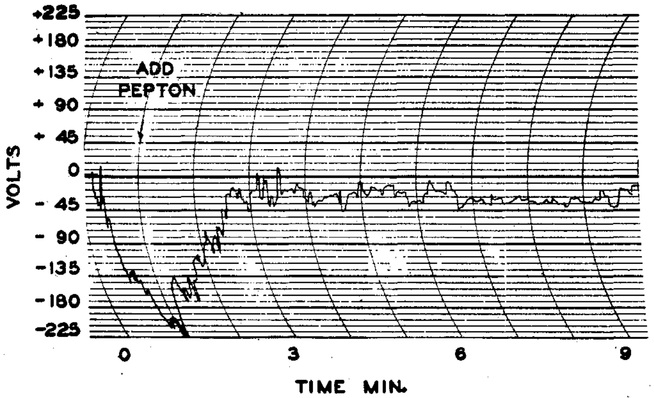

Figure 16. Mastication Curve for GR-S 10-16 with 3% Pepton

Side probe

and rubber is not continuous, such as may be the case with the door probe when the rubber is stiff and nervy, the polarity indicated may be opposite to that actually present on the rubber. When the probe is in substantially continuous contact with the rubber, as is usually the case with the side probe, the polarity and magnitude of the potential is the same as that of the rubber. Since the rubber is in more intimate contact due to greater pressure against the door probe and, also, due to the fact that the rubber is under greater stress, contact potentials usually are higher for the door probe than for the side probe. This enables contact potentials on 80% zinc oxide masterbatches to be measured.

Tests with two electrostatic probes have given a keener insight into the differences in mixing mechanism for plastic and nervy compounds. They also have pointed to the possible ideal location of the probe where maximum continuous pressure of rubber against probe will be realized—namely, in the bottom of the ram.

Application of the electrostatic contact potential theory of mixing, which involves the attractive forces between the positive pigments and the negative rubber in promoting rapid incorporation and the uniformity of electrical charge on pigments in promoting good dispersion, has resulted in the production of coated zinc oxide pigments which produce better quality stocks at reduced mixing costs.

Electrostatic mastication charts on different samples indicate:

It may be possible to develop this equipment for raw material control purposes.

. Substantial contact potentials for both vinyl plastics and silicone rubber point the way for the possible application of this equipment to the processing of these materials.

The action of the chemical plasticizer, Pepton, is similar to mastication, and its action is probably one of oxidation.

This equipment may be of value in reducing costs by determining the proper sequence and timing of mixing operations and in improving quality through better pigment dispersion.

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Preparation of Six- and Eight-Membered Ring Dimers of Butadiene

ENGINEERING
AND PROCESS
DEVELOPMENT

JOHN C. HILLYER AND JAMES VIRGIL SMITH, JR.
Phillips Petroleum Co., Bartlesville, Okla.

THE monomer 1,3-butadiene is readily converted by thermal action into a cyclic dimer, which consists primarily of 4-vinyl-1-cyclohexene (*10, 14*). The reaction has been the subject of several thorough kinetic investigations (*12, 13, 16, 22, 26*) and is now familiar as a result of the greatly expanded interest in butadiene arising from its large scale manufacture for use in synthetic rubber. Most investigators have reported, in addition to this vinyl cyclohexene, smaller amounts of apparently isomeric dimers and of trimers and higher boiling products (*5, 6, 11, 15, 17, 18, 20, 23–26*).

In the course of an investigation on certain phases of the dimerization reaction carried out by the authors of this paper and other associates in this laboratory several years ago, careful distillations were made of the total products from dimerization runs made under a variety of liquid- and vapor-phase conditions. In general, the results of these studies were in accord with the observations reported in the literature. Between the major product, 4-vinyl-1-cyclohexene, and the smaller amounts of trimer and heavy polymers, some intermediate boiling material was observed. In particular, at certain conditions of operation a fairly long plateau in the boiling point curve of the product at 300° F. accounted for more than half this intermediate material. It was shown to be the eight-membered ring compound, 1,5-cyclo-octadiene, resulting from 1,4- condensation of both of the butadiene molecules entering the dimer.

Historical

1,5-Cyclo-octadiene was first reported by Willstätter in 1905 (*27*); it was isolated in studies on the pelletierine alkaloids.

Relatively little was done with it until recently when the work of Reppé (*21*) on the polymerization of acetylene to cyclo-octatetrene became known and aroused great interest (*1*, *2*). In these researches, cyclization of a four-carbon hydrocarbon to a cyclo-octadiene ring was first accomplished using chloroprene to yield 2,6-dichloro-1,5-cyclo-octadiene (*1*). Application of the reaction to butadiene itself was reported briefly by Harries (*9*) in 1912. Concurrently with these researches, Ziegler (*28*) reported 1,5-cyclo-octadiene among the intermediate boiling products of thermal dimerization of butadiene. Subsequently, Ziegler and Wilms (*29*) have shown it to be the cis-cis isomer; Foster and Schreiber (*7*, *8*) have described the product of thermal dimerization of butadiene at 100° to 120° C. as vinylcyclohexene containing 1 to 5% of an eight-membered ring compound whose structure was not determined but which hydrogenated to cyclo-octane.

Table I. Composition of Liquid Products of Dimerization

(Run at 700° F., 40 lb./sq. inch gage, 20 seconds contact time)

Fraction	Boiling Point, ° F. at 760 Mm. Hg	Liquid, Vol. %
I (4-vinyl-1-cyclohexene)	262–267	80.0
II	267–321	9.7
III	321–496	7.7
IV (residue)	Above 195 at 1 mm.	2.6

Because this type of hydrocarbon is still relatively little known and might be of practical interest, an investigation was made of the conditions under which the eight-membered ring formation is most favored, and of the stability and interconversion of the dimers.

Isolation from Crude Dimer Fractions

In one series of tests on vapor-phase dimerization of 1,3-butadiene under pressures in the range 30 to 40 pounds per square inch gage and at temperatures of 700° to 900° F., samples sufficiently large to allow of close fractionation of the higher boiling products were prepared. In one test made at 40 pounds per square inch gage, 22 seconds contact time, and a temperature in the range 775° to 850° F., a yield of 10% of a 298° to 310° F. fraction was obtained. The distillation of another such typical product, prepared at 40 pounds per square inch gage and 700° F. yielded the results shown in Table I.

Since cut II amounted to nearly 10% of the product and half the material boiling above vinylcyclohexene, and there was evidence that most of it distilled on a plateau, it was carefully refractionated. A 40 × 1 inch column packed with 1/8-inch glass helices was first used at 10 to 1 reflux ratio. A final redistillation of the portion of the first distillate boiling in this range was then made at 20 to 1 reflux ratio. Figure 1 shows the distillation curve obtained. The plateau at 297° to 300° F. comprised 68% of the charge and was 6.8% of the total dimerizate. The constants obtained for samples of the purified material from this plateau agree very well with those given in the literature (*1*, *3*) for 1,5-cyclo-octadiene (boiling point, 298.5° to 300° F., $n_D^{20} = 1.4964$, $d_4^{20} = 0.8564$; found, boiling point 300° F., $n_D^{20} = 1.4938$, $d_4^{20} = 0.8570$). The boiling point admitted equally well of 1-vinyl-1-cyclohexene; and molecular weight determination, absorption of 2 moles of bromine and hydrogenation by 2 moles of hydrogen to a saturated compound did not differentiate between the two. The hydrogenation product, however, did not correspond to ethylcyclohexane and was not identical with an authentic sample of this reduction product. The physical constants found (boiling point, 302° F., $n_D^{20} = 1.4580$) corresponded closely with those recorded (*4*) for cyclo-octane. If the original compound was a cyclo-octadiene the 1,5- isomer seemed most probable. Identification was completed by a negative test with maleic anhydride which eliminated the conjugated 1,3- isomer as a possibility, and finally by ozone oxidation to yield 2 moles of succinic acid per mole of cyclo-octadiene.

Process Studies

Since varying amounts of the isomeric dimer were observed in these large samples of product, prepared under somewhat different and rather poorly controlled conditions, an investigation of the effect of the process variables—temperature, pressure, and contact time—was undertaken. Flow-type experiments were used and studies were confined to vapor-phase conditions, since it was known that lower temperature liquid-phase tests yielded only 2 or 3% of material boiling above 270° F., chiefly heavy polymer. The ranges 660° to 1200° F. and atmospheric to 150 pounds per square inch gage pressure were investigated.

In the first tests a large reactor tube (2450 ml.) was used. Various schemes for controlling the temperature were tried but were not wholly satisfactory. A smaller reactor was then incorporated in a new assembly of apparatus, which performed very well. This apparatus is diagramed in Figure 2.

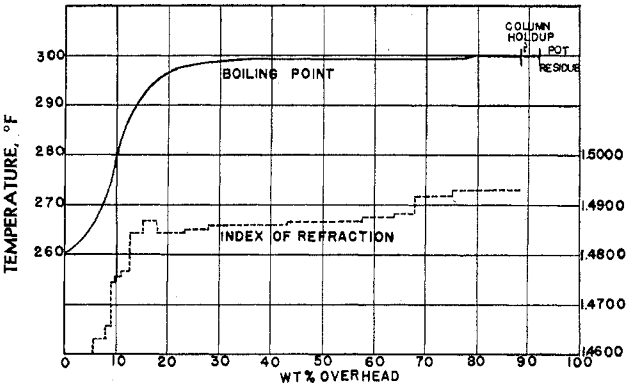

Figure 1. Distillation Curve for Fraction II

1,3-Butadiene feed was Phillips Petroleum Co., Pure Grade, 99+% purity, containing less than 10 p.p.m. peroxides. The principal impurity was 1-butene. Regular analyses for dimer were performed and whenever results showed dimer present, a fresh tank was taken. It was contained in cylinder *A*, fitted with an induction tube reaching to the bottom and an inlet line through which a nitrogen blanket was maintained on the hydrocarbon feed, at a pressure 100 pounds per square inch in excess of the reactor pressure selected for each experiment. The liquid feed to the vaporizer-preheater, *C*, was controlled by the Taylor recording-flow controller, *B*. The instrument was calibrated before each run. The preheater, in which the feed was vaporized and heated to within 50° F. of reaction temperatures, consisted of a 4-foot section of 1/4-inch stainless steel tubing, surrounded by a 1/4-inch pipe. This outer pipe was wrapped with an electrical resistance heater, and the whole covered with insulation. The feed then passed into the reactor, *D*, which was 1.0-inch stainless steel tube. It had a volume of 400 ml.

The heat of reaction was absorbed as latent heat of vaporization of Dowtherm, which was used in the jacket. By varying the pressure on the Dowtherm jacket, the boiling point could be adjusted to match any selected reaction temperature. The jacket was heated by five 5.0-ampere heaters on the outside. Temperatures were recorded on the temperature recorder, *E*, at three points in the reactor jacket, at the preheater outlet, and at the reactor inlet.

The products passed into a receiver, *F*, maintained at reaction pressure and cooled by circulating cold acetone in a surrounding coil. After completing a test the condensate was drained off and the butadiene allowed to boil off. The resulting polymeric products were fractionated in vacuo. The column (not shown) had a diameter of 3/4 inch and a packed section 20 inches long filled with 1/4-inch glass helices. In operation, a 10 to 1 reflux ratio was generally used.

Table II. Effect of Conditions on Product Composition in Thermal Dimerization

Run No.[a]	Temp., ° F.	Pressure, Lb./Sq. In. Gage	Contact Time, Sec.	Total Conversion, %	Calcd. Dimerization[b], %	Product Composition[c], Vol. %: Light ends	Vinyl cyclohexene	Intermediate	Cyclo-octadiene	Heavy ends	Duration, Hr.
1	800	2	3.3	..	3.1	..	..	..	0[d]	..	3
2	775	2	5.4	..	3.6	..	..	..	0[d]	..	2
3	800	0	8.4	..	7.2	..	..	..	0[d]	..	5
4	800	0	11.6	..	9.2	..	..	..	0[d]	..	2
6	865	0	4.2	4.7	9.2	3.5	87.0	0.0	0.0	9.5	4
9	840	0	13.7	10.9	16.6	2.0	89	0.9	2.0	6.1	5
10	860	0	12.8	19.0	18.1	1.5	88	0	0	10.5	5
12	900	0	10.9	31.0	22.9	4.5	85	0.8	0.7	9.0	8
13	950	0	14.8	47.8	43.1	5.0	80	0	0	15.0	3
14	720	40	18.7	15.5	20.2	1.6	85.8	4.2	5.6	3.8	2
15	800	38	47.7	38.2	57.0	1.0	83	2.2	0.6	13.2	4
16	700	39	45	33.5	32.6	3.1	82	1.3	2.0	11.6	2.5
18	750	149	8.7	32.7	31.3	4.0	63.1	2.6	1.9	28.4	2
19	660	100	4.8	5.5	5.6	1.8	81.8	1.6	5.5	9.2	2
20	695	100	5.0	6.6	8.5	2.9	77.1	6.7	3.8	9.6	2
21	690	60	5.0	8.5	6.4	2.7	73.5	5.9	5.0	13.3	2
22	740	60	4.7	11.9	9.7	1.5	78.0	2.3	7.7	10.0	3
23	775	60	2.5	10.7	8.5	3.4	85.5	2.1	3.5	5.5	2.5

[a] Runs 1-16 made in 2450-ml. reactor; runs 18-23 in 400-ml. reactor shown in Figure 2.
[b] Calculated using the equation: $\log K = -8330/T + 7.66$.
[c] Fractions taken as follows: light ends, up to 247° F.; vinylcyclohexene, 247-266° F.; intermediate, 266-290° F.; 1,5-cyclo-octadiene, 290-302° F.; heavy ends, 302° F. and above.
[d] No cyclo-octadiene found in these distillations; no exact determination of volumes of other products made.

In tests at atmospheric pressure, runs 1 through 13 in Table II, no fraction corresponding to cyclo-octadiene was found in the products, except for the small yield in run 9. At progressively increasing temperatures, from 840° to 950° F., the amount of the vinylcyclohexene in the product steadily decreased. There was a corresponding upward trend in the light liquid products (C_6 to 265° F.) obtained. Similarly, there was an upward trend in the trimer and heavier liquid polymer obtained. In the runs made initially in the range 775° to 800° F., accurate data on the yields of products other than cyclo-octadiene were not taken, but it was observed qualitatively that the vinylcyclohexene fraction was substantially the entire product.

Formation of a little solid polymer was observed in all cases, averaging 0.5 to 1% of the total effluent. However, this was sufficient to plug the reactor tube and force termination of the runs. It did not melt and drain from the tube at temperatures above 700° F., although the literature indicated it would do so.

Additional runs at atmospheric pressure were attempted in the temperature range 950° to 1200° F. They were all of very short duration because of rapid plugging with solid polymer. This was the major product in addition to much reduced yields of vinylcyclohexene.

In the experiments in which cyclo-octadiene was first isolated, a small pressure had been employed, so attention was next turned to runs under superatmospheric pressures. In Table II, runs 14 through 23, tests under these conditions all show appreciable formation of isomeric dimers, including a cyclo-octadiene fraction. Temperatures and contact times were adjusted to give a wide range of total conversion.

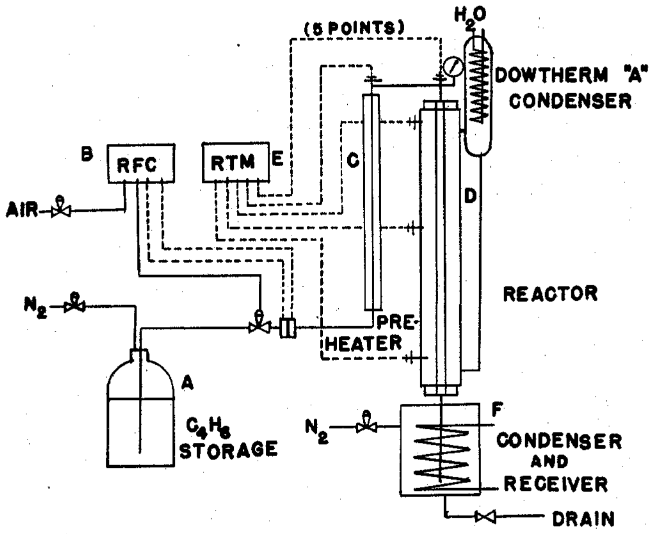

Figure 2. 1,5-Cyclo-octadiene Apparatus

At 40 pounds per square inch gage, low conversion runs, as exemplified by run 14, gave the highest yield of dimers, both six- and eight-membered rings. More heavy polymer and less of the isomeric dimers formed at high conversions. At 60 pounds per square inch gage runs 22 and 23 indicated a higher purity vinylcyclohexene, with less of all the by-products, when equivalent conversion was obtained by the use of higher temperature and shorter contact time.

When pressure was further increased to 100 pounds per square inch gage, fairly good yields of cyclo-octadiene could still be produced by maintaining low conversion (runs 19 and 20). At 150 pounds per square inch gage even moderate temperature and short contact time resulted in very high conversions, with large yields of trimers, etc., but with the amounts of both C_8 and C_6 dimers markedly reduced. Run 18 is typical of tests at 150 pounds per square inch and above.

Conditions best suited to conversion of a portion of the butadiene to cyclo-octadiene appeared to be in the range 40 to 100 pounds per square inch gage at temperatures of 775° to 650° F., respectively, and with total conversion held near 10%. The maximum yield in this series of tests, 7.7%, was obtained at 60 pounds per square inch gage and 740° F. and a total conversion of about 12%.

Isomerization Tests

The rather narrow temperature limits within which cyclo-octadiene was found to occur suggested that isomerization to vinylcyclohexene as a more stable compound might occur above or below this range. Accordingly, two tests were carried out to determine the stability of cyclo-octadiene.

The hydrocarbon was vaporized into a stream of nitrogen as a carrier gas and passed through a heated borosilicate glass tube at atmospheric pressure. Products were collected and carefully examined. In the first test at 600° F. and 23 seconds contact time the entire amount of cyclo-octadiene was recovered unchanged, no gas was formed, and the boiling point of the product was unchanged. On the other hand, in the second test at 800° F. and 18 seconds contact time conversion was substantially complete. No product boiling in the range for cyclo-octadiene remained. Yields of 53% vinylcyclohexene and 19% butadiene were recovered, with 8% heavy polymer. The butadiene recovered was examined by infrared spectroscopy and found to be extremely pure and free of other C_4 hydrocarbons.

Cracking to butadiene and recombination to vinylcyclohexene can be ruled out as the major reaction mechanism. Reaction rate equations (*19*) show that, had the entire feed cracked instantaneously to butadiene, the yield of dimer to be expected in 18 seconds contact time would be only 4.2%. The effect of pressure on the equilibrium has not yet been studied in superatmospheric tests.

Similar tests on vinylcyclohexene did not yield detectable amounts of cyclo-octadiene.

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ENGINEERING
AND PROCESS
DEVELOPMENT

Chemical Production of Lactic and Other Acids from Molasses

Reaction Conditions

REX MONTGOMERY[1] AND RICHARD A. RONCA[2]

Sugar Research Foundation, Inc., New York 5, N. Y., and Eastern Regional Research Laboratory, Philadelphia 18, Pa.

CERTAIN carbohydrates undergo degradation in the presence of alkaline reagents. A systematic study of the reactions involved was first made by Nef (*34, 35*) and extended in more recent years, principally by Evans and coworkers (*12, 13*). These workers found that the principal product from such a reaction was lactic acid, but other acidic compounds were identified, among them acetic, formic, α,γ-dihydroxybutyric (*35*), saccharinic (*12*), and glucic acid (*43*). The theoretical yield of lactic acid from sugars is 2 equivalents per mole of hexose, and 1 equivalent per mole of pentose or triose. Nef (*35*) showed that tetroses rearrange in alkaline media to form saccharinic acids almost exclusively. Glucose, fructose, and invert sugar have been converted to lactic acid to the extent of 60 to 67% of the theoretical value (*25, 45, 50*).

The first extensive work on the formation of lactic acid from sucrose was done by Wolf (*4, 54*), who used calcium oxide, sodium hydroxide, and barium hydroxide reagents at temperatures of about 200° C. Lactic acid was obtained in yields up to 73% of the theoretical value but was isolated as the pure zinc salt only in 60% yield. Haworth, Gregory, and Wiggins (*22*) isolated pure zinc lactate from sucrose in yields of 71% of the theoretical amount. More recently the yields of lactic acid from cane sugar and refiner's blackstrap molasses have been investigated by Miyake, Hayashi, and Sano (*28*), who reported their highest yield as 61.5% from sucrose and 61.3% from molasses, but did not isolate the acid in this yield. Only Braun (*6*) has patented the production of lactic acid from sucrose and molasses without previous inversion, claiming that the reaction mixture from sucrose contained 72 to 75% of the theoretical yield of acid, which was isolated in 45% yield as calcium lactate and 50% yield as the zinc salt.

Although it has been known for some time that acids other than lactic acid are produced by alkaline degradation of carbohydrate materials, little work has been reported on the isolation of these acids. With a view to finding the extent to which lactic acid and the unknown acids are formed from molasses and raw sugar, the action of calcium oxide and calcium hydroxide on Cuban blackstrap molasses, refiner's blackstrap molasses, beet molasses,

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[1] Present address, University of Minnesota, University Farm, St. Paul 1, Minn.

[2] Present address, Sharp and Dohme, West Point, Pa.