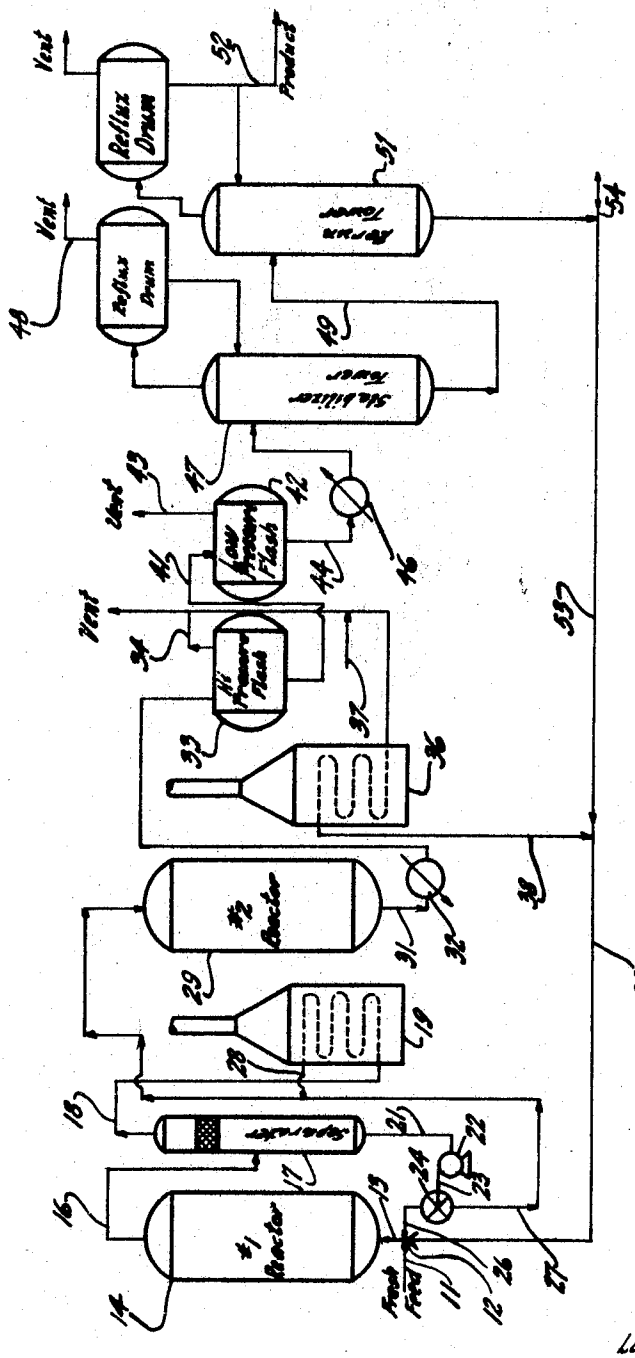
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PYROLYSIS GASOLINE HYDROGENATION

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PYROLYSIS GASOLINE HYDROGENATION

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ABSTRACT OF THE DISCLOSURE

An improved process is described for the continuous hydrogenation of hydrocarbon charge stocks containing high concentrations of polymerizable materials, particularly those stocks typified in full range pyrolysis naphthas. The improvements are obtained through the use of selected methods and conditions conducive to the hydrogenation of polymerizable components before they form polymers. These improvements include up-flow flooded liquid phase operation in a first reaction zone with high dilution of fresh feed and rapid temperature adjustment of the incoming charge through the expedient of abnormally high liquid recycle around the first reaction zone.

BACKGROUND OF THE INVENTION

Petrochemical and petroleum refining operations have broad and important positions in today's technology. One aspect concerns the provision of various components of and ingredients for the plastics industry. Among such components and ingredients are olefinic hydrocarbons which are polymerized or otherwise processed into plastics and polymerics having wide distribution and considerable utility in many forms.

One such olefinic hydrocarbon, for example, is ethylene. As a precursor for polyethylene this olefin is a major petrochemical product. Producers of this petrochemical can use a variety of processes. One type of such process is that of pyrolysis or steam cracking of a naphtha-type charge stock where under appropriate conversion conditions commercially important quantities of ethylene are produced. However, not all the product is the desired ethylene. By-products are produced in sizable quantities. While such by-products can be employed as low grade fuel such usage gives only a minimal value to such materials.

One such by-product comprises hydrocarbons higher boiling than the ethylene. The typical material has normally liquid state and a boiling range including the C_5 hydrocarbons and extends upwardly to above about 400° F. E.P. In the industry this material is known by several terms, the more common being pyrolysis naphtha, aromatic distillate or dripolene. Frequently the quantity of pyrolysis naphtha is of sufficient magnitude to merit serious consideration. While such material boils generally in the gasoline boiling range and has high octane quality it can not be used directly as motor fuel because of the presence of relatively large amounts of objectionable components, including gum formers. Its use as a material other than mere low grade heating fuel is where the problem lies.

Pyrolysis naphtha comprises a multitude of hydrocarbons, including mono-olefins and di-olefins, such that it is a mixture of valuable hydrocarbons but not a valuable

mixture of hydrocarbons. The problem of converting the mixture into a more valuable form has ridden the shoulders of the industry for many years with only modest success in provision of answers.

Two of the areas of potential value in such pyrolysis naphthas when suitably converted are as a source of aromatics, such as benzene, and the other is as a power source, e.g., gasoline, for internal combustion engines. The art is discussed below, and while successful to some extent in being good enough in some instances to be practiced commercially the various attendant problems are serious enough to make appreciable inroads into the profit picture, product quality and utilization of the full range pyrolysis naphtha.

DESCRIPTION OF THE ART

The prior art shows a number of processes have been developed and disclosed wherein the objective is to achieve continuous hydrogenation of charge stocks containing relatively large quantities of polymerizable components.

One embodiment of the prior art is that described in U.S. Patent No. 3,216,924, to J. D. McKinney et al. In the described system improvements are effected in the processing of pyrolysis naphthas through the expedients of controlling the heating of such naphthas, first to a moderate temperature of less than about 260° F. and through direct heat exchange, with a refractory stock preheated to a higher temperature, to an elevated temperature suitable for the following selective hydrogenation of olefinic components in a down-flow, trickle-type reactor containing a suitable hydrogenation catalyst. In a modification, a further quantity of the preheated refractory stock may be added, for further temperature adjustment, to the reaction zone at a level where the hydrogenation is substantially complete. This type of system is in commercial operation and enjoys some success, particularly with pyrolysis naphthas characterized in relatively low levels of readily polymerizable components.

Another art form is that shown in British Patent No. 1,080,586 whereby pyrolysis naphthas are treated to produce relatively high yields of benzene by method generally comprising subjecting such a naphtha to a selective hydrogenation of diolefinic components at elevated pressure in the presence of a hydrogenation catalyst at a relatively low temperature in the range of up to 250° C., further elevated pressure hydrogenation at a temperature in the range of 500°–800° C. and thereafter further hydrotreating at a temperature in the range of 100–250° C. over a hydrodesulfurization catalyst, again at elevated pressure. Several variations along similar lines have been proposed including one version where the charge stock is vaporized and passed over a fixed bed of catalyst. Each of these several schemes employ some type of hydrogenation catalyst such as cobalt-molybdate, nickel on cobalt-molybdate or other.

All of these several process schemes involve some degree of vaporization of the feed stock. Because of the relatively high concentration of polymerizable components in such charges some polymerization can occur simultaneously along with the vaporization. When such polymer is formed it may then deposit either in the inlet lines and preliminary introduction section of the reaction vessel or be deposited in and/or on the catalyst, or both. Such residue, depending on its rate of formation can accumulate to the point where the normal design flow rate

is hindered and the pressure drop increases to a point where practical operation is no longer possible. At this point, if not earlier, the systems have to be shut down and the polymeric material removed by suitable and available means.

The prior art has attempted to circumvent these difficulties by a wide variety of means, one of the most practical of which appears to have been the elimination from the pyrolysis naphtha of all or part of the higher boiling (300–400° F.) fraction. Even so it has been possible to operate commercial units of this type of catalytic reaction for periods no nonger than about 60 days and more usually for periods in the range of 40 days or less. It has been found further that the nature of the accumulated polymeric deposit is such that regeneration systems of the type normally employed in hydrocarbon processing usually cannot be employed to remove such deposits and that physical means have to be employed to clear the lines and frequently to break up practically solid phase of catalyst cemented with the polymeric materials for removal from the system. Such cleaning and rehabilitation of the unit may easily run to seven operating days, thus presenting a serious loss area in the refinery.

SUMMARY OF THE INVENTION

In accordance with this invention a system is provided for the hydrogenation of a full range pyrolysis naphtha under conditions substantially preventing the formation and accumulation of polymeric materials prior to and/or during such selective hydrogenation. This is accomplished in part by simultaneously raising the charge stock to reaction temperature in the order of 400–600° F. by admixture with appropriate temperature-adjusted liquid components comprising at least five times the volume of the fresh feed of high boiling liquid of low olefinicity and as recycle from a first reaction zone. Such admixture, including the fresh feed, is passed at upflow conditions while substantially in the liquid phase and in the presence of an effective amount of hydrogen, such as a hydrogen-containing gas stream with at least 40% as hydrogen, in an amount equivalent to at least two moles of hydrogen per mol of unsaturate in the charge, through a fixed bed of hydrogenation catalyst at a linear velocity of the admixture in excess of 0.1 linear foot per minute with the temperature in the range of 400–600° F. and pressure (600–1000 p.s.i.g.) consistent with the maintenance of the fresh feed components substantially in the liquid phase. The effluent from the first reaction zone, exclusive of any portion recycle, is thereafter adjusted in temperature by suitable interstage heating means to a temperature within the range of 500–600° F. and thereafter passed through a second reactor, containing a hydrogenation catalyst, under mixed phase conditions including temperatures ranging from about 500–700° F. at the inlet to about 550–750° F. at the outlet. The operating pressure is in the range of 700–1200 lb./in.^{2} gage (p.s.i.g.) The reactor effluent from the second reactor may be processed in any of many standard ways for any of a variety of purposes to which the composition of the product may be advantageously adapted.

While the diluent liquid employed in the first reaction zone may comprise any suitable relatively high boiling range, i.e. 300–700° F., non-olefinic hydrocarbons relatively free of readily polymerizable constituents, for reasons of availability and economics it is preferred to recycle a major portion of the liquid effluent which meets these requirements from the first reaction zone. This is advantageously performed by submitting all of the effluent from the first reaction zone to a separator wherein gases and light products are taken overhead and liquid is taken off from the bottom of the separator. The liquid portion thereafter is introduced for controlled flow of a major portion thereof as recycle to the first reactor and the balance as required and desired is directed to the second reactor. Novel heating and control of the temperature of the stream to the second reaction is effected, preferably, by passing the overhead gaseous components of the stream from the separator to an interstage heater and introducing into such gaseous stream a suitable amount of heat such that when it is re-introduced to the normally liquid portion of the feed stream to the second reactor the admixture therewith provides total stream temperature at the desired temperature level in the range of 500–700° F.

PROCESS CONCEPTS

While we do not intend to be held to the concepts and theories expressed hereinafter, such concepts and theories may be found helpful in a rationalization of the unexpected results obtained with operation in accordance with the described practice.

Kinetic studies on various stocks show that the rate of polymerization is dependent on temperature, pressure, polymer precursor concentration, and time. With exception of pressure, the rate of polymerization increases as each of these variables increases independently or collectively. Quantitatively the rate of polymerization responds as follows:

$$\gamma p = A_1 e^{-\frac{B_1}{T}} [p]^n [H_2]^{-m}$$

where:

γp is the rate of polymerization
A_1 and B_1 are positive constants
$[p]$ is the polymer precursor concentration
n is a positive constant >1
$[H_2]$ is the H_2 partial pressure
m is a constant $\geqq$ than zero

Similarly it can be shown that the rate of hydrogenation of the polymer precursor is quantitatively described by:

$$\gamma H = A_2 e^{-\frac{B_2}{T}} [p]^u [H_2]^v$$

where:

γH is the rate of hydrogenation
A_2 and B_2 are positive constants
u is a constant, $0 \leqq u \leqq 1.0$
v is a constant, $0 \leqq v$.

Therefore, any process concept reducing the relative rate of polymerization to hydrogenation will be favorable and described by:

$$\frac{\gamma p}{\gamma H} = \frac{A_1}{A_2} e^{-\left(\frac{B_1 - B_2}{T}\right)} [p]^{n-u} [H_2]^{-(m+v)}$$

Thus, the described system provides a unique combination of innovations to reduce the rate of polymerization relative to hydrogenation.

(1) Utilization of steps to reduce the polymer precursor concentration $[p]$ to decrease γ_p/γ_H because n is greater than u.

(2) Employing high H_2 partial pressure $[H_2]$ reduces γ_p/γ_H because m and v are positive. Thus, high pressure is beneficial.

(3) Employing a predominantly liquid phase type contacting helps keep the catalyst polymer-free because polymers deposited on the surface of the catalyst can be dissolved and removed by hydrocarbon solvents when the polymers are contacted before coke is produced.

(4) Obtaining at least in part such predominantly liquid phase through the introduction of diluent liquid, or wash oil, as a solvent, non-volatile at the reaction conditions such as boiling in the range of about 450 to 650° F., in an amount equivalent to about 0.5 to 1.0 volume of wash oil per volume of fresh feed. The wash ail may be employed on a once-through basis or recycled in part or in toto as part of the recirculated intermediate liquid product described below.

(5) Liquid phase coverage of the catalyst particles assures practically negligible surface evaporation to dryness. Any polymer formed and deposited on the catalyst surface is thus removed by the solvent action of the liquid phase oil rather than being "dried" and converted to coke.

(6) The recirculation of intermediate liquid product from the first stage of the hydrogenation (near zero in polymer precursor concentration) introduces substantially no polymer precursor and operates to substantially reduce the concentration of the fresh feed thereby decreasing the rate to polymerization relative to the rate of hydrogenation.

(7) The introduction of the feed as a cold stream, mixing it with hot product recycle and minimizing the contact time before the catalyst zone is reached all serve to minimize the formation of polymer and shorten the interval to hydrogenation.

In any event operation in accordance with this invention meets the requirements of dilution, temperature control and product quality with attendant reduction in polymerization rates with desirable savings in heat requirements whereby the historic evils of the system are successfully minimized almost to extinction and long term operation in excess of 6 months, such as for years, may be obtained.

DRAWINGS

Assistance in understanding the described invention can be had through reference to the figure which shows an idealized flow diagram with the major vessels and flow lines suitably identified. The figure is an embodiment effective in the execution of a process with the type herein described and it must be understood that the drawing is indicative in general terms rather than is specific types, sizes or qualities.

Fresh dripolene charge at ambient temperatures is introduced through line **11** to mixing T, or jet mixer, **12** and thereafter through line **13** into reactor **14**. If mixing T**12** is positioned at the bottom of reactor **14** it is possible to eliminate line **13**. Reactor **14** contains a fixed bed of sulfided cobalt molybdate on alumina catalyst and the hydrogenation reaction or a suitable portion thereof is effected at elevated temperature and pressure such that substantially all of the hydrocarbon portion of the charge stock is maintained at liquid phase conditions. The hydrogenated or partially hydrogenated effluent from reactor **14** is transferred through line **16** to separator **17** which may be any of a variety of known devices capable of performing an effective separation of material charged thereto into an overhead fraction containing substantially only normally gaseous components and a bottoms fraction containing normally liquid components.

The gaseous overhead fraction from separator **17** comprising mainly hydrogen is transferred through line **18** to interstage heater **19** in which the gaseous stream is heated to a level such that on subsequent recombination with an appropriate liquid stream, as described subsequently, the resultant temperature of the admixture is at about the level required for a subsequent processing step. The bottoms fraction from separator **17** passes through line **21**, pump **22** and line **23** into flow splitter **24** from which approximately 80% is transferred through line **26** as recycle to reactor **14** after passing through mixing T **12**. The remaining 20% of the liquid bottoms from separator **17** are taken from flow splitter **24** through line **27** for admixture with the heated gas from interstage heater **19** introduced to line **27** through line **28**. The temperature-adjusted stream enters reactor **29** for further hydrogenative treatment over a fixed bed of hydrogenation catalyst.

The hydrogenated product from reactor **29** is removed through line **31** and after temperature adjustment in heat exchanger **32** enters the high pressure flash drum **33**. High pressure flash gas overhead is removed from the flash separator **33** through line **34** and with or without venting as desired goes to heater **36**. Hydrogen make-up gas as desired or required may be introduced into line **34** through line **37**. Heated gas from heater **36** is returned through lines **38** and **39** to the mixing T **12** for admixture with fresh feed introduced through line **11** and recycled stock introduced through line **26**. The liquid portion from the high pressure flash separator **33** is transferred through line **41** to low pressure flash separator **42**. The low pressure flash gas portion is vented through line **43** while the low pressure flash drum liquid portion from **42** is transferred by line **44** through heat exchanger **46** and is introduced to the stabilizer tower **47**.

In known manner the charge introduced from line **44** is stablized through removal of extraneous gaseous components vented through line **48** and the liquid or higher boiling portion is transferred through line **49** to re-run tower **51**. Operation of the re-run tower **51** is such that the major fraction is desired product removed through line **52** to storage or further processing stages as shown. Bottoms from the re-run tower **51** are removed through line **53** and are combined with the hot hydrogen-containing gas from line **38** and the mixture forwarded through line **39** to mixing T **12**. Line **54** may be used to introduce make-up wash oil into line **53** or to remove excess wash oil from line **53** as may be required to maintain proper balance in the quantity of recirculated wash oil.

While the figure is a diagrammatic representation of one preferred system for the operation of the present invention it is to be understood that other methods of operation are feasible within the scope of the invention and may be employed as circumstances require. Associated necessary equipment has not been described or indicated inasmuch as its utilization is well understood in the art and as such forms no particular part of this invention except as it may contribute to the normal practical operation thereof. Changes other than in equipment are also contemplated, such as in the operation of the second reactor substantially liquid phase upflow conditions and in other portions of the system changes and regulations that may be desirable in the selection, formation and utilization of various fractions and portions of the process streams other than as shown but within the scope of the invention.

The preferred hydrogenation catalyst is of the type described as sulfided cobalt molybdate supported on alumina. Such preferred catalyst is one containing, prior to sulfidation, 10 to 20% by weight of the oxides of cobalt and molybdenum; the MoO_3 being 3 to 5 times that of the CoO by weight. Sulfidation of the catalyst can be effected by pretreatment with H_2S. However, common practice with sulfur-bearing stocks employed in this invention involves simply allowing the sulfur in the charge to effect the sulfidation of the catalyst. A typical cobalt molybdate catalyst for use in the hydrogenation reactor is that described in Example 1 of U.S. Patent No. 3,207,802. Catalysts containing small amounts of other metal oxides or sulfides of the iron group, particularly nickel, in addition to cobalt may be employed also, such catalysts being of the type described in U.S. Patent No. 2,880,171.

The following exemplary material is described in terms relatable to the drawing and is to be taken as indicative of possibilities within the scope of limitations otherwise described and claimed.

In Table 1, below, two representative dripolene naphthas are identified. The material, charge stock A, represents one type of charge which has been prepared by commercial processing without some of the higher boiling range components. It is termed a full range naphtha and includes those components notoriously known to be prone to polymerization and coke formation. Charge stock B is another representative full range dripolene naphtha the use of which in standard processing opera-

tions would result in drastically foreshortened operable stream time.

TABLE 1

	Full Range Dripolene Naphtha	
Charge Stock	A	B
API, Degrees	37.1	22.4
ASTM Distillation, Vol. Percent:		
IBP	128	181
50%	232	285
90%	341	398
EP	385	580
Bromine No.	50.5	49.5
Elemental Sulfur, Wt. Percent	0.036	0.090
Chemical Comp., Vol. Percent:		
Paraffins	8.4	
Olefins:		
Mono, 11.5; Di, 4.0; Styrenes, 13.0; Indenes, 2.9	31.4	
Mono, 2.3; Di, 21.0; Styrenes, 13.0; Indenes 0.2		36.5
Aromatics:		
Monocyclic, 57.4; Dicyclic, 2.8	60.2	
Monocyclic, 50.1; Dicyclic 10.1		60.2
Coumarone		3.0
Thiophenes and Sulfur Compounds		0.3
Total	100.0	100.0
Octane Number:		
F-1	102.1	
F-1+3cc. TEL	103.3	

While there are many variants possible in charge stocks comprising dripolene naphthas, these stocks are representative for practical purposes and are employed as indicated in the following examples.

Example I

A dripolene naphtha, described in Table 1 as charge stock A, was processed in a conventional manner known to the art. The catalyst employed in this system was a 3.2 mm. sulfided cobalt-molybdena on activated alumina support containing 2.36% cobalt and 10.0% molybdenum. The fresh dripolene naphtha was charged to a first downflow reactor through a mixing T at the top of the reactor after preheating to 250° F. by indirect heat exchange. Joining this stream at the T, a mixture of recycle wash oil, makeup wash oil and recycle gas entered after being preheated to 560° F. to give a combined reactor inlet charge temperature of 450° F. The gas-liquid mixture passed down through the catalyst giving trickle contact. The effluent from the first reactor was heated to provide an inlet temperature of 550° F. to a second reactor. The heated gas-liquid mixture was charged to the second reactor downflow and trickle contacted. Separation of products and recovery of wash oil for circulation was achieved in conventional fractionation equipment. The operating conditions were as shown in Table 2, following.

TABLE 2.—OPERATING CONDITIONS FOR EXAMPLE I

	Reactor 1	Reactor 2	
Mode of Operations, both reactors	Downflow,	Trickle,	Mixed Phase
LHSV (based on naphtha)	3		1
Inlet Temp., ° F	450		550
Pressure, p.s.i.g.	850		850
S.c.f. H_2/bbl. dripolene naphtha		1,200	
Fresh or makeup wash oil rate, vol./vol. of dripolene naphtha		0.14	
Wash oil recycle rate, vol./vol. of dripolene naphtha		0.86	
Recycle gas hydrogen purity, Mole percent		80	
Yield of hydrogenated gasoline, Vol. percent of naphtha charged			96.0

The initial gasoline product bromine number was 0.7 which rose gradually to a level of 3.7 after 29 days of operation at constant conditions. This modest change in product saturation resulted from a small decrease in catalyst activity. However, on the 29th day an increasing pressure drop across the first reactor as observed which further increased rapidly with time and reached 90 p.s.i before the end of the day. At this point the pressure drop became abruptly so great that all inlet flows to the first reactor stopped. Operation had to be discontinued and the unit was allowed to cool and was then opened. Examination of the contents of the first reactor showed the presence of a solid catalyst-carbonaceous plug in the top 15% of the catalyst bed. Regeneration in the normal sense through controlled oxidation was impossible because of the plugged condition. The catalyst-carbonaceous plug was broken up and the entire material removed from the reaction zone.

Example II

A dripolene naphtha, described in Table 1 as charge stock A, was processed in a manner consistent with this invention in a system similar to that shown in the flow diagram of the figure. The catalyst employed in reactors **1** and **2** was sulfided Co-Moly supported on alumina of the same type as described in Example I. Fresh dripolene naphtha at a temperature below 90° F. was charged through a mixing T to the bottom of the first reactor. At this point it was joined by the sum flows of recycle wash oil, makeup wash oil and fresh hydrogen which had been preheated to a temperature of 600° F. to give the desired reactor inlet temperature. This resulted in a nearly instantaneous increase in the dripolene naphtha temperature along with a nearly instantaneous dilution of the fresh feed with decrease in the concentration of polymer precursors, an operation which at all times minimized the potential driving force for polymerization.

The thus-mixed stream entered the bottom of reactor **1** and flowed upward through a flooded fixed bed of catalyst. Although two phases (liquid and gas) were present, the hydrocarbons were all substantially in liquid phase and catalyst particle wetting by the liquid portion of the stream was greater for the upflow operation than obtained in downflow in Example I.

A substantial fraction, approximately 80% of the first reactor liquid effluent was recycled to the first reactor inlet to provide along with approximately 10 volume percent of added wash oil a total diluent to fresh feed ratio of 10 to 1. The net liquid and gas effluent from reactor **1** was preheated to achieve an inlet temperature of 550° F. to the second reactor where again an upflow system was used. Separation of the products and recovery of wash oil for circulation was achieved using conventional fractionation. Operating conditions are set forth in Table 3.

TABLE 3.—OPERATING CONDITIONS FOR EXAMPLE II

	Reactor 1	Reactor 2	
Mode of Operation::	Liquid Phase Upflow	Upflow	Mixed Phase
LHSV (based on naphtha)	1		1
Inlet Temperature, ° F	550		550
Pressure, p.s.i.g.	800		800
S.c.f. H_2/bbl. dripolene naphtha	1,010		1,010
Mole Percent H_2 Purity	100		100
Fresh or makeup wash oil rate, vol./vol. of dripolene naphtha		0.05	
Wash oil recycle rate, vol./vol. of dripolene naphtha		0.95	
Reactor effluent circulation rate, vol./vol. of dripolene naphtha		10	
Rate of Btms. reject, vol./vol. of dripolene naphtha		0.05	
Yield of hydrogenated gasoline, vol. percent of naphtha charged			103.0

The initial gasoline product bromine number from this run was 0.1 which increased almost linearly to a value

of 0.5 after 123 days on-stream at constant operating conditions. Inspection of the reactor internals at this time (123 days) revealed no evidence of polymer formation or reactor plugging. The coke content of the catalyst was found to be 7 wt. percent which is less than ⅓ of the catalyst's full coke capacity. Operation was not continued beyond this point even though from the standpoint of catalyst activity, the absence of polymer accumulation and percent coke on catalyst, operation could have continued for an almost indefinite period. Of particular merit is the gasoline product yield amounting to seven percent more than obtained in the process of Example I.

Example III

A dripolene naphtha described in Table 1 as charge stock A, was processed in a manner which embraced only part of the improvements cited herein. Pertinent operating conditions are given in Table 4. The same catalyst described in Example I was employed.

Fresh dripolene naphtha at a temperature below 90° F. was charged through a mixing T at the top of the reactor. At this point the dripolene naphtha was joined by the sum flows of once-through wash oil, recycle wash oil, hydrogen and methane, all of which had first been preheated to achieve a reactor inlet temperature of 550 F. The same abrupt changes in dripolene concentration and temperature were effected as described in Example II. All streams entered the top of the reactor resulting in down flow through the fixed bed reactor.

At reactor outlet conditions a hot separation was made between reactor effluent gas and liquid. A fraction of the liquid recovered at this point was circulated to the reactor inlet to achieve the desired dilution effect as described in Example II.

TABLE 4.—OPERATING CONDITIONS FOR EXAMPLE III

	Reactor 1
Mode of operation	Downflow
LHSV (based on naphtha)	1.5
Inlet temperature, ° F.	550
Pressure, p.s.i.g.	850
S.c.f. H_2/bbl. dripolene naphtha	1010
S.c.f. CH_4/bbl. dripolene naphtha	430
Mole percent H_2 purity	70
Once-through fresh wash oil rate, vol./vol. of dripolene naphtha	1
Reactor effluent circulation rate, vol./vol. dripolene naphtha	10

The net reactor effluent streams were separated and recovered. No product wash oil was returned to the system. The initial gasoline product bromine number was 11 which increased to a value of 26 after 45 days of operation. On the 46th day a severe pressure drop across the reactor developed in a matter of a few hours which ended with complete blockage of flow. Further operation was not possible. Inspection of the reactor showed that the interstices between the catalyst pellets were completely choked off with carbonaceous polymer in the top half of the reactor.

Example IV

A dripolene naphtha, described in Table 1 as charge stock A, was processed in a manner including all of the improvements described in Example II and modified in being processed in a single reactor with appropriate related changes as described. Pertinent operating conditions are given in Table 5. The apparatus of Example I was employed with the modifications indicated as follows. Fresh dripolene naphtha at a temperature below 90° F. was charged through a mixing T at the bottom of the reactor. At this point the dripolene naphtha was joined by the sum flows of recirculated effluent, once-through wash oil, hydrogen and methane, all of which had first been preheated to achieve a reactor inlet temperature of 550° F. The same abrupt changes in dripolene concentration and temperature were effected as described in Example II. All streams entered the bottom of the reactor resulting in predominantly liquid phase upflow through the fixed bed reactor.

At reactor outlet conditions a hot separation was made between reactor effluent gas and liquid. A fraction of the liquid recovered at this point was circulated to the reactor inlet as part of the sum flow stream providing the desired dilution effect as described in Example II. The operating conditions appear in Table 5, below.

TABLE 5.—OPERATING CONDITIONS FOR EXAMPLE IV

	Reactor 1
Mode of operation	Upflow, mixed phase
LHSV (based on naphtha)	1.0
Inlet temperature, ° F.	550
Pressure, p.s.i.g.	800
S.c.f. H_2/bbl. dripolene naphtha	1010
S.c.f. CH_4/bbl. dripolene naphtha	432
Mole percent H_2 purity	70
Once-through fresh wash oil rate, vol./vol. dripolene naphtha	1
Reactor effluent circulation rate, vol./vol. dripolene naphtha	10

The net reactor effluent streams were separated and recovered. No product wash oil was returned to the system. The initial gasoline product bromine number was 4.8 which increased to a level of 13.5 after 65 days on-stream, at which time this operation was discontinued. No evidence of polymerization or plugging was found.

In general considerations, operation in accordance with this invention may show various processing advantages when one reactor is employed in the processing of the less intractable type of charge stock and/or when product requirements are less stringent in allowing higher bromine number or the like. Two reactor operations can provide processing advantages with particularly difficult charge stocks and/or in the provision of highly hydrogenated products. Either system is amenable to adaption in the satisfactory processing of dripolene charge stocks to high quality products for either or both gasoline usage and aromatic products.

Example V

A dripolene naphtha charge, described in Table 1 as charge stock B, is processed in a system similar to that shown in the figure differing in that the second reactor is operated at upflow conditions. The catalyst in reactors **1** and **2** is sulfided cobalt molybdenum supported on alumina catalyst similar to that employed in Example II. The fresh dripolene naphtha at ambient temperature is admixed with the sum flows of recycle wash oil, makeup wash oil, re-run tower bottoms and hydrogen containing gas. The total admixture having a temperature of approximately 540° F. is introduced directly into the first reactor for selective hydrogenative reaction at upflow, substantially liquid phase conditions.

The liquid effluent from the first reactor after removal of light gases is divided, with approximately 80% being recycled to the first reactor inlet and 20% being charged to the second reactor after recombination with the reheated light gases recovered overhead from the separator intermediate at first and second reactor. This admixed stream having the temperature of 550° F. is passed for upflow, substantially mixed phase reaction in the presence of the hydrogenation catalyst in the second reaction zone. Separation of products from the second reactor and recovery of all fractions is achieved through conventional

fractionation. The operating conditions are set forth in Table 6.

TABLE 6.—OPERATING CONDITIONS FOR EXAMPLE V

	Reactor 1	Reactor 2	
Mode of Operation::	Liquid Phase Upflow	Upflow	Mixed Phase
LHSV (based on naphtha	1		1
Inlet Temperature, ° F	550		550
Pressure, p.s.i.g	800		800
S.c.f. H_2/bbl. dripolene naphtha	1,000		1,000
Mole Percent H_2 Purity	100		100
Fresh or make-up wash oil rate, vol./vol. of dripolene naphtha		0.05	
Wash oil recycle rate, vol./vol. of dripolene naphtha		0.95	
Reactor effluent circulation rate, vol./vol. of dripolene naphtha		10	
Rate of Btms, reject, vol./vol. of dripolene		0.05	
Yield of hydrogenated gasoline, vol. percent of naphtha charged		93	

After an on-stream operating period of 90 days an examination of the reactors and associated equipment discloses the absence of any plugging or substantial accumulation of carbonaceous deposits capable of growth into flow-detrimental proportions within any reasonable or foreseeable future. The product quality from the 90 day operational period is evidenced by a bromine number of less than 1.0, a substantially linear increase from an initial bromine number of 0.1. Coke content of the catalyst after 90 days on-stream is approximately 12.0% which is approxiamtely half of the total capacity of the catalyst, thus indicating an operable time of approximately six months before regeneration of the catalyst would be required.

Obviously, many modifications and variations of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

What is claimed is:

1. In a process for the conversion of pyrolysis naphtha to product of enhanced utility by selective hydrogenation in at least two stages of catalyzed reaction, the improvement comprising

(a) simultaneously diluting fresh feed pyrolysis naphtha and obtaining a mixture adjusted in temperature to desired level for introduction to a first catalytic reaction zone by admixing the fresh feed of a temperature level below that at which thermal polymerization of diolefins occurs with a liquid stream of normally liquid hydrocarbons substantially free of polymerizable components and having a temperature level above the desired introduction temperature level and a gaseous stream containing at least 40% free hydrogen and relatively free of other reactive gases, said liquid stream being at least five times the volume of said fresh stream and said gaseous stream containing at least twice the amount of free hydrogen stoichiometrically needed to effect complete hydrogenation of all olefinic components of said fresh feed, said temperatures of the several streams forming the final admixture being such as to produce a temperature level in the range desired for introduction to said first reaction stage;

(b) introducing said admixture directly into said first reaction stage maintained at conditions, including a temperature in the range of 400–600° F. and a pressure in the range of 600–1000 p.s.i.g., ensuring maintenance of the normally liquid components of said admixture in liquid phase and for effecting the selective hydrogenation of substantially all of the diolefinic components originally present in said admixture, said admixture being passed through said first reaction zone, containing a fixed bed of particulate hydrogenation catalyst, in substantially flooded upflow and at a superficial flow rate in excess of 0.1 linear foot per minute;

(c) passing the effluent from said first reaction zone to a separation zone and separating said effluent into at least two streams, said first stream comprising no more than ⅓ of the normally liquid components of said effluent and substantially all of the lighter components other than those dissolved in the normally liquid components separated, and said second stream comprising at least ⅔ of said normally liquid components;

(d) subjecting said first stream to temperature adjustment and passing said temperature-adjusted stream to and through a second reaction stage, containing a fixed bed of particulate hydrogenation catalyst, operating at conditions, including a temperature in the range of 500 to 750° F. and a pressure in the range of 700 to 1200 p.s.i.g.;

(e) recovering effluent from said second reaction stage substantially free of olefinic components and having a bromine number no greater than 1;

(f) and processing said last-mentioned effluent to a product form having utility enhanced over that of said fresh feed.

2. The process in accordance with claim 1 further characterized in that said second stream from said separation of step (c) is recycled at least in part as said liquid stream in step (a).

3. The process in accordance with claim 1 further characterized in that the particulate hydrogenation catalyst in the several reaction stages is of substantially the same type and composition.

4. The process in accordance with claim 3 further characterized in that said catalyst is sulfided cobalt molybdate hydrogenation catalyst.

5. The process in accordance with claim 1 further characterized in that the operating conditions are those yielding effluent from said second stage readily processed to gasoline product.

6. The process in accordance with claim 1 further characterized in the use of operating conditions yielding desired product continuously for a time period of at least six months.

7. In a process for the conversion of pyrolysis naphtha to product of enhanced utility by selective hydrogenation in the presence of hydrogenation catalyst, the improvement comprising

(a) simultaneously diluting fresh feed pyrolysis naphtha and obtaining a mixture adjusted in temperature to desired level for introduction to a catalytic reaction zone by admixing the fresh feed of a temperature level below that at which thermal polymerization of diolefins occurs with a liquid stream of normally liquid hydrocarbons substantially free of polymerizable components and having a temperature level above the desired introduction temperature level and a gaseous stream containing at least 40% free hydrogen and relatively free of other reactive gases, said liquid stream being at least five times the volume of said fresh stream and said gaseous stream containing at least twice the amount of free hydrogen stoichiometrically needed to effect complete hydrogenation of all olefinic components of said fresh feed, said temperatures of the several streams forming the final admixture being such as to produce a temperature level in the range of 400 to 600° F. desired for introduction to said catalytic reaction zone;

(b) introducing said admixture into said catalytic reaction zone maintained at conditions including a temperature in the range of 400–600° F. and a pressure in the range of 600–1000 p.s.i.g. ensuring maintenance of the normally liquid components of said admixture in liquid phase and for effecting selective hydrogenation of substantially all of the diole-

finic components and a major portion of the monoolefinic components present in said fresh feed portion of said admixture, said admixture being passed through said catalytic reaction zone containing a fixed bed of particulate hydrogenation catalyst in substantially flooded up-flow and at a superficial flow rate in excess of 0.1 linear foot per minute;

(c) passing the effluent from said catalytic reaction zone to a separation zone and separating said effluent into at least two fractions comprising a relatively lower boiling fraction and a relatively higher boiling fraction;

(d) recycling at least a major portion of said relatively higher boiling fraction to said catalytic reaction zone as at least a portion of said liquid stream of normally liquid hydrocarbons substantially free of polymerizable components; and

(e) recovering said relatively lower boiling fraction

as selectively hydrogenated product of enhanced utility.

8. The process in accordance with claim 7 further characterized in that said hydrogenation catalyst is sulfided cobalt molybdate supported on alumina.

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208—144; 260—677

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,498,907 Dated March 3, 1970

Inventor(s) Louis C. Doelp, Jr. 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 3, line 12, "nonger" should be -- longer --.

Column 3, line 57, insert -- . -- after "(psig)".

Column 5, line 12, after "rate", "to" should be -- of --.

Column 5, line 35, after "than", "is" should be -- in --.

Column 5, line 37, after "in" insert a hyphen.

Column 8, line 4, "as" should be -- was --.

Column 9, line 46, "430" should be -- 432 --.

Column 11, line 8, after "naphtha" insert --) --.

SIGNED AND
SEALED
AUG 4 - 1970

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

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Commissioner of Patents