 500	500	550	
Pressure at Section Inlet, p.s.i.a.	19.4	18.5	18.0	
Pressure at last Section Outlet, p.s.i.a.				17.45

It can be seen from the foregoing data that a major proportion of heat input occurs in the last sections when the dimer concentrate vapors are at temperatures in the range of 500-575° F. In these last sections the cross-sectional area of the vapor stream is increased, the fluid velocity is greatly increased with respect to the velocity in the initial section and the residence time of the vapors in the last sections where the vapors are heated to above 500° F. is less than 5% of the total residence time on the furnace, e.g. 1.7 seconds of a total of 100 seconds. Preferably the final section temperature is in the range of 540° to 560° F.

Each section may be made up of a number of interconnected tubes in series to give the desired length of tubes. It is not important to have the tubes of the initial

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section supplied with direct radiant heat while the temperature of the vapors flowing through these tubes are being heated up to 500° F. It is desirable to have uniform direct radiant heat on the final section of tubes in which the vapors are heated above 500° F. and are exposed to heating for a relatively short period of about 1 to 2 seconds.

In the kind of operation described, the amount of water present with the feed is preferably kept low to avoid creating pressures in the cracking tubes.

Along with more nearly uniform pressures in each section of the cracking tubes, a more nearly level temperature is obtainable in the sections where the vapors reach a temperature of 500° to 575° F. This, in a preferred operation with the vapors under a total pressure of 0 to 50 p.s.i.g., heating in initial section at temperatures in the range of 300° to 500° F. is carried with minor heat input compared to the heating in a subsequent section where the vapors are heated to above 500° F. for a short time in the tubes receiving more of the radiant heat.

The invention described is claimed as follows:

1. A process for cracking a C₅ to C₈ cyclodiene dimer concentrate, which comprises passing said concentrate in vapor phase at a pressure of 0 to 50 p.s.i.g. through a

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series of interconnected cracking tubes of consecutively increasing cross sectional area, the largest cracking tubes having from 2 to 4 times the cross sectional area of the smallest tubes, and the pressure drop through the cracking tubes being below 20 p.s.i., and maintaining temperatures in the range of 500 to 575° F. by heating each of the tubes uniformly with radiant heat.

2. A process as defined in claim 1, wherein the number of tubes through which the vapors pass is increased as the vapors flow from an initial section of the series of tubes through a final section to give the vapors an overall increased cross-sectional area as they progressively undergo cracking in passing through said tubes.

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