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PROMOTED PYROLYSIS PROCESS

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This invention relates to the cracking of certain olefins. More specifically, it relates to method of improving the cracking of certain olefins. Most specifically, it relates to methods of improving the efficiency of cracking of olefins to form specific diolefins and paraffinic hydrocarbons or to form certain other specific olefins.

It is known that certain olefins may be thermally decomposed or cracked by subjecting them to relatively high temperatures. By the terms "crack," "cracking," "decomposing," "decompose," "decomposed" or "cracked," etc., as employed throughout this application and appended claims, is meant that the olefin molecule splits into two or more fragments, these fragments themselves form molecules of other hydrocarbons as explained later in greater detail. The olefins with which this invention is concerned are those olefins which will crack or decompose upon the application of heat. Olefins, if they are to crack at all, must contain in their molecules a double bond which is 2 carbon atoms removed from another carbon-to-carbon single bond. Another way of stating this is that if olefins are to crack at all they crack at the carbon-carbon single bond which is in the beta position to the double bond.

This thermal decomposition or cracking of olefins is usually conducted within a closed zone or reactor in the absence of oxygen. Temperatures employed to crack olefins usually range from about 300° C. to about 1000° C. Usually olefins are cracked while in a gaseous state and may be fed to the cracking zone either relatively pure, as mixtures of olefins, in mixture with other hydrocarbons usually saturated, for instance, mixed feed streams of pentane-pentene, or in mixture with diluents such as nitrogen, steam and the like. The thermal decomposition of olefins usually results in the formation of two lower molecular weight materials. There is usually a predominance of a diolefin and a paraffinic hydrocarbon or a predominance of two other olefins formed in most olefin cracking operations.

The particular materials which predominate when olefins are cracked depend largely upon the configuration of the olefin which is cracked. By configuration is meant the position of the double bond and the position of the side chains, if any. For instance, an olefin containing six carbons with a side chain, i.e. a methyl group attached to the second carbon atom of the main or straight chain portion of the olefin and the double bond in the 2 position, such an olefin is 2-methyl pentene-2, when subjected to cracking, will upon decomposition produce as the predominant products 2-methyl butadiene-1,3 or isoprene, a diolefin, and methane, a paraffin. On the other hand another 6 carbon olefin having a methyl group attached to the second carbon of the straight chain and the double bond in the 1 position, such an olefin is 2-methyl pentene-1, when cracked will produce two other olefins, isobutylene and ethylene. When still another isomeric hexene such as 4-methyl pentene-1 is cracked two mols of propylene are produced. These differences in products obtained when different isomeric forms of methylpentene or branched hexenes are cracked are due to the fact that olefins crack at the carbon-to-carbon single bond which is in the position beta to the double bond. That is, the scission occurs in the single bond that is in the position beta to the double bond. Another way of stating this is that the split occurs between the two carbon atoms that are second and third removed from the double bond. Further, in an efficient cracking process, the sum of the carbon atoms of the main or predominant products of the cracking is usually equal to the number of carbon atoms contained in the olefin which was subjected to the cracking. In 2-methyl pentene-2, when it is cracked, only one carbon atom is broken away from the 6 carbon olefin; in 2-methyl pentene-1, two carbon atoms are broken away; in 4-methyl pentene-1, three carbon atoms are broken away. This is because of the location of carbon-to-carbon single bond in the beta position to the double bond. Thus, the particular olefin employed usually dictates the main or predominant products which result from the cracking of olefins. It is signficant that since olefins crack at the bond beta to the double bond, an olefin, if it is to crack easily, or at all, must have in its molecule a carbon-to-carbon single bond in the beta position to the carbon-to-carbon double bond. Examples of olefins which do not have this molecular make-up are ethylene, propylene, butene-2, isobutene, 2-methyl butene-2 and 2,3-dimethyl butene-2. These six aforementioned olefins, since they do not crack easily, are not within the scope of the olefins which are to be cracked in accordance with this invention.

In these thermal cracking processes employing the most favorable conditions conducive to cracking olefins efficiently to form the desired products, it has been found that olefins decompose at a very low rate per pass through the cracking zone. The conditions which have an effect on the cracking are the temperature, the residence time in the cracking zone, and the ratio of the olefin to the gaseous diluent, if any be employed, and, of course, the olefin being cracked. It is usually the practice to increase the decomposition of olefins and of the yield of desired end products by separating the unreacted or undecomposed olefin from the products resulting from the cracking and returning or recycling the unreacted or undecomposed olefin to the cracking zone. Usually, however, regardless of how many recycles are carried out, the ultimate yield or ultimate efficiently of the olefin is not greater than about 50 mol percent of the olefin being converted or decomposed to form the desired products. The remaining 50 mol percent usually is converted into undesirable products as the result of side reactions caused by repeated exposure to high temperature or long residence times or both in the cracking zone.

It is, therefore, an object of this invention to provide a method whereby the yield of the desired products produced by cracking olefins is increased. Another object is to provide a method whereby the cracking of olefins to desired products per pass is increased. Another object is to increase the ultimate yield of desired products from the cracking olefins. Another object is to provide a method whereby the residence time of cracking of olefins may be decreased. Another object is to provide a method whereby the promotion of undesirable side reactions during the cracking of olefins is decreased. Another object is to provide a method whereby olefins may be cracked efficiently at lower temperatures. Another object is to provide a promoter for the cracking of olefins to the desired products. Still another object is to provide a method whereby the cracking of the olefins is promoted. Still another object is to provide a promoted cracking method whereby the cracking promoter is more easily handled. Still another object is to provide a cracking method whereby the cracking promoter may be recovered and recycled for further use.

Still other objects will become apparent as the description proceeds.

According to this invention it has been found that these and other objects are accomplished by (A) providing a cracking mixture comprising (1) at least one olefin having in its molecule a carbon-to-carbon single bond which is in a position beta to the double bond and (2) at least one material resulting from the reaction of one mol of hydrogen sulfide and at least one and not more than two mols of an amine, said material being present in an amount of at least 0.005 mol per mol of olefin, (B) cleaving a carbon-to-carbon single bond which is in a position beta to the double bond of said olefin by subjecting said mixture to suitable conditions of temperature ranging from about 500° C. to about 850° C. and periods of time varying from between about 3 minutes to about 0.001 second.

Contemplated to be within the scope of the term "amine" in the above statement of invention are aliphatic, aromatic, mixed aromatic-aliphatic amines, hydrazine and ammonia. Another way of defining the materials which react with hydrogen sulfide to form the cracking promoter of this invention, would be to refer to these materials as ammonia, aryl derivatives of ammonia, alkyl derivatives of ammonia and amine derivatives of ammonia.

The reaction product of one mol of hydrogen sulfide and one mol of an amine results in a hydrosulfide of the corresponing amine. The reaction product of one mol of hydrogen sulfide and two mols of an amine results in the sulfide of the corresponding amine. By the term "corresponding hydrosulfide" or "corresponding sulfide" is meant simply that the amine and the hydrogen sulfide form a simple addition compound. Thus, whatever the amine may be, either it be aliphatic, aromatic, a mixed aromatic aliphatic amine, hydrazine or ammonia, the amine will react directly with the hydrogen sulfide to form a simple addition compound.

By the term "amine" above is meant alkyl amines, aryl amines, aryl alkyl amines, ammonia and hydrazine. Representative of suitable alkyl amines but by no means limiting are: methylamine, dimethylamine, trimethylamine, ethylamine, diethylamine, triethylamine, methylethylamine, dimethylethylamine, diethylmethylamine, n-propylamine, di-n-propylamine, tri-n-propylamine, isopropylamine, methylisopropylamine, methyl - n - propylamine, ethylisopropylamine, ethyl-n-propylamine, n-butylamine, isobutylamine, methyl-n-butylamine, methylisobutylamine, ethyl-n-butylamine, ethylisobutylamine, t-butylamine, and the like. Representative of suitable aryl amines but by no means limiting are: aniline, p-toluidine, o-toluidine, m-toluidine; 2,3-xylidine; 2,4-xylidine; 2,6-xylidene; 3,4-xylidene; 3,5-xylidene; p-ethylaniline, m-ethylaniline, o-ethylaniline, benzylamine and the like. Representative of suitable mixed aryl alkyl amines but by no means limiting are: phenylmethylamine, phenylethylamine, benzylmethylamine and the like. Hydrazine will also react with hydrogen sulfide to form a water soluble salt. The hydrazine may be simple hydrazine or it may be a substituted hydrazine as well. Representative of such but by no means limiting are hydrazine, methylhydrazine, ethylhydrazine, dimethylhydrazine, diethylhydrazine, phenylhydrazine and the like. Ammonia will also react with hydrogen sulfide to form a water soluble salt, i.e., ammonium hydrosulfide or ammonium sulfide in a manner similar to that of the amines or the hydrazines.

One particular interesting embodiment of the invention of this application is the use of a process which comprises providing a cracking mixture comprising (1) at least one olefin having in its molecule a carbon-to-carbon single bond which is in a position beta to the double bond and (2) at least one material selected from the group consisting of (a) ammonium hydrosulfide, (b) ammonium sulfide and (c) at least one ammonuim polysulfide, said material being present in an amount of at least 0.005 mol per mol of olefin, cleaving a carbon-to-carbon single bond which is in a position beta to the double bond of said olefin by subjecting said mixture to suitable conditions of temperature ranging from about 500° C. to about 900° C. and periods of time varying between about 5 minutes to about 0.001 second. The ammonium hydrosulfide results from the reaction of one mol of ammonia and one mol of hydrogen sulfide. The ammonium sulfide results from the reaction of one mol of hydrgen sulfide and two mols of ammonia. Ammonium polysulfide is usually prepared by adding sulfur to the reaction mixture of ammonium sulfide.

These materials, water soluble salts of amines and hydrogen sulfide, may be prepared in various ways. One embodiment which has been found successful is the preparation by the reaction of one mol of hydrogen sulfide and one mol or two mols of an amine to form the corresponding amine hydrosulfide or sulfide of the particular amine employed. By the term "corresponding hydrosulfide" or "corresponding sulfide" is meant simply that the amine and hydrogen sulfide form simple addition compounds of the particular amine employed to form the particular amine hydrosulfide or particular amine sulfide. Examples of this are illustrated by the use of the methylamine (CH_3NH_2) when one mol of this amine is reacted with one mol of hydrogen sulfide (H_2S) the resulting product is methylamine hydrosulfide

$$((CH_3NH_3)SH)$$

When two moles of this material is reacted with one mol of hydrogen sulfide, methylamine sulfide ($((CH_3NH_3)_2S$) is the resulting product. Still another embodiment of the cracking promoter of this invention are the amine polysulfides. They may be prepared by reacting one mol of hydrogen sulfide and two mols of an amine and adding sulphur to the reaction mixture. Again, using methylamine as an example, methylamine polysulfide

$$((CH_3NH_3)_2S_x)$$

where x equals at least two up to about five depending on the amount of excess sulfur added. Likewise, two mols of dimethylamine reacts with one mol of hydrogen sulfide to form dimethylamine sulfide.

The amount of cracking promoter employed in the practice of this invention is not particularly critical, but it should be realized that sufficient cracking promoter should be employed to effect sufficient promotion to make its addition worthwhile. It has been found that usually about 0.005 mol per mol of olefin to be cracked is sufficient. There is no upper limit to the amount of promoter, but from a practical standpoint no more than about 0.5 mol per mol of olefin need be used. Thus, the range could be said to be from about 0.5 to about 50 mol percent.

The employment of the reaction products of at least one and not more than two mols of amine and one mol of hydrogen sulfide as cracking promoters offer a number of advantages over other promoted olefin processes. Some of these advantages are the ease of processing and economy. The reaction products of one or two molds of amine and one mol of hydrogen sulfide are soluble in water. This means that these cracking promoters can be charged into the process in the form of a water solution. This water is then heated to form steam which is employed as a cracking diluent. Because the reaction products of amines and H_2S are soluble in water the amounts employed can be easily metered and easily handled as well as stored for indefinite periods of time. The compounds employed as cracking promoters in this invention are cheap, thus resulting in considerable economy. These compounds are also recoverable since in the application as a cracking promoter they are relatively indestructible and recoverable in water soluble forms. They are not soluble in the hydrocarbon phase and therefore do not give rise

to purification problems. Furthermore, the promoters employed in this invention do not require expensive materials of construction for the cracking furnace and the quenching equipment in that they are less corrosive and thereby allow the use of lower cost alloys. Additionally, the promoters of this invention do not form by-products which in turn must be removed in the purification operation, thereby adding to the expense of purification.

In general the cracking of olefins in accordance with the practice of this invention may be carried out in any conventional manner usually employed in the art of olefin cracking. Generally the conditions which may be employed in this invention may be widely varied depending upon a number of factors. These conditions depend upon the particular olefin to be cracked, the products desired, the type and amount of diluent employed, if any, the desired rate of conversion of the reactant to products and the desired reaction efficiency to desired products and the type and amount of promoter employed.

For instance, the cracking temperature may be varied broadly from about 500° C. to about 850° C. with a preferred range of from about 600° C. to about 800° C. A still more preferred range may be from about 625° C. to about 775° C. with the most preferred range being between about 650° C. and about 725° C.

The pressures at which the olefins may be cracked may vary broadly from about 1 millimeter of mercury to about 500 pounds per square inch gauge (p.s.i.g.). However, a preferred pressure is one from about 100 millimeters of mercury to about 250 p.s.i.g. A more convenient range is from about 1 atmosphere to about 100 to 150 p.s.i.g.

The reaction time during which olefins are cracked is usually referred to as residence times. The residence time is defined as the time required for one mol of incoming gas, whether it be pure olefin, olefins in mixtures with other hydrocarbons, other olefins or diluents to pass through the cracking zone. In the practice of this invention these times may be varied broadly from about 3 minutes to about 0.001 second with a preferred range of from about 1 minute to about 0.003 second and a more preferred range of from about 1 second to about 0.005 second and a more preferred range of about 0.75 second to about 0.01 second, and a most preferred range of 0.5 to 0.05 second.

The olefins employed in the practice of this invention are fed to the cracking reactor as pure olefins, in mixture with other olefins; in mixture with other hydrocarbons; or in mixture with some inert diluent; or in mixture with a combination of these. If it is desirable to employ an inert diluent such diluents as steam, nitrogen, carbon dioxide, methane, ethane or hydrogen may be employed. Other hydrocarbons which do not crack at the temperatures employed may be also utilized as diluents. Examples of such diluents are the refractory olefins and certain paraffinic hydrocarbons which are uneffected at the temperatures employed in the cracking process. In fact, any diluent that does not have an adverse effect upon the process may be employed. Of these it is usually preferred to employ steam in the practice of this invention as matter of convenience (the promoter being soluble in water) and for reasons of economy. The ratio of diluent to olefin employed in the practice of this invention may be widely varied from about 0.5/1 to about 15/1 or more mols of diluent per mol of olefin. However, if more than about a 15/1 ratio is employed the process tends to become uneconomical. It is preferred to use a diluent to olefin ratio ranging from about 2.0/1 to 4.0/1. The olefins may also be cracked without diluent.

The practice of this invention is illustrated by the following experiments which are to be interpreted as representative rather than restrictive of the scope of this invention. The results and conditions of the cracking experiments are reported in table form.

All of the cracking experiments were performed in a reactor assembly consisting of a "hairpin" coil prepared from ¼-inch O.D. 316 stainless steel tubing. This coil reactor was immersed in a bed of fluidized heat transfer powder which was microspheroidal silica-alumina cracking catalyst. The heat transfer powder was heated both by electrical resistance heaters and by combusting a natural gas flame in the fluidized powder bed. The temperature gradient from top to bottom of the bed was never more than 5 to 6° C. and the gradient from the fluidized bed to the tube walls was about 5–6° C. The temperatures within the fluidized bed were measured by conventional thermocouple techniques as were the temperatures within the cracking zone. The procedure employed was to bring the heat transfer powder up to about 500° C. employing the electrical resistance heaters while fluidizing the heat transfer powder with air. Then the natural gas burner was employed to bring the heat transfer powder up to the desired cracking or operating tempertaure. The cracking promoters, being water soluble, were added to the water which is employed to produce the diluent steam. The water, including the promoter and the olefin, were pumped at the proper rates necessary to produce the H_2O/hydrocarbon ratio and amount of promoter desired and to give the desired residence time of the materials in the cracking zone or cracking reactor. When all variables had been adjusted to give the desired operating conditions, the products of the cracking were collected, if liquid, by means of cooled receivers and, if gas, were metered at atmospheric and room temperature conditions. The products were analyzed for content and yields by conventional analytical methods. Conventional recycle techniques were employed to obtain the ultimate yield of efficiency.

Example I

In this example several experiments were conducted in which 2-methylpentene-2 was pyrolyzed continuously employing methylamine sulfide $(CH_3NH_2)_2S$ as a cracking promoter. A control was employed in which no cracking promoter was present and this control represents the thermal pyrolysis of 2-methylpentene-2. Steam was employed as a diluent at a ratio of 3 mols of steam per mole of 2-methylpentene-2. The pressure employed was atmospheric. The conditions of temperature, time and the amount of promoter, as well as the yield and efficiencies are reported in the following table. Column 1 is the run number, column 2 is the mol percent of promoter employed, column 3 is the residence time in seconds, column 4 is the temperature in degrees C., column 5 is the mol percent of isoprene obtained per pass and column 6 is the reaction efficiency in percent isoprene obtained per mol of 2-methylpentene-2 pyrolyzed.

Run No.	Mol Percent Promoter	Residence Time	Temperature	Mol Percent Isoprene	Efficiency
1	6	0.15	650	18.4	54.1
2	6	0.20	640	11.9	52.4
3	0 (control)	0.15	626	7.5	44.9

Example II

In this example a series of experiments were conducted in which 2-methylpentene-2 was continuously pyrolyzed at various temperatures employing various amounts of ammonium sulfide as the cracking promoter. At each of the various temperatures controls were run in which no cracking promoter was present and these controls consisted of thermal pyrolysis of 2-methylpentene-2. Steam was employed as an inert diluent at a ratio of 3 mols of diluent per mol of olefin. The pressure was about atmospheric. The results are reported in the table below in which column 1 lists the experiment number; column 2 lists the average cracking temperature in degrees centigrade; column 3 lists the average residence time in seconds; column 4 lists the cracking promoter used and amount employed in mol percent if any was

used (none was used in the control runs); column 5 lists the yield in mol percent of the isoprene obtained per pass through the cracking zone; column 6 lists the reaction efficiency in percent of isoprene obtained employing recycle techniques and is the mols of isoprene obtained per mol of 2-methylpentene-2 pyrolyzed.

1 Exp. No.	2 Temp., °C.	3 Res. Time, Seconds	4 Promoter and Amount—Based on 2-MePe-2	5 Isoprene Yield/Pass, Mole Percent	6 Reaction Eff., Percent
1	600.5	.192	Thermal (Control)	3.65	46.12
2	606.7	.146	$(NH_4)_2S$ (2.54)	4.22	48.40
3	625.7	.154	Thermal (Control)	7.45	44.88
4	630.3	.146	$(NH_4)_2S$ (2.54)	8.30	55.32
5	660.5	.150	Thermal (control)	10.70	53.15
6	661.6	.145	$(NH_4)_2S$ (3.71)	19.06	56.71
7	675.4	.149	Thermal (Control)	13.56	51.26
8	681.9	.140	$(NH_4)_2S$ (3.71)	25.94	55.99
9	682.2	.141	$(NH_4)_2S$ (6.06)	29.79	58.41
10	707.5	.188	Thermal (Control)	25.82	40.90
11	702.3	.138	$(NH_4)_2S$ (6.06)	38.14	57.84

As evidenced by the results of the above experiments considerable improvement in yield per pass and reaction efficiency is obtained by the use of the catalyst of this invention. This is particularly true when optimum conditions are attained relative to isoprene yield per pass. Thus it can be seen that use of the cracking promoters of this invention not only exihibit extremely good promotion activity but have the added advantage of being water soluble and recoverable and therefore add to the economy of the cracking process in this regard.

Similar results may be obtained employing the general techniques of the representative examples above and the teachings found elsewhere in this application.

The list of olefins below, which are representative but by no means limitative, are the olefins which, when cracked or pyrolyzed in accordance with the practice of this invention, the results will exhibit improvements in both yield and efficiencies as compared to the thermal cracking of these olefins. These olefins are grouped in a manner so as to indicate the predominance of the products formed upon their decomposition.

Representative among the olefins that will decompose to form predominantly 2-methyl pentadiene-1,3 and 4-methyl pentadiene-1,3 are: 2-methyl hexene-3; 2-ethyl pentene-1; 2,4-dimethyl pentene-2; 2-methyl heptene-3; 4,4-dimethyl hexene-2; 2-propyl pentene-2; 2-methyl-3-ethyl pentene-1; 2,6-dimethyl heptene-3 and 2-propyl hexene-1 and hexene-3.

Representative among the olefins which will decompose to form predominantly 3-methyl pentadiene-1,3 are 3-methyl hexene-3; 3-methyl heptene-3; 3,4-dimethyl hexene-2; 3,6-dimethyl heptene-3.

Representative among the olefins which decompose to form predominantly 2,3-dimethyl butadiene-1,3 are 2,3-dimethyl pentene-2; 2,3,3-trimethyl butene-1; 2-isopropyl pentene-1; 2,3,3-trimethyl pentene-1; and 2,3-dimethyl-heptene-2.

Representative among the olefins which decompose to form predominantly 2-ethyl butadiene-1,3 are 2-ethyl pentene-2; 3-ethyl pentene-2; 3-methyl-2-ethyl butene-1; 3-ethyl hexene-2; 3-methyl-2-ethyl pentene-1.

Representative among the olefins which will decompose to form predominantly butadiene-1,3 are: pentene-2; hexene-2; 3-methyl pentene-1; cyclohexene; 3-methyl butene-1; 2-heptene; 3-methyl hexene-1; 5-methyl hexene-2; 2-octene; 5-methyl heptene-2; 3,5-dimethyl hexene-1; 3,4,4-trimethyl pentene-1; 6-methyl heptene-2; nonene-2 and 3-methyl octene-1.

Representative among the olefins which will decompose to form predominantly isoprene are: 2-methyl pentene-2; 3-methyl pentene-2; 2-ethyl butene-1; 3,3-dimethyl butene-1; 2,3-dimethyl butene-1; 2-methyl hexene-2; 3-methyl hexene-2; 2-ethyl pentene-1; 2,3-dimethyl pentene-1; 3,3-dimethyl pentene-1; 2-methyl heptene-2; 3-methyl heptene-2; 2-ethyl hexene-1; 3,3-dimethyl hexene-1; 2,5-dimethyl hexene-2; 3,5-dimethyl hexene-2; 4-methyl-2-ethyl pentene-1; 2,3,4-trimethyl pentene-1; 3,3,4-trimethyl pentene-2; 2-methyl octene-2; 3-methyl octene-2; 3,3-dimethyl heptene-1; 2,5-dimethyl heptene-2; 2,6-dimethyl heptene-2; 5-methyl-2-ethyl hexene-1; 3,3,5-trimethyl hexene-1; and 2,5,5-trimethyl hexene-2.

Representative among the olefins that will decompose to form predominantly piperylenes are: hexene-3; 4-methyl pentene-2; heptene-3; 4-methyl hexene-2; octene-3; 4-methyl heptene-2; 6-methyl heptene-3; 3-ethyl hexene-1; 4-methyl-3-ethyl pentene-2; 4,5-dimethyl heptene-2; and 4,5,5-trimethyl hexene-2.

Representative among the olefins which will decompose to form ethylene as a major product are: pentene-1; 2-methyl pentene-1.

Representative among the olefins which will decompose to form propylene as a major product are: pentene-1; hexene-1; 4-methyl pentene-1; heptene-1; 2-methyl hexene-1; 4-methyl hexene-1; 5-methyl hexene-1; 2,4-dimethyl pentene-1; 4,4-dimethyl pentene-1; octene-1; 4-methyl heptene-1; 5-methyl heptene-1; 6-methyl heptene-1; and 4-ethyl hexene-1.

Representative among the olefins which will decompose to form isobutylene as a major product are: 2-methyl pentene-1; 2-methyl hexene-1; 5-methyl hexene-1; 2,4-dimethyl pentene-1; and 4,4-dimethyl pentene-1.

Representative of the olefins which will decompose to form butene-1 and/or butene-2 as major products are: heptene-1; 4-methyl hexene-1; 2-methyl heptene-1; and 2,4-dimethyl hexene-1.

Representative of the olefins which will decompose to form 2-methyl butene-1 and/or 3-methyl butene-1 and/or 2-methyl butene-2 as major products are: 5-methyl heptene-1; 6-methyl heptene-1; 4,4-dimethyl hexene-1; 4,5-dimethyl hexene-1; and 2,6-dimethyl heptene-1.

Representative of the olefins which will decompose to form pentene-1 and/or pentene-2 as major products are: 4-methyl heptene-1; 4-ethyl hexene-1; and 2-methyl octene-1.

Representative of the olefins which will decompose to form 2,3-dimethyl butene-1 and/or 2,3-dimethyl butene-2 as major products are: 4,4,5-trimethyl hexene-1 and 2,5,6-trimethyl heptene-1 or 2.

Of these olefins it is particularly desired to form isoprene by the practice of this invention by cracking 2-methyl pentene-2; 3-methyl pentene-2; 2-ethyl butene-1; 3,3-dimethyl butene-1 and 2,3-dimethyl butene-1 while employing the cracking promoter of this invention.

While certain representative embodiments and details have been shown for the purpose of illustrating the invention, it will be apparent to those skilled in this art that various changes and modifications may be made therein without departing from the spirit or scope of the invention.

What is claimed is:

1. A cracking process which comprises (A) providing a cracking mixture comprising (1) at least one olefin having in its molecule a carbon-to-carbon single bond which is in a position beta to the double bond and (2) at least one cracking promoter resulting from the reaction of one mol of hydrogen sulfide and at least one and not more than two mols of an amine, said material being present in an amount of at least 0.005 mol per mol of said olefin, (B) cleaving the carbon-to-carbon single bond which is in a position beta to the double bond of said olefin by subjecting said mixture to suitable conditions of temperature ranging from about 500° C. to about 850° C. for periods of time varying from between about 3 minutes to about 0.001 second.

2. The process according to claim 1 in which the cracking process is conducted in the intimate presence of an inert diluent.

3. The process according to claim 2 in which the inert diluent is steam.

4. A piperylene production process which comprises (A) providing a cracking mixture of (1) at least one olefin selected from the group consisting of hexene-3; 4-methyl pentene-2; heptene-3; 4-methyl hexene-2; octene-3; 4-methyl heptene-2; 6-methyl heptene-3; 3-ethyl hexene-1 and 4-methyl-3-ethyl pentene-2, and (2) at least one cracking promoter resulting from the reaction of one mol of hydrogen sulfide and at least one and not more than two mols of an amine, said material being present in an amount of at least 0.005 mol per mol of said olefin, (B) cleaving the carbon-to-carbon single bond which is in a position beta to the double bond of said olefin by subjecting said mixture to suitable conditions of temperature ranging from about 500° C. to about 850° C. for periods of time varying from between about 3 minutes to about 0.001 second.

5. A butadiene-1,3 production process which comprises (A) providing a cracking mixture of (1) at least one olefin selected from the group consisting of pentene-2; hexene-2; 3-methyl pentene-1; cyclohexene; 3-methyl butene-1; 2-heptene; 3-methyl hexene-1 and 5-methyl hexene-2, and (2) at least one cracking promoter resulting from the reaction of one mol of hydrogen sulfide and at least one and not more than two mols of an amine, said material being present in an amount of at least 0.005 mol per mol of said olefin, (B) cleaving the carbon-to-carbon single bond which is in a position beta to the double bond of said olefin by subjecting said mixture to suitable conditions of temperature ranging from about 500° C. to about 850° C. for periods of time varying from between about 3 minutes to about 0.001 second.

6. A 2-ethyl butadiene-1,3 production process which comprises (A) providing a cracking mixture of (1) at least one olefin selected from the group consisting of 3-ethylpentene-2; 2-ethylpentene-2; 3-methyl-2-ethylbutene-1; 3-ethyl hexene-2 and 3-methyl-2-ethyl pentene-1, and (2) at least one cracking promoter resulting from the reaction of one mol of hydrogen sulfide and at least one and not more than two mols of an amine, said material being present in an amount of at least 0.005 mol per mol of said olefin, (B) cleaving the carbon-to-carbon single bond which is in a position beta to the double bond of said olefin by subjecting said mixture to suitable conditions of temperature ranging from about 500° C. to about 850° C. for periods of time varying from between about 3 minutes to about 0.001 second.

7. An isoprene production process which comprises (A) providing a cracking mixture of (1) at least one olefin selected from the group consisting of 2-methyl pentene-2; 3-methyl pentene-2; 2-ethyl butene-1; 2,3-dimethyl butene-1; 3,3-dimethyl butene-1; 2-methyl hexene-2; 3-methyl hexene-2; 2,3-dimethyl pentene-1; 3,3-dimethyl pentene-1; 2-methyl heptene-2; 3-methyl heptene-2; 2-ethyl hexene-1; 3,3-dimethyl hexene-1; 2,5-dimethyl hexene-2; 3,5-dimethyl hexene-2; 4-methyl-2-ethyl pentene-1; 2,3,4-trimethyl pentene-1 and 3,3,4-trimethyl pentene-2, and (2) at least one cracking promoter resulting from the reaction of one mol of hydrogen sulfide and at least one and not more than two mols of an amine, said material being present in an amount of at least 0.005 mol per mol of said olefin, (B) cleaving the carbon-to-carbon single bond which is in a position beta to the double bond of said olefin by subjecting said mixture to suitable conditions of temperature ranging from about 500° C. to about 850° C. for periods of time varying from between about 3 minutes to about 0.001 second.

8. A cracking process according to claim 1 in which the cracking promoter is ammonium hydrosulfide.

9. A cracking process according to claim 1 in which the cracking promoter is ammonium sulfide.

10. A cracking process according to claim 1 in which the cracking promoter is methylamine sulfide.

11. A cracking process according to claim 1 in which the cracking promoter is dimethylamine sulfide.

12. A piperylene production process according to claim 4 in which the olefin is hexene-3.

13. A piperylene production process according to claim 4 in which the olefin is 4-methyl pentene-2.

14. A butadiene production process according to claim 5 in which the olefin is pentene-2.

15. A butadiene production process according to claim 5 in which the olefin is hexene-2.

16. A 2-ethyl butadiene-1,3 production process according to claim 6 in which the olefin is 3-ethyl pentene-2.

17. A 2-ethyl butadiene-1,3 production process according to claim 6 in which the olefin is 2-ethyl pentene-2.

18. An isoprene production process according to claim 7 in which the olefin is 2-methyl pentene-2.

19. An isoprene production process according to claim 7 in which the olefin is 3-methyl pentene-2.

20. A method of preparing isoprene which comprises (A) providing a mixture of (1) 2-methyl pentene-2, (2) ammonium sulfide in an amount varying between about 1 mol percent and about 10 mol percent based on the mols of 2-methyl pentene-2, (3) steam as an inert diluent in an amount of from about 2/1 to about 4/1 mols of diluent to olefin, (B) cleaving a carbon-to-carbon single bond which is in a position beta to the double bond of said 2-methyl pentene-2 by subjecting said mixture to temperatures ranging between about 625° C. to about 775° C. for periods of time ranging from about 0.01 to about 0.75 second to demethanate the said 2-methyl pentene-2 and form isoprene.

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