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**OLEFIN CRACKING PROMOTED BY
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of Ohio****No Drawing. Filed Sept. 7, 1962, Ser. No. 222,177****9 Claims. (Cl. 260-680)**

This invention relates to a promoted cracking process for certain olefins. More specifically it relates to a method of improving the cracking of certain olefins. Most specifically it relates to methods of improving the efficiency of cracking of certain 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 elevated temperatures, for instance olefins which have in their molecular make-up a carbon-carbon bond which is in a position beta to the double bond will under proper conditions of heat, time and pressure undergo a scission of the carbon-carbon bond in the position beta to the double bond. By the terms "cracking," "decomposing," "cracked," or "decomposed" as employed throughout this specification and claims is meant that the olefin molecule splits into two or more fragments at the carbon-carbon bond which is in a position beta to the double bond. This will be explained in more detail later.

The thermal decomposition or cracking of olefins is usually conducted in a closed zone or reactor and is usually conducted in the absence of oxygen. The temperatures employed usually vary from about 300 to about 1,000° C. Usually this thermal cracking process is conducted while the olefins are in a gaseous state. The olefins may be cracked in relatively pure form or a diluent may be employed.

Employing the most favorable conditions conducive to the cracking of olefins, these conditions being temperature, residence time in the cracking zone, the ratio of the olefin to the diluent if any be employed, it has been found that olefins decompose at fairly low yields and to fairly low efficiency. As employed in this application the term "yield" is meant to connote the decomposition of the olefin feed stock per pass through the cracking zone and the term "efficiency" is meant to connote the total decomposition to the desired end product employing well known recycle techniques.

It is therefore the object of this invention to provide a method whereby the yield of the desired products produced by cracking these olefins is increased. Another object is to increase the ultimate yield or efficiency of the desired product. Another object is to provide a method whereby the residence time in the heating zone and the temperature of the heating zone may be decreased to prevent undesirable side reactions from taking place. Still other objects are to provide cracking promoters which will allow greater yields and greater efficiencies to be obtained in the cracking of these olefins. Still other objects will be apparent as the description proceeds.

To further explain what is meant by a carbon-to-carbon bond in a position beta to the double bond, the following discussion is intended to be illustrative and not restrictive of the scope of this invention. The particular materials

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which predominate when olefins are cracked depend largely upon the configuration of the particular olefin cracked. By "configuration" is meant the location of the double bond and the location of the side group on the chain if any be present. It is believed that this best can be illustrated by the following discussion. When an olefin containing 6 carbon atoms with a side group, i.e. a methyl group attached to the second carbon atom of the main or straight portion of the chain, and the double bond is in the 2 position, such as olefin being 2-methyl pentane-2, is subjected to cracking conditions, the predominant products obtained are 2-methyl butadiene-1,3 (isoprene) which is a diolefin, and methane, a paraffin. On the other hand if a 6 carbon olefin such as 2-methyl pentane-1 which has the double bond in the 1 position and the methyl group in the 2 position is cracked, it will yield as the predominant products two other olefins, isobutylene and ethylene. When still another isomeric hexene such as 4-methyl pentene-1 is cracked, two moles of the olefin propylene are formed. These differences in products obtained, when different isomeric forms of olefins containing the same number of carbon atoms are cracked, are due to the fact that olefins crack at the position beta to the double bond, that is to say the carbon-carbon bond which is two carbon atoms removed from the double bond, is the carbon-to-carbon bond at which the scission occurs. There are certain olefins which do not contain in their molecular make-up a carbon-carbon bond in the position beta to the double bond and, therefore, do not undergo the same reactions when subjected to thermal decomposition conditions. These olefins are ethylene, propylene, butene-2, isobutene, 2-methyl butene-2, and 2,3-dimethyl butene-2, and are usually referred to as refractory olefins. Since these olefins do not undergo similar chain scission as do olefins which contain in their molecule a carbon-to-carbon bond in the beta position to the double bond, these refractory olefins are not considered to be within the scope of the olefins which are to be cracked in accordance with this invention.

It has been found that the objects of this invention are accomplished by subjecting olefins, which have in their molecule a carbon-carbon bond which is in a position beta to the double bond, to conditions of temperature and time suitable or sufficient to cleave the carbon-carbon bond which is in a position beta to the double bond, while said olefin is in the presence of an olefin cracking promoter comprising methylene chloride.

In general the practice of this invention may be carried out in any conventional manner which is usually employed in the thermal cracking of olefins.

Generally the conditions which may be employed in the practice of this invention may vary widely, for instance the cracking temperature may vary broadly from about 400° C. to about 900° C. However, more preferred cracking temperatures are from about 600° C. to about 750° C. The time in which the olefins are in the cracking zone may range broadly from about 0.001 to about 3.0 seconds. However, it is more preferable to employ times varying from about 0.05 to about 0.5 second. These times which are referred to are usually called residence times and are defined as the time required for one mol of gas whether it be pure olefin or in mixture with the diluents to pass through the cracking zone.

As was stated above, generally olefins are cracked either as pure hydrocarbons or as mixtures with other

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diluent gases. These diluent gases may be such materials as steam, carbon dioxide, hydrogen, paraffins, the refinery olefins, or any other inert gaseous substance which does not materially affect the cracking process or react with either the feed stock or products other than to act generally as a diluent. The ratio of this diluent gas may be widely varied depending on conditions, but it is usually employed in mol ratios of from about 0.5/1 to about 15/1 moles of diluent per mol of olefin. If more than about 15/1 mol ratio is employed, the process tends to become uneconomical. Therefore, it is preferred to use a diluent to olefin mol ratio ranging from about 2/1 to about 4/1.

The pressure employed in the cracking zone may be varied from a low of 10 milliliters of mercury to 500 pounds per square inch gauge or even higher. However, it is usually preferred that the pressure range from about atmospheric to about 100 p.s.i. with about 1-2 atmospheres being preferred.

As was stated previously the olefin cracking promoter employed in this invention is methylene chloride. The amount of methylene chloride employed in the practice of this invention has not been found to be too critical. Of course, sufficient promoter should be employed to obtain some beneficial effect, on the other hand, for the sake of economy, no more promoter should be employed than is necessary. Generally it has been the practice to employ from about 0.5 to about 50 mole percent of methylene chloride based on the total moles of olefin desired to be cracked, with about 5 to 10 mol percent being preferred.

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 1/4-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 temperature. The methylene chloride was added to the olefin feed stream. (It could have been added separately to the cracking reactor.) The water and the olefin were pumped at the proper rates necessary to produce the H₂O/hydrocarbon ratio 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 resulting from the cracking operation were collected by means of cooled receivers, if liquid, and were metered at atmospheric and room temperature conditions, if gas. The products were analyzed for content and yields by conventional analytical methods. Conventional recycle techniques were employed to obtain the ultimate yield.

The results of each of the experiments in the following examples as well as the operating conditions are reported in tables below. Column 1 is the experiment number; column 2 is the residence time in seconds; column 3 is the temperature employed in the cracking operation

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in degrees Centigrade; column 4 is the material employed as the cracking promoter with the amount employed in mol percent based on the olefin to be cracked; (Where no promoter was employed this column lists "none"); column 5 is the mol percent yield of isoprene per pass based on the 3-methyl pentene-2 charged; column 6 is the reaction efficiency or ultimate yield and is the amount of isoprene obtained based on the 3-methyl pentene-2 charged using conventional recycle techniques.

Example

In this example 3-methyl pentene-2 was the olefin cracked. Steam was used as a diluent at a mole ratio of water to hydrocarbon of approximately 3/1.

Experiment No.	Time	Temperature	Promoter	Yield	Efficiency
1.-----	0.15	675	None-----	15.33	60.5
2.-----	0.15	676	CH ₂ Cl ₂ -5%-----	25.40	68.4
3.-----	0.15	672	CH ₂ Cl ₂ -9%-----	26.45	69.0

From the above experiments it can be seen that the practice of this invention (as exemplified by Runs 2 and 3) shows a marked increase in the yield of isoprene obtained per pass and a higher reaction selectivity (efficiency) to isoprene than that obtained in a true thermal cracking operation (exemplified by Run No. 1).

Other similar improvements may be obtained when the general techniques of these examples and the other specific teachings mentioned elsewhere in this application are applied to other olefins having in their molecules a carbon-carbon bond in a position beta to the double bond.

The list of olefins set forth below are representative examples of olefins, the cracking of which may be enhanced by the promoter of this invention.

Representative among the olefins which will decompose to form predominantly butadiene-1,3 when cracked in accordance with the practice of this invention 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 2-methyl butadiene-1,3 or isoprene when cracked in accordance with the practice of this invention 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 which will decompose to form predominantly 2-ethyl butadiene-1,3 when cracked in accordance with the practice of this invention are 3-ethyl pentene-2; 2-ethyl pentene-2; 3-ethyl hexene-2; 3-methyl-2-ethyl pentene-1.

Representative among the olefins which will decompose to form predominantly 2,3-dimethyl butadiene-1,3 when cracked in accordance with the practice of this invention are 2,3-dimethyl pentene-2; 3-methyl-2-ethyl butene-1; 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 will decompose to form predominantly 3-methyl pentadiene-1,3 when cracked in accordance with the practice of this invention are 3-methyl hexene-3; 3-methyl heptene-3; 3,4-dimethyl hexene-2; 3,6-dimethyl heptene-3.

Representative among the olefins which will decompose to form predominantly 2-methyl pentadiene-1,3 and 4-methyl pentadiene-1,3 when cracked according to the practice of this invention are 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.

Representative among the olefins which will decompose to form predominantly piperylenes when cracked in accordance with the practice of this invention 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.

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. An isoprene producing process which comprises providing a mixture of (a) at least one olefin from the group of 2-methyl pentene-2; 3-methyl pentene-2; 2-ethyl butene-1; 2,3-dimethyl butene-1; 2-methyl hexene-2 and 3-methyl hexene-2 and (b) at least 0.5 mol percent, based on the total mols of said olefin, of methylene chloride, subjecting said mixture to temperatures ranging from about 400° C. to about 900° C. for periods of time ranging from about 0.05 to about 0.5 second at pressures not exceeding about 100 p.s.i., to cleave the carbon-to-carbon single bond which is in the position beta to the double bond of said olefin, thereby forming isoprene and recovering said isoprene.

2. The method of preparing isoprene which comprises subjecting 3-methyl pentene-2 in the presence of steam at a mole ratio of water to hydrocarbon of approximately 3/1 and methylene chloride in the amount of from about 5 to 10 mole percent based on the total moles of said 3-methyl pentene-2 to temperatures varying from about 600 to about 750° C. for times varying from about 0.05 to about 0.5 second, thereby cleaving the carbon-to-carbon bond in the position beta to the double bond to form isoprene.

3. The method of preparing isoprene which comprises subjecting 2-methyl pentene-2 in the presence of steam at a mole ratio of water to hydrocarbon of approximately 3/1 and methylene chloride in the amount of from about 5 to 10 mole percent based on the total moles of said 2-methyl pentene-2 to temperatures varying from about 600 to about 750° C. for times varying from about 0.05 to about 0.5 second, thereby cleaving the carbon-to-carbon bond in the position beta to the double bond to form isoprene.

4. A butadiene-1,3 producing process which comprises providing a mixture of (a) at least one olefin from the group of pentene-2 and hexene-2; and (b) at least 0.5 mol percent, based on the total mols of said olefin, of methylene chloride, subjecting said mixture to temperatures ranging from about 400° C. to about 900° C. for periods of time ranging from about 0.05 to about 0.5 second at pressures not exceeding about 100 p.s.i., to cleave the carbon-to-carbon single bond which is in the position beta to the double bond of said olefin, thereby forming butadiene-1,3 and recovering said butadiene-1,3.

5. A 2-ethyl butadiene-1,3 producing process which comprises providing a mixture of (a) at least one olefin from the group of 3-ethyl pentene-2; 2-ethyl pentene-2 and 3-ethyl hexene-2 and (b) at least 0.5 mol percent, based on the total mols of said olefin, of methylene chloride, subjecting said mixture to temperatures ranging from

about 400° C. to about 900° C. for periods of time ranging from about 0.05 to about 0.5 second at pressures not exceeding about 100 p.s.i., to cleave the carbon-to-carbon single bond which is in the position beta to the double bond of said olefin, thereby forming 2-ethyl butadiene-1,3 and recovering said 2-ethyl butadiene-1,3.

6. A piperylene producing process which comprises providing a mixture of (a) at least one olefin from the group of hexene-3; 4-methyl pentene-2; heptene-3 and 4-methyl hexene-2 and (b) at least 0.5 mol percent, based on the total mols of said olefin, of methylene chloride, subjecting said mixture to temperatures ranging from about 400° C. to about 900° C. for periods of time ranging from about 0.05 to about 0.5 second at pressures not exceeding about 100 p.s.i., to cleave the carbon-to-carbon single bond which is in the position beta to the double bond of said olefin, thereby forming piperylene and recovering said piperylene.

7. A 2,3-dimethyl butadiene-1,3 producing process which comprises providing a mixture of (a) at least one olefin from the group of 2,3-dimethyl pentene-2; 3-methyl-2-ethyl butene-1 and 2,3-dimethyl heptene-2 and (b) at least 0.5 mol percent, based on the total mols of said olefin, of methylene chloride, subjecting said mixture to temperatures ranging from about 400° C. to about 900° C. for periods of time ranging from about 0.05 to about 0.5 second at pressures not exceeding about 100 p.s.i., to cleave the carbon-to-carbon single bond which is in the position beta to the double bond of said olefin, thereby forming 2,3-dimethyl butadiene-1,3 and recovering said 2,3-dimethyl butadiene-1,3.

8. A 3-methyl pentadiene-1,3 producing process which comprises providing a mixture of (a) at least one olefin from the group of 3-methyl hexene-3; 3,4-dimethyl hexene-2 and 3-methyl heptene-3 and (b) at least 0.5 mol percent, based on the total mols of said olefin, of methylene chloride, subjecting said mixture to temperatures ranging from about 400° C. to about 900° C. for periods of time ranging from about 0.05 to about 0.5 second at pressures not exceeding about 100 p.s.i., to cleave the carbon-to-carbon single bond which is in the position beta to the double bond of said olefin, thereby forming 3-methyl pentadiene-1,3 and recovering said 3-methyl pentadiene-1,3.

9. A 2-methyl pentadiene-1,3 producing process which comprises providing a mixture of (a) at least one olefin from the group of 2,4-dimethyl pentene-2; 2-methyl heptene-3 and 2-propyl pentene-2 and (b) at least 0.5 mol percent, based on the total mols of said olefin, of methylene chloride, subjecting said mixture to temperatures ranging from about 400° C. to about 900° C. for periods of time ranging from about 0.05 to about 0.5 second at pressures not exceeding about 100 p.s.i., to cleave the carbon-to-carbon single bond which is in the position beta to the double bond of said olefin, thereby forming 2-methyl pentadiene-1,3 and recovering said 2-methyl pentadiene-1,3.

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