

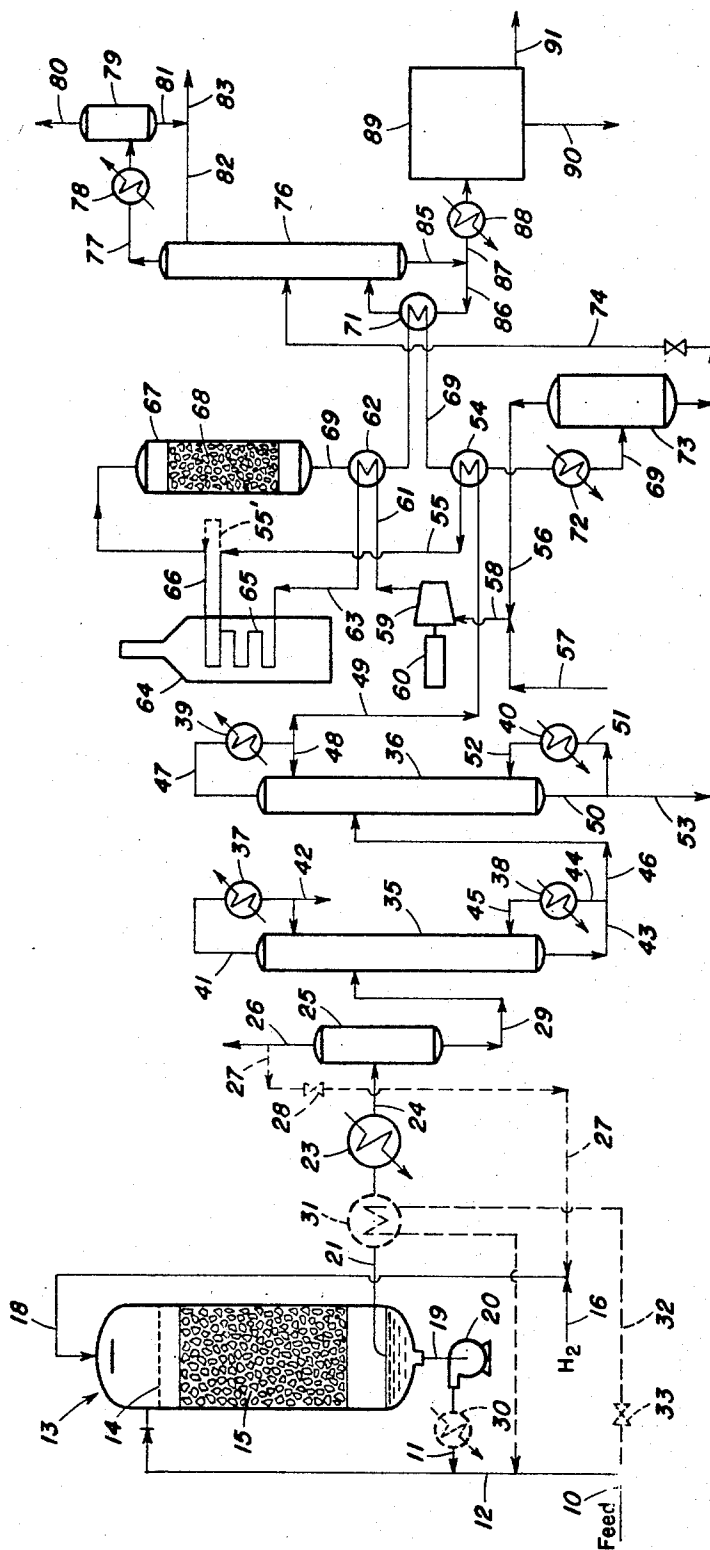
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TWO-STAGE HYDROTREATING OF DRIPOLENE

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1

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TWO-STAGE HYDROTREATING
OF DRIPOLENE

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ABSTRACT OF THE DISCLOSURE

Process for hydrotreating a liquid hydrocarbon fraction containing predominantly C_6 - C_8 aromatic hydrocarbons wherein the polymerizable components in the fraction are substantially instantaneously vaporized by effecting mixing thereof with a hot hydrogen-containing stream. The mixture is then introduced into a hydrotreating zone containing a suitable hydrotreating catalyst. The fraction may be obtained from an effluent produced by the hydrotreating of dripolene in the presence of a noble metal catalyst at a temperature between 120° and 400° F.

This invention relates to the production of benzene, toluene and xylene from dripolene or pyrolysis gasoline, and more particularly, to the production of benzene, toluene and xylenes by the selective hydrogenation of diolefins, olefins and styrenes contained in the byproduct dripolene or pyrolysis gasolines obtained from the production of olefins by the pyrolysis of hydrocarbons.

During the production of olefins by the pyrolysis of hydrocarbons, such as ethane and propane, there is produced in addition to the desired olefins, a considerable quantity of a normally liquid mixture of hydrocarbons commonly termed "dripolene" that contains almost all classes of hydrocarbons, but predominantly olefinic and aromatic hydrocarbons. Diolefins present are butadiene, isoprene, cyclopentadiene and its dimer, etc., while residual amounts of olefins are found, such as pentene, hexene, heptene, styrene, etc. Additionally, large quantities of aromatic compounds, such as benzene, toluene, ethylbenzene and xylenes are contained in dripolene, which are of value if recovered in high purity.

Similarly, the pyrolysis of virgin light, heavy or full boiling range naphtha or even heavier distillate stocks for ethylene and propylene production yields a hydrocarbon mixture in the normal gasoline boiling range which has a composition similar to dripolene. Such a mixture is known as pyrolysis gasoline.

Generally for the production of aromatic compounds, such as benzene, toluene and xylenes, from dripolene or pyrolysis gasoline the following sequence of steps are performed:

(1) First-stage hydrotreating of the pyrolysis gasoline to saturate the diolefins and styrenes while minimizing the hydrogenation of olefins;

(2) Fractionation of the hydrotreated product into three fractions, one fraction constituting a pre-benzene cut boiling below 150° F., a second fraction containing C_6 to C_8 hydrocarbons boiling between about 150 to about 300° F., and a third fraction constituting a post-xylene cut boiling from about 300 to 400° F.;

(3) Second-stage hydrotreating of the C_6 to C_8 fraction to saturate the olefins and to remove essentially all sulfur; and

(4) Extraction of the hydrotreated C_6 to C_8 fraction to produce benzene, toluene and xylenes.

As mentioned in copending application Ser. No. 376,358, filed June 19, 1964, now abandoned, in order to use pyrolysis gasolines in gasoline blending, it is neces-

2

sary to eliminate substantially all of the diolefins and styrenes, and this can be accomplished by hydrogenating the styrenes to the corresponding aromatics, and the conjugated diolefins to the corresponding monoolefins. In fact, for gasoline blending purposes, it is not desirable to hydrogenate the diolefins completely to form saturated hydrocarbons, since saturated hydrocarbons of the paraffin type usually have lower octane ratings than the corresponding monoolefins.

Significant quantities of dicyclopentadiene are contained in dripolene obtained by the pyrolysis of a very light hydrocarbon, such as ethane or propane. In the hydrotreating of such a feed stock, it has been found that dicyclopentadiene behaves as an olefin and consequently, is not completely hydrotreated in the first stage. During fractionation of the hydrotreated product, some of the dicyclopentadiene splits to cyclopentadiene under the influence of heat at the higher temperature, and is subsequently withdrawn from the fractionation zone in the C_6 to C_8 fraction. Second stage hydrotreating of the C_6 to C_8 fraction in the normal manner, i.e., mixing the same with hydrogen at ambient temperature and the subsequent preheating of the mixture has resulted in polymer or coke deposition in the preheater tubes and the second stage hydrotreating reactor. Such depositions shorten the on-stream factor and may render the unit inoperable.

It is an object of the invention to provide an improved process and reactor system for hydrogenating diolefins and styrenes contained in a dripolene, pyrolysis gasoline, and the like.

Another object of the invention is to provide an improved process and reactor system for purifying hydrocarbon streams boiling in the methyl naphthalene range (approximately 360° to 500° F.) for recovery of aromatics such as benzene, toluene and naphthalenes, after hydrodealkylation.

Still another object of the invention is to provide an improved process for producing benzene, toluene and xylenes from dripolene or a pyrolysis gasoline which substantially eliminates polymer and coke deposition during second stage hydrotreating of a C_6 to C_8 fraction separated from the product of first stage hydrotreating of the pyrolysis gasoline.

Yet another object of the invention is to provide an improved process for selectively hydrogenating the diolefins and styrenes present in dripolene or a pyrolysis gasoline.

Still another object of the invention is to provide a hydrogenation reactor system such that the reaction temperature can be controlled within narrow limits at the optimum range for selective hydrogenation of the diolefins and styrenes contained in pyrolysis gasoline obtained by the pyrolysis of hydrocarbons.

Further objects and advantages of the invention will become apparent from the following description taken in conjunction with the accompanying drawing which is a schematic flow diagram of the invention.

In accordance with our invention, dripolene or a pyrolysis gasoline, obtained from a plant preparing olefins by the pyrolysis of a hydrocarbon or hydrocarbon mixture is introduced into a first stage hydrotreating zone where the feed stock is hydrotreated in the liquid phase with a noble metal catalyst to selectively hydrogenate the diolefins and styrenes contained in the feed. The first stage reactor is operated at a temperature and pressure of about 120° to about 400° F., and of from 200 to 1000 p.s.i.g., respectively, depending upon the feed stock, its sulfur content and the hydrogen gas purity (i.e., hydrogen content). Fresh feed to the reactor is mixed with recycled hydrotreated gasoline directly from the bottom of the reactor which has already been stabilized and is introduced into

the top of the reactor and passed cocurrently with hydrogen in the presence of the noble metal catalyst. In this manner, the fresh feed is brought to reaction temperature without passing through any tubular preheating exchanger. At least, indirect preheat above 175° F., at which the tendency to polymerize is essentially nil, is not required. The net reactor effluent comprising a vapor-liquid mixture is cooled and the stabilized product separated from the uncondensed gases. The noble metal catalysts that can be used include platinum and palladium on a suitable support.

The hydrogenation of diolefins is highly exothermic, and depending on the quantity of diolefins and styrenes contained in the feed, the temperature rise between the inlet and outlet of the reactor may be as much as 200° to 400° F. Since it is desirable to operate at as nearly isothermal conditions as possible in order to obtain high selectivity and minimize catalyst deposits, isothermal conditions are approached by recycling a portion of the liquid effluent from the reactor. Such recycled portion is not cooled prior to admixing the same with the feed, as distinguished from known processes. By maintaining a recycle ratio of from 1:1 to 10:1, reactor effluent to reactor fresh feed, it is possible to reduce the temperature rise within the reactor to 100° F., or less. With lower diolefins content and feed stocks requiring less hydrogen absorption, the heat liberated is less, and lower recycle ratios may be used to give the desired temperature control. Thus, the pyrolysis gasoline may be easily hydrotreated in the liquid phase with high selectivity at the preferred temperature range and with the elimination of any need for a tubular surface. Additionally, the reactor system is readily adaptable to periodic regeneration of the catalyst in situ since there is no requirement of a tubular surface. Also, because of the excellent temperature control, it has been found that small increments in temperature rise can be easily regulated to compensate for increased sulfur content of the feed stock. For example, when the reactor is shifted from a feed containing 40 p.p.m. sulfur to one containing 330 p.p.m., an increase in operating temperature of about 50° F. compensates for the deactivating effect of sulfur on the catalyst. In fact, hydrogenation of the diolefins and styrenes appear to be more selective. It is actually advantageous at times to add some sulfur purposely to a low sulfur feed and operate at a higher temperature in order to obtain better selectivity.

One additional surprising result is that at the recycle ratios considered, there is no need to increase the amount of catalyst required. In other words, it is surprising to find that the only important space velocity is the space velocity based on the fresh feed; the dilution effect or presence of recycle appears to have no significant effect on the extent and/or selectivity of the hydrogenation.

The product from the first stage hydrotreating zone is passed through a fractionation zone wherein such product is separated into (a) a prebenzene fraction boiling below about 150° F., (b) a C₆ to C₈ fraction boiling between about 150 to about 300° F., and (c) a postxylene fraction boiling above 300° F.

A hydrogen-containing gaseous stream is preheated to a temperature of about 400° to about 650° F. and subsequently heated in a furnace to a temperature of about 1000° to about 1200° F. The C₆-C₈ fraction is preheated to a temperature below about 420° F., and preferably below 375° F., is introduced into the coil of the furnace and intimately admixed with the hydrogen stream to rapidly vaporize the C₆-C₈ fraction. The quantity and temperature of the hydrogen containing gaseous stream admixed with the C₆-C₈ fraction may be varied but must effect the rapid vaporization of the feed (i.e., so that the resulting gas mixture is above its dew point) or at least so much of the feed as contains any polymerizable components. Generally about 6,000 to 14,000 standard cubic feet of a hydrogen containing gaseous stream is admixed with one barrel of the feed. As hereinafter described, the

hydrogen containing gaseous stream is a recycle stream obtained from downstream processing equipment. Only small quantities of make-up hydrogen need be added, since hydrogen consumption is nominal for the hydrotreating of the C₆-C₈ fraction. An additional benefit of lowered energy requirements is derived from using such a recycled hydrogen stream, since the stream is recovered at the system pressure, and only the pressure drop through the system must be overcome. The resulting mixture, at a temperature of between about 625° to about 800° F., preferably 650 to 750° F. is withdrawn from the furnace and introduced into a second stage hydrotreating reactor which contains a cobalt and molybdenum oxide catalyst on a suitable support. Rapid vaporization of the C₆ to C₈ fraction substantially eliminates polymer and coke deposition in the tubes of the preheater and in the second stage hydrotreating zone.

The effluent from the second stage hydrotreating zone, after treatment to remove lighter components such as hydrogen and C₅ and lighter hydrocarbons, is introduced into an aromatic separation zone wherein such product is treated in a conventional manner, such as by liquid-liquid extraction, azeotropic distillation, or adsorption forming a product comprising nitration grade benzene, toluene and xylenes.

Referring to the drawing, a pyrolysis gasoline in line 10 obtained from the recovery unit of a plant (not shown) for the pyrolysis of hydrocarbons, is mixed with recycle reactor effluent in line 11, as more fully hereinafter described, and introduced through line 12 into reactor, generally indicated at 13.

The reactor 13 includes a vapor-liquid distributor plate 14 and catalyst zone, generally indicated as 15. The catalyst zone is filled with a noble metal catalyst, such as platinum or palladium on a suitable support. Hydrogen, or a mixture of hydrogen and light hydrocarbons such as methane, is admitted through line 16 and is introduced through line 18 into reactor 13, and the hydrogen stream and the liquid feed in line 12 are passed cocurrently through reactor 13. A temperature of between 120° to about 400° F. is maintained in reactor 13, preferably 150° to 370° F., and a pressure of from 200 to 1000 p.s.i.g. is maintained on reactor 13, preferably 400 to 900 p.s.i.g.

As hereinbefore described, the preferred reactor temperature range depends upon the feed stock and its sulfur content. Higher sulfur requires higher operating temperatures. A feed containing more cyclohexadiene requires higher hydrogenation temperature than one containing isoprene or cyclopentadiene. The required reactor pressure depends upon hydrogen purity and reactor temperature. Lower hydrogen purity requires higher total pressure to provide the desired hydrogen partial pressure. In order to keep at least 75% of the feed in the liquid phase, higher pressure is needed at higher temperatures.

A portion of the liquid effluent from the reactor 13 is withdrawn through line 19 by pump 20 and constitutes the liquid recycle reactor effluent in line 11. The recycle ratio of reactor effluent to fresh feed may be from 1:1 to 10:1, preferably from 2:1 to 5:1. In this manner, isothermal conditions within the reactor may be more closely approached with a temperature rise of 100° F. or less during passage of the feed in line 12 through the reactor 13. Net reactor effluent consisting of vapor and liquid is withdrawn from reactor 13 through line 21 to heat exchanger 23 wherein the effluent is cooled to near ambient temperatures of from 85° to 100° F. so as to condense substantially all of the hydrocarbons boiling above methane.

The now cooled effluent is withdrawn from heat exchanger 23 through line 24 and is passed to separator 25. An overhead gaseous stream including methane and unreacted hydrogen is withdrawn from separator 25 and vented through line 26. Should a low partial pressure of hydrogen be desired, a portion of the gaseous stream in line 26 may be recycled through line 27 under the con-

trol of valve 28 to line 18. Generally, the concentration of unreacted hydrogen is insufficient to justify recycle of any portion of the gaseous stream in line 26 so as to maintain the concentration of methane below about 50% in reactor 13. A stabilized product is withdrawn from separator 25 through line 29.

Depending on the feed stock, the hydrogen absorption and therefore heat of reaction, it may be necessary to include a cooler 30 in line 11, and/or a fresh feed preheater 31 in line 21 to provide for flexibility of operation. Should the feed stock have a high hydrogen absorption, the recycle stream should be passed through cooler 30 prior to admixing the same with the feed stock. Conversely, should the hydrogen absorption of the feed stock be too low, it may be necessary to preheat the feed stock by passages through line 32 under the control of valve 33 to preheater 31, and thence into line 12. It is apparent from the foregoing that the cooler 30 and preheater 31 are not used at the same time, and are operated when the feed stock has a high or low hydrogen absorption, respectively.

The stabilized product in line 29 is passed to a fractionation zone comprised of fractionation towers 35 and 36. Fractionation tower 35 includes reflux condenser 37, and reboiler 38; and fractionation tower 36 includes reflux condenser 39 and reboiler 40. In fractionation tower 35 the stabilized product in line 29 is fractionated into an overhead containing C_5 and lighter hydrocarbons which are withdrawn as overhead in line 41 and passed to condenser 37. After satisfying the reflux requirements of the fractionation tower 35, the net overhead is withdrawn through line 42. The C_6 and heavier hydrocarbons are withdrawn as bottoms through line 43. A portion of the bottoms are passed through line 44, reboiler 38, and thence through line 45 to fractionation tower 35 to provide the reboil requirements for fractionation tower 35. The net bottoms in line 46 are introduced into fractionation tower 36 and separated into a C_6 to C_8 aromatic fraction and a residual gasoline fraction.

The C_6 to C_8 aromatic fraction is withdrawn as overhead from fractionation tower 36 through line 47 and passed to reflux condenser 39. A portion of the liquid stream withdrawn from condenser 39 is passed through line 48 to provide the reflux requirements for fractionation tower 36. The net overhead from tower 36 is withdrawn through line 49 and passed to subsequent processing units as more clearly hereinafter described. The bottoms of fractionation tower 36 withdrawn through line 50, with a portion thereof being passed through line 51, reboiler 40, and reintroduced into fractionation tower 36 through line 52. The net bottoms constituting a residual gasoline fraction are withdrawn from fractionation tower 36 through line 53 and passed to storage and blending units (not shown).

The C_6 - C_8 aromatic fraction in line 49 is passed to heat exchanger 54 wherein such fraction is passed in heat exchange relationship with the effluent from the second stage hydrotreating reactor as is more fully hereinafter described. In heat exchanger 54, the aromatic fraction is heated to a temperature of less than about 420° F., preferably about 375° F. A hydrogen-containing gaseous stream in line 56, together with make-up hydrogen in line 57 are combined and passed through line 58 to compressor 59 driven by suitable drive means 60. In compressor 59, the hydrogen-containing gaseous stream is compressed to a pressure of about 750 to 800 p.s.i.g. The now compressed hydrogen-containing gaseous stream is passed from compressor 59 through line 61 to heat exchanger 62 wherein the stream is heated to a temperature of about 400° to about 650° F. and is thereafter passed through line 63 to heater 64 wherein the hydrogen-containing gaseous stream is further heated in furnace coil 65 to a temperature of about 1000° to about 1200° F. At this point, the aromatic fraction in line 55 is injected into the hydrogen-containing gaseous stream and mixed within the

furnace coil 65 whereby the temperature of the combined stream is raised to about 575° to about 650° F., with substantially instantaneous vaporization of the aromatic fraction. Practically, injection generally takes place outside the furnace and the mixture returns immediately to the furnace. The resulting vapor mixture is additionally heated in the final portion of the furnace coil 65 and withdrawn from the furnace 64 through line 66 at a temperature of about 650° to about 750° F.

As noted hereinabove, it is essential that vaporization be substantially instantaneous, but whether or not vaporization must be complete depends on the composition of the aromatic fraction in line 55. In other words, as long as all of the polymerizable components are quickly vaporized, trouble will be avoided. As one skilled in the art will recognize, the volume of hydrogen-containing gas required in the system will be less if complete vaporization is not required, and less volume of recycle gas means lower energy requirements for compressor 59 and heater 64. Determination of the required vaporization must be made, therefore, for the particular liquid being treated for most economic operation.

It has been found that where vaporization is less than total, the injection of the aromatic fraction as described above is satisfactory. Where total vaporization is required and the mixture of vaporized aromatic fraction and hydrogen has a dew point about equal to the desired second stage reactor inlet temperature, it is better to pass the gas all the way through heater 64 and into line 66 prior to injection. In this instance, the aromatic fraction is introduced directly into line 66 via line 55'.

The effluent in line 66 is passed to a second stage hydrotreating reactor 67 including catalyst reactor bed 68 comprised of a conventional hydrogenation catalyst, such as a cobalt and molybdenum oxide on a suitable support. During passage through reactor 67, any cyclopentadiene or dicyclopentadiene present is hydrogenated to cyclopentane or pentanes. Reactor 67 is maintained at a temperature within the range of about 625° to 800° F., preferably 650° to 700° F. The reactor effluent in line 69 is passed through heat exchangers 62, 71, 54 and 72, consecutively. In heat exchanger 62, the reactor effluent is passed in heat exchanger relationship with the hydrogen-containing stream to preheat such stream to a temperature of from 400° to about 650° F. The reactor effluent in line 69 also provides the heat necessary in heat exchanger 71 to provide the reflux requirements for a stripping column as more clearly hereinafter described. In heat exchanger 54, the reactor effluent preheats the C_6 to C_8 fraction in line 49 withdrawn from fractionating tower 36 prior to introduction into the furnace 64. The reactor effluent is further cooled in heat exchanger 72 and introduced into separator 73 wherein hydrogen and methane are separated from the reactor effluent and withdrawn through line 56, which, together with required make-up hydrogen from line 57, constitutes the hydrogen-containing gaseous stream admixed in heater coil 65 with the C_6 to C_8 fraction in line 55.

The bottoms from separator 73 is withdrawn through line 74 and introduced into stripping column 76. An overhead fraction containing C_5 and lighter hydrocarbons is withdrawn through line 77 and passed through condenser 78 and subsequently passed into surge drum 79. The lighter hydrocarbons, such as hydrogen and methane, are withdrawn from surge drum 79 through line 80, while the heavier hydrocarbons are withdrawn through line 81. A portion of the liquid stream in line 81 is passed through line 82 to provide the reflux requirements for stripping column 76, while the remaining portion is withdrawn and passed through line 83 to subsequent units (not shown).

The bottoms from stripping column 76, primarily C_6 to C_8 aromatic hydrocarbons, predominantly benzene, toluene and xylene are withdrawn through line 85 with a portion being passed through line 86 and heat exchanger 71 to provide the reboil requirements for stripping col-

umn 76. The remaining portion of the bottoms in line 85 is passed through line 87 and heat exchanger 88 and is introduced into an aromatics extraction zone, generally indicated as 89.

As hereinbefore mentioned, in aromatic extraction zone 89, the aromatic components of the C₆ to C₈ fraction are treated for example by liquid-liquid extraction, azeotropic distillation, or adsorption to separate and produce an aromatic product containing nitration grade benzene, toluene and xylenes, which is withdrawn from the extraction zone through line 90. The other components contained within the C₆ to C₈ fraction are withdrawn from the aromatic extraction zone through line 91 and passed to subsequent processing units (not shown) for treatment as dictated by the composition of such products. In some instances it may be desirable to also pass such product to the blending and storage units for subsequent inclusion in various gasolines.

EXAMPLE

To further illustrate our invention, 1700 cc. per hour of a liquid dripolene stream at a temperature of 85° F. obtained from the pyrolysis of propane and having the characteristics set forth in Table A below was mixed with 5950 cc. per hour of recycle reactor effluent at a temperature of 320° F. and introduced into reactor 13 at a resulting temperature of 270° F. The catalyst bed of the reactor contained 283 cc. of $\frac{3}{16}$ " x $\frac{1}{8}$ " catalyst pellets of palladium supported on alumina.

Table A

Boiling range, ° F.	124-377
Octane No. (research method, clear)	100+
Bromine No.	65
Diene value ¹	46
Sulfur, p.p.m.	80
Existent gum, mg./100 cc.	47
Induction period, min.	120

¹ Calculated from component analysis.

A gaseous stream in line 18, at a temperature of 150° F. and comprising 11.12 s.c.f. per hour of 65 vol. percent hydrogen and 35 vol. percent methane, was introduced into the reactor 13. The outlet temperature of the reactor was 320° F. and the outlet pressure was 880 p.s.i.g. The net reactor effluent consisting of hydrotreated feed plus unreacted hydrogen was withdrawn through line 21 and subsequently cooled to a final temperature of 100° F. during passage through heat exchanger 23. Approximately 70% of the hydrogen was found to have combined with the feed stock.

The thus cooled reactor effluent was introduced into separator 25 from which an overhead gaseous stream containing hydrogen and methane was withdrawn. A stabilized product having the composition set forth in Table B was withdrawn from separator 25.

Table B

Boiling range, ° F.	124-377
Octane No. (research method, clear)	100
Bromine No.	26
Diene value	0.7
Sulfur, p.p.m.	N.A.
Existent gum, m./100 cc.	1.6
Induction period, min.	1400+

The hydrotreated stream in line 29 was introduced into fractionation tower 35 wherein a C₅/C₆ separation was effected with 0.33 lb. per hour of the C₅ and lighter hydrocarbons being withdrawn as fractionation tower overhead in line 41 and 2.91 lb. per hour of the C₆ and heavier hydrocarbons being withdrawn as net tower bottoms in line 46.

The C₆ and heavier hydrocarbon fraction in line 46 was passed to fractionation tower 36 wherein a C₈/C₉ separation was effected. 2.31 lb. per hour of a C₆ to C₈ fraction boiling in the range of 150° to 300° F. was with-

drawn as net tower overhead in line 49 and had a composition set forth in Table C.

Table C

Boiling range, ° F.	150-300
Bromine No.	21
Diene value	1.0
Sulfur, p.p.m.	60

The C₆ to C₈ hydrocarbon fraction in line 49 at a temperature of 85° F. was preheated in heat exchanger 54 to a temperature of 375° F. Ninety and six-tenths (90.6) s.c.f. per hour of a hydrogen-containing gaseous stream (60% hydrogen, 40% methane) and 5.83 s.c.f. per hour of a makeup hydrogen-containing gas (67% hydrogen, 33% methane) was compressed in compressor 59 to a pressure of 675 p.s.i.g., and passed through heat exchanger 62 wherein the compressed hydrogen-containing gaseous stream was preheated to a temperature of 650° F. The preheated hydrogen-containing gaseous stream was then introduced into the coil 65 of the furnace 64 and, heated to a temperature of 1000° F. At this point the preheated C₆ to C₈ hydrocarbon fraction was injected into the hydrogen-containing gaseous stream in furnace 64 resulting in the rapid vaporization of the C₆ to C₈ fraction. The effluent from the furnace 64 at a temperature of 710° F. was passed through line 66 into reactor 67 containing a catalyst consisting of cobalt and molybdenum oxides supported on alumina. Over an extended period of time, there was no indication of pressure buildup nor any effect on catalyst activity.

The reactor effluent at a temperature of 750° F. and a pressure of 670 p.s.i.g. in line 69 was passed serially through heat exchanger 62, 71, 54 and 72 wherein the reactor effluent was cooled to a temperature of 100° F. The now cooled reactor effluent was introduced into separator 73 wherein 2.31 lb. per hour of a liquid hydrocarbon fraction was withdrawn through line 74 and had following properties as set forth in Table D.

Table D

Color	Water white
Bromine No.	0.9
Thiophene, p.p.m.	<1

Ninety and six-tenths (90.6) s.c.f. per hour of a hydrogen containing gaseous stream were withdrawn through line 56, and passed to compressor 59. The liquid hydrocarbon fraction in line 74 was introduced into stripping column 76 wherein C₅ and lighter hydrocarbons were withdrawn as tower overhead in line 77. 2.30 lb. per hour of a stabilized C₆ to C₈ fraction having a composition as set forth in Table E was withdrawn through line 87 and passed to aromatic separation zone 84.

Table E

Boiling range, ° F.	150-300
Bromine No.	<1
Thiophene, p.p.m.	<1

The C₆ to C₈ fraction was contacted with diethylene glycol solvent. The raffinate is taken out at line 91 and the extract after separation from the solvent is removed through line 90 as a pure aromatic stream containing essentially only benzene, toluene and xylenes. This stream may be contacted with clay to improve its acid color property and then fractionated to yield high purity nitration grade products.

The aromatic products from the separation zone 89 met nitration grade specifications.

Although the present invention has been described and illustrated with reference to specific examples, it is understood that modifications and variations may be made by those skilled in the art within the principles and scope of the invention as expressed in the appended claims. Moreover, those skilled in the art will recognize that while the invention has been described with particular reference to the treatment of dripolene and pyrolysis gasolines, the

second-stage hydrotreating has much broader application. In particular, it may be employed generally for sulfur and olefin removal from hydrocarbon streams boiling in the range of methyl naphthalenes (about 360° to 500° F.).

What is claimed is:

1. A process for hydrotreating dripolene, containing aromatic hydrocarbons and unsaturated components, including, monoolefins, diolefins and styrenes, to recover the aromatic compounds essentially free of the unsaturated components and with the essential elimination of coke and gum formation which comprises:

(a) mixing heated hydrotreated product with dripolene to directly heat said dripolene to a first hydrotreating reaction zone inlet temperature;

(b) introducing said heated fraction, containing hydrotreated product, and a first gaseous stream containing hydrogen into the first hydrotreating reaction zone containing a noble metal catalyst, said reaction zone being maintained at a temperature between about 120° F. and about 400° F.;

(c) withdrawing a hot first hydrotreated product, essentially free of the diolefins and styrenes of the dripolene and containing the other aromatic hydrocarbons and mono-olefins, from said zone, said hot first hydrotreated product being at a temperature greater than the temperature of the dripolene mixed in step (a);

(d) passing a portion of said hot first hydrotreated product to step (a) as the heated hydrotreated product to heat said dripolene;

(e) fractionating the remaining portion of said first hydrotreated product to form a hydrocarbon fraction containing predominantly C₆ to C₈ aromatic hydrocarbons and unsaturated components;

(f) injecting said hydrocarbon fraction at a temperature less than about 420° F. into a second gaseous stream containing hydrogen, the temperature and quantity of said second gaseous stream and rate of injection being at a value such that at least the unsaturated components of said hydrocarbon fraction are substantially instantaneously vaporized;

(g) passing the gaseous mixture of step (f) through a second hydrotreating reaction zone containing a hy-

drotreating catalyst and maintained at a temperature between about 625° F. and about 800° F.; and

(h) recovering a second hydrotreated product from said second reaction zone, containing the C₆-C₈ aromatic hydrocarbons of the dripolene and essentially free of unsaturated components.

2. The process as defined in claim 1 wherein in step (f) the hydrocarbon fraction is substantially instantaneously heated to above the dew point thereof.

3. The process as defined in claim 2 wherein the hydrocarbon fraction is heated in step (f) to a temperature between about 575° F. and about 650° F.

4. The process as defined in claim 3 wherein the second gaseous stream is at a temperature between about 1000° F. and about 1200° F.

5. The process as defined in claim 4 wherein about 6000 to about 14,000 s.c.f. of said second gaseous stream containing from about 50 to about 100 mol percent hydrogen is admixed with one barrel of said hydrocarbon fraction.

6. The process as defined in claim 3 wherein the first reaction zone is maintained at a pressure of from about 200 to about 1000 p.s.i.g., the dripolene in step (a) prior to mixing is at a temperature below about 175° F. and the heated hydrotreated product is employed in step (a) in an amount between about 1:1 and about 10:1 based on the dripolene.

7. The process as defined in claim 1 wherein the hydrocarbon fraction in step (f) is heated to the second hydrotreating reaction zone temperature.

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