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CONVERSION OF HYDROCARBONS

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This invention relates to conversion of hydrocarbons and particularly to the conversion of higher boiling hydrocarbons into lower boiling hydrocarbons or the conversion of hydrocarbons into hydrocarbons containing less hydrogen in the molecule.

One of the objects of this invention is to provide an improved method for converting hydrocarbons into lower boiling hydrocarbons.

Another object of the invention is to provide catalysts or sensitizers which can be used in conventional types of cracking processes to accelerate the rate of cracking or to make possible cracking of hydrocarbons at lower temperatures.

Other objects of the invention will become apparent from the following detailed description.

In accordance with our invention, the hydrocarbon to be converted is passed through a reaction zone together with a small amount of an aliphatic organic compound containing a member of the halogen group of elements and a member of the oxygen family. We have found that aliphatic hydrocarbons containing both halogen and oxygen, sulfur, selenium or tellurium substituted in the molecule have a marked effect in accelerating cracking of hydrocarbon oils and gases into lower boiling hydrocarbons and into more unsaturated hydrocarbons. Halogenated derivatives of the following general groups of compounds are effective: alcohols, aldehydes, acids, ethers, ketones and esters. The halogen may be substituted for hydrogen in one or more alkyl or other radicals although from our experience we prefer those compounds in which halogen is substituted for one or more hydrogen atoms of an alkyl radical. For purposes of brevity the term oxy-halogenated will hereinafter be used to mean compounds containing halogen and one or more members of the oxygen family, viz., oxygen, sulfur, selenium and tellurium.

As specific examples of compounds which we have found will accelerate the cracking of hydrocarbons are ethylene bromohydrin, ethylene chlorohydrin, chloral, dichloracetylchloride, chloromethyl ether and ethyl chloracetate.

In carrying out our invention, the hydrocarbons undergoing reaction should contain in admixture therewith from 0.1 to 5 mol percent of the oxy-halogenated aliphatic compound, although we prefer to use from .25 to 3 mol percent. Higher or lower amounts of sensitizer may be used but within the range above specified the increase in reaction rate is very marked and formation of undesirable amounts of halogen and/or oxygen reaction products is avoided.

Although oxy-halogenated compounds in which chlorine is substituted for any element or radical in the molecule are effective, we have found that bromine-substituted compounds are much more effective than chlorine substituted compounds.

Our invention may be carried out in conventional cracking apparatus either of the straight thermal or catalytic type. The sensitizer may be mixed with the hydrocarbon oil, vapor or gas undergoing conversion prior to charging it to the reaction zone, or the sensitizer may be injected directly into the reaction zone. Although we prefer to use sensitizers which are in the same physical state as the hydrocarbons at reaction temperature, compounds may be used which exist in a different physical state from the hydrocarbons at reaction temperature. The sensitizer, if soluble in the hydrocarbons undergoing conversion, may be dissolved therein prior to passage through the reaction zone, or may be dissolved in a small portion of the hydrocarbons undergoing reaction and fed into the main stream of hydrocarbons in desired proportions. If the sensitizer is insoluble in the hydrocarbon undergoing reaction, a slurry of the sensitizer in a portion of the hydrocarbon oil may be prepared and fed in desirable proportion into the main stream of oil. Where it is desired to crack gases or oil in vapor phase, a sensitizer is preferably selected which vaporizes readily and can be mixed with the vapors undergoing conversion. We prefer to introduce the sensitizer into the mixture undergoing reaction in such manner that decomposition of the sensitizer does not occur until it is in contact with the hydrocarbons undergoing decomposition at reaction temperature. One method of doing this is to flash inject the sensitizer into the reaction chamber without appreciably preheating it.

Cracking with sensitizers in accordance with our invention may be carried out under subatmospheric, atmospheric or super-atmospheric pressure and at temperatures from the lowest temperatures at which cracking will occur to temperatures of approximately 2000° F., depending upon the type of product of hydrocarbon oil is duce. Where cracking of hydrocarbon oil is conducted for the purpose of making lighter oil, such as gasoline, temperatures ranging from approximately 650° to 1200° F. may be used. Where cracking of hydrocarbon oils or gases for the

purpose of making aromatic hydrocarbons is practiced, temperatures of approximately 1000 to 1500° F. may be used. Where it is desired to produce butadiene from hydrocarbon oils, temperatures from the vicinity of 1300 to 1600° F. may be used, and where it is desired to crack hydrocarbon oils to gases, hydrocarbon temperatures of from approximately 1500° to 2000° F. may be used.

In order to demonstrate the invention, a series of runs were made using normal butane as charging stock. The runs were all made at a temperature of 525° C. in laboratory apparatus constructed of Pyrex glass. Before each run, the reaction vessel was evacuated to 0.001 mm. or less of mercury while maintaining the temperature at the desired reaction level. Normal butane admixed with the desired amount of sensitizer was then charged to the reaction chamber until the pressure therein was approximately atmospheric pressure. Pressure increases in the reaction chamber were noted at definite intervals ranging from 0.5 to 2 minutes until a pressure increase of 25% had been attained. At the time the pressure increase reached 25%, the reaction chamber was quickly evacuated and the reaction products were analyzed for carbon dioxide or acidic constituents by absorption in caustic potash solution, for unsaturates by absorption in fuming sulfuric acid, for hydrogen by contraction in volume due to water formation, and for carbon monoxide by oxidation followed by absorption in caustic potash solution.

In addition to the runs made with various sensitizers a number of blank runs were made in which only normal butane without sensitizer was charged to the reaction vessel.

Table I contains, in tabulated form, the results obtained on the various runs made. The blank runs in each case represent an average of at least two runs made shortly before the runs with the particular sensitizer.

TABLE I

Run No.	Sensitizer	Mol per cent sensitizer	Time in minutes required for pressure increase of—			Sensitization factors for ΔP of—		
			5%	12.5%	25%	5%	12.5%	25%
Blank-1			2.1	6.9	18.7			
1 A	dichloroacetylchloride	.25	1.0	4.3	13.1	2.2	1.6	1.4
1 B	do	.50	0.7	3.3	10.5	3.2	2.1	1.8
1 C	do	1.00	0.4	1.7	6.8	5.9	4.1	2.8
Blank-2			2.1	7.0	19.3			
2 A	Chloral	.25	0.4	2.3	10.3	4.8	3.1	1.9
2 B	do	.50	0.4	1.4	6.7	5.9	5.1	2.9
2 C	do	1.00	0.3	0.8	3.7	7.3	8.9	5.3
Blank-3			1.63	6.22	17.73			
3 A	Chloromethyl ether	.25	0.3	2.3	12.12	5.43	2.70	1.46
3 B	do	.50	0.19	0.47	6.28	8.6	13.2	2.8
3 C	do	1.00	0.16	0.40	3.45	10.2	15.6	5.1
3 D	Ethyl chloroacetate	.25	1.7	6.0	17.02	.96	1.04	1.04
3 E	do	.50	.85	4.29	13.42	1.9	1.5	1.3
Blank-4			2.1	7.1	19.6			
4 A	Ethylene chlorohydrin	.25	1.5	5.6	15.8	1.4	1.3	1.2
4 B	do	.50	1.5	5.6	16.1	1.4	1.3	1.2
Blank-5			1.9	6.6	17.9			
5 A	Ethylene bromohydrin	.25	0.7	2.4	6.9	2.6	2.7	2.6
5 B	do	.50	0.9	2.6	6.9	2.2	2.5	2.6

The sensitization factor for pressure changes of 5%, 12.5% and 25% pressure increases are obtained by dividing the time required for the particular pressure increase on the blank run by time required for the same pressure increase with sensitizer. The sensitization factor is, therefore, a direct indication of the rate of acceleration of the reaction caused by the sensitizer. As shown in the table, with a mixture containing as little as .25 mol % of sensitizer, the reaction was accelerated to a marked extent. In the case of ethylene bromohydrin, the reaction was accelerated 260%. The highest rate of acceleration shown on the table was attained with 1% of chloromethyl ether. This sensitizer increased the speed of reaction 1560% for 12.5% pressure increase. However, ethylene chlorohydrin and ethylene bromohydrin possess an advantage over chloromethyl ether in that the sensitization factor is fairly constant for all pressure increases, that is, at all stages of the reaction, whereas chloromethyl ether reaches a maximum and drops off rapidly.

The reaction products formed during the various runs are fairly uniform regardless whether or not a sensitizer is used.

Table II is a tabulation of the reaction products obtained by analysis of the reaction mixture from the various runs tabulated in Table I.

TABLE II

Analysis of reaction products

Run No.	Mol per cent CO_2	Mol per cent unsaturates	Mol per cent CO	Mol per cent H_2	Mol per cent residue
Blank-1	0.0	22.5	0.1	0.6	76.8
1A	0.0	22.9	0.1	1.2	75.8
1B	0.1	22.4	0.1	0.6	76.8
1C	0.1	21.6	0.2	0.5	77.6
Blank-2	0.0	22.6	0.3	0.9	76.2
2A	0.1	24.4	1.2	0.7	73.6
2B	0.1	22.5	0.4	0.9	76.1
2C	0.0	24.1	Sample lost		
Blank-3	0.1	21.7	0.3	1.0	76.9
3A	0.0	22.8	0.1	0.6	76.5
3B	0.4	21.8	0.2	0.8	76.8
3C	0.1	21.6	0.0	0.6	77.7
3D	0.0	22.9	0.0	1.5	75.6
3E	0.1	20.9	0.0	0.6	78.4
Blank-4	0.0	22.2	0.4	0.5	76.9
4A	0.0	21.0	0.2	0.7	78.1
4B	0.2	22.0	0.2	0.8	76.8
Blank-5	0.0	22.4	0.1	0.7	76.8
5A	0.0	22.6	0.1	0.6	76.7
5B	0.3	22.1	0.0	0.5	77.1

Our invention is applicable to improvement of various types of thermal cracking operations now in commercial use and also of catalytic cracking processes of known commercial types. Thus it is possible to improve present commercial cracking operations without the necessity of changing the process and apparatus except to make provision for charging a small amount of sensitizer to the operation.

We claim:

1. The method of cracking hydrocarbons which comprises heating the hydrocarbons to reaction temperature and causing the hydrocarbons to re-

act in the presence of a small amount of a non-metal-containing oxyhalogenated aliphatic organic compound.

2. The method in accordance with claim 1 in which the oxyhalogenated aliphatic organic compound is selected from the group consisting of halogenated alcohols, ketones, ethers, acids, aldehydes and esters.

3. The method in accordance with claim 1 in which the oxyhalogenated aliphatic organic compound is a halogenated ether.

4. The method in accordance with claim 1 in which the oxyhalogenated aliphatic organic compound is chloromethyl ether.

5. The method in accordance with claim 1 in which the oxyhalogenated aliphatic organic compound is a halogenated aldehyde.

6. The method in accordance with claim 1 in which the oxyhalogenated aliphatic organic compound is chloral.

7. The method in accordance with claim 1 in which the oxyhalogenated aliphatic organic compound is an alkylene halohydrin.

8. The method in accordance with claim 1 in which the oxyhalogenated aliphatic organic compound is ethylene bromohydrin.

9. The method in accordance with claim 1 in which the oxyhalogenated aliphatic organic compound is present in the reaction mixture in approximately 0.1 to 5 mol percent of the mixture.

10. The method in accordance with claim 1 in which the oxyhalogenated aliphatic organic compound is present in the reaction mixture in substantial amount but not more than about 3 mol percent of the mixture.

11. The method of cracking hydrocarbons which comprises heating said hydrocarbon to temperatures of approximately 650° to 2000° F. and causing the heated hydrocarbons to crack in the presence of from approximately 0.1 to 5 mol percent of a sensitizer selected from the group of non-metal-containing oxyhalogenated aliphatic hydrocarbons.

12. Method in accordance with claim 11 in which the sensitizer is chloromethyl ether.

13. Method in accordance with claim 11 in which the sensitizer is chloral.

14. Method in accordance with claim 11 in which the sensitizer is ethylene bromohydrin.

15. Method in accordance with claim 11 in which the sensitizer is selected from the group consisting of halogenated alcohols, ketones, ethers, acids, aldehydes and esters.

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