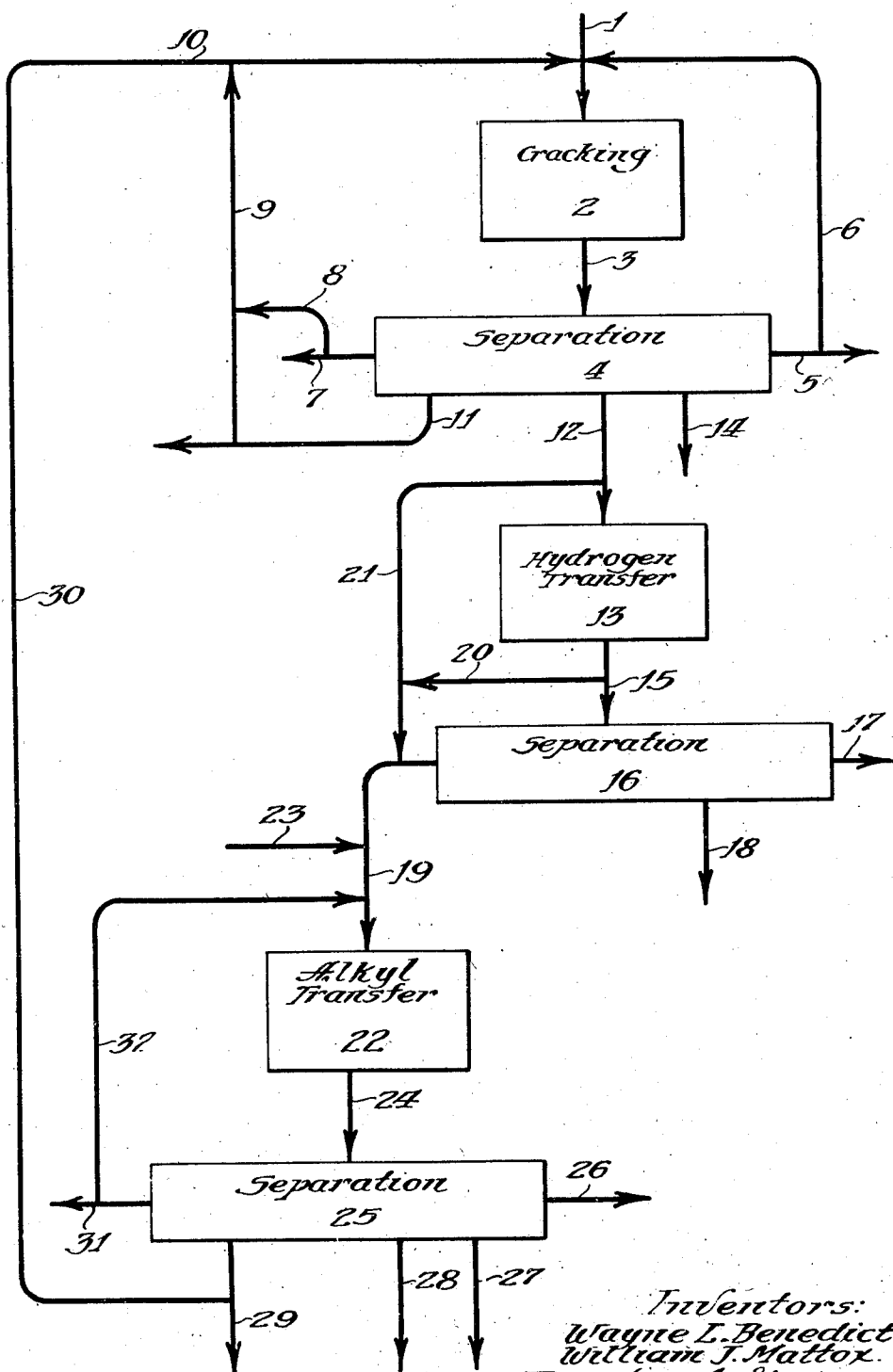


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CONVERSION OF HYDROCARBONS

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CONVERSION OF HYDROCARBONS

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This invention relates to a combination of interdependent and cooperative steps for the conversion of hydrocarbons into gasoline and alkyl aromatics.

In its broadest aspect, the invention comprises the cracking of hydrocarbon oil boiling above the range of gasoline primarily for the purpose of producing gasoline, and reacting at least a portion of the gasoline, which contains poly-alkylated aromatics, with benzene under conditions to effect transfer of alkyl groups from the poly-alkylated aromatics to the benzene and thereby to produce selected monoalkylated aromatics.

The invention is particularly applicable to a process for the production of aviation gasoline and selected mono-alkylated aromatics, such as toluene, ethylbenzene and the like. According to one embodiment of the invention, olefin-free alkylated aromatic hydrocarbons may be produced.

In one specific embodiment, the present invention comprises subjecting oil boiling above the range of gasoline to cracking in the presence of a cracking catalyst to produce a substantially saturated gasoline product, subjecting at least a portion of said gasoline to interaction with benzene in the presence of a catalyst to effect a transfer of alkyl groups from poly-alkylated aromatics contained in said gasoline to said benzene, recovering a substantially saturated gasoline product suitable for use in aviation fuel from the first step of the process, and recovering selected mono-alkylated aromatic hydrocarbons from the second step of the process.

In another specific embodiment, the invention comprises subjecting oil boiling above the range of gasoline to cracking in the presence of a cracking catalyst to produce a substantially saturated gasoline product, subjecting at least a portion of said gasoline to contact with a catalyst to effect saturation of the olefinic hydrocarbons contained in said gasoline, subjecting the olefin-free gasoline fractions to interaction with benzene in the presence of a catalyst to effect a transfer of alkyl groups from the poly-alkylated aromatics contained in said gasoline to said benzene, and recovering a substantially saturated gasoline product suitable for use in aviation fuel from the first step of the process, and recovering selected mono-alkylated aromatic hydrocarbons which are substantially olefin-free from the last step of the process.

The particular conditions of operation to be employed in each step of the process will depend

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primarily upon the charging stock to the first step of the process which, in turn, will affect the materials to be supplied as charging stocks to the subsequent steps of the process, and the operating conditions will also depend upon the particular products desired. For example, if motor fuel is desired, the first step of the process may comprise a non-catalytic cracking operation or it may comprise a catalytic operation in which the cracking is conducted under conditions to produce an olefinic type of distillate. On the other hand, if a substantially saturated gasoline product is desired for use in aviation fuel, the first step of the process will comprise a catalytic step in which the cracking is conducted under conditions to produce a substantially saturated distillate. In any event, the distillate product will contain varying percentages of aromatics, olefins, naphthenes, and paraffins. If substantially olefin-free toluene, ethylbenzene, etc., is desired, the distillate from the first step of the process is subjected to the hydrogen transfer step prior to being subjected to the alkyl transfer step of the process. When the products from the cracking step of the process have a sufficiently low olefin content, the second step of the process may be omitted in cases where the final alkylated aromatic product meets the desired specifications as to olefin content.

It is understood, of course, that the various operations herein disclosed are not necessarily equivalent in their results and that the particular choice will depend upon the considerations heretofore mentioned.

The invention will be explained in detail in connection with the accompanying diagrammatic flow drawing which illustrates several specific embodiments of the invention, although it is understood that various modifications to the particular flow described may be made within the scope of the broad teachings of the present invention.

Referring to the drawing, the charging stock is introduced to the process through line 1 and is directed into cracking zone 2. As heretofore described, the cracking operation will depend upon the charging stock and upon the type of products desired, and thus cracking zone 2 may be of any suitable type of known cracking processes. Non-catalytic cracking operations are usually conducted at temperatures within the range of from about 800 to about 1200° F. and under pressures of from about atmospheric to 1000 pounds or more. Catalytic operations are usually conducted at temperatures within the range of from about

600 to about 1200° F. or more and under pressures of from about atmospheric to 1000 pounds or more. In catalytic operations the hourly weight space velocity is usually within the range of from about .3 to about 5. The hourly weight velocity as used herein is defined as the weight of oil per hour per weight of catalyst in the reactor.

For non-catalytic operations the cracking zone usually comprises a heater, reaction chamber, flash chamber, fractionating and condensing equipment. For catalytic operations the process may be either of a fixed bed or moving bed type, the latter being either of the fluidized type in which the hydrocarbons move at a faster rate within the reactor than does the catalyst, or of the slurry type in which a suspension of oil and catalyst is passed to the heating and/or reaction zones. It is understood that any suitable type of cracking operation may be employed and, since no novelty is claimed herein for the cracking reaction per se, it is not believed necessary to describe the cracking process in detail.

When catalytic cracking is desired, any suitable cracking catalyst may be employed within the scope of the present invention. The catalyst may be of either natural or synthetic origin. A particularly suitable catalyst is of the silica-alumina type and comprises silica composited with alumina, zirconia and/or thoria, or the like, and these catalysts may be prepared in any suitable manner.

The products from zone 2 are directed through line 3 into separation zone 4. Separation zone 4 may comprise one or a plurality of suitable flashing, fractionating, distilling, absorbing and/or stripping zones whereby the products introduced thereto may be separated into the desired fractions. Non-condensable gases may be removed from the upper portion of zone 4 and withdrawn from the process through line 5 or all or a portion of these products may be returned by way of lines 6 and 1 to the cracking zone. This type of operation is particularly desired when the cracking is conducted in the presence of hydrogen or other gases. Higher boiling residue may be withdrawn from the lower portion of zone 4 through line 7 and removed from the process. When desired, and particularly when the cracking is conducted in the presence of catalysts, all or a portion of the residue may be returned by way of lines 8, 9, 10, and 1 to the cracking step for further conversion therein. A lower boiling recycle oil, when desired, may be separated in zone 4 and removed therefrom through line 11 and withdrawn from the process. Preferably, however, at least a portion of this recycle oil is returned by way of lines 9, 10, and 1 to the cracking zone for further conversion therein.

Depending upon the particular type of operation selected, the gasoline fractions, which may or may not contain higher boiling material and thus have an end boiling point of between about 400 and about 500° F. or more, may be withdrawn from zone 4 through line 12, and in one embodiment of the invention, are directed into hydrogen transfer zone 13. When it is desired to produce aviation gasoline, the material boiling within or slightly above the gasoline range may first be fractionated to separate a fraction having an end boiling point between about 250 and about 350° F., which fraction may be removed from zone 4 through line 14 and separately recovered for use in aviation fuel. In this operation the material withdrawn through line 12 will have an initial boiling point of between about 250 and about 350°

F. and an end boiling point of between about 400 and about 500° F. or more.

All or a portion of the gasoline directed through line 12 in the manner heretofore described is subjected to treatment in zone 13 in the presence of a suitable catalyst and under controlled conditions to effect saturation of the olefins contained therein. This zone may likewise assume any suitable form and it may contain any suitable catalyst. A particularly effective catalyst comprises silica composited with alumina, zirconia, and/or thoria, or the like, as heretofore described in connection with the cracking step of the process. However, with these catalysts, the temperature employed in this step of the process is within the range of about 400° to about 950° F. and preferably from about 400° to about 800° F. and usually at relatively low super-atmospheric pressures. The hourly weight space velocity is within the broad range of .3 to 5. The reaction which occurs in the step of the process is one of hydrogen transfer; that is, the olefins are saturated by the hydrogen liberated from some of the other hydrocarbons in the reaction zone. However, it is not intended to limit the invention to this particular reaction since other reactions, such as isomerization, cyclization, dehydrogenation, etc. may also occur. The conditions in this step of the process, furthermore, are controlled so that substantially no cracking occurs, and thus a high recovery of liquid products is obtained with substantially no gas formation.

The products from zone 13 are directed through line 15 into separation zone 16, which zone may comprise one or more fractionating, distilling, or other suitable zones whereby the products introduced thereto may be separated into the desired fractions. Line 17 is provided for the removal of any lighter products, although as heretofore described, the lighter products will in most cases be of negligible amount and, when desired, line 17 may be omitted. In one embodiment of the invention, the products may be separated in zone 16 into an aviation gasoline cut having an end boiling point within the range of from about 250 to about 400° F., and this fraction may be withdrawn from the process through line 18. This operation is particularly suitable when an aviation gasoline is not withdrawn through line 14 in the manner heretofore described, although it is within the scope of the invention to utilize the same even though the prior separation is made. In the latter case it may be desirable to blend the two streams withdrawn from lines 14 and 18.

The remaining products are withdrawn from zone 16 through line 19. In case it is not desired to separate an aviation gasoline cut in zone 16, the stream withdrawn through line 19 will contain the total products subjected to reaction in zone 13, either with or without lighter gases depending on whether line 17 is utilized. In case an aviation gasoline cut is withdrawn through line 18, the stream withdrawn through line 19 will contain the higher boiling constituents. In another embodiment of the invention, when desired, the total products from zone 13 may be directed through lines 15, 20, 21 and 19 into alkyl transfer zone 22. As heretofore mentioned, in cases where the olefin content of the cracked gasoline is sufficiently low, hydrogen transfer zone 13 may be omitted and the products withdrawn from zone 4 through line 12 may be directed through lines 21 and 19 to alkyl transfer zone 22.

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The products being supplied through line 10 will contain poly-alkylated aromatic hydrocarbons and are commingled with benzene in sufficient amounts to effect a transfer of alkyl groups from the poly-alkylated aromatics to the benzene. Preferably an excess of benzene should be introduced at this step of the process but there should preferably be at least one mol of benzene per mol of xylene or other di-alkylated aromatic, at least two mols of benzene for every tri-alkylated aromatic, 3 mols of benzene for every tetra-alkylated aromatic, etc. Further, when the alkyl chains on the aromatic ring are relatively long, the chains may undergo de-poly-alkylation; that is, removal from the benzene ring and de-polymerization into two or more alkyl radicals, in which case there should preferably be sufficient benzene present to accept the alkyl radicals available for transfer to the benzene. The benzene may be introduced to the process through line 23 and is directed through line 19 into zone 22.

Zone 22 may likewise be of any suitable form and may contain any suitable catalyst whereby to effect the transfer of alkyl groups from the poly-alkylated aromatic hydrocarbons to the benzene. A particularly suitable catalyst comprises silica composited with alumina, zirconia and/or thorium or the like, as heretofore described. The catalyst in this instance, however, is preferably of synthetic origin. The reaction is usually effected at temperatures within the range of from about 800 to about 1300° F., and preferably within the range of from about 1000 to about 1200° F. Likewise, relatively low superatmospheric pressures are employed and in most cases substantially atmospheric pressure is utilized. The hourly weight space velocities are usually less than 5. Satisfactory hourly weight space velocities are within the range of 0.5 to 2. The exact conditions of operation to be employed in this step of the process will depend upon the characteristics of the material being directed through line 19 into zone 22.

The products from zone 22 are directed through line 24 into separation zone 25. Likewise, zone 25 may comprise one or a plurality of flashing, fractionating, distilling, absorbing and/or stripping zones whereby the products introduced thereto may be separated into the desired fractions. Light gases may be removed from the upper portion thereof through line 26 and may be withdrawn from the process or, when desired, these gases may be recycled to either zone 2 or zone 22 in any suitable manner not illustrated. The toluene fraction is withdrawn from zone 25 through line 27. Ethylbenzene may be withdrawn from zone 25 through line 28. Although not illustrated in the drawing, other selected alkylated aromatics, such as isopropylbenzene, etc., may be separated from the products in zone 25 and withdrawn therefrom in any suitable manner. When desired, a substantially aliphatic fraction may be separated from the products of zone 25 and withdrawn therefrom through line 29. All or a portion of this fraction is preferably recycled by way of lines 30, 10, and 1 to cracking zone 2 for further conversion within the process. Higher boiling alkylated products are withdrawn from zone 25 through line 31 and may be removed from the process, but preferably at least a portion of these products is recycled by way of lines 32 and 19 to zone 22 for further conversion therein.

A modified operation which may be employed within the scope of the present invention includes

separating one or more selected mono-alkylated aromatics such as toluene, ethylbenzene, isopropylbenzene, butylbenzene, etc., from the products in zone 4 and removing the same by way of line 14. In this particular operation hydrocarbons containing six or less carbon atoms to the molecule may be removed from zone 4 through line 5 while the selected mono-alkylated aromatic may be removed therefrom through one or more points such as line 14. This operation is particularly advantageous when a substantially olefin-free alkylated aromatic is produced in the first step of the process. In this operation the material boiling above the range of the mono-alkylated aromatic will be directed through line 12 either to zone 13 or preferably to zone 22 for conversion therein.

In still another modification either one or more selected mono-alkylated aromatics may be separated in zone 4 and directed through line 12 to hydrogen transfer reaction in zone 13 to saturate the olefins and to subsequently withdraw an olefin-free alkylated aromatic from zone 16 through line 18. In this operation the higher boiling material will be directed, by well known means not illustrated, to the alkyl transfer step of the process.

The following examples are introduced for the purpose of further illustrating the invention but not with the intention of unduly limiting the same.

Example I

A Gulf Coast gas oil having an A. P. I. gravity of 30.2, an initial boiling point of 426° F., and an end boiling point of 740° F. was subjected to cracking in the presence of a silica-alumina catalyst at a temperature of 814° F. under a pressure of about 5 pounds per square inch and at an hourly weight space velocity of 1.08 in a fluidized type operation to produce 28.2% by volume of a 300° F. end point gasoline fraction having a clear octane number of 81.8 by the A. S. T. M. method, and about 7% of naphtha boiling substantially within the range of 300 and 400° F. This naphtha contained 78% aromatics and 3% olefins, the rest being paraffins and naphthenes. The remaining products of the cracking operation comprised incondensable gases, recycle stock, coke, and loss.

The above mentioned 300 to 400° F. naphtha was subjected to alkyl transfer reaction by being mixed with two volumes of benzene and contacted with a silica-alumina catalyst at a temperature of 1022° F. under atmospheric pressure and at a space velocity of 1 for a one hour process cycle. 92.5% of liquid hydrocarbons were recovered, the uncondensed gases amounting to 4% and the carbon to 3.4% by weight. Of the liquid hydrocarbons recovered, toluene comprised 24.9 weight per cent of the charge to the second step of the process. An ethylbenzene-xylene fraction was recovered, which fraction comprised 28.3 weight per cent of the naphtha charge to the second step of the process. By recycling the higher boiling alkylated aromatics to the alkyl transfer step, additional yields of toluene, ethylbenzene and xylene may be obtained.

Example II

A hydrocarbon fraction boiling within the range of 176° F. to 392° F. and comprising 72% aromatics and 23% olefins was subjected to treatment with a silica-alumina catalyst at a temperature of 662° F. at a space velocity of 0.5. No gas was formed and the hydrocarbon recov-

ered amounted to 95.3% by weight of the charge to this step of the process. The recovered hydrocarbons as produced contained 1% olefins. However, by fractionating to remove the light hydrocarbons boiling below 167° F., which amounted to 3% of this treated fraction, the aromatic concentrate contained no olefins. The above fraction may be mixed with two volumes of benzene and subjected to contact with a synthetically prepared silica-alumina catalyst at a temperature of about 1000° F. under atmospheric pressure and with a space velocity of 1 to yield high concentrations of olefin-free toluene and olefin-free ethylbenzene and xylenes.

We claim as our invention:

1. A combination process for the production of gasoline and alkyl aromatic hydrocarbons which comprises cracking a fresh hydrocarbon oil and an aliphatic recycle stock obtained as hereinafter described, separating from the resultant products a gasoline fraction having an end point of from about 250° F. to about 350° F. and a naphtha fraction boiling above the range of said gasoline fraction and having an end point of from about 400° F. to about 500° F., said naphtha fraction containing poly-alkylated benzene and olefins, converting olefins present in said naphtha fraction to more saturated hydrocarbons and separating a substantially olefin-free naphtha fraction, commingling benzene with said substantially olefin-free naphtha fraction and reacting said benzene with poly-alkylated benzene contained therein to effect the transfer of alkyl groups to said benzene, separating unconverted aliphatic hydrocarbons and a substantially olefin-free mono-alkylated benzene from the products of the last named step, recovering said mono-alkylated benzene, and recycling said aliphatic hydrocarbons to the cracking step.

2. A combination process for the production of gasoline and alkyl aromatic hydrocarbons which comprises cracking a fresh hydrocarbon oil and an aliphatic recycle stock obtained as hereinafter described, separating from the resultant products a fraction having an end point of from about 400° F. to about 500° F., converting olefins present in said last named fraction to more saturated hydrocarbons, separating from the resultant products a substantially saturated gasoline fraction having an end point of from about 250° F. to about 350° F. and a higher boiling naphtha fraction having an end point of from about 400° F. to about 500° F., said naphtha fraction being substantially olefin-free and containing poly-alkylated benzene, commingling benzene with

said naphtha fraction and reacting said benzene with poly-alkylated benzene contained therein to effect the transfer of alkyl groups to said benzene, separating unconverted aliphatic hydrocarbons and a substantially olefin-free mono-alkylated benzene from the products of the last named step, recovering said mono-alkylated benzene, and recycling said aliphatic hydrocarbons to the cracking step.

3. The process of claim 1 wherein toluene is separated from the products of the last step.

4. The process of claim 1 wherein ethyl benzene is separated from the products of the last step.

5. The process of claim 1 wherein the cracking step is effected in the presence of a silica-containing catalyst.

6. The process of claim 1 wherein said reaction of benzene with poly-alkylated benzene is effected in the presence of a silica-containing catalyst.

7. The process of claim 1 wherein said step of converting olefins present in said naphtha fraction to more saturated hydrocarbons is effected in the presence of a silica-containing catalyst.

8. The process of claim 2 wherein said step of converting olefins to more saturated hydrocarbons is effected in the presence of a silica-containing catalyst.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Country	Date
2,242,960	Sachanen, et al.	May 20, 1941
2,234,984	Sachanen, et al.	Mar. 18, 1941
2,290,211	Shaad	July 21, 1942
2,306,218	Marks	Dec. 22, 1942
2,308,792	Thomas	Jan. 19, 1943
2,335,596	Marschner	Nov. 30, 1943
2,343,870	Kaplan	Mar. 14, 1944
2,349,834	Schmerling, et al.	May 30, 1944
2,222,632	Sachanen, et al.	Nov. 26, 1940
1,324,143	Brooks	Dec. 9, 1919
2,010,948	Egloff	Aug. 13, 1935
2,010,949	Egloff	Aug. 13, 1935
2,367,535	Sowa	Jan. 16, 1945
2,297,773	Kanhofer	Oct. 6, 1942
2,283,854	Friedman, et al.	May 19, 1942
2,323,899	Day, et al.	July 13, 1943