

July 8, 1947.

H. O. FOLKINS ET AL
CRACKING OF HYDROCARBONS IN THE PRESENCE
OF HALOGEN-CONTAINING SENSITIZERS
Filed June 11, 1945

2,423,494

3 Sheets-Sheet 1

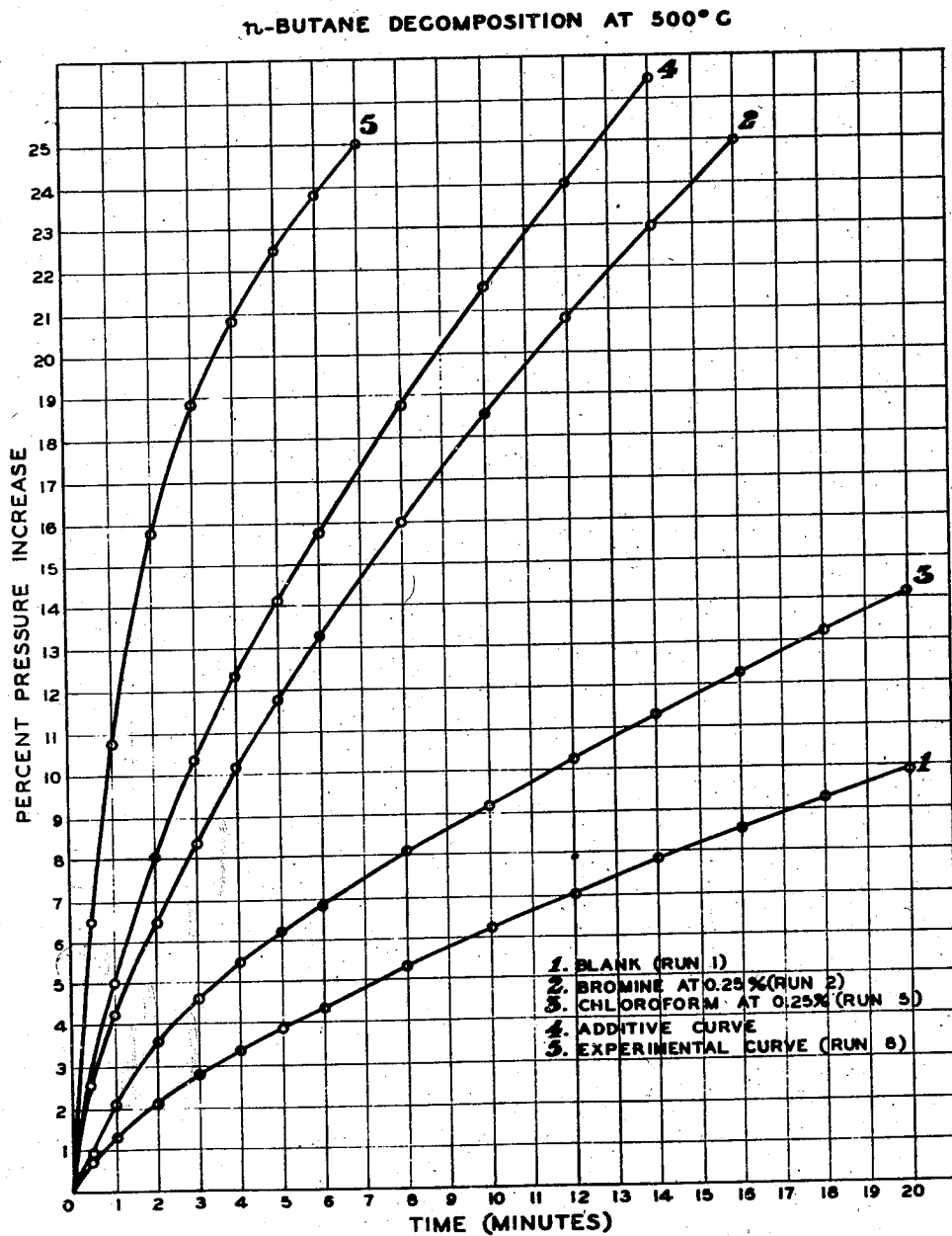


Fig. 1

INVENTORS
Hillis O. Folkins
Carlisle M. Thacker
BY *Edward H. Lang*
ATTORNEY

July 8, 1947.

H. O. FOLKINS ET AL
CRACKING OF HYDROCARBONS IN THE PRESENCE
OF HALOGEN-CONTAINING SENSITIZERS
Filed June 11, 1945

2,423,494

3 Sheets-Sheet 2

n-BUTANE DECOMPOSITION AT 500°C

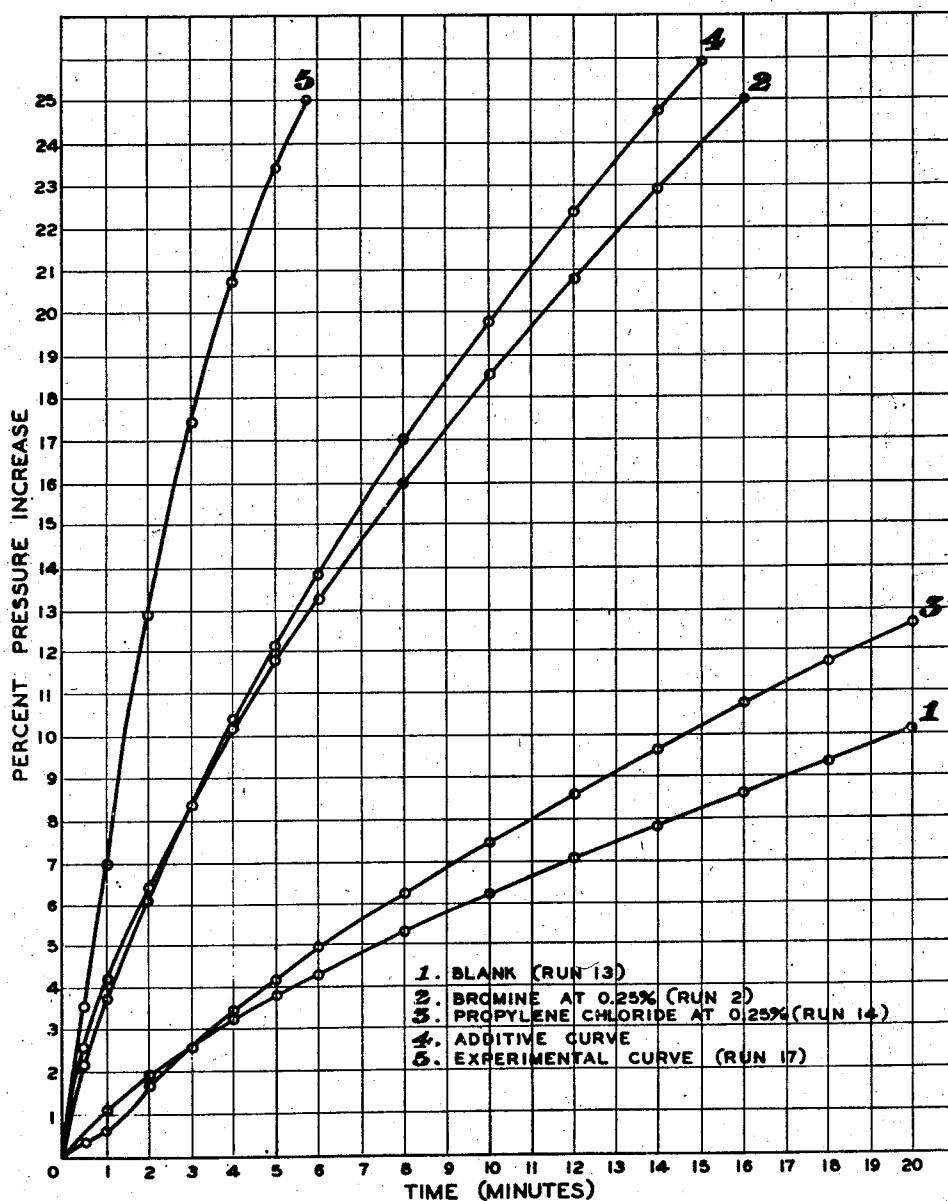


Fig. 2

INVENTORS
Hillis O. Folkins
Carlisle M. Thacker
BY **Edward H. Jung**
ATTORNEY

July 8, 1947.

H. O. FOLKINS ET AL
CRACKING OF HYDROCARBONS IN THE PRESENCE
OF HALOGEN-CONTAINING SENSITIZERS
Filed June 11, 1945

2,423,494

3 Sheets-Sheet 3

n-BUTANE DECOMPOSITION AT 500° C

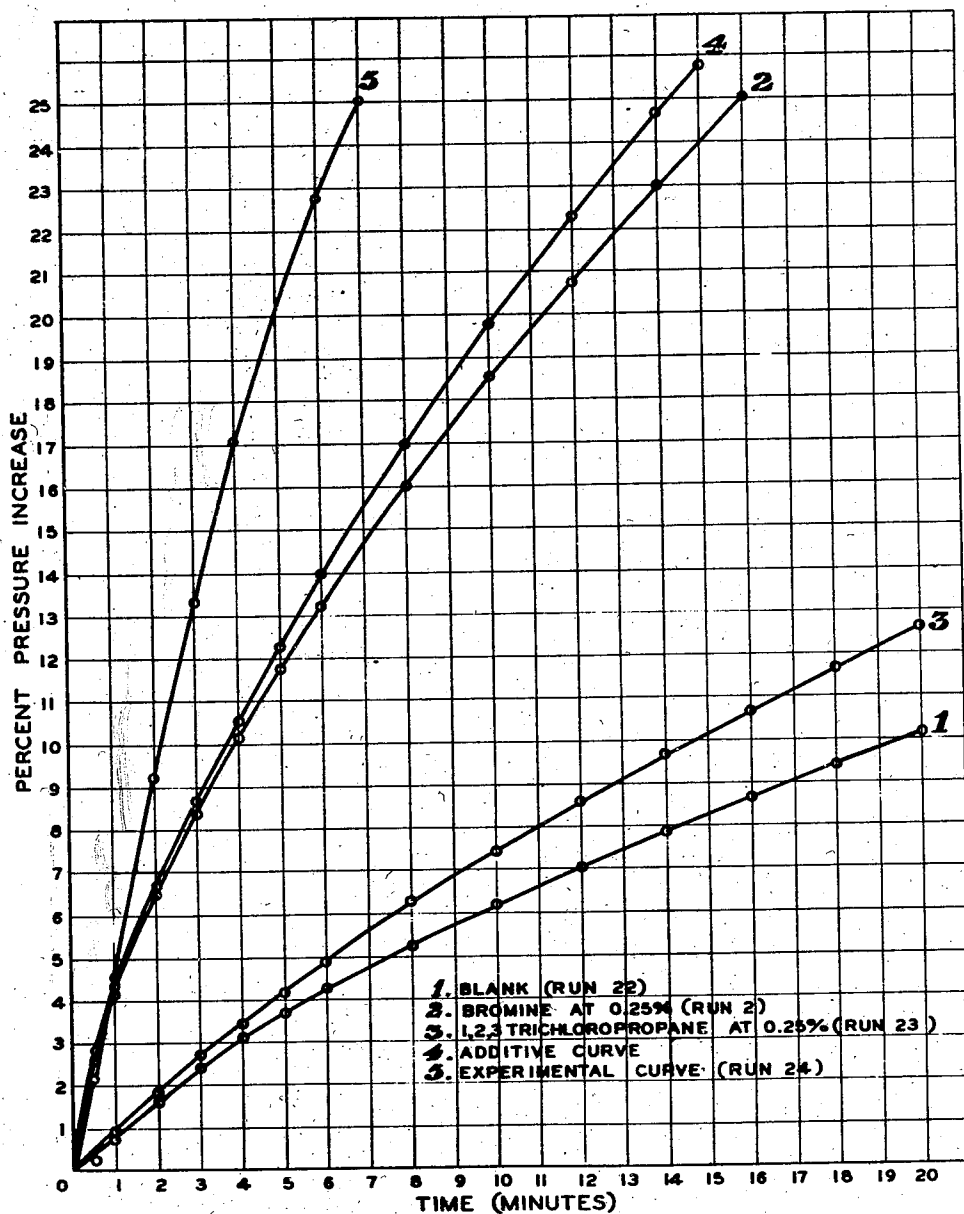


Fig. 3

INVENTORS
Hillis O. Folkins
Carlisle M. Thacker
BY Edward H. Long.
ATTORNEY

UNITED STATES PATENT OFFICE

2,423,494

CRACKING OF HYDROCARBONS IN THE
PRESENCE OF HALOGEN-CONTAINING
SENSITIZERSHillis O. Folkins, Skokie, and Carlisle M. Thacker,
Highland Park, Ill., assignors to The Pure Oil
Company, Chicago, Ill., a corporation of OhioApplication June 11, 1945, Serial No. 598,706
In Canada February 24, 1945

16 Claims. (Cl. 196-52)

1

This invention relates to cracking of hydrocarbons and is more particularly concerned with a method for converting higher boiling hydrocarbons into lower boiling hydrocarbons and for making unsaturated hydrocarbons from saturated hydrocarbons.

We have discovered that if thermal conversion of hydrocarbons is carried out in the presence of a small amount of a poly-chlorinated aliphatic organic compound, particularly a poly-chlorinated hydrocarbon of the paraffin series in which some or all of the hydrogen atoms in the hydrocarbon have been replaced by chlorine, admixed with a small amount of bromine or iodine or both, the cracking of the hydrocarbon is greatly accelerated so that it is possible to obtain larger yields of cracked hydrocarbons under the same time-temperature-pressure conditions than it is possible to obtain in thermal cracking of the hydrocarbons without sensitizer, and it is possible to obtain yields at lower temperatures which are commensurate with yields obtainable at higher temperatures without sensitizers. Our invention is applicable to either batch or continuous methods of cracking. In continuous cracking methods by operating under usual thermal cracking conditions in the presence of a sensitizer, not only can increased yields be obtained but higher octane gasoline can be produced. By using a sensitizer, a larger through-put of charging stock through a given size unit can be effected because of the acceleration in the cracking reaction caused by the sensitizer.

An object of our invention is to provide a method for conversion of hydrocarbons.

Another object of our invention is to provide a method for accelerating cracking of hydrocarbons.

Still another object of our invention is to provide a method for increasing octane number of motor fuel made by cracking of hydrocarbons.

A further object of our invention is to provide a sensitizer which will accelerate the decomposition of hydrocarbons.

A still further object of our invention is to provide a method for improving thermal cracking of hydrocarbons.

Other objects of the invention will become apparent from the following description and the accompanying drawings, of which

Figure 1 is a graphical representation of data showing the unexpected results obtained from using a combination of bromine and chloroform as cracking sensitizer;

Figure 2 is a graphical representation of data

2

showing the unexpected results obtained from using a combination of bromine and propylene dichloride as sensitizer; and

Figure 3 is a graphical representation of data showing the unexpected results obtained from using a combination of bromine and 1,2,3-trichloropropane as cracking sensitizer.

In accordance with the invention, a small amount of a poly-chlorinated aliphatic hydrocarbon, such as chloroform, carbon tetrachloride, ethylene dichloride, propylene dichloride, and 1,2,3-trichloropropane, and bromine and/or iodine are mixed with the hydrocarbons subjected to decomposition. The poly-chlorinated aliphatic hydrocarbon and the halogen may be mixed with the hydrocarbons prior to charging them to the reaction zone or they may be injected directly into the reaction zone. The total sensitizer mixture may be used in concentrations from approximately .055 mole percent to 5 mole percent based on the total charge and should contain not less than about .005 mole percent of bromine and/or iodine, and not less than about .05 mole percent of poly-chlorinated aliphatic hydrocarbon. Higher concentrations of sensitizers may be used, but within the limits above set forth the reaction progresses rapidly without causing accumulation of undesirably large amounts of the sensitizers and their decomposition products in the motor fuel or other product which it is desired to produce. In our experimental work it has been found that a mixture containing from .03 mole percent of bromine up to 2 mole percent of bromine and from .25 percent of a poly-chlorinated aliphatic organic compound up to 2 percent of a poly-chlorinated aliphatic hydrocarbon gives unusually good results. When cracking hydrocarbon oils to gasoline boiling hydrocarbons, it is preferred to keep the combined amount of catalyst below 1% by weight based on the oil cracked.

The invention is useful in conjunction with conventional types of thermal cracking in which the hydrocarbons are cracked at temperatures within the range of approximately 375° C. to 750° C. and is applicable to conversion of hydrocarbon gases such as propane and butane as well as to the conversion of liquid hydrocarbons such as heavy naphtha, kerosine and gas oil. The combination of the bromine and/or iodine with a poly-chlorinated aliphatic hydrocarbon accelerates the cracking reaction to an extent far in excess of that which would be expected from the additive effect of the poly-chlorinated aliphatic hydrocarbon and the bromine or iodine alone.

In order to demonstrate this fact a number of runs were made using normal butane as charging stock. The butane had a purity of 99%. The runs were all made in a Pyrex glass reaction vessel at a temperature of 500° C. Before starting each run the reaction vessel was heated to the desired reaction temperature and then evacuated by means of a vacuum pump to a pressure below 0.001 mm. of mercury. Sufficient butane in admixture with the desired amount of sensitizer composition was then charged to the evac-

the end of the run. The figures appearing in the table for 5% and 12.5% pressure increases were taken from curves of individual runs in which percent pressure increases were plotted against time. In the table the figures given under the heading "Time in minutes for ΔP of 25%" are in some cases recorded and in other cases are interpolated from curves based on recorded pressures because in certain runs the pressure rose above 25% increase too rapidly to obtain a reading at the exact point.

Table

Run No.	Sensitizer		Time in Minutes for ΔP of—			Sensitization Factors			Reaction Products, Mole Per cent				
	Name	Mole, Per cent	5%	12.5%	25%	5%	12.5%	25%	CO ₂	Unsat.	CO	H ₂	Residue
1	None ¹		7.41	27.90	73.32				0.1	23.0	0.3	1.1	75.5
2	Br ₂	0.25	1.30	5.50	16.02	5.7	5.1	4.6	0.1	24.1	0.3	1.0	74.5
3	do	0.5	1.00	4.10	11.52	7.4	6.8	6.2	0.0	23.7	0.0	0.6	75.7
4	do	1.0	0.41	2.75	9.13	18.1	10.1	8.0	0.2	26.8	0.1	0.7	72.2
5	CHCl ₃	0.25	3.45	16.47	47.55	2.1	1.7	1.6	0.0	22.6	0.9	1.0	75.5
6	do	0.5	2.01	10.50	32.55	3.7	2.7	2.2	0.0	22.8	0.3	0.6	76.3
7	do	1.0	1.35	5.59	20.27	5.5	5.0	3.6	0.2	24.2	0.2	0.9	74.5
8	Br ₂	0.25	0.37	1.30	6.95	20.0	21.5	10.5	0.0	24.1	0.0	1.0	74.9
9	CHCl ₃	0.25	0.24	0.85	3.90	30.9	32.8	18.8	0.0	22.8	0.1	0.5	76.6
10	Br ₂	0.5	0.22	0.78	3.28	33.7	35.8	22.4	0.1	23.6	0.1	0.5	75.7
11	CHCl ₃	0.25	0.25	0.89	4.12	29.6	31.3	17.8	0.0	23.2	0.1	0.5	76.2
12	Br ₂	0.25	0.20	0.72	2.73	37.1	38.8	26.9	0.1	23.7	0.1	0.6	75.5
13	CHCl ₃	1.0	7.39	27.41	73.44				0.1	22.6	0.0	1.2	76.1
14	None ¹	0.25	6.09	19.64	54.17	1.2	1.4	1.4	0.0	22.3	0.1	0.8	76.8
15	C ₃ H ₇ Cl ₂	0.5	4.97	14.82	39.90	1.5	1.9	1.8	0.0	23.3	0.0	0.7	76.0
16	C ₃ H ₇ Cl ₂	1.0	3.27	9.47	25.20	2.3	2.9	2.9	0.0	23.4	0.2	1.3	75.1
17	Br ₂	0.25	0.71	1.94	5.75	10.4	14.1	12.8	0.1	24.4	0.0	0.7	74.8
18	C ₃ H ₇ Cl ₂	0.25	0.51	1.49	4.35	14.5	18.4	16.9	0.0	23.7	0.0	0.4	75.9
19	Br ₂	0.5	0.49	1.33	3.95	15.1	20.6	18.6	0.0	24.2	0.0	0.5	75.3
20	C ₃ H ₇ Cl ₂	0.25	0.52	1.49	4.05	14.2	18.4	18.1	0.0	22.6	0.0	0.7	76.7
21	Br ₂	0.25	0.50	1.23	3.13	14.8	22.3	23.5	0.0	23.4	0.0	0.2	76.4
22	C ₃ H ₇ Cl ₂	1.0	7.47	27.17	72.75				0.1	23.0	0.1	1.0	75.8
23	None ¹	0.25	6.09	19.83	54.32	1.2	1.4	1.3	0.1	23.2	0.2	1.8	74.7
24	C ₃ H ₇ Cl ₂	0.25	1.09	2.79	7.02	6.9	9.7	10.4	0.1	23.7	0.1	0.9	75.2
25	Br ₂	0.5	0.72	1.99	5.07	10.4	13.7	14.3	0.0	25.9	0.0	0.3	73.8
26	C ₃ H ₇ Cl ₂	1.0	0.51	1.52	3.97	14.6	17.9	18.3	0.0	24.5	0.1	0.3	75.1

¹ Average of 2 or more runs.

Runs 5-12, CHCl₃ is chloroform.

Runs 14-21, C₃H₇Cl₂ is propylene dichloride.

Runs 23-26, C₃H₇Cl₃ is 1,2,3-trichloropropane.

uated vessel until the pressure in the vessel approximated atmospheric pressure. The reaction was permitted to proceed in the closed reaction vessel while the temperature was maintained at 500° C. until a pressure increase of 25 percent above the initial pressure was observed, whereupon the reaction gases were rapidly removed from the reactor and analyzed. In some runs where the acceleration in reaction was extremely rapid the pressure increase somewhat exceeded 25 percent before the reaction was terminated.

A number of runs were also made without any sensitizer and other runs were made using only a poly-chlorinated paraffin and only bromine as sensitizer.

In each of the runs the initial pressure was calculated, a pressure reading was made 0.5 minute after the run began, thereafter pressure readings were made at intervals of 1 minute from the beginning of the run until 6 minutes thereafter, from that point readings were made at 2 minute intervals until 20 minutes after the run began, and when it was necessary to run in excess of 20 minutes to obtain 25% pressure increase, readings were taken at 5 minute intervals during the period from 20 to 40 minutes and at 10 minute intervals beyond 40 minutes until

The sensitization factors recorded in the table are obtained by dividing the time required for a particular pressure increase without sensitizer by the time required for the same pressure increase with sensitizer.

By referring to the table, it is evident that chloroform, propylene dichloride and 1,2,3-trichloropropane alone sensitize the cracking of butane to some extent. The table also shows that bromine is a more active sensitizer than the chlorinated hydrocarbons. However, by using a combination of bromine with a poly-chlorinated hydrocarbon, the sensitizing effect is much greater than can be anticipated from the additive effect of the chlorinated hydrocarbons and bromine when used alone. In fact, the mixture of a small amount of a poly-chlorinated hydrocarbon with bromine will increase the sensitizing effect of the bromine far above the value which an amount of bromine equivalent to the combined amounts of bromine and chlorinated hydrocarbon gives. For example, one-half percent of bromine (run 3) gave a sensitization factor for 25 percent pressure increase of 6.2; whereas, .25 percent of bromine mixed with .25 percent of chloroform (run 8) gave a sensitization factor of 10.5. Similarly, 0.25 percent of

5

bromine mixed with 0.25 percent of propylene dichloride (run 17) gave a sensitization factor for 25 percent pressure increase of 12.8, as against 6.2 for one-half percent of bromine. A mixture of bromine and 1,2,3-trichloropropane in amounts of .25 percent each (run 24) gave a sensitization factor of 10.4 as against 6.2 for one-half percent of bromine. Thus, it is apparent that the poly-chlorinated hydrocarbons which are poorer sensitizers than bromine when used alone, enhance the sensitization effect of bromine when mixed therewith to an extent considerably above that of an equivalent amount of bromine alone.

In order to further demonstrate the remarkable enhancement in sensitization obtained by using a mixture of bromine and poly-chlorinated aliphatic hydrocarbon, curves were plotted for several runs with time in minutes as abscissae and pressure increase as ordinates.

Referring to Figure 1, curve 1 is a curve for the average of several blank runs, data for which is given in the table under run No. 1. Curve 2 is the curve based on data recorded for run No. 2. Curve 3 is the curve for data recorded in run No. 5. Curve 4 represents the hypothetical or additive results which would be expected from using a mixture of .25 mole percent of chloroform and .25 percent of bromine as sensitizer, and is obtained by adding the pressure increase without sensitizer at a selected time (from curve 1), the pressure increase over that of the blank run caused at the same time by the presence of chloroform alone (curve 3 minus curve 1) and the pressure increase caused at the same time by the presence of bromine alone (curve 2 minus curve 1), and plotting on the graph the figures obtained for a sufficient number of different time periods to be able to draw a curve through the points. As an example, referring to Figure 1, at a time approximately 7 minutes after the beginning of the run, pressure increase without any sensitizer (obtained from curve 1) is 4.8 percent. At the same time the pressure increase in the run sensitized by chloroform alone is 7.5 percent (obtained from curve 3) and the pressure increase in the run sensitized by bromine alone is 14.7 (obtained from curve 2). Pressure increase due to the presence of chloroform is therefore, 7.5 minus 4.8 or 2.7 percent. Pressure increase due to the presence of bromine is, therefore, 14.7 minus 4.8 or 9.9 percent. The pressure increase that might be expected from the combination of chloroform and bromine at a time seven minutes after the run begins is the sum of the pressure increase at the same time without sensitizer and the pressure increases caused by each of the sensitizers or 4.8 plus 2.7 plus 9.9 or 17.4 percent. By referring to curve 4, it will be seen that 7 minutes after the run begins the pressure increase is approximately 17.4 percent.

Curve 5 represents the actual experimental data obtained in the run using the combination sensitizer. At a period 7 minutes after the run began, it will be seen that the actual pressure increase was 25 percent as against an expected increase of 17.4 percent.

Considering the effect in another way, in order to get a pressure increase of approximately 25 percent, it was necessary to permit the reaction to continue for a period of 7 minutes, whereas from the additive results of the individual sensitizers, this pressure increase would not have been

6

expected until the reaction had continued for approximately 13 minutes.

Referring now to Figure 2, the curves are similar to those in Figure 1, with the exception that the data are recorded in connection with a mixture of bromine and propylene dichloride. As is apparent from the curves, the sensitization factor of a mixture of bromine and propylene dichloride in amounts of .25 percent each is even greater than that of the mixture of bromine and chloroform. The same is true for the mixture of bromine and 1,2,3-trichloropropane, results of which are shown graphically in Figure 3.

In order to further demonstrate the effectiveness of mixtures of bromine and poly-chlorinated aliphatic hydrocarbons in the sensitization of hydrocarbons, Pennsylvania gas oil was subjected to cracking in a continuous laboratory cracking apparatus at 525° C. under approximately atmospheric pressure at a through-put of approximately 165 grams of charging stock per hour. In a run in which no sensitizer was used, using a once-through operation, 10.7 percent by weight of gas oil was converted to liquid hydrocarbon boiling below 400° F. and 6.2 percent by weight was converted to gas. Under similar conditions using a mixture of 0.1 percent by weight of bromine and 0.5 percent by weight of propylene dichloride, 14.8 percent by weight of the gas oil was converted to liquid hydrocarbon boiling below 400° F. and 9.1 percent by weight of the gas oil was converted to gas. Under the same conditions a mixture of 0.1 percent by weight of bromine and 0.5 percent by weight of 1,2,3-trichloropropane converted 15.6 percent by weight of the gas oil to liquid hydrocarbon boiling below 400° F. and 9.7 percent by weight of the gas oil to gas.

From the analyses of the reaction products appearing in the table, the reaction is predominantly one of splitting the carbon to carbon bond as shown by the relatively large amount of unsaturated hydrocarbons formed and the small amount of hydrogen formed in the reaction. The nature of the reaction products obtained is essentially the same regardless of whether or not sensitizer is used.

The invention is useful in connection with known types of mineral oil thermal cracking without catalyst. It is also useful in catalytic cracking operations wherein a known solid comminuted catalyst, such as natural or synthetic alumina-silica compositions, is used. The invention may also be used in connection with cracking of gases to make unsaturated hydrocarbons, such as cracking of propane to ethylene, cracking of butane to ethylene and propylene or the cracking of liquid hydrocarbons to olefins or diolefins such as butadiene.

Wherever the terms poly-chlorinated aliphatic hydrocarbon or poly-chlorinated paraffin are used, they are intended to include compounds in which all hydrogen has been replaced by chlorine atoms, as for example, carbon tetrachloride, hexachloroethane and octachloropropane.

This application is a continuation-in-part of our application Serial No. 521,596, filed February 9, 1944, entitled Hydrocarbon conversion.

It is claimed:

1. The method of cracking hydrocarbons comprising subjecting hydrocarbons to suitable cracking conditions of time, temperature and pressure in the presence of a small amount of a halogen selected from the group consisting of bromine and iodine and a small amount of a poly-chlorinated aliphatic hydrocarbon.

2. Method in accordance with claim 1 in which the halogen is bromine and the poly-chlorinated aliphatic hydrocarbon is a poly-chlorinated paraffinic hydrocarbon.

3. Method in accordance with claim 1 in which the amount of halogen present is at least .005 mole percent and the amount of poly-chlorinated aliphatic hydrocarbon is at least .05 mole percent.

4. Method in accordance with claim 1 in which the minimum amount of halogen and poly-chlorinated aliphatic hydrocarbon present is about .005 and .05 mole percent, respectively, and the maximum combined amount of the two is about 5 mole percent.

5. The method of cracking hydrocarbons containing at least 3 carbon atoms per molecule comprising subjecting said hydrocarbons to temperature of approximately 375° to 750° C. in the presence of a small amount of bromine and a poly-chlorinated aliphatic hydrocarbon.

6. Method in accordance with claim 5 in which the poly-chlorinated aliphatic hydrocarbon is 1,2,3-trichloropropane.

7. Method in accordance with claim 5 in which the poly-chlorinated aliphatic hydrocarbon is chloroform.

8. Method in accordance with claim 5 in which the poly-chlorinated aliphatic hydrocarbon is propylene dichloride.

9. Method in accordance with claim 5 in which the bromine is present in an amount of approximately .03 to 2 mole percent and the poly-chlorinated hydrocarbon is present in amounts of approximately 0.25 to 2 mole percent.

10. The method of cracking C₄ hydrocarbons comprising subjecting said hydrocarbons to temperatures of the order of 500°-750° C. in the presence of small amounts of bromine and a poly-chlorinated aliphatic hydrocarbon.

11. Method in accordance with claim 10 in which the amount of bromine is not less than .005 mole percent and the amount of poly-chlo-

rated aliphatic hydrocarbon is not less than .05 mole percent and the maximum combined amount of the two is about 5 mole percent.

12. Method in accordance with claim 5 in which the hydrocarbons are normally liquid hydrocarbons.

13. The method of cracking hydrocarbon oil comprising subjecting said oil to temperatures within the range of approximately 375 to 750° C. in the presence of a mixture of bromine and a poly-chlorinated aliphatic hydrocarbon, the bromine being present in amount not less than .03 mole per cent and the polychlorinated aliphatic hydrocarbon being present in an amount not less than 0.25 mole per cent, the combined amount of the bromine and polychlorinated aliphatic hydrocarbon being less than 1% by weight of the oil.

14. Method in accordance with claim 13 in which the amount of bromine is about 0.1% by weight of the oil and the amount of polychlorinated aliphatic hydrocarbon is about 0.5% by weight of the oil.

15. Method in accordance with claim 13 in which the polychlorinated aliphatic hydrocarbon is 1,2,3-trichloropropane.

16. Method in accordance with claim 13 in which the polychlorinated aliphatic hydrocarbon is propylene chloride.

HILLIS O. FOLKINS.
CARLISLE M. THACKER.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,221,952	Pier et al. _____	Nov. 19, 1940
1,925,421	Van Peski _____	Sept. 5, 1933
2,122,903	Winkler _____	July 5, 1938
2,063,133	Tropsch _____	Dec. 8, 1936
2,213,345	Marschner _____	Sept. 3, 1940