May 13, 1941. P. S. DANNER 2,241,393

PROCESS OF TREATING HYDROCARBONS

Filed March 14, 1938 2 Sheets-Sheet 1

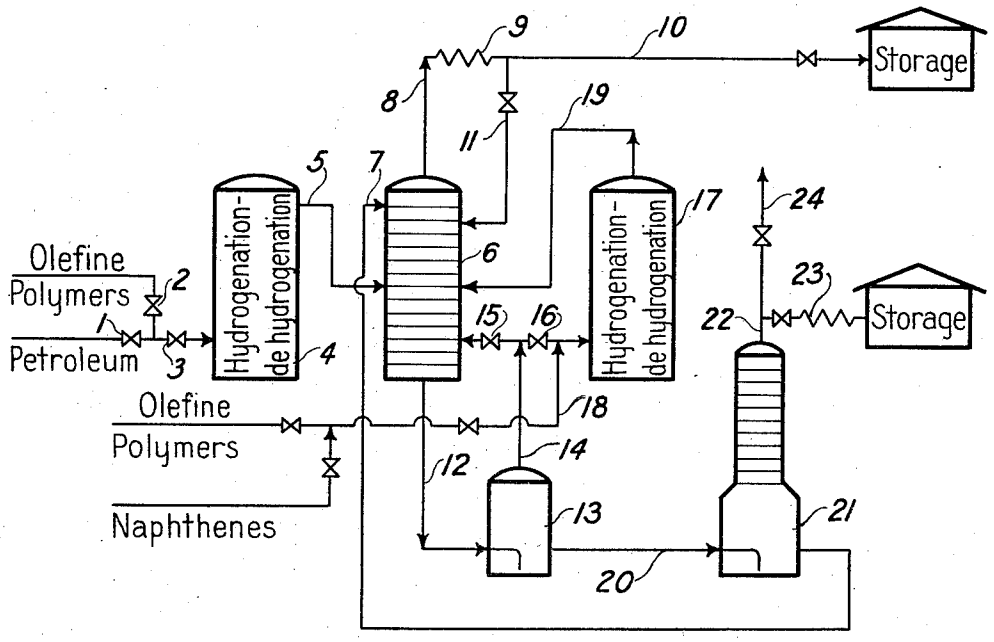


Fig. 1

Philip S. Danner
INVENTOR

BY

ATTORNEY

May 13, 1941. P. S. DANNER 2,241,393

PROCESS OF TREATING HYDROCARBONS

Filed March 14, 1938 2 Sheets-Sheet 2

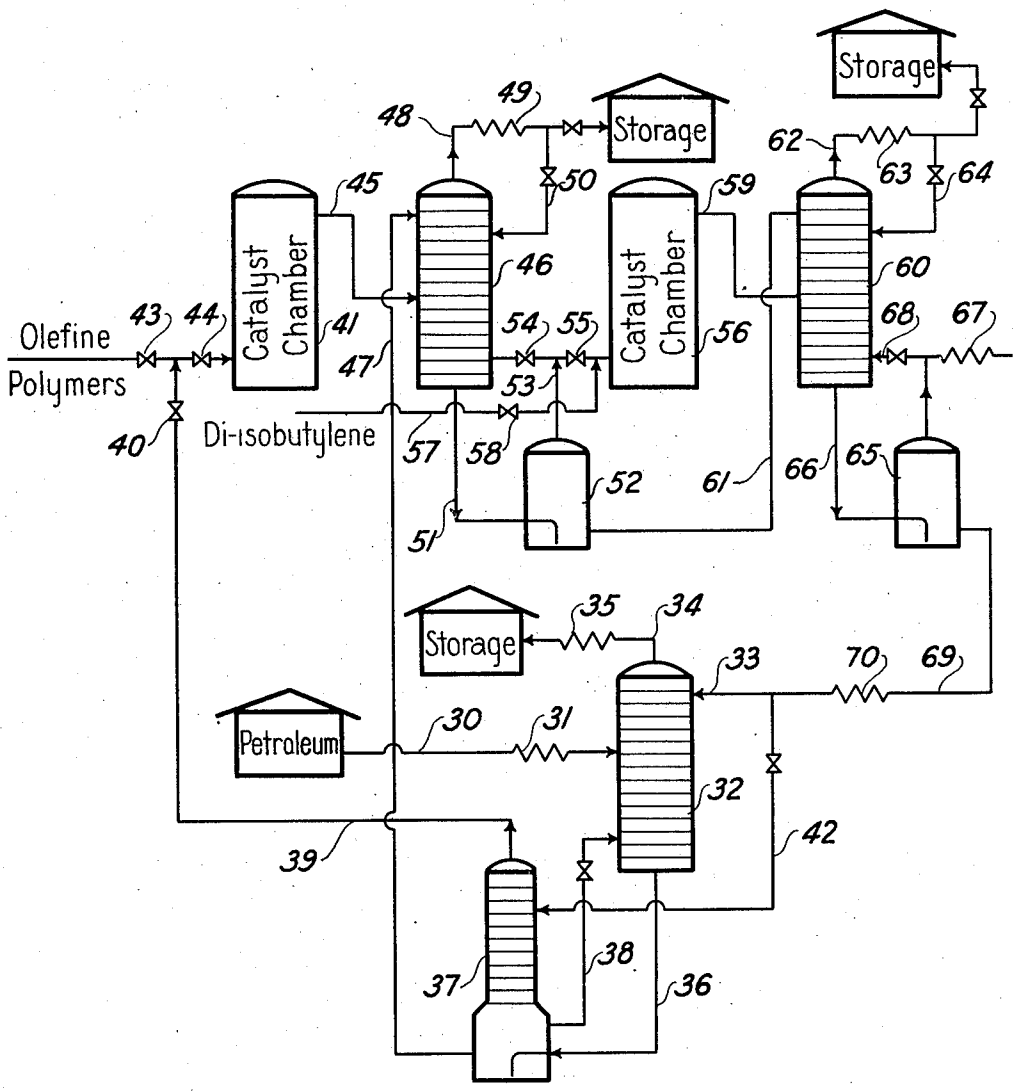


Fig. 2

Philip S. Danner
INVENTOR

BY J. Adams

ATTORNEY

Patented May 13, 1941 2,241,393

UNITED STATES PATENT OFFICE

2,241,393

PROCESS OF TREATING HYDROCARBONS

Philip S. Danner, Berkeley, Calif., assignor to Standard Oil Company of California, San Francisco, Calif., a corporation of Delaware

Application March 14, 1938, Serial No. 195,860

8 Claims. (Cl. 260—668)

This invention relates to a new and improved process for treating hydrocarbons, and more particularly to a process which involves the simultaneous production of a high octane motor fuel and a low aniline point highly aromatic solvent or thinner useful in coating compositions or wherever a petroleum fraction comprising a large proportion of aromatic compounds is desired.

An object of the invention is to provide a new and improved process of treating hydrocarbons. A further object is to provide an efficient method for producing high octane paraffinic motor fuels and highly aromatic petroleum fractions.

Another object of the invention is to provide a combination process in which a mixture of olefine polymers and a naphthenic petroleum fraction is passed through a series of alternate extraction and hydrogenation-dehydrogenation zones, the vapors from each hydrogenation-dehydrogenation zone supplying the heat necessary in a vapor phase selective solvent extraction zone, and the quenching of the vapors in the selective solvent, together with the selective removal of reaction products, serving to halt undesirable side reactions such as polymerization.

An additional object is to provide a process for catalytically treating olefine polymers in which catalyst poisoning is minimized by vapor phase solvent extraction of a petroleum fraction prior to and/or subsequent to admission in each catalytic zone.

A further object of the invention is to selectively remove desired reaction products from the reaction mixture as it flows from a hydrogenation-dehydrogenation zone, thereby enabling the desired reactions to be carried further than would otherwise be feasible and minimizing side reactions.

Another object is to provide a process in which reaction products of olefine polymers and naphthenes are quenched in a liquid phase selective solvent and undesirable side reactions are thereby stopped.

Figure I is a diagrammatic flow sheet illustrating a process utilizing two catalytic hydrogenation-dehydrogenation zones and a single vapor phase selective solvent extraction zone. Figure II illustrates a multi-stage process in which olefine polymers and highly naphthenic petroleum fractions are reacted in a series of hydrogenation-dehydrogenation zones and the reaction mixture from each zone extracted with a selective solvent prior to treatment of unreacted portions thereof in subsequent catalytic treating zones.

In Figure I, a petroleum fraction flows through valve 1 and an olefine polymer through valve 2 by way of mixing valve 3 to catalytic chamber 4. The mixture of hydrocarbons is treated in catalytic chamber 4 to simultaneously convert the olefine polymers to paraffins by hydrogenation and the naphthenic hydrocarbons therein to aromatic and/or cyclic olefine compounds by dehydrogenation. The reaction mixture from the catalytic treatment is immediately passed from chamber 4 through line 5 into extraction tower 6 where the mixture is quenched in a high boiling selective solvent of the type hereinafter more particularly disclosed. The selective solvent in extraction tower 6 is preferably maintained at a temperature above the initial boiling point of the hydrogenated olefines formed by the catalytic treatment, but is preferably no more than 60° F. above the dew point of the unconverted naphthenes under the conditions existing in the extraction tower. The heat released by the quenched vapors in tower 6 serves to selectively vaporize the hydrogenated olefines and other paraffins of the same boiling range from the mixture of hydrocarbons in the presence of the selective solvent. Also, the immediate quenching of the reaction mixture in tower 6 inhibits undesirable side reactions which may normally occur at the higher temperatures involved in the catalytic treating zone.

The high boiling selective solvent, which is admitted to tower 6 by line 7, flows downwardly in liquid phase selectively extracting aromatic, naphthenic and unsaturated compounds from the upwardly flowing hydrocarbon vapors. A simultaneous liquid phase selective solvent extraction and a fractional distillation effect serves to give an efficient separation of the hydrogenated olefine polymers from the non-paraffinic constituents of the reaction mixture. The hydrogenated olefine polymers may comprise high octane compounds, and a high octane motor fuel may thus be removed from the top of tower 6 and passed in vapor phase through line 8 to condenser 9 and valve controlled line 10 to storage. A valve controlled reflux line 11 is provided for returning a portion of the overhead to the top of extraction tower 6.

The downwardly flowing selective solvent, together with its dissolved aromatic, naphthenic and unsaturated compounds, is removed from the bottom of the tower through line 12 to vaporizer 13. A controlled portion of the dissolved hydrocarbons is vaporized in heater 13 and flows through conduit 14 either by way of

valve 15 to tower 6, where the vapors serve to control the temperature in the tower and are again extracted by the selective solvent, or by way of valve 16 to catalyst chamber 17 or the vapors from line 14 may be split and flow both to the tower and the catalyst chamber.

Naphthenic hydrocarbons are more easily vaporized from the selective solvent than are aromatic compounds of corresponding boiling range, and it is preferred to control the temperature in vaporizer 13 to preferentially vaporize the dissolved naphthenic hydrocarbons and preferentially retain the aromatic hydrocarbons in the selective solvent. By so doing, a highly naphthenic vapor which may also contain olefine polymers is obtained and may be admitted to chamber 17. Olefine polymers or naphthenes or both, as may be required, are admitted through valve controlled line 18, and the mixture of naphthenes and olefine polymers converted to a mixture of high octane paraffins and aromatic hydrocarbons by the simultaneous hydrogenation of the olefine polymers and dehydrogenation of the naphthenes in the same manner as in catalyst chamber 4. The reaction mixture from chamber 17 flows through line 19 back to tower 6 where the mixture is quenched and extracted by the selective solvent.

The selective solvent in vaporizer 13, together with the remaining dissolved compounds, flows through line 20 to still 21 where the dissolved hydrocarbons are distilled from the solvent and pass by way of line 22 through condenser 23 to storage. In some cases the entire olefine content is not hydrogenated in catalyst chambers 4 and 17. Where the proportion of such olefines in the mixture from still 21 is large, it is often desirable to separate these olefines by a suitable fractionating column, e. g. of the same type as tower 6, and a valve controlled line 24 is provided for passing the vapors from still 21 to such an extraction tower rather than to storage. The olefines obtained from this separation may be returned to catalyst chamber 4 or 17 for the hydrogenation-dehydrogenation treatment.

As previously indicated, the extract fraction obtained by the above process from still 21 is highly aromatic in composition and comprises an excellent solvent for coating compositions or may be used as a blending agent in motor fuels to increase the octane number thereof. The undissolved vapor phase fraction obtained from extraction tower 6 constitutes a high octane motor fuel when dimers of normally gaseous olefines, such as butene, isobutene dimers and copolymers of the butenes, comprise the olefines fed into the system, and this fraction is useful as an aviation fuel or wherever high octane paraffinic compounds are desired. Thus the process produces simultaneously a highly paraffinic high octane motor fuel which may contain a large proportion of iso-octane and a highly aromatic hydrocarbon fraction of greater economic value than the original petroleum.

In the modified form of the process illustrated by the flow diagram in Figure II, a petroleum fraction flows from storage through line 30 and heater 31, where it is converted to vapor phase, into extraction tower 32. A high boiling selective solvent is admitted to the top of this tower from line 33 and flows downwardly countercurrently extracting the petroleum vapors and simultaneously fractionating the same. By proper control of conditions in tower 32 a major proportion of the paraffinic hydrocarbons originally present in the petroleum may be selectively vaporized and passed through line 34 and condenser 35 to storage. The selective solvent, together with extracted hydrocarbons dissolved therein, flows from the bottom of tower 32 by way of conduit 36 to still 37. Valve controlled pipe 38 is provided for supplying vapors from still 37 to the bottom of tower 32 for maintaining the temperature in said tower at the required level.

Hydrocarbon vapors are separated and fractionated in still 37 and pass through line 39 and valve 40 to the inlet line for catalyst chamber 41. It is preferred to admit a portion of the high boiling selective solvent at the top of the fractionating column of still 37. Valve controlled conduit 42 is provided for this purpose. By admission of a selective solvent at this point and careful control of the temperature in fractionating still 37, a highly naphthenic hydrocarbon fraction substantially free of aromatic compounds may be obtained as overhead for admission to catalyst chamber 41. Sharp fractionation in still 37 also serves to further eliminate potential catalyst poisons, such as sulfur and nitrogen compounds by retaining them in the selective solvent, as well as to supply substantial pure naphthenes to the catalytic treating zone.

Olefine polymers in vapor phase pass by way of valve 43 and, together with the naphthenic hydrocarbon fraction, through mixing orifice 44 into the catalytic treating zone represented by catalyst chamber 41. The reaction mixture from chamber 41 flows through conduit 45 to fractionating tower 46. Inlet pipe 47 serves to admit a high boiling selective solvent to the top of tower 46 for extraction and simultaneous distillation of the reaction mixture. The vapor phase raffinate from tower 46 comprises high octane hydrogenated olefine polymers and flows from the top of the tower by way of line 48 and condenser 49 to storage. A valve controlled reflux line 50 is provided for returning a portion of the overhead to the top of the extraction tower. The selective solvent passes from the bottom of the tower into pipe 51 and vaporizer 52. A controlled portion of the dissolved compounds is vaporized and flows through conduit 53 either by way of valve 54 to the bottom of tower 46, where the vapors serve to control the temperature in the tower and are again extracted, or by way of valve 55 to catalyst chamber 56, or the vapors may be split and pass both to the tower and the catalyst chamber. It is preferred to control the temperature in vaporizer 52 so as to preferentially vaporize the dissolved naphthenes and preferentially retain the aromatics in the selective solvent. By so doing, di-isobutylene can be admitted through line 57 controlled by valve 58, mixed with the naphthenes and converted to a mixture of iso-octane and aromatic compounds in catalyst chamber 56 by the simultaneous hydrogenation of the di-isobutylene and dehydrogenation of the naphthenes in the same manner as in previous catalyst zones.

The reaction mixture from chamber 56 then flows through line 59 to extraction tower 60 of the same type as tower 46. Selective solvent from vaporizer 52 passes to the top of tower 60 by way of pipe 61 and extracts the aromatic compounds from said reaction mixture. Substantially pure iso-octane may be obtained as overhead and flows by way of line 62 and condenser 63 to storage. Valve controlled reflux line 64 is also provided for tower 60. The extract from this tower comprising substantially pure aromatic hydrocarbons dissolved in the selective solvent flows to

vaporizer 65 by way of conduit 66. The aromatic hydrocarbons are vaporized from the solvent and pass through condenser 67 to storage. A portion of these vapors is returned to the bottom of tower 60 by way of valve controlled line 68 for the purpose of controlling temperature in the tower. The selective solvent, stripped of its dissolved hydrocarbons, passes through conduit 69 and cooler 70 to inlet 33 of tower 32, as previously described.

The reaction occurring in the hydrogenation-dehydrogenation zone is believed to be represented by the following equation:

3 olefines+1 naphthene→3 paraffins+1 aromatic

For purposes of illustration, the following comprise specific examples of catalysts and conditions of operation which are suitable for the hydrogenation-dehydrogenation zones:

Table I

Catalyst	Temperature of experiment	Pressure	Space velocity	Stock treated
	°F.	*Lbs./sq. in.*	*Vols. liq./vol. cat. per hour*	
Copper chromite	870–900	Atmos.	0.37	77% 200-300° F. cut natural petroleum + 23% aviation cut butylene polymers.
Copper chromite	900	200	0.33	57% 200-300° F. cut natural petroleum + 43% aviation cut butylene polymers.
Nickel chromite	900	200	0.25	Do.
Nickel chromite	900	200	0.17	Do.
Nickel chromite	900	300	0.25	Do.
50% nickel chromite 50% copper chromite	900	200	0.33	Do.
Do	800	200	0.33	Do.

In general, it has been found that the temperature in the catalytic chambers should be maintained below approximately 1000° F. Temperatures as low as 400° F. are operative with some catalysts and on some stocks. Catalysts which promote both hydrogenation and dehydrogenation reactions in this temperature range may be utilized. Additional examples are nickel and molybdenum sulfide. A number of such catalysts are known to those skilled in the art and the present invention is not concerned with the catalysts per se.

Although specific mention has been made of the treatment of di-isobutylene and although the invention at present finds its greatest utility in the treatment of dimers of two to five carbon olefines, the broader aspects of the invention are not so limited and include treatment of high polymers of these compounds, such as high boiling polymers useful as and/or in synthetic and compounded lubricants. Dimers formed by polymerization or copolymerization of propylene, butylenes, pentenes and mixtures of these compounds when contacted with polymerization catalysts such as phosphoric acid, hot sulfuric acid, aluminum chloride, metal phosphate catalysts such as calcium phosphate, cadmium phosphate and metaphosphates, comprise a most suitable source of olefine polymers for production of high octane paraffinic motor fuels by the process of the present invention. It is to be understood that conjoint polymers or copolymers of the isomeric butenes, of butenes and propylene, of pentenes and propylene, of ethylene and butenes, and of ethylene, propylene and butenes, as well as various other mixtures, are operative in the present process. Where high octane paraffins are desired butene polymers should be utilized.

When high boiling olefine polymers are treated in the present process a high boiling highly paraffinic hydrogenated product results which, in those cases that involve a boiling range above the initial boiling point of the selective solvent, requires a modification of the solvent extraction stage of the process. Since it is not feasible to separate the high boiling hydrogenated olefines as vapor phase, these compounds may be removed from the tower as a separate liquid phase. The unconverted naphthenes may be removed as vapor phase overhead and the aromatics separated with the selective solvent as dissolved therein. Thus, a three-way separation is obtainable in a single extraction tower, namely, naphthenes and olefines as vapor phase raffinate, high boiling paraffins as liquid phase raffinate, and aromatics as liquid phase extract. These separate fractions will be handled in the same way as the corresponding fractions in flow sheets Figures I and II, the only difference being the point at which they are removed from the solvent extraction stage.

The petroleum stocks which may be utilized in the present process may vary greatly in type as well as in boiling range so long as a substantial proportion of naphthenic compounds is contained therein. In order to avoid various difficulties and minimize side reactions, it is preferred to utilize a natural petroleum cut from a highly naphthenic type crude, but Mid-Continent crudes and even cracked naphthas are operative in the process, particularly if the species of operation illustrated by Figure II is adopted. In the specific examples previously tabulated a 200 to 300° F. cut was adopted. It is to be understood that this boiling range merely comprises one example of a suitable material and that other petroleum fractions may be selected depending upon the aromatic compounds or compounds which it may be desired to produce. When, for example, one wishes to synthesize benzene, a narrow cut in the benzene boiling range will be selected and supplied as stock to be treated in the process. Likewise when toluenes or xylenes are desired, corresponding sharply fractionated petroleum cuts may be selected. Similarly, when very high boiling aromatics of unknown or polynuclear constitution are to be synthesized, petroleum fractions boiling in the selective range will be adopted. When a lacquer diluent of low aniline point is to be produced a stock having a boiling range of from 200 to about 265° F. may be selected, and if a paint thinner is desired a 300 to 400° F. cut may be processed. An aromatic type aviation gasoline can be simultaneously produced with the paraffinic type high octane gasoline by processing a petroleum cut having, for example, a 50% point at about 212° F. and a 90% point at 275° F. The above examples will suffice to guide one skilled in the art in the selection of the stocks to be treated.

The relative proportion of petroleum fraction to olefine generally should be such that there is at least one naphthene ring for each three olefine bonds to be hydrogenated. An excess of naphthenes is generally desirable, at least in the first stages of a multi-stage process, in order to afford the most economic utilization of the olefine polymers. In those cases where production of aromatics is the primary object, an excess of olefines may be utilized.

The vapor phase selective solvent extraction stages of the process may be carried out in any known suitable type of fractionating column whether it be a tower filled with a packing of refractory earthenware, glass, etc., or a tower constructed in the same manner as an ordinary fractionating column of the bubble cap type. In order to better understand this stage of the process, the action on a bubble plate will be considered in some detail.

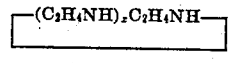
The reaction mixture from a catalytic stage enters the tower in vapor form and is quenched in the liquid phase selective solvent flowing across the bubble plate. The temperature of the solvent in the tower may be maintained above the boiling point of the hydrocarbon mixture under the conditions of extraction by controlling the temperature of the selective solvent entering the top of the tower, by controlling the temperature of the reaction mixture admitted to the tower and by controlling the amount of vapors recirculated from the vaporizer connected to the bottom of the tower. The selective solvent should be maintained at a temperature below that at which the aromatic hydrocarbons will be vaporized from the selective solvent. This temperature may vary widely depending upon the ratio of solvent to aromatics. In general, although higher temperatures are operative, a practical upper limit of temperature is the end point of the stock being extracted and temperatures in the order of 20 to 60° F. above the dew point of the aromatic components of the stock under the conditions existing in the extraction tower are preferable.

By controlling the temperature, as previously indicated, the hydrocarbon vapors are simultaneously selectively extracted as they pass through the selective solvent and are fractionated as they pass upwardly through the fractionating column. The vapor phase hydrocarbons from the catalytic stage are sufficiently hot to serve as a source of heat for the fractionation in the extraction column. At the same time the vapors are giving up their heat to produce fractionation of those hydrocarbons which have been previously condensed, these hotter vapors are being quenched by direct contact with the cooler selective solvent. Inasmuch as the volume of selective solvent is usually two or more times that of the hydrocarbons being extracted (measured as liquid phase) the dissolution of unsaturated compounds, for example, serves to dilute the mixture, and by reason of this dilution to decrease the rate at which various undesirable side reactions may progress. Furthermore, the sudden cooling of the hydrocarbon reaction mixture also tends to prevent or decrease undesired side reactions, particularly polymerization, and consequently reduces the extent of gum formation and the extent of catalyst poisoning by preventing the initial formation of such poisons.

A selective solvent useful for the present process should be highly selective and should have a boiling point well above the end point of the petroleum stock to be treated. A boiling point above approximately 300° F. will generally be found desirable in the treatment of the lower boiling hydrocarbon mixtures. Preferably, the solvents should not form constant boiling mixtures with the hydrocarbons being treated but, in some cases where constant boiling mixtures are formed, the solubility characteristics are such that complete recovery by water extraction is possible and the solvent is therefore suitable for use in such a modified method of treatment. The following comprises a list of high boiling selective solvents which are operative in the extraction stage of the present invention:

Solvent	B. P.
	°F.
Resorcinol	529.
Diacetin	349 at 40 mm.
Tetraethylene glycol	293 at 0.1 mm.
Phenol	360.
Triethylene glycol	550.
Tetramine	511.
Anisidine	435–484.
Diethylene glycol	472.
"Carbitol"	396.
Acetamide	432.
Triacetin	498.
Xylidine	412–439.
Acetanilide	579.
Diethanolamine	514.
Nitrobenzene	412.
Aniline	361.
"Chlorex"	352.
Diaminopropanol	246 at 4 mm.
Tri-cresylphosphate	507 at 20 mm.
Benzaldehyde	355.
Triethanolamine	531 at 150 mm.
Eugenol	487.
Diphenyl amine	576.
Acetophenone	396.
Xylenol	450.
"Carbitol" acetate	424.
Butyl carbitol	448.
Phenetidine	444–489.
Dibutyl phthalate	410 at 20 mm.

Tetraethylene glycol and triethylene glycol have high selectivity factors, high boiling points, and comprise examples of preferred solvents. Ethylene amines, such as tetramine, constitute an additional example of an efficient high boiling solvent. These compounds comprise a generic group which may be represented by the general formula $NH_2C_2H_4(C_2H_4NH)_xNH_2$. Corresponding ring compounds are of the type formula



Although a number of specific examples of suitable selective solvents have been given and although triethylene glycol and tetramine constitute preferred examples of solvents, it should be apparent to those skilled in the art that the broader aspects of the invention include the use of a multitude of other high boiling selective solvents.

It is to be understood that the process of this invention may be carried out under sub-atmospheric, atmospheric or super-atmospheric pressures, and that the drawings are merely diagrammatic in character, no attempt having been made to illustrate an apparatus embodying all the necessary details such as valves, pumps, and pressure control devices. The provision of suitable apparatus for carrying out the process is regarded as within the skill of a petroleum technician. Common forms of catalyst chambers, supports for catalyst beds, heating and cooling means to control the temperature of the catalyst and the temperature of the petroleum vapors may be utilized.

While the character of this invention has been described in detail and numerous illustrative examples given, this has been done by way of ex-

emplification only and with the intention that no limitation should be imposed upon the invention thereby. It will be apparent to those skilled in the art that numerous modifications and variations may be effected in the practice of the invention which is of the scope of the claims appended hereto.

I claim:

1. A process which comprises forming a mixture of olefins and naphthenes, passing said mixture at an elevated temperature over a catalyst in a hydrogenation-dehydrogenation zone whereby naphthenes are dehydrogenated to aromatics and olefines are hydrogenated to paraffins, quenching the vapors leaving said zone by direct contacting with a high boiling organic selective solvent for cyclic hydrocarbons in liquid phase to simultaneously stop undesired side reactions and effect a separation of paraffin from cyclic hydrocarbons, separating said solvent containing dissolved cyclic hydrocarbons from undissolved paraffinic vapors, and recovering naphthenes and aromatics from said solvent.

2. A process which comprises forming a mixture containing naphthenes and a polymerization product of two to five carbon olefins, passing said mixture at an elevated temperature over a catalyst in a hydrogenation-dehydrogenation zone whereby naphthenes are dehydrogenated to aromatics and said olefin polymers are hydrogenated to paraffins, quenching the vapors leaving said zone by direct contacting with a high boiling organic selective solvent for cyclic hydrocarbons in liquid phase to simultaneously stop undesired side reactions and effect a separation of paraffin from aromatic hydrocarbons, separating said solvent containing dissolved aromatic hydrocarbons from undissolved paraffinic vapors, and recovering aromatics from said solvent.

3. A process which comprises forming a mixture containing naphthenes and di-isobutylene, passing said mixture at an elevated temperature over a catalyst in a hydrogenation-dehydrogenation zone whereby naphthenes are dehydrognated to aromatics and said di-isobutylene is hydrogenated to paraffins, quenching the vapors leaving said zone by direct contacting with a high boiling organic selective solvent for cyclic hydrocarbons in liquid phase to simultaneously stop undesired side reactions and effect a separation of paraffin from aromatic hydrocarbons, separating said solvent containing dissolved aromatic hydrocarbons from undissolved paraffinic vapors, and recovering aromatics from said solvent.

4. A process which comprises forming a mixture of olefins and naphthenes which boil substantially in the range of motor fuel, passing said mixture over a catalyst in a hydrogenation-dehydrogenation zone at a temperature of from approximately 400° F. to approximately 1000° F. whereby naphthenes are dehydrogenated to aromatics and olefins are hydrogenated to paraffins, quenching the vapors leaving said zone by direct contacting with a high boiling organic selective solvent for cyclic hydrocarbons in liquid phase to simultaneously stop undesired side reactions and effect a separation of paraffinic from cyclic hydrocarbons, separating a vapor phase hydrogenated olefin fraction, separately removing a naphthenic hydrocarbon fraction from solution in said selective solvent, returning said last fraction to a hydrogenation-dehydrogenation zone, and vaporizing the remaining aromatic compounds from said selective solvent.

5. A process which comprises mixing a petroleum fraction containing naphthenic hydrocarbons with a high boiling organic selective solvent for cyclic hydrocarbons, selectively vaporizing a highly naphthenic hydrocarbon fraction from said selective solvent whereby catalyst poisons are selectively dissolved and said naphthenic hydrocarbons are substantially freed of sulfur and nitrogen compounds, forming a mixture of an olefin and said naphthenic fraction, passing said mixture at an elevated temperature over a catalyst in a hydrogenation-dehydrogenation zone whereby naphthenes are dehydrogenated to aromatics and olefins are hydrogenated to paraffins, quenching the vapors leaving said zone by direct contacting with a high boiling organic selective solvent for cyclic hydrocarbons in liquid phase to simultaneously stop undesired side reactions and effect a separation of paraffin from cyclic hydrocarbons, separating said solvent containing dissolved hydrocarbons from undissolved paraffinic vapors, and recovering aromatics from said solvent.

6. A process which comprises extracting a mixture containing aromatic, naphthenic and paraffinic hydrocarbons with a high boiling organic selective solvent for cyclic hydrocarbons to selectively dissolve aromatic and naphthenic hydrocarbons from said mixture in said solvent, selectively distilling naphthenic hydrocarbons from said high boiling organic selective solvent, mixing a polymerization product of two to five carbon olefins with said distilled naphthenic hydrocarbons, passing said mixture at an elevated temperature over a catalyst in a hydrogenation-dehydrogenation zone whereby naphthenes are dehydrogenated to aromatics and olefins are hydrogenated to paraffins, quenching the vapors leaving said zone by direct contacting with a high boiling organic selective solvent for cyclic hydrocarbons in liquid phase to simultaneously stop undesired side reactions and effect a separation of paraffin from cyclic hydrocarbons, separating said solvent containing dissolved aromatic hydrocarbons from undissolved paraffinic vapors, and recovering aromatics from said solvent.

7. A process which comprises forming a mixture containing an olefin and a naphthalene, alternately passing said mixture at an elevated temperature over a catalyst in a hydrogenation-dehydrogenation zone whereby naphthenes are dehydrogenated to aromatics and olefins are hydrogenated to paraffins and quenching the vapors leaving each of the alternate hydrogenation-dehydrogenation zones by direct contacting with a high boiling organic selective solvent for cyclic hydrocarbons in liquid phase to simultaneously stop undesired side reactions and effect a separation of aromatic hydrocarbons, separating said solvent containing dissolved aromatic hydrocarbons from undissolved vapors, and recovering aromatics from said solvent.

8. A process which comprises forming a mixture of olefins and paraffins, passing said mixture at an elevated temperature over a catalyst in a hydrogenation-dehydrogenation zone whereby naphthenes are dehydrogenated to aromatics and olefins are hydrogenated to paraffins, quenching the vapors leaving said zone by direct contacting with a high boiling organic selective solvent for cyclic hydrocarbons in liquid phase to simultaneously stop undesired side reactions and effect a separation of paraffin from cyclic hydrocarbons, maintaining said selective solvent at

a temperature above the initial boiling point of the reaction mixture but below the boiling point of the highest boiling paraffin hydrocarbons contained therein whereby aromatic hydrocarbons are dissolved in said selective solvent, naphthenic hydrocarbons are vaporized, and high boiling paraffin hydrocarbons comprise an undissolved raffinate phase, returning said vapor phase naphthenes to a hydrogenation-dehydrogenation zone, separating said high boiling liquid phase paraffin hydrocarbons from said selective solvent, and recovering dissolved aromatic hydrocarbons from said solvent.

PHILIP S. DANNER.