

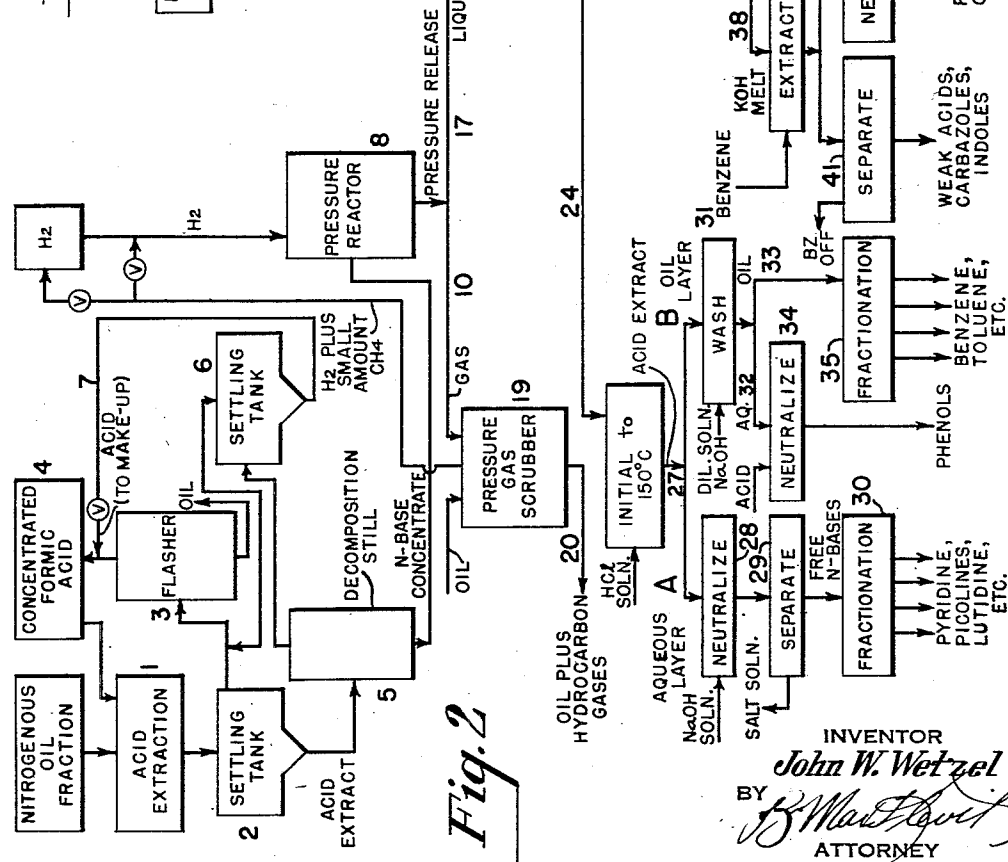
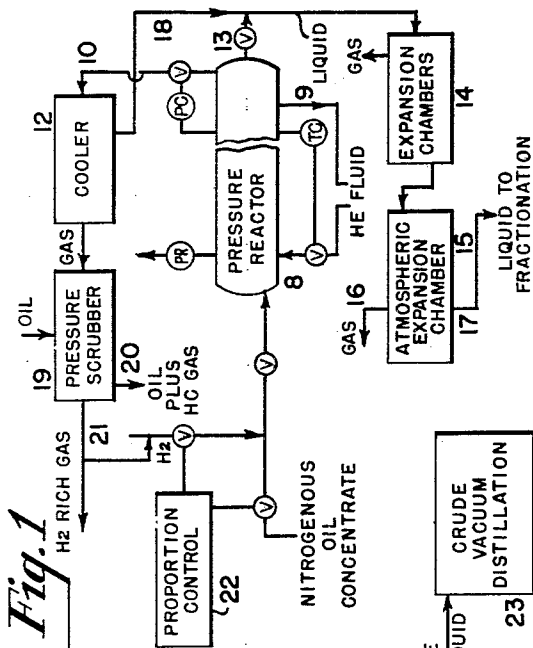
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PYROLYTIC HYDROGENOLYSIS OF NITROGEN BASES

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PYROLYTIC HYDROGENOLYSIS OF NITROGEN BASES

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8 Claims. (Cl. 260—283)

The present invention relates to pyrolytic hydrogenolysis of heterocyclic nitrogen bases and of crude oil fractions and concentrates rich in nitrogen bases, to produce desired conversion products including lower molecular weight heterocyclic N-compounds. There can be recovered from the reaction mixture when starting from natural oil distillates or extracts, in addition to heterocyclic N-bases, valuable non-nitrogenous cyclic compounds formed by the reaction or otherwise present in the reaction mixture.

Many crude petroleum oils and distillate fractions thereof contain heterocyclic nitrogen compounds such as higher homologues of pyridine, quinoline and isoquinoline, which have been found to interfere with the catalytic cracking of these oils. These nitrogen compounds when present even in relatively small amounts in a hydrocarbon charge stock subjected to catalytic cracking, act either as transitory "poisons" or deactivants for the catalyst, and/or demonstrate an inhibitory effect on the cracking reactions, resulting in lower conversion rates and in reduced yields of desired conversion products. The presence of these nitrogenous compounds in oil fractions or distillates which are not ordinarily employed as cracking stocks, also may be undesirable in certain particular uses of these oils; for instance in lubricants, fuel oils, medicinal oils, transformer oils, etc. Nitrogenous compounds of the type described are found not only in petroleum oil fractions and distillates, but also in shale oils, coal tar oils, and distillates therefrom.

Lower molecular weight heterocyclic N-compounds such as pyridine, picolines, lutidines and to a lesser extent leucolines, if present, can be separated comparatively easily from hydrocarbon oils, such as by simple aqueous extraction. The higher homologues are removable to greater or less extent depending upon the nature of the oil, by selective adsorption as with silica gel or by treatment with strong mineral acids, or with selective reactants such as sulfur dioxide or furfural. Such processes of treating nitrogenous oils have not been economically attractive and have been utilized commercially only to limited extent, not only because of the initial cost of reagents, but also because of the simultaneous removal, of other non-nitrogenous constituents of the oil, with consequent loss of valuable and desirable products therefrom. Recovery of useful nitrogen compounds from the concentrated extracts thus obtained, becomes complicated and costly.

In accordance with the present invention heterocyclic N-bases boiling above about 260° F. in selected hydrocarbon oil fractions comparatively rich in such bases, particularly such hydrocarbon oil fractions boiling above the gasoline range, are subjected to pyrolytic hydrogenolysis at temperatures of about 800–1200° F. and under selected conditions hereinafter described, including high pressures and large excess of hydrogen, resulting in dealkylation and perhaps other carbon-carbon scission of these higher molecular weight bases without excessive destruction of the N-hetero ring structure. The obtained reaction mixture is separated for separate treatment into basic and non-basic fractions. The basic fractions can be further fractionated to recover desirable simpler N-hetero bases present therein, such as pyridine, quinolines, and mono- or di-methyl and ethyl homologues of these, such as picolines, lutidines, quin-aldines, etc., while the non-basic fractions particularly when starting from a hydrocarbon oil fraction may contain aromatic and other carbocyclic compounds often

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together with five- and/or six-membered ring compounds containing a hetero sulfur atom, and may also include hydroxy compounds such as phenols and cresols. From the non-basic fractions there can be separated, depending upon the boiling range of the starting material, such compounds as benzene, toluene, xylene, naphthalene, anthracene, thiophene, etc.

The recovered nitrogen bases as well as the compounds recovered from the non-basic fraction have extensive and important uses as solvents, pharmaceutical agents, and as intermediates in organic synthesis for the preparation of dyes and medicinals.

Although a whole crude oil such as petroleum or shale oil, or a selected distillate fraction thereof, may be directly subjected to hydrogenolysis under the described conditions, it is preferred in practice of the invention to treat an extract therefrom more concentrated in nitrogen compounds. By acid extraction, as with sulfuric or formic acid of below 95% concentration, comparatively smaller quantities of aromatics including benzene ring and condensed benzene ring compounds are extracted than in the case of SO₂ extraction, for instance according to the known Edeleanu process. Furfural extraction may also be used, particularly in refining heavier or more viscous oils, as those in the lube oil range.

In the treatment of a hydrocarbon charge stock such as a reduced petroleum crude to improve the crackability of the stock by removal of interfering nitrogen compounds therefrom, such removal of the nitrogen compounds is best carried out with concentrated acid or even with anhydrous acid, such as sulfuric, formic or acetic acid. The existing objections to the use of highly concentrated acids based on economic considerations because of the simultaneous removal of aromatic and certain naphthenic components of the stock are more than overcome, by the subsequent recovery of valuable components from the extract. In cases in which the production of a raffinate for cracking is not among the primary objectives, aqueous acid solution such as those of sulfuric or formic acid of 20 to 30% concentration or higher may be employed. As the concentration and/or proportion of acid is increased and with elevation of treating temperature, larger quantities of hydrocarbon and other non-nitrogenous components go into the extract, while more reactive olefinic constituents may thus be polymerized to tarry residues.

Separation of the nitrogenous extract from the acid or solvent treated crude oil may be effected in known manner, for instance by neutralization of the acid extract and water washing. Preferably the oil is extracted with formic acid to form an acid extract containing nitrogen addition compounds. On distillation of the formic acid extract the addition compounds are split to form the free nitrogen bases with the release of the acid, which acid can then be recycled to the extraction step.

There is thus obtained a nitrogen base-free hydrocarbon fraction and a concentrate rich in nitrogenous compounds. The hydrocarbon fraction may be cracked or otherwise treated or stored for use as such, depending upon the boiling range of the starting material. The nitrogen-rich concentrate is subjected to pyrolytic hydrogenolysis under the selected conditions hereinafter more fully described.

The reaction products from hydrogenolysis are then condensed, and fixed gases including saturated lower molecular weight hydrocarbon gases such as methane and ethane, and unreacted hydrogen are thus separated. From the condensates the nitrogenous compounds can be separated, as by water washing, or dilute acid extraction, leaving a substantially nitrogen-free oil. The gaseous fraction may be recycled to the hydrogenation reactor, after at least a simple treatment to roughly separate out a portion of the hydrocarbons therein, and with the addition of fresh hydrogen to replace that used up in the hydrogenation process.

The nitrogen-free oil may be fractionated in known manner to separate the same into products of required boiling range, and if desired, the various fractions may be further fractionated and purified to recover the desired aromatic hydrocarbons. Thus, there may be separated concentrates of benzene, toluenes, xylenes, naphthalene,

anthracene, etc., and in some instances sulfur-containing ring compounds such as thiophenes.

The addition salts in the acidic nitrogenous extract from hydrogenolysis are readily hydrolyzed to reform the free nitrogen bases. The mixture of nitrogen bases from such hydrolysis may then be separated into its various components by known fractionation procedures, and individual fractions concentrated; or these may be further fractionated and purified, if desired, to isolate the various simpler heterocyclic nitrogen bases, such as pyridine, picoline, quinolines, quinaldines, ethyl pyridines, dimethyl-pyridines, etc. The residual heavier nitrogen bases in the bottom fraction may be returned to the hydrogenolysis step for further reaction therein, or may be separately subjected to further fractionation and recovery of valuable products therein.

The invention will be best understood by reference to the accompanying drawings showing schematically a method of operation that can be employed in practice of the invention. In these drawings:

Figure 1 is a schematic flow diagram of the hydrogenolysis reactor section of the process with which the present invention is more particularly concerned, showing certain of the adjacent associated and auxiliary portions of the system; and

Figure 2 is an illustrative flow diagram showing the relation and position of the hydrogenolysis reaction step in a preferred sequence of operations, starting from a suitable raw material and recovering ultimate desired valuable compounds.

It will be understood that the illustrated flow diagrams are merely representative and are not to be construed as limiting the scope of the operation. The reference characters on the drawings refer to various steps of the process as identified or explained at the corresponding numbers in the description which follows.

In the operation illustrated in Figure 2, a nitrogenous oil is initially extracted with formic acid 1, as for instance with 85% formic acid employing 10 volumes of the 85% acid per 100 volumes of the oil. The acid-oil mixture is run to a settling tank 2 wherein it is permitted to stratify and the oil layer separated from the aqueous layer. The oil layer is sent to a flasher 3 operating at about 300° F. wherein the formic acid in the oil is flashed off to return to storage 4. The oil fraction thus freed from formic acid is returned to separate storage for any desired use.

The aqueous acid extract from the settling tank 2 is sent to a decomposition still 5, wherein it is heated to a temperature effecting decomposition of the formic acid addition compounds of the nitrogen bases; for instance the still may be operated at an initial temperature of about 200° F. and over a distillation range up to a maximum of about 400 to 500° F. The overhead from the decomposition still including light hydrocarbons and reconstituted formic acid is condensed and sent to a settling tank 6 wherein the materials which steam distill with formic acid are separated into an aqueous layer and an oil layer. The aqueous layer comprising chiefly formic acid is returned to the formic acid supply reservoir, with intermediate purification or fortification, if desired. The oil layer from settling tank 6 is added to the oil from settling tank 2 and sent together therewith to flasher 3.

There is thus obtained a nitrogen base-free hydrocarbon fraction from the flasher 3 and a concentrate rich in nitrogenous compounds. The latter is sent to a suitable furnace or heat exchanger (not shown) to be heated to reaction temperature and then to a pressure reactor 8, while the hydrocarbon fraction may be cracked or otherwise treated or stored for use without further treatment, depending upon the boiling range of the starting material and the use to be made of that fraction. In the pressure reactor 8 the nitrogen rich concentrate is subjected to pyrolytic hydrogenolysis under selected conditions. Thus, the nitrogen-base concentrate is heated to a temperature in the range of about 800–1200° F., preferably above 900° F., and hydrogen run in, maintaining a pressure in the range of 500–3000 pounds per square inch gauge or somewhat above during the reaction, preferably above 1500 pounds per square inch. Pressures above 1500 pounds per square inch are generally preferred, and if the recovery of light heterocyclic bases such as pyridine is a controlling objective, the total pressure should not be permitted to exceed about 2500 pounds per square inch gauge. It is important that hydrogen be maintained in

considerable excess of its stoichiometric requirements, since it was found that coke formation could thereby be reduced to very low levels. As a rule, in practical operation of the process, 5 to 20 or more mols of hydrogen per mol (average molecular weight) of the charge is advised, corresponding to a partial pressure of not less than about 1250 pounds per square inch in the preferred operating range, but short of that causing such high partial pressure of hydrogen at the temperatures and pressures of the reaction to hydrogenate the heterocyclic nucleus with consequent breaking down of the ring structure. At high temperatures in the order of about 1025° F. a partial pressure of hydrogen may be used up to about 2700–2800 pounds per square inch. The reaction may be carried out under conditions of throughput rates affording a residence time of reactants corresponding to a liquid hourly space velocity (based on reactor volume) of the oil in the range of about 0.1 to 3.0. Lower space rates, as that corresponding to a residence time of 15 minutes or more, are not recommended, since abnormally high yields of gas result with concomitant increased losses of nitrogen as ammonia and volatile amines.

The operation of the hydrogenolysis step will be better understood from Figure 1 of the accompanying drawings. The net result of the reactions taking place in reactor 8 is exothermic so that it may be desirable to provide means for controlling the temperature of the reaction not to exceed a set maximum. This may be accomplished in known manner by the provision of a temperature controlling jacket surrounding the reactor or better by the provision of coils in the reactor circulating an indirect heat exchange medium 9; the temperature being readily controlled by the rate of flow of the medium responsive to a temperature sensitive flow control means such as a thermostat, as indicated at TC. The addition of unheated hydrogen assists in keeping the reaction temperature down, reducing cooling requirements in the reactor to a minimum; in some instances indirect cooling may be omitted entirely. The vaporous reaction effluent from the reactor is withdrawn 10 at a fixed pressure under control of pressure controller (PC), and is sent to a pressure cooler 12. The liquid products from pressure reactor 8 are separately withdrawn 13 and sent to an expansion chamber for the separation of gases evolved as a result of depressuring of the liquid. Instead of bringing the reaction liquid from its initial pressure as discharged from the reactor to atmospheric pressure in a single expansion chamber, it is preferred to employ a series of such chambers operating at consecutively decreased pressures, as diagrammatically indicated for instance at 14 and 15, the final chamber being at atmospheric pressure. The gas evolved in the initial expansion chamber 14 will contain any unreacted hydrogen accompanying the liquid oil together with some dissolved low molecular weight hydrocarbon gases. This gas may be added to the gases 10 sent from the reactor to the cooler or to the final hydrogen rich gas obtained in the subsequent treatment of these gases. From the final expansion chamber 15 there is obtained an overhead 16 of previously unseparated products which are gaseous at atmospheric temperature, and a liquid product 17 withdrawn through a suitable line and sent to fractionation as will be hereinafter described.

In the cooler 12 the gases may be cooled down to about 500° F. or lower, and any liquid condensed is withdrawn 18, and added to the liquid product 13 discharged directly from the reactor. The uncondensed gas from the cooler 12 is sent to a pressure scrubber 19 wherein the same may be contacted with oil for the removal of hydrocarbon gases 20, the undissolved hydrogen-rich gas being withdrawn overhead 21. The latter gas may be recycled directly to the line supplying hydrogen to the reactor 8 or may be returned to the hydrogen supply reservoir with or without further purification. In order to maintain the desired ratio of hydrogen and nitrogenous oil concentrate supplied to the reactor 8 these may be automatically controlled in known manner by suitable proportionating control devices 22.

The liquid product 17 is separated into desired fractions of different boiling range for appropriate individual treatment to break each of these fractions down into desired recoverable concentrates or components of required purity. Returning now to Figure 2, in accordance with the preferred procedure, the liquid fraction is subjected to crude distillation separating the same into three cuts: (I)

an initial cut 24 boiling at atmospheric pressure say up to 150° C.; (II) a fraction 25 obtained by reducing the pressure say to 1 to 3 mm. of mercury, and collecting the effluent boiling up to about 115° C.; and (III) a residual fraction 26 boiling at the reduced pressure between about 115° C. to 150° C. The crude distillation may be effected in a reflux column equipped for evacuation and employing about 1 or 2 theoretical plates. The above fractions correspond roughly to a pyridine fraction containing monomethyl and some dimethyl pyridines; an intermediate quinoline fraction containing also alkyl quinolines and higher alkyl pyridines; and a heavy fraction containing polycyclic bases and substituted quinolines boiling above that of the intermediate fraction. The residue may be recycled to hydrogenolysis for further splitting.

The first fraction (I), containing the products boiling up to 150° C. at atmospheric pressure, is subjected to acid extraction 27. In this step there may be employed a hydrochloric acid solution of the concentration obtained by diluting reagent grade hydrochloric acid (38% HCl) with equal parts water by volume, which acid solution may be used in the proportions of 2-3 volumes of oil distillate per volume of acid. The acid-oil mixture separates on standing to form an aqueous layer (A) and an oil layer (B) which are separately treated as follows. The aqueous layer is neutralized with sodium hydroxide solution 28, effecting the release of free nitrogen bases from the acid addition salts present, and the formation of a sodium chloride salt solution, which assists in salting out the otherwise water soluble pyridine and methyl pyridine compounds. The salt solution is separated from the free nitrogen bases 29 and the latter subjected to fractional distillation 30 to separate the same into desired cuts. Thus, the cuts may be taken at boiling ranges predominating in (a) pyridine, (b) alphapicoline and (c) a cut comprising chiefly gamma and beta picoline and 2-6 lutidine, which latter cut finds important uses as a mixed fraction as such, or may be further treated to effect additional separation of components.

The oil layer (B) comprising chiefly hydrocarbons is washed with a dilute alkaline solution 31, which may be for example a 10% solution of sodium hydroxide, causing separation of the product into an aqueous layer 32 and an oil layer 33. The aqueous layer is neutralized with acid 34 effecting separation of low boiling phenols. The oil layer is subjected to vacuum fractionation to recover aromatic hydrocarbon fractions therein which may comprise benzene, toluene and C-2 alkyl benzenes.

The intermediate fraction (II) is collected 36 and is treated with solid KOH to form a fusion melt 37, the solid 38 being readily separated from the liquid oil layer 39 by decantation, filtration or centrifuging. The melt is extracted with water and benzene 40, the benzene solution being withdrawn and treated to drive off the benzene 41, leaving a residue of weak acids, such as carbazoles and indoles. The aqueous layer is neutralized with acid 42, recovering cresols and other alkyl phenols.

The liquid oil layer from which the KOH melt was separated is extracted with hydrochloric acid 43 forming an aqueous layer and an oil layer. The aqueous layer is then treated 44 similarly to the aqueous layer (A) from the light fraction as by neutralization with alkaline solution with the resulting separation of a mixture of free bases including quinolines and higher alkyl pyridines, which may be recovered as concentrates or components of desired purity, for instance by vacuum fractionation.

The oil layer from acid extraction is washed in alkaline solution and otherwise treated 45 similarly to the oil layer B in the initial light fraction, except for the step of separation of phenolic compounds (compare step 42), the washed oil comprising hydrocarbons boiling in the range of C₃ alkyl benzenes, naphthalenes, mono and dimethylnaphthalenes, which may include some acenaphthenes. The oil may be further fractionated into concentrates or components, as desired.

Fraction III, is fused with solid potassium hydroxide 46 in the same manner as the middle cut was treated under step 37 above, the melt being separated and extracted with water and benzene, and the oil separated from the melt extracted with acid. Further treatment of the separated portions may follow the same procedure as in fraction II, and resulting in the ultimate separation of a neutral fraction comprising higher polycyclic hydrocarbons, a basic fraction consisting largely of nitrogen bases of the type of acridine and benzoquinoline, and an acid fraction sepa-

rable into weak acids of the carbazole type on the one hand and stronger acidic materials among which higher alkyl phenols are typical.

Example I

An Edeleanu extract of 0.3% N content (15.6° API gravity) from a diesel cut of a nitrogenous gas oil fraction (about 20% by volume boiling in the range up to 500° F.) was charged to a copper lined reactor together with 7.1 moles of hydrogen per mol of oil at a liquid hourly space velocity of 0.7 liter of oil per liter of reactor capacity per hour, at an average temperature of 970° F. and an average pressure of 1925 lbs. per square inch gauge, the run being continued for 90 minutes. Condensation of the effluent yielded a liquid product constituting 78.5% by weight of the charge of which 49% distilled in the range of up to 500° F.

Example II

(a) An Edeleanu extract of a diesel cut of the same nitrogenous gas oil as in the preceding example was extracted with 85% formic acid employing 0.10 part by volume of the acid to the oil, to provide an extract highly concentrated in nitrogen bases. The acid layer thereby formed was separated from the oil layer and distilled to split off formic acid from the addition salts formed. This gave a nitrogenous oil product of 4.4% N content which was subjected to hydrogenolysis in a copper lined reactor under conditions and with the yields reported below.

Conditions	Run #1	Run #2
Temperature, ° F.	1,040	1,040
Pressure, p. s. i. g. avg.	3,000	3,040
LHSV, vol./hr./vol.	0.2	0.2
H ₂ /oil, mole/mole.	13.3	13.7
Length of Run, on stream min.	595	700
Products: Liquid, wt percent.	47.4	49.3

Inspection	Liquid Product		Charge Stock
	Run #1	Run #2	
Distillation:			
Init. to 150° C. atm., wt per cent.	21.6	19.5	0
150° C. atm. to 136° C. at 3 mm., wt per cent.	51.6	57.1	27

(b) The individual fractions of the several runs were then composited and the initial and intermediate fractions extracted with reagent grade concentrated hydrochloric acid (38% HCl) diluted with an equal volume of water. The free bases were regenerated from the aqueous hydrochloric acid solution by solid sodium hydroxide. The free bases were ether extracted from the excess caustic and salt solution. The ether extract was dried over solid caustic and vacuum fractionated in a high temperature Poddelniak column. The approximate analysis based on distillation characteristics is given below:

	Wt. percent of liquid product
Pyridine	2.1
Alpha-picoline	0.7
Beta-picoline	1.0
Gamma-picoline	0.1
2,6-lutidine	0.5
Bases b. r. 146/1 atm.-83°/150 mm.	8.2
Quinoline	9.9
Isoquinoline	3.4
Quinaldine	2.3
Bases b. r.:	
93-109° F./4 mm.	3.7
109/4-115°/1 mm.	3.2

(c) The non-basic middle oil fraction from (b) above was extracted with 10% NaOH solution to remove phenolic materials which were recovered by acidification and ether extraction. They amounted to 1.1 weight per cent of liquid product.

(d) The remaining oil of the neutral middle oil from (c) above was extracted repeatedly with concentrated

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sulfuric acid diluted with water (2:1); a reddish tarry acid layer was obtained which amounted to 4.5 weight per cent of liquid product.

(e) The oil remaining after acid extraction in (d) above was then treated at 140°–150° C. with solid potassium hydroxide and the resulting precipitate was removed by filtration and washed with ether. The weak acids so removed amounted to 0.9 weight per cent of the liquid product.

(f) The filtrate separated from the potash precipitate above (e) was dried over anhydrous sodium sulfate and vacuum fractionated in a high temperature Podbielniak column. The approximate analysis based on the distillation is as follows:

	Weight per cent of liquid product
Benzene	7.5
Toluene	2.9
Xylenes	2.4
Naphthalenes	5.8
Methylnaphthalenes	4.1
Neutral b.r.:	
250°–310°	3.7
300°/1 atm.–115°/1 mm.	0.9

(g) A qualitative examination of the heavy oil boiling above 115°/1 mm. (24.5 weight per cent of liquid product) showed the presence of carbazole, phenanthrene, anthracene, and acridine.

Example III

A Los Angeles basin gas oil of 21.1° A. P. I. gravity and boiling in the range of (vacuum assay) 615° F. initial to 90% at 910° F. was distilled, and the lower boiling half up to about 850° F. was collected. This light boiling fraction was extracted with 85% formic acid, employing one part of the acid to 10 parts of the oil by volume, giving a nitrogenous oil concentrate of 22.5° A. P. I. comprising about 2.25% of the crude oil subjected to extraction, and having a 4.1% N content.

After removal of formic acid as in the preceding example, the nitrogenous oil concentrate was subjected to hydrogenolysis at an average temperature of 1040° F. and an average pressure of about 3000 p. s. i. g., at a liquid hourly space velocity of 0.20, employing 12.8 mols per hydrogen per mol of oil.

The liquid products condensed from the reactor effluent were combined with the liquid product from another run at approximately the same conditions, and the mixture divided into a light oil fraction boiling up to 150° C. under atmospheric pressure, a middle oil fraction (plus traps) collected under a vacuum of 1 mm. mercury boiling at this reduced pressure up to 115° C., and a residual oil fraction. The light to middle oil fractions were separated into acidic, basic and neutral portions using the techniques described in the preceding example. The composition of each of these portions is given in the following table.

Light Oil (to 150° C.):		Per cent
Neutral compounds		8.8
Bases		3.2
Acids		.05
Water		1.2
Losses		.5
Totals		13.8
Middle Oil (+ Traps) (to 115°/1 mm.):		
Neutral compounds		12.2
Bases, approx.		20.1
Phenols and acids; ether sol.		1.3
Acids, insol. in ether (ca.)		.1
Very weak acids (K-salt completely decomposed by water)		1.8
Losses, approx.		0.9
Totals		36.4
Heavy oil		49.7
Grand total		99.9

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The basic and non-basic portions were distilled separately and by using a combination of the chemical and distillation characteristics, the following approximate analysis of the liquid product was made:

	Weight per cent crude liquid product
Basic portion, light and middle oil:	
Pyridine	0.8
Alpha-picoline	1.3
Beta and gamma-picoline, 2,6 lutidine	0.9
Bases, B. P. 150–225° C.	2.7
Quinoline, isoquinoline, quinaldine	6.4
Higher bases and loss	11.2
Total bases, light and middle oils	23.3
Non-basic portion, light and middle oil:	
Benzene	1.8
Toluene	2.1
Xylenes and cumenes	3.3
B. P. 155–210° C. (neutral)	1.3
Naphthalene	4.2
Methyl naphthalenes	3.4
Neutral:	
B. P. 250–270° C.	0.6
B. P. 270–300° C.	0.6
Higher, in middle oil	1.2
Removed by 70% H ₂ SO ₄	3.0
Removed by fused KOH (weak acids)	1.8
Phenols	1.5
Losses+water	2.6
Total, non-basic portion, light and middle oil	27.4
Heavy oil residue	49.7
Total	100.4

Example IV

The whole Los Angeles Basin gas oil of 21.1 API gravity was subjected to formic acid extraction and the extract subjected to hydrogenolysis at 104° F., 2980 p. s. i. g., liquid hourly space velocity of 0.2 and hydrogen to oil ratio molar ratio of 15.3. A liquid recovery of over 63% was obtained. In this reaction the product obtained was somewhat higher boiling than in the hydrogenolysis of the lower boiling fraction in the preceding example. The main differences were found in the pyridine-picoline fraction.

The liquid portion from this run was combined with the liquid portions from several other runs at approximately the same conditions, and the mixture fractionated into cuts, as follows:

- I. Initial to 150° C./atm.
- II. 150° C. atm. to 115° C./1 mm.
- III. 115° C./1 mm. to 150° C./1 mm.

Cuts I and II were then individually treated as in the preceding example to separate the same into acidic, basic and non-basic portions which were further extracted similarly to the corresponding portions in the previous example.

Based on the chemical and distillation characteristics, the liquid product was found to have the following approximate analysis:

	Weight per cent liquid product
Basic portion:	
Pyridine	0.5
Alpha-picoline	0.5
Beta, gamma-picoline	0.5
2,6-lutidine	2.6
Bases, b. r. 150–225° C.	4.0
Quinoline, isoquinoline	1.6
Quinaldine	
Higher bases	
Total bases	9.2

Non-basic portion:	Weight per cent liquid product
Benzene	7.1
Toluene	1.9
Neutral, b. r. 112-210° C.	3.4
Naphthalene	3.2
Methylnaphthalene	1.5
Higher boiling neutral	9.3
Acidic compounds	4.8
Total non-basic	31.2
Fraction 115°-150°/1 mm.	8.6
Heavy oil bottoms	51.9
Total	100.9

Example V

The basic charge described in Example IV was subjected to hydrogenolysis at 1055° F., 2010 p. s. i. g., liquid hourly space velocity of 0.1 and a hydrogen to oil mol ratio of 12.6. The liquid product was treated as described in the above example except that the KOH fusion was omitted. The approximate analysis is given below:

Basic portion:	Weight per cent liquid product
Pyridine	0.9
Picolines and 2,6-lutidine	1.2
Bases, b. r. 150-225° C.	2.5
Quinoline	3.0
Iso-quinoline	1.2
Quinaldine	1.1
Higher bases	2.1
Total bases	12.0
Non-basic portions:	
Benzene	8.7
Toluene	3.9
Neutral, b. r. 112-210° C.	4.5
Naphthalenes	5.9
Methylnaphthalenes	2.8
Higher boiling neutral	5.9
Acidic compounds	0.3
Total non-basic	32.0
H ₂ O+dist. losses	1.6
Frac. 115-150°/1 mm.	12.1
Heavy oil bottoms	42.6
Total	100.3

The described conditions of hydrogenolysis are also generally applicable for the conversion of individual higher molecular weight heterocyclic nitrogen bases as such and mixtures thereof to simpler heterocyclic compounds.

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.

I claim as my invention:

1. The method which comprises subjecting a hydrocarbon oil fraction rich in nitrogen content and containing heterocyclic nitrogen compounds including higher homologues of quinoline and pyridine, to pyrolytic hydrogenolysis in the absence of catalyst in a reaction zone under selected conditions favoring carbon-carbon scission without excessive destruction of the N-hetero ring structures present in such fraction, said selected conditions including temperatures in the range of 800-1200° F., a total pressure of about 500-3000 pounds per square inch gauge, relatively high throughput rates of the oil corresponding to a residence time in the reaction zone of less than 15 minutes, and the addition of hydrogen in an amount corresponding to 5-20 moles per mole of oil fraction charged.

2. The method as defined in claim 1 wherein said relatively high throughput rates correspond to a liquid hourly space velocity of said oil based on volume capacity of reaction zone between 0.1 and 3.0.

3. The method as defined in claim 1 wherein said selected conditions include a partial pressure of the added

hydrogen of not less than about 1250 pounds per square inch.

4. The method of converting to lower boiling heterocyclic nitrogen bases those higher boiling heterocyclic nitrogen bases boiling above about 260° F. and normally present in nitrogenous petroleum oils, which comprises subjecting a nitrogenous petroleum oil containing such higher boiling bases to pyrolytic hydrogenolysis in the absence of catalysts in a reaction zone at a temperature in the range of 900-1200° F. at a total pressure of 1500 to 2500 pounds per square inch gauge and in the presence of added hydrogen present during the reaction at a partial pressure of hydrogen of at least 1250 pounds per square inch, the residence time of said bases in said reaction zone corresponding to a liquid hourly space velocity based on volume capacity of said reaction zone between 0.1 and 3.0.

5. The method of pyrolytic hydrogenolysis of nitrogenous oils containing higher homologues of pyridine and quinoline for recovery of monocyclic hetero nitrogen compounds therefrom which comprises heating such an oil in the absence of catalysts to a temperature of 900-1200° F. and a pressure of 1500-2500 pounds per square inch gauge, in the presence of at least 5 moles hydrogen per mole of oil, recovering the normally liquid products of hydrogenolysis, and separating from such liquid products the desired monocyclic hetero nitrogen compounds.

6. The method of claim 5 wherein said liquid products of hydrogenolysis are fractionated to recover products of desired boiling range, leaving a higher boiling residual oil containing nitrogenous compounds, which oil is recycled to pyrolytic hydrogenolysis.

7. The method of treating naturally nitrogenous petroleum oils, including components boiling above the range of gasoline and including heterocyclic nitrogen bases, which method comprises contacting such an oil with formic acid to form therein addition compounds of nitrogen bases present in the oil, stratifying the obtained mixture into an oil fraction and an aqueous acid fraction, the latter containing said addition compounds, separating the recited fractions, heating the aqueous acid fraction to a temperature above the decomposition temperature of said addition compounds to split off the formic acid as vapors which are separated from the remaining oil concentrated in thus reconstituted nitrogen bases, and subjecting the said remaining oil to pyrolytic hydrogenolysis in the absence of catalysts at a temperature of 800-1200° F. in the presence of hydrogen at a partial hydrogen pressure of at least 1250 pounds per square inch.

8. The method of treating naturally nitrogenous petroleum oils boiling above the range of gasoline, and containing heterocyclic basic nitrogen materials boiling above the range of gasoline, which comprises extracting such an oil with concentrated acid to obtain an oil fraction rich in nitrogen compounds, removing acid from said oil fraction, subjecting the nitrogen-rich oil fraction to pyrolytic hydrogenolysis in the absence of catalyst, at a temperature of 900-1200° F. and at a total pressure of 1500 to 3000 pounds per square inch, in the presence of hydrogen added at the rate of 5 to 20 mols per mol of the oil charged, collecting the normally liquid effluent from hydrogenolysis step, separating the liquid effluent into basic and non-basic portions by acid extraction, removing acid from the non-basic portion, thereby causing such portion to separate into an aqueous layer containing phenolic compounds and an oil layer, separating the oil layer, and fractionating the oil raffinate to recover aromatic hydrocarbons therein of desired boiling range.

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