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(54) Titre : EXTRACTION DU SOUFRE PAR DISTILLATION CATALYTIQUE
(54) Title: SULFUR REMOVAL BY CATALYTIC DISTILLATION

(57) **Abrégé/Abstract:**

A product of reduced sulfur content is produced from a feedstock which is comprised of a mixture of hydrocarbons and contains organic sulfur compounds as unwanted impurities. The process comprises converting at least a portion of the sulfur-containing impurities to sulfur-containing products of higher boiling point by treatment with an alkylating agent in the presence of an acid catalyst and removing at least a portion of these higher boiling products by fractional distillation. The process can be carried out in a distillation column reactor wherein the acid catalyzed reaction and fractional distillation are carried out simultaneously. Suitable alkylating agents include alcohols and olefins.



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(54) Title: SULFUR REMOVAL BY CATALYTIC DISTILLATION (57) Abstract A product of reduced sulfur content is produced from a feedstock which is comprised of a mixture of hydrocarbons and contains organic sulfur compounds as unwanted impurities. The process comprises converting at least a portion of the sulfur-containing impurities to sulfur-containing products of higher boiling point by treatment with an alkylating agent in the presence of an acid catalyst and removing at least a portion of these higher boiling products by fractional distillation. The process can be carried out in a distillation column reactor wherein the acid catalyzed reaction and fractional distillation are carried out simultaneously. Suitable alkylating agents include alcohols and olefins.		

Sulfur Removal by Catalytic Distillation

Field of the Invention

10 This invention relates to a process for producing a product of reduced sulfur content from a liquid feedstock wherein the feedstock is comprised of a mixture of hydrocarbons and contains organic sulfur compounds as unwanted impurities. More particularly, it involves the catalyzed conversion of at least a portion of the organic sulfur compounds in the feedstock to products of a higher boiling point and removing
15 these high boiling products by fractional distillation. The process can be carried out in a distillation column reactor wherein the catalyzed conversion and fractional distillation are carried out simultaneously.

Background of the Invention

20 The catalytic cracking process is one of the major refining operations which is currently employed in the conversion of petroleum to desirable fuels such as gasoline and diesel fuel. The fluidized catalytic cracking process is an example of this type of process wherein a high molecular weight hydrocarbon feedstock is converted to
25 lower molecular weight products through contact with hot, finely-divided solid catalyst particles in a fluidized or dispersed state. Suitable hydrocarbon feedstocks typically boil within the range of from about 205° C to about 650° C, and they are usually contacted with the catalyst at temperatures in the range from about 450° C to about 650° C. Suitable feedstocks include various mineral oil fractions such as light
30 gas oils, heavy gas oils, wide-cut gas oils, vacuum gas oils, kerosenes, decanted oils,

residual fractions, reduced crude oils and cycle oils which are derived from any of these as well as fractions derived from shale oils, tar sands processing, and coal liquefaction. Products from the process are typically based on boiling point and include light naphtha (boiling between about 10° C and about 221° C), kerosene
5 (boiling between about 180° C and about 300° C), light cycle oil (boiling between about 221° C and about 345° C), and heavy cycle oil (boiling at temperatures higher than about 345° C).

Not only does the catalytic cracking process provide a significant part of the gasoline pool in the United States, it also provides a large proportion of the sulfur
10 that appears in this pool. The sulfur in the liquid products from this process is in the form of organic sulfur compounds and is an undesirable impurity which is converted to sulfur oxides when these products are utilized as a fuel. These sulfur oxides are objectionable air pollutants. In addition, they can deactivate many of the catalysts that have been developed for the catalytic converters which are used on automobiles
15 to catalyze the conversion of harmful emissions in the engine exhaust to gases which are less objectionable. Accordingly, it is desirable to reduce the sulfur content of catalytic cracking products to the lowest possible levels.

The sulfur-containing impurities of straight run gasolines, which are prepared by simple distillation of crude oil, are usually very different from those in cracked
20 gasolines. The former contain mostly mercaptans and sulfides, whereas the latter are rich in thiophene derivatives.

Low sulfur products are conventionally obtained from the catalytic cracking process by hydrotreating either the feedstock to the process or the products from the process. The hydrotreating process involves treatment with elemental hydrogen in
25 the presence of a catalyst and results in the conversion of the sulfur in the sulfur-containing organic impurities to hydrogen sulfide which can be separated and converted to elemental sulfur. Unfortunately, this type of processing is typically quite expensive because it requires a source of hydrogen, high pressure process equipment, expensive hydrotreating catalysts, and a sulfur recovery plant for
30 conversion of the resulting hydrogen sulfide to elemental sulfur. In addition, the hydrotreating process can result in an undesired destruction of olefins in the

feedstock by converting them to saturated hydrocarbons through hydrogenation. This destruction of olefins by hydrogenation is undesirable because it results in the consumption of expensive hydrogen, and the olefins are valuable as high octane components of gasoline. As an example, naphtha of a gasoline boiling range from a catalytic cracking process has a relatively high octane number as a result of a large olefin content. Hydrotreating such a material causes a reduction in the olefin content in addition to the desired desulfurization, and octane number decreases as the degree of desulfurization increases.

During the early years of the refining industry, sulfuric acid treatment was an important process that was used to remove sulfur, precipitate asphaltic material, and improve stability, color and odor of a wide variety of refinery stocks. At page 3-119 of the *Petroleum Processing Handbook*, W.F. Bland and R.L. Davidson, Ed., McGraw-Hill Book Company, 1967, it is reported that low temperatures (-4° to 10° C) are used in this process with strong acid, but that higher temperatures (21° to 54° C) may be practical if material is to be rerun. It is disclosed in the *Oil and Gas Journal*, November 10, 1938, at page 45 that sulfuric acid treatment of naphtha is effective in removing organic sulfur-containing impurities such as isoamyl mercaptan, dimethyl sulfate, methyl-*p*-toluene sulfonate, carbon disulfide, *n*-butyl sulfide, *n*-propyl disulfide, thiophene, diphenyl sulfoxide, and *n*-butyl sulfone. The chemistry involved in sulfuric acid treatment of gasoline is extensively discussed by G.E. Mapstone in a review article in the *Petroleum Refiner*, Vol. 29, No. 11 (November, 1950) at pp. 142-150. Mapstone reports at page 145 that thiophenes may be alkylated by olefins in the presence of sulfuric acid. He further states that this same reaction appears to have a significant effect in the desulfurization of cracked shale gasoline by treatment with sulfuric acid in that a large proportion of the sulfur reduction obtained occurs on the redistillation of the acid treated gasoline, with the re-run bottoms containing several percent of sulfur.

U.S. Patent No. 2,448,211 (Caesar et al.) discloses that thiophene and its derivatives can be alkylated by reaction with olefinic hydrocarbons at a temperature between about 140° and about 400° C in the presence of a catalyst such as an activated natural clay or a synthetic adsorbent composite of silica and at least one

amphoteric metal oxide. Suitable activated natural clay catalysts include clay catalysts on which zinc chloride or phosphoric acid have been precipitated. Suitable silica-amphoteric metal oxide catalysts include combinations of silica with materials such as alumina, zirconia, ceria, and thoria. U.S. Patent No. 2,469,823 (Hansford et al.) teaches that boron trifluoride can be used to catalyze the alkylation of thiophene and alkyl thiophenes with alkylating agents such as olefinic hydrocarbons, alkyl halides, alcohols, and mercaptans. In addition, U.S. Patent No. 2,921,081 (Zimmerschied et al.) discloses that acidic solid catalysts can be prepared by combining a zirconium compound selected from the group consisting of zirconium dioxide and the halides of zirconium with an acid selected from the group consisting of orthophosphoric acid, pyrophosphoric acid, and triphosphoric acid. It is further disclosed that thiophene can be alkylated with propylene at a temperature of 227° C in the presence of such a catalyst.

U.S. Patent No. 2,563,087 (Vesely) discloses that thiophene can be removed from mixtures of this material with aromatic hydrocarbons by selective alkylation of the thiophene and separation of the resulting thiophene alkylate by distillation. The selective alkylation is carried out by mixing the thiophene-contaminated aromatic hydrocarbon with an alkylating agent and contacting the mixture with an alkylation catalyst at a carefully controlled temperature in the range from about -20° C to about 85° C. It is disclosed that suitable alkylating agents include olefins, mercaptans, mineral acid esters, and alkoxy compounds such as aliphatic alcohols, ethers and esters of carboxylic acids. It is also disclosed that suitable alkylation catalysts include the following: (1) The Friedel-Crafts metal halides, which are preferably used in anhydrous form; (2) a phosphoric acid, preferably pyrophosphoric acid, or a mixture of such a material with sulfuric acid in which the volume ratio of sulfuric to phosphoric acid is less than about 4:1; and (3) a mixture of a phosphoric acid, such as orthophosphoric acid or pyrophosphoric acid, with a siliceous adsorbent, such as kieselguhr or a siliceous clay, which has been calcined to a temperature of from about 400° to about 500° C to form a silico-phosphoric acid combination which is commonly referred to as a solid phosphoric acid catalyst.

U.S. Patent No. 2,943,094 (Birch et al.) is directed to a method for the removal of alkyl thiophenes from a distillate which consists predominately of aromatic hydrocarbons, and the method involves converting the alkyl thiophenes to sulfur-containing products of a different boiling point which are removed by
5 fractional distillation. The conversion is carried out by contacting the mixture with a catalyst at a temperature in the range from 500 to 650° C, wherein the catalyst is prepared by impregnating alumina with hydrofluoric acid in aqueous solution. It is disclosed that the catalyst functions to: (1) convert alkyl thiophenes to lower alkyl thiophenes and/or unsubstituted thiophene by dealkylation; (2) effect the
10 simultaneous dealkylation and alkylation of alkyl thiophenes; and (3) convert alkyl thiophenes to aromatic hydrocarbons.

U.S. Patent No. 2,677,648 (Lien et al.) relates to a process for the desulfurization of a high-sulfur olefinic naphtha which involves treating the naphtha with hydrogen fluoride to obtain a raffinate, defluorinating the raffinate, and then
15 contacting the defluorinated raffinate with HF-activated alumina. The treatment with hydrogen fluoride is carried out at a temperature in the range from about -51° to -1° C under conditions which result in the removal of about 10 to 15% of the feedstock as a high sulfur content extract, and about 30 to 40% of the feedstock is simultaneously converted by polymerization and alkylation to materials of the gas oil
20 boiling range. After removal of HF from the raffinate, the raffinate is contacted with an HF-activated alumina at a temperature in the range from about 316 to 482° C to depolymerize and dealkylate the gas oil boiling range components and to effect additional desulfurization.

U.S. Patent No. 4,775,462 (Imai et al.) is directed to a method for converting
25 the mercaptan impurities in a hydrocarbon fraction to less objectionable thioethers which are permitted to remain in the product. This process involves contacting the hydrocarbon fraction with an unsaturated hydrocarbon in the presence of an acid-type catalyst under conditions which are effective to convert the mercaptan impurities to thioethers. It is disclosed that suitable acid-type catalysts include: (1) acidic
30 polymeric resins such as resins which contain a sulfonic acid group; (2) acidic intercalate compounds such as antimony halides in graphite, aluminum halides in

graphite, and zirconium halides in graphite; (3) phosphoric acid, sulfuric acid or boric acid supported on silica, alumina, silica-aluminas or clays; (4) aluminas, silica-aluminas, natural and synthetic pillared clays, and natural and synthetic zeolites such as faujasites, mordenites, L, omega, X and Y zeolites; (5) aluminas or silica-aluminas which have been impregnated with aluminum halides or boron halides; and (6) metal sulfates such as zirconium sulfate, nickel sulfate, chromium sulfate, and cobalt sulfate.

U.S. Patent No. 3,629,478 (Haunschild) discloses a method for the separation of linear olefins from tertiary olefins by selectively converting the tertiary olefins in the feedstock to ethers by reaction with an alcohol in a distillation column reactor and fractionating the resulting products in the distillation column reactor. The reaction is catalyzed by a heterogeneous catalyst which is located in a plurality of zones within the distillation column reactor.

U.S. Patents No. 4,232,177 (Smith), 4,307,254 (Smith) and 4,336,407 (Smith) are directed to a method for simultaneously conducting a catalyzed chemical reaction and separating the reaction products through the use of a distillation column reactor which contains a fixed bed of the catalyst as a column packing. The reactants are contacted with the catalyst under reaction conditions, and the resulting products are separated by fractional distillation within the distillation column reactor concurrently with their formation. These patents broadly disclose that this type of process can be used with organic reactions such as dimerization, etherification, isomerization, esterification, chlorination, hydration, dehydrohalogenation, alkylation and polymerization. U.S. Patent No. 4,232,177 teaches that the process can be used to produce isobutene by catalytically converting methyl tertiary butyl ether to methanol and isobutene over an acid cation exchange resin and concurrently separating the products by fractional distillation. U.S. Patent No. 4,307,254 teaches that the process can be used for the production of methyl tertiary butyl ether wherein an acid cation exchange resin is used as a catalyst in combination with methanol and a mixture of isobutene and normal butene as feedstocks. Finally, U.S. Patent No. 4,336,407 teaches that the process can be used to produce ethers by reacting C₄ to C₅ olefins with C₁ to C₆ alcohols over an acidic cation exchange resin.

U.S. Patent No. 4,242,530 (Smith) is also directed to a method for simultaneously conducting a catalyzed chemical reaction and separating the reaction products through the use of a distillation column reactor which contains a fixed bed of the catalyst as a column packing. More specifically, this patent teaches that such a process can be used to separate an isoolefin, such as isobutene, from the corresponding normal olefin by contacting a mixture of the olefins with an acidic cation exchange resin to convert the isoolefin to a dimer which is concurrently separated by fractional distillation.

10

Summary of the Invention

Hydrotreating is an effective method for the removal of sulfur-containing impurities from hydrocarbon liquids such as those which are conventionally encountered in the refining of petroleum and those which are derived from coal liquefaction and the processing of oil shale or tar sands. Liquids of this type, which boil over a broad or narrow range of temperatures within the range from about 10° C to about 345° C, are referred to herein as "distillate hydrocarbon liquids." For example, light naphtha, heavy naphtha, kerosene and light cycle oil are all distillate hydrocarbon liquids. Unfortunately, hydrotreating is an expensive process and is usually unsatisfactory for use with highly olefinic distillate hydrocarbon liquids. Accordingly, there is a need for an inexpensive process for the removal of sulfur-containing impurities from distillate hydrocarbon liquids. There is also a need for such a process which can be used to remove sulfur-containing impurities from highly olefinic distillate hydrocarbon liquids.

25

We have found that many of the sulfur-containing impurities which are typically found in distillate hydrocarbon liquids can be easily and selectively converted to sulfur-containing materials of a higher boiling point by treatment with an acid catalyst in the presence of olefins or alcohols. We have also found that a large portion of the resulting higher boiling sulfur-containing materials can be removed by fractional distillation. The catalyzed formation of these higher boiling sulfur-containing materials and their removal is conveniently carried out in a

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distillation column reactor wherein the catalyzed reaction and fractional distillation are carried out simultaneously.

One embodiment of the invention is a method for producing a product of reduced sulfur content from a liquid feedstock, wherein said feedstock is comprised of a mixture of hydrocarbons which boils below about 345° C and contains a minor amount of organic sulfur compounds, and wherein said process comprises: (a) adjusting the composition of said feedstock so that it contains an amount of alkylating agent which is at least equal on a molar basis to that of the organic sulfur compounds, and wherein said alkylating agent is comprised of at least one material selected from the group consisting of alcohols and olefins; (b) passing said mixture to a distillation column reactor which contains at least one fixed bed of acidic solid catalyst; (c) contacting the feedstock with said catalyst under conditions which are effective to convert at least a portion of the sulfur-containing impurities in the feedstock to a sulfur-containing material of higher boiling point; (d) fractionating within the distillation column reactor the products of said contacting; (e) withdrawing at least a portion of the sulfur-containing material of higher boiling point in a high boiling fraction from the distillation column reactor; and (f) withdrawing a fraction from the distillation column reactor which has both a lower boiling point than that of said high boiling fraction and a reduced sulfur content relative to that of said feedstock.

Another embodiment of the invention is a process which comprises: (a) catalytically cracking a hydrocarbon feedstock which contains sulfur-containing impurities to produce volatile catalytic cracking products which include sulfur-containing impurities; (b) preparing a second feedstock which is comprised of at least a portion of said volatile catalytic cracking products and wherein said second feedstock contains both organic sulfur compounds as impurities and at least 1 weight percent of olefins; (c) passing the second feedstock to a distillation column reactor which contains at least one fixed bed of acidic solid catalyst; (d) contacting the second feedstock with said catalyst under conditions which are effective to convert at least a portion of the sulfur-containing impurities in the second feedstock to a sulfur-containing material of higher boiling point; (e) fractionating within the distillation

column reactor the products of said contacting; (f) withdrawing at least a portion of the sulfur-containing material of higher boiling point in a high boiling fraction from the distillation column reactor; and (g) withdrawing a fraction from the distillation column reactor which has both a lower boiling point than that of said high boiling
5 fraction and a reduced sulfur content relative to that of said second feedstock.

An object of the invention is to provide a method for the removal of sulfur-containing impurities from distillate hydrocarbon liquids which does not involve hydrotreating with hydrogen in the presence of a hydrotreating catalyst.

An object of the invention is to provide an inexpensive method for producing
10 distillate hydrocarbon liquids of a reduced sulfur content.

Another object of the invention is to provide a method for the removal of mercaptans, thiophene and thiophene derivatives from hydrocarbon liquids.

Another object of the invention is to provide an improved method for the removal of sulfur-containing impurities from catalytic cracking products.

15 A further object of the invention is to provide a method for the removal of sulfur-containing impurities from the light naphtha product of a catalytic cracking process without significantly reducing its octane.

Another object of the invention is to provide a method for catalyzing the conversion of sulfur-containing impurities in a distillate hydrocarbon liquid to higher
20 boiling sulfur-containing products and simultaneously removing these products by fractional distillation.

Brief Description of the Drawings

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FIG. 1 of the drawings illustrates the use of a solid phosphoric acid catalyst on kieselguhr to increase the boiling point of sulfur-containing impurities in a stabilized heavy naphtha feedstock that was blended with a mixture of C₃ and C₄ olefins.

FIG. 2 of the drawings illustrates the use of a solid phosphoric acid catalyst on kieselguhr to increase the boiling point of sulfur-containing impurities in an olefin-containing, stabilized, heavy naphtha feedstock.

FIG. 3a of the drawings illustrates the distribution of sulfur content as a function of boiling point in a low olefin content synthetic hydrocarbon feedstock which contains 2-propanethiol, thiophene, 2-methylthiophene, and isopropyl sulfide as impurities. FIG. 3b illustrates the use of a solid phosphoric acid catalyst on kieselguhr to increase the boiling point of the sulfur-containing impurities in this synthetic feedstock.

FIG. 4a of the drawings illustrates the distribution of sulfur content as a function of boiling point in a high olefin content synthetic hydrocarbon feedstock which contains 2-propanethiol, thiophene, 2-methylthiophene, and isopropyl sulfide as impurities. FIG. 4b illustrates the use of a solid phosphoric acid catalyst on kieselguhr to increase the boiling point of the sulfur-containing impurities in this synthetic feedstock.

FIG. 5 of the drawings illustrates the ability of six different solid acidic catalysts to increase the boiling point of sulfur-containing impurities in a synthetic feedstock (which contained 12.9 wt. % of C₆ and C₇ olefins) both before and after the feedstock was blended with propene at a 0.25 volume ratio of propene to synthetic feedstock.

FIG. 6 of the drawings illustrates the increased catalyst life that can be obtained by removing basic nitrogen-containing impurities from the feedstock.

Detailed Description of the Invention

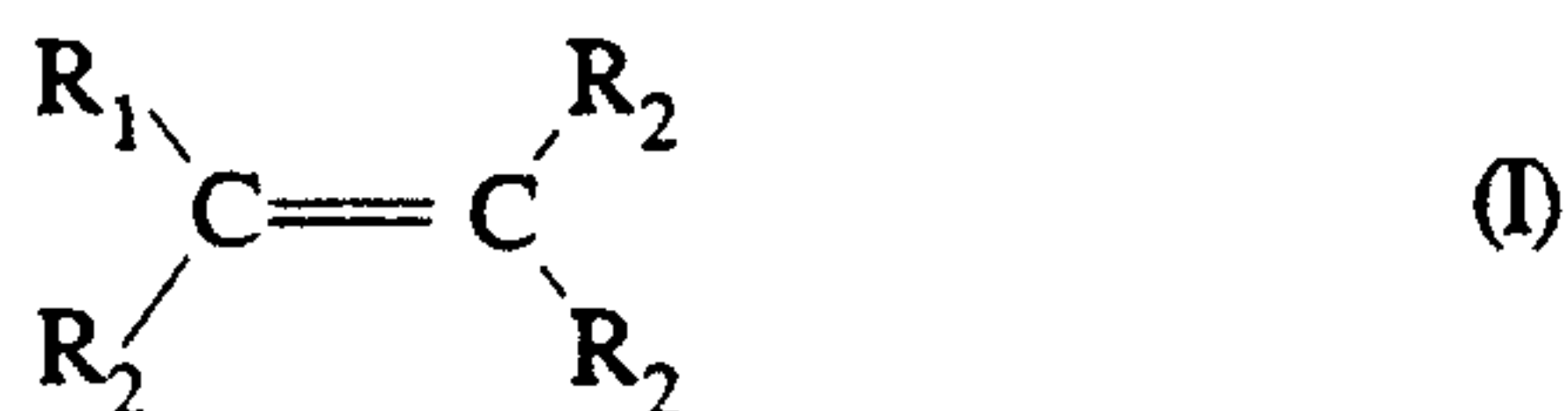
We have discovered a process for the production of a product of reduced sulfur content from a liquid feedstock wherein the feedstock is comprised of a mixture of hydrocarbons and contains organic sulfur compounds as unwanted impurities. This process comprises converting at least a portion of the sulfur-containing impurities to sulfur-containing products of a higher boiling point by

treatment with an alkylating agent in the presence of an acid catalyst and removing at least a portion of these higher boiling products by fractional distillation. The acid catalyzed conversion and removal of the higher boiling products is conveniently carried out in a distillation column reactor wherein the acid catalyzed reaction and

5 fractional distillation are carried out simultaneously. The distillation column reactor contains at least one fixed bed of acidic solid catalyst which is used to catalyze the conversion of sulfur-containing impurities to higher boiling products, and the separation of these higher boiling products is carried out by fractional distillation of the resulting reaction mixture within the distillation column reactor.

10 Suitable alkylating agents for use in the practice of this invention include both alcohols and olefins. However, olefins are generally preferred since they are usually more reactive than alcohols and can be used in the subject process under milder reaction conditions. Suitable olefins include cyclic olefins, substituted cyclic olefins, and olefins of formula I wherein R_1 is a hydrocarbyl group and each R_2 is

15 independently selected from the group consisting of hydrogen and hydrocarbyl groups. Preferably, R_1 is an alkyl group and each R_2 is independently selected from the group consisting of hydrogen and alkyl groups. Examples of suitable cyclic



olefins and substituted cyclic olefins include cyclopentene, 1-methylcyclopentene,

20 cyclohexene, 1-methylcyclohexene, 3-methylcyclohexene, 4-methylcyclohexene, cycloheptene, cyclooctene, and 4-methylcyclooctene. Examples of suitable olefins of the type of formula I include propene, 2-methylpropene, 1-butene, 2-butene, 2-methyl-1-butene, 3-methyl-1-butene, 2-methyl-2-butene, 2,3-dimethyl-1-butene, 3,3-dimethyl-1-butene, 2,3-dimethyl-2-butene, 2-ethyl-1-butene, 2-ethyl-3-methyl-

25 1-butene, 2,3,3-trimethyl-1-butene, 1-pentene, 2-pentene, 2-methyl-1-pentene, 3-methyl-1-pentene, 4-methyl-1-pentene, 2,4-dimethyl-1-pentene, 1-hexene, 2-hexene, 3-hexene, 1,3-hexadiene, 1,4-hexadiene, 1,5-hexadiene, 2,4-hexadiene, 1-heptene, 2-heptene, 3-heptene, 1-octene, 2-octene, 3-octene, and 4-octene.

Secondary and tertiary alcohols are highly preferred over primary alcohols because

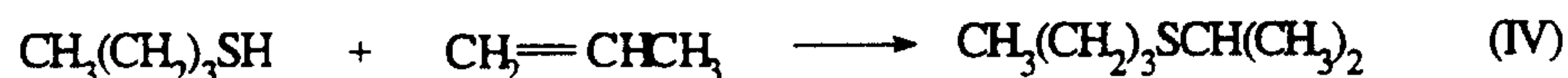
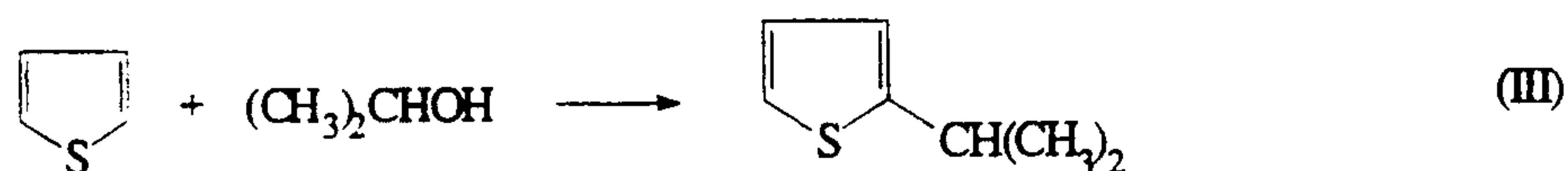
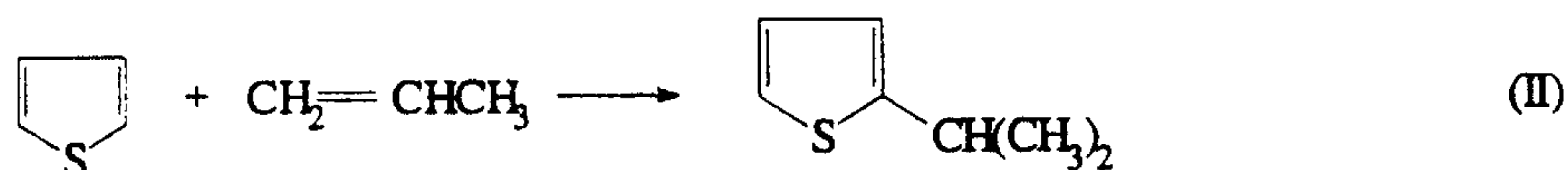
they are usually more reactive than the primary alcohols and can be used under milder reaction conditions. Materials such as ethylene, methanol and ethanol are less useful than most other olefins and alcohols in the practice of this invention because of their low reactivity.

5 Preferred alkylating agents will contain from about 3 to about 20 carbon atoms, and highly preferred alkylating agents will contain from about 3 to about 10 carbon atoms. The optimal number of carbon atoms in the alkylating agent will usually be determined by both the boiling point of the desired liquid hydrocarbon product and the boiling point of the sulfur-containing impurities in the feedstock. As
10 previously stated, sulfur-containing impurities are converted by the alkylating agents of this invention to sulfur-containing materials of a higher boiling point. However, alkylating agents which contain a large number of carbon atoms ordinarily result in a larger increase in the boiling point of these products than alkylating agents which contain a smaller number of carbon atoms. Accordingly, an alkylating agent must be
15 selected which will convert the sulfur-containing impurities to sulfur-containing products which are of a sufficiently high boiling point that they can be removed by distillation. For example, propylene may be a highly satisfactory alkylating agent for use in the preparation of a liquid hydrocarbon product of reduced sulfur content which has a maximum boiling point of 150° C but may not be satisfactory for a
20 liquid hydrocarbon product which has a maximum boiling point of 345° C.

In a preferred embodiment, a mixture of alkylating agents, such as a mixture of olefins or of alcohols, will be used in the practice of this invention. Such a mixture will often be cheaper and/or more readily available than a pure olefin or alcohol and will often yield results which are equally satisfactory to what can be
25 achieved with a pure olefin or alcohol as the alkylating agent. However, when it is desired to optimize the removal of specific sulfur-containing impurities from a specific hydrocarbon liquid, it may be advantageous to utilize a specific olefin or alcohol which is selected to: (1) convert the sulfur-containing impurities to products which have a sufficiently increased boiling point that they can be easily removed by
30 fractional distillation; and (2) permit easy removal of any unreacted alkylating agent, such as by distillation or by aqueous extraction, in the event that this material must be

removed. It will be appreciated, of course, that in many refinery applications of the invention, it will not be necessary to remove unreacted alkylating agent from the resulting distillate products of reduced sulfur content.

Although the invention is not to be so limited, it is believed that the principal
 5 mechanism for conversion of the sulfur-containing impurities to higher boiling products involves the alkylation of these impurities with the alkylating agent. By way of example, simple alkylation of an aromatic sulfur compound such as thiophene would yield an alkyl-substituted thiophene. This type of reaction is illustrated in equations II and III wherein the conversion of thiophene to 2-isopropylthiophene is
 10 illustrated using propene and 2-propanol, respectively, as the alkylating agent. It will be appreciated, of course, that monoalkylation of thiophene can take place either α or β to the sulfur atom, and that polyalkylation can also take place. The alkylation of a mercaptan would yield a sulfide, and this type of reaction is illustrated in equations IV and V wherein the conversion of *n*-butylmercaptan to isopropyl(*n*-butyl)sulfide is
 15 illustrated using propene and 2-propanol, respectively, as the alkylating agent.



The alkylation process results in the substitution of an alkyl group for a hydrogen atom in the sulfur-containing starting material and causes a corresponding
 20 increase in molecular weight over that of the starting material. The higher molecular weight of such an alkylation product is reflected by a higher boiling point relative to that of the starting material. For example, the conversion of thiophene to 2-*t*-butylthiophene by alkylation with 2-methylpropene results in the conversion of

thiophene, which has a boiling point of 84° C, to a product which has a boiling point of 164° C and can be easily removed from lower boiling material in the feedstock by fractional distillation. Conversion of thiophene to di-*t*-butylthiophene by dialkylation with 2-methylpropene results in a product which has an even higher boiling point of about 224° C. Alkylation with alkyl groups that add a large rather than a small number of carbon atoms is preferred since the products will have higher molecular weights and, accordingly, will usually have higher boiling points than products which are obtained through alkylation with the smaller alkyl groups.

Feedstocks which can be used in the practice of this invention include any liquid which is comprised of one or more hydrocarbons and contains organic sulfur compounds, such as mercaptans or aromatic sulfur compounds, as impurities. In addition, a major portion of the liquid should be comprised of hydrocarbons boiling below about 345° C and preferably below about 230° C. Suitable feedstocks include any of the various complex mixtures of hydrocarbons which are conventionally encountered in the refining of petroleum such as natural gas liquids, naphtha, light gas oils, heavy gas oils, and wide-cut gas oils, as well as hydrocarbon fractions derived from coal liquefaction and the processing of oil shale or tar sands. Preferred feedstocks include the liquid products that contain organic sulfur compounds as impurities which result from the catalytic cracking or coking of hydrocarbon feedstocks.

Aromatic hydrocarbons can be alkylated with the alkylating agents of this invention in the presence of the acidic catalysts of this invention. However, aromatic sulfur compounds and other typical sulfur-containing impurities are much more reactive than aromatic hydrocarbons. Accordingly, in the practice of this invention, it is possible to selectively alkylate the sulfur-containing impurities without significant alkylation of aromatic hydrocarbons which may be present in the feedstock. However, any competitive alkylation of aromatic hydrocarbons can be reduced by reducing the concentration of aromatic hydrocarbons in the feedstock. Accordingly, in a preferred embodiment of the invention, the feedstock will contain less than 50 weight percent of aromatic hydrocarbons. If desired, the feedstock can contain less than about 25 weight percent of aromatic hydrocarbons or even smaller amounts.

Catalytic cracking products are preferred feedstocks for use in the subject invention. Preferred feedstocks of this type include liquids which boil below about 345° C, such as light naphtha, heavy naphtha, distillate and light cycle oil. However, it will also be appreciated that the entire output of volatile products from a catalytic cracking process can be utilized as a feedstock in the subject invention. Catalytic cracking products are a desirable feedstock because they typically contain a relatively high olefin content, which makes it unnecessary to add any additional alkylating agent. In addition, aromatic sulfur compounds are frequently a major component of the sulfur-containing impurities in catalytic cracking products, and aromatic sulfur compounds are easily removed by means of the subject invention. For example, a typical light naphtha from the fluidized catalytic cracking of a petroleum derived gas oil can contain up to about 60% by weight of olefins and up to about 0.5% by weight of sulfur wherein most of the sulfur will be in the form of aromatic sulfur compounds. A preferred feedstock for use in the practice of this invention will be comprised of catalytic cracking products and will be additionally comprised of at least 1 weight percent of olefins. A highly preferred feedstock will be comprised of catalytic cracking products and will be additionally comprised of at least 5 weight percent of olefins. Such feedstocks can be a portion of the volatile products from a catalytic cracking process which is isolated by distillation.

The sulfur-containing impurities which can be removed by the process of this invention include but are not limited to mercaptans and aromatic sulfur compounds. Examples of aromatic sulfur compounds include thiophene, thiophene derivatives, benzothiophene, and benzothiophene derivatives, and examples of such thiophene derivatives include 2-methylthiophene, 3-methylthiophene, 2-ethylthiophene and 2,5-dimethylthiophene. In a preferred embodiment of the invention, the sulfur-containing impurities in the feedstock will be comprised of aromatic sulfur compounds and at least about 20% of these aromatic sulfur compounds are converted to higher boiling sulfur-containing material upon contact with the alkylating agent in the presence of the acid catalyst. If desired, at least about 50% or even more of these aromatic sulfur compounds can be converted to higher boiling sulfur-containing material in the practice of this invention.

Any acidic material which can catalyze the reaction of an olefin or alcohol with mercaptans, thiophene and thiophene derivatives can be used as a catalyst in the practice of this invention. Solid acidic catalysts are particularly desirable, and such materials include liquid acids which are supported on a solid substrate. The solid
5 acidic catalysts are generally preferred over liquid catalysts because of the ease with which the sulfur-containing feedstock can be contacted with such a material in a distillation column reactor. For example, the feedstock can simply be passed through one or more particulate fixed beds of solid acidic catalyst at a suitable temperature wherein the fixed beds are used as a column packing in a distillation column. By
10 insertion of the catalyst into the distillation column, the column becomes a distillation column reactor. As a consequence, the catalyzed conversion and fractional distillation of this invention can be carried out simultaneously by contacting the feedstock with the catalyst within the distillation column and fractionating the resulting products in the presence of the catalyst.

15 Catalysts which are suitable for use in the practice of the invention can be comprised of materials such as acidic polymeric resins, supported acids, and acidic inorganic oxides. Suitable acidic polymeric resins include the polymeric sulfonic acid resins which are well-known in the art and are commercially available.

Amberlyst[®] 35, a product produced by Rohm and Haas Co., is a typical example of
20 such a material.

Supported acids which are useful as catalysts include, but are not limited to, Brönsted acids (examples include phosphoric acid, sulfuric acid, boric acid, HF, fluorosulfonic acid, trifluoromethanesulfonic acid, and dihydroxyfluoroboric acid) and Lewis acids (examples include BF_3 , BCl_3 , AlCl_3 , AlBr_3 , FeCl_2 , FeCl_3 , ZnCl_2 ,
25 SbF_5 , SbCl_5 and combinations of AlCl_3 and HCl) which are supported on solids such as silica, alumina, silica-aluminas, zirconium oxide or clays. When supported liquid acids are employed, the supported catalysts are typically prepared by combining the desired liquid acid with the desired support and drying. Supported catalysts which are prepared by combining a phosphoric acid with a support are highly preferred and are
30 referred to herein as solid phosphoric acid catalysts. These catalysts are preferred

because they are both highly effective and low in cost. U.S. Patent No. 2,921,081 (Zimmerschied et al.) discloses the preparation of solid phosphoric acid catalysts by
5 combining a zirconium compound selected from the group consisting of zirconium oxide and the halides of zirconium with an acid selected from the group consisting of orthophosphoric acid, pyrophosphoric acid and triphosphoric acid. U.S. Patent No. 2,120,702 (Ipatieff et al.) discloses the preparation of solid phosphoric acid catalysts by combining a phosphoric acid with a siliceous material. Finally, British Patent No.
10 863,539 also discloses the preparation of a solid phosphoric acid catalyst by depositing a phosphoric acid on a solid siliceous material such as diatomaceous earth or kieselguhr.

Acidic inorganic oxides which are useful as catalysts include, but are not limited to, aluminas, silica-aluminas, natural and synthetic pillared clays, and natural
15 and synthetic zeolites such as faujasites, mordenites, L; omega, X, Y, beta, and ZSM zeolites. Highly suitable zeolites include beta, Y, ZSM-3, ZSM-4, ZSM-5, ZSM-18, and ZSM-20. If desired, the zeolites can be incorporated into an inorganic oxide matrix material such as a silica-alumina. Indeed, equilibrium cracking catalyst can be used as the acid catalyst in the practice of this invention.

20 Catalysts can comprise mixtures of different materials, such as a Lewis acid (examples include BF_3 , BCl_3 , SbF_5 , and AlCl_3), a nonzeolitic solid inorganic oxide (such as silica, alumina and silica-alumina), and a large-pore crystalline molecular sieve (examples include zeolites, pillared clays and aluminophosphates).

Feedstocks which are used in the practice of this invention will occasionally
25 contain nitrogen-containing organic compounds as impurities in addition to the sulfur-containing impurities. Many of the typical nitrogen-containing impurities are organic bases and, in some instances, can cause deactivation of the acid catalyst by reaction with it. In the event that such deactivation is observed, it can be prevented by removal of the basic nitrogen-containing impurities from the feedstock before it is
30 contacted with the acid catalyst.

The basic nitrogen-containing impurities can be removed from the feedstock by any conventional method. Such methods typically involve treatment with an acidic material, and conventional methods include procedures such as washing with an aqueous solution of an acid and the use of a guard bed which is positioned in front of the acid catalyst. Examples of effective guard beds include but are not limited to A-zeolite, Y-zeolite, L-zeolite, mordenite, fluorided alumina, fresh cracking catalyst, equilibrium cracking catalyst and acidic polymeric resins. If a guard bed technique is employed, it is often desirable to use two guard beds in such a manner that one guard bed can be regenerated while the other is being used to pretreat the feedstock and protect the acid catalyst. If a cracking catalyst is utilized to remove basic nitrogen-containing impurities, such a material can be regenerated in the regenerator of a catalytic cracking unit when it has become deactivated with respect to its ability to remove such impurities. If an acid wash is used to remove basic nitrogen-containing compounds, the feedstock will be treated with an aqueous solution of a suitable acid. Suitable acids for such use include, but are not limited to, hydrochloric acid, sulfuric acid and acetic acid. The concentration of acid in the aqueous solution is not critical, but is conveniently chosen to be in the range from about 0.5 to about 30% by weight.

In the practice of this invention, the feedstock which contains sulfur-containing impurities is contacted with the acid catalyst at a temperature and for a period of time which are effective to result in conversion of at least a portion of the sulfur-containing impurities to a higher boiling sulfur-containing material. Desirably, the contacting temperature will be in excess of about 50° C, preferably in excess of 100° C, and more preferably in excess of 125° C. The contacting will generally be carried out at a temperature in the range from about 50° to about 350° C, preferably from about 100° to about 350° C, and more preferably from about 125° to about 250° C. It will be appreciated, of course, that the optimum temperature will be a function of the acid catalyst used, the alkylating agent or agents selected, and the nature of the sulfur-containing impurities that are to be removed from the feedstock. It will also be appreciated that the pressure at which the distillation column reactor is operated can be used to control both the distillation temperature and the temperature at which the catalyst is contacted by the feedstock in the distillation column reactor.

By increasing the pressure, a higher temperature will be required to effect fractional distillation in the distillation column reactor.

The sulfur-containing impurities are highly reactive and can be selectively converted to sulfur-containing products of higher boiling point by reaction with the alkylating agent of this invention. Accordingly, the feedstock can be contacted with the acid catalyst under conditions which are sufficiently mild that most hydrocarbons will be substantially unaffected. For example, aromatic hydrocarbons will be substantially unaffected and significant olefin polymerization will not take place. In the case of a naphtha feedstock from a catalytic cracking process, this means that sulfur-containing impurities can be removed without significantly affecting the octane of the naphtha. However, if desired, the temperature and concentration of alkylating agent can be increased to a point where significant alkylation of aromatic hydrocarbons can also be produced. If, for example, the feedstock contains both sulfur-containing impurities and modest amounts of benzene, the reaction conditions can be selected so that the sulfur-containing impurities are converted to higher boiling products and a major portion of the benzene is converted to alkylation products.

Any desired amount of alkylating agent can be used in the practice of this invention. However, relatively large amounts of alkylating agent relative to the amount of sulfur-containing impurities will promote a rapid and complete conversion of the impurities to higher boiling sulfur-containing products upon contact with the acid catalyst. Before contacting with the acid catalyst, the composition of the feedstock is desirably adjusted so that it contains an amount of alkylating agent which is at least equal on a molar basis to that of the organic sulfur compounds in the feedstock. If desired, the molar ratio of alkylating agent to organic sulfur compounds can be at least 5 or even larger.

In the practice of this invention, the feedstock can be contacted with the acid catalyst at any suitable pressure. However, pressures in the range from about 0.01 to about 200 atmospheres are desirable, and a pressure in the range from about 1 to about 100 atmospheres is preferred. The temperature and pressure at which the feedstock is contacted with the solid acidic catalyst in the distillation column reactor

are selected which are effective to: (1) convert at least a portion of the sulfur-containing impurities in the feedstock to a sulfur-containing material of higher boiling point; and (2) permit fractional distillation of the process stream in the presence of the catalyst.

5 The acidic solid catalyst can be placed in the distillation column reactor in any conventional manner and can be located in a single contacting zone or a plurality of contacting zones within the reactor. For example, the catalyst can be placed on the trays of a conventional distillation column or within at least one conduit which provides a path for the flow of liquid from one zone to another within the distillation
10 column reactor. If desired, such conduits can be located external to the main structure of the distillation column reactor so that each is accessible and can be independently taken out of service for replacement of the acidic solid catalyst without shutting down the distillation column reactor. As noted, it will usually be desirable to use at least two such conduits which contain acidic solid catalyst so that
15 deactivated or spent catalyst in one conduit can be replaced or regenerated while the additional conduit or conduits permit continued operation of the distillation column reactor. Alternatively, the conduits can take the form of downcomers which connect adjacent trays and provide a path for the flow of liquid within a conventional distillation column. The use of downcomers to hold the catalyst in a distillation
20 column reactor is described in U.S. Patents No. 3,629,478 (Haunschild) and 3,634,534 (Haunschild). In a preferred embodiment, the catalyst is used as a packing for the distillation column, and fractionation is carried out, at least in part, in the presence of the catalyst. For example, the solid acidic catalyst can be in the form of pellets, rods, rings, saddles, balls, irregular pieces, sheets, tubes, spirals, packed in
25 bags, or deposited on grills or screens. The use of a catalyst as a packing material in a distillation column reactor is described in U.S. Patents Nos. 4,232,177 (Smith), 4,242,530 (Smith), 4,307,254 (Smith) and 4,336,407 (Smith).

Desirably, the solid acidic catalyst will be used in a physical form which will
30 permit a rapid and effective contacting with the feedstock and alkylating agent. Although the invention is not to be so limited, it is preferred that the catalyst be in

particulate form wherein the largest dimension of the particles has an average value which is in the range from about 0.1 mm to about 2 cm. For example, substantially spherical beads of catalyst can be used which have an average diameter from about 0.1 mm to about 2 cm. Alternatively, the catalyst can be used in the form of rods
5 which have a diameter in the range from about 0.1 mm to about 1 cm and a length in the range from about 0.2 mm to about 2 cm.

This invention represents a method for concentrating the sulfur-containing impurities of a hydrocarbon feedstock into a high boiling fraction which is separated by fractional distillation. As a result of concentration, the sulfur can be disposed of
10 more easily and at lower cost, and any conventional method can be used for this disposal. For example, the resulting high sulfur content material can be blended into heavy fuels where the sulfur content will be less objectionable. Alternatively, this high sulfur content material can be efficiently hydrotreated at relatively low cost because of its reduced volume relative to that of the original feedstock.

15 A highly preferred embodiment of this invention comprises its use to remove sulfur-containing impurities from the hydrocarbon products that occur in the products from the fluidized catalytic cracking of hydrocarbon feedstocks which contain sulfur-containing impurities. The catalytic cracking of heavy mineral oil fractions is one of the major refining operations employed in the conversion of crude oils to desirable
20 fuel products such as high octane gasoline fuels which are used in spark-ignition internal combustion engines. In fluidized catalytic cracking processes, high molecular weight hydrocarbon liquids or vapors are contacted with hot, finely-divided, solid catalyst particles, typically in a fluidized bed reactor or in an elongated riser reactor, and the catalyst-hydrocarbon mixture is maintained at an elevated
25 temperature in a fluidized or dispersed state for a period of time sufficient to effect the desired degree of cracking to low molecular weight hydrocarbons of the kind typically present in motor gasoline and distillate fuels.

Conversion of a selected hydrocarbon feedstock in a fluidized catalytic cracking process is effected by contact with a cracking catalyst in a reaction zone at
30 conversion temperature and at a fluidizing velocity which limits the conversion time to not more than about ten seconds. Conversion temperatures are desirably in the

range from about 430° to about 700° C and preferably from about 450° to about 650° C. Effluent from the reaction zone, comprising hydrocarbon vapors and cracking catalyst containing a deactivating quantity of carbonaceous material or coke, is then transferred to a separation zone. Hydrocarbon vapors are separated from spent
5 cracking catalyst in the separation zone and are conveyed to a fractionator for the separation of these materials on the basis of boiling point. These volatile hydrocarbon products typically enter the fractionator at a temperature in the range from about 430° to about 650° C and supply all of the heat necessary for fractionation.

10 In the catalytic cracking of hydrocarbons, some non-volatile carbonaceous material or coke is deposited on the catalyst particles. As coke builds up on the cracking catalyst, the activity of the catalyst for cracking and the selectivity of the catalyst for producing gasoline blending stocks diminishes. The catalyst can, however, recover a major portion of its original capabilities by removal of most of
15 the coke from it. This is carried out by burning the coke deposits from the catalyst with a molecular oxygen-containing regeneration gas, such as air, in a regeneration zone or regenerator.

A wide variety of process conditions can be used in the practice of the fluidized catalytic cracking process. In the usual case where a gas oil feedstock is
20 employed, the throughput ratio, or volume ratio of total feed to fresh feed, can vary from about 1.0 to about 3.0. Conversion level can vary from about 40% to about 100% where conversion is defined as the percentage reduction of hydrocarbons boiling above 221° C at atmospheric pressure by formation of lighter materials or coke. The weight ratio of catalyst to oil in the reactor can vary within the range from
25 about 2 to about 20 so that the fluidized dispersion will have a density in the range from about 15 to about 320 kilograms per cubic meter. Fluidizing velocity can be in the range from about 3.0 to about 30 meters per second.

A suitable hydrocarbon feedstock for use in a fluidized catalytic cracking process in accordance with this invention can contain from about 0.2 to about 6.0
30 weight percent of sulfur in the form of organic sulfur compounds. Suitable feedstocks include, but are not limited to, sulfur-containing petroleum fractions such

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as light gas oils, heavy gas oils, wide-cut gas oils, vacuum gas oils, naphthas, decanted oils, residual fractions and cycle oils derived from any of these as well as sulfur-containing hydrocarbon fractions derived from synthetic oils, coal liquefaction and the processing of oil shale and tar sands. Any of these feedstocks can be
5 employed either singly or in any desired combination.

One embodiment of the present invention involves passing volatile products from the catalytic cracking of a sulfur-containing feedstock to a distillation column reactor wherein: (1) the volatile products are contacted with an acidic solid catalyst within the distillation column reactor under conditions which are effective to convert
10 at least a portion of their sulfur-containing impurities to a sulfur-containing material of higher boiling point; (2) the products resulting from contact with said catalyst are fractionated within the distillation column reactor; (3) at least a portion of the sulfur-containing material of higher boiling point is separated as a component of a high boiling fraction or bottoms from the distillation column reactor; and (4) a product of
15 reduced sulfur content relative to that of the feedstock to the distillation column reactor is separated as a lower boiling fraction or overhead from the reactor.

The following examples are intended only to illustrate the invention and are not to be construed as imposing limitations on the invention.

20

EXAMPLE I

Polymeric sulfonic acid resin.-- A macroreticular, polymeric, sulfonic acid resin was obtained from the Rohm and Haas Company which is sold under the name Amberlyst[®] 35 Wet. This material was provided in the form of spherical beads
25 which have a particle size in the range from 0.4 to 1.2 mm and has the following properties: (1) a concentration of acid sites equal to 5.4 meq/g; (2) a moisture content of 56%; (3) a porosity of 0.35 cc/g; (4) an average pore diameter of 300 Å; and a surface area of 44 m²/g. The resin was used as received and is identified herein as Catalyst A.

30

EXAMPLE II

Solid phosphoric acid alkylation catalyst on kieselguhr.— A solid phosphoric acid catalyst on kieselguhr was obtained from UOP which is sold under the name SPA-2. This material was provided in the form of a cylindrical extrudate having a nominal diameter of 4.75 mm and has the following properties: (1) a loaded density of 0.93 g/cm³; (2) a free phosphoric acid content, calculated as P₂O₅, of 16 to 20 wt. %; and (3) a nominal total phosphoric acid content, calculated as P₂O₅, of 60 wt. %. The catalyst was crushed and sized to 12 to 20 mesh size (U.S. Sieve Series) before use, and is identified herein as Catalyst B.

EXAMPLE III

Preparation of ZSM-5 Zeolite.— A solution of 1.70 kg of sodium hydroxide, 26.8 kg of tetrapropyl ammonium bromide, 2.14 kg of sodium aluminate, and 43.5 kg of silica sol (Ludox HS-40^{*} manufactured by E.I. duPont de Nemours Co. Inc.) in 18.0 kg of distilled water was prepared in an autoclave. The autoclave was sealed and maintained at a temperature of about 149° C, autogenous pressure, and a mixer speed of about 60 rpm for a period of about 120 hours. The slurry was filtered and washed, and the resulting filter cake was dried in an oven at 121° C for a period of 16 hours. The dried filter cake was then calcined at 538° C for a period of 4 hours. The calcined material was ion exchanged three times with ammonium nitrate in water by heating, under reflux, to a temperature of about 85° C for a period of one hour, cooling while stirring for 2 hours, filtering, and washing with 1 liter of water, and reexchanging. The resulting solid was washed with 4 liters of water, dried in an oven at 121° C for a period of 4 hours and calcined at 556° C for 4 hours to yield ZSM-5 zeolite as a powder.

Preparation of alkylation catalyst comprised of ZSM-5 zeolite in an alumina matrix.— A 166 g portion of the above-described ZSM-5 zeolite was mixed with 125 g of Catapal SB^{*} alumina (alpha-alumina monohydrate manufactured by Vista). The mixture of solids was added to 600 g of distilled water, mixed well and dried in an

^{*}Trademark

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oven at 121° C for a period of 16 hours. The solids were then moistened with distilled water and extruded as a cylindrical extrudate having a diameter of 1.6 mm. The extrudate was dried at 121° C for 16 hours in a forced air oven and calcined at 538° C for 4 hours. The resulting material was crushed and sized to 12-20 mesh size (U.S. Sieve Series). This material, which is comprised of ZSM-5 zeolite in an alumina matrix, is identified herein as Catalyst C.

EXAMPLE IV

10 Preparation of beta zeolite.-- A solution of 0.15 kg of sodium hydroxide, 22.5 kg of tetraethyl ammonium hydroxide, 0.90 kg of sodium aluminate, and 36.6 kg of silica sol (Ludox HS-40 manufactured by E.I. duPont de Nemours Co. Inc.) in 22.5 kg of distilled water was prepared in an autoclave. The autoclave was sealed and maintained at a temperature of about 149° C, autogenous pressure, and a mixer speed of about 60 rpm for a period of about 96 hours. The slurry was filtered and washed, and the filter cake was dried in an oven at 121° C for a period of 16 hours. The resulting solid was ion exchanged three times with ammonium nitrate in water by heating, under reflux, to a temperature of about 60° C for a period of three hours, cooling while stirring for 2 hours, decanting and reexchanging. Upon drying in an oven at 121° C for a period of 4 hours, the desired beta zeolite was obtained as a powder.

20 Preparation of alkylation catalyst comprised of beta zeolite in an alumina matrix.-- An 89.82 g portion of the above-described beta zeolite powder was mixed with 40 grams of Catapal SB alumina (alpha-alumina monohydrate manufactured by Vista). The mixture of solids was added to 300 g of distilled water, mixed well and dried at 121° C for 16 hours in a forced air oven. The solids were then moistened with distilled water and extruded as a cylindrical extrudate having a diameter of 1.6 mm. The extrudate was dried at 121° C for 16 hours in a forced air oven and calcined at 538° C for 3 hours. The resulting material was crushed and sized to 12 to 20 mesh size (U.S. Sieve Series). This material, which is comprised of beta zeolite in an alumina matrix, is identified herein as Catalyst D.

EXAMPLE V

Preparation of silica-alumina alkylation catalyst.-- A 75.0 g portion of
5 tetraethyl orthosilicate and 500 g of *n*-hexane were mixed with 375 g of a low silica
alumina which had a surface area of 338 m²/g and was in the form of a cylindrical
extrudate having a diameter of 1.3 mm (manufactured by Haldor-Topsoe). The *n*-
hexane was allowed to evaporate at room temperature. The resulting material was
dried in a forced air oven at 100° C for 16 hours and then calcined at 510° C for 8
10 hours. The calcined material was impregnated with a solution containing 150 g of
ammonium nitrate in 1000 ml of water, allowed to stand for 3 days, dried in a forced
air oven at 100° C for 16 hours and calcined at 538° C for 5 hours. The resulting
material, which is comprised of silica-alumina, is identified herein as Catalyst E.

15

EXAMPLE VI

Preparation of alkylation catalyst comprised of Y zeolite in an alumina
matrix.-- A 100.12 g portion of LZY-82 zeolite powder (LZY-82 is an ultrastable Y
zeolite manufactured by Union Carbide) was dispersed in 553.71 g of PHF alumina
20 sol (manufactured by Criterion Catalyst Company), and the dispersion was dried in a
forced air oven at 121° C for 16 hours. The resulting material was moistened with
distilled water and was then extruded as a cylindrical extrudate having a diameter of
1.6 mm. The extrudate was dried at 121° C for 16 hours in a forced air oven and then
calcined at 538° C for 3 hours. The resulting material was crushed and sized to 12-20
25 mesh size (U.S. Sieve Series). This material, which is comprised of LZY-82 zeolite
in an alumina matrix, is identified herein as Catalyst F.

EXAMPLE VII

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The data which are set forth below for the sulfur content of samples as a
function of boiling point were obtained using a gas chromatograph equipped with a

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flame ionization detector, a wide-bore fused-silica capillary column, direct injector, and a sulfur chemiluminescence detector. The analytical method is based on a retention time versus boiling point calibration of the chromatographic system.

The ability of various acidic solid catalysts to convert the sulfur-containing impurities in a hydrocarbon feedstock to sulfur-containing products of a higher boiling point was evaluated using the following feedstocks:

Stabilized Heavy Naphtha-- This material, boiling over the range from -21° to about 249° C, was obtained by: (1) partial stripping of the C₄ hydrocarbons from a heavy naphtha that was produced by the fluidized catalytic cracking of a gas oil feedstock which contained sulfur-containing impurities; and (2) treatment with caustic to remove mercaptans. Analysis of the stabilized heavy naphtha using a multicolumn gas chromatographic technique showed it to contain on a weight basis: 4% paraffins, 18% isoparaffins, 15% olefins, 15% naphthenes, 45% aromatics, and 3% unidentified C₁₃₊ high boiling material. The total sulfur content of the stabilized heavy naphtha, as determined by X-ray fluorescence spectroscopy, was 730 ppm. This sulfur content, as a function of boiling point, is set forth in Table I. The principal sulfur-containing impurities were identified chromatographically by discrete peak identification, and these results are set forth in Table II.

Except where otherwise stated, experiments with the stabilized heavy naphtha feedstock were carried out using the following procedure. A 7 g portion of the selected catalyst was packed into a 9.5 mm internal diameter tubular reactor which was constructed of stainless steel and held in a vertical orientation. The catalyst bed was placed in the reactor between beds of silicon carbide which were held in place with plugs of quartz wool. Operating temperatures were varied from 93° to 204° C, and the pressure within the reactor was maintained at 75 to 85 atm. The feedstock was introduced at the top of the reactor and was passed downward through the catalyst bed at a space velocity of 1-2 LHSV. A syringe pump was used to inject the feedstock into the reactor. The experimental apparatus included a back-pressure regulator which was downstream from the reactor and was positioned at a higher

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TABLE I. Sulfur Content of Heavy Naphtha Feedstock
as a Function of Boiling Point.

Amount of Sulfur in Higher		
	Boiling Fractions, wt. %	Temperature, ° C
5	95	113
	90	114
	85	132
	80	139
10	75	142
	70	163
	65	168
	60	182
15	55	201
	50	219
	45	220
	40	220
20	35	226
	30	227
	25	229
	20	232
25	15	233
	10	247
	5	264
	1	365

elevation than the top of the catalyst bed in order to ensure that the catalyst bed was completely filled with liquid.

30 Synthetic Feedstocks.-- Two synthetic feedstocks, one of low olefin content and the other of high olefin content, were prepared by blending model compounds

TABLE II. Principal Sulfur-Containing Impurities In
Stabilized Heavy Naphtha Feedstock.

5	Component	Component Concentration, ppm
	Thiophene	18
	2-Methylthiophene	33
	2-Ethylthiophene	15
	3-Ethylthiophene	21
10	Benzothiophene	111
	Tetrahydrothiophene	4
	2,5-Dimethylthiophene	11

15 which were selected to represent the principal groups of organic compounds which
are found in a typical heavy naphtha which is produced by the fluidized catalytic
cracking process. The proportions of these principal groups in the high olefin content
synthetic feedstock are typical of what would be expected in such a heavy naphtha
from a fluidized catalytic cracking process. The synthetic feedstocks are very similar
20 in composition except that the low olefin content synthetic feedstock contains very
little olefin. The compositions of these synthetic feedstocks are set forth in Table III.

Experiments with the synthetic feedstocks were carried out using the
following procedure. A 10 cm³ volume of the selected catalyst was packed into a
1.43 cm internal diameter tubular reactor which was constructed of stainless steel and
25 held in a vertical orientation. The catalyst bed was placed in the reactor between
beds of alpha alumina which were held in place with plugs of quartz wool. Prior to
use, catalysts C, D, E and F were activated in the reactor at a temperature of 399° C
in a stream of nitrogen at a flow rate of 200 cm³/min for one hour. Operating
temperatures were varied from 93° to 204° C, and the pressure within the reactor was
30 maintained at either 17 or 54 atm. The feedstock was introduced at the bottom of the
reactor and was passed upward through the catalyst bed.

TABLE III. Composition of Synthetic Feedstocks.

5	Component	Component Concentration, wt. %	
		High Olefin	Low Olefin
		Content Feedstock	Content Feedstock
	2-Propanethiol	0.39	0.22
	1-Hexene	4.10	0.38
	Methylcyclopentane	8.54	6.81
	2,3-Dimethyl-2-butene	4.17	0.44
10	Benzene	10.32	13.44
	Thiophene	0.49	0.41
	1-Heptene	4.63	0.56
	<i>n</i> -Heptane	43.37	47.86
	Toluene	22.53	28.74
15	2-Methylthiophene	0.45	0.50
	Isopropyl sulfide	0.48	0.29

EXAMPLE VIII

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The stabilized heavy naphtha feedstock was blended with a mixed C₃/C₄ stream (containing, on a weight basis, 55% propane, 27% propene, 9.5% 2-butene, 6% 1-butene and 2.5% 2-methylpropene) at a 1.0 volume ratio of C₃/C₄ stream to naphtha. The resulting blend was contacted, as described above, with Catalyst B
 25 (solid phosphoric acid catalyst on kieselguhr) at a pressure of 85 atm and a space velocity of 2 LHSV. The effect of temperature was evaluated in a series of three experiments by carrying out the contacting at temperatures of 93°, 149° and 204° C. The distribution of sulfur content as a function of boiling point in the feedstock and in the products obtained at reaction temperatures of 93°, 149° and 204° C is set forth
 30 in FIG. 1 (boiling point is plotted as a function of the percentage of the total sulfur

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content which is present in higher boiling fractions). These results demonstrate that, at a reaction temperature of either 149° or 204° C, the sulfur-containing impurities in the feedstock are converted to higher boiling sulfur-containing products, and that this increase in boiling point is about 25° C over the entire boiling range of the naphtha.

- 5 In contrast, there is relatively little conversion of the sulfur-containing impurities to higher boiling products at a reaction temperature of 93° C.

EXAMPLE IX

- 10 The stabilized heavy naphtha was contacted with Catalyst B (solid phosphoric acid catalyst on kieselguhr) at a pressure of 75 atm, a temperature of 204° C and a space velocity of 1 LHSV. The distribution of sulfur content as a function of boiling point in the feedstock and in the product is set forth in FIG. 2 (boiling point is plotted as a function of the percentage of the total sulfur content which is present in higher
- 15 boiling fractions). These results demonstrate that the olefin content of this heavy naphtha feedstock from a catalytic cracking process is sufficiently high to permit conversion of the sulfur-containing impurities to higher boiling sulfur-containing products. It will also be noted that 30% of the sulfur in the product boils above 288° C in contrast to only about 20% in the product which was obtained when the
- 20 feedstock was blended with a mixture of propene and butenes as described in Example VIII. It is believed that the higher molecular weight olefins present in the feedstock yield sulfur-containing products which are higher in boiling point than the products that are obtained when large amounts of C₃ and C₄ olefins are added to the feedstock as in Example VIII.

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EXAMPLE X

- A low olefin content synthetic feedstock having the composition which is set forth in Table III was contacted, as described above, with Catalyst B (solid
- 30 phosphoric acid catalyst on kieselguhr) at a pressure of 54 atm, a temperature of 204° C, and a space velocity of 2 LHSV. The distribution of sulfur content as a function

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of boiling point in the low olefin content synthetic feedstock is set forth in FIG. 3a (boiling point is plotted as a function of the percentage of the total sulfur content which is present in higher boiling fractions). FIG. 3b sets forth the sulfur distribution as a function of boiling point in the product from this feedstock. Comparison of
5 FIGS. 3a and 3b, demonstrates that there was very little conversion of the sulfur-containing components of the synthetic feedstock to higher boiling sulfur-containing products.

EXAMPLE XI

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A high olefin content synthetic feedstock having the composition which is set forth in Table III was contacted, as described above, with Catalyst B (solid phosphoric acid catalyst on kieselguhr) at a pressure of 54 atm, a temperature of 204° C, and a space velocity of 2 LHSV. The distribution of sulfur content as a function
15 of boiling point in the high olefin content synthetic feedstock is set forth in FIG. 4a (boiling point is plotted as a function of the percentage of the total sulfur content which is present in higher boiling fractions). FIG. 4b sets forth the sulfur distribution as a function of boiling point in the product from this feedstock. Comparison of FIGS. 4a and 4b demonstrates that there was substantial conversion of the sulfur-
20 containing components of the synthetic feedstock to higher boiling sulfur-containing products. Except for olefin content, the high olefin content synthetic feedstock of this experiment has a composition which is very similar to that of the low olefin content synthetic feedstock of Example X above. A comparison of the results of this
25 experiment with those of Example X will demonstrate that there is very little conversion of the sulfur-containing feedstock components in the absence of the olefins.

EXAMPLE XII

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Catalysts A, B, C, D, E and F, which are described in detail above and whose properties are briefly summarized in Table IV, were each tested as described above at

a pressure of 17 atm, a temperature of 204° C, and a space velocity of 2 LHSV with the following two feedstocks: (1) a high olefin content synthetic feedstock having the composition which is set forth in Table III; and (2) the same high olefin content synthetic feedstock after blending with propene at a 0.25 volume ratio of propene to

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TABLE IV. Catalyst Characteristics.

	Catalyst	Type	Pore Size	Relative Acidity
10	A	Amberlyst [®] 35 Wet	>6Å	Medium
	B	Solid phosphoric acid on kieselguhr	>6Å	Strong
	C	ZSM-5 zeolite in alumina matrix	<6Å	Strong
15	D	Beta zeolite in alumina matrix	>6Å	Strong
	E	Silica-alumina	>6Å	Medium
	F	Y zeolite in alumina matrix	>6Å	Strong

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synthetic feedstock. In each such test, the conversion of thiophenes (thiophene and 2-methylthiophene) to other materials was determined from an analysis of the resulting product for thiophene and methylthiophene content. The results of these tests are set forth in FIG. 5. These results suggest that the conversion of thiophene and 2-methylthiophene in the absence of added propene is highest over the most acidic catalysts which have a pore size greater than about 6Å (Catalysts B, D and F). Although the invention is not to be so limited, these results suggest that the size of the alkylated product may be too large to form in the pores of the catalyst which has a pore size smaller than about 6Å (Catalyst C) and that the acidity of the moderately acidic catalysts (Catalysts A and E) may be insufficient to fully activate the C₆ and

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C₇ olefins of the high olefin content synthetic feedstock. However, when propene is added to the synthetic feedstock, the conversion of thiophene and 2-methylthiophene over both Catalyst C (<6Å pore size) and the moderately acidic Catalyst E is approximately doubled.

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EXAMPLE XIII

A high olefin content synthetic feedstock having the composition which is set forth in Table III was blended with propene at a 0.13 volume ratio of propene to synthetic feedstock, and the resulting blend was contacted with Catalyst B (solid phosphoric acid catalyst on kieselguhr) at a pressure of 54 atm, a temperature of 149° C, and a space velocity of 2 LHSV. This experiment was then repeated at a temperature of 204° C. In each experiment, the conversion of thiophenes (thiophene and 2-methylthiophene), benzene, and toluene to other products was determined from an analysis of the resulting product. At 149° C, the conversion of thiophenes (thiophene and 2-methylthiophene), benzene and toluene was 54%, 15% and 7%, respectively. At 204° C, the conversion of thiophenes (thiophene and 2-methylthiophene), benzene and toluene was 73%, 36% and 26%, respectively. Accordingly, under these conditions, the aromatic sulfur compounds (thiophene and 2-methylthiophene) are converted in preference to the aromatic hydrocarbons (benzene and toluene).

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EXAMPLE XIV

In a series of tests, the stabilized heavy naphtha was blended with varying amounts of a mixed C₃/C₄ stream (containing, on a weight basis, 55% propane, 27% propene, 9.5% 2-butene, 6% 1-butene, 2.5% 2-methylpropene, and 1500 ppm 2-propanol), and the various blends were contacted with Catalyst B (solid phosphoric acid catalyst on kieselguhr) at a pressure of 82 atm, a temperature of 204° C, and a space velocity of 1 LHSV. The ratio by volume of the mixed C₃/C₄ stream to naphtha used in these tests is set forth in Table V. The product of each test was

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analyzed with respect to: (1) the conversion of sulfur-containing impurities to higher boiling sulfur-containing material; and (2) its content of benzene and cumene. These analytical results are also set forth in Table V. The ratio of cumene to benzene in the product is an indicator of the extent to which the aromatic hydrocarbons in the naphtha feedstock have been alkylated under the conditions of each test (the cumene

TABLE V. Effect of Varying Amounts of Mixed C₃/C₄ Olefins on Alkylation of Heavy Naphtha.

Run No.	Volume Ratio of C ₃ /C ₄ Stream to Naphtha	Sulfur in Products Boiling above 260° C, wt. %	Weight Ratio of Cumene to Benzene
1	0.02	23	0.01
2	0.03	25	0.03
3	0.14	23	0.04
4	0.24	25	0.14
5	0.50	36	0.83
6	1.0	42	1.6

is formed by alkylation of benzene in the naphtha feedstock with propene from the mixed C₃/C₄ stream). For comparison purposes, the feedstock had a 0.01 weight ratio of cumene to benzene and 5 weight percent of its sulfur content had a boiling point above 260° C. The results indicate that the sulfur-containing impurities can be converted to higher boiling sulfur-containing material in a selective manner which does not cause significant alkylation of the aromatic hydrocarbons which are also in the feedstock.

EXAMPLE XV

The removal of nitrogen-containing impurities from the stabilized heavy naphtha feedstock by washing with an aqueous sulfuric acid solution was evaluated

in a series of experiments wherein the sulfuric acid concentration of the aqueous solution was varied. In each experiment, about 80 g of the aqueous sulfuric acid solution was added to about 64 g of the stabilized heavy naphtha in a small separatory funnel, and the resulting mixture was shaken by hand. The aqueous and organic layers were then allowed to separate, and the lower aqueous layer was

TABLE VI. Removal of Nitrogen-Containing Impurities
from Heavy Naphtha with Aqueous Sulfuric Acid.

Composition	H ₂ SO ₄ Content of Aqueous Acid used for Treatment, wt %	Basic Nitrogen Content of Composition, ppm
Untreated Feedstock	---	82
Treated Feedstock	2.7	<5
"	0.27	<5
"	0.14	<5
"	0.027	12

removed. The organic layer was then washed three times in the separatory funnel by the same procedure except using about 100 g portions of distilled water in place of the aqueous acid. The resulting hydrocarbon layer was analyzed for basic nitrogen content, and the results are set forth in Table VI.

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EXAMPLE XVI

The removal of nitrogen-containing impurities from a feedstock which consisted of blend of light and heavy naphthas by treatment with a solid adsorbent was evaluated in a series of experiments wherein a variety of adsorbents were employed. The feedstock was a blend of 20 vol % of a light naphtha (containing <5 ppm of basic nitrogen and boiling in the range from about -21° to about 95° C) with 80 vol % of the stabilized heavy naphtha. In each experiment, a 100 cm³ portion of

the feedstock was mixed with a 6.6 g portion of a solid adsorbent which had been calcined for 3 hours at 538° C. The mixture was shaken and then allowed to stand at room temperature for about 72 hours. The resulting treated feedstock was analyzed for basic nitrogen content, and these results are set forth in Table VII.

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TABLE VII. Removal of Nitrogen-Containing Impurities from Naphtha by Treatment with Various Adsorbents.

Composition	Adsorbent used for Treatment	Basic Nitrogen
		Content of Composition, ppm
Untreated Feedstock	---	65
Treated Feedstock	13X Molecular Sieve	<5
"	Fresh Fluid Catalytic Cracking Catalyst ¹	<5
"	Equilibrated Fluid Catalytic Cracking Catalyst ²	9
"	Activated Alumina ³	15

10 ¹ REDUXION[®] cracking catalyst (manufactured by Engelhard Corporation).

² OCTISIV[®] cracking catalyst (manufactured by Engelhard Corporation).

³ Chromatographic grade.

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EXAMPLE XVII

Basic nitrogen-containing impurities in the untreated feedstock of Example XVI were removed by washing the feedstock with an aqueous sulfuric acid solution which contained 15 wt% H₂SO₄. Analysis showed that the basic nitrogen content of

the acid washed feedstock was below the analytical detection limit of 5 ppm. This acid washed feedstock was contacted with 10 cm³ Catalyst B (solid phosphoric acid catalyst on kieselguhr) at a pressure of 54 atm, a temperature of 204° C and a space velocity of 1 LHSV in accordance with the procedure described in Example VII for the synthetic feedstocks. The contacting was carried out continuously over the same batch of catalyst, and the conversion of thiophene and methylthiophene to higher boiling materials is shown as a function of time in FIG. 6. This experiment was then repeated using the untreated feedstock of Example XVI, and the conversion of thiophene and methylthiophene to higher boiling materials is shown in FIG. 6. The results in FIG. 6 demonstrates that the conversion of thiophene and methylthiophene remained essentially unchanged over a period of 55 days when the acid washed feedstock was used. In contrast, the conversion of thiophene and methylthiophene dropped from about 85% to about 25% over a period of 13 days when the untreated feedstock was used. These results indicate that a relatively rapid deactivation of the catalyst occurred when the untreated feedstock was used.

We Claim:

1. A method for producing a product of reduced sulfur content from a feedstock, wherein said feedstock:
 - (a) is comprised of a mixture of hydrocarbons which boils below about 345 °C;
 - (b) contains a minor amount of organic sulfur compounds which are selected from the group consisting of mercaptans and aromatic sulfur compounds; andcontains an amount of alkylating agent which is at least equal on a molar basis to that of the organic sulfur compounds, and wherein said alkylating agent is comprised of at least one material selected from the group consisting of alcohols and olefins; and wherein said method comprises:
 - (a) passing said feedstock to a distillation column reactor which contains at least one fixed bed of acidic solid catalyst;
 - (b) contacting the feedstock with said catalyst under conditions which are effective to convert at least a portion of the organic sulfur compounds in the feedstock to a sulfur-containing material of higher boiling point;
 - (c) fractionating within the distillation column reactor the products of said contacting;
 - (d) withdrawing at least a portion of the sulfur-containing material of higher boiling point in a high boiling fraction from the distillation column reactor; and
 - (e) withdrawing a fraction from the distillation column reactor which has both a lower boiling point than that of said high boiling fraction and a reduced sulfur content relative to that of said feedstock.
2. The method of claim 1, wherein at least a portion of the acidic solid catalyst is a column packing in the distillation column reactor and at least a portion of said fractionating is carried out in said column packing.
3. The method of claim 1, wherein the acidic solid catalyst is located within a plurality of contacting zones within the distillation column reactor.

4. The method of claim 1, wherein at least a portion of the acidic solid catalyst is located in at least one conduit which provides a path for the flow of liquid from one zone to another within the distillation column reactor.
5. The method of claim 4, wherein a plurality of said conduits are used.
6. The method of claim 1 wherein said feedstock is substantially free of basic impurities.
7. The method of claim 1 wherein the mixture of hydrocarbons boils below about 230 °C.
8. The method of claim 1, wherein the feedstock is contacted with the catalyst at a temperature in the range from about 50 ° to about 350 °C.
9. A process which comprises:
 - (a) catalytically cracking a hydrocarbon feedstock which contains sulfur-containing impurities to produce volatile catalytic cracking products which include sulfur-containing impurities;
 - (b) passing a second feedstock to a distillation column reactor which contains at least one fixed bed of acidic solid catalyst, wherein said second feedstock;
 - (i) is comprised of at least a portion of said volatile catalytic cracking products,
 - (ii) contains organic sulfur compounds as impurities, and
 - (iii) contains at least 1 weight percent of olefins;
 - (c) contacting the second feedstock with said catalyst under conditions which are effective to convert at least a portion of the sulfur-containing impurities in the second feedstock to a sulfur-containing material of higher boiling point;
 - (d) fractionating within the distillation column reactor the products of said contacting;

(e) withdrawing at least a portion of the sulfur-containing material of higher boiling point in a high boiling fraction from the distillation column reactor; and

(f) withdrawing a fraction from the distillation column reactor which has both a lower boiling point than that of said high boiling fraction and a reduced sulfur content relative to that of said second feedstock.

10. The process of claim 9, wherein at least a portion of the acidic solid catalyst is a column packing in the distillation column reactor and at least a portion of said fractionating is carried out in said column packing.

11. The method of claim 9, wherein said second feedstock is treated with an acidic material to remove basic impurities before it is passed to the distillation column reactor.

12. The process of claim 11, wherein said acidic material is a solid particulate cracking catalyst.

13. The process of claim 9, wherein the second feedstock boils below about 345°C.

14. The method of claim 1, wherein said feedstock is comprised of a liquid.

15. The method of claim 1, wherein the feedstock is comprised of hydrocarbons from a catalytic cracking process.

16. The method of claim 15, wherein the feedstock is comprised of a naphtha from a catalytic cracking process.

17. The method of claim 15, wherein the feedstock is comprised of a treated naphtha which is prepared by removing basic nitrogen-containing impurities from a naphtha produced by a catalytic cracking process.

18. The method of claim 17, wherein the feedstock is prepared by combining said

treated naphtha with at least one material selected from the group consisting of alcohols and olefins of from 3 to 10 carbon atoms.

19. The method of claim 17, wherein the feedstock is prepared by combining said treated naphtha with at least one material selected from the group consisting of olefins of from 3 to 10 carbon atoms.

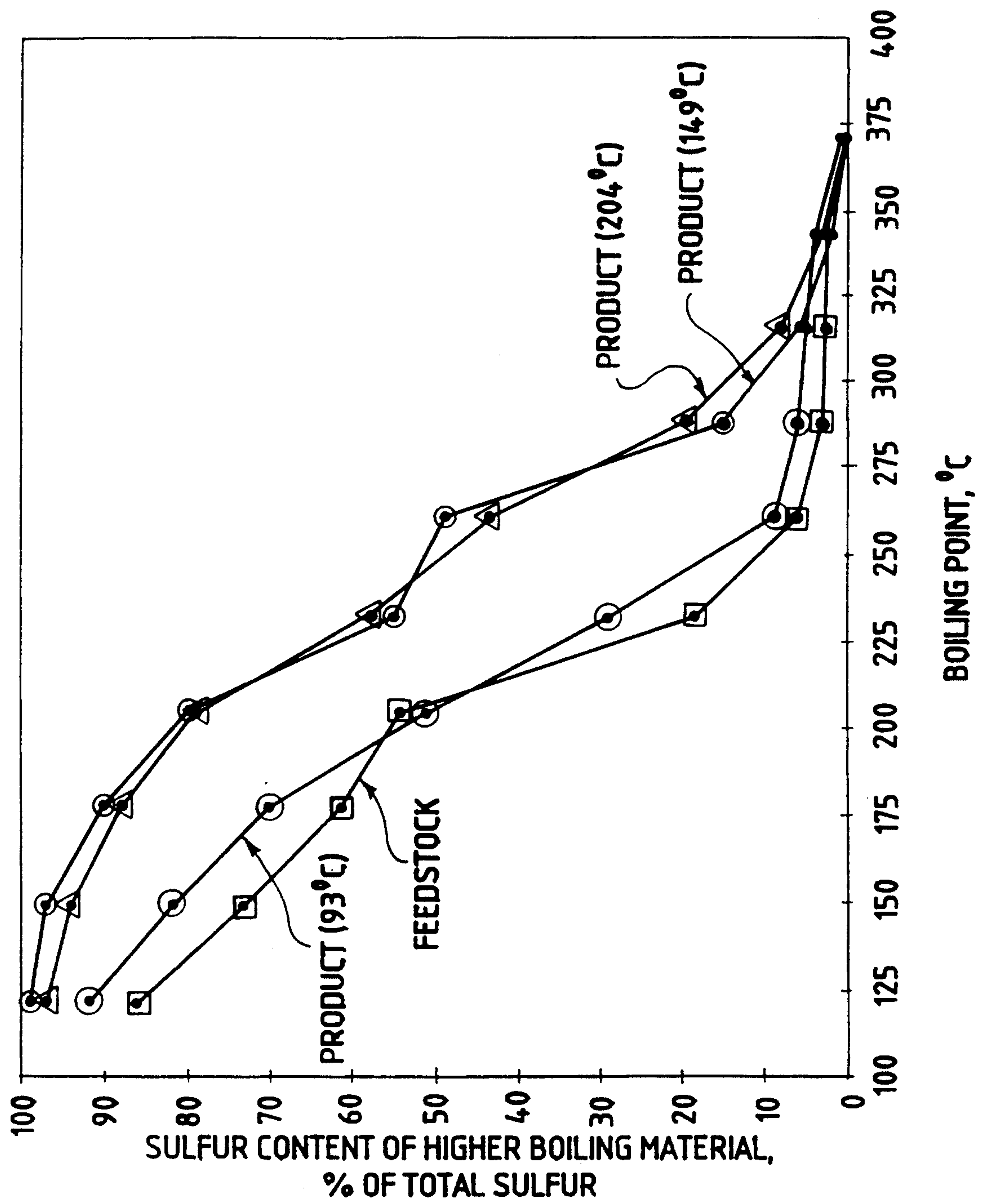
20. The method of claim 17, wherein the feedstock is prepared by combining said treated naphtha with at least one material selected from the group consisting of propene, 2-butene, 1-butene and 2-methylpropene.

21. The method of claim 1, wherein said alkylating agent is comprised of at least one material selected from the group consisting of alcohols of from 3 to 10 carbon atoms.

22. The process of claim 9, wherein the organic sulfur compounds of said second feedstock are comprised of aromatic sulfur compounds.

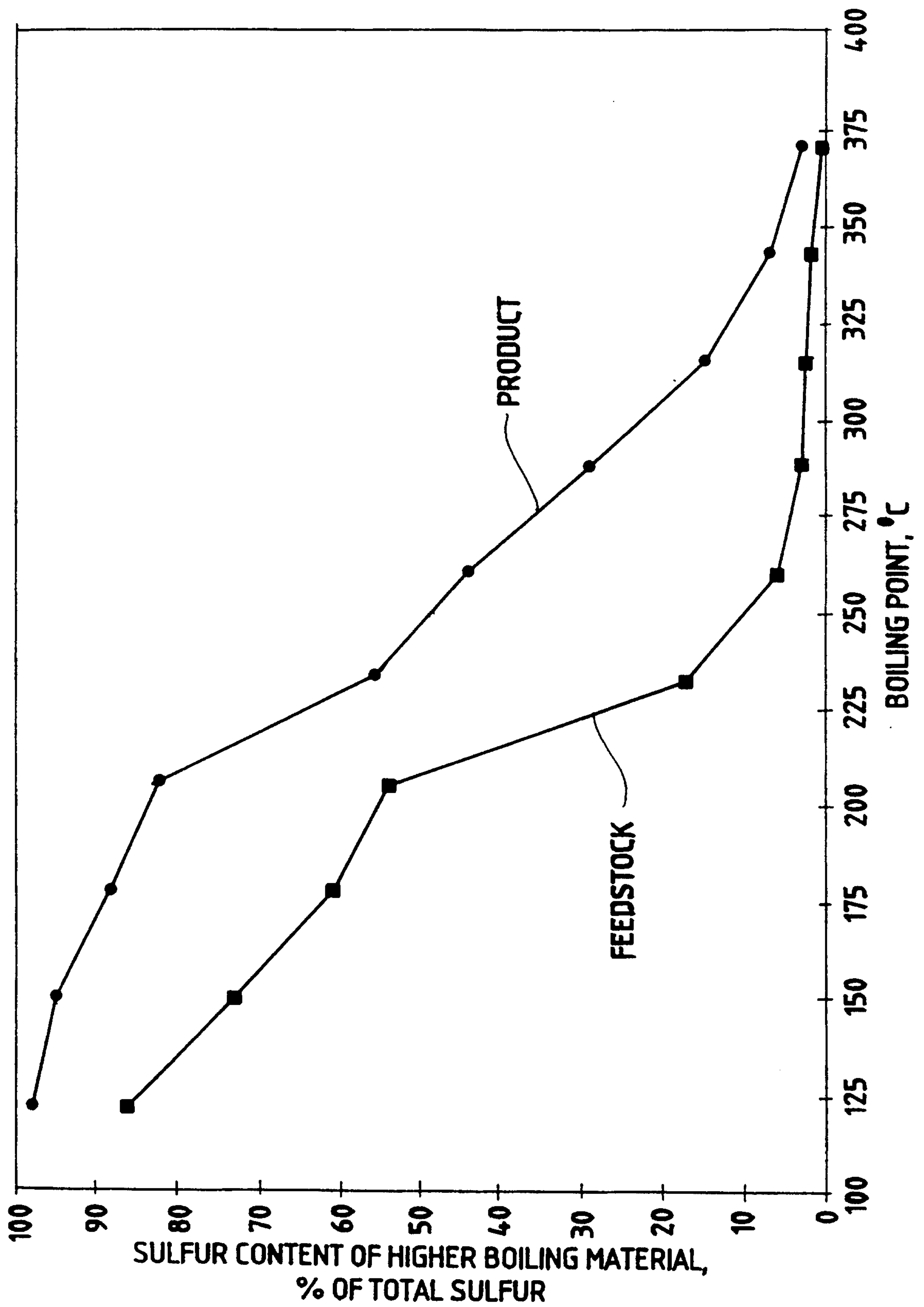
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FIG. 1



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FIG. 2



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FIG. 3a

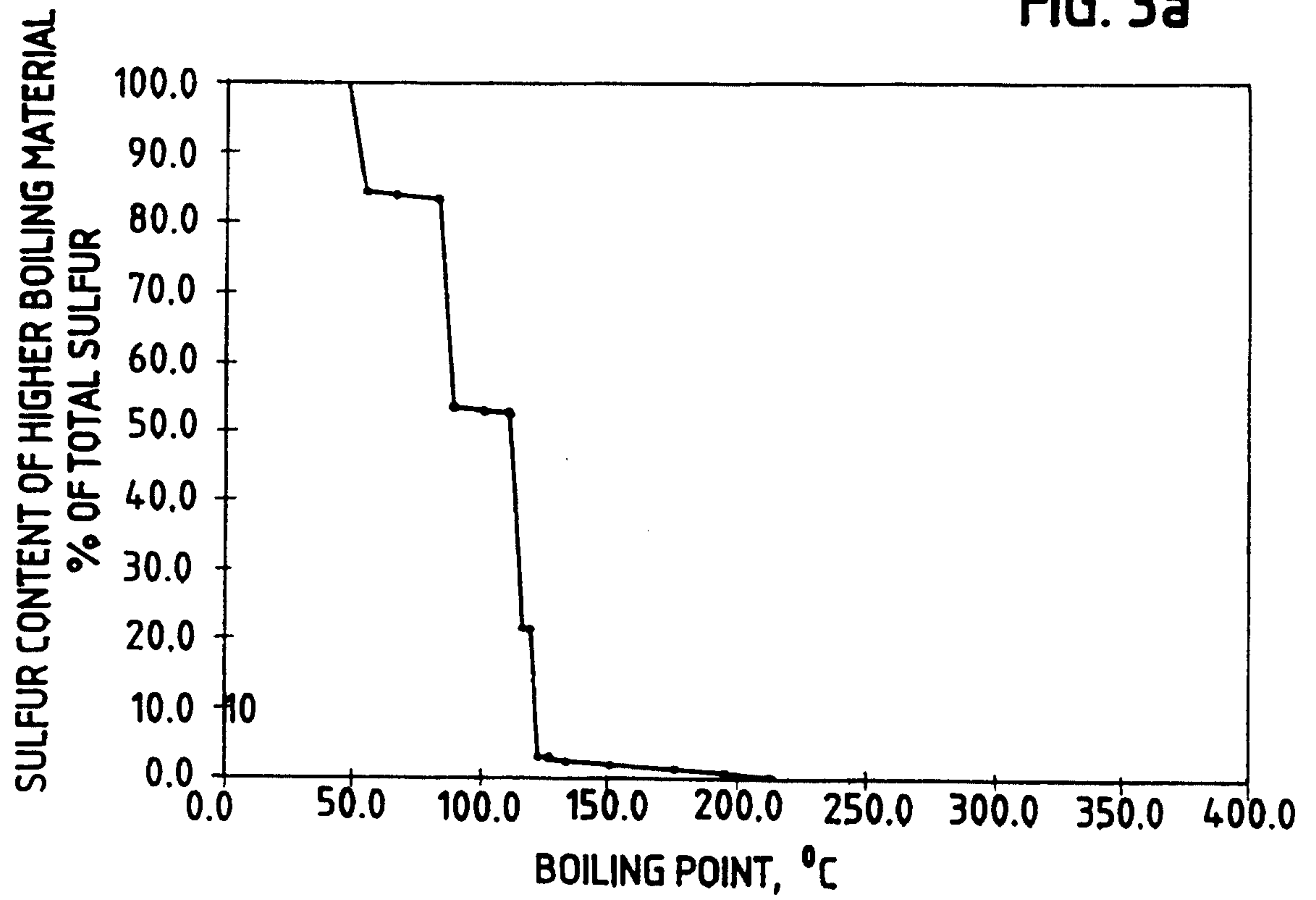
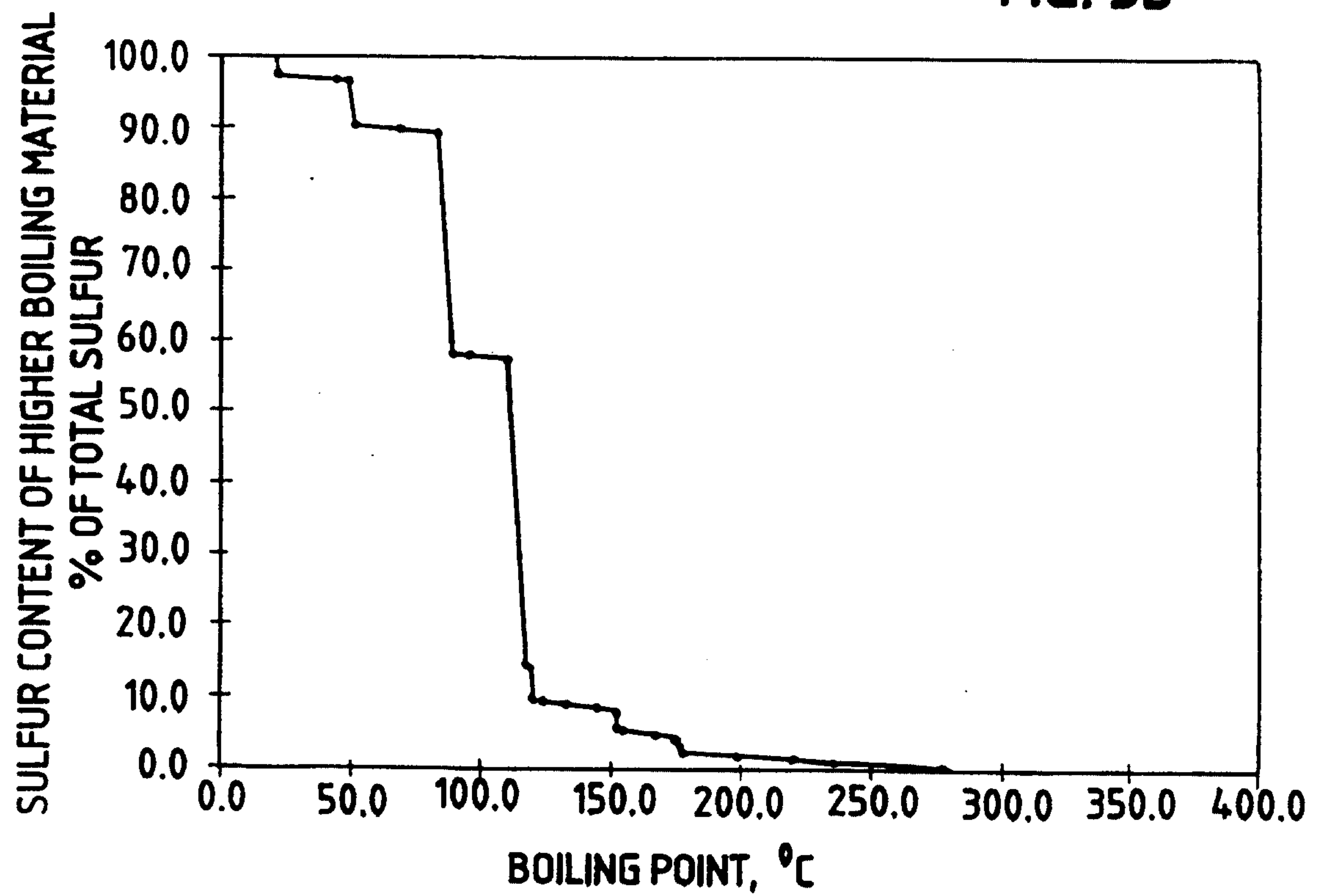


FIG. 3b



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FIG. 4a

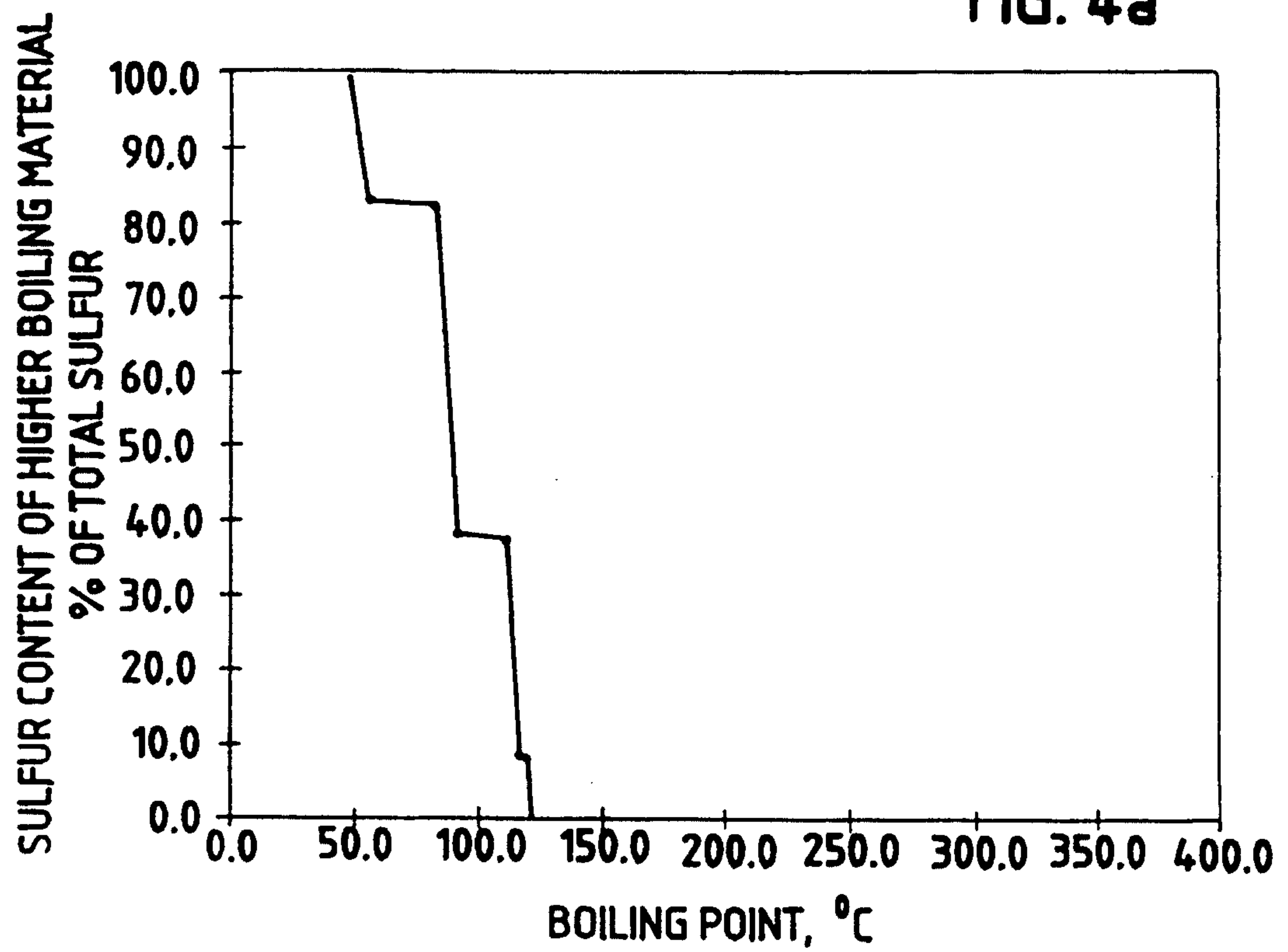
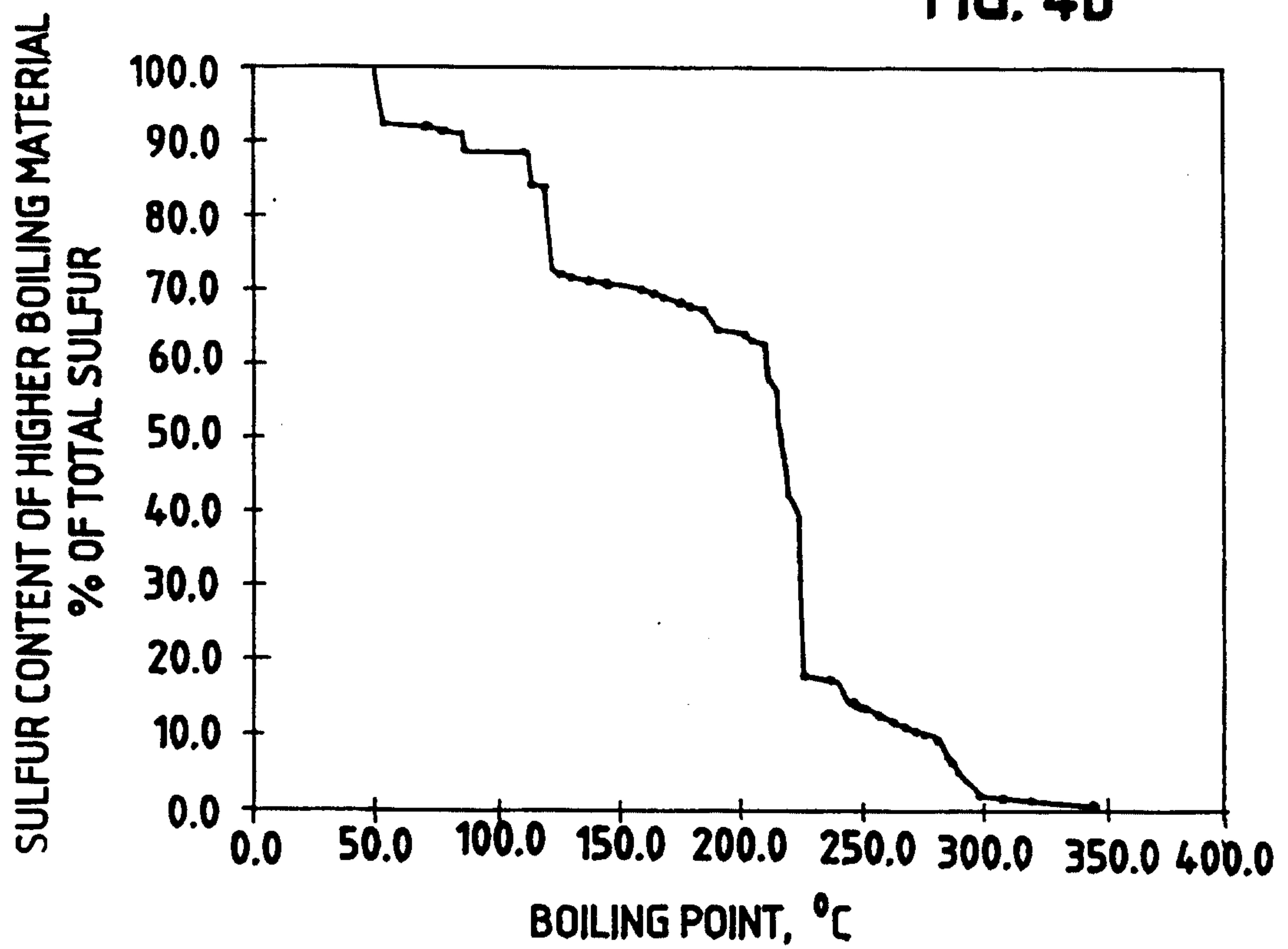
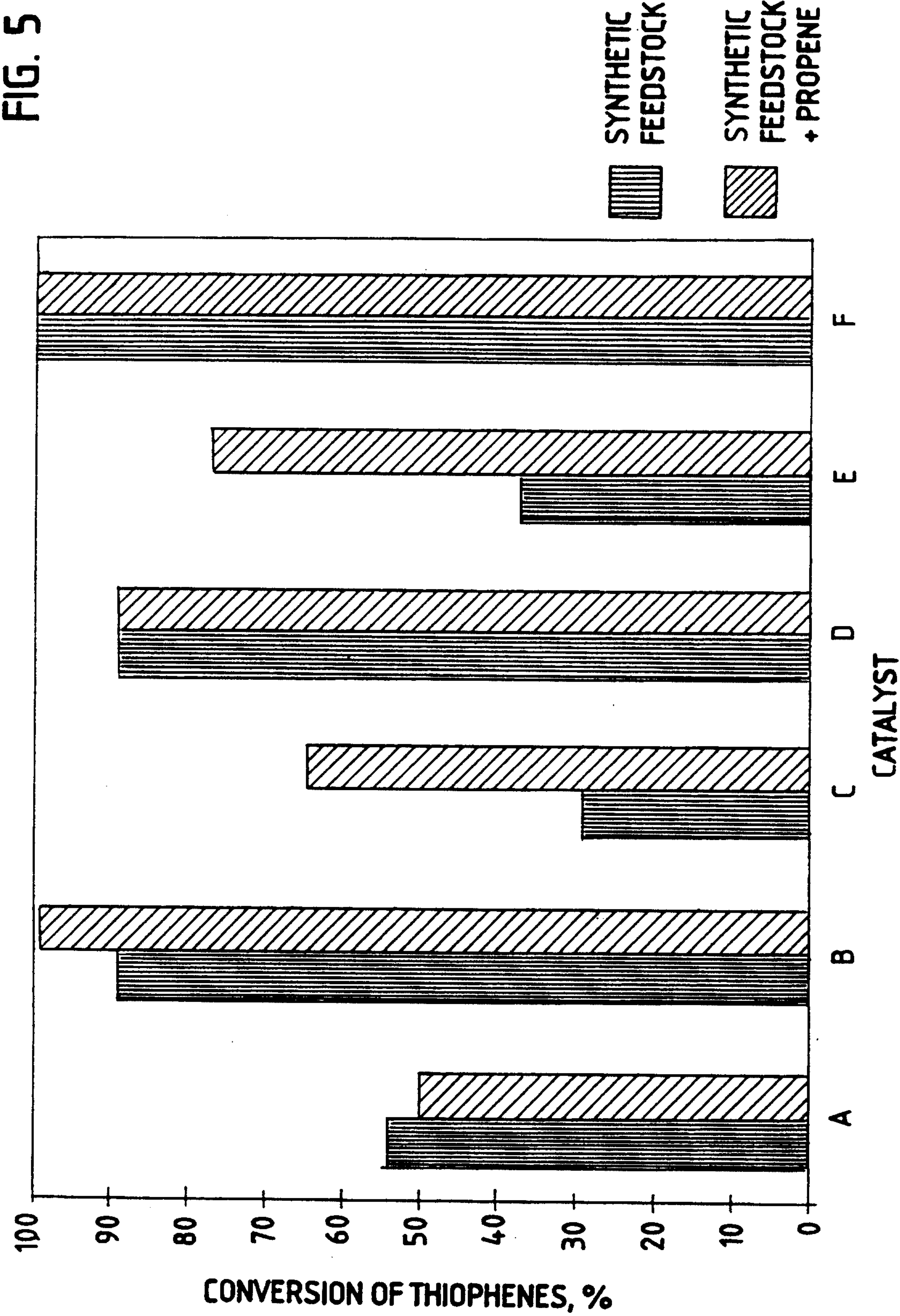


FIG. 4b





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FIG. 6

