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EXTRACTION PROCESS FOR RECOVERY OF AROMATIC HYDROCARBONS UTILIZING PYRIDINE-BF_3 OR PICOLINE-BF_3 AS THE SOLVENT

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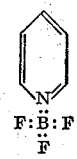
This invention relates to a process for the partial or complete resolution of hydrocarbon mixtures into their components by selective extraction thereof with a solvent selected from the class consisting of pyridine-boron trifluoride and a picoline-boron trifluoride or mixtures thereof. In one particular aspect, this invention relates to the selective extraction of aromatic hydrocarbons from mixtures of aromatic and aliphatic hydrocarbons which are commercially produced as processed or unprocessed petroleum oils or mineral oils, coal tar oils, shale oils and the like. Various aromatic hydrocarbons are valuable as solvents and for the preparation of resins, plasticizers and various other chemical derivatives. The removal of aromatic hydrocarbons from various hydrocarbon stocks may be desired in order to improve their quality for thermal or catalytic cracking, for hydrogenation operations, for use as heater oils and for other purposes.

With the commercial development of new processes for producing aromatic hydrocarbons boiling within the gasoline boiling range by cyclization-dehydrogenation of paraffinic hydrocarbons and by the dehydrogenation of cycloalkanes there has come an increased demand for processes to separate and concentrate the aromatic hydrocarbons thus produced. Thus, with the commercial development of such processes as hydroforming, platinum catalyst reforming of naphthas, and the like, a tremendous potential has been created for the production of nitration-grade aromatics such as benzene, toluene and xylenes for use by both the petroleum and chemical industries.

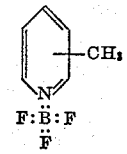
It is an object of my invention to provide a process for the selective extraction of hydrocarbon mixtures with specified novel solvents. Another object of my invention is to provide the art of selective extraction of hydrocarbon mixtures with novel solvents, viz. pyridine-boron trifluoride or picoline-boron trifluorides. A further object of my invention is to provide for the employment of new solvents in a process for the selective extraction of aromatic hydrocarbons from liquid mixtures thereof with aliphatic hydrocarbons, particularly saturated hydrocarbons. A further object is to provide processes for the concentration and purification of aromatic hydrocarbons, particularly those containing not more than about 10 carbon atoms per molecule. An additional object is to provide a process for the selective extraction of aromatic hydrocarbons from mixtures thereof with olefinic hydrocarbons. Yet another object is to provide a process for the selective extraction of olefinic hydrocarbons from saturated hydrocarbons. A further object of this invention is to provide a process for the separation of close-boiling or azeotropic mixtures of aromatic hydrocarbons with saturated hydrocarbons by extraction or extractive distillation with pyridine boron trifluoride or a picoline boron trifluoride. Another object is to provide a process for refining hydrocarbon oils by extraction with novel solvents. These and other objects of my invention will become apparent from the ensuing description thereof.

Pyridine-boron trifluoride is a compound resulting from the exothermic reaction of one mol each of pyridine and

gaseous BF_3, for example in a solvent such as dry benzene ("Boron Trifluoride and Its Derivatives," by H. S. Booth and D. R. Martin—John Wiley & Sons, Inc., New York, 1949—page 47). The structure of pyridine-boron trifluoride is:



The bonding or compound formation is the result of coordination covalent bonding between the two free electrons of nitrogen in pyridine and picoline and the boron atom in BF_3 to complete an octet of electrons about the boron atom. The N–B bond may be partially ionized. Picoline-boron trifluorides have the structure



in which the substituent methyl is ortho-, meta- or para- to the nitrogen atom.

Under otherwise constant operating conditions (temperature, ratio of solvent to feed, extraction temperature, molecular weight of the feed stock, etc.) the solvent power of my novel solvents tends to increase through the series: normal paraffins, isoparaffins, cycloparaffins, acyclic olefins, non-conjugated diolefins, cyclic olefins, aromatics and aromatics containing unsaturated substituents. In general, hydrocarbons of mixed type, for example, alkyl aromatics, have intermediate solubility to the hydrocarbons of the pure structural components (unsubstituted aromatics and paraffins).

In the process of the present invention the selective solvent is employed as a liquid, melt or solution and the feed stock may be charged to the process as a liquid or solution, or, in some instances, as vapors (extractive distillation). The feed stock is preferably dried by conventional methods such as distillation or by contact with adsorbents such as alumina or magnesium silicates before contacting the selective solvent. In extractive distillation, the temperature should be between the dew point of the hydrocarbon mixture and about 240° C. and contacting of the liquid solvent and feed vapors is usually in countercurrent. The solvent concentration of the liquid phase in extractive distillation should be about 5 to about 99 v. percent and the process may be effected at atmospheric or other pressures.

The present extraction process can be applied to numerous hydrocarbon oil fractions derived from petroleum, coal, shale, etc. which are known to contain aromatic hydrocarbons and relatively polar impurities such as organic sulfur compounds whose removal is sought in order to produce refined hydrocarbon oils. Such oils may boil within the boiling range of (and the oils may be generally characterized as) gasoline or naphtha, cracked naphthas, coke still naphthas, kerosene, virgin gas oil, cracked gas oil, hydroformer bottoms, heater oil, furnace oil, diesel fuel, transformer oil, crude oil, reduced crude oil, vis-broken crude oil, lubricating oil distillates, etc. The present process may also be applied to the refining of various coal tar fractions and coal tar distillates, or of neutralized Fischer-Tropsch process fractions.

Other applications of the extraction process of my invention are in the selective absorption of normally gaseous olefins from their mixture with normally gaseous paraffins, for example the selective absorption of ethylene

from gaseous hydrocarbon streams containing ethane and methane, hydrogen, etc., the selective absorption of propylene from propylene-containing gas streams and the like. My invention is likewise applicable to the selective absorption of acetylene from gas mixtures containing the same and methane, hydrogen, ethane, ethylene, etc. By the employment of the extraction or absorption process of the present invention, it is possible to produce normally gaseous unsaturated hydrocarbons of high concentration or purity, which is deemed to be extremely desirable in the further treatment or chemical conversion of said hydrocarbons.

In general, liquid-liquid extraction operations can be conducted at temperatures between about 0° C. and about 200° C., more or less, depending upon the particular charging stock, the particular solvent or solvents, the solvent:feed ratio, the number of extraction stages, the degree of extraction which is sought, the proportions of auxiliary solvents (if any), etc., as will be apparent to one skilled in the art. Usually liquid-liquid extraction is effected at temperatures between about 30° C. and about 150° C. and in the extraction of naphtha boiling range stocks, I prefer to employ temperatures between about 40° C. and about 80° C. Generally, the selection of a suitable extraction temperature is not critical.

The ratio of solvent to hydrocarbon feed stock, in liquid-liquid extractions, must be sufficient to exceed its solubility under the extraction conditions in said feed stock in order to form two distinct liquid phases, viz, a raffinate phase containing little or no solvent and an immiscible extract phase comprising the solvent and extracted hydrocarbons. Generally, I may employ between about 0.5 and about 50 volumes of solvent per volume of hydrocarbon charging stock. Ordinarily, I prefer to employ between about 1 and about 20 volumes of solvent per volume of feed stock, especially in the treatment of naphtha boiling range stocks (about 400° F. end-point). Sufficient pressure is maintained within the extraction zone to prevent substantial volatilization of the hydrocarbon charging stock or solvent under the liquid-liquid extraction conditions. It is obvious that pressure and temperature are related variables in the extraction process. Usually pressures within the range of about 0 to about 100 p.s.i. are sufficient, it being appreciated that the particular pressure which is required in a given case can readily be determined by experiment.

Any means of separating extracted materials from the extract phase and of recovering solvent therefrom may be employed. Thus under certain conditions, it may be desirable to distill extracted materials from the extract phase or to wash them out of the extract layer with a paraffin hydrocarbon having a different boiling point. Also, the solvents may in some instances be recovered from the extract layer by crystallization or by washing with a solvent which is highly selective therefor, such as ethers, etc.

The raffinate phase (or in extractive distillation, the distillate) can be treated by conventional methods to effect further refining thereof. Thus, the raffinate or distillate can be washed with water, aqueous alkalies, etc., treated with adsorbent solids such as activated carbon, activated clays, etc., redistilled, and otherwise prepared for use or sale.

It may be desirable to employ diluents or auxiliary solvents in specific cases in order to modify selectivity of the principal solvent, to lower the melting point of the principal solvent to permit its use at low temperatures, or for other reasons. The amount of auxiliary solvent can be selected with reference to specific cases; ordinarily, between about 1 and about 20 weight percent or even more, based on the principal solvent, may be employed. The auxiliary solvent should be miscible to the desired extent with the principal solvent, and should preferably be a neutral compound. As examples of auxiliary solvents which may be employed, one may mention the

sulfolanes, for example, 2,4-dimethylsulfolane, 2,3-dimethylsulfolane and the like; various nitriles such as acetonitrile, bis-2-cyanoethyl ether and the like; various ethers such as diethyl ether, methyl-tert-butyl ether; glycols or their ethers having the structure $R_1O(CH_2CH_2O)_nR_2$ and

$$R_1O(\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-O)_nR_2$$

wherein R_1 and R_2 are alkyl groups and n is an integer having a value between 1 and 3, inclusive, tetrahydrofuran and the like; halogenated hydrocarbon solvents such as chloroform, carbon tetrachloride, ethylene dichloride, ethylene dibromide, trichloroethane, tetrachloroethane and the like; esters of carbonic acid, monocarboxylic acids, and dicarboxylic acids, for instance, diethyl carbonate, bis-2-hydroxyethyl carbonate, bis-2-chloroethyl carbonate, bis-2-methoxyethyl carbonate, ethylene carbonate, n-butyl formate, methyl furoate, dimethyl oxalate, diethyl succinate, dimethyl phthalate, dimethylisophthalate, and the like; neutral organic nitrogen compounds such as N,N-dialkyl formamides (particularly dimethyl formamide), dimethyl hydantoin and the like, nitro aromatics such as nitrobenzene and the like; ketones, for example, acetone methyl ethyl ketone, methyl isobutyl ketone and the like, aldehydes, for example, furfural, crotonaldehyde and the like; butyrolactone, butyrolactam, etc.

Anti-solvents or diluents may also be employed in the practice of the present invention. Thus, diluents such as saturated hydrocarbons, perfluorocarbons, perfluoroamines, perfluoroethers, etc. may be added to the feed stock to be dearomatized or introduced directly into the extraction zone.

In the extraction, a small proportion of a suitable surface-active agent may be added to increase the efficiency of the extraction equipment. Thus long chain esters of perfluoroalkyl alcohols or perfluoroalkyl acids, perfluoroalkyl amides and amines, etc. may be employed, in suitable concentrations between about 0.0001 and about 1 weight percent, based on the weight of the solvent (note G. B. Blake et al.—paper presented before the Division of Petroleum Chemistry of the American Chemical Society, September 1954, pp. 313 ff.).

The present invention can be carried out in batch, continuous or semi-continuous operating cycles, and in one or more actual or theoretical stages, employing contacting and separation equipment such as has heretofore been employed in the selective solvent refining of petroleum stocks. Various types of liquid-liquid extraction operations and suitable extraction equipment are described, for example, in "Chemical Engineers' Handbook" (McGraw-Hill Publishing Co., Inc., N.Y., 1950), pp. 716 ff. and 474 ff. It should be understood that the specific equipment employed forms no part of the present invention and that any equipment adaptable for the purposes of contacting the solvent with the hydrocarbon charging stock and thereafter separating an extract phase from the refined charging stock can be employed for the purposes of my invention.

The following table shows the results of the extraction of a 50 volume percent n-heptane-50 volume percent toluene feed with an equal volume of pyridine-boron trifluoride and 2-picoline-boron trifluoride solvents. Single-stage extractions were effected with solvent:hydrocarbon feed ratio of one.

Solvent	Temp., ° C.	W. Percent Toluene in Extract	W. Percent Toluene Extracted
Pyridine-BF_3	40	84	90
2-picoline-BF_3	30	88	50

The foregoing examples have illustrated specific aspects of my invention, which is not limited thereto. The extraction process of the present invention is readily appli-

cable to the separation of hydrocarbon mixtures and hydrocarbon types not specifically illustrated in the foregoing examples, e.g., the selective separation of olefins from aromatics, naphthenes from paraffins, naphthenes from aromatics, olefins from saturated hydrocarbons, cycloolefins from acyclic olefins, monoolefins from conjugated diolefins, of conjugated diolefins from nonconjugated diolefins, of diolefins from aromatics, etc.

Having thus described my invention, what I claim is:

1. A process for the selective extraction of an aromatic hydrocarbon from a naphtha fraction containing the same, which process comprises contacting said naphtha in the liquid condition with a solvent selected from the group consisting of pyridine-boron trifluoride and a picoline-boron trifluoride, the molar ratio of pyridine and picoline, respectively, to boron trifluoride being one, said solvent being used in an amount sufficient at least to form a distinct liquid phase, separating a raffinate phase from an extract phase comprising said solvent and said aromatic hydrocarbon, and distilling said aromatic hydrocarbon from said extract phase.

2. The process of claim 1 wherein the extraction is conducted at temperatures between about 40° C. and about 80° C.

3. The process of claim 1 wherein said solvent comprises pyridine-boron trifluoride.

4. The process of claim 1 wherein said solvent comprises a picoline-boron trifluoride.

References Cited in the file of this patent

UNITED STATES PATENTS

2,053,485	Lindeke et al.	Sept. 6, 1936
2,133,691	Francis	Oct. 18, 1938
2,142,939	Francis	Jan. 3, 1939
2,246,257	Kohn	June 17, 1941
2,638,441	Nixon et al.	May 12, 1953
2,639,304	Hazlett	May 19, 1953

OTHER REFERENCES

"Boron Trifluoride and Its Derivatives," Booth and Martin: Published by John Wiley and Sons, Inc., New York, 1949, page 47.