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THERMAL CRACKING OF HYDROCARBONS IN THE PRESENCE OF ADDED SULFUR COMPOUNDS AND NITRIC OXIDE

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ABSTRACT OF THE DISCLOSURE

The addition of a combination of sulfur, a sulfur compound or mixtures thereof and nitric oxide to a vaporized hydrocarbon charge stream gives high conversions of the hydrocarbon stream to lower molecular weight hydrocarbons in the subsequent thermal cracking of such stream as compared with the conversions obtained in the absence of these compounds.

BACKGROUND OF THE INVENTION

The pyrolysis or thermal cracking of hydrocarbons as well as other organic compounds has, of course, been known and practiced for a great many years. As originally conceived the purpose of thermal cracking was to convert normally liquid heavy hydrocarbon stocks into those boiling in the gasoline range, but with the advent of catalytic cracking which was far superior for this purpose, thermal cracking was directed toward the production of C_4 and lighter hydrocarbons for use as petrochemicals from normally liquid hydrocarbon mixtures such as naphthas and gas oils. The term "normally liquid" is conventionally used to describe hydrocarbons liquid at ambient (room) temperature and atmospheric pressure. Thus C_1 to C_4 's are not included and often isopentane is excluded since it boils at about 85° F. and therefore is frequently removed from "normally liquid" charge stocks. The concurrent production of pyrolysis gas oils and naphthas represented a penalty to the process since these were in the same boiling range as the charge hydrocarbons and therefore did not constitute an improvement.

Many early proposals were made to improve the conversion in thermal decomposition reactions, for example, W. L. Roth and G. K. Rollefson in a paper in Journal American Chem. Soc., Vol. 64, p. 1707 et seq. (July, 1942) showed an improvement in the thermal decomposition of acetaldehyde by the use of hydrogen sulfide and nitric oxide to produce methane and carbon monoxide.

Two recent patents, United States Nos. 3,751,514 and 3,751,516 show, respectively, the conversion of isobutane into isobutylene and propylene and the conversion of n-butane into propylene using as a homogeneous catalyst in each process a sulfur compound such as hydrogen sulfide, ammonium sulfide, a mercaptan or the like or a bromine compound. These charge hydrocarbons, i.e. isobutane and n-butane are, however, valuable as chemicals and so such processes are not particularly desirable. They do not show combinations of these catalysts with nitric oxide nor do they show thermal cracking of heavy hydrocarbon charge stocks.

Since most normally liquid hydrocarbon charge stocks contain sulfur compounds and many contain nitrogen compounds as well, it was surprising to find that if a combination of sulfur or a sulfur compound and nitric oxide was added to the vaporized normally liquid hydrocarbon charge prior to thermal cracking, thereafter in the thermal cracking process markedly higher conversions to lighter hydrocarbons are obtained as compared with the thermal cracking in the absence of these compounds.

The results obtained with the combination of sulfur, the sulfur compound or mixtures thereof and nitric oxide

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in relatively small amounts, i.e. up to a total of 9 mole percent for the combination are equivalent to the results obtained with from 10 to 50 mole percent of the sulfur or sulfur compound alone. The combination of the sulfur or sulfur compound with the nitric oxide has been found to give results superior to those obtained by the use of either of these alone.

SUMMARY OF THE INVENTION

In accordance with this invention a combination of sulfur, carbon disulfide, carbonyl sulfide, ammonium sulfide, hydrogen sulfide, mercaptans, alkyl sulfides, alkyl disulfides or mixtures thereof with nitric oxide is added to a vaporized normally liquid hydrocarbon charge before the charge is heated to cracking temperature. The amount of the sulfur or sulfur compound which is added can range from about 2 mole percent to 5 mole percent based on the total charge and the amount of nitric oxide can range from about 1 mole percent to 4 mole percent based on the hydrocarbon charge. The results obtained in utilizing this combination of compounds are higher conversion to the lower boiling hydrocarbons particularly in the C_1 to C_4 range with the corresponding reduction in the amount of material boiling in the same range as the feed stock.

It is an object of this invention therefore to provide an improved method for the thermal cracking of normally liquid hydrocarbons.

It is another object of this invention to provide a method for the thermal cracking of normally liquid hydrocarbons wherein higher conversions to lower molecular weight products are obtained with a corresponding reduction in the amount of products boiling in the same range as the feed stock.

It is another object of this invention to provide an improved hydrocarbon thermal cracking process utilizing a combination of sulfur, a sulfur compound, mixtures of sulfur with a sulfur compound or mixtures of sulfur compounds with nitric oxide added to the hydrocarbon charge.

Other objects of this invention will be apparent from the description of the invention and from the claims.

DESCRIPTION OF THE INVENTION

The charge stocks which can be used in the method of this invention include those ranging from stabilized, i.e. the normally gaseous hydrocarbons have been removed (C_1 to C_4 and in some instances isopentane) crude oils to light naphthas, with preferred charge stocks being the normally liquid gas oils and naphthas with highly paraffinic light naphtha stocks being particularly amenable to treatment by the method of this invention. Naphthas or light naphthas as the terms are used herein refer to fractions containing hydrocarbons ranging from those having 5 carbon atoms in the molecule, i.e. de-butanized and some de-isopentanized naphthas, to hydrocarbons boiling up to 400° F. to 420° F. The gas oils are higher boiling than naphthas and can range from an initial boiling point of about 350° F., but generally above this temperature, to an end point of about 650° F. or above. These ranges are, of course, subject to variations in accordance with the particular crudes being processed by the refiner.

The hydrocarbon charge can range from about 10 mole percent to 50 mole percent based on the total charge with from 20 mole percent to 40 mole percent based on the total charge being preferred.

The sulfur or sulfur compounds which can be utilized in the method of this invention include sulfur, hydrogen sulfide, ammonium sulfide, carbon disulfide, carbonyl sulfide, the mercaptans, alkyl sulfides, alkyl disulfides and mixtures of these. The sulfur can be conveniently added by solution, for example, in carbon disulfide. The mercap-

tans are characterized by having the formula RSH wherein R is an unsubstituted alkyl radical having from 1 to 8 carbon atoms. The alkyl sulfides are characterized by the formula RSR' wherein R and R' may be the same or different unsubstituted alkyl radicals having a total of from 2 to 8 carbon atoms. Although higher molecular weight mercaptans, sulfides and disulfides are operable, they are not preferred, and the most preferred mercaptans, sulfides and disulfides are those having from 1 to 4 carbon atoms. The sulfur or sulfur compound or mixture together with the nitric oxide is added to the charge stock which is in vaporized form before such stock is heated to cracking temperatures. The sulfur or sulfur compounds added can range in amounts from about 2 mole percent to 5 mole percent based on the total charge and the nitric oxide is added in amounts ranging from 1 mole percent to 4 mole percent based on the total charge. Preferably the amount of sulfur or sulfur compound ranges from 3 to 5 mole percent and the amount of nitric oxide ranges from 1 to 3 mole percent. The cracking temperatures employed can range from about 675° C. to 800° C. with a more preferred range being from 700° C. to 775° C. Pressures ranging from 0.5 to 5 atmospheres, preferably from 1 to 2 atmospheres, and contact times of from 0.1 to 2.0 seconds, preferably from 0.5 to 1.2 seconds, are employed. Diluents such as steam or nitrogen can be used to reduce the partial pressure of the mixed charge in amounts ranging from about 5 to 80 mole percent of the total charge.

In the Examples which follow all of the runs were carried out in a tubular quartz reactor packed with tabular alumina granules for improved heat transfer. The tube was heated externally by an electric furnace, and temperatures were measured axially at various points down the bed. The products (except the non-condensibles) were collected in Dry-Ice traps and were analyzed by gas chromatography.

The Examples which follow are provided for illustrating the invention in additional detail but are not to be construed as limiting.

EXAMPLE I

Comparative cracking runs were carried out on a West Texas naphtha having the composition and properties shown in Table I.

TABLE I

Composition, weight percent:

Alkanes:

C ₄	0
<i>i</i> -C ₅	3.3
<i>n</i> -C ₅	29.3
C ₆	29.3
C ₇	8.8
C ₈	5.4
C ₉	0.2
C ₁₀	0

Cycloalkanes.....12.7

Aromatics:

C ₆	1.5
C ₇	0.8
C ₈	2.5
C ₉	0.1

Total.....100.0

Properties:

Density at 20° C.....	0.6742
API gravity at 60° F.....	77.1
Average molecular weight.....	83.13

The conditions used and results obtained are shown in Table II.

TABLE II

Run number.....	1	2	3	4
Temperature, ° C.....	707	706	702	701
Contact time (seconds).....	1.1	1.0	1.0	1.0
Feed composition (volume percent):				
Naphtha.....	29.77	29.43	29.46	29.62
H ₂ S.....	0	3.66	3.39	14.06
NO.....	0	0	1.42	0
N ₂	70.23	66.91	65.73	56.32
Conversion, wt. percent.....	53.8	60.3	70.2	79.71

It can be seen from these results that the nitric oxide serves as an activator for the sulfur compound. In the absence of either the sulfur compound or nitric oxide the conversion shown in Run No. 1 is obtained. The addition of a relatively small amount of sulfur compound gives a marked increase in conversion, Run No. 2 compared with Run No. 1. In the absence of nitric oxide the increase in conversion between 3.66 percent H₂S (Run No. 2) and 14.06 percent (Run No. 4) is almost 20 percent, i.e., the H₂S is more than 4 times as great in Run No. 4 as in Run No. 2 but when only 1.42 percent nitric oxide is added to 3.39 percent H₂S the conversion is increased 10 percent comparing Run No. 2 with Run No. 3.

EXAMPLE II

Comparative runs were made to determine if nitric oxide alone had any effect on conversion. These runs were on the same naphtha employed in Example I. The conditions and results are shown in Table III.

TABLE III

Run number.....	5	6
Reaction conditions:		
Temperature, ° C.....	754	755
Contact time (seconds).....	1.0	1.0
Feed gas composition:		
Naphtha, volume percent.....	29.49	29.74
Nitrogen volume percent.....	68.23	65.14
H ₂ S volume percent.....	0	3.80
NO volume percent.....	2.28	1.32
Conversion, wt. percent.....	76.5	90.6
Production distribution, pounds per 100 pounds of naphtha fed:		
Hydrogen.....	0.84	0.71
Methane.....	11.5	13.3
Ethylene.....	26.6	17.4
Ethane.....	6.7	19.8
Propylene.....	16.9	22.7
Propane.....	0	0
Butadiene.....	4.2	6.2
Butylenes.....	7.6	8.5
Butane.....	1.7	1.6
C ₅ -C ₈ non-aromatics.....	20.7	3.7
Benzene.....	1.7	3.2
Toluene.....	0.3	0.7
CO.....	0.7	1.8
CO ₂	0.5	0.4
Coke.....	0.46	0.41

The conversion obtained with nitric oxide only, Run No. 5, is substantially the same as that obtained by thermal cracking alone at this temperature which gives a conversion of almost 79 weight percent which is not a significant difference. The results obtained in Run No. 6 are substantially the same as obtained when 20 mole percent hydrogen sulfide only is used for increasing the conversion.

The results obtained as shown in the foregoing examples show that the addition of small amounts of nitric oxide greatly reduces the amount of sulfur compound needed to give an increased conversion.

EXAMPLE III

A series of runs were made on the same West Texas naphtha used in Examples I and II comparing the conversions obtained by (1) straight thermal cracking, (2) cracking in the presence of 20 mole percent hydrogen sulfide (based on total feed) and (3) cracking in the presence of approximately 2 mole percent nitric oxide and 5 mole

percent hydrogen sulfide based on total feed. In each run the naphtha amounted to about 29.5 mole percent and the remainder of the feed was nitrogen as the diluent gas.

It was found that at about 700° C. the increase in conversion using 20 mole percent hydrogen sulfide over straight thermal cracking amounted to about 30 weight percent while the 2 mole percent nitric oxide plus 5 mole percent hydrogen sulfide combination exceeded straight thermal cracking conversion by about 23 weight percent. At about 725° C. the 20 mole percent hydrogen sulfide conversion and the 2 mole percent nitric oxide—5 mole percent hydrogen sulfide gave about the same conversion which was about 21 to 22 weight percent higher than the straight thermal cracking. At 775° C. the increase still remains important being about 8 weight percent.

Accordingly, the utility of this invention is clearly demonstrated, namely that the use of small quantities of nitric oxide in combination with a sulfur compound or sulfur greatly reduces the quantity of sulfur compound required to give the desired increase in conversion in thermal cracking processes.

I claim:

1. A method for the thermal cracking of mixtures of normally liquid hydrocarbons having at least 5 carbon atoms in the molecule characterized by increased conversion to lower molecular weight products and decreased production of products boiling in the same range as said normally liquid hydrocarbon charge mixture which comprises adding sulfur, a sulfur compound selected from the group consisting of carbon disulfide, carbonyl sulfide, ammonium sulfide, mercaptans, alkyl sulfides, alkyl disulfides or mixtures thereof together with nitric oxides to a vaporized stream of said normally liquid hydrocarbon charge mixture, thereafter subjecting the resulting sulfur and nitric oxide-containing hydrocarbon stream to thermal cracking conditions and recovering the thermally cracked products.

2. The method according to claim 1 wherein said sulfur, sulfur compounds or mixtures thereof range from about 2 mole percent to 5 mole percent based on the total charge, the nitric oxide ranges from about 1 mole percent to 4 mole percent based on the total charge and a gaseous diluent ranges from about 5 to 80 mole percent based on the total charge.

3. The method according to claim 2 wherein said sulfur, sulfur compounds or mixtures thereof range from about 3 to 5 mole percent based on the total charge and the nitric oxide ranges from about 1 to 3 mole percent based on the total charge.

4. The method according to claim 1 wherein said thermal cracking is carried out at temperatures in the range of from 675° C. to 800° C.

5. The method according to claim 4 wherein said normally liquid hydrocarbon charge mixture is a naphtha having hydrocarbons of 5 carbon atoms and ranging up to

hydrocarbons boiling up to 400° F. to 420° F. and said sulfur compound is hydrogen sulfide.

6. The method according to claim 4 wherein said normally liquid hydrocarbon charge mixture is a gas oil fraction having an initial boiling point of at least 350° F. and said sulfur compound is hydrogen sulfide.

7. The method according to claim 5 wherein said naphtha ranges from about 10 mole percent to 50 mole percent based on the total charge.

8. The method according to claim 6 wherein said gas oil ranges from about 10 mole percent to 50 mole percent based on the total charge.

9. A method for the thermal cracking of normally liquid hydrocarbon mixtures selected from the group consisting of naphthas having hydrocarbons ranging from at least 5 carbon atoms and ranging up to hydrocarbons boiling up 400° F. to 420° F. and gas oils having an initial boiling point of at least 350° F. characterized by increased conversion to lower molecular weight products and decreased production of products boiling in the same range as said normally liquid hydrocarbon charge mixture, said charge mixture ranging from 10 mole percent to 50 mole percent based on the total charge, which comprises adding from 1 mole percent to 5 mole percent based on the total charge of hydrogen sulfide and from 1 mole percent to 4 mole percent based on the total charge of nitric oxide to a vaporized stream of said hydrocarbon charge mixture, thereafter subjecting the resulting hydrogen sulfide and nitric oxide-containing hydrocarbon stream to thermal cracking at temperatures in the range of from about 675° C. to 800° C. and recovering the thermally cracked products.

10. The method according to claim 9 wherein said total charge contains from about 5 to 30 mole percent of nitrogen or steam as a diluent.

11. The method according to claim 10 wherein said thermal cracking is at temperatures in the range of from 700° C. to 775° C.

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