Sept. 6, 1955 I. H. LUTZ ET AL 2,717,231

PROCESS FOR TREATING AROMATIC-DIOLEFIN MIXTURES

Filed May 21, 1954 2 Sheets-Sheet 1

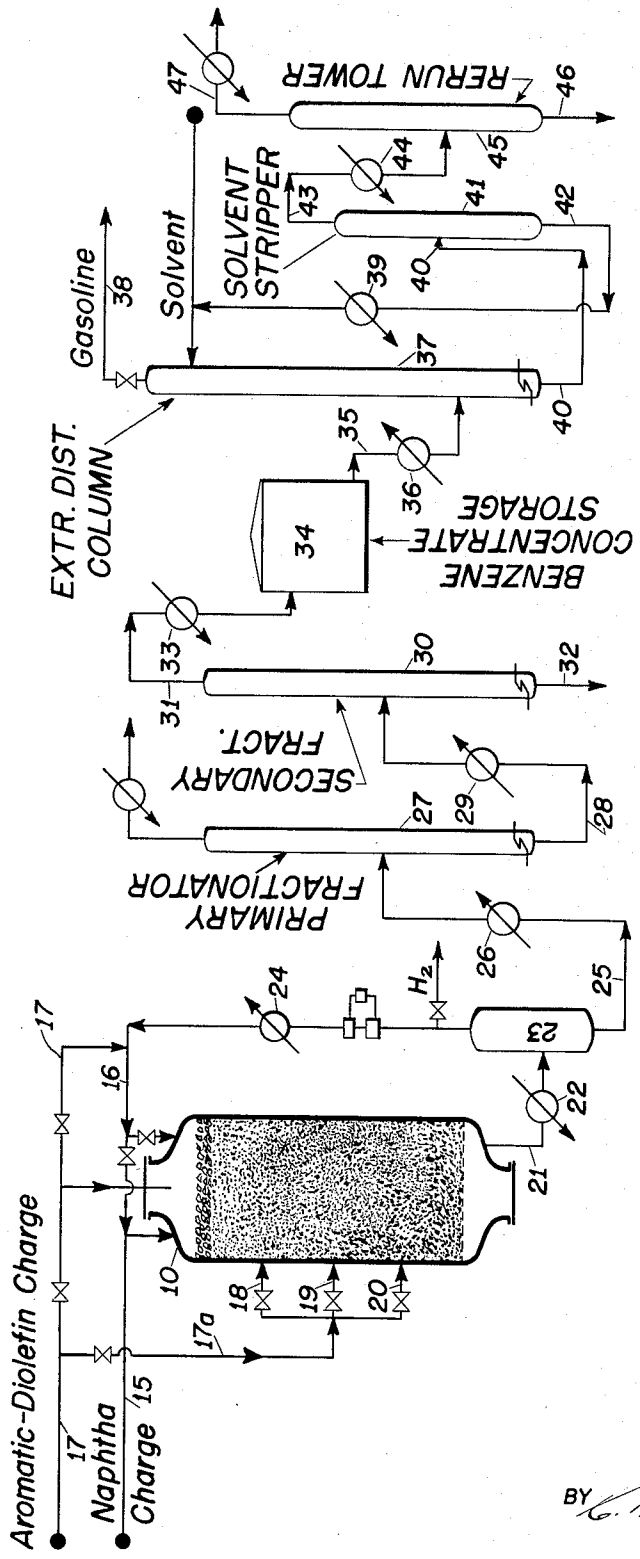


FIG. 1

INVENTORS:
Irvin H. Lutz
Oran W. Collier
David J. Bellman

BY

ATTORNEY

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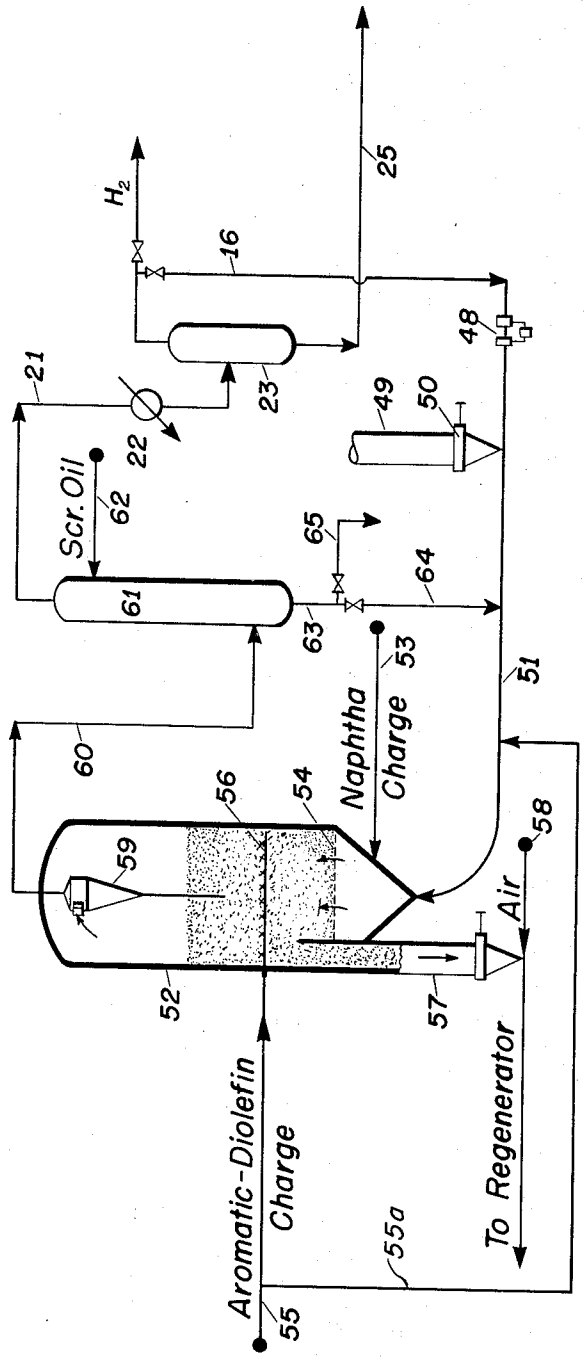


FIG. 2

INVENTORS:
Irvin H. Lutz
Oran W. Collier
David J. Bellman

BY

ATTORNEY

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2,717,231

PROCESS FOR TREATING AROMATIC-DIOLEFIN MIXTURES

Irvin H. Lutz, Galveston, and Oran W. Collier and David J. Bellman, La Marque, Tex., assignors to The American Oil Company

Application May 21, 1954, Serial No. 431,432

13 Claims. (Cl. 196—50)

This invention relates to catalytic refining of hydrocarbon fractions containing substantial proportions of aromatics and diolefins. More particularly, it relates to the recovery of substantially pure aromatics such as benzene from such fractions and to the conversion of diolefins present therein to hydrocarbons suitable for use in internal combustion engine fuel.

A hydrocarbon fraction typical of that which may be refined according to this invention is the liquid product of approximately gasoline boiling range which results from the pyrolysis of an ethane-propane gas stream during the production of ethylene. As a by-product of such a cracking operation there is produced a normally liquid hydrocarbon fraction, usually boiling within the range of from about 100° to about 400° F., which comprises a predominant amount of benzene, a substantial portion of diolefins and some monoolefins. Whereas the present invention has application to similar fractions from other sources which will hereinafter be set forth in detail, the following description will make particular reference to an aromatic-diolefin fraction resulting from such a pyrolysis. Such a product is sometimes referred to in the art as "Drip Oil" or "Dripolene."

Prior efforts to obtain substantially pure aromatics from such complex hydrocarbon fractions have been only partially successful. By the use of conventional techniques such as atmospheric fractional distillation or extractive distillation it is most difficult if not impossible to effect a separation between benzene and closely boiling hydrocarbons which azeotrope therewith or are equally soluble in the solvent employed in extractive distillation. In addition, the diolefins present polymerize readily to resins and high boiling fractions with the evolution of heat which greatly increase the distillation difficulties. Fractional crystallization has been employed but it suffers from the economic standpoint and is not a process readily adapted to large scale operations. Even more important, none of these alternatives offers the possibility of upgrading substantially the entire fraction to premium liquid products. By the process of this invention, however, substantially pure aromatics, particularly benzene, may be recovered and diolefins may be converted to suitable motor fuel components in equipment presently available in many refineries.

It is an object of this invention to recover substantially pure aromatics such as benzene from difficultly separable hydrocarbon fractions containing substantial quantities of aromatics and diolefins such as the liquid fraction of about gasoline boiling range which results from the pyrolysis of a petroleum gas stream. A further object is to convert the diolefins in such an aromatic-diolefin fraction to suitable motor fuel constituents. An additional object is to enhance the value of such aromatic-diolefin by-products by recovering valuable benzene therefrom and by converting the diolefins to suitable motor fuel components. A still further object is to conduct this refining operation in presently available hydroforming equipment

simultaneously with the hydroforming of a virgin naphtha or the like. These and additional objects and advantages will be apparent from the following description and claims taken in conjunction with the attached drawings.

In accordance with the present invention a relatively small amount of a rather narrow boiling fraction containing substantial amounts of olefins, diolefins and aromatics, from which the aromatics are not otherwise readily and economically recoverable in a substantially pure state, is introduced to a hydroforming reactor during the hydroforming of a virgin naphtha or the like. Fractions containing an amount of diolefins substantially greater than occurs in cracked naphthas, e. g. at least about 5% and ordinarily at least about 7 or 8% and a yet substantially greater amount of aromatics, e. g. at least about 20% and usually at least about 30% by volume, may be advantageously refined in accordance herewith. The hydroforming process is now well-known to those skilled in the art and is described in numerous patents such as U. S. Letters Patents 2,320,147, 2,357,365 and 2,388,536. A feature of the conventional hydroforming process is the fact that there is invariably a net production of hydrogen. The extent of hydrogen production depends upon the charging stock employed and to a great extent upon the amount of cracked naphtha, if any, in the charge. By this invention a portion of the net hydrogen normally produced is employed in situ to aid in the recovery of benzene and high octane liquid products from the aromatic diolefin fraction.

Since benzene is the predominant aromatic in the fraction the present invention is described with particular reference to its recovery, but the other aromatics present, such as the xylenes, toluene, etc., may likewise be recovered by this general technique. By introducing the aromatic-diolefin fraction to the hydroformer, substantially all of the benzene present in the fraction may be readily recovered in substantially pure state from the hydroformer product by prefractionation and extractive distillation. Furthermore, the yield of gasoline is increased and in certain instances the octane number thereof is raised.

It is particularly disadvantageous to admix the aromatic-diolefin stream with the naphtha before preheating the naphtha charge because solid deposition in the coils of the preheater, resulting from the rapid thermal polymerization of the diolefins present in the aromatic-diolefin stream, greatly lowers the heat transfer coefficient. Indeed, mixing the two streams at any point where solid deposition will be substantial and cumulative and not subject to periodic removal by burning in the regenerative cycle of the hydroforming process has been found to be essentially unsatisfactory. Whereas cracked naphthas containing minor quantities of diolefins may to some extent result in such difficulties, if so handled, it is apparent how much more serious the treatment of stocks containing 10% and more diolefins can be if not conducted in accordance herewith. In order to avoid such difficulties, the aromatic-diolefin stream should be maintained at a temperature below that at which a substantial amount of polymerization takes place until it is contacted with a substantial amount of uncombined hydrogen which serves to inhibit resin formation and/or reaches a point in the process where periodic burning in the regenerative cycle of the process will remove resins which might be formed. In the preferred embodiment the two streams should be mixed within the reactor and in the presence of an excess of uncombined hydrogen. They may, for example, be mixed in the open space at the top of the reactor in the presence of recycle hydrogen or the aromatic-diolefin stream may be introduced to the reactor at one or more points spaced from the naphtha inlet

and down-stream of the location where the naphtha is introduced where recycle hydrogen and hydrogen produced in situ by dehydrogenation are available. A distributor means is desirable when the two streams are mixed in the top of the reactor prior to contacting the catalyst and when down-stream injection is employed, according to the alternative procedure, the points of injection are preferably chosen to correspond with the reactor level at which the catalyst no longer is efficiently utilized for dehydrogenation. Such loss in efficiency may be caused either by the depletion of naphthene or paraffin content of the charge, as a result of conversion, or by the incidence of such a low temperature, as a result of the endothermic reaction, that the velocity of dehydrogenation is decreased. Surprisingly, no increase in coke on the catalyst or decrease in activity thereof has been noted over considerable periods of time during which the aromatic-diolefin fraction was charged. In certain instances a net decrease in coke on the catalyst has been noted.

In the accompanying drawings:

Fig. 1 is a schematic flow diagram of a fixed bed system for practicing this invention.

Fig. 2 is a schematic flow diagram of fluid system for practicing the invention.

As a specific example of the invention, the hydroforming of a naphthenic heavy naphtha will be described. It should be understood, however, that the invention is not limited to that particular stock but is applicable generally to charging stocks rich in hydrogen which liberate hydrogen in the initial stage of the hydroforming reaction. The second charging stock, comprising a predominant amount of aromatics and a substantial amount of diolefins, is a liquid fraction, having a boiling range of from about 100° to about 360° F., which is a by-product of the pyrolysis of an ethane-propane mixture at a temperature in the range of from about 1300° to 1400° F. Average analytical data for such a material taken on many different samples over a period of about seven months are set forth below:

TABLE I

Gravity, ° API, 60° F	34.7.
Bromine number, cg. Br_2/g	104.1.
Maleic anhydride value, mg. Br_2/g	79.0.
Index of refraction, N_D	1.4830.
ASTM distillation:	
Initial B. P.	100° F.
10%	146° F.
20%	162° F.
30%	178° F.
40%	188° F.
50%	196° F.
60%	206° F.
70%	234° F.
80%	296° F.
90%	340° F.
Final B. P.	360° F.
Dissolved C_3 and C_4 (volume per cent)	Approx. 8.0%.
Pentadienes	7.7%.
Pentylenes	6.3%.
Benzene	34.2%.
Toulene	7.8%.
Xylene	Approx. 1%.
Styrene	Approx. 3%.
Dicyclopentadiene	5%.
Unidentified	29.6%.

Both stocks should boil approximately within the gasoline boiling range, i. e. about 100° to about 400° or 430° F.

Referring to Fig. 1, reactor **10** may correspond to reactor **17** or **17'** in the system illustrated in U. S. 2,388,536 and since the general system is fully described in that patent it will require no further detailed description. In accordance with the present invention, however, there is preferably an open space above the bed of solid catalyst in the reactor so that sufficient space is available to permit rapid dispersion of the aromatic-diolefin stream introduced through line **17** in the hot naphtha which is introduced through line **15**. Whereas the invention is specifically described herein with reference to introduction of the aromatic-diolefin stream to the top of the reactor via line **17**, it may be introduced thereto via line **16** wherein it is admixed with recycle gases containing a large amount of uncombined hydrogen; it may likewise be introduced to the reactor via line **17*a*** and lines **18**, **19** and/or **20**. If such operation is employed the valve in line **17** leading to the reactor will preferably be closed just as the valve in line **17*a*** is preferably closed when the stream is introduced into the top of the reactor via line **17** as is hereinafter specifically described. Alternatively the reactor **10** may be divided into separate beds by catalyst supporting grids so that distributing spaces are provided between the several beds. Whether a solid bed or a reactor having separate beds of catalyst is employed is substantially independent of the method in which the aromatic-diolefin stream is introduced but it is preferred when employing spaced injection via lines **17*a*** and **18**, **19** and/or **20** to employ separate beds and to introduce the stream into the distributing spaces between the several beds. Perforated pipes or other known means may be employed for distributing the aromatic-diolefin stream uniformly throughout the cross sectional area of the bed if the stream is introduced via line **17*a*** to a reactor containing a solid catalyst bed. The charge capacity of the reactor varies somewhat with the type of naphtha introduced, thus for a naphthenic heavy naphtha the total charge, including the aromatic diolefin stream, is about 6300 barrels per day and the same for a so-called high benzene content naphthenic naphtha (herein more fully defined) and for a paraffinic heavy naphtha the total charge is from about 7500 to 7800 barrels per day. The catalyst itself is preferably molybdenum oxide on active alumina as described, for example, in the patents hereinabove referred to; the catalyst may, however, be an equal molecular mixture of nickel and tungsten sulfides, chromium oxide supported by activated alumina or any other hydrogenation-dehydrogenation catalyst suitable for use in the hydroforming reaction.

With the catalyst bed at a temperature of about 900° to 1100° F., preferably about 1000° F. and a pressure of from about 100 to about 500 pounds per sq. inch, the naphtha charging stock is introduced through line **15** at a temperature at from about 950° to 1050° F., e. g., about 1000° F. and recycled hydrogen is introduced through line **16** or if preferred it may be mixed with the naphtha charge prior to introduction to the reactor and introduced through line **15**. It is preferred to carry out the hydroforming reaction at temperatures above about 900° F. because of more desirable equilibrium relationships which favor production of aromatics, particularly benzene. The hydrogen is introduced preferably at a temperature about 50° to 200° higher than the temperature of the introduced naphtha. Usually about 1 to 5, preferably 3 mols of recycled gas is employed per mol of charging stock and the recycle stock contains at least about 35% and preferably upwards about 70 percent hydrogen. The space velocity is within the approximate range of about 0.2 to 2 volumes of total charge (liquid basis) per hour, by volume of catalyst space. In the event spaced injection of the aromatic-diolefin stream through lines **18**, **19** and/or **20** is employed the space velocity may be lower in the upper part of the reactor where only the naphtha is charged then in the lower part of the reactor where the naphtha is supplemented by the diolefin fraction.

An 80 per cent overhead cut of the aromatic-diolefin

fraction, said cut having a boiling range of from about 100° to about 300° F., and containing a somewhat higher concentration of aromatics and diolefins than set forth above for the total stream, is introduced via line **17** to the reactor and is dispersed in the naphtha being charged through line **15** by means of a suitable distribution nozzle at the end of line **17** extending into the top of the reactor. The amount of this fraction which may be introduced will depend, apart from mechanical limitations, upon the amount of hydrogen that is made available by dehydrogenation of the naphtha, the particular naphtha charged, catalyst bed temperature limitations, etc. In general it has been found desirable to substitute the aromatic-diolefin fraction, essentially barrel for barrel, for a portion of the naphtha charge, i. e., a barrel of naphtha is withheld from the charge for each barrel of aromatic-diolefin introduced. Since the naphtha preheater on most hydroformers is ordinarily designed for a throughput corresponding to the capacity of the reactor it is not entirely satisfactory to reduce the amount of naphtha charged to a point much below the design figure. It may be said, however, that in general as much of the aromatic-diolefin fraction may be charged as is permissible from the engineering standpoint, taking into consideration capacity of the reactor, the amount of hydrogen available for hydrogenation of the unsaturated material in the aromatic-diolefin charged and for use in purging the reactors, the reactor temperature limitations, etc. In the particular reactor employed (substantially as described in U. S. 2,388,536) it has been found that from about 5 to about 30 per cent by volume of the total charge may constitute aromatic-diolefin fraction when operating with a naphthenic heavy naphtha. With a high benzene content naphthenic naphtha from about 5 to about 20 per cent by volume may be charged while with a paraffinic heavy naphtha from about 5 to about 18 per cent by volume of the aromatic-diolefin may be introduced. Thus, depending upon the particular naphtha charged, from about 5 to about 30 volume per cent of the total charge may constitute aromatic-diolefin fraction.

The total products are withdrawn through line **21** and cooler **22**, then introduced into a separator **23** from which hydrogen is recycled through heater **24** and line **16** back to the reactor while the liquid product is withdrawn through line **25**, passed through heater **26** prior to preliminary fractionation in column **27** from which a prebenzene fraction is withdrawn overhead for blending in gasoline. The bottoms from prefractionator **27** pass through line **28** via heater **29** and are then introduced to fractionator **30** wherein a benzene concentrate is produced which is taken overhead from column **30** via line **31** through cooler **33** to benzene concentrate storage **34**.

Benzene concentrate is fed through line **35** to heater **36** and then introduced to the extractive distillation column **37** where it is distilled and contacted countercurrently with phenol introduced via line **42**. The raffinate is withdrawn via line **38** for blending in gasoline. The solution of benzene in phenol passes through line **40** to solvent stripper **41** wherein the phenol is stripped substantially free of benzene and the stripped phenol solvent is recycled through line **42** to the extractive distillation column **37** via cooler **39**. The benzene distillate goes overhead from column **41** via line **43** and may optionally be rerun in column **45** to recover pure benzene. In general the final rerunning step has been found unnecessary because substantially pure benzene comes overhead from stripper **41**. The method of recovering benzene from the hydroformer product is that which is preferred but it is not intended that this invention be limited thereto since other suitable methods known to the art may be employed if desired, such as azeotropic distillation, etc. In addition to the use of phenol as the solvent various other solvents may be employed such as resorcinol, cresylic acid, etc.

In Table II below are set forth comparative runs wherein each of three different type naphthas were charged to the hydroformer with and without the aromatic-diolefin fraction. The so-called high benzene content naphthenic naphtha is a rather low boiling fraction (about 150° to about 275° F.) containing a relatively high percentage of benzene, methylcyclopentane and cyclohexane. The naphthenic heavy naphtha is a higher boiling naphtha fraction (about 250° to about 425° F.) which contains essentially no benzene, methylcyclopentane or cyclohexane. The paraffinic naphtha is a stock boiling in about the same range as the heavy naphthenic naphtha (from about 200° to about 410° F.) which likewise contains substantially no benzene, methylcyclopentane or cyclohexane but comprises paraffins to a large extent. As may be seen from Table II, the conversion of total hydroformer charge to gasoline from each of these naphthas is substantially improved by the addition of the aromatic-diolefin fraction as herein described. It should be understood that the percentage gasoline yields given in the table are based on the total charge less benzene in the aromatic-diolefin fraction. A surprising feature of this invention as evidenced by the data in Table II lies in the fact that in addition to recovering substantially all of the benzene from the aromatic-diolefin fraction and producing more gasoline, there is substantially no increase in polymer and coke deposition remains the same or is decreased. In addition it should be noted that the amount of make-gas (hydrogen) is greatly reduced with increased amounts of aromatic-diolefin charged.

TABLE II

	High Benzene Content Naphthenic Naphtha*				Naphthenic Naphtha*				Paraffinic Naphtha*	
	1	2	3	4	5	6	7	8	9	10
Naphtha Charge	6,551	6,663	6,470	5,898	6,314	6,268	5,827	5,826	7,740	7,280
Aromatic-Diolefin	0	0	300	528	0	0	448	448	0	500
Total charge	6,551	6,663	6,770	6,426	6,314	6,268	6,275	6,274	7,740	7,780
Percent Conversion to Gasoline**	76	77.5	77.2	83.7	78.5	79.3	83.4	83.3	78.7	83.5
Benzene in Aromatic-Diolefin Charge			159	251			230	230		238
Benzene in Naphtha	268	240	207	223	Nil	Nil	Nil	Nil	Nil	Nil
Benzene Produced From Non-Benzene Stock	708	677	606	551	55	65	58	58	79	73
Total Benzene Recovery	976	917	972	1,025	55	65	263	263	79	297
Percent Benzene Recovery From Aromatic-Diolefin Charge			79	83			89	89		94
Polymer	56	56	60	51	152	160	171	171	130	130
Coke, #/D	7,900	6,900	7,900	6,100	12,500	12,550	9,300	10,500	17,000	10,500
Make Gas, MCF/D	4,880	4,600	5,080	2,570	4,230	3,940	3,260	3,120	4,600	3,210

*Barrels per day unless otherwise indicated.
**Based on total charge minus benzene in aromatic-diolefin charge.

In Fig. 2 the application of this invention to a fluid type hydroforming system is illustrated. Recycled hydrogen from line **16** is compressed by compressor **48** and it picks up hot regenerated catalyst from the base of standpipe **49** in amounts regulated by valves **50** and carries this catalyst by line **51** to the base of reactor **52**.

The naphtha may be introduced through line 53 directly into the reactor or it may be introduced into the reactor through line 51. It is preferred to introduce the naphtha via line 53 directly to the catalyst bed at a point above the grid or at least above the point of hydrogen inlet so that the recycle hydrogen may condition the catalyst, to some extent, prior to contact of said catalyst with introduced naphtha. The general operating conditions may be substantially the same as in the previous example but in this case the catalyst is in finely divided form with a particle size chiefly within the range of from about 10 ot 100 microns. The catalyst is uniformly distributed in the reactor by grid 54 and the upward gas velocity in the reactor is of the order of about .2 to 2 feet per second so that the catalyst will form a fluidized liquid-like dense turbulent suspended phase superimposed by a light dispersed catalyst phase. The aromatic-diolefin fraction is introduced through line 55 and distributors 56 at a downstream point in the reactor, preferably at about the middle of the dense turbulent catalyst phase and above the naphtha inlet so as to take advantage of additional hydrogen liberated in the dehydrogenation reactions. Alternatively, the aromatic-diolefin stream may be introduced to the reactor via line 55*a* to line 51 where it is admixed with the recycle gas containing large amounts of uncombined hydrogen. The catalyst is withdrawn for regeneration through standpipe 57 from the base of which it is picked up by air introduced through line 58. The product stream may pass through one or more cyclone separators 59 for knocking back entrained solids and it may then pass by line 60 to scrubber 61 into which a nonvolatile scrubbing oil may be introduced through line 62. The catalyst fines from the products may be withdrawn through line 63 and returned through line 64 and line 51 to the reactor or withdrawn through line 65. The catalyst free-product stream then passes through line 21 and cooler 22 to separator 23 from which hydrogen is recycled through line 16 and the products are withdrawn through line 25 for fractionation and recovery in the same manner as shown in Fig. 1 with respect to fixed bed operation. If the heat of the regenerated catalyst from standpipe 49 is not sufficient for the desired reaction a heater corresponding to heater 24 in Fig. 1 may be employed preferably between compressor 48 and standpipe 49.

The present invention is not limited to refining the liquid product resulting from pyrolysis of ethane and propane but is applicable generally to the treatment of hydrocarbon fractions boiling chiefly in the gasoline boiling range containing a substantial amount of aromatics such as benzene and of diolefins of potential value as motor fuel constituents, i. e., diolefins of such configuration that hydrogenation thereof would produce a substantial yield of suitable motor fuel components. Thus, the invention is applicable to similar fractions produced by the pyrolysis of various liquid petroleum fractions as well as to other such products obtained by pyrolyzing petroleum gases, generally. Typical of such aromatic-diolefin fractions are the liquid fractions boiling chiefly in the gasoline range obtained by pyrolyzing heavy charge stocks such as a reduced crude, a visbreaker tar, etc., at temperatures of from 1200° F. to about 1400° F. Thus, a 7% mixed paraffinic reduced crude having the inspection data set forth below in Table III was cracked at temperatures ranging from about 1200° F. to about 1500° F. by passing the same up through molten lead maintained at such temperatures.

TABLE III

7% reduced crude inspection

Gravity, ° API	15.8.
Viscosity:	
S. F. sec. at 210° F	72.
S. F. sec. at 122° F	
Conradson carbon residue	9.43.
Carbon and hydrogen analysis:	
Wt. per cent C	86.7.
Wt. per cent H	11.84.
Wt. per cent ash	0.10.
Wt. per cent sulfur	0.7.
Refractive index, n_D^{25}	Too dark.
Initial boiling point	850° F. (1 mm. converted).
Iodine No., cg./gm	21.
Flash point	230+.

Set forth in Table IV is inspection and product distribution of the C_6 to 400° F. gasoline fractions obtained at various cracking temperatures.

TABLE IV

Average properties of C_6–400° F. gasoline fractions from bench-scale high temperature cracking of 7 wt. percent mixed paraffinic reduced crude charge rate: Approximately 1 liter/hr. of reduced crude

C_6–400° F. E. P. Gasoline	1,200° F. Cracking	1,300° F. Cracking	1,400° F. Cracking	1,500° F. Cracking
Gravity, °API	48.6	40.9	32.7	30.5
Bromine No., cgs./gm	107	97	52	35
MAV, mg./gm	92	142.	71	53
Wt. Percent Sulfonated	72	91.9		
Aniline Point, ° F	87.2	Below 19.6	Below 19.6	
Wt. Percent Sulfur	0.7	1.0	0.8	0.6
Refractive Index, n_D^{25}	1.4433	1.4529	1.4877	1.4932
Composition, Wt. Percent:				
Total Aromatics	18.1	38.4	70.4	76.4
Benzene	2.7	13.0	33.2	46.4
Toluene	5.3	12.2	23.5	24.3
Xylene and Ethylbenzene	3.7	7.5	10.6	5.7
Mono-olefins	48.2	38.1	17.7	11.1
Diolefins	9.3	14.4	7.3	5.1
Paraffins and Naphthenes (By Difference)	24.4	9.1	4.6	7.4

It is apparent from the above mentioned table that fractions resulting from cracking the reduced crude at temperatures between about 1300° F. and 1400° F. contain the larger quantities of aromatics and diolefins and would, therefore, be especially suitable for treatment in accordance herewith. The gasoline fractions produced by pyrolysis at lower temperatures do contain, however, substantial amounts of both diolefins and aromatics and may be charged to the hydroformer with advantage. The C_4 and C_5 fractions from this pyrolysis also contain some diolefins and may be blended with the C_6 to 400° F. fraction for use in accordance herewith. The introduction of the aforementioned gasoline boiling range aromatic-diolefin mixture to the hydroformer is effected in same manner as discussed above with respect to the 80% overhead fraction of the product resulting from pyrolysis of a gas stream. Thus, such aromatic-diolefin fractions may be handled similarly, regardless of source.

Other stocks somewhat lower boiling than residuums and tars, e. g. cycle oils from catalytic cracking, petroleum naphtha fractions, etc., have also been pyrolyzed at temperatures of about 1200° to 1500° F. to produce fractions boiling chiefly in the gasoline range which contain a substantial quantity of aromatics and diolefins, at least about 5% and higher. Butane, mixtures of butane and other gases, etc., in addition to the gases previously referred to will likewise produce, under similar conditions, products which may advantageously be charged to hydroformers in accordance with the present invention. Moreover, aromatic-diolefin products of the type described herein may be produced in the so-called "Gyro Process" which is a thermal cracking process of the type described in U. S. 2,101,800 and other patents.

It is to be understood that the specific methods of preparing these various aromatic-diolefin stocks suitable for use in accordance herewith are not per se part of the invention but it should be further understood that enumeration of the various charge stocks which may be pyrolyzed is for purpose of illustration and not of limitation. Any liquid pyrolysis product, whether from gaseous or liquid petroleum hydrocarbon fraction, which boils chiefly in the gasoline range and which contains substantially more diolefins than are present in a cracked naphtha and an amount of aromatics substantially in excess of the diolefin content is included within the scope of the present invention, and may be advantageously charged to a hydroformer in accordance herewith.

Although this invention has been specifically described with respect to refining the 80 per cent overhead fraction of the liquid product resulting from the pyrolysis of ethane and propane it may be found more advantageous to treat the entire product or other fractions thereof. The 80% overhead fraction, having an end point of about 300° F. is particularly suitable since the benzene is more concentrated and the heaviest boiling substances, which are of somewhat more doubtful potential value as motor fuel constituents, are eliminated prior to introduction to the hydroformer.

Since aromatics generally have high octane numbers it may be found desirable under certain circumstances to leave the aromatics in the gasoline fraction rather than recovering the same in pure state.

The present application for Letters Patent is a continuation in part of our application for Letters Patent Serial No. 242,512, filed August 18, 1951, and now abandoned.

Alternative embodiments and conditions will be apparent from the above description to those skilled in the art.

Having thus described our invention, what we claim as novel and desire to protect by Letters Patent is as follows:

1. A method which comprises introducing a vaporized petroleum naphtha charge into a space above the catalyst bed in a hydroforming reactor; introducing as a separate stream to said space between about 5% and about 30% by volume, based upon total hydrocarbon charge, of a liquid hydrocarbon fraction resulting from the pyrolysis of a petroleum fraction and boiling chiefly in the gasoline boiling range which contains a volume percentage of diolefins substantially in excess of that present in a cracked naphtha fraction and a volume of aromatics substantially in excess of said diolefin content, said hydrocarbon fraction being introduced at a temperature below the polymerization temperature of said diolefins; introducing into admixture with said naphtha and said hydrocarbon fraction in said space a substantial amount of uncombined hydrogen; and contacting the admixture of naphtha petroleum fraction, normally liquid hydrocarbon fraction and uncombined hydrogen with hydroforming catalyst under hydroforming conditions and recovering an aromatic hydrocarbon, initially present in said hydrocarbon fraction, from the hydroformer product.

2. The method of claim 1 wherein the substantially pure aromatic hydrocarbon is recovered from the hydroformer product by fractionating said product to produce a concentrate of said aromatic hydrocarbon and extractively distilling said concentrate in the presence of a phenolic solvent to separate said aromatic hydrocarbon.

3. The method of claim 1 wherein the hydroforming catalyst comprises molybdenum oxide mounted on active alumina.

4. In a hydroforming process carried out at a temperature of about 900° to about 1100° F., a pressure of about 100 to 500 pounds per square inch and in the presence of a hydroforming catalyst wherein a petroleum naphtha fraction is heated to a temperature of about 950° to about 1050° F. and introduced to a reaction zone containing said catalyst and hydrogen-rich gases are continuously recycled to said reactor, the improvement which comprises introducing between about 5% and about 30% by volume based upon total hydrocarbon charge of a normally liquid hydrocarbon fraction resulting from the pyrolysis of a petroleum fraction stream and comprising substantial amounts of aromatics and diolefins boiling chiefly within the gasoline boiling range, to said hydrogen-rich gases, before such gases are introduced to the reactor, introducing the resulting admixture of normally liquid hydrocarbon fraction and hydrogen-rich gases to said reaction zone wherein said petroleum naphtha fraction is being hydroformed and recovering a substantially pure aromatic hydrocarbon initially present in said normally liquid hydrocarbon fraction from the hydroformer product.

5. The process of claim 4 wherein said substantially pure aromatic hydrocarbon is recovered from the hydroformer product by first fractionating said hydroformer product to concentrate said aromatic hydrocarbon and recovering said aromatic hydrocarbon in substantially pure state from said concentrate by extractively distilling the same in the presence of a phenolic solvent.

6. The method of processing an aromatic-diolefin charge, containing a volume percentage of diolefins substantially in excess of that present in a cracked naphtha fraction and a volume of aromatics substantially in excess of said diolefin content, boiling within the range of 100 to 430° F. and produced by pyrolysis of an ethane-propane mixture at a temperature of about 1300 to 1400° F. which method comprises contacting a naphtha in a reaction zone in the presence of a hydroforming catalyst at a temperature in the range of about 900 to 1000° F. under a pressure of about 100 to 500 p. s. i. in the presence of a recycle hydrogen stream at a volume space velocity in the range of about .2 to 2 and introducing into said reaction zone an amount of said aromatic-diolefin charge in the range of about 5 to 30% by volume based on total hydrocarbon charge, and maintaining said aromatic-diolefin charge at a temperature below diolefin polymerization temperature until it is admixed with hydrogen introduced to the reaction zone.

7. The method of claim 6 wherein the aromatic-diolefin charge is introduced directly into the reactor as a stream which is separate from the introduced naphtha charge.

8. The method of claim 6 wherein the aromatic-diolefin charge is introduced to the reaction zone in the recycled hydrogen stream.

9. In a hydroforming process operated in the presence of a recycled hydrogen stream at a temperature in the range of 900° to 1000° F. and under a pressure in the range of about 100 to 500 p. s. i. wherein a petroleum naphtha charge is heated to a temperature in the range of about 900 to 1050° F. and introduced to a reaction zone containing a hydroforming catalyst, the improved method of operation which comprises replacing about 5 to about 30% of the petroleum naphtha charge with a separately introduced aromatic-diolefin charge resulting from the pyrolysis of a petroleum fraction, boiling chiefly in the gasoline boiling range and containing a volume

percentage of diolefins substantially in excess of that present in a cracked naphtha fraction and a volume of aromatics substantially in excess of said diolefin content, said aromatic-diolefin charge being introduced to the reaction zone at a temperature below the polymerization temperature of diolefin components and said aromatic-diolefin charge being contacted with free hydrogen while its temperature is raised to the temperature maintained in the reaction zone.

10. The method of claim 9 wherein the aromatic-diolefin charge is a by-product of the pyrolysis of an ethane-propane mixture at a temperature in the range of about 1300 to 1400° F.

11. The method of claim 10 in which the aromatic-

diolefin charge boils in the range of about 100 to 300° F.

12. The method of claim 9 wherein the aromatic-diolefin charge is a product of the pyrolysis of a liquid hydrocarbon fraction.

13. The method of claim 12 wherein the liquid hydrocarbon fraction is a reduced crude.

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