

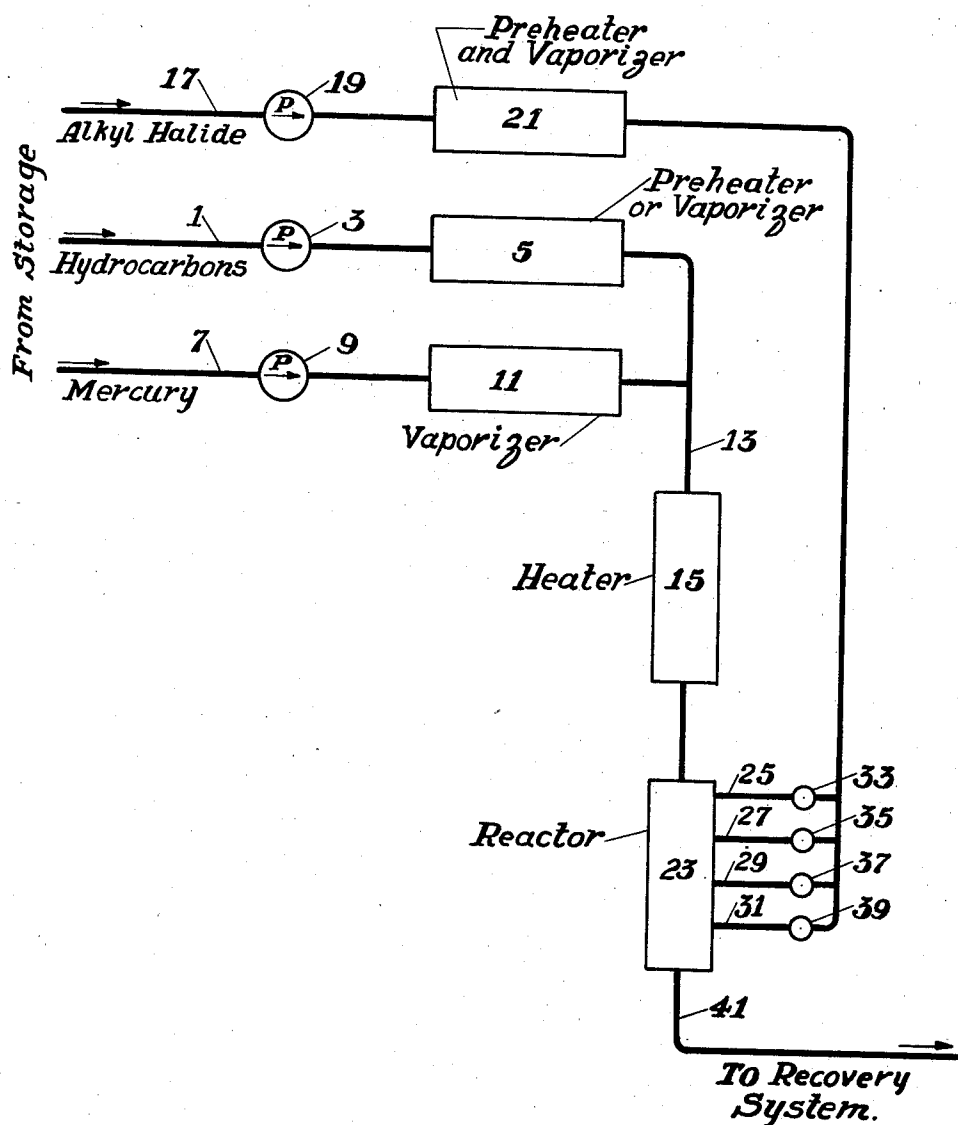
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PROCESS FOR HYDROCARBON CONVERSION

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PROCESS FOR HYDROCARBON CONVERSION

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This invention relates to a method of converting hydrocarbons to hydrocarbons of lower boiling point or to hydrocarbons containing less hydrogen in the molecule and is particularly concerned with conversion of hydrocarbons containing 3 or more carbon atoms in the molecule.

It is well known that hydrocarbons crack at elevated temperatures ranging upward from about 700° F. to produce hydrocarbons of greater unsaturation and/or hydrocarbons of lower boiling point. It is also known that the rate of cracking is proportional to the temperature.

We have discovered that at any particular cracking temperature the rate of cracking can be greatly accelerated by contacting the hydrocarbons undergoing conversion with a mixture of an aliphatic halide and mercury.

One of the objects of the invention is to provide an improved process for cracking hydrocarbons.

Another object of the invention is to provide a process for homogeneous catalysis of hydrocarbon cracking reactions.

A still further object of the invention is to provide an accelerator or sensitizer for catalyzing cracking reactions.

Other objects of the invention will become manifest from the following detailed description of the invention considered in conjunction with the accompanying drawing of which the single figure is a diagrammatic side elevational view.

Referring to the drawing, 1 indicates the feed line through which hydrocarbons are charged to the cracking system by means of pump 3. The process is designed to crack propane, butane, or any mixture of C₃ and C₄ hydrocarbons as well as higher boiling hydrocarbons such as those within the gasoline, kerosene, gas oil or residuum boiling range. It will be understood that in the event the charging stock is composed of normally gaseous hydrocarbons, these gases may be charged to the system either in the liquid or gaseous state. When charged in the gaseous state a compressor will be substituted for the pump 3.

The charging stock is pumped or forced through the preheater or vaporizer 5 where it is heated or vaporized at a temperature below but preferably close to the desired cracking temperature. The cracking temperature will vary with the nature of the charging stock and the nature of the products which it is desired to produce, but in general will range from approximately 700° F. to 1400° F. The lower boiling hydrocarbons will in general require higher temperatures than the higher boiling hydrocarbons, but it will be understood that temperatures for converting the higher boiling hydrocarbons may be just as high as those used for converting the lower boiling hydrocarbons where it is desired to make low boiling unsaturated products such as ethylene, propylene, butylene and butadiene. Even higher temperatures may be resorted to when necessary, as for example in the manufacture of acetylene. In general we prefer to keep the temperature in the preheater or vaporizer 5 below that at which rapid conversion of the hydrocarbons takes place.

Mercury is charged to the cracking system through the line 7 by means of pump 9 and through vaporizer 11 where it is heated to a temperature sufficient to vaporize the mercury. This temperature will depend on the pressure at which the cracking system is operated. The vaporized mercury is then mixed with the preheated hydrocarbons in the line 13 and the mixture charged to preheater 15 where it is heated to the desired reaction temperature. The preheater may take the form of a coil located in a suitable furnace. The amount of mercury mixed with the hydrocarbons may vary widely, but from 1/16 to 10 mole per cent of mercury based on the hydrocarbons is sufficient to produce the desired acceleration in conjunction with the aliphatic halide. Aliphatic halide is charged to the system through line 17 by means of pump 19. The aliphatic halide is preferably first preheated and vaporized in 21 so that it may be injected into the reaction zone in the form of a vapor. The temperature to which the alkyl halide is preheated will depend on the particular halide and the pressure conditions existing in the reaction zone, it being desired merely to vaporize the alkyl halide in vaporizer 21. Any aliphatic halide which may be vaporized at reaction temperature can be used, but we prefer to use those which are liquid at ordinary atmospheric temperatures, vaporize without appreciable decomposition and contain 7 or less carbon atoms in the molecule. Saturated as well as unsaturated halides may be used such as ethyl iodide, ethylene di-bromide, propyl iodide, butyl fluoride, butyl chloride, 3-bromo propyne and 3-iodo propyne. The amount of halide used may vary within wide limits but we prefer to use from 1/16 to 10 mole per cent of halide based on the hydrocarbons charged.

The mixture of mercury vapor and hydrocarbons after being heated to the desired reaction temperature in a coil or heater 15 are charged to the reactor 23, which may take the form of a

steel or refractory chamber, or of a steel coil. The reactor 23 should be of sufficient size to permit the hydrocarbons and accelerators to be subjected to reaction temperature for sufficient period of time to enable the desired reaction to take place. The period for which the hydrocarbons are subjected to reaction temperatures will in general be the same as the periods of time used in purely thermal cracking reactions, or may be somewhat less. Since the sensitizers accelerate the reaction it will be apparent that the same amount of conversion obtained in purely thermal reaction can be obtained in accordance with our invention in a shorter period or a greater percentage conversion can be obtained in the same period of time.

The aliphatic halide in the vapor state may be injected into the reactor through a series of parallel lines 25, 27, 29, and 31 controlled by valves 33, 35, 37, and 39 at different points in the reactor. It is advantageous to distribute the halide throughout the reactor in order to insure that halide is present during substantially all stages of the reaction.

The reaction products are withdrawn from the reactor through the line 41 and are sent to the recovery system to separate the various products therefrom. The recovery of the various reaction products forms no part of this invention and therefore will not be illustrated or described. It may, however, correspond to any known or conventional type of recovery system for recovering products from conversion of hydrocarbon oils and gases.

In order to demonstrate the invention a number of runs were made in laboratory apparatus using any empty stainless steel tube of 1½" inside diameter and having a volume of about 100 ccs., as the reactor. The results on these runs are given in the following table:

TABLE 1
Decomposition of normal butane
[Total pressure on system—750 mm. (approx.)]

	Run No.					
	1	2	3	4	5	6
Reactor temperature, °C.:						
Top.....	572	592	497	599	600	598
Middle.....	575	600	600	600	600	600
Bottom.....	574	599	598	597	599	597
Total gas flow.....ft. ³ /hr.	0.994	0.998	1.000	0.994	1.020	0.995
n-C ₄ H ₁₀ flow.....ft. ³ /hr.	0.994	0.998	1.000	0.986	0.989	0.979
Pressure Hg.....millimeters.	0	0	0	4	0	4
Pressure C ₂ H ₅ I.....do.	0	0	0	0	7.5	7.5
Vol. exit gas + vol. inlet C ₂ H ₅ I.....	1.014	1.052	1.060	1.064	1.172	1.163
Yield ft. ³ unsats. per ft. ³ C ₄ H ₁₀ charged.....	0.035	0.067	0.063	0.065	0.089	0.165
Exit gas, mol percent:						
H ₂	0.9	0.8	0.9	0.6	1.3	0.9
Unsats.....	3.4	6.4	5.9	6.1	7.6	14.2

In all the runs normal butane was used as the charging stock. In those runs where mercury and/or ethyl iodide were used as sensitizers the quantity of mercury was used slightly in excess of ½ mole per cent and the quantity of ethyl iodide was approximately 1 mole per cent. The extent of cracking which occurred is indicated by the yield of unsaturates per cubic foot of butane charged.

Run #1 was a blank run made at a temperature of approximately 575° C. Because of the small amount of conversion which occurred at this temperature blank runs #2 and #3 were made at temperatures of approximately 600° C. and the yield of 0.067 and 0.063 check fairly closely. Run #4 was then made with mercury at 600° C. and

the yield of unsaturates was substantially the same as that obtained in the blank runs.

A run was then made using ethyl iodide as sensitizer at 600° C. and the yield of .089 unsaturates indicates that the ethyl iodide sensitized or accelerated the reaction to the extent of 40%. Run #6 was then made under the same conditions using the combination of ethyl iodide and mercury as sensitizer and a yield of 0.165 cu. feet of unsaturates per cubic foot of butane was obtained, thus indicating an acceleration of the reaction of over 150 per cent.

Thus, it will be seen that the mixture of mercury and ethyl iodide greatly accelerated the cracking reaction. It will also be seen that although a small amount of dehydrogenation occurred the reaction was predominantly one of splitting of the butane molecule to form lower boiling unsaturated hydrocarbons.

Although we have demonstrated one way in which our invention may be carried out it should be understood that the manner and order of mixing the sensitizers with the hydrocarbons undergoing reaction and the particular type of apparatus used may be varied. It should be also understood that a mixture of aliphatic halides may be used instead of a single halide.

The pressure under which the reaction is conducted may be sub-atmospheric, atmospheric or super-atmospheric. For example, where the purpose of the conversion reaction is to prepare acetylenes or diolefins it may be desirable to use sub-atmospheric pressures. Where high boiling hydrocarbons are cracked to form gasoline it may be desirable to use high pressures of the order of those commonly used in purely thermal cracking processes. The conditions of both temperature and pressure will in general correspond to the conditions used in purely thermal operations with respect to the same type of operations.

Our invention is also useful in connection with catalytic cracking processes in which a stationary or moving solid catalyst is used, as for example comminuted co-precipitated alumina-silica and fuller's earth. The mercury-aliphatic halide mixture accelerates solid catalyst reactions in the same manner that it will accelerate conversion of the hydrocarbons in the absence of the solid catalyst.

Although we prefer to use aliphatic halides that vaporize without appreciable decomposition, our invention contemplates the use also of those halides which do decompose appreciably at vaporization temperature but when using such halides we prefer to inject them directly into the reactor 23 without prior vaporization.

We claim:

1. The method of cracking hydrocarbons of 3 or more carbon atoms per molecule at temperatures ranging from 700 to 1400° F. which comprises contacting the hydrocarbons at cracking temperature with a small amount of mercury and a volatile aliphatic halide under pressure conditions such as to maintain the mercury and aliphatic halide in vapor state.

2. The method of cracking hydrocarbons of 3 or more carbon atoms per molecule which comprises subjecting said hydrocarbons to temperatures sufficiently high to produce cracking in the absence of a solid catalyst, in the presence of a small amount of mercury vapor and aliphatic halide vapor.

3. The method of cracking in accordance with claim 2 in which the aliphatic halide is ethyl iodide.

4. The method of cracking hydrocarbons of 3 or more carbon atoms per molecule which comprises mixing said hydrocarbons with a small amount of vaporized mercury, heating the mixture to reaction temperature and then mixing the mixture with a small amount of aliphatic halide.

5. Method in accordance with claim 4 in which the aliphatic halide is injected into the heated mixture at spaced points in the reaction zone.

6. The method of cracking hydrocarbons which

comprises subjecting said hydrocarbons to cracking in the presence of mercury and an aliphatic halide under conditions of temperature and pressure at which mercury and the aliphatic halide are in the vaporized state.

7. Method in accordance with claim 6 in which the amount of mercury and alkyl halide in the reaction mixture is from 0.1 to 10 mole percent of each based on the hydrocarbons in the mixture.

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