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(54) Process for separating N-olefins and N-paraffins from hydrocarbon mixtures.

(57) This invention relates to a separation process for the adsorption-desorption of n-olefin n-paraffin mixtures in zeolites, particularly acid free silicalite molecular sieves. Preferred hydrocarbon feeds for the present separation process are C_9 to C_{19} distillates derived via the thermal cracking of petroleum residua. Such distillates, e.g. light FLEXICOKER and Fluid-coker gas oils contain 1-n-olefins and n-paraffins as the main types of components and minor components of branched olefins and paraffins as well as aromatic hydrocarbons and sulfur compounds. Mixtures mostly consisting of 1-n-olefins and n-paraffins can be separated from such coker distillates containing relatively high concentrations of sulfur compounds via the present process.

The olefin components of n-olefin and n-paraffin mixture products of the present molecular sieve separation can be utilized as reactants in polymerization, alkylation and carbonylation reactions, wherein the unconverted paraffin components are subsequently separated by distillation. Such a three step sieving, conversion, distillation process is particularly attractive as a low cost approach for the preparation of polyolefin based synthetic lubricants.

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PROCESS FOR SEPARATING N-OLEFINS AND N-PARAFFINS FROM HYDROCARBON MIXTURES

This invention relates to a separation process based on the selective adsorption-desorption of n-olefins and n-paraffins in neutral molecular sieves, particularly MFI-framework zeolites such as silicalite, ZSM-5 and compositional variances thereof.

Selective adsorption of hydrocarbons in molecular sieves has been known for more than 25 years. The selective adsorption of n-paraffins by molecular sieves is a widely employed commercial method of separation.

The early sieve adsorbents were crystalline aluminosilicates commonly known as zeolites. However, during the last ten years similar cystalline sieve compounds of different chemical compositions were synthesized. These include aluminophosphates and various microporous crystalline silica, including silicalite, which may contain small amounts of alumina. In the present invention all these shape selective adsorbent compounds are broadly termed as zeolites.

The early aluminosilicate zeolites were mostly active as catalysts, due to their polar, acidic character. They led to olefin isomerization, oligomerization, alkylation, polymerization and cracking reactions. Nevertheless, they were often disclosed as adsorbents for separations applicable in refinery processes where selectivities and the absence of side reactions were less critical. Most of the prior patents were aimed at the separation of n-paraffins.

Eberly and Webb described in U.S. Patent 3,485,748 the separation of normal and branched chain paraffins and olefins from aromatic hydrocarbons, using an acid treated mordenite having an SiO_2/Al_2O_3 molar ratio above 25.

A number of patents assigned to Mobil Oil Corporation disclose the use of ZSM-5 and related zeolites for the separation of normal paraffins. Gorring and Shipman described in U.S. Patents 3,894,938 and 3,980,550 the catalytic hydrodewaxing of gas oil using multivalent transition metal derivatives of ZSM-5 and the like. This process for the production of lubricating oils of reduced pour point was improved by Garwood and Caesar. They disclose in U.S. Patent 4,149,960 that the addition of water to the gas oil feed reduces coke formation. U.S. Patent 4,517,402 by Dessau disclosed a process for the selective separation of linear aliphatic compounds with ZSM-11. Dessau shows the separation of n-paraffins from branched paraffins and aromatics and the separation n-olefins from branched olefins. However, he neither shows nor suggests the separation of an n-paraffin and n-olefin mixture from a feed containing both aliphatic and aromatic hydrocarbons.

U.S. Patent 4,619,758 by Pratt, Sayles, Bowers and Scott discloses the selective adsorption of n-paraffins by zeolites such as ZSM-5, from hydrocarbon mixtures for example vacuum gas oil, followed by cracking of said n-paraffins in the zeolite.

U.S. Patent 3,969,223 by Rosback and Neuzil discloses the separation of olefins from olefin - paraffin mixtures, such as cracked wax by an X zeolite with an amorphous binder previously treated by aqueous sodium hydroxide to increase its sodium cation concentration. The treatment resulted in less olefin dimerization during the separation. However, this large pore diameter zeolite could not be used to separate straight chain and branched chain compounds.

Neuzil and Kulprathipanja were the first to disclose, in U.S. Patent4,455,445, column 1, lines 25 to 32, "that silicalite is able to effect the separation of normal C_4 hydrocarbons from isobutylene with substantially complete elimination of the aforementioned undesired side effects of olefin dimerization and polymerization, particularly when pentene-1 is used to displace the normal C_4 hydrocarbons from the zeolite." Neuzil et al. aimed their process for the separation of isobutylene from C_4 hydrocarbons, since isobutylene is useful e.g. as a gasoline blending agent and as a monomer for the production of polyisobutylene. They neither disclosed nor suggested this separation for the production of useful mixtures of higher n-olefins and n-paraffins.

Kulprathipanja and Neuzil also disclosed in U.S. Patent 4,486,618 the adsorption of normal C_6 olefins from cyclic and branched C_6 olefins using a silicalite with alumina as a binder. 1-Pentene or 1-butene were used for desorption. 1-Octene could never completely displace 1-hexene. In U.S. patent 4,433,195, Kulprathipanja disclosed the separation of a trans-olefin from a cis-olefin via selective adsorption by a silicalite. As an example he described the adsorption of trans-2-butene from a mixture of cis- and trans-2-butenes followed by desorption with 1-pentene.

U.S. patent 4,455,444 by Kulprathipanja and Neuzil disclosed the selective adsorption of n-paraffins in silicalite and their desorption by n-olefins, particularly 1-hexene. However, this patent emphasized that the feeds are limited to hydrocarbons containing little or no olefins. The disclosures of the parent patent by Kulprathipanja and Neuzil, i.e. U.S. patent 4,367,364, were also limited to selective n-paraffin adsorption in silicalites in the presence of little or no olefins. Additionally, the process of this patent and the process of the above discussed subsequent patents by the same inventors were limited to hydrocarbon feeds containing cyclic hydrocarbons having more than six carbons. This excludes benzene which can enter the pores of the silicalite.

Overall the disclosures of the Kulprathipanja and Neuzil patents suggest that all the work was carried out with silicalite plus alumina binder compositions. The results were probably affected by the presence of the acidic alumina even though the Si/Al ratios were above 12 as stated in U.S. patent 4,486,618.

Some of the fundamental information disclosed in the Kulprathipanja and Neuzil patents was previously published in an article announcing the discovery of silicalite: A research group of the Union Carbide Corporation and J.V. Smith of the University of Chicago reported, in volume 271, pages 512 to 516 of Nature, the synthesis, structure and generic adsorption properties of silicalite in 1978. Silicalite was patented in 1977 as a novel composition of matter in U.S. Patent 4,061,724 by R.W. Grose and E.M. Flanigen, assigned to Union Carbide. A more recent publication of this composition by Y.H. Ma and Y.S. Lin appeared as paper No. 68h-21 in the preprints of the 1984 Annual Meeting in San Francisco of the American Institute of Chemical Engineers. It was found that the equilibrium adsorption capacity of silicalite for the investigated hydrocarbon in n-hexene solution decreases in the following order: 1-heptene > cyclohexene > benzene > cyclohexane > n-octane and the presence of alumina binder affected the adsorption in most cases.

The processes disclosed in the prior art are directed either to the separation of olefins or to the separation of paraffins. There are no processes disclosed or suggested for the separation of C_5 to C_{19} n-olefin and n-paraffin mixtures from branched olefins, branched paraffins, aromatic hydrocarbons and sulfur containing compounds by the use of zeolites.

Accordingly the present invention provides a process for the separation of C_5 to C_{19} mixtures of n-olefins and n-paraffins from a feed mixture comprising aliphatic and aromatic hydrocarbons which process comprises contacting said mixture of C_5 to C_{19} aliphatic and aromatic hydrocarbons with a neutral molecular sieve adsorbent under conditions sufficient to effect selective adsorption of n-olefins and n-paraffins, and contacting the resulting sieve containing the adsorbed n-olefin and n-paraffin enriched extract with a more volatile desorbent under conditions sufficient to effect displacement from the sieve of said extract.

This invention provides a new separation approach for obtaining normal olefin, particularly α-olefin reactants, suitable as chemical intermediates. Known chemical methods for the preparation of such olefins are ethylene oligomerization, paraffin cracking and dehydrogenation and alkyl chloride dehydrogenation and alkyl chloride dehydrochlorination. Past separations were directed to the separation of olefins. In contrast, the present invention provides a process which separates a mixture of n-olefins and n-paraffins by a neutral molecular sieve of preferably high silica alumina ratio. The olefin components of this mixture may then be selectively converted to desired higher molecular weight products in a separate step. Finally, the unreacted paraffins may be removed from the reaction mixture by distillation.

In contrast to the prior art, the present invention is directed toward the separation of C_5 to C_{19} n-olefin and paraffin mixtures from branched olefins, branched paraffins, aromatics hydrocarbons and sulfur containing compounds by the use of zeolites. In spite of the negative teachings of the prior art, it was found that the present process could be operated using a mixture comprising open chain and cyclic aliphatic hydrocarbons and benzene.

It was surprisingly found that the present process is applicable to hydrocarbon streams containing relatively large amounts of aromatic sulfur compounds. In particular, thiophene, methylthiophenes and dimethylthiophenes which boil in the C_6 to C_8 carbon range were found to be adsorbed in the zeolite.

Unexpectedly, the process of the present invention is applicable to sulfur containing olefinic distillates derived by the high temperature thermal cracking of petroleum residua. Distillates in the C_9 to C_{19} range, containing mostly aromatic, bulky sulfur compounds such as benzothiophene, are preferred. In this high carbon range, 1-n-olefins were found to be adsorbed with an increased selectivity as compared to other products in the feed stream.

A key process step of the present invention is a molecular sieve separation. Past sieve separation processes were usually aimed at the separation of single types of compounds. Distinct processes were developed for the separation of olefins and normal paraffins. In contrast the present process separates a mixture of n-olefins and n-paraffins.

An attractive feature of the present separation process is that it utilizes low cost olefinic hydrocarbon feeds which contain not only aliphatic hydrocarbons but aromatic hydrocarbon and sulfur compounds as well. Such olefinic hydrocarbon feeds are produced by the high temperature thermal cracking of petroleum residua, particularly vacuum resids. These feeds contain high concentrations of linear thermal (i.e. α-)

olefins of Type I and linear internal olefins of Type II.

Another important feature of the present separation is the use of a neutral molecular sieve. This minimizes olefin side reactions and allows the separation of 1-n-olefin - n-paraffin mixtures without any major terminal, e.g. olefin to internal olefin isomerization. In the present process, preferably low alumina zeolites having less than 5000 ppm alumina are used for selective adsorption.

In the present invention acid-base treated silicalites and sodium ZSM-5 were found to be particularly suitable adsorbents for the separation of mixtures and 1-n-olefins and n-paraffins, because of their reduced olefin isomerization activity.

From the viewpoint of process economics, it is important that the present process can use feeds containing substantial amounts of aromatic components. The preferred feeds of the present separation process are olefinic distillates produced from petroleum residua by high temperature thermal cracking. Such cracked distillates are preferably produced from vacuum residua by Fluid-coking or FLEXICOKING. These distillates contain 1-n-olefins as the major type of olefin components and organic sulfur.

The present invention also provides a process for converting the olefins obtained from the separation process to less volatile products. The combined process converts the olefin components of the separated olefin-paraffin mixtures to higher boiling products and removes the unconverted paraffins thereafter by flash off. This unique combination of process steps has never been contemplated prior to the instant invention.

The present invention relates to a process for the separation of C_5 to C_{19}, preferably C_9 to C_{19}, mixtures of n-olefins and n-paraffins, preferably 1-n- olefins and n-paraffins, from a mixture of aliphatic and aromatic hydrocarbons and, optionally, sulfur containing compounds comprising a mixture of C_5 to C_{19} aliphatic and aromatic hydrocarbons, preferably a mixture also containing organic sulfur compounds, specifically in concentrations equivalent to from 0.05% to 3% sulfur with a neutral molecular sieve, preferably a metal zeolite such as sodium ZSM-5 having a minimum silica to alumina ratio of 20, more preferably a silicalite, most preferably a silicalite substantially free from alumina, which has been preferably pretreated by an acid and then a base, under conditions sufficient to effect selective adsorption from the liquid and/or the gas phase, preferably from the liquid phase under pressure sufficient to maintain liquid phase, and in the temperature range of 10° C to 250° C, more preferably 20° C to 150° C, most preferably 100° C to 140° C, and contacting the resulting sieve containing the n-olefin and n-paraffin enriched extract with a more volatile desorbent gas and/or liquid, preferably liquid, under pressure sufficient to maintain liquid phase preferably an n-olefin and/or n-paraffin, more preferably an n-olefin or n-paraffin under conditions sufficient to effect displacement from the sieve of said extract, preferably under conditions of the adsorption step.

In a preferred embodiment the invention provides a process for the separation of C_9 to C_{19} mixtures of n-olefins and n-paraffins from aliphatic and aromatic hydrocarbons and, optionally, sulfur containing compounds, preferably 1-n-olefins and n-paraffins, comprising containing a mixture of C_9 to C_{19}, preferably C_9 to C_{13}, aliphatic and aromatic hydrocarbons, which preferably also contains sulfur compounds, with a neutral molecular sieve, preferably a zeolite having a minimum silica alumina ratio of 20, sodium ZSM-5 or more preferably a silicalite, in the liquid phase and in the temperature range of 80° C and 200° C preferably 100° C to 150° C for a sufficient time to effect adsorption, and desorbing the resulting n-paraffin and n-olefin enriched extract from the sieve with a more volatile olefin or paraffin as described above.

Advantageously, the present invention provides a process for the separation of C_5 to C_{19}, preferably C_9 to C_{15}, more preferably C_9 to C_{13} mixture of 1-n-olefins and n-paraffins from aliphatic and aromatic hydrocarbons and, optionally, sulfur containing compounds comprising contacting a corresponding olefinic cracked distillate feed produced from petroleum residua by high temperature thermal cracking, preferably Fluid-coking or FLEXI-COKING, and containing 1-n-olefins as the major type of olefin components, the percentage of Type I olefins preferably exceeding 30 wt% of the total olefins, and organic sulfur compounds, preferably in concentration exceeding 0.05%, more preferably in the concentration range of 0.3% to 3% with a neutral molecular sieve, preferably an above described high Si/Al ratio zeolite, more preferably sodium ZSM-5 or a silica molecular sieve in the liquid phase in the temperature range of 10° C and 200° C for a sufficient time to effect adsorption and desorbing the resulting 1-n-olefin - n-paraffin enriched mixture from the sieve with a more volatile n-olefin and/or n-paraffin, preferably n-olefin, under adsorption conditions.

Most advantageously the present invention represents a process for the separation of C_9 to C_{19}, preferably C_9 to C_{15}, mixtures of 1-n-olefins and n-paraffins comprising contacting a C_9 to C_{19} olefinic cracked distillate feed produced from vacuum residua by high temperature thermal cracking in a Fluid-coker or FLEXICOKER unit which contains more than 20% olefins, more than 30% of said olefins being of Type I, and additionally contains organic sulfur compounds in concentrations exceeding 0.3% sulfur, with a neutral molecular sieve, preferably an earlier defined high Si/Al ratio zeolite, more preferably a silicalite in the liquid phase in the temperature range of 80° C and 200° C for a sufficient time to effect adsorption, and desorbing the resulting 1-n-olefin - n-paraffin enriched extract from the sieve with a more volatile n-olefin and/or n-paraffin under adsorption conditions.

The present invention also encompasses a separation - conversion process comprising contacting an olefinic C_5 to C_{19}, preferably C_9 to C_{19} mixture of aliphatic and aromatic hydrocarbon feed, the more preferred feeds being those defined above, with a neutral molecular sieve, preferably a zeolite with a high Si/Al ratio, preferably as defined above, more preferably a silicalite, in the liquid and or gas phase preferably in the liquid phase in the temperature range of 100° to 250° C for a time sufficient to effect a selective adsorption of the 1-n-olefin and n-paraffin components, desorbing the resulting 1-n-olefin and n-paraffin enriched extract with a more volatile n-olefin and/or paraffin, preferably n-olefin, and converting the olefin components of the extract to less volatile products via reactions preferably selected from the group consisting of oligomerization, aromatics alkylation and carbonylation, more preferably oligomerization to products having two to six monomer units, alkylation of benzene to alkyl-benzenes and carbonylation to aldehydes wherein the aldehyde products are preferably further converted to alcohols or carboxylic acids, and removing the unconverted paraffin component from the olefin derived product preferably by distillation.

More specifically, this invention covers a selective separation - conversion process comprising contacting a C_9 to C_{13} olefinic cracked petroleum distillate feed, produced from vacuum residua by high temperature thermal cracking in a Fluid-coker or FLEXICOKER unit, which contains more than 20%, preferably more than 30%, olefins and more than 30% said olefins being of Type I and additionally contains organic sulfur compounds in concentrations exceeding 0.3% sulfur, with a neutral molecular sieve, preferably a silicalite or sodium ZSM-5 in the liquid or gas phase, preferably in the liquid phase, in the temperature range of 100° C to 250° C, preferably 100 to 150° C for a sufficient time to effect selective adsorption of the 1-n-olefin and n-paraffin components, desorbing the resulting 1-n-olefin - n-paraffin rich extract from the sieve with a more volatile n-olefin or/and n-paraffin, preferably n-olefin, converting the olefin components of the thus separated mixture in the presence of an acid catalyst, preferably a boron trifluoride complex, more preferably a boron trifluoride alcohol complex, to selectively produce an oligomer containing 2 to 6 monomer units, hydrogenating the olefinic double bonds of said oligomer to produce an isoparaffin lubricant, and removing the unreacted n-paraffin components from the isoparaffin containing reaction mixture, preferably by distillation.

The specific details of the embodiments of the present invention will be described in terms of the hydrocarbon feeds of the present separation process and the zeolite adsorbents employed. Thereafter, the conditions of the selective adsorption of n-olefin - n-paraffin mixtures will be described. The description of the separation process will conclude with that of the desorption step.

The combined separation - conversion process of the present invention will be detailed regarding the conversion encompassed within the inventive concept. The conversion of the olefin components of the n-olefin - n-paraffin extract to synthetic lubricants will be particularly described.

Hydrocarbon Feeds

The preferred hydrocarbon feeds of the present invention contain major amounts of olefins, paraffins and aromatic compounds. More preferably the feeds also contain significant amounts of sulfur compounds. A detailed description of the most preferred feeds, i.e. distillate feeds, produced from petroleum residua by high temperature thermal cracking processes such as Fluid-coking and FLEXICOKING, is found in U.S. patent 4,711,968.

The olefin compounds of the feed are preferably in concentrations exceeding 10 wt.%, more preferably 20 wt%, most preferably 30%. In preferred olefinic feeds, the normal, i.e. linear, olefins are the major olefin component. More preferably, the largest single type of olefin is Type I, of the formula $RCH=CH_2$, representing 20% or more of the total olefins. The prevalent specific olefins are 1-n-olefins. Some preferred olefin feed components are 1-pentene 3-hexene, 3-methyl-2-pentene, 1-octene, trans-2-decene, tetradecene, 1-octadecene.

The paraffin components are preerably in concentrations similar or lower concentrations than those of the olefins or lower, the normal paraffins being the major paraffin component. Exemplary paraffins are n-pentane, cyclohexane, n-octane, n-decane, 2-methylnonane, decalin, hexadecane.

The aromatic hydrocarbon components preferably represent from 1 to 60 wt.% of the feed more preferably 10 to 60 wt.%. The preferred aromatic hydrocarbons are either unsubstituted or substituted by short C_1 to C_3 alkyl groups such as benzene, p-xylene, 1-methyl-4-ethyl-benzene, 1,2,3-trimethylbenzene, naphthalene, 2-methylnaphthalene, phenanthrene.

The sulfur compounds are usually present as impurities in the hydrocarbon feed. The present process is preferred for feeds of relatively high sulfur content, 0.05 wt.% or above and can handle feeds having sulfur concentrations ranging from 0.3 to 3% sulfur. The sulfur compounds are usually present as thiol and/or aromatic sulfur compounds. Aromatic sulfur compounds, such as thiophenes, benzothiophenes and dibenzothiophenes are preferred. These aromatic sulfur compounds can be substituted by one or more short chain alkyl groups, preferably C_1 to C_3 alkyl, more preferably methyl.

The preferred olefinic distillate feeds of the present invention are produced from petroleum residua by high temperature thermal cracking. The percentage of the most desired 1-n-olefin components of such feeds generally increases with the temperature of cracking. Therefore, the distillate products of high temperature thermal cracking processes such as Fluid-coking and FLEXICOKING are preferred feeds for the present process. Delayed coking which is normally operated at lower temperatures can also produce suitable feeds for the present process although these feeds contain higher concentrations of n-paraffins than 1-n-olefins. Other less preferred, but suitable, generally milder cracking processes to produce feeds for the present invention are the thermal cracking of gas oils and the vis-breaking of vacuum residues.

The preferred feeds of Fluid-coking and FLEXICOKING are highly olefinic with olefin concentrations exceeding 20 wt.%, preferably 30%. The aliphatic hydrocarbons are semilinear in character. The main components are linear, i.e. normal olefins and normal paraffins. The largest specific type of compounds are 1-n-olefins followed by n-paraffins. The majority of olefins are Type I and Type II olefins as indicated by the following tabulation showing approximate concentration ranges determined by proton magnetic resonance spectrometry (NMR),

$RCH=CH_2$	$RCH=CHR$	$R_2C=CH_2$	$R_2C=CHR$	$R_2C=CR_2$
Type I	Type II	Type III	Type IV	Type V
~25-45%	15-25%	10-20%	10-20%	Not indicated

The R groups in the formulas of the various types of olefins can be straight chain or branched alkyl groups. However, the alkyl groups of the preferred coker olefins of Type I and Type II are predominantly either straight chain or monomethyl branched. Additionally, the Type III and Type IV olefin components of these preferred feeds predominantly possess a methyl group as one of the alkyl grups on the completely substituted vinylic carbon. NMR also indicated the presence of minor amounts of conjugated dienes ranging from about 2 to about 10% concentration. The concentration of the various olefins generally decreases with their molecular weight, i.e. carbon number. Therefore, coker distillates having more than 19 carbons per molecule are less preferred.

The paraffin components of the preferred coker distillate feeds are present in concentrations similar to but smaller than the olefin components! The n-paraffins are the major single types of paraffins present. The branched paraffins are largely methyl branched. Monomethyl branched paraffins are prevalent.

The aromatic hydrocarbons of the present feeds have a concentration range from 6% to 50%. The percentage of the aromatic components increases with the carbon number of the distillate fractions. Of course the percentages of olefins and paraffins decrease accordingly. In the preferred C_9 to C_{19} carbon range the concentration of aromatics is between 10 and 50%.

The aromatic hydrocarbon components of these feeds are predominantly unsubstituted parent compounds such as benzene or substituted with methyl groups such as toluene. The concentration of ethyl substituted compounds is much smaller. Propyl substituted aromatics are present in insignificant amounts. Up to 12 carbon atoms, the aromatics are benzenoid hydrocarbons. From C_{12} to C_{15} most aromatics are of the naphthalene type. Among the higher carbon number hydrocarbons most aromatics are three membered fused ring compounds such as anthracenes and phenanthrenes.

The concentration and type of sulfur compounds in the preferred coker distillates depend on their carbon number. The sulfur concentrations range from 0.1% to 3%. In general, sulfur concentrations increase with the carbon number to 3%. In the C_5 to C_7 carbon range there are major amounts of thiols present. The C_8 and higher fractions contain mostly aromatic sulfur compounds, mostly of the thiophene type. The structure of aromatic thiol components is similar to those of the aromatic hydrocarbons. Methyl and ethyl substituted thiophenes are present in decreasing amounts. Alkylthiophenes are the major sulfur compounds in the C_8 to C_{11} range. Benzothiophenes are mostly present in the C_{12} to C_{15} range. In the higher boiling fractions, dibenzothiophenes are major sulfur compound components.

Zeolite Adsorbents

The zeolite adsorbents of the present process are molecular sieves which include not only crystalline alumino-silicates but aluminophosphtates, silicalites and similar crystalline materials. Zeolites either possess an internal pore system comprised of interconnected cagelike voids or a system of one, two or three dimensional channels. The zeolite minerals mordenite and chabazite are examples of these two types. Zeolites are mainly used as catalysts for chemical conversions and adsorbents for separations. They are described as "Molecular Sieves" in Kirk-Othmer's Encyclopedia of Chemical Technology, published by J. Wiley & Sons of New York. More detailed information is available in two monographs, entitled "Zeolite Molecular Sieves" and "Zeolites and Clay Minerals as Sorbents and Molecular Sieves" by D. W. Breck and R. M. Barrer, respectively. These monographs were published by the R. E. Krieger Publishing Co, Malabar, Florida, in 1984 and by Academic Press, New York, N.Y. in 1978.

Separations based on the molecular sieve effect generally employ dehydrated zeolites. Zeolites can selectively adsorb molecules based upon differences in molecular size, shape and other properties such as polarity.

The preferred zeolite adsorbents of the present invention possess pore diameters ranging from 3.5 to 7 Å. Zeolites of this pore diameter range from chabazite to ZSM-5 and silicalite.

Such zeolites can adsorb n-paraffins and 1-n-olefins while rejecting bulky hydrocarbon molecules such as branched olefins, branched paraffins and C_9 and higher aromatic hydrocarbons. The other important characteristics of the preferred zeolites is their reduced polarity which increases their affinity toward aliphatic rather than aromatic hydrocarbons. To produce a reduced polarity, i.e. increased hydrophobic character, the silica to alumina ratio of the present zeolites is preferably above 12, more preferably above 30 such as ZSM-5. U.S. Patent 3,702,886 describes ZSM-5 and is incorporated herein by reference. Similar zeolites are ZSM-11 described in U.S. Patent 3,709,979 and ZSM-12 described in U.S. Patent 3,832,449.

The zeolite frameworks were also classified by the pore structure as described by W. M. Meier and D. H. Olson in a monograph, entitled "Atlas of Zeolite Structure Types" which was published by Polycrystal Book Service in Pittsburgh, Pennsylvania in 1978. According to the nomenclature of Meier and Olson ZSM-5 and silicalite both possess a synthetically occurring MFI framework having two orthogonal interconnected channel systems with minimum diameter of 5.1 and 5.4 Å. The MEL framework of ZSM-11 is similar. Both MFI and MEL structures have pores with 10 ring windows.

A typical silica to alumina ratio for ZSM-5 and ZSM-11 is 30. Although pure silicalite is by definition has an alumina free framework, the silicalites used in the present invention also had a significant alumina content. For the purpose of the present invention sodium ZSM-5 is distinguished from the silicalites employed by its sodium content which results in a lesser olefin isomerization activity than the silicalites have.

The silica to alumina ratio of zeolites can be increased by acid treatment which remove some of the alumina. This reduces the acidity and the polarity of the thus treated zeolite. Acid treatment can also affect pore size. These combined effect increase the adsorptive capacity and selectivity of zeolites while reducing the extent of undesired side reactions.

While protonated aluminosilicate type zeolites of low acidity can be employed as adsorbents in the present invention it is preferred to employ their sodium derivatives, more particularly sodium. Such derivatives can be prepared by the neutralization of protonated zeolites by the appropriate metal base or salt, such as aqueous sodium hydroxide or sodium chloride. Such a base treatment can also affect advantageously the pore diameter and shape of the zeolite. Change in the cations also results in electric field effects, resulting different interactions with adsorbate molecules. For example, the calcium exchanged form of the synthetic zeolite A has a pore diameter of 4.2 Å. This sieve is referred to as 5A. The natural zeolite, chabazite, is another aluminosilicate with a similar pore diameter. The preferred ZSM-5 is a high Si/Al ratio sodium aluminosilicate having a pore diameter above 5 Å. Sodium ZSM-5 can be prepared from either the corresponding quaternary ammonium derivative via thermal decomposition and neutralization or by direct synthesis.

The preferred zeolite adsorbents are silicalites which topologically resemble ZSM-5 and contain the same type of building unit. The two sets of intersecting channels of silicalite have pore sizes ranging from 5.2 to 5.7 Å. It is commonly assumed that silicalites contain no exchangeable metal cations and as such they are highly non polar with high affinity for nonpolar hydrocarbon molecules.

Commercially available silicalite from Union Carbide Corporation contains significant amounts, about 0.5%, aluminum as Al_2O_3. Significant amounts of this impurity can be removed by acid treatment. The resulting low alumina (about 0.3% Al) silicalite is then treated with a base to neutralize and remove acid impurities. The resulting acid-base treated silicalite has improved selectivity and as such is a preferred adsorbent in the present process.

The crystalline zeolite adsorbents are usually formed into spheres or cylindrical pellets which have high mechanical attrition resistance. This is achieved using binders which do not seriously hinder diffusion in the micropores. As binders silica, alumina and crosslinked organic polymers can be employed.

Adsorption

Adsorption by zeolite molecular sieves is performed using gaseous and liquid feeds. In the present process, zeolites are regenerated and used for many adsorption-desorption cycles. The present process is directed at the separation of two rather than one types of molecules and as such does not follow the rules and predictions developed for processes separating a single type of compounds. However, process techniques, such as counter-current liquid phase adsorption, developed for single type hydrocarbons, are applicable.

The present invention comprises the selective adsorption of both n-olefins and n-paraffins from a mixture of aliphatic and aromatic hydrocarbon compounds. The preferred feed mixtures are in the C_5 to C_{19} range. Preferably 1-n-olefins and n-paraffins are mainly adsorbed from a feed richer in terminal 1-n-olefins than internal n-olefins. Such preferred feeds are the distillates produced from petroleum residua by high temperature thermal cracking. These feeds additionally contain sulfur compounds.

The absence of catalytic side reactions such as isomerization is particularly important for recovering a mixture of 1-n-olefins and n-paraffins. 1-n-Olefins are particularly subject to isomerization resulting in internal olefins. In general, internal olefins are less desired than terminal olefins.

Working with an acid-base treated silicalite, it was unexpectedly found in the present invention that the 1-n-olefin components of the C_9 to C_{15} feeds are preferably adsorbed over the corresponding n-paraffins. The trans-isomers of the internal linear olefins and 1-olefins are adsorbed at comparative rates. Little adsorption of the very minor cis-isomers occurs. In case of the minor conjugated linear diene components, such as transpiperylene, a selective adsorption is also observed.

In addition to the selective adsorption of 1-n-olefins and n-paraffins, selective adsorption or rejection of aromatic sulfur compounds was observed, using ZSM-5 and silicalite. It was found that the thiophenic sulfur compound components of C_5 to C_8 cracked distillates derived from residua are selectively adsorbed in the present process. The adsorption of 2,5-dimethylthiophene is surprising in view of the rejection of toluene components of very minor concentrations. The adsorption of these sulfur compounds however, does not interfere with the production of 1-n-olefin plus n-paraffin rich extracts. If desired the minor aromatic sulfur compounds can be removed from the extracts, e.g. by chemically modified adsorbents, before any subsequent chemical conversion. The benzothiophene type sulfur compounds present in the higher carbon distillates were not adsorbed.

It was found that silicalite is a size selective adsorbent for certain monomethyl branched olefins. 3-Methyl-2-pentene was selectively adsorbed, while 2-methyl-2-pentene, 2-methyl-1-pentene and 4-methyl-2-pentene, were not. Some adsorption of C_8 and higher carbon 2-methyl-1-alkenes and 2-methylalkanes was observed. However, their presence in minor amounts in the extracts of coker distillates does not interfere with the use of such extracts in synlube preparation.

The adsorption occurs on contacting the hydrocarbon feed and the zeolite at a temperature wherein the molecules to be adsorbed have a sufficient energy to overcome the repulsive interaction with the zeolite and pass through the aperture of the zeolite channels and reversibly fill the micropores. To achieve sufficient adsorbate diffusion rates, increased temperatures are needed to overcome the activation energy requirements of molecules of increasing size and/or molecular weight.

Generally, preferred adsorption temperatures are in the 10 to 250 °C range. Adsorption of the low molecular weight, C_5 to C_8 distillate, feeds can be carried out at low temperatures, in the 10 to 100 °C regime. The adsorption of C_9 to C_{19} fractions at optimum diffusion rates requires increasing temperatures, ranging from 100 to 200 °C. However, the optimum temperatures of the present adsorption process are limited by the need to avoid 1-n-olefin isomerization and cracking. The choice of adsorption temperature also depends on the carbon range of the hydrocarbon feed. Broad distillate feed cuts are processed at temperatures higher than warranted for their low boiling components.

Gas phase adsorption is carried out preferably at close to atmospheric pressure in a temperature range wherein the feed is in the gaseous state. Similarly, liquid phase adsorption is performed at temperatures where the feed is liquid. When processing a volatile feed, such as C_5, in the liquid phase, above atmospheric pressure may be used. In general, a liquid phase operation is preferred because it can be usually carried out at a lower temperature providing a higher extract yield.

Desorption

Desorption, i.e. the removal of the n-olefin and n-paraffin rich extract from the zeolite adsorbents, can be carried out under varying conditions as part of the adsorption-desorption cycle. A thermal swing cycle comprises desorption at a temperature higher than that for the adsorption. Similarly, a pressure swing cycle employs reduced pressure to effect desorption. An isothermal purge cycle employs a non-adsorbed liquid to strip the adsorbate from the voids and eventually from the pores of the zeolite. Finally, the displacement purge cycle employs a desorbent which is equally or more strongly adsorbed than the adsorbate. This desorbent is then displaced by the adsorbate in the adsorption cycle. For further information, reference is made to an earlier quoted discussion of Molecular Sieves in Kirk-Othmer's Encyclopedia of Chemical Technology.

The preferred desorption is part of a displacement purge cycle. This cycle is preferably practiced as outlined by D.B. Broughton in U.S. patent 2,985,589 and a paper entitled "Continuous Adsorptive Processing-A New Separation Technique", presented at the 34th Annual Meeting of the Society of Chemical Engineers at Tokyo, Japan on April 2, 1969 which are incorporated hereby by reference. Broughton particularly described a simulated moving bed countercurrent process flow scheme preferred in the process of the present invention.

In general, a variety of compounds such as CO_2, NH_3, methane, butane, and butene can be used in the desorption step. However, for a preferred operation in the liquid phase using the displacement purge cycle, n-paraffins and/or n-olefins, particularly 1-n-olefins are the choice desorbents. These preferred desorbents are liquids which are lower boiling than the feed. In a preferred operation, the boiling point of the desorbent should be low enough for easy separation from the feed by distillation but high enough so as to assure that the specific gravity and viscosity of the feed are not drastically different from that of the feed. The latter facilitates smooth feed and extract displacement by liquid flow through the adsorbent bed.

Exemplary desorbing agents include, n-pentane for a C_6 feed, 1-hexene for a C_7 to C_9 feed, 1-n-octene for a C_9 to C_{13} feed. In contrast to the prior art, 1-n-octene is a preferred desorbent in the present process. Even though 1-n-octene may not be completely separated from the 1-n-olefin n-paraffin rich extract, its presence is not objectionable in the subsequent conversions of the olefin components.

In a preferred operation a broad feed fraction, such as C_8 to C_{15}, is employed and the low boiling part of the extract, e.g. a mixture of C_8, C_9 n-olefins and n-paraffins, is used as a desorbent. In such an operation, the low boiling components of the extract are distilled and used as desorbents.

The broad temperature range of desorption is generally the same as that of the adsorption. In the isothermal or nearly isothermal process cycles, such as the preferred displacement-purge cycle and the stripping cycle, the preferred temperature ranges for desorption and adsorption are similar by definition.

With the exception of the pressure swing cycle, the pressure ranges of adsorption and desorption are generally similar. Close to atmospheric cycles are preferred. In a preferred liquid phase cycle, the use of a low boiling desorbent such as n-butane may require superatmospheric pressure.

Adsorption-desorption cycles of the present process are operated in a temperature regime where no significant olefin side reactions take place. Nevertheless, the zeolite adsorbents have finite lifetimes due to minor side reactions resulting in pore plugging. Regeneration of the thus deactivated zeolite is generally possible by calcination which results in the burning off of organic impurities.

Conversion

The olefin components of n-olefin plus n-paraffin mixtures obtained in the present separation process are advantageously converted to higher boiling derivatives and then separated from the unreacted n-paraffins. These conversions generally comprise known chemical reactions and processes. The preferred conversions are oligomerization, alkylation of aromatics and carbonylation. A preferred aspect of the present invention is a unique combination of zeolite separation and selective conversion of n-olefin plus n-paraffin mixtures followed by the separation of the n-paraffin.

The preferred n-olefin-n-paraffin mixtures of the present invention contain 1-n-olefins as the main olefinic components. These 1-n-olefins are the preferred reactants in numerous types of conversions which are more specifically polymerization, oligomerization, alkylation, carbonylation and various other olefin conversions. In the following, mainly the conversions of these olefins will be discussed. n-Olefins generally undergo similar conversions at a lower rate.

The acid catalyzed and free radical oligomerization of 1-n-olefins is widely known. In the present process acid catalysed oligomerization in the liquid phase is preferred. The catalysts are generally strong acids such phosphoric acid, sulfonic acid, aluminum chloride, alkylaluminum dichloride and boron trifluoride complexes. Boron trifluoride complexes are preferably those of protic compounds such as water, alcohols, and protic acids. Using BF_3 complexes, cracking side reactions are avoided.

The oligomerizations are generally carried out in the -100 to 100° C temperature range at atmospheric pressure. Superatmospheric pressure may be used to assure a liquid phase operation. The number of monomer units in the oligomer products is 2 to 30, preferably 2 to 6.

The most preferred oligomerizations produce polyolefin intermediates for synthetic lubricants. The preparation of synthetic lubricants via the polymerization of even numbered, pure 1-n-olefins was reviewed by J.A. Brennan in the journal, Ind. Eng. Chem., Prod. Res. Dev. Vol. 19, pages 2-6 in 1980 and the references of this article. Brennan concluded that isoparaffins, derived from 1-n-decene via trimerization catalyzed by boron trifluoride followed by hydrogenation, possess superior lubricant properties. Due to the position and legnth of their n-alkyl chains these trimers also exhibit superior stability. Their viscosity is relatively insensitive to temperature changes. Based on these and similar studies C_8, C_{10} and C_{12} α-olefin based lubricants, having 30 to 40 atoms per isoparaffin molecule, were developed.

More recently synthetic lubricants were also developed on an internal olefin basis. U.S. patents 4,300,006 by Nelson and 4,319,064 by Heckelsberg et al. discuss the synthesis of such lubricants via the BF_3 catalyzed dimerization of linear internal olefins derived via α-olefin metathesis. Heckelsberg also discloses in U.S. Patent 4,317,948 the synthesis of lubricants via the codimerization of linear internal and terminal, i.e. α-olefins.

According to the present invention, the n-olefin components of a mixture of n-olefins and n-paraffins are converted into oligomers by reacting them in the presence of an acid or a free radical catalyst preferably an acid catalyst. In a preferred conversion step, oligomers containing an average of 3 to 4 monomer units, trimers and tetramers, are produced by reacting a mixture rich in C_9 to C_{13} 1-n-olefins and n-paraffins, in the presence of a boron trifluoride complex. In an alternative step, the 1-n-olefin and internal normal olefin components of a C_{13} to C_{17} mixture of n-olefins and n-paraffins are cooligomerized to produce oligomers containing an average of 2 to 3 monomer units.

Another preferred acid catalyzed oligomerizaiton of n-olefins, produces polyolefins in the C_{15} to C_{50} carbon range. These are subsequently used to alkylate benzene to produce C_{15} to C_{50} alkylbenzene intermediates for the synthesis of oil soluble calcium and magnesium alkylbenzene sulfonate detergents. For these oligomerizations preferably C_5 to C_8 n-olefins are employed.

The unconverted paraffin components of the n-olefin oligomer product mixture are removed preferably by distillation. The distillation is performed either right after the oligomerization or subsequent to the next conversion step comprising either hydrogenation to isoparaffins or benzene alkylation to alkylbenzenes.

Another preferred conversion of the n-olefin components of the n-olefin plus n-paraffin mixtures involves the acid catalyzed alkylation of aromatic compounds. Exemplary reactants are benzene, toluene, o-xylene, naphthalene and phenol.

Benzene alkylation by n-olefins is important in the preparation of the linear alkylbenzene intermediates of biodegradable aqueous alkylbenzene sulfonate detergents and oil soluble linear alkylbenzene sulfonates. Benzene alkylation can be effected with $AlCl_3$ as a catalyst by known methods at temperatures between 0 and 100° C.

Phenol alkylation by n-olefins leads to linear alkylphenol intermediates of ethoxylated surfactants. Phenol is highly reactive and can be readily alkylated in the presence of a crosslinked sulfonated styrene-divinyl benzene resin, Amberlyst 15, at 80 to 150° C.

After the alkylation of the aromatic compounds the unconverted olefins and other volatile components are removed by distillation.

A third preferred conversion is the carbonylation of the n-olefin components of the n-olefin plus n-paraffin extracts. Carbonylation is a reaction with carbon monoxide and an active hydrogen compound to provide a carbonyl derivative of said olefin reactant. In the case of the preferred 1-n-olefin components the main reaction is the following:

$RCH=CH_2 + CO + Hx \rightarrow RH_2CH_2COX$

R = n-alkyl, x = H, OH, OR

The preferred carbonylation catalysts are cobalt and rhodium carbonyl complexes. The preferred carbonylation leading to aldehydes in hydroformylation.

$$RCH=CH_2 \xrightarrow{CO/H_2} RCH_2CH_2CHO + RCH(CH_3)CO$$

The hydroformylation of the olefin components of whole FLEXICOKER distillate feeds is described in the earlier referenced Oswald et al. patent. Similar hydroformylation catalysts and conditions are applicable to the n-olefin plus n-paraffin extracts of the present invention. The preferred feed of the present carbonylations is also FLEXICOKER based. It contains mainly 1-n-olefins and n-paraffins separated from FLEXICOKER distillates.

The preferred n-olefin - n-paraffin mixtures employed as carbonylation feeds are of a relatively narrow carbon range, containing components having 3 different adjacent carbon atoms or less. This allows the separation of the unconverted paraffin components and paraffin by-products from the carbonyl compound products. In the case of hydroformylation the aldehyde product may be hydrogenated to the corresponding alcohols prior to paraffin removal by hydrogenation.

For polymerizations and copolymerizations aimed at producing high molecular weight polymers, 1-n-olefin - n-paraffin mixtures are preferred, wherein the 1-n-olefin and n-paraffin have the same particular number of carbon atoms in the molecule. For example, a mixture of 1-n-hexene and n-hexane produced by the present process can be used to produce an ethylenehexene copolymer. Similar 1-n-olefin - n-paraffins wherein the 1-n-olefin and n-paraffin have the same particular number of carbon atoms in the molecule are preferably used in other olefin conversions such as hydroboration and expoxidation.

The invention shall now be illustrated by the following Examples and with reference to the accompanying drawings in which :

Figure 1 illustrates the capillary gas chromatogram of a sharp C_{10} FLEXICOKER distillate fraction, which was most frequently used as a feed for zeolite separations.

Figure 2 illustrates the desorption, by n-hexane in a pulse test, of aromatic raffinate components and a 1-n-decene plus n-decane extract. This figure is discussed in detail in Example 12.

Figure 3 illustrates the capillary gas chromatogram of a n-decenes plus n-decane extract of the C_{10} FLEXICOKER distillate fraction, said extract having been obtained in the pulse test.

Figure 4 and 5 show the capillary gas chromatograms of a feed mixture of C_9 to C_{12} model compounds and the raffinate derived from it by sodium ZSM-5 adsorption. The details are discussed in Example 17.

Figures 6 and 7 show the gas chromatograms of a C_9 to C_{13} FLEXICOKER distillate feed and its raffinate product. The details of the selective adsorption involved are discussed in Example 18.

EXAMPLES

The following examples are provided to illustrate the presently claimed process but are not intended to limit the scope of the invention. Most of the Examples describe the novel selective adsorption in zeolites, particularly silicalites and sodium ZSM-5, of n-olefin - n-paraffin mixtures. Adsorption studies of feeds consisting of model compounds and 1-n-olefin rich cracked distillates derived from petroleum residua will be presented side by side. The desorption step of the present adsorptive, molecular sieve process will be also illustrated. Finally, an example will be given for the conversion of the olefin components of an n-olefin plus n-paraffin rich product of the present separation process.

Prior to the specific examples, the cracked distillate feed employed and the zeolite adsorbents used will be described. The test methods and analytical techniques, i.e. the gas and liquid phase standard static adsorption tests, and raffinate analysis by capillary gas chromatography, will be discussed.

Feeds, Test Methods and Analyses

The model compound mixtures employed as feeds in the adsorption tests were made up from pure laboratory chemicals representing the main types of compounds present in the feeds of the present separation process.

Preferred feed fractions examined in detail were FLEXICOKER distillates produced by cracking vacuum residua of mixed crudes of South American and Mideastern origin. Fluid-coker distillates similarly derived from Northwest American crude had similar molecular compositions. Both distillates are described in detail int he earlier referred Oswald et al. patent.

The zeolite adsorbents were calcined before use by heating at 40° C overnight. Thereafter, they were stored at 80° C under nitrogen until used.

The majority of the silicalites employed were supplied by Union Carbide Corporation. S115 was microcrystalline silicalite powder, R115 was silicalite pelletized with a silica binder. Similarly P115 was pelletized silica with an alumina binder. A low alumina (less than 200 ppm) microcrystalline silicalite was also employed.

Some of the high alumina (5000 ppm) silicalite powder from Union Carbide Corporation was treated at room temperature at first with an 18% aqueous hydrochloric acid solution overnight 3-4 times, until the supernatant liquid was no longer discolored. Thereafter, the silicalite was treated with a dilute aqueous sodium hydroxide solution of pH 9-10 overnight. These treatments resulted in a significant reduction of its alumina content and the neutralization of acidic impurities. The silicalite resulting from this acid base treatment was calcined as usual.

A laboratory preparation of ZSM-5 sodium aluminosilicate derivative derived from the corresponding quaternary ammonium derivative was also used. The microcrystalline powder was also calcined and employed in some of the adsorption tests. Sodium ZSM-5, made via direct synthesis by Uetikon of Switzerland was also tested.

The model compound mixtures and FLEXICOKER distillate fractions employed as feeds in the adsorption tests and their respective raffinates, i.e. non-adsorbed products of these tests, were analyzed by capillary gas chromatography (GC). High resolution GC analyses were carried out using a 50 m fused silica column coated with non-polar methylsilicones. Thus GC retention times were approximately proportional to the boiling points of the components.

In general, the adsorption tests were carried out with accurately weighed amounts of zeolite and hydrocarbon feed. After contacting the zeolite and the feed, the composition of the rejected hydrocarbon raffinate was analyzed and compared with that of the feed.

Static adsorption tests were carried out in both the gas and the liquid phase, using model compound mixtures and FLEXICOKER fractions of varying carbon ranges. In the gas phase test about 1 g zeolite and 0.2 g hydrocarbon feed were placed into a small closed vial and kept there for four hours at 40° C. With the low, C_5 and C_6, fractions used in these tests, this was sufficient to reach adsorption and gas liquid equilibria. Thereafter, the gas phase of the test mixture representing the raffinate and the feed were both sampled for G.C. analyses.

In the liquid phase tests, the hydrocarbon feed was diluted with a non adsorbing bulky compound, heptamethylnonane or decalin. In the majority of liquid phase tests 2 g of a 10/90 mixture of hydrocarbon and diluent was used per g zeolite. This proportion of the liquids to solids gave rise to a substantial supernatant liquid phase of the test mixture which could be easily sampled. The test mixture was heated for several hours with occasional shaking to reach equilibrium. The supernatant liquid was then analyzed by GC and its composition was compared with that of the feed.

Some of the liquid phase tests were carried out with about 1g of a 30/70 mixture of the feed plus diluent per g zeolite. These mixtures exhibited no significant supernatant liquid phase after settling. The sealed mixtures were heated to reach equilibria as above. Due to the absence of a separate liquid phase, the equilibria were more rapidly established in these tests. After equilibriation, the test mixtures were diluted with about 1g of isooctane, 2,2,4-trimethylpentane, or other suitable bulky compound and thoroughly mixed. After settling, the clear supernatant liquid phase was analyzed by GC as usual.

It is noted that the absence of zeolite microcrystals from the liquids injected to the gas chromatograph is critical for correct compositional analyses of the raffinates. These crystals, if present, are deposited in the high temperature (about 325° C) injection port of the chromatograph and act as cracking catalysts particularly for the 1-n-olefin components.

The FLEXICOKER distillate feeds exhibited complex gas chromatograms with overlapping GC peaks of some components, especially in case of the higher fractions. As a consequence the nominal GC percentages of some small components were dependent on the GC sample size.

The selectivities and capacities of zeolite adsorbents for the components of the test mixtures were estimated by the ratio of their respective concentrations in the raffinate. High ratios indicated selective adsorption while low ratios were signs of rejection by the zeolite.

Example 1

Preparation of Acid Base Treated Silicalite

One liter of 18% by wt. hydrochloric acid, at room temperature, was added to 20g silicalite (S115 from Union Carbide Corporation) with stirring. The liquid-solid suspension was allowed to settle overnight to separate into two phases. The supernatant liquid phase, which had become discolored, was decanted and 1 liter of fresh 18% HCl was added to the solid with stirring and again allowed to settle overnight. This acid washing procedure was repeated a third time, after which the liquid phase remained colorless. The silicalite was collected and washed repeatedly with deionized water until the wash water gave a neutral reaction to litmus. The silicalite was then washed in 1 liter of a mildly basic solution which was prepared by adding 0.3g NaOH to 1 liter water, again allowed to settle, and finally rinsed once with deionized water. The silicalite was dried in air overnight at 90° - 95° C and calcined at 400° C for a minimum of 4 hrs. at which time it was ready for use.

Example 2

Adsorption of n-Pentenes and n-Pentane From C_5 FLEXICOKER Naphtha

A sealed mixture of about 0.2g C_5 FK feed fraction and 1g acid base treated silicalite was heated at 40° C for four hours. Subsequent gas phase analyses of the feed and the raffinate (Raf.) by GC indicated the percentage composition listed in Table I. (The main components are listed in the order of their retention times.)

The data of Table I show that the concentrations of 1-n-pentene, cis- and trans-pentenes and n-pentane are significantly reduced in the raffinate, indicating their selective adsorption. In contrast the concentrations of methyl branched butenes and isopentane (2-methylbutane) are increasing in the raffinate, indicating their rejection.

Table I

Adsorption of C_5 FLEXICOKER Fraction by Acid/Base Treated Silicalite

Name of Component	Component		
	Conc., GC %		Ratio, Feed to Raf.
	Feed	Raf.	
3-Methyl-1-butene	4.5	9.3	0.48
Isopentane	13.4	21.8	0.61
1-n-Pentene	38.1	22.6	1.69
2-Methyl-1-butene	18.4	24.2	0.76
n-Pentane	12.5	6.7	1.86
Isoprene	3.1	4.5	0.69
trans-2-Pentene	4.9	3.1	1.58
cis-2-Pentene	1.8	1.3	1.38
2-Methyl-2-butene	0.8	3.2	0.25

Example 3

Adsorption of n-Hexenes and n-Hexane From a Mixture of C_6 Model Compounds

About 0.2g of a mixture of similar amounts of n-hexenes, n-hexane and 2-methylpentane and 1g acid/base washed silicalite were contacted at 40° C for four hours and analyzed by the gas phase method using GC. The compositions of the resulting raffinate and the starting feed are compared in Table II.

The data of the table indicate that with the exception of cis-2-hexene, all the n-hexenes plus the n-hexane in the mixture were adsorbed. Trans-2-Hexene was preferentially adsorbed over cis-2-hexene.

A rejection of 2-methyl branched 1-pentene was indicated.

Calculations have shown that the approximate capacity of the silicalite for 2-hexenes and 1-hexene was about 4.7 wt.% and 1.9 wt.%, respectively.

Table II

Adsorption of Model Mixture of C_6 Hydrocarbons by Acid/Base Treated Silicalite			
Name of Component	Component		
	Conc., GC %		Ratio, Feed to Raf.
	Feed	Raf.	
2-Methyl-1-pentene	18.5	33.0	0.56
1-n-Hexene	17.0	13.8	1.23
n-Hexane	18.0	12.6	1.43
trans-2-Hexene	22.7	14.7	1.55
cis-2-Hexene	18.8	17.0	1.11

Example 4

Adsorption of n-Hexenes and n-Hexane From C_6 FLEXICOKER Naphtha

A gas phase adsorption test was carried out with a mixture of about 0.2g broad C_6 FLEXICOKER feed fraction and 1g acid/base treated silicalite for four hours at 40° C. Subsequent GC analyses of the feed and the raffinate obtained are shown in Table III.

The data of the table show that, among the C_5 components, cyclopentene and cyclopentane are not adsorbed. In contrast, cis and trans-piperylene appear to get adsorbed among the numerous C_6 hydrocarbons, the n-hexanes exhibited the positive adsorption behavior observed in the C_6 model mixture. The methyl branched pentenes did not get appreciably adsorbed except the 3-methyl branched 2-pentene. Among the C_6 paraffins present, only n-hexane was adsorbed.

Calculation indicated that the approximate capacity of the silicalite for the main two components 1-n-hexane and n-hexane was 3.5% and 1.8%, respectively.

Table III

Adsorption of C_6 FLEXICOKER Fraction by Acid/Base Treated Silicalite

Name of Component	Component		
	Conc., GC%		Ratio, Feed to Raf.
	Feed	Raf.	
n-Pentane	2.2	0.3	7.3
trans-2-Pentene	1.7	0.7	2.4
cis-2-Pentene	1.1	0.6	1.8
2-Methyl-2-butene	3.8	7.3	0.5
trans-Piperylene	1.1	0.2	5.5
cis-Piperylene	0.8	0.2	4.0
Cyclopentene	4.4	7.8	0.6
Cyclopentane	3.4	6.4	0.6
4-Methyl-1-pentene	5.8	10.4	0.6
2-Methylpentane	4.5	7.2	0.6
4-Methyl-2-pentene	2.3	3.8	0.6
3-Methylpentane	1.8	3.1	0.6
2-Methyl-1-pentene	3.6	5.7	0.6^{a}
1-n-Hexene	20.3	5.3	3.8^{a}
n-Hexane	10.1	2.2	4.6
3-Hexenes	1.3	0.5	2.6
trans-2-Hexene	3.0	0.7	4.0^{a}
2-Methyl-2-pentene	2.1	3.4	0.6
3-Methyl-2-pentene	1.5	0.5	3.0
cis-2-Hexene	1.2	1.8	0.7
Methylcyclopentane	3.5	4.7	0.7
Benzene	6.1	7.6	0.8^{a}

[a] GC peak overlap

Example 5

Adsorption of 1-n-Octene and n-Octane From a Mixture of C_8 Model Compounds

About 2.4 g of 10/90 mixture of C_8 model compounds and heptamethylnonane diluent were added to two 1g acid/base washed samples to prepare two test mixtures. These mixtures were then heated at 110°C for 2 hours and at 150°C for 4 hours. The supernatant liquids of these compositions were then analyzed by GC. The GC compositions of the two C_8 raffinate compositions are compared to that of the feed in Table IV.

The data of the table indicate that 1-n-octene and n-octane are selectively adsorbed from a mixture containing C_7 and C_8 aromatic hydrocarbons at both test temperatures. There is only minor isomerization of 1-octene to internal i.e. 2-, 3- and 4-octenes. The aromatic sulfur compounds present, 2-methylthiophene and 2,5-dimethylthiophene, are highly selectively adsorbed. The selectivity as indicated by the ratio of raffinate to feed is particularly high for the less bulky methylthiophene.

Table IV

Adsorption of Model Mixture of C_8 Hydrocarbons by Acid/Base Treated Silicalite

Name of Component	Concentration, GC %			Ratio of Feed to Raffinate	
	Raffinate			to Raffinate	
	Feed	110° C	150° C	110° C	150° C
Toluene	12.7	15.3	18.1	0.8	0.7
2-Methylthiophene	1.3	0.4	0.1	3.4	10.3
1-n-Octene	20.2	10.8	9.7	1.9	2.1
4-Octene	0.1	0.1	0.1	~1.0	~1.0
3-Octene	0.2	0.4	0.4	~0.5	~0.5
n-Octane	28.7	10.6	9.4	2.7	3.0
trans-2-Octene	0.3	0.7	0.7	~0.4	~0.4
cis-2-Octene	0.2	0.9	0.6	~0.2	~0.3
Ethylbenzene	15.7	18.8	21.9	0.8	0.7
2,5-Dimethylthiophene	1.5	0.7	0.3	2.2	7.7
m- & p-Xylenes	26.7	34.0	38.9	0.8	0.7

Example 6

Adsorption of 1-n-Octene and n-Octane from C_8 FLEXICOKER Naphtha

A liquid phase adsorption test was carried out with about 2.2 ml of a 10/90 mixture of a C_8 FLEXICOKER distillate and heptamethylnonane and 1 g acid/base washed silicalite. The mixture was heated at 110° C for 2 hours. The supernatant raffinate was analyzed by GC and its composition compared with that of the feed. The results are shown in Table V.

The data indicate 1-n-octene and n-octane are selectively adsorbed. It appears that some of the 1-n-octene was isomerized to internal octenes. 4-Methyl-1-heptene is apparently not adsorbed appreciably because of the branching in the middle of the chain. The dimethyl branched aliphatic hydrocarbons are completely rejected. Similarly, the aromatic hydrocarbons, toluene and ethylbenzene, appear to be rejected.

Table V

Adsorption of C_8 FLEXICOKER Fraction by Acid/Base Washed Silicalite at 110° in 2 Hours			
Name of Component	Component		
	Conc. GC %		Ratio, Feed to Raf.
	Feed	Raf.	
Toluene	7.2	11.8	0.6
4-Methyl-1-heptene	2.8	4.4	0.6
2-Methylheptane	4.3	2.0	2.1
cis-1,3-Dimethylcyclohexane	4.5	6.5	0.7
2-Methyl-1-heptene [a]	6.1	1.8	3.4
1-n-Octene [a]	17.6	7.2	2.5
4-Octene [b]	2.7	5.4	0.5
3-Octene [b]	1.9	2.2	0.8
n-Octane [b]	13.2	9.5	1.4
trans-2-Octene [b]	2.4	2.0	1.2
Dimethylhexathiene [c]	2.6	5.0	0.5
cis-2-Octene	1.3	0.8	1.7
Dimethylcyclohexene [c]	1.4	2.9	0.5
Ethylbenzene	0.4	0.7	0.5

[a] Partial isomerization may have occurred

[b] Value includes associated GC peaks

[c] Tentative identification

Example 7

Adsorption of 1-n-Nonene and n-Nonane Versus 2-Methylnonene and 2-Methylnonane from a Mixture of C_9 Model Compounds

About 1 g each of a 40/60 mixture of model compounds and decalin diluent were mixed with about 1 g each of acid/base washed silicalite and sodium ZSM-5. The mixtures were heated in closed vials at 150° C for one hour in a liquid phase adsorption test. Thereafter, they were diluted with about 1 mole i-octane. The solid zeolites were then allowed to settle and the supernatant raffinate liquids analyzed by GC. The composition of the raffinates is compared with that of the starting mode mixture in Table VI.

The data of Table VI indicate that 1-n-nonene and n-nonene are strongly and about equally adsorbed on both the silicalite and the sodium ZSM-5 adsorbent. 2-Methyl-1-nonene and 2-methylnonane are only slightly adsorbed. In contrast, both of the trimethylbenzene isomers are completely rejected.

In the presence of the silicalite a slight isomerization of 1-n-nonene to cis-and trans-2-nonenes occurred. Seemingly, a major isomerization of 2-methyl-1-nonene probably to 2-methyl-2-nonene took place in the presence of silicalite. In the presence of sodium ZSM-5, there vas no indication of any isomerization.

The decreased concentrations of 1-n-nonene and n-nonane in the raffinates indicate that the combined capacities for these two compounds of silicalite and sodium ZSM-5 are about 8.3 and 9.2%, respectively.

Table VI

Adsorption of 1-n-Nonene and n-Nonane Versus 2-Methylnonane and 2-Methylnonene by Acid/Base Treated Silicalite and Sodium ZSM-5					
Name of Component	Composition, GC%			Ratio of Feed	
	Raf. 150 °C, 1 hr			to raffinate	
	Feed	Silicalite	ZSM-5	Silicalite	ZSM 5
1-n-Nonene	17.1	12.9	12.1	1.3	1.4
n-Nonane	16.8	12.9	12.2	1.3	1.4
trans-2-Nonene		0.3			
cis-2-Nonene		0.2			
1,3,5- Trimethylbenzene	18.5	23.9	25.8	0.8	0.7
2-Methylnonane	12.3	11.3	10.7	1.1	1.1
2-Methyl-1-nonene	17.9	4.3	15.0		
				1.1	1.2
2-Methyl-2-nonene[a]	0.6	12.5	0.6		
1,2,3-Trimethylbenzene	16.8	21.7	23.6	0.8	0.7

[a] The compound was not conclusively identified

Example 8

Adsorption of 1-n-Decene and n-Decane from Their Mixture With Trimethylbenzenes

About 1.6 g of a 15% solution of 1-n-decene, n-decane, 1,2,4- and 1,2,3-trimethylbenzenes in heptamethylnonane was added to 1 g acid/base washed silicalite. The mixture was heated at 150 °C for 3 hours. A subsequent GC analysis of the supernatant liquid raffinate showed a major change in the composition of the model compounds as shown by Table VII.

The data show a highly selective adsorption of both 1-n-decene and n-decane. A minor isomerization of 1-n-decene is indicated by the readily distinguished GC peaks of 4-decene and trans-2-decene. Based on the decreased concentrations of 1-n-decene and n-decane, the approximate capacity of the silicalite for these compounds together is 10.1%.

Table VII

Adsorption of a Mixture of C_9 and C_{10} Model Compounds by an Acid/Base Washed Silicalite at 150° C for 3 hours

Name of Component	Comp., GC %		Ratio Feed to Raf.
	Feed	Raf.	
1,2,4- Trimethylbenzene	29.7	50.2	0.6
1-Decene	22.1	0.9	24.5
4-Decene		0.1	
n-Decane	22.0	2.8	7.9
trans-2-Decene		0.1	
1,2,3- Trimethylbenzene	25.4	44.5	0.6

Example 9

Adsorption of Isomeric n-Decenes from a Mixture of Model Compounds

About 2.7 g of a 1/1 mixture of C_{10} model compounds and heptamethylnonane was added to a 1 g acid/base washed silicalite. The resulting test mixture was then heated at 150° C for 2 hours. The supernatant raffinate liquid was then analyzed by GC and its composition compared with that of the feed mixture. The results are shown by Table VIII.

The data show that all the n-decenes are adsorbed in contrast to the trimethylbenzene components. However, it is not possible to determine the relative selectivities of their adsorption because of their concurrent isomerization. At a concentration comparable to those of n-decenes, 2,5-dimethylthiophene is adsorbed to a lesser degree although it is clearly not rejected like the trimethylbenzenes.

Table VIII

Adsorption of n-Decenes by an Acid-Base Washed Silicalite at 150° C in 2 Hours

Name of Component	Comp., GC%		Ratio, Feed to Raf.
	Feed	Raf.	
2,5-Dimethylthiophene	10.7	11.8	0.9
1,2,4-Trimethylbenzene	18.0	29.4	0.6
1-n-Decene	11.3	5.7	2.0
4-Decene	12.7	7.0	1.8
3-Decene	3.0	2.4	1.3
trans-2-Decene cis-2-Decene[a]	12.0	8.5	1.4
1,2,3-Trimethylbenzene[a]	26.6	33.5	-

[a] The two GC peaks are not completely resolved.

Example 10

Adsorption of 1-n-Decene and n-Decane from a Mixture of C_{10} Model Compounds by Various Silicalites

About 1 g of each of an about 10/90 mixture of C_{10} model compounds and heptamethylnonane was added to 1 g samples of various silicalites. The resulting mixtures were heated at 150° C for 2 hours and the raffinates analyzed by GC. The data are shown by Table IX.

A comparison of the feed composition with those of the raffinates indicate that all the silicalites tested selectively adsorb 1-n-decene and n-decane. The untreated and acid/base washed silicalites were especially effective in adsorbing 1-n-decene. It is indicated by the low concentration of cis-2-decene in the raffinate, that no significant isomerization of 1-n-decene occurred. The concentration of indene in the raffinate of the mixture with the untreated silicalite is sharply reduced. This is probably due to acid catalyzed dimerization, oligomerization. The reduced concentrations of 2,5-dimethylthiophene indicate its selective adsorption by all the zeolites. It is noted that a selective 2,5- dimethylthiophene adsorption was not observed in the previous example where large amounts of 2,5-dimethylthiophene were employed. The bulkier sulfur compound, benzothiophene, was not adsorbed in either the present or the previous example.

Table IX

Adsorption of C_{10} Model Compounds by Various Silicalites					
Name of Component	Composition, GC % Silicalite at 120° C, 2 hrs				
	Feed	As is	Acid/Base	Silica Binder	Pure
2,5-Dimethylthiophene	1.6		0.2	0.4	0.1
1,3,5-Trimethylbenzene	10.0	30.8	21.5	17.0	20.2
1,2,4-Trimethylbenzene	9.9	26.0	18.7	16.5	19.9
1-n-Decene	25.7		0.4	12.4	8.2
n-Decane	27.9	12.1	7.9	18.3	7.7
cis-2-Decene	0.3	0.3	1.2	0.2	0.2
Indane	0.8	1.9	1.2	1.3	1.5
Indene	11.4	2.4	15.3	16.1	19.0
Naphthalene	8.0	22.0	16.9	13.8	18.7
Benzothiophene	2.0	3.6	3.3	3.2	4.2[a]

Example 11

Adsorption of 1-n-Decene and n-Decane from a Mixture of C_{10} Model Compounds with Sodium ZSM-5 and Silicalite

Adsorption experiments were carried out at 120° C in the manner described in the previous example with sodium ZSM-5 and a silicalite pelleted with alumina binder. The results are shown in Table X.

The data show that ZSM-5 exhibits a similar adsorption behavior to that of the alumina bound silicalite of this example and the silicalites of the previous example. 1-n-Decene and n-decane are selectively adsorbed. 2,5-Dimethylthiophene is adsorbed while benzothiophene is rejected. All the aromatic hydrocarbons are rejected.

A time study of the adsorption with the silicalite showed that the process was essentially complete in 30 minutes or less.

Table X

Adsorption of C_{10} Model Compounds by Na ZSM-5 and a Silicalite with Al_2O_3 Binder			
Name of Compound	Composition, GC %		
		120° C for 1 hr.	
	Feed	ZSM-5	Silicalite
2,5- Dimethylthiophene	1.6	0.5	0.3
1,3,5- Trimethylbenzene	10.0	26.0	19.7
1,2,4- Trimethylbenzene	9.9	24.3	18.7
1-n-Decene	25.7	7.5	13.3
n-Decane	27.9	8.8	17.4
Indane	0.8	1.3	1.3
Indene	11.4	15.2	13.5
Naphthalene	8.0	13.4	13.3
Benzothiophene	2.0	2.8	2.5

Example 12

Adsorption of 1-n-Decene and n-Decane from C_{10} FLEXICOKER Naphtha by Acid/Base Washed Silicalite

About 1.9 g of a 10/90 mixture of a sharp C_{10} FLEXICOKER naphtha fraction, of bp. 165 to 171° C, was added to 1 g acid/base washed silicalite. The resulting test mixture was heated for 4 hours at 150° C. The feed and the supernatant raffinate liquid were then analyzed by GC. The gas chromatogram of the feed is shown by Figure 1. The compositions of the feed and the raffinate are compared in Table XI.

The data of the table show that the concentrations of the main 1-n-decene and n-decane components are drastically reduced on treatment with silicalite. This is apparently due to the selective adsorption of these components. As a consequence of the selective adsorption of the linear aliphatic compounds the concentration of the aromatic components is generally increased.

Table XI

Adsorption of 1-n-Decene and n-Decane From a Sharp C_{10} Fraction of FLEXICOKER Naphtha by Acid/Base Washed Silicalite

Name of Compound	Concentration,GC %		Ratio, Feed to Raf.
	Feed	Raf.	
1-Methyl-3-ethylbenzene	0.69	1.30	0.53
1-Methyl-4-ethylbenzene	0.79	0.82	0.96
1,3,5- Trimethylbenzene	1.90	3.71	0.51
1-Methyl-2-ethylbenzene	2.32	4.15	0.56
1,2,4-Trimethybenzene	12.98	23.41	0.55
1-n-Decene	23.17	0.92	25.18
n-Decane	14.86	3.57	4.16
trans-2-Decene	3.14	2.73	1.15
1,2,3- Trimethylbenzene	7.41	12.82	0.58
Indane	2.96	5.52	0.54
Indene	0.85	0.90	0.94

Example 13

Adsorption-Desorption of n-Decenes and n-Decane from C_{10} FLEXICOKER Naphtha Fraction in a Pulse Test

About 4.51 g acid base washed silicalite, having a bed volume of 5 ml, was packed into a 1 ft. stainless steel column of a diameter of 1/4 in. The resulting adsorbent bed was pre-wetted with n-hexane desorbent at a liquid hourly space velocity [LHSV] of 1.3, i.e. 6.5 ml per hour. After the desired operating conditions, i.e. 140° C and 270 psi, were lined out, a 0.25 ml C_{10} FLEXICOKER feed pulse, of the composition shown in the previous example, was injected into the column. After the injection, the flow of n-hexane desorbent was resumed and the feed components were eluted. Effluent samples were collected periodically and analyzed by GC. Their composition was plotted against the volume of the eluted desorbent as shown by Figure 2.

Figure 2 indicates that the aromatic (and branched aliphatic) hydrocarbon components of the feed were eluted at first, due to their simple displacement by the desorbent from the voids of the silicalite column. This early fraction is the raffinate. Elution of the n-decane and 1-n-decene component rich extract occurred distinctly later. These components of the extract clearly coeluted, due their concurrent displacement from the channels of the silicalite by the desorbent. The 1-n-decene was slightly more difficult to displace than the n-decane. As it is shown by the Figure an in between-cut of the eluent was taken between the raffinate and the extract.

Both the raffinate and the extract were analyzed by GC in some detail. The analysis of the raffinate showed that essentially all the aromatic components of the feed were recovered. The results of the GC analysis of the extract are illustrated by Figure 3.

Figure 3 shows that besides n-decane and 1-n-decene, significant amounts of internal linear decenes (5-,4-and 2-decenes) were recovered in the extract. The latter compounds were in part already present in the feed. Additional amounts were formed via 1-n-decene isomerization during the adsorption desorption process.

The chromatogram of the figure also indicates the presence in the extract of small amounts, about 0.5%, of 2-methyl-1-nonene. Some adsorption by the silicalite of this compound and the related 2-methylnonane was indicated by the model compound experiment described in Example 7.

Example 14

Adsorption of 1-n-Decene and n-Decane from C_9 FLEXICOKER Naphtha by Silicalites and Sodium ZSM-5

About 0.8 g each of an approximately 20/80 mixture of the sharp C_{10} FLEXICOKER distillate fraction of the previous example was added to about 1 g of an appropriate molecular sieve. The resulting test mixtures were heated at 120° C for 1 hour and the raffinates analyzed. The results are shown in Table XII.

The data of the table indicate the concentrations of 1-n-decene, n-decane, trans-2-decene and the major, identified aromatic hydrocarbon components. Compared to the composition of the feed, the percentages of 1-n-decene and n-decane decreased in all the raffinates, indicating their selective adsorption. The concentrations of most aromatic hydrocarbons increased in the raffinate, due to their rejection. The various silicalites and sodium zeolite exhibited a similar adsorption behavior.

Similar tests with different test periods showed that the adsorption is essentially complete in one hour.

Table XII

Adsorption of C_{10} FLEXICOKER Fraction by Silicalites and Sodium ZSM at 120° C in 1 Hour

Name of Component	Composition, GC% Raffinate Silicalite				
	Feed	Acid/Base[a]	Silica[b]	Alumina[b]	Na ZSM- 5
1-Methyl-3-ethylbenzene	0.8	1.2	1.1	1.1	1.2
1-Methyl-4-ethylbenzene	0.8	1.1	1.0	0.7	0.7
1,3,5-Trimethylbenzene	1.9	3.0	3.0	2.9	3.3
1-Methyl-2-ethylbenzene	2.3	3.9	4.0	3.7	3.9
1,2,4-Trimethylbenzene	12.6	19.5	17.6	16.5	19.3
1-Decene	22.7	10.5	7.3	7.6	7.0
n-Decane	14.9	6.7	6.4	7.4	6.2
trans-2-Decene	3.9	3.1	2.1	2.1	1.8
1,2,3-Trimethylbenzene	7.4	10.2	10.0	9.3	10.8
Indane	2.9	4.6	4.4	4.1	3.3
Indene	0.9	1.2	1.2	0.8	0.8

[a] About 0.96 g test solution per g acid/base washed silicalite
[b] About 0.80 g test solution per g pelletized silica
[c] About 1.5 g test solution per g Na ZSM-5 powder

Example 15

Adsorption of 1-n-Dodecene and n-Dodecane from a Mixture of Model Compounds

About 2.5 g of a 10/90 mixture of model compounds and heptamethylnonane solvent was added to 1 g acid/base washed silicalite to obtain a test mixture. This was then heated for 150° C for 2 hours. Thereafter, the supernatant raffinate liquid and the starting feed were analyzed by GC. Their compositions are compared in Table XIII.

The data of the table indicate that 1-n-dodecene and n-dodecane were adsorbed by the silicalite while the aromatic hydrocarbons and benzothiophene of their boiling range were rejected.

Table XIII

Adsorption of 1-n-Dodecene and n-Dodecane from a Mixture of Model Compounds by Acid-Base Washed Silicalite at 150° for 2 Hours			
Name of Component	Composition, GC%		Ratio, Feed to Raf.
	Feed	Raf.	
1,2,3,5-Tetramethylbenzene	26.2	43.9	0.6
Naphthalene	22.3	33.8	0.7
Benzothiophene	4.3	6.4	0.7
1-n-Dodecene	19.6	3.3	5.9
n-Dodecane	24.0	10.0	2.4

Example 16

Adsorption of 1-n-Dodecene and n-Dodecane From C_{12} FLEXICOKER Distillate

About 1.4 g of a 10/90 mixture of a sharp C_{12} distillate fraction of light FLEXICOKER gas oil (of bp. 212° C) and heptamethylnonane were added to 1 g of acid/base washed silicalite. The resulting mixture was then heated at 150° C for two hours. Samples of the supernatant raffinate liquid and the starting feed were then analyzed by GC. The percentages of some of the main components are shown in Table XIV.

The data of the table show decreased concentrations of 1-n-dodecene and n-dodecane and correspondingly increased concentrations of 1,2,3,5-tetramethylbenzene and naphthalene in the raffinate. This, of course, indicates the selective adsorption of the two main linear aliphatic hydrocarbon components. Similar results were obtained when the test mixture was heated at 195° C instead of 150° C.

Table XIV

Adsorption of a C_{12} FLEXICOKER Fraction by Acid/Base Washed Silicalite at 150° C in 2 Hours			
Name of Component	Composition, GC%		Ratio, Feed to Raf.
	Feed	Raf.	
1,2,3,4-Tetramethylbenzene	1.2	2.4	0.5
Naphthalene	3.3	6.4	0.5
1-n-Dodecene	29.1	5.0	5.8
n-Dodecane	17.7	9.2	1.9

Example 17

Adsorption of 1-n-Olefins and n-Paraffins from a Mixture of C_9 to C_{13} Model Compounds by Sodium ZSM-5

About 1 g of a 15/85 mixture of C_9 to C_{13} model compounds and heptamethylnonane was added to sodium ZSM-5. The resulting test mixture was heated at 120° C for 2 hours. Samples taken after 1 and 2 hours were analyzed by GC and their compositions were compared with that of the feed. The capillary gas chromatograms of the feed and the 1 hour raffinate are shown by Figures 4 and 5 to illustrate the results. The quantitative GC compositions of the feed and the raffinates are shown by Table XV.

The data of the table show that the C_9 to C_{13} model feed mixture contained about equal amounts (9 wt.%) of C_9 to C_{12} 1-n-olefins. Also, similar amounts (5,7 wt.%) of C_9 to C_{12} n-paraffins were present in the feed. The concentrations of the rest of the hydrocarbon components were about 3.5% by weight. Due to the different factors of GC detection, the percentages determined by GC were somewhat different but similar.

A comparison of Figures 4 and 5 indicate that the concentrations of all the 1-n-olefins and n-paraffins were decreased in the raffinate due to selective coadsorption. Surprisingly, the decrease of their concentrations increased with their increasing carbon number. The GC concentration of 1-n-nonene decreased from 9.7 to 9.4% while that of 1-n-dodecene decreased from 9.1 to 1.1% in two hours. A similar trend was observed in the case of the n-paraffin components as indicated by a comparison of Figures 4 and 5 and the data of the table.

Based on the changes in their respective concentrations, the slightly branched C_{10} aliphatic hydrocarbons, 2-methylnonane and 2-methyl-1-nonene, were found to be adsorbed somewhat but to a much lesser degree than the linear C_{10} aliphatics, n-decane and 1-n-decene.

The concentrations of the aromatic hydrocarbon components were greatly increased in the raffinate, indicating their rejection from the adsorbate. The two aromatic sulfur components, 2,5-dimethylthiophene and benzothiophene, showed a size dependent behavior. The smaller 2,5-dimethylthiophene was adsorbed somewhat while the larger benzothiophene molecule was not.

A comparison of the compositions of the 1 and 2 hour raffinate samples indicated that most of the adsorption occurs during the first hour. Similar but slower adsorption was found to take place at 80° C. Experiments with a C_6 to C_{13} mixture of model compounds showed a similar effect of the molecular weight on the coadsorption of 1-n-olefins and n-paraffins. The above experiments suggest that the present separation process is applicable to broad carbon range refinery streams such as heavy FLEXICOKER naphtha and light coker gas oil.

Table XV

Adsorption of C_9 to C_{13} Model Compounds by Sodium ZSM-5 at 120°C

Name of Compound	C_9-C_{13} Feed Composition		Raffinate Composition GC%		Ratio Feed to 2 hr. Raf.
	Wt%	GC%	1 hr	2 hr	
2,5- Dimethylthiophene	1.17	0.94	1.11	0.87	1.08
o-Xylene	3.42	3.89	8.55	8.47	0.46
1-n-Nonene	9.12	9.71	9.14	9.38	1.04
n-Nonane	5.70	6.08	5.49	5.57	1.09
1-Methyl-3-ethylbenzene	3.54	3.59	7.65	8.03	0.45
1-Methyl-4-ethylbenzene	3.56	4.43	9.25	9.54	0.46
1,3,5-Trimethylbenzene	3.59	4.03	8.68	9.00	0.45
2-Methylnonane	3.61	3.81	3.59	3.42	1.11
2-Methylnonene	3.76	3.78	3.50	3.29	1.08
1-n-Decene	9.13	0.68	5.77	5.46	1.77
n-Decane	5.72	6.15	3.38	3.15	1.95
Indane	3.45	3.30	6.93	7.32	0.45
1-n-Undecane	9.18	8.36	2.65	2.23	3.75
n-Undecane	5.67	6.13	1.70	1.39	4.41
1,2,4,5-Tetramethylbenzene	3.47	3.95	8.31	8.91	0.44
Naphthalene	3.52	4.19	8.45	9.19	0.46
Benzothiophene	1.18	1.10	2.21	2.37	0.46
1-n-Dodecene	9.12	9.09	1.51	1.11	8.19
n-Dodecane	5.73	6.34	0.82	0.60	10.57
n-Tridecane	6.36	7.02	0.09	-	-

Example 18

Adsorption of 1-n-Olefins and n-Paraffins from a C_9 to C_{13} FLEXICOKER Distillate by Sodium ZSM-5

A C_9 to C_{13} mixture of FLEXICOKER distillates was prepared by combining fractions in the 139 to 234°C boiling range in proportions providing 1-n-olefin concentrations in the 2.1 to 3.1% range. This feed was then diluted with heptamethylnonane to obtain a 21.5% test solution. The molecular sieve employed for adsorption was a sodium ZSM-5 zeolite prepared by Uetikon of Switzerland via direct synthesis. About 1.2 g test solution was added to 1 g zeolite and the mixture was heated at 120°C for 1 hour. The supernatant raffinate liquid was then analyzed by GC and its composition was compared with that of the feed. The capillary gas chromatogram of the feed and the raffinate are shown by Figure 6 and 7, respectively.

A first look at the chromatograms indicated that the 1-n-olefin and n-paraffin components were selectively adsorbed. Their GC peaks were hardly observable in the raffinate. Quantitative data, showing the concentrations of these components and some identified aromatic compounds in the feed and the raffinate, are shown by Table XVI. The data of the table show that as the concentrations of 1-n-olefins and n-paraffins decreased in the raffinate, the concentrations of aromatics increased. The decrease, in the concentration of linear aliphatic compounds due to adsorption, appeared to be greater in the C_9 to C_{11} than in the C_{12}, C_{13} range, probably due to greater aromatic GC peak overlaps in the high carbon range.

Thus the present selective adsorption-desorption process appears applicable to broad as well as narrow carbon range feeds.

Table XVI

Adsorption of C_9-C_{13} FLEXICOKER Fraction by Sodium ZSM-5 at 120°C in 1 Hour

Name of Compound	Composition, GC%		Ratio, Feed to Raf.
	Feed	Na ZSM -5	
Ethylbenzene	0.33	0.23	1.43
m-& p- Xylenes	1.47	1.77	0.83
o-Xylene	1.04	1.81	0.57
1-n-Nonene	2.27	0.35	6.49
n-Nonane	1.92	0.34	5.65
1-Methyl-3-ethylbenzene	0.83	1.40	0.59
1-Methyl-4-ethylbenzene	0.66	0.25	2.64
1,3,5-Trimethylbenzene	0.65	1.19	0.55
1-Methyl-2-ethylbenzene	0.74	1.14	0.65
1,2,4- Trimethylbenzene	1.79	2.75	0.65
1-n-Decene	2.90	0.26	11.15
n-Decane	2.12	0.48	4.42
1,2,3-Trimethylbenzene	1.41	2.21	0.64
Indane	0.73	1.13	0.65
Indene	0.60	0.50	1.20
1,4-Dimethyl-2-ethylbenzene	0.86	0.87	0.99
1,2-Dimethyl-4-ethylbenzene	1.30	2.62	0.50
1-n-Undecene	3.11	0.29	10.72
n-Undecane	2.64	0.60	4.40
1,2,4,5-Tetramethylbenzene	0.67	1.19	0.56
1,2,3,5- Tetramethylbenzene	0.87	1.09	0.80
Methylindane	0.92	1.55	0.59
1,2,3,5- Tetramethylbenzene	0.50	0.92	0.54
Naphthalene	0.41	0.87	0.47
1-n-Dodecane	2.78	0.70	3.97
n-Dodecane	2.06	0.51	4.04
1-n-Tridecene	2.06	0.89	2.31
n-Tridecane	2.13	1.77	1.20

Example 19

Adsorption of Isomeric n-Tetradecenes from a Mixture of Model Compounds

A mixture of model compounds was made up from 5 wt% of each, 1-n-tetradecene, 7-tetradecene, n-tetradecane, 1% benzothiophene and 84% of decalin. About 2.7 g of this mixture was mixed with 1 g of acid/base washed silicalite and heated at 150°C for 2 hours. A subsequent analysis of the supernatant raffinate indicated that all the C_{14} n-aliphatic hydrocarbons were adsorbed by the silicalite. However, the n-tetradecenes were more selectively removed than n-tetradecane.

Example 20

Adsorption of 1-n-Tetradecene and n-Tetradecane from C_{14} FLEXICOKER Distillate

About 1.5 g of a 10/90 mixture of a sharp C_{14} distillate fraction of light FLEXICOKER gas oil of (bp. 248-250° C) and decalin were added to 1 g of acid/base washed silicalite. The test mixture was then heated at 200° C for 1 hour. Subsequent GC analyses of the feed and the supernatant raffinate indicated that, as a result of adsorption by the silicalite, the concentration of 1-n-tetradecane in the C_{14} FLEXICOKER fraction decreased from 15.6 to 0.4% (39 fold decrease). The concentration of n-tetradecane was similarly dropped 19.0 to 0.7% (27 fold decrease). It is noted though that these values were semiquantitative due to the elevated GC baseline. In this high carbon range of coker distillate feeds and raffinates, an exact determination of single compounds is usually impossible on a boiling point type GC column.

Example 21

Isomerization of 1-n-decene by Silicalite in the Presence and Absence of Benzothiophene

The isomerization of excess 1-n-decene by silicalite without acid/base treatment at 120° C in 1 hour was determined in the absence and the presence of about 5% benzothiophene. In the absence of the sulfur compound, 30% of internal n-decenes were found by GC as a consequence of isomerization via double bond migration. In the presence of sulfur, only 10% of the feed was isomerized.

Example 22

Preparation of Synthetic Polyalkene Lubricant from A C_9 to C_{13} n-Olefins Plus n-Paraffins Mixture

A mixture of C_9 to C_{13} n-olefins and n-paraffins is separated from the corresponding broad FLEXICOKER distillate via a molecular adsorption of the type described in Example 12. This mixture, containing C_9 to C_{13} 1-n-olefins as the main reactive components, is then oligomerized using a boron trifluoride complex of an alcohol, i.e. neopentyl alcohol. The oligomerization is carried out in the liquid phase at temperatures and pressures sufficient to convert not only the terminal 1-n-olefin components but most of the internal n-olefins as well to polyolefin oligomers containing olefin trimers as the main components.

The resulting polyolefin - n-paraffin mixture is then hydrogenated in the presence of a sulfur insensitive transition metal sulfide catalyst. This provides an isoparaffin plus n-paraffin mixture which is then separated by distillation. The n-paraffins and the isoparaffin dimers are distilled. The residual isoparaffin product comprising mainly trimers and tetramers is a desirable synthetic lubricant. The n-paraffin distillate is converted via known chlorination - dehydrochlorination reactions to linear olefin intermediates of biodegradable alkylbenzene sulfonate manufacture. The isoparaffin dimers are useful as solvents of low volatility.

Due to the presence of significant amounts of linear internal olefins and minor amounts of monomethyl branched olefins in the feed the polyolefin lubricant products are distinct over products of the prior art. The presence of comparable amounts of even and uneven carbon number olefin reactants in the feed also distinguishes the products over the prior art poly-α-olefin lubricants derived from ethylene via even numbered 1-n-olefins.

Claims

1. A process for the separation of C_5 to C_{19} mixtures of n-olefins and n-paraffins from a feed mixture comprising aliphatic and aromatic hydrocarbons which process comprises contacting said mixture of C_5 to C_{19} aliphatic and aromatic hydrocarbons with a neutral molecular sieve adsorbent under conditions sufficient to effect selective adsorption of n-olefins and n-paraffins, and contacting the resulting sieve

containing the adsorbed n-olefin and n-paraffin enriched extract with a more volatile desorbent under conditions sufficient to effect displacement from the sieve of said extract.

2. The process of claim 1 wherein said adsorption and desorption occurs in the liquid phase.

3. The process of claim 1 or 2 wherein the molecular sieve adsorbent is a silicalite.

4. The process of claim 3 wherein the silicalite adsorbent has been previously acid and base treated.

5. The process of claim 1 or 2 wherein the molecular sieve adsorbent is sodium ZSM-5.

6. The process of any preceding claim wherein both adsorption and desorption are carried out in the temperature range of 10° C and 250° C.

7. The process of any preceding claim wherein the desorbent is a n-olefin and/or n-paraffin.

8. The process of any of claims 1 to 6 wherein the desorbent is an n-olefin.

9. The process of any preceding claim wherein the process is selective for the separation of a mixture of 1-n-olefins and n-paraffins.

10. The process of any preceding claim wherein the hydrocarbon feed contains organic sulfur compounds in concentrations equivalent to from 0.05% to 3% sulfur.

11. The process of any preceding claim wherein the hydrocarbon feed is a distillate produced from petroleum residua by high temperature thermal cracking.

12. The process of claim 11 wherein the distillate contains 1-n-olefins as the major type of olefin component and organic sulfur compounds in concentrations exceeding 0.05% sulfur.

13. The process of any preceding claim which separates C_9 to C_{19} mixtures of n-olefins and n-paraffins from a feed mixture of C_9 to C_{19} aliphatic and aromatic hydrocarbons, the mixture being contacted with the molecular sieve in the liguid phase in the temperature range of 80° C to 200° C.

14. The process of claim 13 wherein the said feed mixture comprises an olefinic cracked petroleum distillate feed produced from vacuum residue by high temperature thermal cracking in a Fluid-coker or FLEXICOKER unit which contains more than 20% olefins and more than 30% of said olefins being 1-n-olefins and additionally contains organic sulfur compounds in concentrations exceeding 0.3% sulfur.

15. The process of any preceding claim wherein, after desorbing the resulting n-olefin and n-paraffin enriched mixture, the olefin components of the enriched mixture are converted to less volatile products via reactions selected from oligomerization, alkylation and carbonylation, and the unconverted paraffin components are removed from the olefin derived product by distillation.

16. The process of claim 15 wherein the olefin components are converted to an alkylbenzene by an alkylation process.

17. The process of claim 15 wherein the olefin components are converted to an alcohol by carbonylation.

18. The process of claim 15 wherein the olefin components are reacted in the presence of an acid catalyst to selectively produce an oligomer containing 2 to 6 monomer units, hydrogenating the olefinic unsaturation of the oligomer to produce an isoparaffinic lubricant, and removing the unreacted n-paraffin components from the isoparaffin-containing reaction mixture by distillation.

19. The process of claim 18 wherein the oligomerization of the olefin components is carried out in the presence of a boron trifluoride alcohol complex.

Figure 1

CAPILLARY GAS CHROMATOGRAM OF A C_{10} FLEXICOKER DISTILLATE FEED

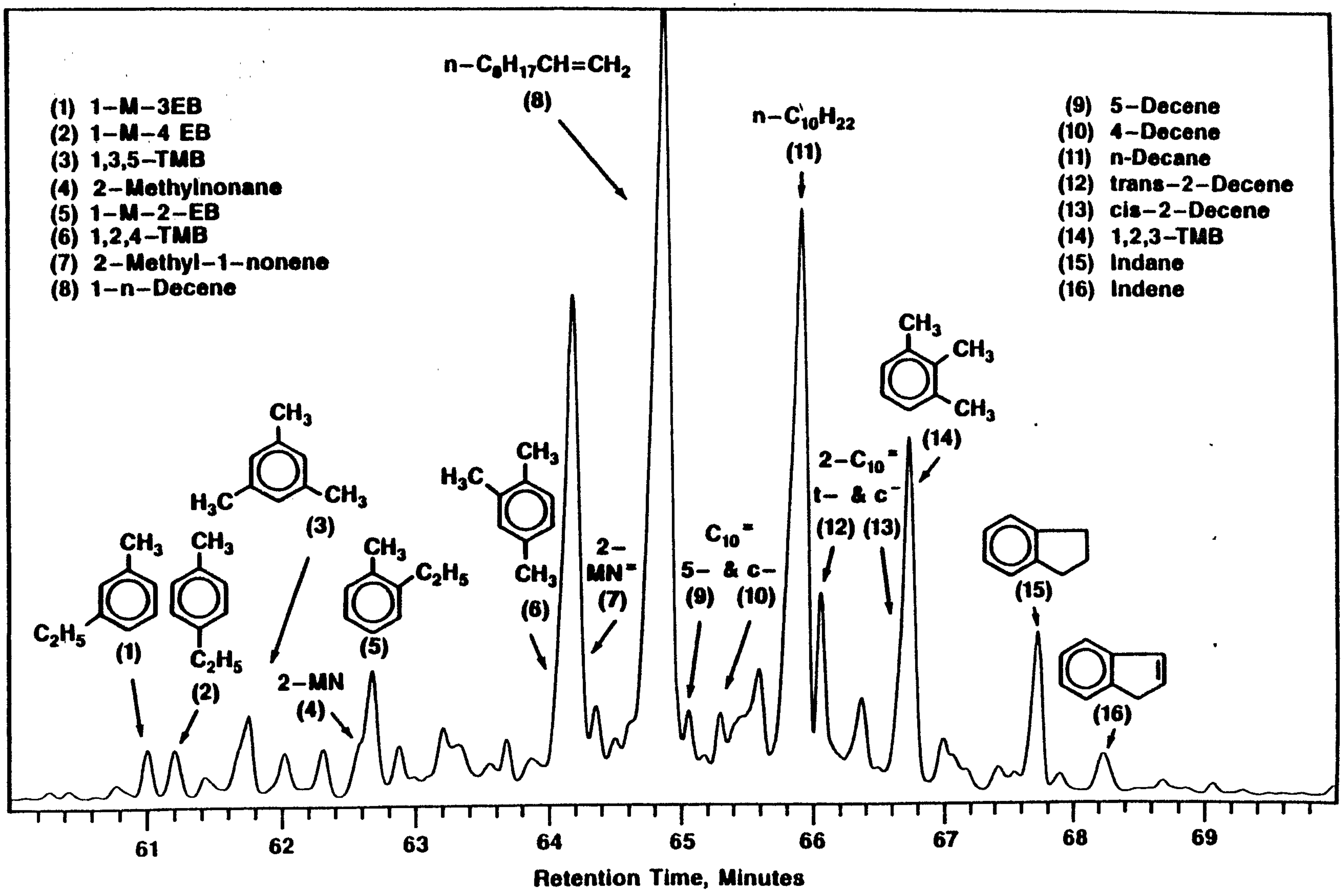


Figure 2

SILICALITE SEPARATION OF 1-n-DECENE AND n-DECANE FROM AROMATIC COMPONENTS OF FLEXICOKER DISTILLATE IN PULSE TEST

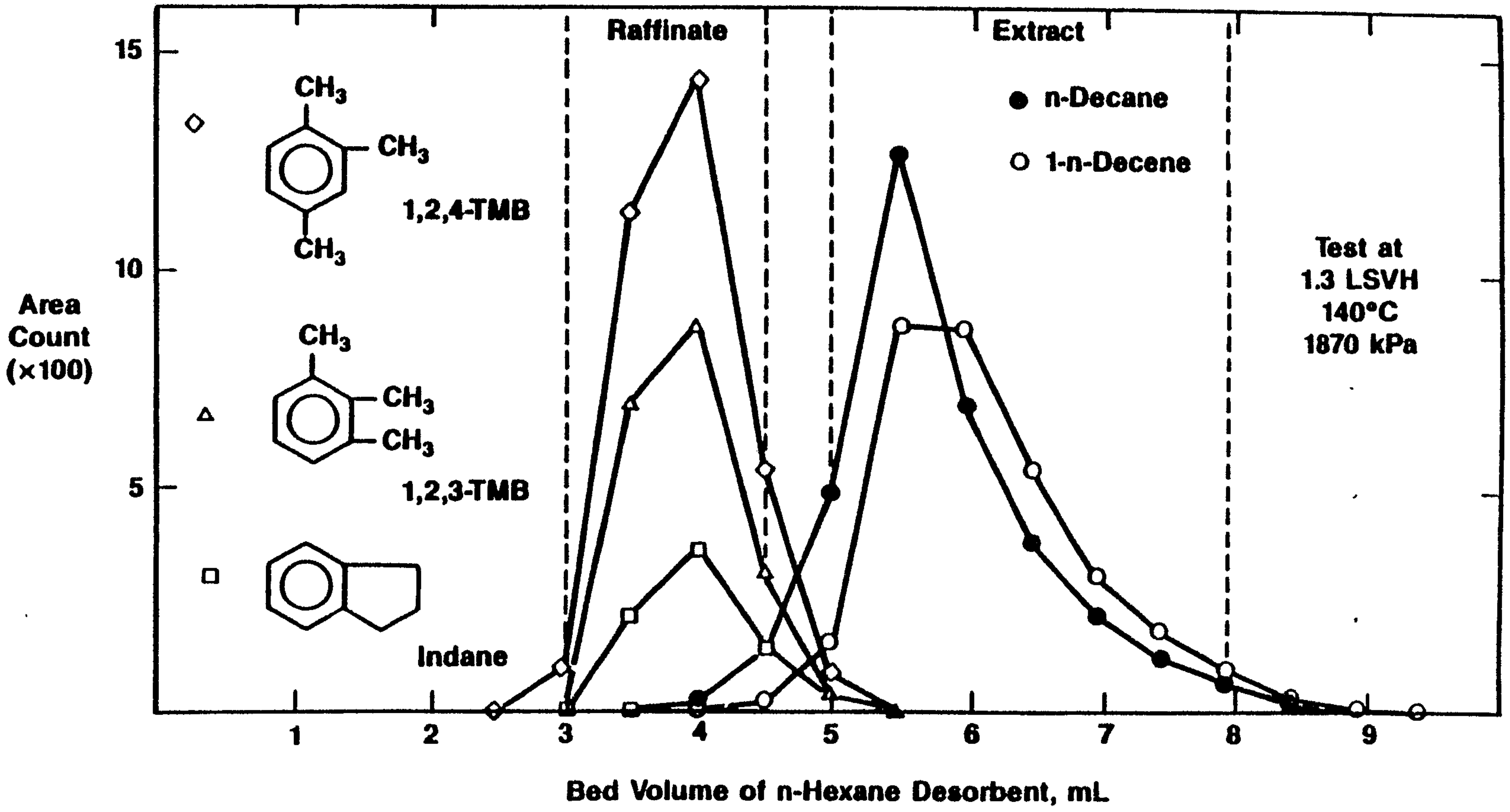


Figure 3

CAPILLARY GAS CHROMATOGRAM OF AN EXTRACT FROM A C_{10} FLEXICOKER DISTILLATE

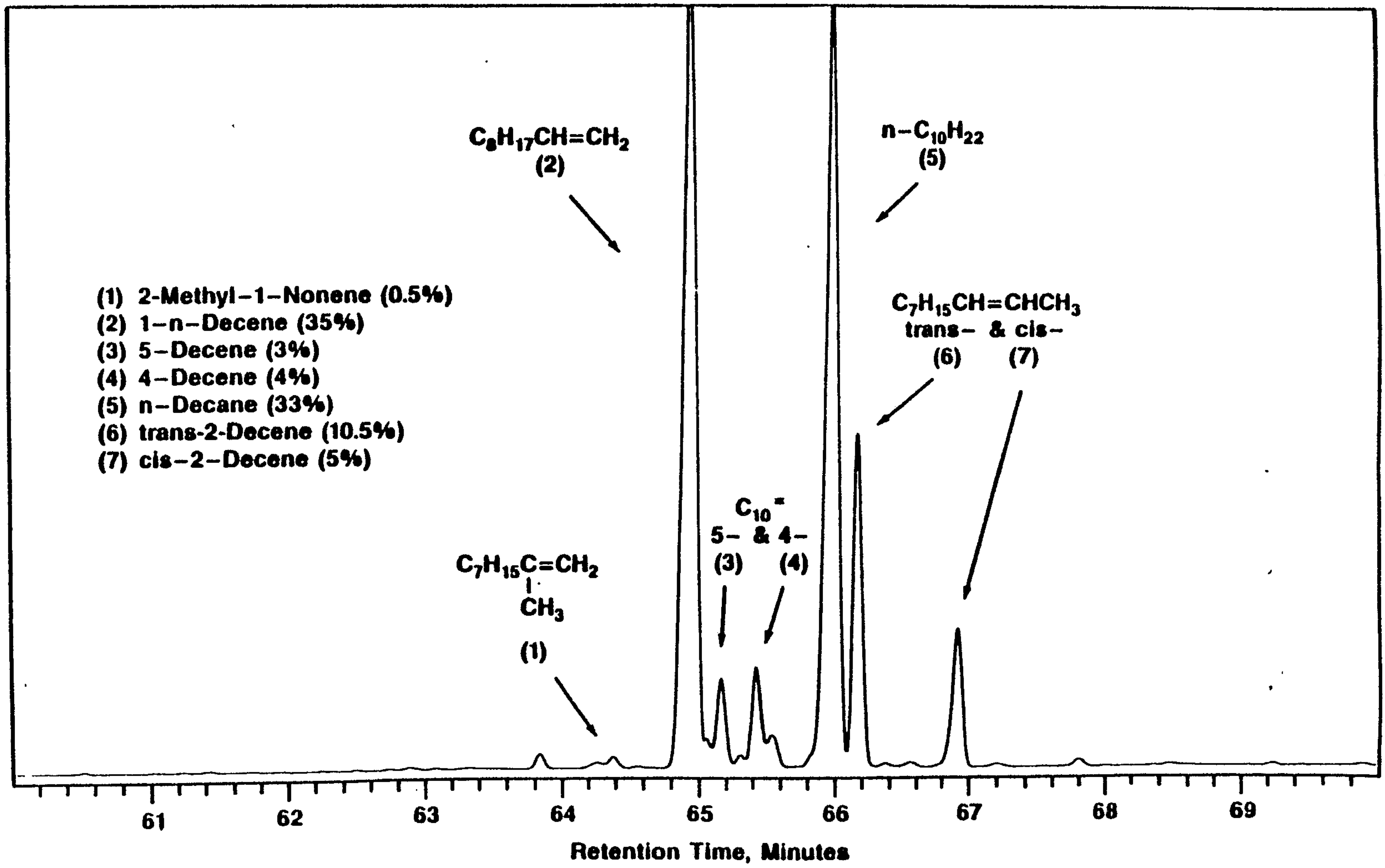


Figure 4
CAPILLARY GAS CHROMATOGRAM OF A MIXTURE OF C_9 TO C_{12} MODEL COMPOUNDS CONTAINING COMPARABLE AMOUNTS OF VARIOUS 1-N-OLEFINS

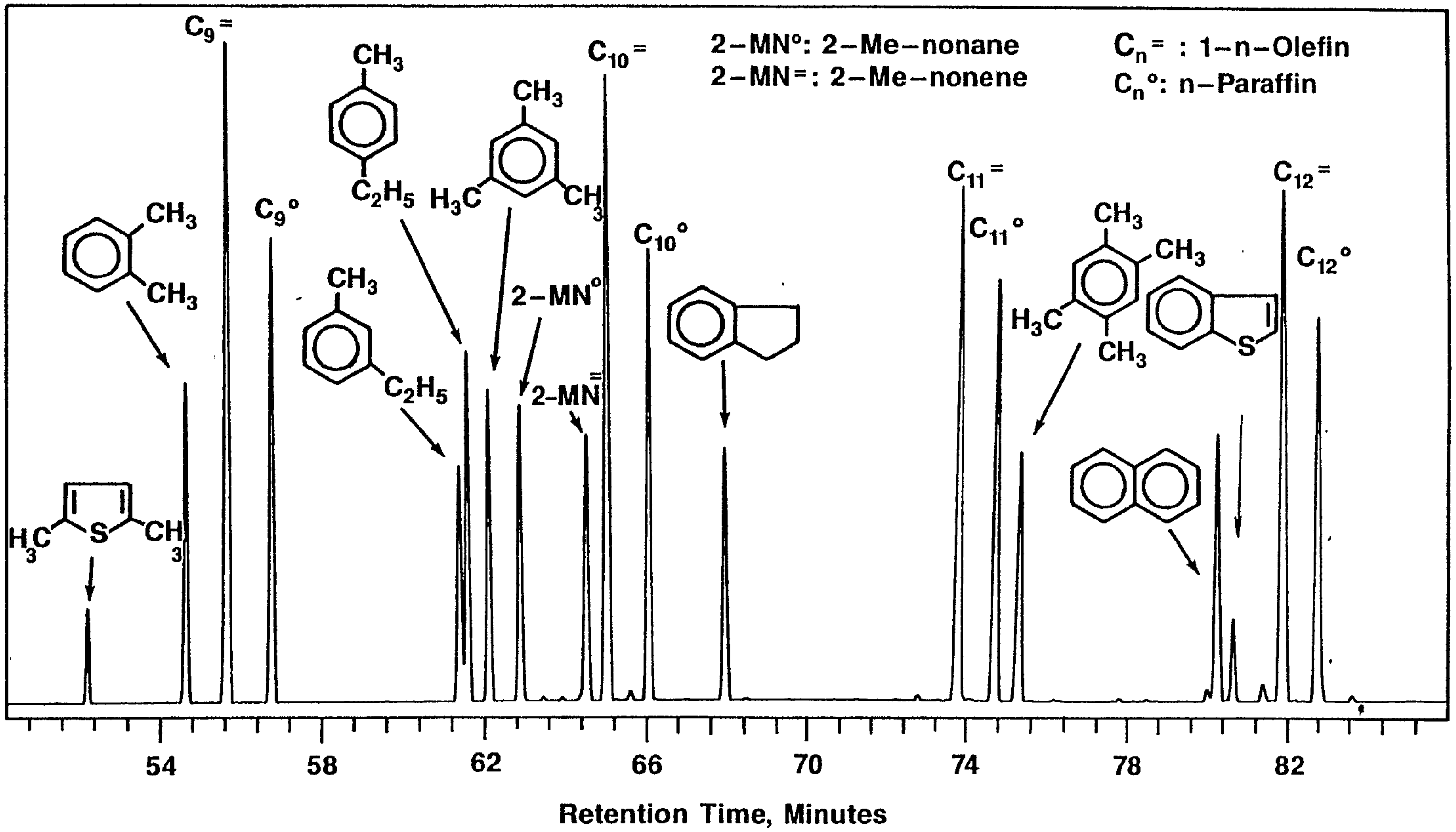


Figure 5

CAPILLARY GAS CHROMATOGRAM OF THE RAFFINATE OF A MIXTURE OF C_9 TO C_{12} MODEL COMPOUNDS CONTAINING DECREASING AMOUNTS OF 1-N-OLEFINS WITH INCREASING CARBON NUMBER

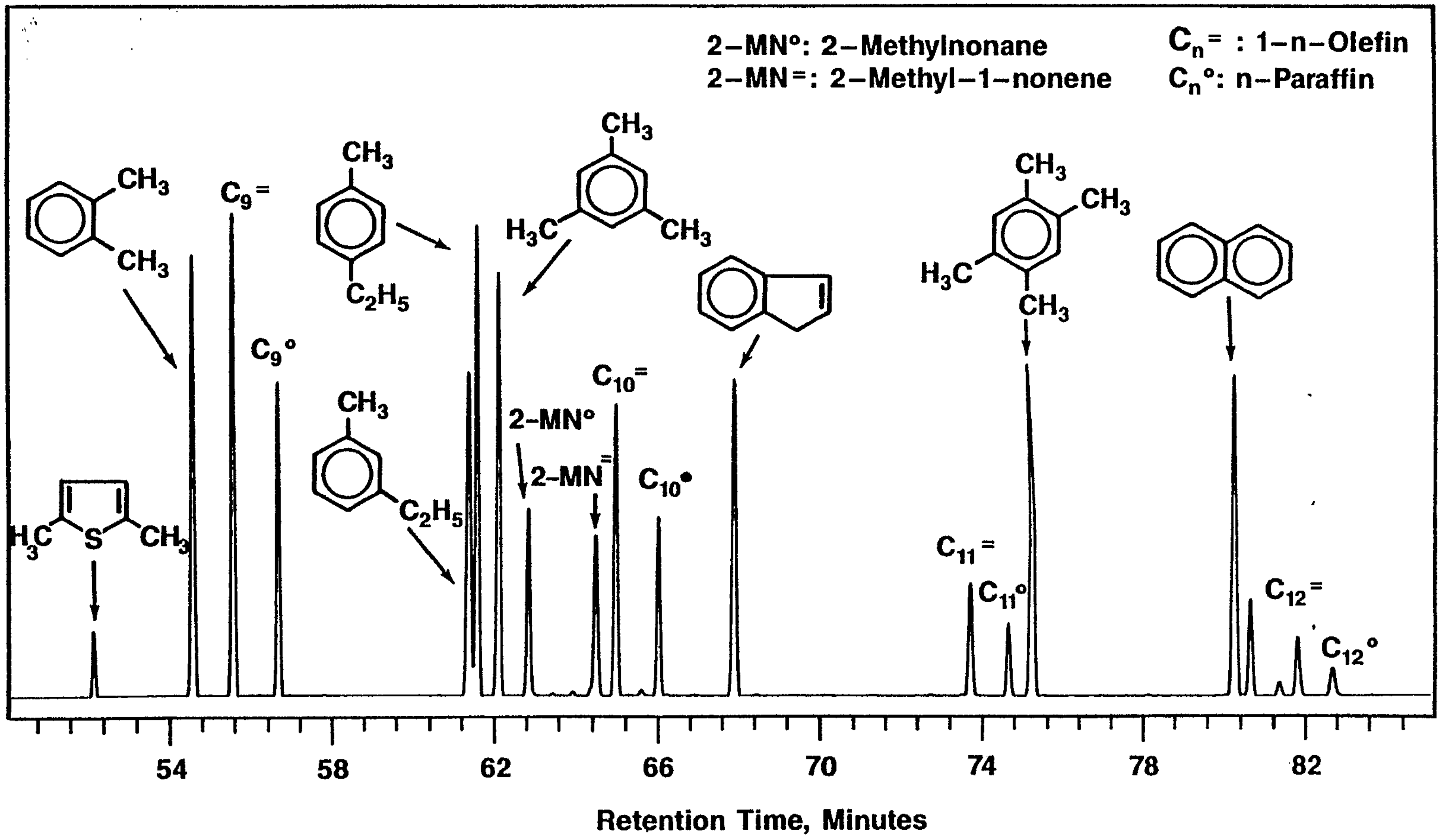


Figure 6

CAPILLARY GAS CHROMATOGRAM OF A LINEAR OLEFINS AND PARAFFINS RICH C_9 TO C_{13} FLEXICOKER DISTILLATE FRACTION EMPLOYED AS FEED IN MOLECULAR SIEVE SEPARATION

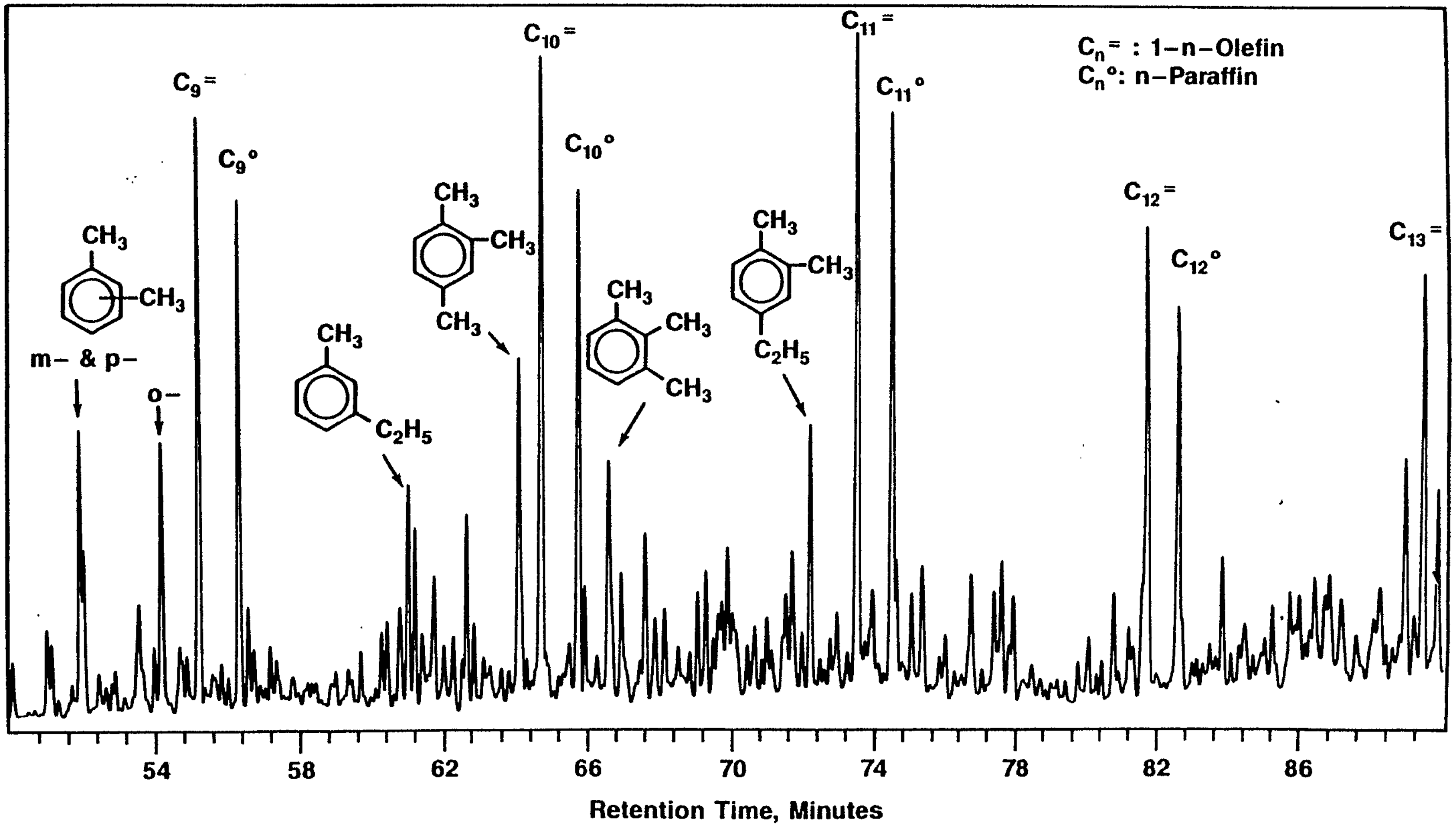
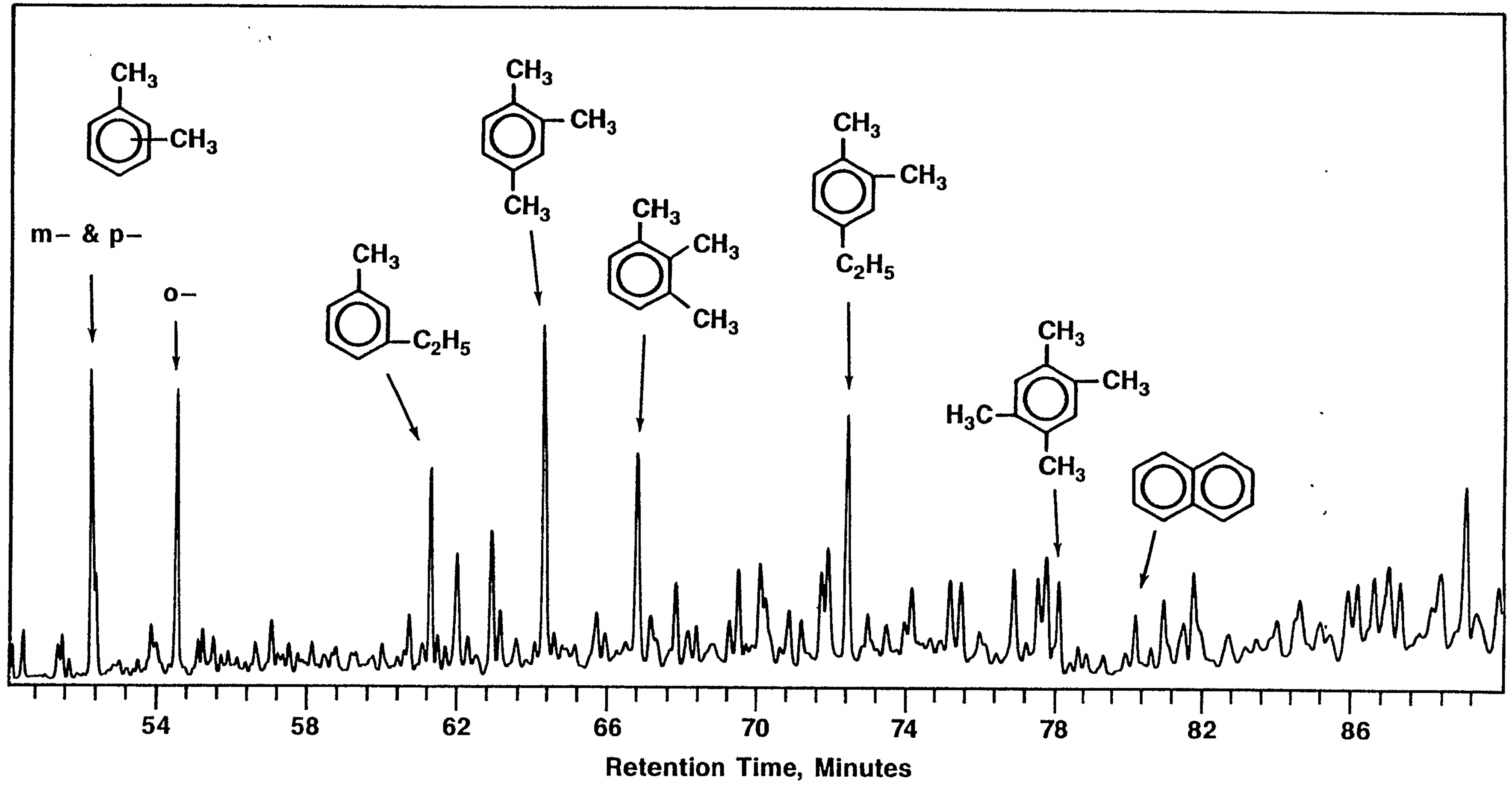


Figure 7
CAPILLARY GAS CHROMATOGRAM OF THE AROMATICS RICH RAFFINATE OF THE SEPARATION OF A C_9 TO C_{13} FLEXICOKER FRACTION



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EUROPEAN SEARCH REPORT

Application Number

EP 89 31 2735

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	EP-A-0 031 676 (MOBIL) * Claims 11-15,61; page 5, line 20 - page 6, line 6; page 11, lines 3-34 * -----	1,2,5,6,9,13	C 10 G 25/03
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C 10 G

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	19-03-1990	DE HERDT O.C.E.

CATEGORY OF CITED DOCUMENTS

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