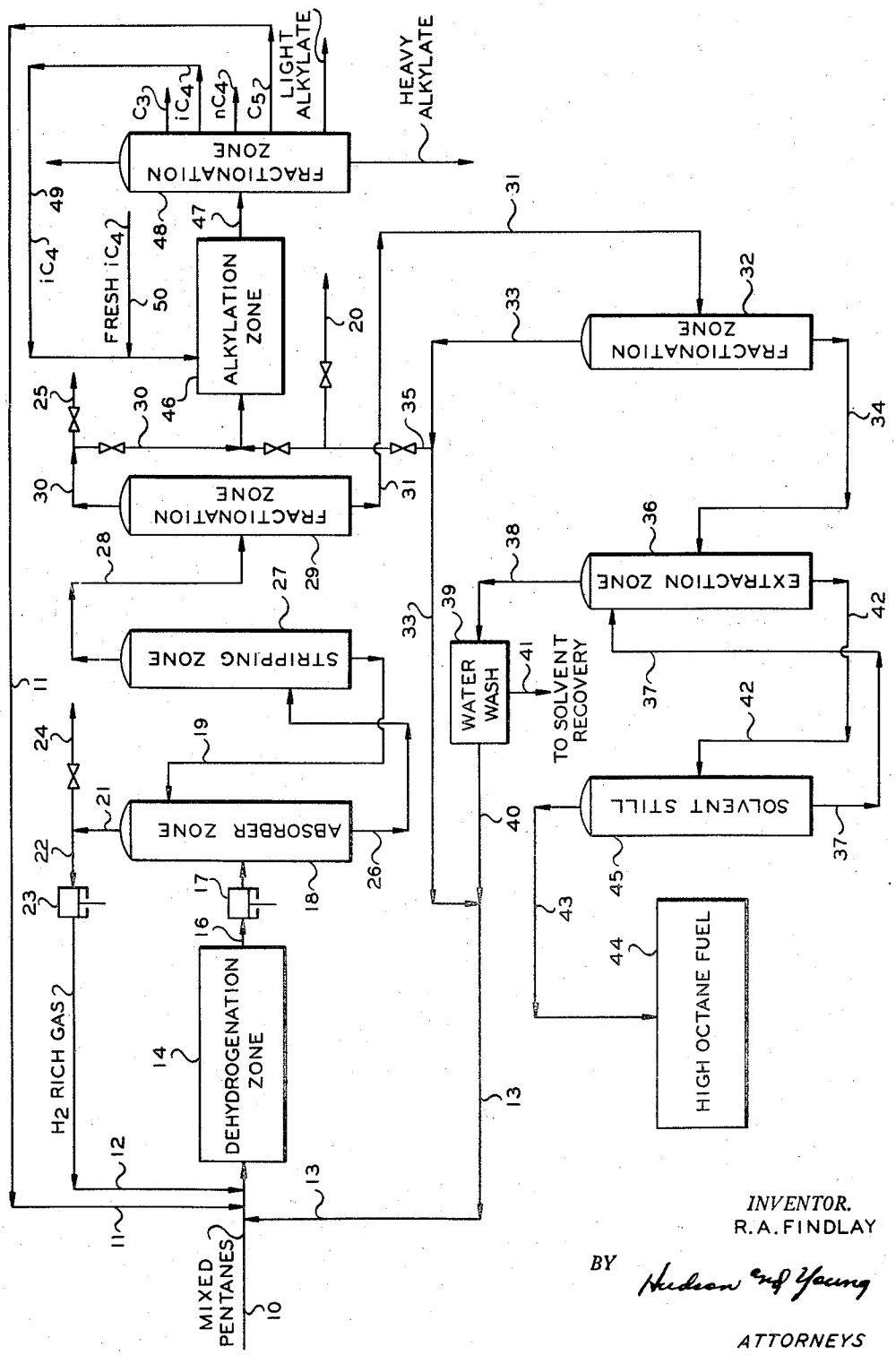
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PRODUCTION OF OLEFINIC C_5 HYDROCARBONS

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PRODUCTION OF OLEFINIC C_5 HYDROCARBONS

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This invention relates to the production of high octane fuels. In one aspect, this invention relates to the dehydrogenation of saturated C_5 hydrocarbons to produce olefinic C_5 hydrocarbons having increased octane numberms. In another aspect, this invention relates to the production of olefinic hydrocarbons by the dehydrogenation of saturated C_5 hydrocarbons, which olefinic hydrocarbons can be used in the blending of high octane fuels or further processed for the production of high octane fuels.

One source of blending stocks for the production of fuels for internal combustion engines, both automotive and aviation, has been the comparatively large supply of the normally liquid hydrocarbons, such as pentanes, isopentanes, etc. However, the amount of said hydrocarbons which can be blended into finished fuels is limited by the relatively low octane number and high volatility of said normally liquid hydrocarbons. In recent years, due to advances in the design of internal combustion engines, there has been an ever increasing demand for higher octane number fuels which has further decreased the amount of these hydrocarbons which can be so used. This has led to the development of processes such as dehydrogenation, isomerization, catalytic reforming, etc. for converting said normally liquid hydrocarbons into other hydrocarbons having increased octane numbers. In some instances, special fractions or cuts have been processed.

The demand for ever increasing octane numbers has created a demand for "super fuels," i. e., fuels having extraordinarily high blending octane numbers which can be used to blend with the lower octane number materials. It has been known that normal pentane and isopentane, having octane numbers of 58 and 91 respectively (research method) can be dehydrogenated to give olefinic C_5 hydrocarbons, for example, 2-pentene and 2-methyl-2-butene, having blending octane numbers within the range of 120 to 150, depending upon the material with which they are blended. The problem in the production of such fuels has been primarily two-fold: (1) separation of the desired olefinic hydrocarbons from the reaction product including other olefinic hydrocarbons and the unreacted saturated hydrocarbon; and (2) increasing the yield of the desired olefinic hydrocarbon.

I have discovered a combination of processing steps which provides for both a more efficient recovery of the desired olefinic C_5 hydrocarbons, and an increased yield of said desired olefinic C_5 hydrocarbons, for example, the 2-pentenes and 2-methyl-2-butene, from the reaction effluent of a saturated C_5 hydrocarbon dehydrogenation process. Herein and in the claims, unless otherwise specified, the term "2-pentene" is used to refer to and include both the cis- and trans- forms of 2-pentene.

An object of this invention is to provide an improved

method for the production of olefinic C_5 hydrocarbons from saturated C_5 hydrocarbons. Another object of this invention is to provide an improved method for separating desired olefinic C_5 hydrocarbons, such as 2-pentene and 2-methyl-2-butene, from the reaction effluent of a saturated C_5 hydrocarbon dehydrogenation process. Still another object of this invention is to increase the production of desired olefinic C_5 hydrocarbons in a saturated C_5 hydrocarbon dehydrogenation process. A still further object of this invention is to provide an improved process for converting relatively high volatility, relatively low octane number, saturated C_5 hydrocarbons into olefinic C_5 hydrocarbons having relatively low volatility and higher octane numbers. Other aspects, objects and advantages of the invention will be apparent to those skilled in the art upon study of this disclosure.

Thus, according to the invention there is provided a method comprising a combination of steps for producing a high octane fuel from a saturated C_5 hydrocarbon. Said saturated C_5 hydrocarbon is dehydrogenated in the presence of a suitable catalyst. Reactor effluent is deethanized and is then fractionated in a first fractionation step to obtain a first overhead fraction comprising paraffinic and olefinic C_3 to C_5 hydrocarbons lower boiling than isopentane, and a first bottoms fraction comprising isopentane, and paraffinic and olefinic C_5 hydrocarbons higher boiling than isopentane. Said first bottoms fraction is then fractionated in a second fractionation step to give a second overhead fraction comprising isopentane and olefinic C_5 hydrocarbons lower boiling than normal pentane, and a second bottoms fraction comprising normal pentane and C_5 olefinic hydrocarbons higher boiling than normal pentane. Said second bottoms fraction is then solvent extracted with a suitable selective solvent to obtain a raffinate comprising normal pentane which is recycled to said dehydrogenation step, and an extract comprising said C_5 olefinic hydrocarbons higher boiling than normal pentane, as a product of the process.

In one embodiment of the invention, the overhead from the first fractionation step, i. e., the paraffinic and olefinic C_3 to C_5 hydrocarbons lower boiling than isopentane, is removed and charged to an alkylation unit wherein the olefinic hydrocarbons are used to alkylate an isoparaffin, such as isobutane, and saturated C_5 hydrocarbons produced in said alkylation process are recycled as a part of the feed to the dehydrogenation step.

In another embodiment of the invention, at least a portion of the overhead from the second fractionation step, i. e., isopentane and olefinic C_5 hydrocarbons lower boiling than normal pentane, is charged to an alkylation unit wherein said unsaturated hydrocarbons are used to alkylate an isoparaffin, such as isobutane, and saturated C_5 hydrocarbons produced in the alkylation process are recycled as a part of the feed to the dehydrogenation step. Said alkylation unit can be the same to which the overhead from the first fractionation step is charged or a different alkylation unit. Since the olefins in the overhead stream from the second fractionation zone are predominately C_5 olefins it will be advantageous in some instances to provide separate alkylation because the alkylate produced from C_4 olefins has a higher octane number than that produced from C_5 olefins.

It is to be noted that in all embodiments of the invention, the overhead stream from the first fractionation step is removed and is not returned to the dehydrogenation step. A conventional method of operation would be to perform only one fractionation step and return

all the overhead stream therefrom, comprising isopentene and lower boiling hydrocarbons, to the dehydrogenation zone. By providing two fractionation steps I decrease the amount of olefins which are recycled to the dehydrogenation zone. In catalytic dehydrogenation processes, the dehydrogenation reaction tends to approach an equilibrium and the presence of excess olefins in the reaction zone will prevent the reaction from proceeding as far toward completion as it normally would in the absence of said olefins. Therefore, by removing said overhead stream from the first fractionation step and not returning it to the dehydrogenation zone I avoid the presence of excess olefins in the dehydrogenation zone and obtain a higher conversion per pass of the paraffin hydrocarbons to olefins.

A further advantage of my improved process is that by combining an alkylation step with the dehydrogenation step, the lower boiling olefinic hydrocarbons and the undesired olefinic hydrocarbons removed overhead from the first and second fractionation steps can be efficiently utilized to produce alkylate having a relatively high octane number and a relatively low volatility. Said alkylate is an excellent blending stock for the production of high octane fuels. A further advantage of my combination of a dehydrogenation step and an alkylation step is that the saturated C_5 hydrocarbons produced in the alkylation step can be dehydrogenated in the dehydrogenation step. Thus, each unit produces feed stock for the other unit. This is real and effective cooperation between the units of the combination.

It is within the scope of the invention to dehydrogenate normal pentane and isopentane separately, or in admixture.

The drawing is a diagrammatic flow sheet illustrating the several embodiments of the invention.

Referring now to the drawing, the invention will be more fully explained. A mixture of pentanes containing about 40 percent isopentane and about 60 percent normal pentane is charged through line **10** into dehydrogenation zone **14**. Pentanes from line **11**, isopentane plus C_5 olefins from line **13**, and a hydrogen rich gas from line **12**, all from sources hereinafter described, are mixed with said mixture of pentanes in line **10** and also charged to dehydrogenation zone **14**. Said dehydrogenation zone **14** can be either a fixed bed type or of the fluidized bed type. It is also to be understood that while shown in the drawing diagrammatically, dehydrogenation zone **14** includes such conventional equipment as a heating furnace and suitable separation equipment not shown in the drawing. Gaseous effluent from said dehydrogenation zone is passed through line **16** and compressor **17**, wherein it is compressed to about 50–150 p. s. i. g., and introduced into absorber zone **18** wherein it is contacted countercurrently with a suitable lean absorbent such as mineral seal oil introduced through line **19**. Said absorber **18** functions primarily as a deethanizer, i. e., normally gaseous hydrocarbons lower boiling than propane, and hydrogen are removed from the top thereof through line **21**. A portion of said gases can be recycled to the dehydrogenation zone via line **22**, compressor **23**, line **12** and line **10** as previously mentioned. Excess gases can be removed through line **24**. Rich absorbent is removed from the bottom of absorber zone **18** through line **26** and introduced into stripping zone **27**. Lean absorbent is recycled from stripping zone **27** via line **19** to said absorber zone **18**. Deethanized effluent is passed via line **28** into first fractionation zone **29** from which there is removed overhead through line **30** a first overhead fraction comprising paraffinic and olefinic C_3 to C_5 hydrocarbons lower boiling than isopentane. A first bottoms fraction is removed through line **31** and comprises isopentane, and paraffinic and olefinic C_5 hydrocarbons higher boiling than isopentane. Said first bottoms fraction is introduced into a second fractionation zone **32** from which there is removed a second overhead fraction via line **33** comprising isopentane and olefinic C_5 hydrocarbons lower boiling than normal pentane.

A second bottoms fraction, comprising norman pentane and C_5 olefinic hydrocarbons higher boiling than normal pentane, is removed from fractionation zone **32** via line **34** and introduced into solvent extraction zone **36** wherein it is contacted countercurrently with a suitable selective solvent introduced through line **37**. Normal pentane and other saturated hydrocarbons are removed overhead as a raffinate phase from zone **36** via line **38**, passed through water washing zone **39** for the removal of solvent, and returned via lines **40** and **13** to dehydrogenation zone **14**. Olefinic hydrocarbons, primarily 2-pentene and 2-methyl-2-butene are removed from zone **36** via line **42** as extract phase and introduced into solvent recovery still **45**. Solvent is removed from said still **45** via line **37** and returned to said extraction zone **36**. Said 2-pentene and 2-methyl-2-butene, are recovered from said still **45** and removed via line **43** to storage **44** as product of the process.

In one embodiment of the invention, the overhead stream in line **30** from the first fractionation zone **29** is introduced into alkylation zone **46**. Isoparaffin, such as isobutane, is introduced through line **50** into said alkylation zone. Butenes from other sources (such as refinery cracking operations) can also be added to alkylation zone **46** through a line not shown. Said hydrocarbons are contacted and admixed in the presence of a suitable alkylation catalyst such as hydrofluoric acid and said isoparaffin is alkylated by said olefins. Alkylation zone effluent is passed via line **47** into fractionation zone **48** wherein it can be fractionated according to any desired separation. The separation shown in the drawing is one most usually effected. Saturated C_5 hydrocarbons in the alkylation zone effluent are recycled via line **11** to dehydrogenation zone **14**. Isobutane is recycled via line **49** to alkylation zone **46**. If it is not desired to alkylate the overhead stream in line **30** said stream can be withdrawn via line **25** for other use.

In another embodiment of the invention, a portion of the overhead stream from the second fractionation zone **32** can be passed via lines **33** and **35** into said alkylation zone **46**. The amount of said second overhead stream passed to said alkylation zone is determined largely by the concentrations of olefins in said overhead stream. It is desirable to prevent buildup of a large olefin recycle so as to suppress diolefin formation and to favor the primary dehydrogenation reaction. The olefins in this stream are alkylated in the manner previously described. It is within the scope of the invention to alkylate the overhead streams from said first fractionation zone and from said second fractionation zone either separately or together.

Any suitable dehydrogenation catalyst can be employed in the dehydrogenation step of the invention. A presently preferred catalyst is an unsupported chromium oxide gel catalyst. Said catalyst can be employed in either pelleted or granular form, or in finely divided form. One advantageous way of preparing said catalyst is as follows. Acetic acid is added to a 10 percent aqueous solution of chromic nitrate until the solution contains 20 percent of acid. Ammonia is then added until in slight excess. The precipitated gel is removed from the supernatant liquid, washed thoroughly with water and slowly dried. The dried gel is dark colored, translucent and vitreous, and possesses a highly developed gel structure which is retained when the gel is heated in use as a catalyst. Further details regarding the preparation of said catalyst can be found in Patent 1,905,383, issued April 25, 1932, to Huppke et al.

The chromium oxide gel catalyst is preferred because it permits operation of the dehydrogenation step at a lower temperature than most other catalysts. It is desirable to carry out the dehydrogenation step at the lowest possible temperature for several reasons. (1) To decrease the

decomposition of the C_5 hydrocarbons to lower paraffin hydrocarbons. (2) To suppress the formation of diolefins which are undesirable because they tend to form gum in motor fuel and also to cause higher acid consumption in the alkylation step. (3) To favor the formation of 2-olefins rather than the formation of 1-olefins (at the lower temperatures, the equilibrium favors isomerization of the double bond toward the middle of the molecule). Other dehydrogenation catalysts which can be used include a 40 percent chromia—10 percent beryllia—50 percent alumina catalyst prepared as disclosed and claimed in Patent 2,483,929, issued October 4, 1949, to J. R. Owen; and a 20 percent chromia—80 percent alumina catalyst disclosed and claimed in Patent 2,606,159, issued August 5, 1952, to J. R. Owen; and other catalysts disclosed and claimed in said patents.

The dehydrogenation step can be carried out at temperatures ranging from 900 to 1150° F. However, in order to achieve the above advantages of low temperature operation, it is preferred to carry out said dehydrogenation step at temperatures within the range of 900 to 1000° F., more preferably at temperatures between 925 and 960° F.

As might be expected from the law of mass action, the dehydrogenation reaction is favored by low absolute or partial pressures. Low absolute pressures, i. e., below atmospheric pressure, while favorable to the dehydrogenation reaction are generally undesirable in commercial operations due to the difficulty of preventing leakage of air into the system. For this reason, it is customary to employ pressures somewhat above atmospheric, i. e., within the range of 0 to 50 p. s. i. g., preferably 0 to 30 p. s. i. g., and more preferably within the range of 0 to 15 p. s. i. g.

The space velocity in the dehydrogenation step will usually be in the range of 800 to 1600 gaseous volumes per volume of catalyst per hour. It is preferred to carry out the dehydrogenation reaction in the presence of hydrogen present in an amount of about 1 mol per mol of feed stock so as to suppress the formation of diolefins and to extend the life of the catalyst. Too much hydrogen should be avoided because the presence of excess hydrogen is unfavorable to the dehydrogenation reaction.

Operating conditions in the two fractionation steps of the invention will depend upon the composition of feed to the fractionation zones and the degree of separation which it is desired to effect as will be understood by those skilled in the art.

Any suitable selective solvent can be employed for the solvent extraction of the bottoms fraction from the second fractionation step, i. e., the separation of the normal pentane from the desired olefinic C_5 hydrocarbons. A presently preferred solvent is methyl Carbitol (diethylene glycol monomethyl ether) containing from 5 to 25 percent water, preferably 10 to 15 percent water. Said solvent is usually employed in a solvent to hydrocarbon ratio within the range of 10 to 20:1, preferably 12 to 15:1. The solvent extraction tower is usually operated at temperatures of about 100° F. and under sufficient pressure to maintain the hydrocarbons in liquid phase, e. g. about 25 p. s. i. g. Other solvents which can be used include furfural, aqueous phenol, and other glycol ethers similar to methyl Carbitol.

Operating conditions in the alkylation zone are generally as follows: isoparaffin to olefin ratio, within the range of 4.5:1 to 8:1 or higher; temperature 80 to 120° F.; and acid to hydrocarbon ratio about 1:1.

The following example will serve to further illustrate the invention.

EXAMPLE I

A mixture consisting essentially of about 40 percent isopentane and about 60 percent normal pentane is vaporized, mixed with hydrogen in an amount of about 1 mol of hydrogen per mol of charge stock, and passed through a dehydrogenation reactor containing a fixed bed of chromium oxide gel catalyst prepared as described above. Said catalyst bed is maintained at a temperature of 935° F. and under a pressure of 10 p. s. i. g. After being compressed and deethanized the effluent from the reaction zone is fractionated in a first fractionation step to give a first overhead fraction comprising C_3 hydrocarbon, 1-butene, 2-butene, butanes, and 3-methyl-1-butene, and a first bottoms fraction comprising isopentane, 1-pentene, 2-pentene, 2-methyl-2-butene and normal pentane. Said first bottoms fraction is then fractionated in a second fractionation step to give a second bottoms fraction comprising normal pentane, 2-pentene, and 2-methyl-2-butene. Said second bottoms fraction is then solvent extracted with 14 volumes of methyl Carbitol solvent containing 10 percent water to yield a raffinate comprising normal pentane, and an extract comprising 2-pentene and 2-methyl-2-butene. Said extract is obtained in a yield of 70.3 mol percent based on the fresh charge to the dehydrogenation step.

Table I below sets forth a material balance for this example.

Table I.—Material balance

	Fresh Charge, Mols	Recycle Stream, Mols	Combined Feed, Mols	Dehydro. Zone Effluent [1], Mols	Fractionator No. 1, Overhead, Mols	Fractionator No. 1, bottoms, Mols	Fractionator No. 2, Overhead, Mols	Fractionator No. 2, Bottoms, Mols	Raffinate, Mols	Extract (Product), Mols	Boiling Point, ° F.
C_3 (Propane, Propylene)				0.3	0.3						−43.9 to −48.3.
Butenes				0.5	0.5						23–26.
Butanes				0.5	0.4						14.3–31.1.
3-Methyl-butene-1				0.8	0.8						77.0.
Isopentane	8.4	32.8	41.2	33.1	0.3	32.8	32.5	0.5	0.3		82.4.
1-Pentene		3.3	3.3	3.3		3.3	3.3				85.5.
2-Methyl-1-butene		2.8	2.8	2.8		2.8	2.8				87.8.
Normal Pentane	12.5	41.5	54.0	41.9		41.9	0.4	41.5	41.1	0.4	97.2.
2-Pentene		0.2	0.2	7.4		7.4	0.1	7.3	0.1	7.2	97.3 Cis, 98.4 Trans.
2-Methyl-2-butene		0.2	0.2	7.7		7.7	0.1	7.6	0.1	7.5	101.5.
C_5 Diolefins		0.3	0.3	1.8		1.8		1.8	0.3	1.5	
Total—Mols	20.9	81.1	102.0	100.0	2.3	97.7	39.2	58.5	41.9	16.6	

[1] 2.0 mols gas (C_2 and lighter) removed in absorber after dehydrogenation.

The extract product of the invention (see Example I and Table I above), comprising 2-pentenes and 2-methyl-2-butene has an especially high blending octane number. When said product is blended with a platformate (obtained by catalytically reforming a straight-run gasoline, obtained from a mixture of West Texas and Gulf Coast crude oils, in the presence of a platinum-containing catalyst) in amounts of as low as only 10 percent by volume, there is a marked increase in the octane number. Table II given below shows tests on (1) said platformate, (2) a blend containing 90 volume percent of said platformate and 10 volume percent of mixed pentanes (the charge stock for Example I), and (3) a blend containing 90 volume percent of said platformate and 10 volume percent of the high octane fuel product of Example I.

Table II.—Blending information on product and feed

	Platformate	90% Platformate, 10% Pentanes (mixed)	90 % Platformate, 10% High-Octane Fuel (2-pentene,2-methyl-2-butene)
Reid Vapor Pressure, lb	4.10	5.70	5.35
Gravity, ° API	50.5	53.7	53.0
ASTM Distillation ° F.:			
IBP	119	99	104
10%	181	150	152
50%	260	253	254
90%	325	323	322
E. P	382	382	389
Octane No., Research +1 ml. TEL	91.5	91.0	94.7

A comparison of the data given above in Table II shows that the original mixed pentanes actually lower the octane number of the platformate when blended therewith; whereas, the high octane fuel product of the invention increases the octane number of said platformate by more than three numbers, showing that the blending octane number of said high-octane fuel product is about 123 in this instance. It is also to be noted that the Reid vapor pressure of the blend containing the high-octane fuel product of the invention is considerably lower than the Reid vapor pressure of the blend containing the mixed pentanes. The lower vapor pressure of the blend containing the high-octane fuel of the invention is an important advantage because more butane, or other desirable blending stocks having a high vapor pressure, can be blended into the final motor fuel. This not only makes it possible to produce more motor fuel but also operates to conserve natural resources such as normally gaseous hydrocarbons like butane, etc.

As will be evident to those skilled in the art, various modifications of the invention can be made, in view of the above disclosure, without departing from the scope of said invention.

I claim:

1. A process for the production of unsaturated C_5 hydrocarbons having increased anti-knock value from saturated C_5 hydrocarbons, which process comprises the combination of steps; contacting said saturated C_5 hydrocarbons with a dehydrogenation catalyst in a dehydrogenation zone to produce a mixture containing paraffinic and olefinic hydrocarbons; fractionating said mixture in a first fractionation zone to obtain a first overhead fraction comprising paraffinic and olefinic C_3 to C_5 hydrocarbons lower boiling than isopentane, and a first bottoms fraction comprising isopentane and paraffinic and olefinic C_5 hydrocarbons higher boiling than isopentane; fractionating said first bottoms fraction in a second fractionation zone to obtain a second overhead fraction comprising iso-pentane and olefinic C_5 hydrocarbons lower boiling than normal pentane, and a second bottoms fraction comprising normal pentane and olefinic C_5 hydrocarbons boiling higher than normal pentane; returning at least a portion of said second overhead stream to said dehydrogenation zone; solvent extracting said second bottoms fraction with a selective solvent to produce a raffinate comprising normal pentane and an extract comprising said C_5 olefinic hydrocarbons higher boiling than normal pentane; returning said raffinate to said dehydrogenation zone; and recovering said extract as product of the process.

2. A process according to claim 1 which comprises, in further combination, the steps of: passing said first overhead fraction to an alkylation zone; passing an isoparaffin to said alkylation zone; alkylating said isoparaffin with the olefins in said first overhead fraction in the presence of an alkylation catalyst under alkylation conditions; recovering unreacted isoparaffin from the effluent from said alkylation zone and returning same to said alkylation zone; recovering substantially saturated C_5 hydrocarbons from said alkylation zone effluent; and returning said C_5 hydrocarbons to said dehydrogenation zone as a portion of the charge stock thereto.

3. A process according to claim 1 which comprises, in further combination, the steps of: passing at least a portion of said second overhead fraction to an alkylation zone; passing an isoparaffin to said alkylation zone; alkylating said isoparaffin with the olefins in said second overhead fraction in the presence of an alkylation catalyst under alkylation conditions; recovering unreacted isoparaffin from the effluent from said alkylation zone and returning same to said alkylation zone; and recovering substantially saturated C_5 hydrocarbons from said alkylation zone effluent and returning said C_5 hydrocarbons to said dehydrogenation zone as a portion of the charge thereto.

4. A process according to claim 2 wherein at least a portion of said second fractionation zone overhead is passed to said alkylation zone.

5. The process of claim 2 wherein said isoparaffin is isobutane and said alkylation catalyst is hydrofluoric acid.

6. A process for the production of 2-pentene and 2-methyl-2-butene from a mixture of normal pentane and isopentane, which process comprises the combination of steps: contacting said mixture with a dehydrogenation catalyst in a dehydrogenation zone to produce a dehydrogenation zone effluent containing paraffinic and olefinic hydrocarbons; fractionating said effluent in a first fractionation zone to obtain a first overhead fraction comprising 1-butene, 2-butene, butanes, and 3-methyl-1-butene, and a first bottoms fraction comprising isopentane, 1-pentene, 2-methyl-1-butene, normal pentane, 2-pentene, and 2-methyl-2-butene; fractionating said first bottoms fraction in a second fractionation zone to obtain a second overhead fraction comprising isopentane, 1-pentene, and 2-methyl-1-butene, and a second bottoms fraction comprising normal pentane, 2-pentene, and 2-methyl-2-butene; returning at least a portion of said second overhead fraction to said dehydrogenation zone; solvent extracting said second bottoms fraction with a selective solvent and recovering a raffinate comprising normal pentane, and an extract comprising 2-pentene and 2-methyl-2-butene; returning said raffinate to said dehydrogenation zone; and recovering said extract as a product of the process.

7. A process according to claim 6 which comprises, in further combination, the steps of: passing said first overhead fraction to an alkylation zone; passing isobutane to said alkylation zone; alkylating said isobutane with the olefins in said first overhead fraction in the presence of hydrofluoric acid alkylation catalyst under alkylation conditions; recovering unreacted isobutane from the effluent from said alkylation zone and returning same to said alkylation zone; recovering substantially saturated C_5 hydrocarbons from said alkylation zone effluent; and returning said C_5 hydrocarbons to said dehydrogenation zone as a portion of the charge stock thereto.

8. A process according to claim 6 which comprises, in further combination, the steps of: passing at least a portion of said second overhead fraction to an alkylation zone; passing isobutane to said alkylation zone; alkylating said isobutane with the olefins in said first overhead fraction in the presence of hydrofluoric acid alkylation catalyst under alkylation conditions; recovering unreacted isobutane from the effluent from said alkylation zone and returning same to said alkylation zone; recovering substantially saturated C_5 hydrocarbons from said alkylation zone effluent; and returning said C_5 hydrocarbons to said dehydrogenation zone as a portion of the charge stock thereto.

9. A process according to claim 7 wherein at least a portion of said second fractionation zone overhead is passed to said alkylation zone.

10. A process according to claim 7 wherein said dehydrogenation catalyst is a chromium oxide gel catalyst; said dehydrogenation zone is operated at a temperature within the range of 900 to 1000° F., a pressure within the range of 0 to 30 p. s. i. g.; and said selective solvent is diethylene glycol monomethyl ether containing from 10 to 15 percent by volume of water.

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