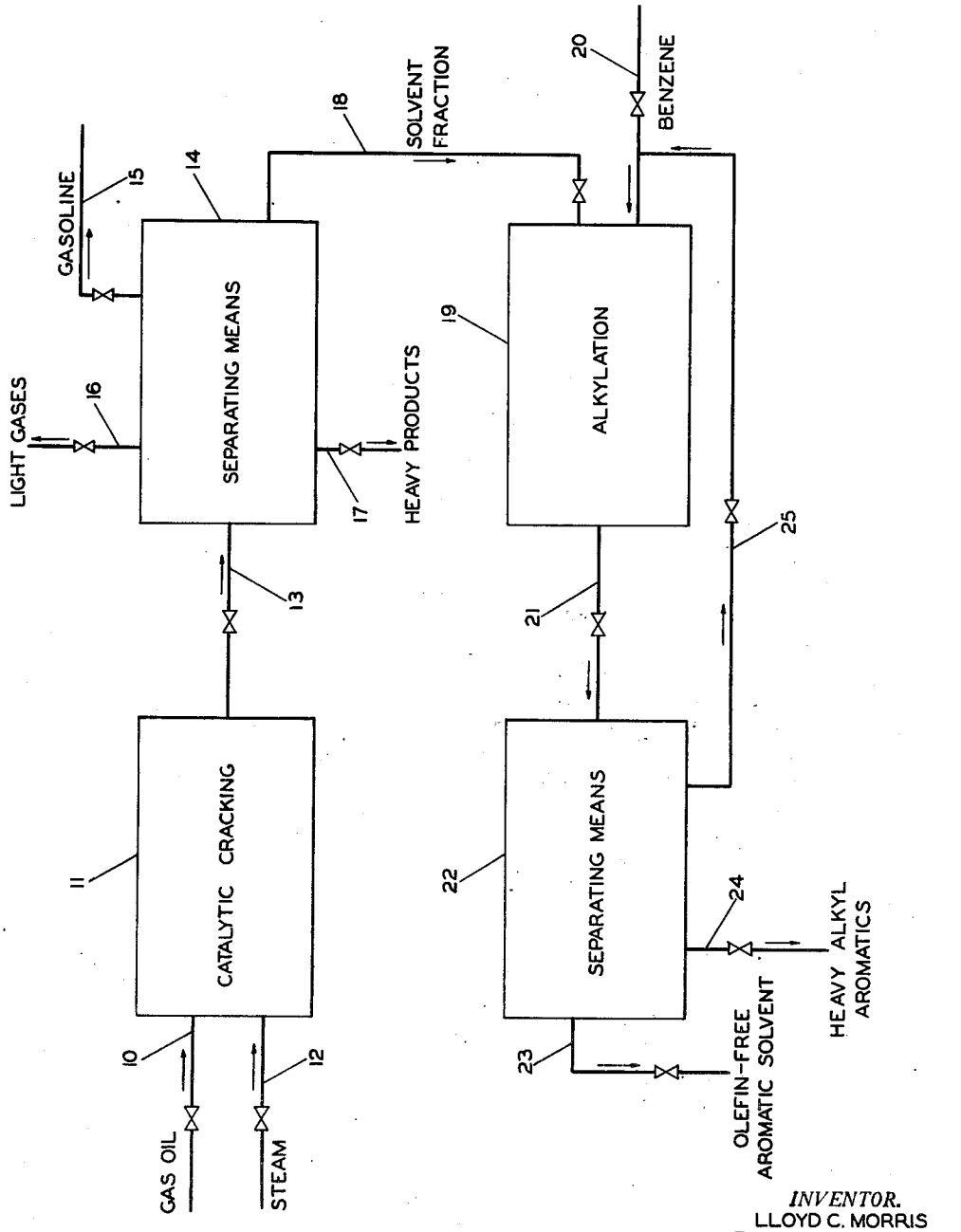
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PROCESS FOR THE MANUFACTURE OF A HYDROCARBON SOLVENT

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INVENTOR.
LLOYD C. MORRIS
FREDRICK M. SMITH

BY

Hudson & Young

ATTORNEYS

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PROCESS FOR THE MANUFACTURE OF A HYDROCARBON SOLVENT

Lloyd C. Morris and Fredrick M. Smith, Bartlesville, Okla., assignors to Phillips Petroleum Company, a corporation of Delaware

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1

This invention relates to the production of high-boiling solvent naphthas. In a preferred specific embodiment it relates to a process for the treatment of a cracked naphtha fraction comprising aromatic and naphthenic constituents in admixture with high-boiling olefins, and boiling in a range between about 250 and about 500° F., wherein olefins in said fraction are removed in an alkylation step to provide residual naphthas in the same boiling range characterized by a high concentration of cyclic constituents and possessing preferred solvent properties.

In the manufacture of gasolines and motor fuels, it has been found that high concentrations of aromatic constituents have desirable effects in increasing octane rating and various processes have been developed for the production of high aromaticity in such fuels. In some instances high-boiling naphthas or gas oils are subjected to controlled temperature catalytic cracking treatment under conditions for the production of a motor fuel of substantial aromatic content.

Naphthas having a high degree of aromaticity are particularly desirable as solvents, but employment of the above-mentioned method for their manufacture provides products which contain high-boiling olefins in relatively large proportions. While these long chain olefins contribute desirable characteristics to the motor fuel, their presence, even in much smaller concentrations, in a solvent material leads to many difficulties such as oxidation, reactions with the solute, and the like.

In recent years there has been a constantly increasing demand for hydrocarbon solvents, not only for conventional uses such as in dry cleaning, the manufacture of paints, varnishes, waterproofing agents, etc., but also for newly developed products and processes involving specialized requirements not met by ordinary commercially available solvent materials. For example, the production of insect repellents and insecticides has created a need for an organic solvent which is capable of carrying in solution a relatively large concentration of active substance and is at the same time free from color and objectionable odor, non-toxic to man and animals, has a high flash point, and is relatively non-volatile.

The solvent value of a hydrocarbon fraction is, in a general sense, determined by its content of cyclic constituents. That is, for example, a paraffinic material such as n-heptane may be said to have a relatively low solvent value in comparison with a cyclic material such as benzene or cyclohexane, while a mixture, say of benzene

2

with n-heptane, will have an intermediate solvent value depending upon the relative proportion of its constituents.

We have now found that by contacting a fraction of catalytically cracked gas oil boiling in the approximate range 250 to 500° F. and comprising aromatic and naphthenic constituents in admixture with long chain olefins, with a lower boiling aromatic substance under alkylating conditions, said olefins are converted to high-boiling alkyl benzenes and residual naphthas of high solvent power can be obtained.

An object of our invention is to decrease the olefin content of a hydrocarbon material containing olefins as minor constituents.

Another object of our invention is to produce a desirable hydrocarbon solvent.

A further object of our invention is to treat a hydrocarbon mixture containing olefin, aromatic, naphthene, and paraffin hydrocarbons to remove substantially all of the olefin hydrocarbons.

Still a further object of the invention is to remove olefin hydrocarbons from admixture with aromatic and naphthene hydrocarbons.

Other objects and advantages of our invention will become apparent, to one skilled in the art, from the accompanying description and discussion.

In a more general embodiment the process of the present invention comprises the steps: (1) preparation of a feed stock comprising aromatic and naphthenic constituents in admixture with long-chain and branched-chain olefins by fractionating a catalytically cracked high-boiling naphtha or gas oil to produce a cut boiling in the approximate range 250 to 500° F.; (2) contacting said fraction with a molar excess of a lower boiling aromatic substance under alkylating conditions whereby substantially all olefins present are converted to high-boiling alkyl benzenes; (3) stripping out unreacted low-boiling aromatic substance for recycling to the reaction; (4) fractionation of the effluent to separate naphthas boiling in the same range as the feed stock and having preferred solvent value.

The feed stock employed comprises a relatively high percentage of aromatic, naphthenic, and condensed ring cyclic constituents, generally substantially more than 50 per cent by volume, in admixture with a substantial per cent by volume of olefins ranging in carbon content from about seven to about sixteen carbon atoms to the molecule and lesser amounts of paraffinic hydrocarbons, and may be prepared by catalytic cracking

of high-boiling naphthas or gas oils, for example, by a "Cycloversion" process, and fractionating the effluent to separate a cut having an initial boiling point not lower than about 250° F. and an end point not greater than about 500° F.

The aromatic substance employed may comprise benzene, benzene homologues, or mixtures thereof, said aromatic substance being so chosen that its boiling point is in a range lower than that of the feed stock by an amount sufficiently great to permit stripping out unreacted portions subsequent to the alkylation operation. The proportion of aromatic substance employed is in substantial molar excess of the olefinic content of the feed stock, generally in a ratio of from about 5:1 to 15:1.

The alkylation catalyst employed may be one of a variety of alkylating catalysts. We generally prefer to use a catalyst comprising a liquid, and more particularly complexes or addition compounds of boron fluoride with water, phosphoric acid, or aqueous hydrogen fluoride, although other types and materials, such as sulfuric acid, various sulfonic acids, hydrofluoric acid, and solid catalysts such as an aluminum halide, alone or as a part of an organic or inorganic complex "solid" phosphoric acid, silica-alumina, etc., are not excluded. Also the employment of starting materials of a suitable nature produced by other methods than the aforementioned catalytic cracking process is within the scope of our invention.

A most significant advantage of our preferred process lies in the superior solvent value of the naphtha produced. Aromatic, naphthenic, and condensed ring cyclic constituents from the feed stock are concentrated in the residual naphtha when olefins are removed in the alkylation step. The relatively high index of refraction and the high density and low aniline number of the product indicate aromaticity substantially above that of ordinary commercially available hydrocarbon solvents boiling in the same range. The superior solvent properties of our product are further indicated by the unusually high kauri-butanol and dimethyl sulfate values, the low bromine number and satisfactory flash point. Other desirable properties are its excellent color, low odor, and substantial freedom from toxicity.

In connection with this invention the boiling range, initial boilnig point, end point, and the like are to be determined by the well-known A. S. T. M. procedures. The kauri-butanol values are determined substantially as described by Gardner in "Physical and Chemical Examination of Paints, Varnishes, Lacquers and Colors," published by the National Paint, Varnish and Lacquer Association. A high kauri-butanol value indicates a high solvent power. The dimethyl sulfate values are determined substantially as described by the same author in the same publication, and give directly the percentage of aromatic constituents and unsaturated aliphatic hydrocarbons of the olefin series. The value should be high for a good lacquer solvent, although, as discussed herein, the olefin content should be low, as indicated by a low bromine number. By the proper practice of our invention it is possible to reduce the olefin content so that the bromine number is not greater than 1.0, and it will usually be somewhat less than this value.

Since the total product from our process boils in a relatively broad range, selected fractions may be separated for various specific uses. For example, a fraction boiling between about 400 and 450° F. provides a superior solvent for insect repellents and insecticides since it embodies substantially all the specific properties required for the preparation of highly effective solutions of these recently developed products which are non-staining, free from objectionable odor, and of excellent lasting quality.

A fraction boiling between about 300 and 425° F. provides Stoddard solvent of superior grade, suitable for employment in the dry-cleaning industry. Painters' and varnish-makers' naphtha is obtained in the cut boiling between about 250 and 425° F. By suitable adjustment of the boiling range solvents applicable to many other uses are available.

A further advantage in the present process lies in the production of valuable alkyl benzenes as by-products from the alkylation step. Other advantages inherent in the invention will be evident from the description of the accompanying sketch which illustrates in diagrammatic form one type of apparatus in which the objects of our invention can be accomplished.

Referring now to the drawing, a high-boiling naphtha or gas oil is passed through pipe 10 to catalytic cracking unit 11. A typical charge stock is a gas oil separated from a Mid-Continent crude having an initial boiling point of about 250 to 300° F., a 90 per cent distillation point of about 700° F., and a gravity of about 36° A. P. I. Catalytic cracking unit 11 will contain one or more catalytic reaction chambers filled with a catalyst such as granular bauxite. The charge is heated to a temperautre between about 950 and 1050° F. and is then passed through the catalyst bed at a pressure between about 70 and about 100 pounds per square inch gage. The flow rate of the gas oil will be between about 5 and about 10 barrels of oil per ton of catalyst per hour. If desired steam or some other gaseous diluent may be added to the charge through pipe 12. If steam is used a suitable flow rate will be between about 0.2 and about 0.5 pound per pound of gas oil per hour and the bed of catalyst can be used for between about 3 and about 8 hours before sufficient carbon has accumulated on it to require stopping of the flow of reactants and regeneration of the catalyst bed. Reaction effluents pass through pipe 13 to separating means 14, which will comprise suitable heat exchangers, fractionating columns, pumps, heaters, coolers, accumulators, and the like as can be supplied in any particular instance by one skilled in the art. In such a conversion substantial quantities of hydrocarbon products boiling in the gasoline range will be produced and can be recovered as a product of the process through pipe 15. Normally gaseous constituents will also be produced and can be removed through pipe 16. Such products will comprise substantial amounts of olefin hydrocarbons which can be used as desired, for example, for alkylation by reaction with isobutane to produce additional hydrocarbon materials suitable for inclusion in a gasoline product. Any undesired heavy products can be discharged through pipe 17.

A hydrocarbon fraction boiling preferably above 250° F. and not higher than about 500° F. is removed through pipe 18 as a raw material for the production of a hydrocarbon solvent. This fraction will generally contain over 50 per cent of aromatic and naphthene hydrocarbons. It will contain a smaller but substantial quantity

of olefin hydrocarbons, such as between about 10 and 30 per cent by volume. Generally also it will contain a somewhat smaller amount of paraffin hydrocarbons. This fraction is passed to alkylation step 19 wherein it is mixed with a suitable lower-boiling aromatic hydrocarbon, such as benzene, introduced through pipe 20. This material should be introduced in an amount in excess of that molecularly equivalent to the olefins present in the hydrocarbon material passing through pipe 18. The resulting hydrocarbon mixture is intimately mixed with an alkylation catalyst under alkylation conditions which include a reaction time sufficient for substantially complete reaction of the olefins in the charge stock. A suitable reaction temperature between about 50 and 150° F. and sufficient pressure to maintain the reactants in liquid phase is also generally used. Effluents of the alkylation are passed through pipe 21 to separating means 22 which will also include suitable separation and fractional distillation equipment. Unreacted benzene can be separated and returned to alkylation 19 through pipe 25. Heavy hydrocarbons comprising primarily high-boiling aromatic alkyl hydrocarbons produced in the alkylation step are separated through pipe 24. In many instances these alkyl aromatic hydrocarbons can be readily sulfonated and the resulting sulfonic acids have excellent detergent properties. An olefin-free hydrocarbon solvent which will have a high content of aromatic and naphthene hydrocarbons is recovered as a product of the process through pipe 23.

As will be readily appreciated, each of the reaction units has been shown only diagrammatically. Each such unit involves processes which are not novel to the present invention per se and operate under conditions and in equipment which can be readily determined and supplied by one skilled in the art. Such equipment includes catalytic cracking reactors, heating furnaces, waste heat boilers, means for supplying air for catalyst regeneration, means for supplying steam, or combustion gas or the like, as diluent material both for the catalytic cracking operation when such is desired and for the catalyst regeneration step. As previously mentioned separating means 14 and 22 will each comprise suitable fractional distillation equipment and associated heaters, coolers, pumps, and the like. Alkylation unit 19 will include alkylation reactors, catalyst separators, cooling equipment, pumps, and the like.

We have found that a particularly desirable solvent is ultimately obtained through pipe 23 when the catalytic cracking carried out in cracking unit 11 is similar to that known to the art as "Cycloversion." A more detailed discussion of the operation has been discussed by Schulze and Helmers in the Oil and Gas Journal for April 13, 1944. However, we have also determined that desirable solvent fractions can be produced by the practice of our invention from high-boiling hydrocarbon fractions obtained from effluents of any of the well-known commercial catalytic cracking operations such as those employing a so-called fluid cracking catalyst, the T. C. C. catalytic cracking process, and similar processes. If a charge stock containing cyclic hydrocarbons and smaller quantities of olefin hydrocarbons is available from any other source it may likewise be employed as a charge for the process of our invention.

Example

The following is an example of our invention.

A virgin gas oil obtained from a Texas Panhandle crude oil was catalytically cracked in a "Cycloversion" unit. This gas oil had a boiling range of 450 to 750° F., an aniline point of 187.8° F., and a gravity of 36.5° A. P. I. It was cracked by being passed through a fixed bed of granular bauxite at a rate of 7.6 barrels per ton of catalyst per hour, in admixture with steam passed at a rate of 40 pounds per barrel of gas oil. The temperature at the inlet of the catalyst chamber was 1015° F. and at the outlet was 940° F., and the pressure at the inlet was 95 pounds per square inch gage. The unit was operated for periods of six hours between catalyst regenerations. Effluents of the process were subjected to fractional distillation, and there was separated a cut boiling in the approximate range of 400 to 450° F. This material had the properties shown in column A of the following table, and had the following approximate composition:

	Per cent by volume
Olefins	25
Aromatics	30
Naphthenes	35–40
Paraffins	5–10

A sample of this fraction weighing 17,510 grams was mixed with 17,590 grams of benzene and 1600 cc. of catalyst prepared by saturating hydrofluoric acid with boron fluoride. The mixture was maintained at a temperature between 120 and 130° F. for one hour with mechanical stirring. The catalyst was separated by gravity, the effluent washed to remove traces of catalyst, dried over solid sodium hydroxide and unreacted benzene removed by distillation. The product was then fractionated to yield 12,910 grams of oil boiling in the range of 400 to 450° F. Properties of the oil are shown in column B in the following table. For purposes of comparison, similar properties of a commercial hydrocarbon solvent are shown in column C and of a typical Mid-Continent kerosene in column D. All values were obtained on fractions boiling in the 400 to 450° F. range.

	A	B	C	D
Gravity, °A. P. I. @ 60° F.	39.2	40.5	46.9	42.2
Index of Refraction @ 68° F. (20° C.)	1.4612	1.460	1.441	1.421
Bromine Number	18.6	0.6	3.0	(2)
Aniline Point, °C. (°F.)	43.5	49.7 (121.5)	73.6 (164.5)	67.7 (153.9)
Kauri-Butanol Value, cc.	42.3	43.0	28.1	31.6
Solvent power, per cent [1]	17.0	15.4	2.0	6.0
Dimethyl sulfate value		16.0	3.0	4.0
Saybolt color		+26	+13	+21
Total Sulfur		0.013	0.044	0.024
Flash Point, °F	170	170	181	137

[1] Based on benzene as 100 and n-heptane as zero.
[2] Less than 1.

It will be appreciated that various modifications of our invention can be practiced without departing from the scope and spirit of the disclosure and teachings, and without departing from the scope of the claims.

We claim:

1. An improved process for the production of an olefin-free, aromatic hydrocarbon fraction, which comprises subjecting a gas oil petroleum fraction to catalytic cracking at an elevated temperature to produce a hydrocarbon material boiling between about 250 to about 500° F. containing at least 50 per cent by volume of aromatic and naphthene hydrocarbons and the remainder primarily olefin and paraffin hydrocarbons, said olefin hydrocarbons being 10 to 30 per cent by

volume of said hydrocarbon material, separating such a hydrocarbon material from effluents of said catalytic cracking, adding to said material a lower-boiling aromatic hydrocarbon in an amount in excess of that molecularly equivalent to the olefin content of said hydrocarbon material such that the ratio of said aromatic to the olefin will be in the range 5:1 to 15:1, subjecting the resulting liquid mixture to the action of an alkylation catalyst under alkylation conditions for a time sufficient to react by alkylation substantially the entire olefin content of said mixture, and recovering from effluents of said alkylation an olefin-free aromatic hydrocarbon material with an initial boiling point not less than about 250° F. and an end point not greater than about 500° F. containing the first said paraffin, naphthene, and aromatic hydrocarbons and also being free from reaction products of said alkylation.

2. An improved process for removing olefins from a hydrocarbon material boiling above 250° F. and containing substantially more than 50 per cent by volume of aromatic and naphthene hydrocarbons and also 10 to 30 percent by volume of olefins as undesired constituents, which comprises adding to said material a lower-boiling aromatic hydrocarbon in an amount greater than that molecularly equivalent to the olefin content of said hydrocarbon material such that the ratio of said aromatic to the olefin will be in the range 5:1 to 15:1, subjecting the resulting liquid mixture to the action of an alkylation catalyst comprising hydrofluoric acid saturated with boron trifluoride under alkylation conditions for a time sufficient to effect substantially complete reaction of said olefins, and recovering from effluents of said alkylation a hydrocarbon fraction boiling above 250° F. having a bromine number less than 1.0 and containing substantially all of the aromatic and naphthene hydrocarbons present in said original hydrocarbon material and being free from reaction products of said alkylation.

3. An improved process for treating a hydrocarbon mixture boiling between 400 and 450° F., obtained from effluents of a process for cracking heavier hydrocarbons to produce lighter hydrocarbons and comprising paraffin, naphthene, aromatic, and 10 to 30 per cent by volume of olefin hydrocarbons, to produce a hydrocarbon mixture

boiling within the same range and sufficiently free from olefin hydrocarbons as to have a bromine number not greater than 1.0, which comprises adding benzene to said hydrocarbon mixture in an amount at least five times the molecular equivalent of the olefins in said mixture, subjecting the resulting liquid mixture to the action of an alkylation catalyst at a reaction temperature not greater than 150° F. while under a pressure sufficient to maintain the reactants in liquid phase for a time sufficient to effect complete reaction of the olefin content of said hydrocarbon mixture by alkylation, and recovering from effluents of said alkylation a hydrocarbon mixture boiling between 400 and 450° F. and having a bromine number not greater than 1.0 as a product of the process, said product containing said paraffin, naphthene and aromatic hydrocarbons and being free from reaction products of said alkylation.

LLOYD C. MORRIS.
FREDRICK M. SMITH.

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