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Gomi et al.

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[54] **PROCESS FOR TREATING BY-PRODUCT HEAVY FRACTIONS FORMED IN THE PRODUCTION OF OLEFINS**

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[51] **Int. Cl.** **C10g 37/00**

[58] **Field of Search** ..... 209/57, 67, 44; 260/671, 260/671 P, 668 F

[56] **References Cited**

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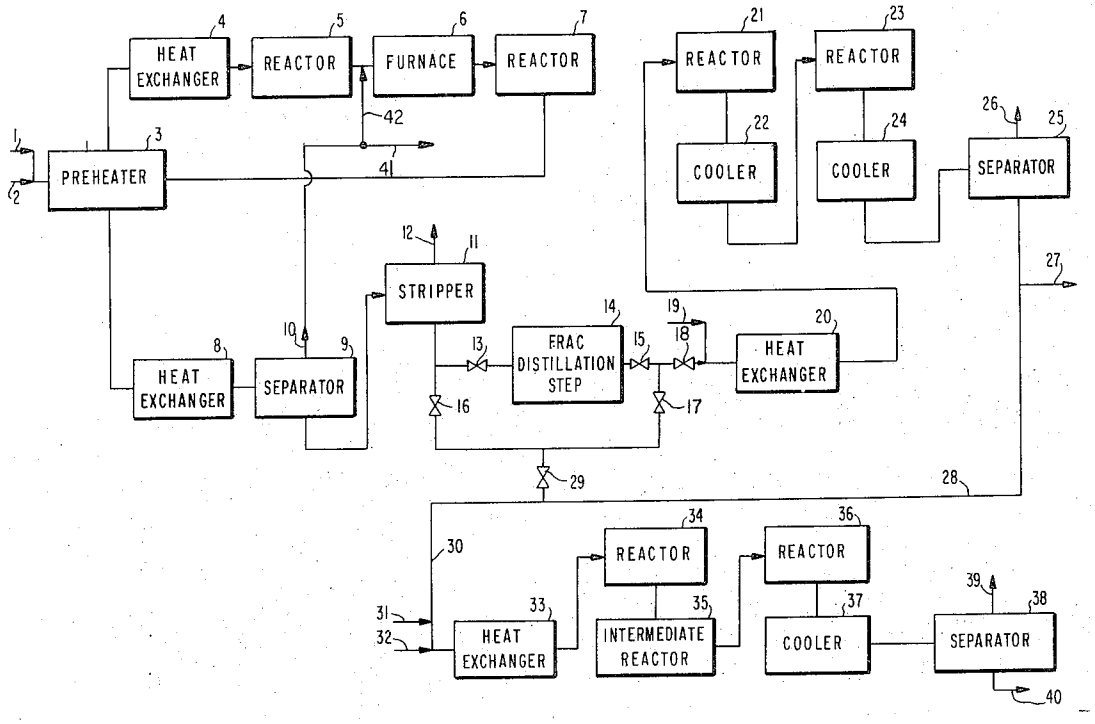
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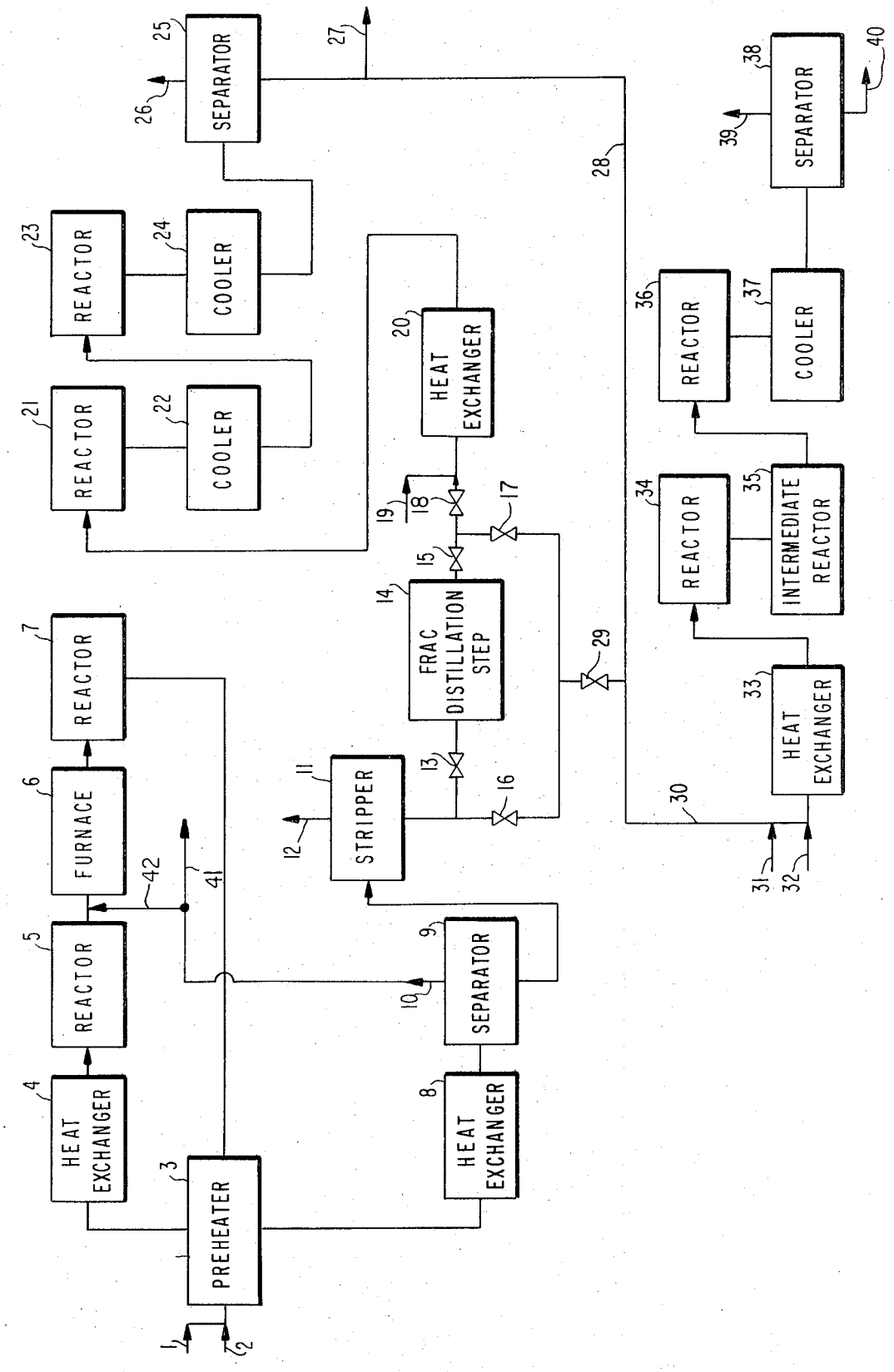
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[57] **ABSTRACT**

A process for obtaining improved hydrocarbon oil products by treating by-product heavy fractions, formed in the production of olefins and having initial boiling point of above 160°C and a 75 percent distill-off point of below 450°C, with hydrogen at a temperature of from 40° to 200°C and a pressure of from 5 to 300 kg/cm² G using a nickel-containing catalyst which has been pre-treated with organic sulfur compounds, to thereby impart thermal stability to the oil, then subjecting the resulting oil to a hydrorefining followed by hydrogenation is disclosed.

1 Claim, 1 Drawing Figure




PREHEATER
HEAT EXCHANGER
REACTOR
FURNACE
REACTOR
SEPARATOR
HEAT EXCHANGER
STRIPPER
FRAC DISTILLATION STEP
HEAT EXCHANGER
REACTOR
COOLER
REACTOR
COOLER
SEPARATOR
REACTOR
INTERMEDIATE REACTOR
HEAT EXCHANGER
REACTOR
COOLER
SEPARATOR
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PROCESS FOR TREATING BY-PRODUCT HEAVY FRACTIONS FORMED IN THE PRODUCTION OF OLEFINS

RELATED APPLICATION

This application is a divisional of U.S. Application Ser. No. 97,231 filed Dec. 11, 1970, now U.S. Pat. No. 3,689,401 issued Sept. 5, 1972.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a process for the treatment of heavy oil fractions formed as by-products in the production of olefins.

2. Description of the Prior Art

The amount of liquid oil formed as by-products in the production of gaseous olefins by high temperature cracking of naphtha and like hydrocarbons increasingly becomes larger, the larger the scale of the olefin producing plant. Accordingly, increasingly larger amounts of residual by-product heavy fractions are formed after the B.T.X. fraction (benzene, toluene and xylene) is distilled off.

In addition, the trend toward shifting the feed hydrocarbon from naphtha to increasingly heavier fractions or crude oils increases the yield of by-product heavy fractions to a greater extent than that obtained at the present time. It will therefore become a serious problem in the near future to utilize effectively such heavy fraction by-products.

However, there are many deficiencies in the by-product heavy fractions such as the following:

Since the heavy fraction contains many types of unstable compounds, polymerization upon heating tends to occur, causing plugging of the pipings in the equipment for treating the by-product heavy fractions. Consequently, this leads to forced shut-downs of the operation. In addition, deactivation of the catalyst used occurs.

These unstable compounds cannot be removed by simple distillation due to the highly complex nature of their composition as well as a pronounced tendency toward polymerization.

As was stated hereinabove, the by-product heavy fractions have not been utilized efficiently due to their disadvantageous properties. They have only been evaluated with calorific bases as fuels or at least been utilized in the production of carbon blacks. In Japanese Patent Publication No. 12504/65, a process is disclosed for the treatment of the by-product residual oil formed in the thermal cracking of petroleum naphtha. The process involves the stabilization of the feed residual oil using a simple hydrogenation procedure, subsequently a reforming treatment and a distillative separation to thereby recover a portion of the naphthalene contained in the feed oil. However, the process of this Japanese Pat. No. 12504/64 inevitably is accompanied by undesirable nuclear hydrogenation in addition to desirable saturation of conjugated double bonds of polymerizable compounds, which invites not only the generation of an excessive exothermic heat of reaction and an acceleration of polymerization but also a reduction in the yield of naphthalene due to its conversion into hydronaphthalenes.

As is apparent in the above Japanese Patent, the only technique proposed for the treatment of the residual cracked oil involves the production of a single compound, for example, naphthalene, but no technique has been proposed yet for the production of hydrocarbon oils having high additional values and consisting of a mixture of various substances, by applying a series of processes to the by-product heavy fractions having highly complicated properties.

An object of the process of this invention is the treatment of the by-product heavy fractions by the application thereto of a sequence of a plurality of process steps involving a hydrogenating step in which the polycondensed aromatic hydrocarbon compounds in the feed stock are mainly hydrogenated without any change in their ring structures. In this hydrogenating step, it is already known in the art to use sulfides of tungsten and molybdenum as the catalyst for the nuclear hydrogenation.

Generally, however, these sulfide type catalysts have a poor nuclear hydrogenating activity requiring more severe hydrogenating reaction conditions. For instance, the hydrogenation of coal-tar so as to obtain a hydrogenated product with 90 percent nuclear hydrogenation is reported to require reaction conditions including a temperature of from 420° to 430°C, a pressure of from 200 to 250 kg/cm^{2}G and a feed rate of 1 kg of coal-tar per hour per liter of the catalyst (COAL-TAR, Vol. 14, No. 10, 1962).

With regard to reaction of olefins with hydrocarbons, the reaction of a pure aromatic hydrocarbon with an olefin, known as an alkylation process, for example, the alkylation of benzene with ethylene in the presence of anhydrous aluminum chloride and like catalysts produces ethyl benzene and also naphthalene is converted to α- and β-naphthalenes (U.S. Pat. No. 2,515,237, U.S. Pat. No. 2,570,263, Japanese Patent Publication No. 7731/63).

There is also reported in the literature studies on the formation of α,β-isomers by the reaction of naphthalene with propylene and butylene [*Journal of Organic Chemistry*, Vol. 34, No. 10, 3211 (1969)].

Every one of these reports has as its object obtaining pure ethyl naphthalene and propyl naphthalene as the product to be formed by additively reacting an olefin with substantially pure naphthalene, and therefore essentially differs from the process of the present invention in that in the present invention a mixture of diverse compounds as in the above-described by-product heavy fractions reacted with an olefin to give a diversity of products accompanying various reactions of the olefin with the respective compounds contained in the heavy fraction.

SUMMARY OF THE INVENTION

The process of this invention comprises a process for the treatment of by-product heavy fractions formed in the production of olefins in which the by-product heavy fractions formed in the production of gaseous olefins by the thermal cracking of hydrocarbons are thermally stabilized in a first step by a treatment using a specific catalyst having superior selectivity, then the resulting heavy fractions are treated using a hydrorefining step, therafter the product is treated by reacting with olefin and/or by hydrogenation in a subsequent step to thereby obtain improved hydrocarbon oil products having excellent anti-freezing properties, thermal stability, oxidation stability at elevated temperatures, solubility, electric properties and a good color appearance.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is a process for the treatment of by-product heavy fractions formed in the production of olefins. More particularly, the present invention is a process for the treatment of the by-product heavy fractions which are obtained upon the thermal cracking of such hydrocarbons as crude oil, asphalt, heavy oil, kerosene, naphtha and liquefied petroleum gas at a temperature above 700°C to produce acetylene and gaseous olefins, such as ethylene and propylene, in which the by-product heavy fractions have an initial boiling point of above 160°C and have a 75 percent distill-off point of below 450°C.

According to the process of the present invention, the above-described by-product heavy fractions used as the raw feed stock are firstly treated with hydrogen under reaction conditions of a temperature of from 40° to 200°C, a pressure of from 5 to 300 kg/cm²G, and a liquid residence time of from 0.1 to 2.0 hours using a nickel-containing catalyst which has been reduced to the metallic state followed by a treatment with organic sulfur compounds consisting exclusively of carbon hydrogen and sulfur atoms, to thereby impart to the by-product heavy fractions thermal stability; then the resulting stabilized oils are subjected to hydrorefining at a temperature of from 250° to 450°C, a pressure of from 5 to 300 kg/cm²G and a liquid residence time of from 0.1 to 5.0 hours using a catalyst containing at least two components selected from the group consisting of cobalt, molybdenum, tungsten and nickel to thereby cause desulfurization and denitrogenation; thereafter the resulting hydrorefined material is subjected to a procedure in which the material is reacted with an olefin at a temperature of from 40° to 380°C, a pressure of from 0 to 150 kg/cm²G, a liquid residence time of from 0.1 to 5.0 hours using a solid acid catalyst, and/or a procedure in which hydrogen is reacted at a temperature of from 100° to 400°C, a pressure of from 10 to 300 kg/cm²G, and a liquid residence time of from 0.1 to 5.0 hours in the presence of a solid hydrogenating catalyst to give a hydrocarbon oil having improved properties.

Since the by-product heavy fractions to be treated according to the process of this invention are obtained by the thermal cracking of hydrocarbons at a temperature above 700°C, the by-product heavy fractions are rearranged so as to contain predominantly an aromatic-rich fraction, and can be utilized quite advantageously depending upon the method of their treatment. On the other hand, they contain a fairly large proportion of thermally unstable substances which are readily converted into resinous materials upon heating to cause deposition on the walls of the equipment, such as heat exchangers, and on the catalyst surface. The formation of such undesirable resinous materials becomes increasingly serious causing eventual plugging of the pipings and the reactors and a deactivation of the catalyst within a short period of time especially when the by-product heavy fractions contain a small amount of air admixed therein or have at one time been contacted with air.

The by-product heavy fractions to be treated according to the process of this invention not only include normally liquid oils but also include those existing as solids at normal temperatures.

Embodiments of the process of this invention comprise mainly treatments including a step in which thermal stability is imparted to the product heavy fractions and a hydrorefining step, and further treatments in the step of reaction with an olefin and/or the step of hydrogenation.

The following three types of combinations are given as illustrative practical embodiments of the processes of this invention:

1. (a) A thermal stability imparting step,
(b) A hydrorefining step,
(c) An olefin reacting step;
2. (a) A thermal stability imparting step,
(b) A hydrorefining step,
(c) A hydrogenating step;
3 (a) A thermal stability imparting step,
(b) A hydrorefining step,
(c) An olefin reacting step,
(d) A hydrogenating step.

By employing any one of above three combinations, it is possible to produce a hydrocarbon oil having better properties and more advantageous performance characteristics than that of untreated by-product heavy fractions, i.e., a considerably lower pour-point, a higher viscosity index as well as improved thermal stability, electric properties, color appearance and solubility. The product hydrocarbon oil thus obtained exhibits superior properties which are especially suited for use as lubricating oils, heat transfer media, electrical insulating oils (condenser oils, ultrahigh voltage cable oils, high voltage transformer oils), paint vehicles, solvents, plasticizers, rubber processing oils, jet engine fuels, and the like.

As was stated hereinabove, the process of the present invention in particular concerns treatment of the by-product heavy fractions formed upon the production of olefins whereby a hydrocarbon oil having superior performances can be obtained by the treatment in a sequence of characteristic procedures of the by-product heavy fractions, which have been scarcely utilized efficiently due to particularly complicated properties of the components contained therein.

The present invention has now found great industrial significance in the efficient utilization of by-product heavy fractions which are produced in increasing quantity especially due to the increasing capacity of ethylene production as well as the shifting trend towards heavier feed stocks for cracking feeds.

DESCRIPTION OF THE ACCOMPANYING DRAWINGS

The accompanying Drawing sets forth diagramatically embodiments of the process of this invention in the form of a block flow sheet.

DESCRIPTION OF PREFERRED EMBODIMENTS

The respective reaction steps of the process of this invention will be explained in greater detail according to the accompanying drawing showing embodiments of the process of the present invention.

i. In the step for imparting thermal stability in the drawing, the feed material is pumped to line 1 under a pressure of from 5 to 300 kg/cm²G and heated after being mixed with compressed hydrogen from 2, at from 40° to 150°C using preheater 3 and heat exchanger 4.

A reactor 5 is provided so as to impart thermal stability and packed with a nickel-containing catalyst which has been previously treated in a specific manner. The process of the present invention is not only characterized in the treatment of the heavy fraction material by the use of a specifically pretreated nickel catalyst but also in the method for the preparation of afore said nickel catalyst.

More particularly, the pretreated catalyst is prepared by contacting a solid catalyst containing at least 1 percent by weight (preferably not less than 5 percent by weight) of nickel in its reduced form at a temperature below 150° C in the presence of or absence of hydrogen, with an organic sulfur compound consisting exclusively of carbon, hydrogen and sulfur atoms, such as mercaptans, for example, propyl mercaptan, phenyl mercaptan and benzyl mercaptan; sulfides, for example dimethyl sulfide and dibutyl sulfide; disulfides, for example, dibenzyl disulfide, polysulfides and thiophene, either directly or, if desired, as a diluted mixture with hydrocarbons, in the gaseous or liquid phase in a ratio of at least 0.01 sulfur atom per nickel atom. Then the catalyst is allowed to stand for a period of not less than 10 seconds.

It is also possible to use the feed stock itself for the pretreatment of the solid catalyst containing the nickel in the reduced state, since the feed material contains at least one of such organic sulfur-containing compounds as described previously.

It is further possible to add copper and chromium as promoters to the nickel-containing catalyst. In this case, the total amount of copper and chromium is preferably not greater than 10 percent by weight based on the nickel in the catalyst, and the ratio of copper to chromium is preferably about 1 : 1.

Noble metals such as palladium can be used instead of the nickel catalyst, but the use of the nickel catalyst is more advantageous since it is much more resistant to deactivation even in the presence of carbon monoxide and small amounts of hydrogen sulfide, and it is less expensive than palladium.

By using the nickel catalyst pretreated with the organic sulfur compounds in this reaction step, it is now possible to avoid any saturation of non-conjugated olefins as well as to avoid hydrogenation of the aromatics. It is also to prevent the reaction from going out of control due to an excessive increase in the reaction temperature arising from exothermic heat resulting in various hydrogenation reactions of the hydrocarbons, particularly hydrogenolysis, which leads to considerable loss of the useful components in the feed stock. Thus, the reaction takes place smoothly under milder temperature conditions unaccompanied by polymerization of the thermally unstable components to thereby keep the preheater and catalyst clean over an extended period of time. This has never been attained using conventional nickel sulfide catalysts which necessarily must be operated at temperatures as high as 200° C or above due to their lower catalytic activity. The reaction conditions to be employed in this step involve a temperature of from 40° to 200° C, a pressure of from 5 to 300 kg/cm²G and a liquid residence time of from 0.1 to 2.0 hours.

ii. Hydrorefining Step. The oil which has been stabilized in the preceding step is heated in furnace 6 and treated in hydrorefining reactor 7 wherein desulfurization and denitrogenation are accomplished simultaneously. Sulfur compounds poison the nickel-containing catalyst used in the later hydrogenation step, described hereinafter, and basic nitrogen-containing compounds poison the catalyst used in the reaction with olefins. For these reasons, the hydrorefining step is necessary to remove poisonous sulfur-containing and basic nitrogen-containing compounds. This hydrorefining step is carried out at a temperature of from 250° to 450° C, a pressure of from 5 to 300 kg/cm²G, and a liquid residence time of from 0:1 to 5.0 hours using a catalyst which contains at least two components selected from the group consisting of tungsten, cobalt, molybdenum and nickel, for example, a cobalt-molybdenum-alumina catalyst, a nickel-molybdenum-alumina catalyst, a nickel-tungsten-alumina catalyst and a sulfided catalyst thereof. The composition at the outlet of 7 is determined such that the molar ratio of hydrogen to the oil material is not less than 0.1.

The hydrorefined oil withdrawn from the reactor 7 is cooled in 3 and heat exchanged in 8 and separated into the gas and liquid phases in separator 9. The hydrogen-rich gas obtained at line 10 is recirculated via line 42 while a portion of the gas is released via line 41 from the system. The refined oil obtained at 9 is heated, if necessary, and passed to stripper 11 in which the hydrogen sulfide dissolved is stripped off and the off gases are vented at 12.

iii. Step for reacting with an olefin. The hydrorefined oil thus obtained is then sent to a step for reaction with an olefin by being passed through valves 16, 17 and 18, mixed with an olefin fed from line 19 and heated or cooled at 20 to bring it to the necessary temperature of from 40° to 380° C.

As a practical matter, the refined oil can be passed through valve 13, and then introduced to fractional distillation 14 so as to recover a desirable fraction which is successively passed to the olefin-reacting step through valves 15 and 18.

The refined oil or fractionated oil is then mixed with an olefin supplied from line 19, heated or cooled at 20 to the necessary temperature of from 40° to 380° C, and introduced into a reactor 21 operated under a pressure of from 0 to 150 kg/cm²G, a liquid residence time of from 0.1 to 5.0 hours and an olefin to refined oil molar ratio of from 0.1 to 10 to thereby effect the reaction with the olefin.

The mole ratio of the olefin to aromatics can be varied depending upon the types and uses of the products, but usually from 1 to 4 moles on the average are required. The number of moles of the olefin added can be adjusted by controlling the reaction temperature, pressure, residence time, and the ratio of olefin to hydrorefined oil. The reactor 21 is packed with a solid acid catalyst having an acid content in the range of from 0.01 to 10 meq/g, determined by the amine titration method using an indicator having a $pKa = 0.8$. Typical solid acid catalysts which can be used include, for example, silica-alumina, crystalline aluminosilicate, nickel oxide-silica, silver-oxide silica-alumina, silica-magnesia, alumina-boria and solid phosphoric acid.

Since the olefin-addition reaction is exothermic, the use of only one reactor is sometimes thermally insufficient to complete the required reaction. In such a case, an additional reactor, for example, a second reactor 23 may be connected from the primary reactor 21 after controlling the temperature of the reaction material in cooler 22. A plurality of such a combination of an adia-

batic reactor with an inter cooler may be installed if desired.

The product which has been reacted with the olefin is then passed to separator **25** from which an excess of olefin obtained at line **26** is recycled to the reactor with or without the release of a portion thereof. The degree of gas-liquid separation in this procedure is facilitated by providing cooler **24.**

The reaction product is withdrawn from line **27** and conveyed to, if necessary, a separating section including distillation under reduced pressure and the like, or passed via line **28** to the following hydrogenation step.

The olefin to be used can contain impurities such as nitrogen, hydrogen, carbon monoxide, lower saturated hydrocarbons, and the like.

When the hydrorefined oil to be treated in this step contains in excess of 30 ppm (by weight), as nitrogen, of basic nitrogen-containing compounds, it is preferred to preliminarily treat the material at a temperature of from 50° to 350° C by adsorption with a solid acidic substance, such as active clay, silica-alumina and solid phosphoric acid, having an acid content in the range of from 0.01 to 10 meq/g according to amine titration method using an indicator having a pKa value below 3.3, so as to reduce the content of the basic nitrogen-containing compounds.

iv. Hydrogenating Step. The hydrorefined oil is passed via valve **29** and line **30,** and the olefin-reacted oil is passed via lines **28** and respectively to the hydrogenating step together with hydrogen fed from line **31.** If necessary, the hydrorefined oil after having been preliminarily distilled at **14** via **13** to give the desired fractions, can be passed to this step via **15, 17, 29** and **30** depending upon the type and specification of the product required.

The hydrogenation in this step is carried out by reacting at least one of the above pretreated oils with hydrogen at a temperature of from 100° to 400° C, a pressure of from 10 to 300 kg/cm^{2}G and a liquid residence time of from 0.1 to 5.0 hours, using a solid hydrogenating catalyst. A hydrogenating reactor **34** employed in this step is packed with a solid hydrogenating catalyst, one of which consists of Group VI metals of the Periodic Table, such as molybdenum and the like, and Group VIII metals, such as nickel, palladium and platinum, or of a Group VIII metal alone. The use of these catalysts in this step enables a smooth hydrogenating reaction, because the catalyst is readily stabilized by the action of sulfur-containing compounds which are often present in the feed stock, and out of control operation with respect to the temperature due to excessively high initial catalytic activity can be avoided effectively.

If the oil to be treated in the hydrogenating step contains only a small amount of the sulfur compounds, the temperature goes out of control due to an excessively high initial activity of the catalyst which leads to a degradation of the catalyst and makes safe operation impossible. In such a case, the solid hydrogenation catalyst to be used in this step can be pretreated according to the following procedure.

A nickel-containing catalyst having a nickel content of at least 1 percent by weight is charged in the hydrogenating reactor **34,** then reduced with hydrogen supplied from **31** after being heated at **33** to a temperature of about 150° C. Thereafter, the catalyst is treated under pressure with a sulfur-containing hydrocarbon oil fed from line **32** or with a hydrorefined oil passed via **29** and **30** after being heated at from 180° to 300° C in **33** in the presence or absence of hydrogen or in the presence of an inert gas to thereby prepare a pretreated nickel-containing catalyst. The pretreatment in the presence of hydrogen is often accompanied by an exothermic hydrogenation reaction, although this is dependent upon the nature of the sulfur-containing hydrocarbon oil, so that it is necessary to control the inlet temperature of the reactor at approximately 180° C. The nickel-containing catalyst having a nickel content of at least 1 percent by weight used in this step is a powdery or shaped catalyst consisting of nickel and a carrier material of inorganic oxides such as silica, silica-alumina, magnesia and diatomaceous earth. A small amount of copper, chromium, cobalt and the like can be added to the catalyst if desired. The sulfur-containing hydrocarbon oil to be used for the pretreatment of the catalyst has a sulfur content, calculated as sulfur, in the range of from 0.001 to 3.0 percent by weight, an initial boiling point above 160° C and is substantially free from hydrogen sulfide, carbon disulfide, mercaptans, sulfides, disulfides, polysulfides and thiophene. Examples of such hydrocarbon oils include by-product oils from high temperature cracking, hydrorefined heavy cycle oils from fluidized catalytic cracking, kerosene, light oil and the like, which essentially should not contain the above-described hydrogen sulfide, carbon disulfide, mercaptans, sulfides, disulfides, polysulfides and thiophene.

The hydrorefined oil passed via lines **29** and **30** satisfies the above requirements well in view of its characteristics and by the fact that it has undergone the hydrorefining treatment. By using such a nickel-containing catalyst pretreated in the manner described hereinabove, it is now possible to carry out the nuclear hydrogenation alone selectively due to the stabilized activity of the catalyst. This catalyst has a high activity sufficient to carry out the nuclear hydrogenation smoothly at a temperature of from 100° to 400° C, a pressure of from 10 to 300 kg/cm^{2}G, and a liquid residence time of from 0.1 to 5.0 hours.

To the thus prepared catalyst the oil passed through **30** and hydrogen from **31** are introduced, and the hydrogenation takes place usually under a pressure of from 10 to 300 kg/cm^{2}G, at a temperature from 100° to 400° C, and with a liquid residence time of from 0.1 to 5.0 hours in reactor **34.**

The composition at the outlet of the hydrogenating reactor **34** is controlled in that the molar ratio of hydrogen to the feed oil (being passed through **30**) is kept above a value of 0.2.

Though the degree of the nuclear hydrogenation needed for the product will vary depending upon the uses and applications of the product desired, it generally reaches at least 40 percent. When the heat of the reaction becomes too large to carry out the reaction in a single reactor, depending upon the requisite degree of nuclear hydrogenation, it is preferred to provide a second reactor **36** after the reaction mixture has been cooled in an intermediate reactor **35.** By employing a plurality of combinations of such adiabatic reactors with the intercoolers, it is possible to attain a desired degree of nuclear hydrogenation.

The product thus formed is then cooled, if necessary, in a cooler **37,** freed from excess hydrogen at **38,** and thereafter withdrawn at **40.** Hydrogen from **39** is par-

tially released and the remainder is recycled for re-use. The product from 40 can be further separated, if desired, into the desired types of products after distillation under reduced pressure.

The processes of this invention and advantages effected thereby will now be described by reference to the following examples.

EXAMPLE 1

A stainless steel reactor having an inner diameter of 100 mm and a length of 5 mm was packed with a mixture of aluminum grains of 1 mm in diameter with catalyst particles of 3 mm in both diameter and in height and containing 55 percent by weight of nickel and a small proportion of chromium and copper supported on diatomaceous earth. Purified hydrogen gas was then passed through the reactor at 180° C, under a pressure of 20 atm. at a flow rate of 5,000 litres (NTP) per hour for a period of 4 hours so as to reduce and activate the catalyst. The hydrogen gas was then replaced by nitrogen while cooling the reactor. To this reactor, liquid n-heptane containing 2 mole percent of dibutyl sulfide was passed for 20 minutes at a rate of 20 liters per hour under nearly atmospheric pressure while controlling the temperature of the catalyst all over the reactor to within 80° C ± 2° C.

After allowing to stand for two hours, n-heptane was passed at the same rate for an hour to thereby prepare a catalyst to be used in the step for imparting thermal stability.

Next, a series of steps including a step for imparting thermal stability, a hydrorefining step, an olefin-reacting step and a hydrogenating step were successively caried out using as the material by-product heavy oils formed upon non-catalytic cracking of naphtha to produce ethylene.

The properties of this material were as follows:

(1) Distillation Characteristics

Initial Boiling Point	180°C
10% Distill-off Point	203°C
30% Distill-off Point	226°C
50% Distill-off Point	265°C
70% Distill-off Point	330°C
90% Distill-off Point	420°C

(2) Nuclear Magnetic Resonance Spectrum

Ar - $\underline{H}$	45.8%	Ar - $\underline{CH_3}$	26.7%
Ar - $\underline{CH}=CH_2$	8.3%	Ar - $\underline{C}-CH_3$	10.6%
Ar - $\underline{CH_2}-C$	5.9%		

(wherein Ar represents an aromatic radical)
The above-described numerical values refer to the ratio, in percentages, of the underlined proton(s) to the total protons

(3) Sulfur-containing Compounds (as sulfur) 300 ppm

(4) Basic Nitrogen-containing Compounds (as nitrogen) 35 ppm

(5) Specific Gravity
d_4^{15} 1.013

This material was passed to the reactor containing the catalyst prepared previously and treated with hydrogen under a hydrogen pressure of 40 kg/cm²G, at an oil feed rate of 50 liters/hr. at an inlet reactor temperature of 80° C.

The reaction tube used was externally heated with electric heaters.

The oil was then hydrorefined in a reactor containing a sulfurized cobalt-molybdenum catalyst (3 mm in diameter) under a hydrogen pressure of 40 kg/cm²G, a temperature of 380° C, and an oil feed rate of 50 lit/hr. The hydrorefined oil had the following properties. The distillation characteristics somewhat differed from that of the material oil since it had been flushed after the reaction in a high temperature gas-liquid separator so as to remove high boilers.

(1) Distillation Characteristics

Initial Boiling Point	160°C
10% Distill-off Point	175°C
30% Distill-off Point	198°C
50% Distill-off Point	232°C
70% Distill-off Point	275°C
90% Distill-off Point	356°C

(2) Sulfur-containing compounds (as sulfur) 104 ppm

(3) Basic Nitrogen-containing Compounds (as nitrogen) 12 ppm

(4) Specific Gravity
d_4^{15} 1.005

The hydrorefined oil was then reacted with ethylene under a reaction pressure of 40 kg/cm²G, at an oil feed rate of 50 liters/hr, and an ethylene to oil molar ratio of from 3 to 5 using a silica-alumina catalyst (3 mm in diameter). The properties of the reaction product thus obtained were as follows:

(1) Distillation characteristics

Initial Boiling Point	162°C
10% Distill-off Point	183°C
30% Distill-off Point	228°C
50% Distill-off Point	270°C
70% Distill-off Point	320°C
90% Distill-off Point	410°C

(2) Nuclear magnetic Resonance Spectrum

Ar - $\underline{H}$	5.4%
Ar - $\underline{CH_2}-C$	26.0%
Ar - $\underline{C}-CH_3$	40.5%

(3) Specific Gravity
d_4^{15} 0.968

The resultant product had reduced aromatic protons and increased methylenes attached to the aromatic as well as methyl protons in comparison to the material. This indicates clearly the addition of olefin to aromatics.

It was also found as a result of a mass analysis that new peaks appeared at points where an ethyl group is added to the material peaks, that is, at a mass number 28 greater than the material peaks. There were of course other peaks where two or three ethyl groups were added, or at points of mass numbers 56 or 84 greater than that of the material peaks.

According to the results of various analyses as shown above, it was assumed that an average of about two moles of ethyl group was added per mole of the material.

The properties of the product determined on the fraction boiling from 325° to 338° C (calculated at normal pressure) obtained by distillation under reduced pressure, are as follows:

(1) Kinematic Viscosity
30°C 23 cst
70°C 4.5 cst

(2) Flash Point
180°C

-Continued

(3) Pour Point
−32.5°C

For use an an electric insulating oil, the electrical properties of the resultant product are shown as follows:

Tan δ (80°C)	0.12%
Volume Resistance (80°C)	$2 \times 10^{13}\Omega$cm
Dielectric Constant (80°C)	2.7

Other fractions than the above fraction were found to possess properties suited for use as heat-transfer media and paint vehicles.

Next, the hydrogenation was carried out using a heavy fraction obtained by flushing after the hydrorefining treatment. The distillation characteristics of this heavy fraction were as follows:

(1) Distillation Characteristics	
Initial Boiling Point	225°C
10% Distill-off Point	247°C
30% Distill-off Point	273°C
50% Distill-off Point	335°C
70% Distill-off Point	420°C

The hydrogenation is carried out using the procedures described as follows:

Twenty five liters of a nickel-diatomaceous earth catalyst was packed to the first and into the second reactors and reduced with hydrogen gas at a temperature of 180° C for 5 hours. Then the reduced catalyst was wetted with a hydrorefined catalytic cracking cycle oil and heated at a temperature of 180° C for 5 hours in the presence of nitrogen while continuously passing the cycle oil over it. Thereafter, the hydrogenation was continuously carried out under a hydrogen pressure of 100 kg/cm²G at an oil flow rate of 50 liters/hr. while maintaining the inlet temperature of both the first and the second reactors at **180°** C and keeping the outlet temperature of the first reactor and the second reactor at 300° C and 290° C respectively.

The effluent product oil thus treated according to the above procedure had a markedly increased transparency. The hydrogenated product had the following distillation properties:

(1) Distillation Characteristics:	
Initial Boiling Point	166°C
10% Distill-off Point	182°C
30% Distill-off Point	209°C
50% Distill-off Point	264°C
70% Distill-off Point	352°C

A fraction boiling in the range of from 260° to 350° C was collected from the hydrogenated product. The properties of this fraction measured were as follows:

Specific Gravity	d^{15}	1.0303
Refractive Index	n_D^{25}	1.6064
Kinematic Viscosity	30°C	5.7 cst, 70°C 2.2 cst
Flash Point	120°C	
Pour Point	below −50°C	

The electric properties were as follows:

Tan δ (80°C)	0.05%
Volume Resistance (80°C)	$5 \times 10^{15}\ \Omega$ cm
Dielectric Constant (80°C)	2.35

As is apparent from the above results, the hydrogenated product thus obtained was found to be especially well suited for use as a superior electrical insulating oil.

Moreover, other fractions than the fraction boiling at 260° to 350° C exhibited characteristic properties and were found to be utilizable suitably as paint vehicles, plasticizers and as jet engine fuels.

COMPARATIVE EXAMPLE 1

Hydrorefining treatment so as to effect desulfurization and denitrogenation as in Example 1 was carried out without applying the pretreatment step with hydrogen at a low temperature for imparting thermal stability.

Although the hydrorefined oil obtained had a similar character to that obtained in Example 1, the hydrorefining operation suffered due to an increase in the pump delivery pressure from 42 kg/cm²G at start up to 48 kg/cm²G after about 20 hours of operation while carrying out the reaction under a hydrogen pressure of 40 kg/cm²G, at an oil flow rate of 50 liters/hr., and at an inlet temperature of 380° C. This indicates that the differential pressure between pressures at the entrance and exit of the reactor has increased from the initial 2 Kg/cm² at the beginning of operation to 8 Kg/cm².

This pressure difference quickly increased after the duration of 20 hours to such an extent that supplying the oil became impossible. In addition, the temperature of the catalyst bed in the middle of the reactor was about 50° C higher than the inlet temperature of 380° C. A large amount of a coke-like powder and a pitch-like mass was found plugging and deposited inside the pipings on inspection of the preheating zone after the termination of the oil supply. The same disadvantage was also observed in the catalyst bed of the reactor. Furthermore, the sulfur content of the refined oil sampled immediately before the shut-down showed an increase as high as 180 ppm. These phenomena are believed to be based on a lowering of the catalyst activity due to the deposition of carbonaceous materials on the catalyst.

This was proved by the fact that the content of the carbon in the catalyst removed from the reactor reached in excess of 20 percent by weight.

EXAMPLE 2

Total fractions of hydrorefined oil obtained in Example 1 were reacted with propylene, and thereafter subjected to nuclear hydrogenation.

First, propylene was reacted with the refined oil using a silica-alumina catalyst under a pressure of 8 kg/cm²G, at a temperature of from 200° to 250° C and at an oil flow rate of 2 lit/hr. using a reaction tube of a diameter of 20 mm.

The product showed an increase in the 50 percent distill-off point of about 70° C and a decrease of nearly 0.058 in the specific gravity at 15° C. The product oil was found to exhibit better electrical properties than the product obtained by reacting with ethylene according to Example 1.

The resultant product was then nuclear hydrogenated using a nickel-diatomaceous earth catalyst diluted with an equal amount of aluminum grain at a hydrogen pressure of 100 kg/cm²G, a reactor inlet temperature of 170° C, a reactor outlet temperature of 280° C and at an oil flow rate of 2 liters/hr. The effluent

oil was returned to the reactor so as to make a total time of contact with the nickel-diatomaceous of one hour. The transparency of the oil increased as the sum total of the contact time increased. After contact for an hour, the 50 percent distillation point was about 75° C lower than that of the product oil.

The thus obtained hydrogenated product was also found to be desirable as an electrical insulating oil based on the following electric properties.

	Product	Hydrogenated Product
Tan δ (80°C)	0.04%	0.003%
Volume Resistance (80°C)	$5 \times 10^{15}\Omega$cm	$5 \times 10^{16}\Omega$cm
Dielectric Constant (80°C)	2.7	2.3

EXAMPLE 3

The state of deactivation of the catalyst to be used for reacting with olefin was determined by taking the decrease in the specific gravity of the material as a measure. The propriety of employing such a simple and convenient method is explained as follows:

It has been found that the correlation between the specific gravity of the product and the average number of added olefins has a nearly linear relationship, although it differs somewhat depending upon the type of the feed stock. The average number was calculated by analyzing the number of olefins added to the material with various data obtained by NMR analysis, H/C ratio, mass spectrum analysis and gas chromatography after reacting the olefin at a variety of degrees with the unreacted material which has been previously measured to determine its specific gravity. Accordingly, the degree of the deactivation can be estimated by comparing the difference of the specific gravity between the material and the product at the initial stage of the catalyst with that at the intermediate and at the last stage of the catalyst.

Seria crude oil was thermally cracked at 1,050° C at a contact time of 5×10^{-3} seconds by using a high temperature stream to give a by-product heavy oil from which a fraction having an initial boiling point of 178° C and a 95 percent distill-off point of 370° C was obtained and used as the material for imparting thermal stability and successively for the hydrorefining treatment.

The catalyst used in this thermal stability-imparting step was a reduced and activated one, identical to the one described in Example 1, and prepared by passing for 20 minutes a hydrorefined oil obtained in Example 1 and containing an added 2 mole percent of dibutyl sulfide, under a pressure nearly equal to atmospheric at a rate of 20 liters per hour for 4 hours while controlling the catalyst temperature all over the reactor to within the range of 80° C ± 2° C, then allowing to stand for additional 2 hours followed by treating again with the hydrorefined oil at the same rate for an hour.

The conditions employed for imparting thermal stability were the same as those employed in Example 1.

The following hydrorefining treatment was carried out under a hydrogen pressure of 30 kg/cm²G, at a temperature of 400° C and at the liquid residence time of 1.0 hour using a cobalt-molybdenum catalyst.

Next, the hydrorefined oil thus obtained was adsorptively treated with a low temperature grade activated clay of a particle size of 10 to 30 mesh which had been previously dried at 200° C with hot air. The acid content of this low temperature-grade activated clay was 0.1 meq/g. determined according to an amine titration method using dimethyl yellow as an indicator.

This adsorptive treatment was carried out at a temperature of 100° C at a flow rate of the refined oil of 50 volumes per volume of the activated clay.

The thus treated oil contained 2.7 ppm by weight of basic nitrogen-containing compounds (calculated as nitrogen) and 45 ppm of sulfur compounds (calculated as sulfur). The oil was then reacted with ethylene at 300° C, under a pressure of 30 kg/cm²G, at a liquid residence time of 0.5 hr., at an ethylene to oil molar ratio of from 3 to 6 in the presence of a SiO_2-Al_2O_3 catalyst having an Al_2O_3 content of about 25 wt. percent, an acid content of 0.55 meq/g and shaped in a size of from 0.5 to 1.5 mm in diameter and from 3 to 5 mm length by extrusion, followed by calcinating at 600° C. The relation of the oil feed multiple number to the reaction result (indicated by multiplying 10^4 by the decrease of the specific gravity as described previously) was as follows:

Feed Oil Multiple Number (Cumulative volume of the oil fed per volume of the catalyst)	Reaction Result
1	395
10	366
50	332
100	310

As can be seen from the above results a smooth reaction of ethylene can be effected for a prolonged period.

COMPARATIVE EXAMPLE 2

The procedures of imparting thermal stability and hydrorefining as in Example 3 were repeated using the same by-product heavy oil and employing the same reaction conditions. Then the product was directly reacted with ethylene under the same conditions as used in Example 3 but eliminating the adsorption treatment. The oil obtained after the hydrorefining treatment had a sulfur content of 45 ppm (by weight) and a basic nitrogen-containing compound content calculated as nitrogen was 35 ppm by weight. This result corresponded to the reaction result of 116 at an oil feed multiple number of 100 in which the value reached was as small as three-eighths when compared to the result obtained in Example 3 where the adsorptive treatment was adopted. In this example, a smooth reaction of ethylene could not be expected.

EXAMPLE 4

Light naphtha was thermally cracked at a temperature of 950° C in an atmosphere of steam with a residence time of 0.2 second to give a liquid product which was used as the feed stock of this example. This material was successively treated in a step for imparting thermal stability, a step of hydrorefining and a step of hydrogenation to thereby produce a nuclear hydrogenated product.

The properties of the liquid feed stock were as follows:

Initial Boiling Point	280°C
30% Distill-off Point	346°C
50% Distill-off Point	352°C
70% Distill-off Point	364°C
90% Distill-off Point	394°C
97% Distill-off Point	420°C
Paraffin	NEG
Olefin	1.0 wt %
Aromatics	99.0 wt %
Sulfur	0.045 wt %

The first step for imparting thermal stability was carried out by using the same reactor as used in Example 1, a catalyst prepared according to the same procedure as employed in Example 3 under the reaction conditions including a temperature of 130° C, a hydrogen pressure of 45 kg/cm²G, and a liquid residence time of 0.1 hour. Next, the stabilized oil was passed through two reactors connected in series each containing 25 liters of a cobalt-molybdenum-alumina catalyst under a reaction pressure of 40 kg/cm²G, an average temperature of 400° C, an oil feed rate of 45 liters/hr, and hydrogen feed rate of 60 NM³/hr so as to effect hydrorefining. The sulfur content of the resultant hydrorefined oil showed a reduction to 32 ppm. By analysis, it was found that this sulfur was not present as compounds such as hydrogen sulfide, carbon disulfide, mercaptan sulfides, disulfides, polysulfides or thiophene.

This hydrorefined oil was further hydrogenated using a packed nickel-diatomaceous earth catalyst. This catalyst was prepared by a preliminary reduction with hydrogen at 160° C for 6 hours, thereafter the hydrogen was discontinued and the temperature was increased to 260° C while passing the refined oil at the rate of 50 liters/hr. for 12 hours. Then the hydrogenating reaction was started by gradually increasing the pressure to 100 kg/cm²G while compressing the hydrogen at a temperature of from 260° to 300° C. The resultant hydrogenated oil had a markedly higher transparency than that of the starting material. The degree of nuclear hydrogenation determined by the refractive index, the nuclear magnetic resonance spectrum (NMR), a H/C analysis and the like was 96.5 percent and the properties of the hydrogenated product were as follows:

Initial Boiling Point	230°C
30% Distill-off Point	292°C
50% Distill-off Point	301°C
70% Distill-off Point	312°C
90% Distill-off Point	332°C
97% Distill-off Point	401°C
Aromatics	below 3.5%
Saturates	96.5%

After running the hydrogenating reaction for 48 hours, the degree of hydrogenation remained nearly constant within the range of experimental error.

This proves the fact that the catalyst used for the hydrogenation has strong resistance against sulfur and can be used over a prolonged period with a practical level of activity.

What is claimed is:

1. A process for the preparation of hydrocarbon oils of improved quality by treatment of by-product heavy fractions having an initial boiling point of above 160° C and a 75 percent distill-off point of below 450° C and obtained in the production of gaseous olefins by the thermal cracking of hydrocarbons at temperatures above 700° C which comprises:

1. imparting thermal stability to said by-product heavy fractions by treating said fractions with hydrogen at a temperature of from 40° to 200° C, a pressure of from 5 to 300 Kg/cm²G and a liquid residence time of from 0.1 to 5.0 hours in the presence of a metallic nickel-containing catalyst, containing at least 1 percent by weight of reduced nickel and not more than 10 percent by weight, based on the nickel, of a promoter consisting of copper and chromium, said catalyst being prepared by treatment with organic sulfur compounds consisting exclusively of carbon, hydrogen and sulfur atoms to obtain thermally stabilized heavy fractions,
2. hydrorefining the thermally stabilized heavy fractions at a temperature of from 250° to 450° C, a pressure of from 5 to 300 Kg/cm²G and a liquid residence time of from 0.1 to 5.0 hours in the presence of a catalyst containing at least two components selected from the group consisting of cobalt, molybdenum, tungsten and nickel to cause desulfurization and denitrogenation, and
3. reacting the hydrorefined material with hydrogen at a temperature of from 100° to 400° C, a pressure of from 10 to 300 Kg/cm²G and a liquid residence time of from 0.1 to 5.0 hours in the presence of a solid hydrogenating catalyst.

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