Patented Feb. 11, 1947

UNITED STATES PATENT OFFICE

2,415,477

CONVERSION OF HYDROCARBONS

Hillis O. Folkins, Skokie, and Carlisle M. Thacker, Highland Park, Ill., assignors to The Pure Oil Company, Chicago, Ill., a corporation of Ohio

No Drawing. Application December 26, 1942, Serial No. 470,304

1 Claim. (Cl. 260—683)

1

This invention relates to a method for converting higher boiling hydrocarbons into lower boiling hydrocarbons and to a method of producing unsaturated hydrocarbons from saturated hydrocarbons.

An object of the invention is to convert higher boiling hydrocarbons into lower boiling hydrocarbons.

Another object of the invention is to provide a method of accelerating the rate of conversion of higher boiling into lower boiling hydrocarbons.

A still further object of the invention is to provide a method for preparing unsaturated hydrocarbons from saturated hydrocarbons.

A further object of the invention is to accelerate the cracking of saturated to unsaturated hydrocarbons.

Still another object of the invention is to provide a method of accelerating cracking of hydrocarbons under known thermal conditions and in present types of cracking apparatus.

Other objects and advantages inherent in the invention will become apparent from the following description.

We have discovered that thermal conversion of hydrocarbons into lower boiling hydrocarbons and/or into unsaturated hydrocarbons can be accelerated by introducing into the hydrocarbons undergoing conversion a small amount of sulfur, hydrogen sulfide, and/or organic sulfur compounds, preferably mercaptans, sulfides, disulfides and other alkyl sulfur compounds.

The particular compound or compounds selected as sensitizers should preferably be in the same phase (liquid or vapor) as the charging stock at the temperature of reaction. As examples of sulfur compounds, which we have found useful, may be mentioned methyl, ethyl, n-propyl, isopropyl, n-butyl, iso-butyl, tertiary butyl, n-amyl and iso-amyl mercaptans; methyl, ethyl, n-propyl, allyl, methyl ethyl, methyl n-butyl and ethyl n-butyl sulfides; and methyl and ethyl disulfides.

2

For the purpose of this invention organic compounds are those having both carbon and hydrogen in the molecule.

We have found that when sulfur, hydrogen sulfide and/or organic sulfur compounds are mixed with hydrocarbons undergoing conversion in an amount of 3 molal per cent or less, a marked acceleration in the rate of cracking occurs at temperatures above 375° C. Sensitizers, in accordance with our invention, are effective at sub-atmospheric, atmospheric and super-atmospheric pressure.

In order to demonstrate the effectiveness of various compounds falling within the scope of our invention, a number of tests were made in both a Pyrex reaction vessel and in a stainless steel reaction vessel. The results of these tests are set forth in Tables I, II and III. In the great majority of tests normal butane was used as the charging material. Some of the tests were conducted with pentane as the charging stock. The tests were carried out by heating the reaction vessel to reaction temperature (either 500° or 525° C.), evacuating it, injecting into the evacuated vessel sufficient butane (or pentane), containing the desired amount of sensitizer, to produce the desired initial pressure (usually about 1 atmosphere), allowing the reaction to proceed until a pressure increase of 25% over the initial pressure was obtained, and then rapidly removing reaction gases for analysis. The time required for an increase in pressure of 5, 12.5 and 25 per cent was recorded. A number of blank runs in which no sensitizer was used were made in order to obtain a comparison with the sensitized runs. In the last column of the tables the sensitization factor is the quotient of the time required for 25 per cent pressure increase for a non-sensitized run divided by the time required for the same pressure increase in a sensitized run. In Table I the tests were all carried out at a temperature of 525° C.

TABLE I

Run No.	Charge	Sensitizer		Time in minutes required for pressure increase of—			Sensitization factor for 25% pressure increase
		Compound	Per cent	5%	12.5%	25%	
240	$N\text{-}C_4H_{10}$			2.35	7.70	20.7	
244	do	$N\text{-}C_4H_9SH$	1	1.27	3.92	10.4	2.0
245	do	do	0.5	1.53	5.04	13.65	1.5
246	do	do	0.25	1.72	5.68	15.65	1.3
248	do	$Iso\text{-}C_4H_9SH$	1	1.05	3.68	10.7	1.9
249	do	do	0.5	1.39	4.91	13.7	1.5
250	do	do	0.25	1.71	5.80	16.25	1.3
252	do			1.97	7.12	20.0	
253	do	$N\text{-}C_5H_{11}SH$	1.0	1.25	3.81	10.83	1.9
254	do	do	0.5	1.52	4.89	13.92	1.4
255	do	do	0.25	1.69	5.74	16.17	1.2
257	do	CH_3SH	1.0	1.50	3.94	9.75	2.1
258	do	do	0.5	1.53	4.77	13.03	1.5
259	do	do	0.25	1.95	6.16	16.50	1.2
261	do	C_2H_5SH	1.0	1.35	3.73	10.12	2.0
262	do	do	0.5	1.45	4.52	12.83	1.6
263	do	do	0.25	1.67	5.53	15.50	1.3
265	do	$Iso\text{-}C_5H_{11}SH$	1.0	1.40	4.23	11.46	1.8
266	do	do	0.5	1.74	5.38	14.50	1.4
267	do	do	0.25	1.96	6.32	17.06	1.2
269	do	$N\text{-}C_3H_7SH$	1.0	1.20	3.80	10.42	1.9

TABLE I—Continued

Run No.	Charge	Sensitizer		Time in minutes required for pressure increase of—			Sensitization factor for 25% pressure increase
		Compound	Per cent	5%	12.5%	25%	
271	$N\text{-}C_3H_7SH$	$Iso\text{-}C_3H_7SH$	1.0	1.12	3.70	10.6	1.9
272	do	do	0.5	1.42	4.82	14.10	1.4
273	do	do	0.25	1.80	6.16	17.1	1.2
275	do	$Ter\text{-}C_4H_9SH$	1.0	0.87	3.45	10.25	2.0
276	do	do	0.5	1.41	5.15	14.35	1.4
277	do	do	0.25	1.63	5.92	17.1	1.2
279	do	SH-conc.[1]	1.0	1.26	3.82	10.7	1.9
280	do	do	0.5	1.70	5.26	14.5	1.4
286	do			2.26	7.82	20.7	
287	do	$(CH_3)_2S$	1.0	1.08	3.28	8.5	2.4
288	do	do	0.5	1.44	4.54	12.5	1.7
289	do	do	0.25	1.51	5.13	14.6	1.4
291	do	$(C_2H_5)_2S$	1.0	0.75	2.25	6.47	3.2
292	do	do	0.5	0.96	2.90	8.78	2.4
293	do	do	0.25	1.08	3.58	11.60	1.8
295	do	$N\text{-}(C_3H_7)_2S$	0.5	1.22	3.73	11.90	1.7
296	do	do	0.25	1.10	4.00	13.15	1.6
298	do	$(C_3H_5)_2S$	1.0	1.30	4.37	12.60	1.6
299	do	do	0.5	1.66	5.65	15.6	1.3
300	do	do	0.25	1.92	6.63	18.2	1.1
302	do	$(CH_3)_2S_2$	1.0	1.41	3.61	8.97	2.3
303	do	do	0.5	1.55	4.33	11.95	1.7
304	do	do	0.25	2.15	6.15	15.70	1.3
306	do	$(C_2H_5)_2S_2$	0.25	2.48	6.92	17.75	1.1
308	do			2.20	7.40	20.3	
309	do	$CH_3\text{-}S\text{-}C_2H_5$	1.0	0.88	2.51	6.81	3.0
310	do	do	0.5	1.22	3.60	10.23	2.0
311	do	do	0.25	1.60	5.15	14.67	1.4
313	do	$CH_3\text{-}S\text{-}N\text{-}C_4H_9$	1.0	1.02	3.10	9.22	2.2
314	do	do	0.5	1.40	4.44	13.74	1.5
315	do	do	0.25	1.50	4.93	14.95	1.4
317	do	$C_2H_5\text{-}S\text{-}N\text{-}C_4H_9$	0.5	1.15	3.90	12.41	1.6
318	do	do	0.25	1.55	5.10	15.65	1.3
320	do	CS_2	1.0	2.32	7.80	21.15	1.0
321	do	do	3.0	2.36	7.75	21.0	1.0
323	do			2.28	7.64	20.8	
324	do	H_2S	1.0	1.33	4.00	10.5	2.0
325	do	do	0.5	1.52	5.00	13.75	1.5
326	do	do	0.25	1.90	6.30	17.0	1.2

[1] Mixed mercaptans extracted from sour gasoline with aqueous caustic soda solution and stripped from the caustic soda with steam.

TABLE II

Run No.	Charge	Sensitizer		Time in minutes required for pressure increase of—			Sensitization factor for 25% pressure increase
		Compound	Per cent	5%	12.5%	25%	
332[1]	$N\text{-}C_4H_{10}$			6.60	24.90	67.0	
340	do			7.4	30.0	85.0	
343	$N\text{-}C_5H_{12}$			4.33	16.44	40.8	
344	do	$(C_2H_5)_2S$	1.0	2.0	6.22	16.6	2.5
345	do	H_2S	1.0	2.67	8.0	19.7	2.1
346	$N\text{-}C_4H_{10}$	do	1.0	3.95	14.23	40.7	2.1
347	do	$(C_2H_5)_2S$	1.0	1.75	6.25	18.8	4.5
348[1]	do	do	1.0	1.50	4.85	19.6	4.6
353[1]	do	$(CH_3)_2S$	1.0	2.52	8.32	22.60	3.0
354	do	do	1.0	3.08	10.70	29.2	2.9
355	do	do	1.0	2.70	8.85	21.2	1.9

[1] Initial pressure slightly above atmospheric.

TABLE III

Gas analyses by volume

Run No.	Per cent acid constituents	Per cent C_nH_{2n}	Per cent CO	Per cent H_2	Per cent res.	Run No.	Per cent acid constituents	Per cent C_nH_{2n}	Per cent CO	Per cent H_2	Per cent res.
240	0.0	22.3	0.1	0.6	77.0	258	0.1	22.4	0.1	0.6	76.8
244	0.2	22.4	0.0	0.3	77.1	259	0.0	22.6	0.1	0.5	76.8
245	0.2	21.9	0.2	0.2	77.5	261	0.3	23.4	0.0	0.3	76.0
246	0.1	22.2	0.0	0.4	77.3	262	0.3	22.9	0.4	0.2	76.2
248	0.4	23.6	0.3	0.3	75.4	263	0.1	21.8	0.4	0.6	77.1
249	0.0	22.4	0.1	0.4	77.1	265	0.2	22.4	0.7	0.3	76.4
250	0.1	22.1	0.1	0.3	77.4	266	0.1	23.0	0.2	0.3	76.4
252	0.3	22.6	0.0	0.4	76.7	267	0.0	22.8	0.1	0.2	76.9
253	0.1	22.7	0.0	0.3	76.9	269	0.0	21.9	0.0	0.1	78.0
254	0.1	22.5	0.1	0.8	76.5	271	0.1	22.9	0.1	0.2	76.7
255	0.2	22.4	0.1	0.4	76.9	272	0.1	22.6	0.1	0.2	77.0
257	0.1	22.6	0.1	0.2	77.0	273	0.2	21.9	0.5	0.7	76.7

TABLE III—Continued

Gas analyses by volume

Run No.	Per cent acid constituents	Per cent C_nH_{2n}	Per cent CO	Per cent H_2	Per cent Res.
275	0.3	23.7	0.4	0.4	75.2
276	0.0	23.1	0.4	0.7	75.8
277	0.3	22.8	0.2	0.9	75.8
279	0.0	23.3	0.2	0.4	76.1
280	0.1	22.0	0.2	0.8	76.9
286	0.0	21.8	0.3	0.7	77.2
287	0.1	22.4	0.1	0.6	76.8
288	0.0	22.8	0.1	0.5	76.6
289	0.1	20.3	0.5	0.8	78.3
291	0.1	22.7	0.4	0.5	76.3
292	0.1	23.4	0.3	0.7	75.5
293	0.1	22.2	0.3	0.7	76.7
295	0.2	23.5	0.3	0.9	75.1
296	0.0	21.7	0.4	0.7	77.2
298	0.2	23.9	0.1	0.8	75.0
299	0.0	22.9	0.6	0.6	75.9
300	0.0	23.1	0.4	0.7	75.8
302	0.3	23.2	0.2	0.7	75.6
303	0.2	23.6	0.3	0.7	75.2
304	0.1	22.5	0.1	0.8	76.5
306	0.0	22.3	0.0	1.0	76.7
308	0.0	22.7	0.1	0.8	76.4
309	0.2	22.3	0.1	0.8	76.6
310	0.0	23.0	0.3	0.6	76.1
311	0.1	23.1	0.1	0.8	75.9
313	0.0	22.4	0.2	0.7	76.7
314	0.1	22.7	0.0	1.2	76.0
315	0.0	22.9	0.2	0.9	76.0
317	0.0	22.0	0.2	0.7	77.1
318	0.0	22.9	0.0	0.7	76.4
320	0.0	21.7	0.5	0.6	77.2
321	0.1	23.4	0.6	0.3	75.6
323	0.0	21.1	0.1	0.6	78.2
324	0.5	23.8	0.1	0.6	75.0
325	0.1	21.8	0.0	0.4	77.7
326	0.0	22.5	0.3	0.9	76.3
332	0.0	21.1	0.2	0.7	78.0
340	0.0	18.8	0.7	0.7	79.8
343	1.0	21.7	1.0	1.0	75.3
344	0.4	21.3	1.0	0.8	76.5
345	0.2	21.2	0.7	0.2	77.2
346	0.0	19.5	0.2	0.7	79.6
347	0.0	20.9	0.2	0.5	78.4
348	0.1	21.9	0.3	1.0	76.7
353	0.1	21.8	0.1	0.8	77.2
354	0.2	19.8	0.4	0.9	78.7
355	0.2	23.2	0.6	1.9	74.1

Although mercaptans, sulfides, disulfides and hydrogen sulfide all generally accelerated the rate of cracking of normal butane, as shown in Table I,

the sulfides appear to have the greatest sensitizing effect.

The runs tabulated in Table II were all performed at 500° C. and had an initial pressure of approximately 400 mm. with the exception of those runs marked with an asterisk.

Table III is a tabulation of the gas analyses by volume per cent of the gases produced in the runs tabulated in Tables I and II. The gas analyses demonstrate that the composition of the gas produced in the cracking operation is fairly uniform, regardless of whether or not a sensitizer is used. The analyses also show that a considerable portion of the butane and pentane charged in the various runs was converted to unsaturated hydrocarbons and that very little hydrogen was produced in these runs, thereby demonstrating that the cracking took place between the carbon bonds rather than between carbon and hydrogen.

In order to demonstrate the efficacy of sensitizers in accordance with our invention, when used in a continuous type process, a series of runs were made using Stoddard's solvent as a charging stock in a flow apparatus. The Stoddard's solvent had an A. P. I. gravity of 48.1, an initial boiling point of 305, and an end point of 390. The total sulfur content was .03 and the solvent contained no mercaptan sulfur. The results of these runs are recorded in Table IV. In making these runs the Stoddard's solvent was preheated in a stainless steel tube of ¼" diameter and was then charged to a stainless steel reactor having a diameter of 3" and a length of 9¼". The temperatures of the preheater and reactor were maintained by an external electric heating element.

Runs 415 and 420 are blank runs. Runs 416 and 423 were carried out with hydrogen sulfide as the sensitizer. Run 425 was carried out with methyl sulfide as the sensitizer. The sensitizer was added to the Stoddard's solvent before it was charged to the preheater coil.

TABLE IV

Run No	415	416	420	423	425
Reactor:					
Top	501	501	475	476	501
Middle	499	499	476	474	495
Temp., ° C.: Bottom	501	501	475	475	502
Preheater: Temp., ° C	325	330	301	300	329
Pres. p. s. i. gauge	500	502	500	500	500
Gal./hr. charged	1.000	0.995	0.252	0.251	1.006
Wt. per cent sensitizer	-------	0.142 H_2S	-------	0.122 H_2S	0.47 Me_2S
Liquid product per gal. charge (lbs.)	6.31	6.25	6.26	6.22	6.29
Cu. ft. gas per gal. charge	2.044	3.088	3.038	3.508	2.749
Wt. per cent liquid prod	96.9	96.2	96.4	95.7	96.7
Wt. per cent gas. prod	3.1	3.8	3.6	4.3	3.3
A. P. I. gravity of liquid	49.4	49.7	49.2	49.3	49.1
A. P. I. distillation of liquid:					
I. B. P	132	120	132	128	128
5%	243	186	217	197	224
10%	297	264	280	256	285
20%	320	310	315	305	315
30%	331	322	330	326	331
40%	338	334	337	337	337
50%	344	342	344	345	343
60%	349	347	351	352	349
70%	355	354	357	357	355
80%	362	362	365	366	361
90%	374	375	378	380	372
95%	395	398	394	404	389
E. P	424	437	445	454	428
Per cent recovered	97.0	97.0	98.0	97.8	97.5
Per cent residue	0.8	0.8	1.0	1.5	1.1
Per cent loss	2.2	2.2	1.0	0.7	1.4
A. S. T. M. octane No	42.2	43.6	49.0	51.0	47.1
Bromine No	13.0	17.2	16.3	19.1	14.0
Sulfur compounds in liquid:					
Per cent H_2S	-------	0.010	-------	0.005	None
Per cent S as RSH	-------	0.007	-------	0.009	0.019
Sulfur compounds in liquid after caustic soda wash:					
Per cent H_2S	-------	None	-------	None	None
Per cent S as RSH	-------	0.002	-------	0.004	0.005
Per cent free S	-------	None	-------	-------	None
Per cent S as R_2S_2	-------	0.001	-------	0.001	None
Per cent as R_2S	-------	0.007	-------	0.007	0.056
Per cent res. S	-------	0.009	-------	0.006	0.008

From the results tabulated in Table IV it will be seen that sensitizer produced a liquid product which had a lower initial boiling point and a higher octane number than the product prepared without a sensitizer, thereby definitely showing that higher cracking took place with the sensitizer in the same period of time than without the sensitizer. A further indication of the greater extent of cracking in the sensitized runs is the bromine number showing a larger proportion of unsaturates in the distillate made in the sensitized runs than in the non-sensitized runs.

The analyses of the liquid product for sulfur compound indicate that by a simple aqueous caustic soda wash of the distillate the amount of sulfur compounds in the distillate can be reduced to a point where they are unobjectionable.

The invention is applicable to cracking of both low boiling and high boiling hydrocarbons within the range of 375° C. to approximately 700° C. The sensitizers are effective in very small amounts and when cracking gasoline or higher boiling hydrocarbons, should be used in amounts below 1 per cent by weight of the charge since larger amounts not only cause corrosion difficulties but deleteriously affect the quality of the product. Good results are obtained by using from 0.25 to 1 molal per cent of the sensitizer.

The sensitizer may be added to the hydrocarbons under going cracking prior to charging the latter to the heating zone or may be injected directly into the reaction zone either alone or in admixture with a small amount of solvent.

The invention is useful in connection with conventional thermal cracking operations to accelerate the rate of cracking or may be used in connection with catalytic cracking operations of the stationary or moving bed catalyst type, or in conjunction with vapor suspended solid catalyst type of operation, in which solid, comminuted catalytic clays or synthetic alumina-silica or other solid catalysts are used.

What is claimed is:

The method of cracking butane to lower boiling unsaturated hydrocarbons which comprises subjecting it to temperatures above 375° C. in the presence of a small amount of ethyl sulfide.

H. 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
1,221,698	Day	Apr. 3, 1917
2,168,840	Groll	Aug. 8, 1939
2,268,094	Russell	Dec. 30, 1941
1,925,421	Peski	Sept. 5, 1933
2,232,909	Gohr	Feb. 25, 1941
2,115,336	Krauch et al.	Apr. 26, 1938

OTHER REFERENCES

A. P. C. Application of Woog, Ser. No. 330,613, Published May 18, 1943.