Jan. 15, 1974 R. L. BANKS 3,785,956
SELECTIVE OLEFIN DISPROPORTIONATION AND THE USE THEREOF TO PRODUCE HIGH OCTANE GASOLINES
Filed Dec. 10, 1971 2 Sheets-Sheet 1

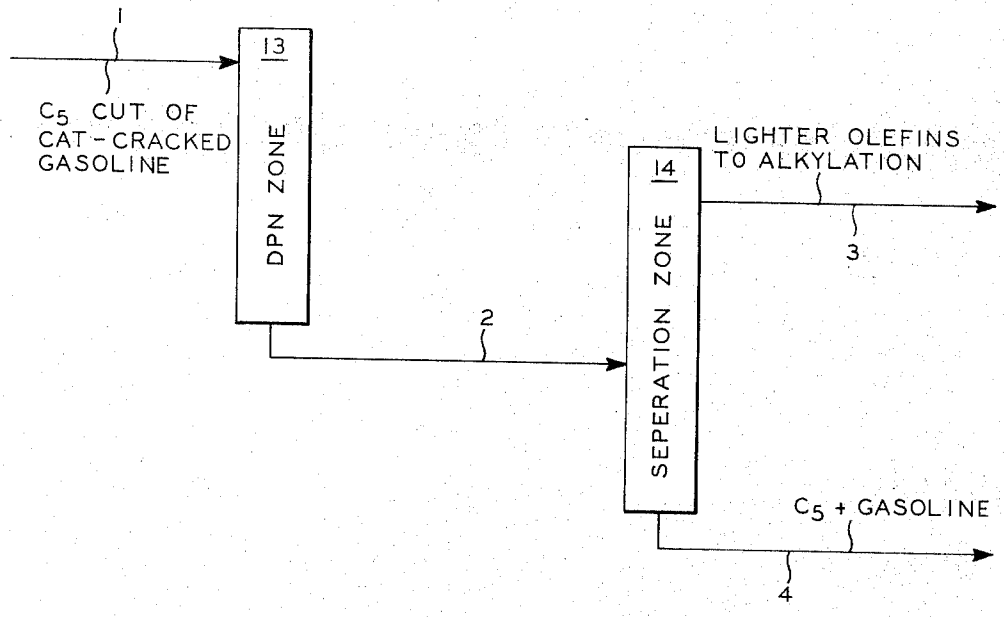

FIG. 1

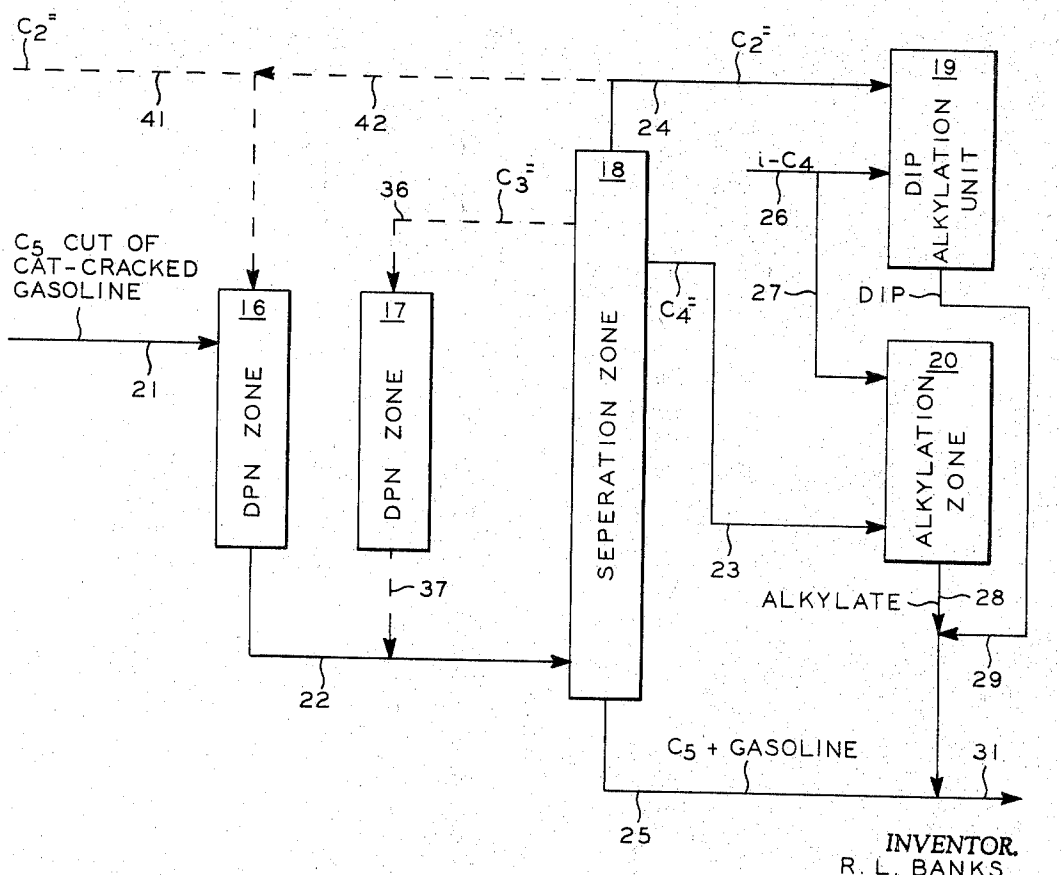

FIG. 2

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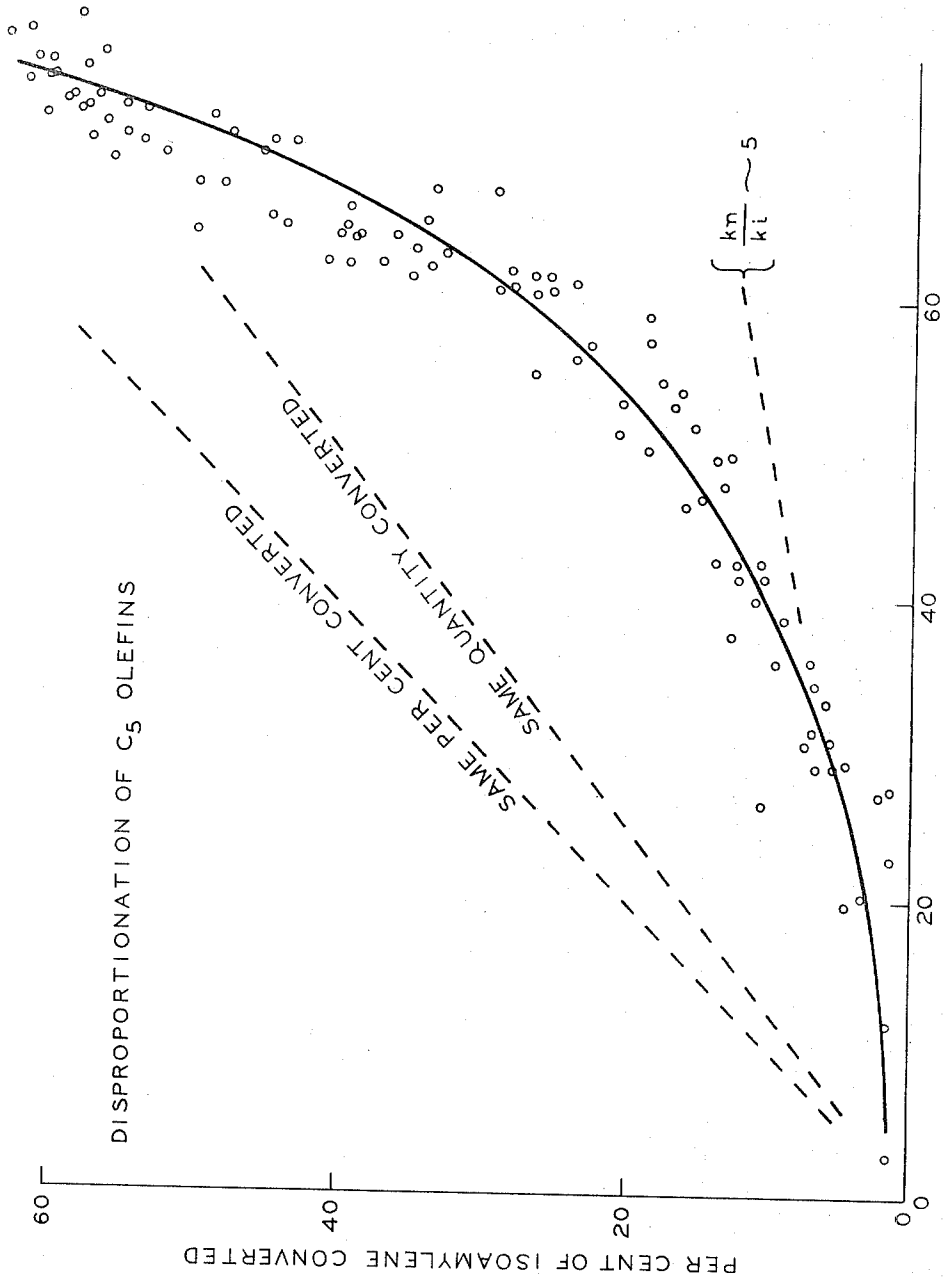

FIG. 3

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United States Patent Office 3,785,956 Patented Jan. 15, 1974

3,785,956

SELECTIVE OLEFIN DISPROPORTIONATION AND THE USE THEREOF TO PRODUCE HIGH OCTANE GASOLINES

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Filed Dec. 10, 1971, Ser. No. 206,734
Int. Cl. C07c 3/62; C10g 37/06
U.S. Cl. 208—93 12 Claims

ABSTRACT OF THE DISCLOSURE

The disproportionation of mixtures of branched and unbranched disproportionatable olefins in the presence or absence of ethylene is improved by adjusting the conversion to a specified level thereby increasing the selectivity of the reaction to the conversion of the unbranched olefins. The process has particular utility in increasing of the quality of olefinic gasoline streams in that the lower octane-rated unbranched olefins can be selectively removed from the gasoline by conversion to other olefins while substantially retaining the higher octane-rated branched olefins. In this aspect, a process for increasing the octane value of olefinic gasoline streams is provided which comprises the steps of separating a C_5 fraction from an olefinic gasoline stream, the C_5 fraction containing both pentenes and isopentenes, selectively disproportionating the C_5 stream, with or without the presence of added ethylene, to convert more of the normal pentenes than the isopentenes, alkylating the resulting butenes and lighter olefins with isobutane, and combining the alkylate and remaining gasoline to provide a high octane gasoline having a reduced light olefins content. In a modification of the above described multistep process produced propylene is disproportionated in a second olefin disproportionation zone, to provide additional butenes for alkylation and ethylene for reaction with n-pentenes in the first step of the process.

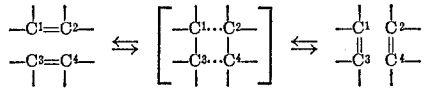
BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to olefin disproportionation. In a further aspect this invention relates to a method of increasing the octane value of olefinic gasoline streams using olefin disproportionation and alkylation steps.

Description of the prior art

The reaction of olefinic materials to produce other olefinic materials wherein the reaction can be visualized as the breaking of two existing double bonds between first and second carbon atoms, and between third and fourth carbon atoms, respectively, and the formation of two new double bonds, such as between the first and third carbon atoms and the second and fourth carbon atoms, respectively, and wherein the two new double bonds can be on the same or different molecules, has been called "the olefin reaction." The breaking and formation of these bonds can be visualized by using a mechanistic scheme involving a cyclobutane transition state. Thus, two unsaturated pairs of carbon atoms combine to form a 4-center (cyclobutane) transition state which then disassociates by breaking either set of opposing bonds. This reaction can be illustrated by the following formulas:



Other terms have been utilized to describe the reactions of olefinic materials which are within the scope of the olefin reaction as defined above. These include such terms as

"olefin disproportionation," "olefin dismutation," "transalkylidenation," and "olefin metathesis." Throughout the specification and claims the term "olefin disproportionation" is used as a matter of choice and is deemed to be equivalent to the above-mentioned terms, including the olefin reaction terminology. Numerous catalyst systems have been reported which effect this reaction, including the catalyst of U.S. Pats. 3,261,879, Banks (1966), and 3,365,513, Heckelsberg (1968).

One important embodiment of the olefin disproportionation reaction is the process wherein propylene is smoothly and efficiency converted to approximately equimolar amounts of ethylene and n-butenes. Similarly, other olefins such as pentenes, hexenes, and heptenes can also be disproportionated, either singly or in mixtures to produce other olefins of both higher and lower molecular weight. The disproportionation of n-pentenes to produce other olefins such as octenes, heptenes, hexenes, butenes, propylene, and ethylene is also a reaction which has been reported in the prior art.

Still another important aspect of the olefin disproportionation reaction is the embodiment wherein a mixture of ethylene and a suitable higher olefin is disproportionated. The presence of ethylene in the reaction mixture changes the nature of the olefinic products such that the higher olefin is converted into a lower olefin. Such a result has been term "ethylene cleavage" or "etheneolysis." Thus, olefins such as n-pentenes can be converted to a lower olefin such as propylene. This result is often promoted by the presence of some double bond isomerization activity within the reaction zone.

Today, the oil industry faces the problem of upgrading the octane values of gasoline produced in refinery operations. This problem had its genesis in the heavily industrialized countries of the world because of pollution of the atmosphere by automobile exhaust emissions. Technological development to abate such pollution has resulted in the use of catalytic exhaust gas treators. These catalytic mufflers employ conversion catalysts which are sensitive to lead compounds in the exhaust. Thus the use of lead in gasolines has been greatly curtailed. Therefore, the producers of gasolines have been requested to upgrade the octane value of their refinery gasolines to meet the high performance requirement of the modern internal combustion engine without the assistance of added alkyl lead compounds.

OBJECTS OF THE INVENTION

It is an object of this invention to modify the products obtained from the disproportionation of mixtures of branched and linear olefins. It is a further object of this invention to upgrade olefinic gasolines to gasolines having higher octane values. Other objects and advantages of the present invention will be apparent to those skilled in the art from the following summary of the invention, detailed description of the invention and the claims.

SUMMARY OF THE INVENTION

I have discovered that the olefin disproportionation reaction, when converting a mixture of branched and linear disproportionation olefins, either in the presence or absence of added ethylene, can be made selective for the linear olefins in the reactant mixture by adjusting the level of conversion in the olefin disproportionation reaction zone. By adjusting the level of conversion to a range of from about 30 to about 50 percent of the unbranched olefins in the mixture, a relatively small amount of the branched olefins are converted. Accordingly, the process of my invention comprising passing a mixture of linear and branched acylic olefins over an olefin disproportionation catalyst under reaction conditions such that the level

of conversion of the linear olefins is in the range of from about 30 to about 50 percent.

In a further aspect of my invention, the octane value of an olefinic gasoline is increased by first subjecting the gasoline to separation to provide a stream rich in C_5 olefins, subjecting the C_5 rich olefin stream to olefin disproportionation in the absence of added ethylene as mentioned above to selectively convert a substantial amount of the lower octane-rated linear C_5 olefins to heavier and lighter acyclic olefins, while substantially retaining the higher octane-rated branched olefins, and then separating the lighter olefins from the effluent of the reaction to provide a stream comprising the lighter olefins and stream comprising C_5^+ olefins. Additionally, the lighter olefins stream, e.g., propylene and butenes, can be alkylated with isobutane to provide high octane alkylates which can then be blended with C_5^+ olefins. Additionally, the lighter olefin stream, e.g., propylene and butenes, can be alkylated with isobutane to provide high octane alkylates which can then be blended with the C_5^+ olefin stream and with the remaining portion of the original olefinic gasoline.

In a further aspect of my invention, the octane value of an olefin containing gasoline stock is increased by first subjecting the gasoline to a separation step to provide a C_5 cut rich in olefins. The C_5 stream is then contacted with an olefin disproportionation catalyst, preferably in the presence of ethylene, under selective reaction conditions, to convert a substantial amount of the lower octane-rated linear C_5 olefins to olefins, while substantially retaining the higher octane-rated branched olefins, lighter olefins of ethylene, propylene and butenes. The olefin disproportionation reactor effluent is separated to provide an ethylene stream, a butenes stream, and an isoolefin-enriched C_5 gasoline stream. The ethylene stream is passed to an alkylation unit wherein the ethylene and isobutane are converted to diisopropyl (DIP). Alternatively, a portion of the ethylene stream is returned to the disproportionation zone as a recycle. The butenes stream is passed to an alkylation zone wherein the butenes and isobutenes are converted ot a high octane C_8 alkylate. The high octane C_8 alkylate stream, the diisopropyl stream and the C_5 gasoline stream can be combined with the original olefin gasoline stock to provide a high octane gasoline as a product of the process.

In still a further aspect of my invention, the separation of the olefin disproportionation effluent as discussed above also provides a propylene stream. This propylene stream is passed to a second olefin disproportionation unit to provide additional ethylene and butenes for increased production of diisopropyl and C_8 alkylate.

BRIEF DESCRIPTION OF DRAWING

The three figures of the drawing illustrate certain aspects of my invention. FIG. 1 is a simplified flow diagram of my process showing the selective olefin disproportionation of a C_5 cut from an olefinic cat-cracked gasoline. FIG. 2 is a simplified flow diagram of my process showing the steps of selective olefin disproportionation, a second olefin disproportionation step, and ethylene-isobutane alkylation and butene-isobutane alkylation steps. FIG. 3 is a graph of data showing the conversion of isoamylenes versus the conversion of n-amylenes when a mixed amylene stream is passed over an olefin disproportionation catalyst. The data were obtained over a variety of reaction conditions.

DETAILED DESCRIPTION OF THE INVENTION

A starting material for the process of my invention is an olefinic gasoline having at least about 10 weight percent of olefin hydrocarbons. The gasoline will preferably have a boiling end point which does not exceed 450° F. The olefin content is advantageously from about 20 to about 70 weight percent. Such streams are readily available in refinery operations and are generally available as a product from a catalytic cracker unit. Preferably, the feed is a full range cat-cracked gasoline. However, a full range cat-cracked gasoline can be fractionated to provide suitable gasoline fractions for my process which are high in olefin and low in aromatics.

My processes have the unique advantages of producing generally increased octane values and a reduced lower olefin content while substantially increasing the volume of gasoline which is available for motor fuel when compared to the volume and octane value of the cat-cracked gasoline starting material.

This advantage is obtained by adjusting the reaction conditions of the olefin disproportionation reaction zone to provide a conversion of the normal feed olefins within the range of from 30 to 50 percent. At this level, the conversion of n-amylenes is much greater than the conversion of isoamylenes. This relationship is true both in the presence and absence of added ethylene. Thus, the effluent from the disproportionation zone retains the higher octane-rated branched olefins, while the newly formed ethylene, propylene and butenes result primarily from the conversion of the lower octane-rated linear amylenes.

Although the use of selected conditions in the olefin disproportionation reaction is especially suitable for the preparation of high octane gasolines, this aspect of my invention has much broader applicability. Thus, a mixture of branched and unbranched olefins having from 4–20 carbon atoms, preferably 4–8 carbon atoms, per molecule can be subjected to disproportionation conditions such that a substantial quantity of the unbranched olefins are converted while substantially retaining the branched olefins. Suitable olefins include the butenes, pentenes, hexenes, heptenes, octenes, and the like. It is not necessary that the mixed feed stream contain branched and unbranched isomers of only one carbon number. Thus, a stream comprising linear pentenes, and isohexenes can be selectively disproportionated such that substantial amounts of the linear olefins (e.g. n-pentenes) are converted while relatively small amounts of the branched olefins (e.g. isohexenes) are converted, thus enriching the mixture in branched olefins.

Those skilled in the olefin disproportionation art are aware that the extent of conversion is largely dependent upon the reaction conditions such as temperature, the catalyst selected, and reaction time or space velocity. Accordingly, the exact conditions employed within the reaction zone will be dependent, for example, on the particular catlyst chosen and on the temperature range at which it exhibits optimum activity and selectivity. Preferably, however, the particular olefin disproportionation catalyst is employed at a temperature which is optimum for that catalyst. The space rate is then adjusted to bring the conversion level within the above specified range, preferably about 40 percent.

In view of the above, it is readily apparent that the use of any specific olefin disproportionation catalyst is not critical to my invention. As a matter of fact any catalyst which has the ability to disproportionate propylene to ethylene and butenes can be employed. Those solid catalysts which exhibit disproportionation activity at a temperature in excess of 400° F. are particularly suitable because they are characteristically more resistant to catalyst poisons sometimes associated with the feed.

Accordingly, I prefer to use catalysts such as molybdenum oxide on alumina, on silica or on aluminum phosphate; a tungsten oxide on silica, on alumina, or on aluminum phosphate; or rhenium oxide on alumina or on aluminum phosphate. The preparation, activation, maintenance and use of these catalysts have been reported in the prior art.

Of course, these catalysts can also be modified by various treatments also reported in the prior art. For example, treatment with alkali metals or alkaline earth metals, or admixtures with suitable double bond isomerization catalysts, or treatment with reducing gases such as H_2 or other gases including CO, all have been reported.

Any of these treatments can be employed in my process.

The conditions in each of the olefin disproportionation zones include reaction pressures in the range 0–2000 p.s.i.g., preferably 25–500 p.s.i.g.; space rates of 0.1–1000 WHSV, preferably 1–500 WHSV, and reaction temperatures broadly in the range of −60 to about 1200° F., but generally dependent upon the specific olefin disproportionation catalyst chosen. The following table illustrates some reaction temperatures for some specific catalysts.

Disproportionation catalyst	Temperature, ° F.	
	Broad	Preferred
WO_3/SiO_2	400–1,100	600–900
MoO_3/SiO_2	400–1,100	800–1,000
MoO_3/Al_2O_3	150–500	250–400
WO_3/Al_2O_3	100–750	550–650
Re_2O_7/Al_2O_3	−60–1,000	100–500
$WO_3/AlPO_4$	600–1,200	800–1,000
$Re_2O_7/AlPO_4$	−69–1,000	50–250
$MoO_3/AlPO_4$	600–1,200	800–1,000

Because of its high activity and high durability, the WO_3/SiO_2 catalyst is the presently preferred olefin disproportionation catalyst.

Of particular importance to my process is the admixture of a disproportionation catalyst with a suitable solid double bond isomerization catalyst because these combination catalysts generally provide increased conversions particularly when ethylene is in the feed olefin mixture. Some suitable double bond isomerization catalysts are MgO, ZnO, and alumina. Thus, my most preferred catalyst is a combination of magnesium oxide and tungsten oxide on silica where the amount of double bond isomerization catalyst is from about 2:1 to 10:1 parts by weight per part of the olefin disproportionation catalyst.

The alkylation steps employed in my process are equally well known in the prior art. Thus the diisopropyl alkylation step and the butene-isobutane alkylation step can employ any suitable catalyst reported in the prior art to convert isobutane and ethylene (in the presence or absence of propylene) and butenes to high octane alkylate. Suitable catalysts include sulfuric acid, $AlCl_3$, BF_3, HF, and the like, and mixtures thereof. For example, in a typical HF-alkylation process, a typical temperature is 80–100° F., with a 1–10 minute contact time and with an isobutane to olefin ratio of 6–15.

My invention can best be understood by reference to the drawing. FIG. 1 of the drawing illustrates one embodiment of my invention wherein a C_5 cut from a full range cat-cracked gasoline is used as feed in line **1** to the olefin disproportionation zone **13**. Therein, the mixed amylene stream is contacted under reaction conditions which result in a relatively high conversion of n-amylenes, and in a relatively low conversion of isoamylenes. The effluent from zone **13** is passed to separation zone **14** by way of line **2**. The effluent includes ethylene, propylene, and butenes, unconverted amylenes and a C_5^+ material which boils in the gasoline range. Separation zone **14**, removes the ethylene, propylene and butenes in line **3**, while the C_5^+ gasoline material is removed in line **4**. The C_5^+ gasoline can then be blended with depentanized cat-cracked gasoline to provide a gasoline having a greatly reduced light olefin content and the remaining olefins being enriched in isoolefins.

Another embodiment of my invention is illustrated in FIG. 2 of the drawing. A debutanized full range cat-cracked gasoline is subjected to fractionation (not shown) to provide a C_5 cut rich in olefins. The C_5 cut is passed via line **21** to disproportionation zone **16** wherein it is converted under the selective disproportionation conditions discussed previously. The effluent is withdrawn from zone **16** and passed in line **22** to separation zone **18**, In zone **18**, ethylene (and optionally propylene) is separated and removed via line **24**, butenes are separated and removed via line **23**, and a C_5^+ gasoline material is removed from line **25**.

Diisopropyl unit **19** receives ethylene (and optionally propylene) from line **24** and isobutane from line **26**. In the presence of a suitable alkylation catalyst and reaction conditions in zone **19** these materials are converted to diisopropyl alkylate which is removed by line **29**. Alkylation zone **20** receives isobutane from line **27** and butenes from line **23**. In zone **20**, the feed materials are catalytically converted to high octane C_8 alkylate which is removed from zone **20** by line **28**. The diisopropyl and C_8 alkylate are combined in line **28** and passed to line **24** for admixture with the C_5^+ gasoline in line **24**. A high octane gasoline having increased octane and increased volume is produced when the hydrocarbon mixture in line **31** is combined (not shown) with the depentanized cat-cracked gasoline used as the starting material to my process.

In another modification of my process, two additional steps are employed in the process as discussed above for FIG. 2 of the drawing. In the first step, propylene is removed from separation zone **18** via line **36** and passed to a second disproportionation zone **17**. This zone employs a suitable olefin disproportionation catalyst of the same type discussed above in this disclosure. However, the use of a double bond isomerization catalyst is optional, and preferably not employed to reduce catalyst expense. In zone **17**, the propylene feed is converted to ethylene and butenes and the effluent of this reaction zone is returned to separation zone **18** via lines **37** and **22**. This additional disproportionation unit greatly increases the amounts of ethylene and butenes available for alkylation and therefore, increases the quality of alkylate in line **31**.

The second modification feeds ethylene into the first olefin disproportionation zone **16** by way of line **41** and/or **42**. The amount of ethylene employed will be on the order of about 1 to about 20, preferably 2–10, moles of ethylene per mole of C_5 olefin feed. The ethylene cleavage of the mixed isoamylene and n-amylene stream under selective conditions provides still greater quantities of the light olefins for alkylation. If desired, a certain amount of the ethylene in line **24** can be returned to zone **16**, via line **42**, thus reducing the make-up ethylene requirements.

One additional advantage of my process resides in the fact that alkylation units require high purity feedstocks to operate at peak efficiency. The olefin disproportionation reaction is uniquely compatible with these units as the products from the reaction zones of the olefin disproportionation steps are free from contaminants often encountered in refinery streams using direct separation techniques which adversely affect the alkylation reaction.

Those skilled in the art will understand that the simplified flow diagrams of my process have omitted many items which are actually needed to operate the process. Thus, the use of pumps, fractionators, controls, and the like, have been omitted to simplify the discussion of my invention. The use of these apparatus and other steps is well within those skilled in the art. Thus, for example, it may be advantageous to hydrotreat the cat-cracked gasoline under very mild conditions to prevent contamination of the disproportionation catalyst. Similarly, it may be advisable to treat the feed by percolation through activated beds of materials such as alumina, mole sieves, magnesia, and the like, at low temperatures to purify contaminants of the feed to the first disproportionation zone.

My invention can be further understood by the following examples which are presented to illustrate the process of my invention. They should not be construed to limit the disclosure of my invention as provided above.

EXAMPLE I

A series of runs were performed on the C_5 cuts of different cat-cracker gasolines. Numerous variables were studied in these runs including different levels of feed purification, different process conditions including reaction temperature, pressure, and flow rates, and different combinations of olefin disproportionation catalysts

(WO_3/SiO_2)

and double bond isomerization catalysts (MgO). The results of these runs were then plotted on a graph as set forth in FIG. 3 of the drawing. That is, in FIG. 3, the points plotted thereon each represent the results of analysis of a sample taken during these runs calculated to percent conversion of isoamylenes versus percent conversion of n-amylenes.

The test reported below is representative of the runs used to provide the data reported in FIG. 3 of the drawing.

A C_5 cut of a cat-cracker gasoline was prepared and found to contain 23.3 percent n-pentene and 28.2 percent isopentene by analysis. The catalyst was 8 percent WO_3. 92 percent SiO_2 olefin disproportionation catalyst operated at a temperature of 750° F., 300 p.s.i.g., and 75 weight hourly space velicity. The catalyst was initially activated in air at 1100° F. for 2 hours, flushed with N_2, and then treated with carbon monoxide at 1100° F. for 15 minutes. The reactor was cooled to reaction temperature by flushing with N_2. The same activation procedure was subsequently used to regenerate the catalyst.

The system was operated for about 2 hours, the catalyst was then regenerated, and operated for 6 hours. Samples for each of the hours of operation during the 6 hour run were taken and analyzed by gas-chromatography.

A bed of activated MgO was then placed in the feed line to the reactor to further purify and dry the feed, the catalyst was again regenerated, and an additional 6 hour run was made taking sample each hour of the second 6 hour run (samples 7–12). The conversions of n-amylenes and isoamylenes are given below in Table I.

TABLE I

	Percent conversion	
	n-Amylenes	Isoamylenes
Sample:		
1	64.0	39.3
2	62.5	39.5
3	62.2	36.9
4	62.5	34.0
5	65.0	34.2
6	60.6	27.9
7	54.7	26.4
8	30.2	7.4
9	45.9	16.2
10	40.9	12.1
11	32.2	6.0
12	38.3	9.4

The above conversion results are a portion of the data plotted in FIG. 3. This example demonstrates that when the n-amylenes conversion level is in the range of 30–50 percent, very low amounts of isoamylenes are destroyed.

Also reported in FIG. 3 of the drawing are dashed lines which show the expected results if the rates of reaction of the isoamylenes and n-amylenes are equal. The upper dashed line shows the expected results for the equal percent conversion and the lower dashed line shows the expected results for the equal quantity converted with respect to the above-described C_5 stream. That the curve obtained by actual runs is far removed from the dashed lines signifying the expected results is strong testimony for the unexpected nature of the present invention.

In addition, these data enable one to calculate that the ratio of rate of reaction of n-amylenes (k_n) to the rate of isoamylenes (k_i) is about 5. This is also shown in FIG. 3 of the drawing as the lowest dashed line.

EXAMPLE II

A full range debutanized cat-cracked gasoline is used as the starting material for my process as illustrated in FIG. 1. The debutanized cat-cracked gasoline is fractionated to yield a C_5 cut having the composition given in the table below. The feed is passed over a catalyst of 1000 pounds of 8 percent tungsten oxide and 92 percent silica activated in flowing air prior to use at a temperature of from 1000 to 1100° F. Conditions in the disproportionation reactor **13** are a temperature of 720° F., a pressure of 350 p.s.i.g. and a space velocity of 125 pounds of feed per hour per pound of catalyst. Under these conditions, the conversion of C_5 olefins is about 27 percent, the conversion of isoamylenes is about 7 percent, and the conversion of n-amylenes is about 50 percent.

The material balance of Table II below illustrates the results achieved with my invention.

TABLE II

	Pounds per hour			
Stream number	1	2	3	4
Hydrocarbon:				
Ethylene		188	188	
Propylene		1,937	1,937	
Butenes	4,750	10,125	9,587	538
Butanes	1,375	1,375	1,325	50
Isopentane	39,625	39,625	1,128	38,437
n-Pentane	7,625	7,625	75	7,550
Isopentenes	32,250	29,963	588	29,375
n-Pentenes	27,875	13,937	275	13,662
C_6^+	8,500	20,225		20,225
Total	125,000	125,000	15,164	109,837

The above example illustrates how the present olefin disproportionation process can selectively convert a substantial amount of n-pentenes while retaining a substantial amount of the isopentenes from a mixture containing approximately equal amounts of each.

EXAMPLE III

A full range cat-cracked gasoline containing 67 percent olefin content is used as a feed to my process as illustrated in FIG. 2 of the drawing. In this example, ethylene is not used as additional feed. The cat-cracked gasoline is subjected to fractionation in the same manner as Example II to provide a C_5 cut. Reactor **16** uses the same catalyst and same conditions as reported above in Example II. Reactor **17** uses 160 pounds of 8 percent tungsten oxide and 92 percent silica catalyst activated in the same manner as the catalyst in Example II. The conditions in reactor **17** are a temperature of 725° F., a pressure of 325 p.s.i.g. and a space rate of 30 pounds of feed per hour per pound of catalyst. The material balance for the process is presented below in Table III.

TABLE III

	Pounds per hour						
Stream number	21	22	25	36	37	23	24
Hydrocarbon:							
Ethylene		188		35	648		801
Propylene		1,937		4,587	2,727	70	7
Butenes	4,750	10,125	538	117	1,327	10,797	
Butanes	1,375	1,375	50	30	30	1,325	
Isopentane	39,625	39,625	38,437			1,188	
n-Pentane	7,625	7,625	7,550			75	
Isopentenes	35,250	29,963	29,375			588	
n-Pentenes	27,875	13,937	13,662		37	312	
C_6^+	8,500	20,225	20,225				
Total	125,000	125,000	109,837	4,769	4,769	14,355	808

Stream **23** is the feed to the HF alkylation **20** unit along with isobutane. The alkylate produced in zone **20** and removed by line **28** is produced in the following yields and has the following properties:

Yield, barrels/barrel of butenes	1.75
Research octane number (RON)—clear	96.8
Motor octane number (MON)—clear	94.0

Stream **24** is the feed to the diisopropyl unit **19**. Alkylation with isobutane produces a diisopropyl effluent in line **29**. Streams **29**, **28**, and **25** are combined in line **31**. The line **31** effluent is then combined with the full range cat-cracked gasoline feed.

This process results in an increase in the MON value of 3–4 units, and the volume of gasoline range material is increased about 25 percent. RON value of the feed full range cat-cracked gasoline as compared to the processed gasoline blend are about the same.

EXAMPLE IV

A full range cat-cracked gasoline containing 65 percent olefin content is once again fractionated to provide a C_5 cut and processed as depicted in FIG. 2 of the drawing. In this example, ethylene is also provided to the disproportionation reactor **16** via line **41**. In this case all of the ethylene is placed on recycle through line **42**. That is, zone **19** is not included in the process.

The catalyst in reactor **16** is 15,000 pounds of 8 percent tungsten oxide and 92 percent silica disproportionation catalyst. It is intimately mixed with 75,000 pounds of MgO double bond isomerization catalyst. Reaction conditions in reactor **16** include a temperature of 750° F., a pressure of 350 p.s.i.g. and a weight hourly space velocity of 26. The catalyst in reactor **17** is 2,400 pounds of the same catalyst as used in reactor **16**. Reaction conditions in reactor **17** include a temperature of 725° F., a pressure of 325 p.s.i.g. and WHSV of 30. Each catalyst is activated in flowing air at a temperature of 1000–1100° F. prior to use.

The material balance for this process is given in Table IV below.

TABLE IV

	Pounds per hour							
Stream number	21	41	42	22	25	23	36	37
Hydrocarbon:								
Ethylene		10,997	176,203	166,960			1,700	10,943
Propylene	20			28,150		140	68,656	40,646
Butenes	7,110			27,520		25,727	274	18,481
Butanes	370			2,400		2,400	30	30
C_5^+ isoolefins	95,520			84,070	83,230	840		
C_5^+ n-olefins	35,870			16,990	16,820	170		560
C_5 saturates [1]	64,870			64,870	64,220	650		
Total	203,760	10,997	176,203	390,960	164,270	50,487	70,660	70,660

[1] Includes aromatics.

Stream **23** is the feed to HF alkylation unit **20**. The results of this step are shown above in Example III. When the alkylate in line **28**, the C_5^+ gasoline in line **25** and the remaining depentanized cat-cracked gasoline used to provide the C_5 feed to the process are combined, the following results are achieved. (1) Gasoline volume is increased 27 percent, (2) The clear motor octane rating is 84.3 compared to 79.1 of the original cat-cracked gasoline; clear research octane rating of both are about 94, (3) The olefin content of the combined gasoline is 39 percent compared to 65 percent for the original gasoline.

Reasonable variations and modifications of my process will be readily apparent to those skilled in the art without departing from the spirit or scope of my invention.

I claim:

1. In a process of disproportionating a feed stream comprising ethylene and a mixture of branched and linear disproportionable olefins in the presence of an olefin disproportionation catalyst, wherein the olefin disproportionation catalyst is tungsten oxide on silica, alumina, or aluminum phosphate; molybdenum oxide on alumina, silica, or aluminum phosphate; or rhenium oxide on alumina, silica, or aluminum phosphate, the improvement comprising selectively converting the linear olefin by maintaining the conversion of the linear olefin over the catalyst within a range of from about 30 to about 50 percent.

2. The process of claim **1** wherein the feed stream is a C_5 cut from fractionating a full range cat-cracked gasoline.

3. The process of claim **1** wherein the feed stream comprises a mixture of normal and isoamylenes.

4. The process of claim **1** wherein the olefin disproportionation catalyst is tungsten oxide on silica.

5. The process of producing a high octane gasoline stock by the steps of

(1) separating from a gasoline stream containing at least 10 weight percent olefin hydrocarbons a stream comprising isoamylenes and normal amylenes, and a C_6^+ gasoline stream;

(2) passing the stream comprising isoamylenes and normal amylenes over an olefin disproportionation catalyst, wherein the olefin disproportionation catalyst is tungsten oxide on silica, alumina, or aluminum phosphate; molybdenum oxide on alumina, silica, or aluminum phosphate; or rhenium oxide on alumina, silica, or aluminum phosphate, under reaction conditions which are adjusted to maintain the conversion of the normal amylenes in the range from about 30 to about 50 percent whereby the conversion is made selective for the conversion of normal amylenes, and to provide an effluent stream comprising ethylene, butenes, and a C_5^+ gasoline;

(3) separating the effluent from step (2) to provide a stream comprising the C_5^+ gasoline blending stock;

(4) combining the C_5 gasoline with the C_6^+ gasoline stream of step (1).

6. The process of claim **5** wherein the olefin disproportionation catalyst is tungsten oxide on silica.

7. A process for the preparation of a high octane gasoline by the steps of:

(1) separating a gasoline stream containing at least 10 weight percent olefin hydrocarbons to provide a stream comprising normal amylenes and isoamylenes and a stream comprising a C_6^+ gasoline;

(2) passing the C_5 stream of step (1) over an olefin disproportionation catalyst, wherein the olefin disproportionation catalyst is tungsten, oxide on silica, alumina, or aluminum phosphate; molybdenum oxide on alumina, silica, or aluminum phosphate; or rhenium oxide on alumina, silica, or aluminum phosphate, under reaction conditions which are adjusted to maintain the conversion of the normal isoamylenes in the range of from about 30 to 50 percent whereby the conversion is made selective for the conversion of normal amylenes, and to provide an effluent stream comprising ethylene, propylene, butenes and a C_5^+ gasoline;

(3) separating the effluent stream of step (2) to provide a stream of ethylene, a stream of propylene, a stream of butenes, and a C_5^+ gasoline stream;

(4) passing the stream of butenes from step (3) in admixture with isobutane to an alkylation zone con-

taining an alkylation catalyst to provide an effluent stream comprising a high octane alkylate;

(5) combining the C_6^+ gasoline stream of step (1), the C_5^+ gasoline stream of step (3) and the high octane alkylate stream of step (4) to provide a high octane gasoline having a motor octane value greater than the initial gasoline stream having at least 20 weight percent olefins.

8. The process of claim **7** further including the steps of:

(6) passing the stream of propylene from step (3) to an olefin disproportionation zone wherein the stream is catalytically converted to an effluent stream comprising ethylene and propylene, and

(7) returning the effluent stream to separation step (3) to provide increased quantities of ethylene and butenes.

9. The process of claim **7** further including the steps of:

(8) passing the stream comprising ethylene in admixture with isobutane to an alkylation zone to provide an effluent stream comprising diisopropyl alkylate, and

(9) combining the diisopropyl alkylate with the combined streams of step (5).

10. The process of claim **7** wherein step (2) is accomplished in the presence of added ethylene.

11. The process of claim **8** wherein step (2) is accomplished in the presence of ethylene, and the stream comprising ethylene of (3) is returned to step (2).

12. The process of claim **11** wherein the olefin disproportionation catalyst is tungsten oxide on silica.

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U.S. Cl. X.R.

208—79; 260—683 D, 683.4 R, 683.48

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 3,785,956

DATED : January 15, 1974

INVENTOR(S) : Robert L. Banks

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 10, line 65, delete "isoamylenes" and insert --- amylenes ---.

Signed and Sealed this

sixteenth Day of December 1975

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks