

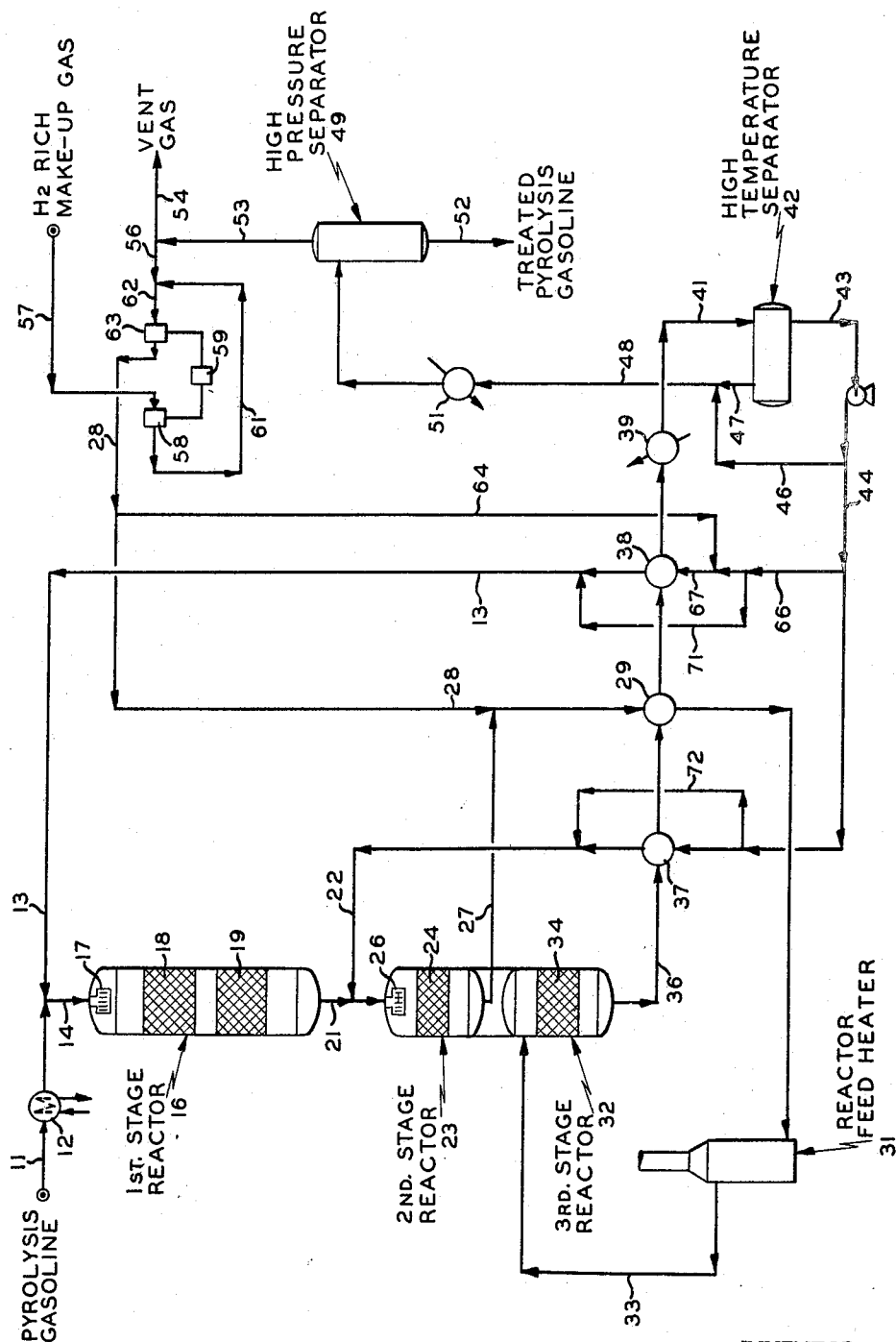
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HYDROTREATING PYROLYSIS GASOLINE

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1

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HYDROTREATING PYROLYSIS GASOLINE

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ABSTRACT OF THE DISCLOSURE

A full boiling-range pyrolysis gasoline containing styrene and C_5 and lighter hydrocarbons is hydrotreated with a sulfided nickel catalyst under conditions which produce either stable gasoline in a single zone or a substantially olefin-free, sulfur-free product in two or more reaction zones. The initial hydrotreating zone employs relatively mild hydrogenation including relatively low temperatures. The two- and three-zone processes are directed to relatively more severe hydrogenation conditions without the serious problems of equipment fouling and catalyst aging which are problems previously associated with diolefinic compounds.

This invention relates to upgrading pyrolysis gasoline and, more particularly, to a method for catalytically hydrotreating pyrolysis gasoline to produce either stable high octane gasoline or suitable feedstock for aromatic extraction.

Steam pyrolysis of hydrocarbons under conditions suitable to produce normally gaseous olefins such as ethylene and propylene produces a by-product boiling in the gasoline range which is generally termed "pyrolysis gasoline." This by-product gasoline is characterized by unusually high concentrations of unsaturated hydrocarbons relative to straight run and ordinary cracked gasolines. Thus, pyrolysis gasoline contains generally between about 2 and about 20 mol percent of diolefins, between about 3 and about 40 mol percent of mono-olefins and between about 20 and about 80 mol percent of aromatic hydrocarbons. The precise amounts of each type of hydrocarbon will vary somewhat depending upon the nature of the hydrocarbons subjected to steam pyrolysis and the conditions used. Typical properties of uninhibited pyrolysis gasoline as produced are:

Octane number, CFRR Clear	85-105
Bromine number	30-70
Maleic anhydride value, mg./g.	70-150
Gum, existent mg./100 cc.	15-40
Induction period, minutes	0-50

Pyrolysis gasoline is potentially valuable as motor fuel because of its high octane number. Furthermore, because of its high aromatic content, pyrolysis gasoline is also potentially valuable as a feedstock for aromatic extraction to recover benzene, toluene and the xylenes which are useful as solvents and for other purposes. Unfortunately, however, pyrolysis gasoline is unsuitable for direct use in either of these applications. Its high diolefin content, as indicated by maleic anhydride values, is associated with a tendency to form gums, as indicated by the values for existent gum and induction period, which interfere with its use in either application. From the standpoint of using pyrolysis gasoline as a feedstock for aromatic extraction, the presence of olefins, as indicated by values of bromine number, creates a further problem because these materials are associated with poor extraction selectivity.

The large number of processes which have been developed for upgrading ordinary cracked gasolines and other

2

relatively saturated feeds are unsuitable for upgrading pyrolysis gasoline. The highly unsaturated character of pyrolysis gasoline creates special problems of equipment fouling and catalyst aging not solved by such processes. A few special processes have been proposed for upgrading pyrolysis gasoline to motor fuels and extraction feeds. Commercially, the more important of these processes involve hydrotreating, i.e., catalytic hydrogenation. Thus, some processes are available for selectively hydrogenating the high diolefin content of pyrolysis gasoline to produce a high octane motor fuel. Unfortunately, these processes are not completely satisfactory in that it has been found necessary to add inhibitors to the gasoline product or to the feed in order to meet stability specifications in terms of existent gum and induction period. The use of inhibitors adds to the cost of the process and the product and may create a separate problem of engine deposits when the product is subsequently burned as fuel. Other processes have been developed for hydrotreating pyrolysis gasoline to prepare an extraction unit feedstock. These processes too are not completely satisfactory because they are limited to treating selected fractions of the pyrolysis gasoline and not applicable to treating a full boiling-range pyrolysis gasoline such as one containing C_5 and lighter hydrocarbons and/or one containing styrene. A common disadvantage of the various processes now available is that they are not sufficiently flexible to be used at times to make motor fuel and at other times to make extraction feedstock. Furthermore, it is characteristic of these prior processes that the catalyst requires fairly frequent regeneration or replacement due to the formation of deposits on the catalyst. Frequent interruption of the process for regeneration or replacement is costly and therefore undesirable.

The present invention has as its general object the provision of a process for hydrotreating pyrolysis gasoline which overcomes the foregoing disadvantages of prior art processes. Other and more detailed objects and advantages of the invention will be apparent to those skilled in the art from the following detailed discussion and description.

The improved method of the invention comprises contacting pyrolysis gasoline with hydrogen-containing gas in the presence of a nickel sulfide catalyst in a first hydrotreating zone at relatively low temperatures and under other conditions which assure that at least a substantial portion of the hydrocarbons is in liquid phase, whereby a gasoline product, stable without inhibition, is obtained, and then contacting effluent of the first hydrotreating zone with an active hydrogenation catalyst in a second hydrotreating zone at relatively higher temperatures to produce a feed for aromatic extraction. When a stable high-octane gasoline only is desired, the second hydrotreating zone is by-passed and the products of the first hydrotreating zone are recovered directly.

The feed to the process comprises pyrolysis gasoline having a boiling range of up to 425° F. ASTM end point. The initial boiling point can be as low as about 95° F. ASTM. The pyrolysis gasoline boils essentially below 400° F. with not more than about 10 volume percent boiling above 400° F. An important advantage of the invention resides in the ability of the process to hydrotreat feeds containing C_5 and lighter hydrocarbons including butadiene and/or ones containing styrene, without undue equipment fouling and catalyst aging. Although a full-boiling range pyrolysis gasoline can be treated by the process of the invention, it is within the scope thereof to treat any selected fraction of the full boiling range pyrolysis gasoline. Depending upon the process of which the pyrolysis gasoline is a by-product, it may also contain varying but small quantities of impurities such as sulfur.

The hydrogen-containing gas supplied can also introduce impurities such as carbon monoxide. These impurities do not interfere with the process and, in the case of sulfur, are removed by the process.

The pyrolysis gasoline feed is initially contacted in the presence of a supported nickel sulfide catalyst containing about 5 to about 40 percent by weight of nickel calculated as the element. The selection of a nickel sulfide catalyst is important. It is an active but relatively mild hydrogenation catalyst as compared with elemental nickel and nickel oxide catalyst. Because of the highly unsaturated character of the pyrolysis gasoline feed, the initial catalyst must have relatively mild hydrogenation properties to prevent excessive non-selective hydrogenation of the pyrolysis gasoline. At the same time, it must be sufficiently active to promote substantially complete conversion of diolefins to more saturated hydrocarbons at the relatively low temperatures required. Excessive non-selective hydrogenation must be avoided both in order to avoid serious impairment of the octane number of the gasoline through saturation of mono-olefins and aromatics and in order to prevent excessive temperature rise which will induce deposition of gums and other solids on catalyst surfaces. Generally, any of the several available methods of preparing the nickel sulfide catalyst can be used. A preferred method of preparation involves reducing a nickel oxide catalyst using hydrogen and sulfiding the elemental nickel catalyst by passing hydrogen sulfide or reactive organic sulfur compounds such as mercaptans thereover. An example of a suitable organic compound is tertiary butyl mercaptan. This material is a liquid at ambient conditions which allows for easy storage.

The reaction in the presence of nickel sulfide catalyst is carried out over a restricted temperature range. Generally, temperatures of about 200° F. to about 500° F. are used. Preferably, temperatures are between about 350 and about 475° F. The minimum temperatures must be observed at the inlet to the catalyst bed because temperatures lower than these are not sufficient to cause significant hydrogenation. The reaction threshold temperature varies somewhat with the specific characteristics of the catalyst and the pyrolysis gasoline being treated. The higher temperature limits must be observed in order to avoid hydrocracking of the pyrolysis gasoline which is appreciable at temperatures above about 525° F. Hydrocracking produces gas and coke at the expense of yield and catalyst life. In general, all operating conditions in the first hydrotreating zone are selected to cause substantially complete hydrogenation of diolefins, i.e., to produce a product having a maleic anhydride value of no more than about 3.0, with a minimum of hydrogenation of mono-olefins and aromatics. Such a result involves a net hydrogen consumption depending upon the initial diolefin content of about 75 to about 250 standard cubic feet of hydrogen per barrel of pyrolysis gasoline (s.c.f./b.). There will be a temperature rise proportionate to the hydrogen consumed because the hydrogenation reaction is exothermic. In use, the nickel sulfide catalyst gradually loses activity which is compensated for by raising inlet temperature. Outlet temperatures will rise accordingly but should not be allowed to exceed the upper temperature limits previously stated. When the maleic anhydride value specification can no longer be met by raising inlet temperature in view of the temperature limitations stated, operation should be discontinued and the catalyst should be regenerated.

It is essential to the success of the process that at least a substantial portion of the hydrocarbons remain in liquid phase throughout the first hydrotreating zone. Experiments have shown that in the absence of substantial amounts of material in liquid phase the catalyst ages, i.e., loses activity very rapidly. At the temperatures prevailing in the first hydrotreating zone, a pressure above about 550 p.s.i.g. should be used in order to maintain a substantial portion of the hydrocarbon in liquid phase. Pref-

erably, pressures of about 600 to about 1000 p.s.i.g. are used. Additional assurance of maintaining a liquid phase can be obtained by carrying out the reaction in the presence of added stable liquid hydrocarbons having a boiling range no lower than that of pyrolysis gasoline and preferably a somewhat higher boiling fraction. The term "stable liquid hydrocarbons" embraces normally liquid hydrocarbons substantially free of diolefins. The added stable liquid hydrocarbons can be for example an extraneous gas oil fraction which is continuously recycled in the process. A more preferred and convenient source of added stable liquid hydrocarbons is the heavier portion of the stable product of the process itself, a portion of which can be recycled for phase control. Temperature control is also facilitated by recycling stable liquid hydrocarbons. Thus, the recycle stream can be preheated to a temperature sufficient to provide the desired reactor inlet temperature upon admixture with the pyrolysis gasoline feed. Furthermore, the exothermic heat of the hydrotreating reaction will be taken up in part as latent heat of vaporizing hydrocarbons initially in liquid phase thus reducing the net temperature rise.

Catalyst requirements and contact time in the first hydrotreating zone are expressed in terms of liquid hourly space velocity (LHSV). In general, LHSV of about 0.5 to about 10.0 volumes of pyrolysis gasoline calculated as liquid per volume of catalyst per hour is used. Preferably, a LHSV of about 1.0 to about 3.0 is used on this basis. Where added stable liquid hydrocarbons are used as recycled product or otherwise, the volumetric ratio thereof to pyrolysis gasoline is about 0.5 to about 3.0. The total amount of hydrogen-containing gas supplied to the first hydrotreating zone is in substantial excess of stoichiometric requirements in order to minimize coke formation but not so great as to cause non-selective hydrogenation. On this basis, a ratio of total hydrogen to pyrolysis gasoline of about 500 to about 3000 s.c.f./b. is used. Ordinarily, the bulk of the hydrogen-containing gas is obtained by separating and recycling the unreacted hydrogen. A portion of the recycle gas is vented and fresh hydrogen-rich gas is added to make up the net hydrogen consumed and to maintain the level of hydrogen above about 55 mol percent. The ratio of recycle gas to pyrolysis gasoline is about 650 to about 4000 s.c.f./b. or about 0.5 to about 4.2 mols per mol.

As indicated, the presence of a quantity of liquid phase throughout the course of the treatment over nickel sulfide catalyst in the first hydrotreating zone is essential to successful operation of the process. Experiments have been made which establish that the catalyst ages rapidly and that hydrogenation of diolefins to mono-olefins is incomplete where essentially vapor phase conditions exist. The principle involved appears to be that a certain amount of the conjugated diolefins and related materials present in pyrolysis gasoline polymerize or otherwise react readily to form varnish-like films on catalyst surfaces so that the liquid phase is necessary to wash catalyst surfaces and prevent rapid build-up of deposits on the catalyst. On this basis, the minimum amount of liquid phase required is that amount sufficient to wet the catalyst. The amount of liquid required for wetting will vary with the physical characteristics of the catalyst and the configuration of the catalyst bed. In view of the great variation which is possible in this regard, it is impractical to attempt a listing which will cover every case. It will be appreciated by those skilled in the art that a few simple experiments with the specific catalyst, bed configuration and reaction conditions to be used will establish the amount of liquid required in a given case. The latter will be so whatever the mechanism involved may be. It should be understood that the invention is not to be limited by any theory here advanced since, in any case, a substantial amount of liquid phase is essential.

As a result of the process carried out in the first hydrotreating zone, an excellent product, boiling in the

5

gasoline range, is produced. Typical properties of the uninhibited gasoline-boiling-range product are as follows:

Octane number, CFRR clear -----	83-103
Bromine number -----	20-45
Maleic anhydride value, mg./g. -----	0-2.0
Gum, existent mg./100 cc. -----	0-1.0
Induction period, minutes -----	Above 250

As is apparent from the values which bear upon stability, inhibitors against gum formation are not required to meet usual gasoline stability specifications. Although there can be some decline in the octane number due to partial hydrogenation of mono-olefins, as shown by decline in the bromine number, the lead susceptibility of the treated gasoline is improved with respect to the untreated gasoline. Hence, on a leaded basis, the gasoline product can and frequently will have an octane rating as high or higher than the feed. The low maleic anhydride values indicate that substantially no diolefinic compounds remain after the first stage of hydrotreating. It is also important to note that the aromatic content of the pyrolysis gasoline is essentially unaffected by the first stage treatment.

In the production of a suitable feedstock for aromatic extraction, the products of the first hydrotreating zone are contacted in a second hydrotreating zone under relatively more severe but controlled hydrotreating conditions using an active hydrogenation catalyst. Conditions are controlled to cause selective hydrogenation of the remaining traces of diolefinic compounds and of monoolefinic compounds and to cause desulfurization.

Any hydrogenation catalyst active under the more severe hydrogenation conditions maintained in the second hydrotreating zone can be used. Such catalysts are well known and include a group VI metal compound including, for example, the oxide and/or sulfide of the left-hand elements thereof, specifically, chromia and/or molybdenum trioxide supported on alumina; the group VI metal compound can be promoted with a compound of a metal of group VIII having an atomic number not greater than 28 such as for example, the oxides and/or sulfides of iron, cobalt and nickel or the latter can be used alone on a support. A preferred catalyst is one containing about 2 to about 5 weight percent cobalt and about 5 to about 15 weight percent molybdenum on a support. This catalyst will normally become sulfided in use. Conditions used in the second hydrotreating zone include temperatures of about 650 to about 800° F., pressures of about 550 to about 1000 p.s.i.g., space velocities on the basis of liquid pyrolysis gasoline feed of about 0.5 to about 10.0 LHSV, and a ratio of recycle gas to pyrolysis gasoline of about 500 to about 3000 s.c.f./b. The pressure used is preferably substantially that of the first hydrotreating zone in order to minimize compression requirements for the recycle gas.

In a preferred method of practicing the invention, the hydrotreating process is carried out in three stages, the first and third of which correspond to the operation of the first and second hydrotreating zones discussed above, and the second of which functions as an intermediate hydrotreating zone. In the second stage or intermediate hydrotreating zone, the products of the first stage are contacted with hydrogen-containing gas in the presence of an active hydrogenation catalyst such as one of the catalysts previously indicated for the second hydrotreating zone under conditions such that, at least at the inlet to the catalyst bed, a portion of the hydrocarbon is in liquid phase. Temperatures in the intermediate hydrotreating zone are intermediate those of the first and second zones. Suitable temperatures are about 475 to about 600° F. Temperature and phase control can be achieved by use of added stable liquid hydrocarbons, preferably a further portion of the stable product stream, the use of

6

which in connection with the first hydrotreating zone has been previously described. With the exception of higher temperatures and any use made of further stable liquid hydrocarbons, the conditions used in the intermediate hydrotreating zone are as set forth for the first hydrotreating zone. In this way the maleic anhydride value of the pyrolysis gasoline is reduced essentially to zero as the small remaining quantities of diolefinic compounds are hydrogenated in the presence of a liquid phase. Hydrogenation can then be continued under relatively high temperatures and in vapor phase without the serious problems of equipment fouling and catalyst aging associated with diolefinic compounds.

The stable products of the intermediate hydrotreating zone are then heated and treated in the second hydrotreating zone. The recycle gas quantities specified are provided in part by unreacted gas in the effluents of the intermediate and first hydrotreating zones and the balance is added. Hydrogen consumption is about 100 to about 500 s.c.f./b. on the basis of pyrolysis gasoline which corresponds to a temperature rise of about 25 to about 75 Fahrenheit degrees. As a result of the several stages of treatment a stable, desulfurized and saturated product suitable for aromatic extraction is obtained. Typical properties of this uninhibited product are as follows:

Bromine number -----	0-2.0
Maleic anhydride value -----	0-0.2
Gum, existent mg./100 cc. -----	0-1.0
Induction period, min. -----	Above 420
Sulfur -----	Below 25 p.p.m.

The original content of aromatics is essentially unaffected by the treatment so that the ultimate recovery of benzene, toluene and xylenes from the raw pyrolysis gasoline is limited essentially only by the efficiency of the extraction process.

Under the indicated conditions of operation, extended catalyst life is obtained and problems of fouling are minimized. The catalysts are responsive to standard regeneration techniques which are found to restore catalyst activity and selectivity even after the catalyst has been permitted to become severely deactivated.

As mentioned, the multi-stage process can be practiced without undue fouling on a full-boiling-range feed including one containing styrene, contrary to the experience of others. This result appears to be due to the substantially complete initial removal of diolefinic and acetylenic materials prior to exposing the pyrolysis gasoline to the active hydrogenation catalyst and relatively severe hydrogenation conditions of the second hydrotreating zone. It further appears that the latter result is due to the combination of catalyst, conditions used and the presence of liquid phase in the first hydrotreating zone. Again however it should be noted that the invention is not to be limited by this or any other suggested explanation of its success.

For a better understanding of the invention and a specific example of its use, reference is had to the accompanying drawing which illustrates suitable apparatus in diagrammatic form for carrying out a preferred embodiment of the invention.

Referring now to the drawing, pyrolysis gasoline is introduced to the process through line 11. The pyrolysis gasoline feed is derived as a by-product of a process for the steam pyrolysis of naphtha for the production of ethylene and propylene. The feed in line 11 is heated to about 300° F. by indirect heat exchange with low-pressure steam in exchanger 12. The preheated feed is then joined by a saturated recycle liquid-recycle gas stream from line 13 which is at a higher temperature and brings the mixture in line 14 to the desired initial reaction temperature. The feed in line 14 is introduced into first stage reactor 16 by means of a suitable distributor 17 which distributes the charge uniformly over the surface of the nickel sulfide catalyst bed 18. A second nickel sulfide

catalyst bed 19 is used which permits redistribution of the reactants between the beds. The saturation reaction in first stage reactor 16 is exothermic thereby causing an increase in temperature.

The essentially diolefin-free stream leaving the first stage reactor 16 through line 21 is combined with additional saturated recycle liquid from line 22 prior to entering the second stage reactor 23. The combined feed is introduced uniformly over a bed of cobalt molybdate catalyst 24 by means of distributor 26. In catalyst bed 24 of second stage reactor 23, the balance of the diolefins are saturated and a part of the olefins are saturated. Once again, a temperature rise occurs in the bed due to the exothermic reaction.

To accomplish complete saturation of olefins, the effluent of second stage reactor 23 in line 27 is combined with the balance of the recycle gas in line 28, heated by indirect heat exchange with effluent of the final reactor in heat exchanger 29 and further heated in the reactor feed heater 31 prior to entering the third stage reactor 32 through line 33. The third stage reactor 32 contains a bed of cobalt molybdate catalyst 34 which causes further reaction and a further temperature rise.

The substantially olefin-free effluent from catalyst bed 34 of third stage reactor 32 is withdrawn through line 36 and cooled in a series of heat exchange steps in heat exchangers 37, 29, 38 and 39 to an intermediate temperature such that the heavier components of the effluent are condensed at the prevailing reactor pressure. The partially condensed effluent is introduced via line 41 into high-temperature separator 42 in which a liquid-vapor separation is made. The liquid fraction from the high temperature separator 42 is withdrawn through line 43 and is recycled through line 44 to first and second stage reactors 16 and 23 for phase and temperature control. A portion of the condensed liquid can be passed through line 46 to join the uncondensed fraction in line 47 from high-temperature separator 42. The uncondensed fraction from line 47 together with any liquid from line 46 are passed through line 48 to high-pressure separator 49 after being cooled to about 70° F. in heat exchanger 51. A liquid-vapor separation is effected in high-pressure separator 49. The liquid phase separated is withdrawn through line 52 and is the treated pyrolysis gasoline product of the process. It is further processed by standard recovery techniques for the purpose of adjusting its boiling range to values consistent with the requirements of the aromatics extraction process to which it is to be charged.

The flashed vapor from high-pressure separator 49 is recycled via lines 53 and 56 to the process, a portion being vented through line 54. Fresh hydrogen rich make-up gas is introduced through line 57 and is compressed in a first stage 58 of a two-stage compressor 59. The partially compressed make-up gas in line 61 joins with the recycle gas in line 56 and the combined recycle gas stream in line 62 is compressed in second stage 63 of compressor 59 to the required reactor pressure.

A portion of the recycle gas in line 64 is combined with a portion of the recycle liquid from line 44 in line 66. The combined stream in line 67 is heated in exchanger 38 and passed through line 13 as aforesaid to combine with the fresh pyrolysis gasoline feed to first stage reactor 16. A second portion of the recycle gas is passed through line 28 as aforesaid to combine with the effluent of second stage reactor 23 for providing the recycle gas requirement of third stage reactor 32. The amount of the recycle gas vented through line 54 and the amount of hydrogen rich make-up gas introduced through line 57 are adjusted to prevent the build-up of normally gaseous hydrocarbons, to supply the net hydrogen consumed by the reaction and to maintain the desired hydrogen concentration in the recycle gas.

Various standard items of equipment such as pumps, valves and control instruments are used but are not shown. Since the need for such equipment is well known as is its

manner of use, these items are omitted from the drawing and discussion in the interest of simplicity.

EXAMPLE I

A pyrolysis gasoline having the composition and characteristics set forth in Table I below, when processed according to the flow sequence illustrated on the drawing and previously described, produces a stable high-octane gasoline product from first stage reactor 16 and an olefin-free and desulfurized product from third stage reactor 32, the composition and characteristics of which are also set forth in Table I below:

TABLE I

	Raw Pyrolysis Line 11 Gasoline	Stable Line 21 Gasoline	Olefin-Free Line 36 Desulfurized Product
°API.....	44.5	44.5	45.1
ASTM distillation, ° F.:			
IBP.....	130	130	128
10%.....	176	180	181
30%.....	208	208	209
50%.....	234	236	235
70%.....	265	264	265
90%.....	304	306	304
E.P.....	408	464	458
Maleic anhydride value, mg./g.....	76.2	1.9	Zero
Bromide number.....	49.2	29.1	0.6
Induction period, min.....	Zero	>390	>420
Existent gum, mg./100 ml.....	23.6	0.6	0.2
Sulfur, wt. percent.....	0.02	0.02	0.002
Aromatics:			
C ₆	14.7	14.7	14.4
C ₇	16.3	16.6	16.7
C ₈	14.3	14.1	14.5
C ₉	3.7	3.6	3.6
Octane numbers:			
CFRR-Clear.....	93.8	92.0	185.5
+3 cc.....	99.7	98.8	196.3
CFRM-Clear.....	79.3	79.2	
+3 cc.....	85.0	86.3	
Hydrogen consumption, s.c.f./bbl.....		190	320

¹ On 375° F. end point material.

The conditions used in achieving these results are set forth in Table II below:

TABLE II

Reactor.....	16	23	32
Inlet operating pressure (clean catalyst), p.s.i.g.....	850	830	800
Operating temperature, F.:			
Bed inlet (at start—at end of run).....	350—425	475—505	705
Bed outlet (at start—at end of run).....	405—475	500—530	750
Liquid hourly space velocity (Basis: pyrolysis gasoline feed).....	1.0	2.5	1.65
Volumetric recycle ratio, recycle liquid to pyrolysis gasoline feed.....	1.0	2.0	2.0
Recycle gas ratio, mol/mol charge of pyrolysis gasoline.....	1.66	1.66	2.48
Recycle gas ratio, s.c.f./bbl. of pyrolysis gasoline.....	1800	1800	2700
Recycle gas H ₂ content, mol percent.....	74	74	74
Type of catalyst.....	Ni ₂ S ₂	Co-Mo	Co-Mo
Catalyst Size, mesh (dia. in.).....	4-8	(1/8 x 1/8)	(1/8 x 1/8)

The operating conditions in high-temperature separator 42 are 370° F. and 725 p.s.i.g. and the recycle liquid is the condensate at this dew point. The operating conditions in high-pressure separator 49 are 70° F. and 700 p.s.i.g. The hydrogen rich make-up gas in line 57 contains about 79 mol percent hydrogen. It will be noted that the temperatures in the reactors, except for third stage reactor 32, are increased in the course of the run. This is done to compensate for the gradual loss of activity of the catalyst. Temperature control in first stage reactor 16 is achieved by controlling the temperature of the recycle gas-recycle liquid stream in line 13. Thus, the amount of recycle liquid passing through line 67 to exchanger 38 can be varied by controlling the amount of the recycle liquid from line 66 which bypasses exchanger 38 through line 71. The temperature of the recycle stream in line 13 will vary on this basis between about 380° F. and about 566° F. In like fashion, the temperatures in second stage reactor 23 are adjusted by controlling the temperature of the recycle liquid in line 22 which in turn is adjusted by controlling

the amount of recycle liquid which bypasses heat exchanger 37 through line 72. At the flow rates indicated in Table II, the temperature of the recycle liquid in line 22 varies between about 600° F. and about 655° F. In addition to the function performed by the recycle streams in line 13 and 22 of achieving temperature control, these streams also serve to provide phase control. Thus, at the flow rates indicated in Table II and the temperatures involved, liquid phase will be present in substantial amount throughout first stage reactor 16. With regard to second stage reactor 23, liquid phase will be present at the top of catalyst bed 24. At the lower bed outlet temperature, liquid phase will also be present at the bottom of bed 24 but at the higher bed outlet temperatures all of the reactants will have become substantially completely vaporized at the bottom of bed 24.

It will be noted from Table I that substantially all of the diolefinic materials are hydrogenated in first stage reactor 16 as shown by the low maleic anhydride value. At the same time, there is some hydrogenation of monoolefinic compounds as shown by the decline in the bromine number, but this does not materially affect the octane number of the gasoline, particularly on a leaded basis. The aromatic and sulfur contents of the stable gasoline product in line 21 are not substantially different from those of the feed. With regard to the further hydrogenation carried out in second and third stage reactors 23 and 32, it will be noted that substantially all olefinic materials have been hydrogenated as shown by the maleic anhydride value and the bromine number. The content of aromatics is again substantially unaffected, indicating the excellent selectivity obtained by the process. However, the data show that the final product is substantially desulfurized. It will be apparent from the foregoing that the process is readily adapted to process pyrolysis gasoline for the production of stable gasoline and/or an extraction feedstock without having to practice an intermediate fractionation, i.e., the process is a simple and unitary one having the flexibility to meet varying marketing needs.

EXAMPLE II

Experimental work was done to determine the conditions essential to the success of the process. For the experimental investigation, a synthetic blend of hydrocarbons was prepared to stimulate the composition of pyrolysis gasoline. The composition of the blend studied was as follows:

TABLE III

Component:	Weight percent (Nominal)
1,3-butadiene	4
Isobutene	10
1-butene	12
Pentadiene	4
n-Heptane	30
Benzene	33
Dicyclopentadiene	2
Styrene	5

The catalyst used was a commercial nickel catalyst having the following characteristics and composition:

TABLE IV

Ni, wt. percent	30.8
Al ₂ O ₃ , wt. percent	54.2
Ignition loss at 1200° C., wt. percent	2.11
Surface area, m. ² /g.	43

The experimental apparatus included a small electric furnace containing a one-inch reactor tube of stainless steel having a heated capacity of approximately 250 cc. A 50 cc. batch of catalyst was weighed and placed in the lower part of the reactor. The unit was pressure-tested cold and hot (700° F.) with nitrogen and hydrogen. The nickel catalyst was treated with hydrogen flowing at 3 s.c.f.h. and 750° F. at atmospheric pressure for 12 hours. The reduction of nickel catalyst was followed by a sulfiding treat-

ment at 350° F. with a stream containing 2% H₂S and the balance hydrogen for 12 hours at atmospheric pressure at a rate of 4 s.c.f.h. In operation, the synthetic blend was pumped at a pre-determined rate to the inlet of the reactor to which fresh feed gas or recycle gas was also fed in metered quantity. The top section of the one-inch reactor was used as a combined preheater-vaporizer for the combined stream prior to reaching the catalyst. The product stream was cooled and the liquid and vapor separated in a high pressure receiver. The high pressure off gas went to recycle and/or through a backpressure regulator to vent. The high pressure liquid was drawn down into bombs and either analyzed, weathered or debutanized. Temperatures were monitored and maintained at predetermined values by controlling the heating accomplished by the furnace.

With this apparatus and procedure, the test unit was operated for about 545 hours on oil without regeneration at 800 p.s.i.g., at temperatures controlled at 250, 300 and 350° F., at space velocities of 2 and 6 LHSV and at once-through hydrogen rates of 2000 s.c.f./b. Under these conditions, liquid phase was present in substantial amount throughout. For most of this period, the synthetic blend was charged although Dripolene was charged for a total of about 80 of these hours on oil. Dripolene is pyrolysis gasoline obtained by steam-pyrolysis of propane. The products were analyzed for pentadiene and butadiene and the percentages of these diolefins on the basis of C₄'s were taken to reflect the activity of the catalyst. Throughout the 545 hour run, the percentage of pentadiene on the basis of C₄'s was essentially nil, while the percentage of butadiene on the basis of C₄'s was essentially 0.1, indicating good catalyst activity and good maintenance of activity. At 545 hours on oil, the unit pressure was dropped from 800 p.s.i.g. to 400 p.s.i.g. and operations were continued for about 59 hours on the synthetic blend at 350° F., 2 LHSV and 3000 s.c.f. hydrogen per barrel of charge. Under these conditions, little or no liquid phase was present. During this latter period, there was a rapid linear rise in the concentrations, in the effluent, of pentadiene and butadiene to final values of about 1.5 and about 2.4 respectively on the basis of C₄'s. Therefore, the catalyst aged rapidly in the absence of liquid phase and became severely deactivated over only a short space of time.

The deactivated catalyst was then regenerated. For this purpose, the hydrocarbon was blown down with hydrogen at atmospheric pressure while raising catalyst temperatures to 800° F. After lining out at 800° F., the unit was flushed with nitrogen and the catalyst was regenerated with 1% oxygen in nitrogen at 200 p.s.i.g., flowing at 2 s.c.f.h. After burning was substantially complete (no further indication of carbon dioxide formation), the inlet gas composition was raised gradually to full air. The regenerated catalyst was then subjected to the same reduction and sulfiding treatment as fresh catalyst. With the regenerated catalyst, operation was resumed on the synthetic blend at 800 p.s.i.g., 350° F., 2000 s.c.f./b. and 2 LHSV and the results indicated full restoration of the activity of the catalyst.

With regard to the specific flow arrangement shown in the drawing and the specific examples given, it should be understood that various other arrangements and operating conditions can be used, as will be apparent to those skilled in the art from the foregoing, without departing from the scope of the invention.

What is claimed is:

1. A process for upgrading pyrolysis gasoline which comprises contacting a full boiling-range pyrolysis gasoline containing styrene and C₅ and lighter hydrocarbons with hydrogen-containing gas in the presence of a sulfided nickel catalyst under conditions which assure that at least a substantial portion of the hydrocarbons is in liquid phase including a pressure above about 550 p.s.i.g., temperatures in the range of about 200 to about 500°

F., a space velocity of about 0.5 to about 10.0 LHSV and a ratio of hydrogen to pyrolysis gasoline of about 500 to about 3000 s.c.f./b., whereby a gasoline product, stable without inhibition, is obtained.

2. A process for upgrading pyrolysis gasoline which comprises contacting a full boiling-range pyrolysis gasoline containing styrene and C_5 and lighter hydrocarbons with hydrogen-containing gas in the presence of added stable liquid hydrocarbons and of a sulfided nickel catalyst under conditions which assure that at least a substantial portion of the hydrocarbons is in liquid phase including a pressure above about 550 p.s.i.g., temperatures in the range of about 200 to about 500° F., a space velocity of about 0.5 to about 10.0 LHSV on the basis of pyrolysis gasoline, a ratio of hydrogen to pyrolysis gasoline of about 500 to about 3000 s.c.f./b. and a volumetric ratio of added stable liquid hydrocarbons to pyrolysis gasoline of about 0.5 to about 3.0, whereby a gasoline product, stable without inhibition, is obtained.

3. A process for upgrading pyrolysis gasoline which comprises contacting a full boiling-range pyrolysis gasoline containing styrene and C_5 and lighter hydrocarbons with hydrogen-containing recycle gas in the presence of added stable liquid hydrocarbons and of a sulfided nickel catalyst in a hydrotreating zone under conditions which assure that at least a substantial portion of the hydrocarbons is in liquid phase including a pressure of about 600 to about 1000 p.s.i.g., temperatures in the range of about 200 to about 500° F., a space velocity of about 0.5 to about 10.0 LHSV on the basis of pyrolysis gasoline and a ratio of recycle gas to pyrolysis gasoline of about 650 to about 4000 s.c.f./b., whereby a gasoline product, stable without inhibition, is obtained, cooling effluent of said hydrotreating zone to condense at least the heavier components thereof, passing cooled effluent to a separation zone and there separating condensed and uncondensed fractions, recycling separated condensed fraction from said separation zone to said hydrotreating zone as said added stable liquid hydrocarbons in an amount sufficient to provide a volumetric ratio of added stable liquid hydrocarbons to pyrolysis gasoline of about 0.5 to about 3.0 and recycling at least a portion of the separated uncondensed fraction from said separation zone to said hydrotreating zone to provide at least a portion of said hydrogen-containing recycle gas.

4. A process for upgrading pyrolysis gasoline which comprises contacting a full boiling-range pyrolysis gasoline containing styrene and C_5 and lighter hydrocarbons with hydrogen-containing gas in the presence of a sulfided nickel catalyst in a first hydrotreating zone under conditions which assure that at least a substantial portion of the hydrocarbons is in liquid phase including a pressure above about 550 p.s.i.g., temperatures in the range of about 200 to about 500° F., a space velocity of about 0.5 to about 10.0 LHSV and a ratio of hydrogen to pyrolysis gasoline of about 500 to about 3000 s.c.f./b., and contacting effluent of said first hydrotreating zone with hydrogen-containing gas in the presence of an active hydrogenation catalyst in a second hydrotreating zone at a pressure above about 550 p.s.i.g., temperatures in the range of about 650 to about 800° F., a space velocity of about 0.5 to about 10.0 LHSV and a ratio of recycle gas to pyrolysis gasoline of about 500 to about 3000 s.c.f./b., whereby a substantially olefin-and-sulfur-free product is obtained.

5. A process for upgrading pyrolysis gasoline which comprises contacting a full boiling-range pyrolysis gasoline containing styrene and C_5 and lighter hydrocarbons with hydrogen-containing recycle gas in the presence of added stable liquid hydrocarbons and of a sulfided nickel catalyst in a first hydrotreating zone under conditions which assure that at least a substantial portion of the hydrocarbons is in liquid phase including a pressure of about 600 to about 1000 p.s.i.g., temperatures in the range of about 200 to about 500° F., a space velocity

of about 0.5 to about 10.0 LHSV on the basis of pyrolysis gasoline and a ratio of recycle gas to pyrolysis gasoline of about 650 to about 4000 s.c.f./b., and contacting effluent of said first hydrotreating zone with hydrogen-containing gas in the presence of an active hydrogenation catalyst in a second hydrotreating zone at a pressure substantially the same as that of said first hydrotreating zone, temperatures in the range of about 650 to about 800° F., a space velocity of about 0.5 to about 10.0 LHSV on the basis of pyrolysis gasoline and a ratio of recycle gas to pyrolysis gasoline of about 500 to about 3000 s.c.f./b., whereby a substantially olefin-and-sulfur-free product is obtained, cooling effluent of said second hydrotreating zone to condense at least the heavier components thereof, passing cooled effluent to a separation zone and there separating condensed and uncondensed fractions, recycling separated condensed fraction from said separation zone to said first hydrotreating zone as said added stable liquid hydrocarbons in an amount sufficient to provide a volumetric ratio of added stable liquid hydrocarbons to pyrolysis gasoline of about 0.5 to about 3.0 and recycling at least a portion of the separated uncondensed fraction from said separation zone to said first and second hydrotreating zones to provide at least a portion of said hydrogen-containing recycle gas.

6. A process for upgrading pyrolysis gasoline which comprises contacting a full boiling-range pyrolysis gasoline containing styrene and C_5 and lighter hydrocarbons with hydrogen-containing gas in the presence of a sulfided nickel catalyst in a first hydrotreating zone under conditions which assure that at least a substantial portion of the hydrocarbons is in liquid phase including a pressure above about 550 p.s.i.g., temperatures in the range of about 200 to about 500° F., a space velocity of about 0.5 to about 10.0 LHSV and a ratio of hydrogen to pyrolysis gasoline of about 500 to about 3000 s.c.f./b., contacting effluent of said first hydrotreating zone with hydrogen-containing gas in the presence of an active hydrogenation catalyst in an intermediate hydrotreating zone under conditions which assure that at least at the inlet thereto a portion of the hydrocarbon is in liquid phase including a pressure above about 550 p.s.i.g., temperatures in the range of about 475 to about 600° F., a space velocity of about 0.5 to about 10.0 LHSV and a ratio of hydrogen to pyrolysis gasoline of about 500 to about 3000 s.c.f./b., and contacting effluent of said intermediate hydrotreating zone with hydrogen-containing gas in the presence of an active hydrogenation catalyst in a second hydrotreating zone at a pressure above about 550 p.s.i.g., temperatures in the range of about 650 to about 800° F., a space velocity of about 0.5 to about 10.0 LHSV and a ratio of recycle gas to pyrolysis gasoline of about 500 to about 3000 s.c.f./b., whereby a substantially olefin-and-sulfur-free product is obtained.

7. A process for upgrading pyrolysis gasoline which comprises contacting a full boiling-range pyrolysis gasoline containing styrene and C_5 and lighter hydrocarbons with hydrogen-containing recycle gas in the presence of added stable liquid hydrocarbons and of a sulfided nickel catalyst in a first hydrotreating zone under conditions which assure that at least a substantial portion of the hydrocarbons is in liquid phase including a pressure of about 600 to about 1000 p.s.i.g., temperatures in the range of about 200 to about 500° F., a space velocity of about 0.5 to about 10.0 LHSV on the basis of pyrolysis gasoline and a ratio of recycle gas to pyrolysis gasoline of about 650 to about 4000 s.c.f./b., contacting effluent of said first hydrotreating zone with hydrogen-containing recycle gas in the presence of further added stable liquid hydrocarbons and of an active hydrogenation catalyst in an intermediate hydrotreating zone under conditions which assure that at least at the inlet thereto a portion of the hydrocarbon is in liquid phase including a pres-

13

sure substantially the same as that of said first hydro-
treating zone, temperatures in the range of about 475
to about 600° F., a space velocity of about 0.5 to about
10.0 LHSV on the basis of pyrolysis gasoline and a ratio
of recycle gas to pyrolysis gasoline of about 650 to about
4000 s.c.f./b., contacting effluent of said intermediate
hydrotreating zone with hydrogen-containing recycle gas
in the presence of an active hydrogenation catalyst in a
second hydrotreating zone at a pressure substantially
the same as those of said first and intermediate hydro-
treating zones, temperatures in the range of about 650
to about 800° F., a space velocity of about 0.5 to about
10.0 LHSV on the basis of pyrolysis gasoline and a
ratio of recycle gas to pyrolysis gasoline of about 500
to about 3000 s.c.f./b., whereby a substantially olefin-
and-sulfur-free product is obtained, cooling effluent of
said second hydrotreating zone to condense at least the
heavier components thereof, passing cooled effluent to a
separation zone and there separating condensed and un-
condensed fractions, recycling separated condensed frac-
tion from said separation zone to said first hydrotreating
zone as said added stable liquid hydrocarbons in an
amount sufficient to provide a volumetric ratio of added
stable liquid hydrocarbons to pyrolysis gasoline in the
range of about 0.5 to about 3.0, recycling separated con-
densed fraction from said separation zone to said inter-
mediate hydrotreating zone as said further added stable
liquid hydrocarbons in an amount sufficient to provide
a volumetric ratio of total added stable liquid hydrocar-
bons to pyrolysis gasoline within said last-mentioned
range, and recycling at least a portion of the separated
uncondensed fraction from said separation zone to said
first, intermediate and second hydrotreating zones to pro-
vide at least a portion of said hydrogen-containing gas.

8. A process as defined in claim 7 in which portions
of said separated uncondensed fraction are recycled from
said separation zone separately to said first and second
hydrotreating zones.

9. A process as defined in claim 7 in which tempera-
tures in said first hydrotreating zone are raised within
the temperature limits set forth as the sulfided catalyst
becomes aged by raising the temperature of the separated
condensed fraction recycled to said first hydrotreating
zone from said separation zone.

10. A process as defined in claim 7 in which tempera-
tures in said first and intermediate hydrotreating zones
are maintained by preheating the separated condensed
fraction which is recycled to each of said zones from
said separation zone in indirect heat exchange with ef-
fluent of said second hydrotreating zone and by control-
ling the amount of said preheated fraction which is re-
cycled.

11. A process as defined in claim 7 in which said
active hydrogenation catalyst used in said intermediate
and second hydrotreating zones is a catalyst containing
cobalt and molybdenum in each case.

12. A process for upgrading pyrolysis gasoline having
a boiling range of about 95 to about 425° F. ASTM ob-
tained as a by-product from the steam pyrolysis of hydro-
carbons to produce ethylene and propylene which com-
prises contacting a mixture consisting essentially of said
pyrolysis gasoline, hydrogen-containing recycle gas, and
added stable liquid hydrocarbon in the presence of a sul-
fided nickel catalyst in a hydrotreating zone under suitable
conditions to obtain substantially complete conversion of
diolefins and partial conversion of mono-olefins to more
saturated hydrocarbons and to assure that at least a sub-
stantial portion of the hydrocarbons is in the liquid phase
including a pressure above about 600 to about 1000
p.s.i.g., temperatures in the range of about 200 to about
500° F., a space velocity of about 0.5 to about 10.0 LHSV
on the basis of pyrolysis gasoline and a ratio of recycle
gas to pyrolysis gasoline of about 650 to about 4000
s.c.f./b., whereby a gasoline product having an octane num-
ber not substantially lower than the octane number of

14

said pyrolysis gasoline and having a maleic anhydride
value of no more than about 3.0, stable without inhibi-
tion, is obtained and a net hydrogen consumption of about
75 to about 250 standard cubic feet per barrel of pyrolysis
gasoline results, cooling effluent of said hydrotreating
zone to condense at least the heavier components thereof,
passing cooled effluent to a separation zone and there
separating condensed and uncondensed fractions, recycl-
ing separated condensed fraction from said separation
zone to said hydrotreating zone as said added stable liquid
hydrocarbons in an amount sufficient to provide a volu-
metric ratio of added stable liquid hydrocarbons to
pyrolysis gasoline of about 0.5 to about 3.0 and recycling
at least a portion of the separated uncondensed fraction
from said separation zone to said hydrotreating zone to
provide at least a portion of said hydrogen-containing re-
cycle gas.

13. A process for the selective nondestructive hydro-
genation of a liquid hydrocarbon feed containing styrene,
C₅ and lighter hydrocarbons, said feed boiling below about
425° F. and containing aromatic hydrocarbons, olefins,
diolefins and sulfur compounds which comprises passing
said feed in the liquid phase and hydrogen through an
initial hydrogenation zone in contact with a porous solid
sulfided nickel hydrogenation catalyst while controlling
hydrogenating conditions in said zone to provide a hydro-
genation effluent from said zone in which a substantial
amount of the diolefins have been at least partially satu-
rated and in which a substantial part of said liquid feed
and products thereof are in the liquid phase, passing ef-
fluent hydrocarbons from said initial hydrogenation zone
together with hydrogen through an intermediate hydro-
genation zone in contact with a porous solid hydrogenation
catalyst having a high hydrogenation activity at a tem-
perature substantially higher than the average tem-
perature in said initial zone under conditions controlled to
maintain a portion of the hydrocarbon in the liquid phase
at least at the inlet to said intermediate hydrogenation
zone and to further hydrogenate said effluent from the
initial hydrogenation zone, passing the effluent from said
intermediate zone through a subsequent conversion zone
at a suitable desulfurization temperature in contact with
a porous solid sulfur-resistant conversion catalyst having
at least moderate hydrogenation activity and a high de-
sulfurization activity, and regulating conditions in said
conversion zone to produce a substantially desulfurized
conversion effluent with a normally liquid fraction having
a substantial lower Bromine Number than said liquid
feed.

14. A process for the selective nondestructive hydro-
genation of a liquid hydrocarbon feed containing styrene,
C₅ and lighter hydrocarbons, said feed boiling below
about 425° F. and containing aromatic hydrocarbons, ole-
fins, diolefins and sulfur compounds which comprises
passing said feed in the liquid phase and hydrogen through
an initial hydrogenation zone in contact with a porous
solid sulfided nickel hydrogenation catalyst while control-
ling hydrogenating conditions in said zone to provide a hy-
drogenation effluent from said zone in which at least about
35% of the diolefins have been at least partially saturated
and in which a substantial part of said liquid feed and
products thereof are in the liquid phase, passing effluent
hydrocarbons from said initial hydrogenation zone to-
gether with hydrogen through an intermediate hydrogenation
zone in contact with a porous solid hydrogenation
catalyst having a high hydrogenation activity at a tempera-
ture high enough for olefin saturation and substantially
higher than the average temperature in said initial zone
under conditions controlled to maintain a portion of the
hydrocarbon in the liquid phase at least at the inlet to
said intermediate hydrogenation zone and to further hy-
drogenate said effluent from the initial hydrogenation zone
whereby the diolefin content of the normally liquid frac-
tion thereof is less than about 50% of that of said liquid
feed, withdrawing the effluent from said intermediate zone

at a temperature suitable for desulfurization, passing said intermediate effluent through a subsequent conversion zone in contact with a porous solid sulfur-resistant conversion catalyst having at least moderate hydrogenation activity and a high desulfurization activity, and controlling conversion conditions in said conversion zone to produce an effluent with a normally liquid fraction having a Bromine Number less than about 4 and an organic sulfur content below about 25 p.p.m.

15. A process according to claim 14 in which the temperature in said intermediate zone is also high enough for desulfurization.

16. A process according to claim 14 in which at least about 50% of the more reactive diolefins are at least partially saturated in said initial zone and the diolefin content of the normally liquid fraction of said intermediate effluent is less than about 40% of that of said liquid feed.

17. A method according to claim 14 in which said intermediate and conversion catalysts each contain a metal of the iron group and a metal in Group VI-B of said Periodic Table.

18. A method according to claim 14 in which said intermediate zone and said conversion zone are located in a single closed reaction vessel.

19. A method according to claim 14 in which said intermediate catalyst and said conversion catalyst are employed in volumetric ratios between 1:20 and 20:1, respectively.

20. A method according to claim 14 in which the conditions controlled within said initial zone include maintaining a pressure above about 550 p.s.i.g., an hourly space velocity within the range of about 0.5–10.0 based on the volume of said liquid feed, a hydrogen charge within the range of about 500–3000 s.c.f./b. of said liquid feed and a temperature within the broad range of about 200 to about 500° F., the conditions controlled in said intermediate zone include maintaining a pressure above about 550 p.s.i.g., an hourly space velocity within the range of about 0.5 to about 10 based on the volume of said liquid feed, a total hydrogen charge within the range of about 500–3000 s.c.f./b. of said liquid feed and a temperature within the range of about 475 to about 600° F.; and the conditions controlled in said conversion zone include maintaining an hourly space velocity between about 0.5 and about 10 based on the volume of said liquid feed and an average reaction temperature not substantially below the temperature of the intermediate zone.

21. A method according to claim 20 in which said temperature of the initial zone is maintained at a relatively low value within said broad range while said catalyst is fresh and said temperature is increased within the limits of said broad range to maintain said diolefin saturation as the hydrogenation activity of said initial catalyst decreases with continued use, and said temperature of the intermediate zone is maintained at a relatively low value within the wide range while said intermediate and conversion catalysts are fresh and said temperature is increased within said wide range as the activity of said catalysts decreases with continued use in order to maintain said organic sulfur content and Bromine Number in said conversion effluent fraction.

22. A method according to claim 14 in which the conditions controlled within said initial zone include maintaining a pressure within the range of about 600 to about 1000 p.s.i.g., an hourly space velocity within the range of about 0.5 to above 10 based on the volume of said liquid feed, a hydrogen charge within the range of about 500 to about 3000 s.c.f./b. of said liquid feed and a temperature within the range of about 350 to about 475° F. to provide a hydrogenation effluent from said zone in which the Bromine Number of the normally liquid fraction thereof is at least 25% below that of the liquid feed and at least about 50% of the diolefins have been at least partially saturated and in which at least an amount equal to at least about 60% of the liquid feed is

in the liquid phase; the conditions controlled in said intermediate zone include maintaining a pressure within the range of about 600 to about 1000 p.s.i.g., an hourly space velocity within the range of about 0.5 to about 10 based on the volume of said liquid feed, a total hydrogen charge within the range of about 500 to about 3000 s.c.f./b. of said liquid feed and a temperature within the range of about 475 to about 600° F. to provide an intermediate zone effluent with a normally liquid fraction in which the diolefin content is less than about 40% of that of said liquid feed; and the conditions controlled in said conversion zone include maintaining an hourly space velocity between about 0.5 to about 10 based on the volume of said liquid feed and an average reaction temperature not substantially below the inlet temperature of the intermediate zone to produce an effluent with a normally liquid fraction having a Bromine Number less than about 2.0 and an organic sulfur content below about 25 p.p.m.

23. A process for the selective nondestructive hydrogenation of a liquid hydrocarbon feed containing styrene, C₅ and lighter hydrocarbons, said feed boiling below about 425° F. and containing aromatic hydrocarbons, olefins, diolefins and sulfur compounds which comprises passing said feed substantially in the liquid phase and hydrogen through an initial hydrogenation zone in contact with a porous solid sulfided nickel hydrogenation catalyst while controlling hydrogenating conditions in said zone including pressure within the range of above about 550 p.s.i.g., hourly space velocity within the range of about 0.5–10.0 based on the volume of liquid feed, the hydrogen charge within the range of about 500–3000 s.c.f./b. of the liquid feed and temperature within the broad range of about 200 to about 500° F., said hydrogenating conditions being regulated to provide a hydrogenation effluent from said zone in which at least about 35% of the diolefins have been at least partially saturated and in which a substantial amount of said effluent is in the liquid phase, effecting controlled vaporization of at least a portion of the liquid phase of said hydrogenation effluent, passing hydrogen together with material derived from vaporization step through a subsequent conversion zone in contact with a porous solid conversion catalyst of at least moderate hydrogenation activity and high desulfurization activity at a substantially higher average temperature than in said initial zone while controlling conversion conditions in said conversion zone including pressure within the range of about 500 to about 1000 p.s.i.g., hourly space velocity within the range of about 0.5 to about 10.0 based on the volume of said liquid feed, the total hydrogen charge within the range of about 500–3000 s.c.f./b. of said liquid feed and temperature within the range of about 650 to about 800° F., said conversion conditions being regulated to produce a substantially desulfurized conversion effluent having a substantially lower Bromine Number than said liquid feed.

24. A process for the selective nondestructive hydrogenation of a liquid hydrocarbon feed containing styrene, C₅ and lighter hydrocarbons, said feed boiling below about 425° F. and containing aromatic hydrocarbons, olefins, diolefins and sulfur compounds which comprises passing said feed in the liquid phase and hydrogen through an initial hydrogenation zone in contact with a porous solid sulfided nickel hydrogenation catalyst while controlling hydrogenating conditions in said zone to provide a hydrogenation effluent from said zone in which a substantial amount of the diolefins have been at least partially saturated and in which a substantial part of said liquid feed and products thereof are in the liquid phase, passing the resulting mixed phase together with hydrogen through an intermediate hydrogenation zone in contact with a porous solid hydrogenation catalyst having a high hydrogenation activity at a temperature substantially higher than the average temperature in said initial zone under conditions controlled to further hydrogenate said mixed phase, pass-

17

18

ing the effluent from said intermediate zone through a subsequent conversion zone at a suitable desulfurization temperature in contact with a porous solid sulfur-resistant conversion catalyst having at least moderate hydrogenation activity and a high desulfurization activity, and regulating conditions in said conversion zone to produce a substantially desulfurized conversion effluent with a normally liquid fraction having a substantial lower Bromine Number than said liquid feed.

25. A process for the selective nondestructive hydrogenation of a liquid hydrocarbon feed containing styrene, C₅ and lighter hydrocarbons, said feed boiling below about 425° F. and containing aromatic hydrocarbons, olefins, diolefins and sulfur compounds which comprises passing said feed in the liquid phase together with added stable liquid hydrocarbon and hydrogen through an initial hydrogenation zone in contact with a porous sulfided nickel hydrogenation catalyst while controlling hydrogenating conditions in said zone to provide a hydrogenation effluent from said zone in which a substantial amount of the diolefins have been at least partially saturated and in which a substantial part of the hydrocarbons are in the liquid phase, passing effluent hydrocarbons from said initial hydrogenation zone together with hydrogen through an intermediate hydrogenation zone in contact with a porous solid hydrogenation catalyst having a high hydrogenation activity at a temperature substantially higher than the average temperature in said initial zone under conditions controlled to maintain a portion of the hydrocarbon in the liquid phase at least at the inlet of said intermediate hydrogenation zone and to further hydrogenate said effluent from the initial hydrogenation zone,

passing the effluent from said intermediate zone through a subsequent conversion zone at a suitable desulfurization temperature in contact with a porous solid sulfur-resistant conversion catalyst having at least moderate hydrogenation activity and a high desulfurization activity, and regulating conditions in said conversion zone to produce a substantially desulfurized conversion effluent with a normally liquid fraction having a substantial lower Bromine Number than said liquid feed.

26. A process according to claim 25 in which further stable liquid hydrocarbon is passed with the effluent hydrocarbons from said initial hydrogenation zone through said intermediate hydrogenation zone.

27. A process according to claim 23 in which stable liquid hydrocarbon is passed with said feed through the initial hydrogenation zone.

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U.S. Cl. X.R.

208—210, 211, 216

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,492,220 Dated January 27, 1970

Inventor(s) F.L. Lempert et al.

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

Column 4, line 35, for "a" read --to--;
Column 8, Table I, first column, eleventh entry, for "Bromide"
read "Bromine";
Column 9, line 45, for "stimulate" read --simulate--;
Column 10, line 7, for "preheater-vaporized" read --preheater-vaporiz
Column 13, line 41, after "sulfided" insert --nickel--;
Column 15, line 41, for "an" read --and--;
Column 16, line 48, for "500" read --550--.

Signed and sealed this 4th day of January 1972.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Acting Commissioner of Patents