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METHOD FOR CONVERTING HYDROCARBONS

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This invention relates to the conversion of hydrocarbons and more particularly to the cracking of hydrocarbons containing three or more carbon atoms per molecule to hydrocarbons of lower boiling point or to hydrocarbons of higher degree of unsaturation.

This application is a continuation-in-part of application Serial No. 520,536, filed January 31, 1944, entitled Method for converting hydrocarbons.

We have discovered that esters, and particularly esters of aliphatic alcohols and fatty acids, in which one or more bromine atoms are substituted for one or more hydrogen atoms, are effective as sensitizers in accelerating the decomposition of hydrocarbons when the brominated ester is present in the reaction zone in small amounts. Examples of brominated esters which may be used in accordance with our invention are: methyl bromoacetate, ethyl bromoacetate, β-bromoethyl acetate, ethyl dibromoacetate, bromomethyl acetate, ethyl-α-bromo-n-butyrate, ethyl-α-bromo-iso-butyrate, ethyl-α-bromopropionate, ethyl-β-bromopropionate, methyl-α, β-dibromopropionate, methyl-β-bromopropionate, β-bromo-n-propyl acetate. Esters of inorganic acids, such as di-octyl acid pyrophosphate, in which bromine is substituted for one or more hydrogen atoms, may be used. Compounds containing more than one bromine atom are preferred over compounds which contain only one bromine atom since the poly-brominated esters are more active. The brominated ester may be added to the charging stock before charging it to the heating and conversion zone or it may be injected directly into the conversion zone. Brominated esters are effective as cracking accelerators or sensitizers in amounts equivalent to as low as 0.001% by weight of bromine based on the charging stock. Amounts between 0.005 and 3% by weight of sensitizer may be used effectively, although larger amounts may be used if desired. We prefer not to use amounts in excess of 3% by weight since amounts below 3% will provide satisfactory acceleration of the cracking reaction without causing the presence of objectionable amounts of brominated compounds in the resulting product. Our experiments indicate that an amount of brominated ester of 1% or less will give a large increase in acceleration of the cracking reaction.

Where the invention is used for cracking hydrocarbon liquids of higher boiling range, as for example gas oil, to gasoline or gasoline boiling hydrocarbons, or used to reform naphtha to gasoline of higher octane rating, and particularly

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where cracking is carried out under superatmospheric pressure, we prefer to use an amount of the brominated ester equivalent to not more than 0.1% by weight of bromine. Brominated esters in amounts equivalent to 0.001 to 0.1% of bromine by weight give a greater increase in yield of gasoline boiling hydrocarbons per unit weight of sensitizer than is obtained with larger amounts. In other words, although the yield of cracked gasoline increases up to a certain point with increase in the amount of sensitizer used, the increase is not sufficiently great to justify the use of larger amounts.

Sensitizers, in accordance with our invention, are useful in thermal cracking processes at either subatmospheric, atmospheric, or super-atmospheric pressure. Cracking of hydrocarbon oils and/or gases may be carried out with brominated esters at temperatures of approximately 650 to 2000° F., depending upon the nature of the charging stock and the type of product desired. Where cracking of hydrocarbon oils to gasoline is practiced, the temperature may range from approximately 650 to 1200° F. When gases or oils are cracked to aromatic hydrocarbons, temperatures of approximately 1000 to 1500° F. may be resorted to. When it is desired to crack hydrocarbon oils or gases to butadiene, temperatures of the order of 1300 to 1600° F. may be used. Where cracking of oils or gases to lower molecular weight gaseous hydrocarbons is practiced, such as, cracking of propane to ethylene, temperatures of 1200 to 2000° F. may be used.

In carrying out our invention, we prefer to use brominated esters which are volatile at reaction temperatures. Where brominated esters are used which are unstable at temperatures at or below cracking temperature, it may be desirable to inject the sensitizer directly into the reaction zone in order to prevent decomposition thereof before the cracking stock with which it is mixed reaches cracking temperature.

In order to demonstrate the effectiveness of brominated esters as cracking sensitizers, a number of runs was made in a Pyrex glass reaction vessel at 977° F. using butane of 99% purity as charging stock. Each run was made by heating the reaction vessel to 977° F. and evacuating the vessel by means of a vacuum pump to a pressure of 0.001 millimeter of mercury. Butane when mixed with the desired amount of sensitizer was then charged to the evacuated vessel until the pressure therein was approximately atmospheric.

Readings were made as to the time required to

attain a pressure increase of 5%, 12.5%, and 25%. When the pressure increase had reached 25% the reaction products were rapidly evacuated from the vessel and analyzed.

A number of runs was also made in the same manner without any sensitizers to enable a comparison to be made in the acceleration rate with and without the sensitizer. Data for the various runs are tabulated in the following table:

Table

Run No.	Initial pressure cm. Hg	Sensitizer		Time in minutes for ΔP of—			Sensitization factor for ΔP of—			Mole per cent reaction products				
		Name	Per cent	5%	12.5%	25%	5%	12.5%	25%	Acids	Unsat.	CO	H_2	Residue
1														
2														
3														
Avg.	78.55	None		2.03	7.18	19.69				0.1	22.0	0.1	1.2	76.6
4	79.50	Ethyl bromo acetate	0.25	0.50	1.90	5.60	4.1	3.8	3.5	0.1	22.5	0.4	0.9	76.1
5														
6														
7														
8														
9														
10														
Avg.	80.45	None		1.99	7.76	21.90				0.1	23.0	0.1	1.3	75.5
11	82.10	Methyl bromo acetate	0.5	0.39	1.04	2.97	5.1	7.5	7.4	0.2	24.3	0.4	1.3	73.8
12	81.90	Methyl bromo acetate	0.25	0.43	1.24	3.63	4.6	6.3	6.0	0.0	24.1	0.2	1.2	74.5
13	82.40	Methyl bromo acetate	0.25	0.52	1.40	3.97	3.8	5.5	5.5	0.2	24.0	0.2	1.2	74.4
14														
15														
16														
Avg.	81.65	None		2.11	7.89	21.91				0.1	22.0	0.1	1.6	76.2
17	82.10	Ethyl bromo actate	0.25	0.50	2.25	7.02	4.2	3.5	3.1	0.1	22.7	0.1	1.4	75.7
18	82.00	Ethyl bromo acetate	0.25	0.49	2.14	6.70	4.3	3.7	3.3	0.1	22.8	0.1	1.5	75.5
19														
20														
21														
22														
23														
24														
25														
Avg.	80.20	None		2.08	7.83	21.61				0.1	22.4	0.1	1.4	76.0
26	79.95	β-Bromo-ethyl acetate	0.5	0.66	2.68	7.83	3.2	2.9	2.8	0.0	23.0	0.0	1.3	75.7
27	81.60	β-Bromo-ethyl acetate	0.25	0.74	3.05	8.70	2.8	2.6	2.5	0.1	22.7	0.2	1.2	75.8

Sensitization factor is obtained by dividing the time required to attain a given pressure increase without sensitizer by the time required to attain the same pressure increase with sensitizer. The average of figures for non-sensitized runs appearing in the table immediately before the sensitized runs is used as a basis for determining sensitization factor.

From the table it will be seen that ethyl and methyl bromo acetate and β-bromo-ethyl-acetate accelerated the reaction to a considerable extent. Of the brominated esters appearing in the table, methyl-bromo-acetate is the most effective.

Although our invention is applicable to all known types of hydrocarbon cracking processes, catalytic and purely thermal, it is particularly adapted for use in purely thermal operations in which no solid catalyst is used. The invention may be adapted to present types of thermal cracking processes without modifying operation or apparatus in which they are conducted, except to the extent to provide for the addition of the sensitizer to the charging stock or to the reaction vessel.

We claim:

1. The method of cracking hydrocarbons which comprises subjecting said hydrocarbons to suitable cracking conditions of time, temperature and pressure in the presence of a small amount of a brominated ester.

2. Method in accordance with claim 1 in which the brominated ester contains at least two bromine atoms.

3. Method in accordance with claim 1 in which the ester is an ester of an aliphatic alcohol and fatty acid in which bromine is substituted for hydrogen.

4. The method of cracking hydrocarbons having at least three carbon atoms in the molecule to lower boiling hydrocarbons which comprises subjecting said hydrocarbons to temperatures of 650° F. to 2000° F. in the presence of a small amount of an organic acid ester in which bromine is substituted for at least one hydrogen atom.

5. Method in accordance with claim 4 in which the amount of brominated ester present in the mixture undergoing reaction is between 0.005 and 3% by weight.

6. Method in accordance with claim 4 in which the amount of brominated ester present in the mixture undergoing reaction is between .005 and 1% by weight.

7. Method in accordance with claim 4 in which the amount of brominated ester present in the mixture undergoing reaction is not in excess of 1% by weight.

8. Method in accordance with claim 4 in which the hydrocarbons comprise a large portion of propane.

9. Method in accordance with claim 4 in which the brominated ester is methyl bromoacetate.

10. Method in accordance with claim 4 in which the brominated ester is ethyl bromoacetate.

11. Method in accordance with claim 4 in which the brominated ester is β-bromoethyl acetate.

12. The method of cracking hydrocarbons having at least three carbon atoms to the molecule which consists in subjecting said hydrocarbons to thermal cracking temperature in the presence

of approximately from 0.005 to 3% by weight of a brominated ester.

13. The method of cracking hydrocarbon liquids to gasoline boiling hydrocarbons comprising subjecting said hydrocarbon liquids to suitable cracking conditions of time and temperature in the presence of sufficient brominated ester to accelerate the rate of cracking but not in excess of an amount equivalent to about 0.1% by weight of bromine.

14. Method in accordance with claim 13 in which the brominated ester is present in an amount equivalent to about 0.001 to 0.1% by weight of bromine.

15. The method of cracking hydrocarbon oil boiling above the gasoline range to hydrocarbons boiling within the gasoline range comprising subjecting said oil to temperatures of approximately 650 to 1200° F. in the presence of an amount of brominated ester sufficient to accelerate the rate of cracking but less than an amount equivalent to 0.1% by weight of bromine.

16. Method in accordance with claim 15 in which ester is a polybrominated ester.

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