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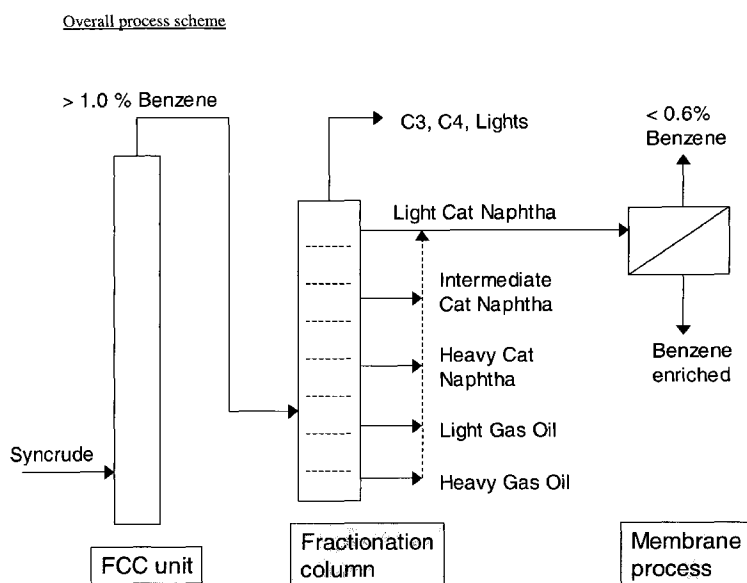
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(54) **Title:** CATALYTIC CRACKING FOR ENHANCED PROPYLENE YIELD AND REDUCED BENZENE NAPHTHA FRACTIONS

FIG. 1



(57) **Abstract:** A process in which a catalytic cracking unit is operated to crack a hydrocarbon feedstock in a manner to enhance light olefin yields. The accompanying benzene-containing naphtha product stream is further processed through a benzene selective membrane to provide a low content benzene stream. Refiners frequently operate their cracking units to optimize light olefin yields, e.g., propylene, in response to needs in the petrochemical industry, and it has been discovered that units operated in this manner frequently produce naphtha containing increased amounts of benzene. The method of this invention therefore allows one to operate the unit when it is desired to optimize light olefin yields, yet at the same time produce a naphtha yield having a low benzene content. The invention is particularly useful when the cracking unit utilizes pentasil zeolites at increased concentrations to enhance light olefins yield.

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**PROCESS FOR ENHANCED PROPYLENE YIELD FROM CRACKED  
HYDROCARBON FEEDSTOCKS AND REDUCED BENZENE IN RESULTING  
NAPHTHA FRACTIONS**

**BACKGROUND OF THE INVENTION**

[0001] The invention relates to catalytic cracking processes conducted to produce light olefins. The invention further relates to methods for reducing benzene in naphtha fractions produced in such processes.

[0002] Benzene is a known carcinogen that arises in the production of gasoline. Regulations in the European Union, US, and other locations require less than 1% benzene in gasoline. Gasoline is produced at a refinery by blending component streams, including butane, isopentane, alkylate, isomerate, straight run naphtha, hydrocrackate, catalytic naphtha, steam cracked naphtha, coker naphtha, pyrolysis gasoline, catalytic reformat, vacuum gas oil, and oxygenates. The naphthas formed from catalytic cracking, e.g., fluidized catalytic cracking (FCC), can be further fractionated into light cat naphtha, intermediate cat naphtha, and heavy cat naphtha.

[0003] The product distribution from current FCC processes comprises a number of constituents in addition to gasoline naphtha. While gasoline is of primary interest to most refiners, light olefins and LPG are also found in the FCC product, and are increasingly becoming of interest to refiners as those products become more valuable. The light olefins produced can be used for a number of purposes, e.g., they are upgraded via sulfuric or HF alkylation to high quality alkylate. LPG is used for cooking and/or heating purposes. Accordingly, operators of FCC units can vary the content of their products depending upon the markets they are serving and the value associated with each of the components found in an FCC product.

[0004] Propylene is a particular light olefin in high demand. It is used in many of the world's largest and fastest growing synthetic materials and thermoplastics. Refiners are relying more and more on their FCC units to meet the increased demand for propylene, thus shifting the focus of the traditional FCC unit away from transportation fuels and more toward petrochemical feedstock production as operators seek opportunities to maximize margins. Indeed, the FCC unit provides one third of the world's propylene, and being able to increase propylene output from the unit is of value when propylene prices are high.

[0005] If a refinery cannot expand its existing FCC unit, the unit's operators have rather limited options for increasing light olefin production. Reported options include:

- (a) using additive ZSM-5 catalyst and/or additive in the FCC unit; and
- (b) increasing the severity of the conditions, e.g., temperature, in the unit, e.g., production of cracked gas from gas oil over pentasil zeolites, e.g., ZSM-5.

[0006] It has been noted, however, that processes such as the above typically produce a product that, when fractionated to the gasoline naphtha streams, have higher concentrations of benzenes compared to units run at conditions to maximize gasoline yields. Naphtha fraction from a FCC unit operated to enhance light olefin yields can contain more than 2% benzene. The source of increased benzene is not readily recognized by refiners.

[0007] Accordingly, there can be reluctance to rely on FCC units for substantially meeting olefin needs, or reluctance to maximize the use of the pentasil additive catalysts. The reluctance is further reinforced given that when refiners use pentasil additives to enhance olefin yields, gasoline yields are often sacrificed. In other words, the refiner is facing the additional issue that the yield of a valuable product is being reduced in addition to the fact the process will require processing the product to remove the increased amount of benzene.

[0008] Polymeric membranes have been reported to separate aromatics.

[0009] US Patent 2,930,754 (Stuckey), US Patent 2,958,656 (Stuckey), US Patent 3,370,102 (Carpenter et al.), US Patent 4,115,465 (Elfert et al.), US Patent 4,944,880 (Ho et al.), US Patent 5,028,685 (Ho et al.), US Patent 5,063,186 (Schucker), and US Patent 5,635,055 (Sweet et al.) all relate to membranes for aromatic/non-aromatic separations, but none address benzene removal from hydrocarbon streams.

[0010] US Patent 6,180,008 (White) and US Patent 6,187,987 (Chin et al.) refers to polyimide membranes and processes using hyperfiltration to recover aromatic solvents. Benzene removal from hydrocarbon streams, however, is not addressed.

[0011] US 5,914,435 (Streicher and Prevost) describe a process where a sidestream from a distillation column enriched in benzene is treated with a membrane permeation zone in order to reduce the benzene content of the treated hydrocarbon stream. The membrane is selective for benzene, and at least part of the retentate low in benzene is divided into two streams and recycled to two different levels in the distillation column. It is believed that the distillation column is a naphtha pre-fractionating column designed to separate C<sub>5</sub> to C<sub>10</sub> hydrocarbons, wherein the those hydrocarbons having a boiling point in the range of 150 to 200°C are collected at the bottom of

the column and hydrocarbons having a boiling point of about 50°C are collected off the top of the column.

[0012] A publication titled “Reduce Your Tier 2 Gasoline Compliance Costs with Grace Davison S-Brane™ Technology” and presented at the Spring 2002 NPRA meeting (AM-02-21) by J. Balko describes reducing sulfur content in gasoline by employing S-Brane® membranes. See also U.S. Patent 6,896,796 (White, Wormsbecher, and Lesemann). Balko generally mentions retentate aromatics level (particularly benzene) is substantially reduced by the process using the S-Brane membrane, but there is no mention of doing so in connection with a gasoline stream relating to olefin production, and sulfur reduction was the primary purpose of using the S-Brane membrane. Indeed, Balko does not provide supporting data on benzene removal.

[0013] The following references also describe using membranes to remove sulfur from hydrocarbon feeds. Except for the '761 to Balko, these references do not mention benzene removal. US Patent 6,649,061 (Minhas et al.); US 7,048,846 (White et al.); and US 7,267,761 (Balko).

[0014] Jonquière, R. Clément, P. Lochon, J. Néel, M. Dresch, and B. Chrétien; “Industrial state-of-the-art of pervaporation and vapour permeation in the western countries”; J. Membrane Sci. 206 (2002) 87-117, states that “the petrochemical industry is now considering these new separation processes as very good candidates to take up the coming world-wide challenge of aromatics removal from gasoline that remains one of the current great issues of public health”, but no additional references or information is given. See also, A. Jonquière, R. Clément, and P. Lochon; “Permeability of block copolymers to vapors and liquids”; Prog. Polym. Sci. 27 (2002) 1803-1877.

[0015] US Patent 6,232,518 (Ou) refers to using cyclodextrins for removal of benzene from hydrocarbon streams.

[0016] J. Garci Villaluenga and A. Tabe-Mohammadi; “A review of the separation of benzene/cyclohexane mixtures by pervaporation processes”; J. Membrane Sci. 169 (2000) 159-174 reviews existing technologies for recovery of benzene. Removal of benzene to low levels, however, is not addressed.

[0017] New regulations are calling for lower levels of benzene in gasoline. Since the FCC unit produces blending components for gasoline, keeping the benzene levels low is critical to a refiner. It would therefore be desirable to have a process that allows for increased propylene production

while simultaneously lowering the benzene levels in FCC gasoline produced during that production. As evidenced from above discussion, a practical solution to this dilemma has not been disclosed or suggested.

### **BRIEF DESCRIPTION OF THE DRAWINGS**

[0018] Figure 1 is schematic illustration showing one embodiment of the invention wherein light cat naphtha is treated with a membrane to reduce the amount of benzene in the stream.

[0019] Figure 2 is a graph illustrating the invention's performance in reducing benzene concentrations with respect to membranes M1 and M2 described in Example 3.

### **SUMMARY OF INVENTION**

[0020] We have found that a membrane process can be used to address the undesirable build-up of benzene when cracking feedstocks to light olefins, e.g., propylene, using pentasil zeolite catalysts or other conditions known to enhance light olefin yields, thereby allowing for process conditions that improves light olefin yield from an FCC unit, while at the same time providing a more environmentally friendly naphtha stream that can be blended into the gasoline pool. Light olefins are intended herein to mean ethylene, propylene and butylenes, i.e., olefins containing two to four carbons (C<sub>2</sub> to C<sub>4</sub>).

[0021] The invention comprises introducing a hydrocarbon feedstock into a reaction zone of a catalytic cracking unit, which feedstock is characterized as having an initial boiling point from about 120°C with end points up to about 850°C. The feedstock is cracked in the reaction zone of the unit by contacting the feedstock with a cracking catalyst under conditions of temperature, catalyst to oil ratio, pressure, steam dilution and space velocity such that a light olefin yield from the unit is enhanced compared to that of the same unit operating at more typical conditions, e.g., those listed below.

Temperature, °C	500-535
Cat./Oil	5 to 10
Pressure, atmospheres	1 to 4
Steam Dilution, wt% of feed	1 to 5

WHSV, hr <sup>-1</sup>	125-200
Pentasil zeolite crystal content, wt% catalyst	0-1

[0022] The unit thereby produces a product comprising light olefin, naphtha and benzene, wherein the product comprises about 6 to about 20% propylene based on the weight of the hydrocarbon feedstock introduced in the cracking step above. The product is then fractionated into at least an light olefin-containing fraction, and a benzene-containing naphtha fraction. Such streams can include full range cat naphtha (boiling point in the range of 50°C to about 220°C, and 0.6 to about 3% by weight benzene) or light cat naphtha (boiling point in the range of 50°C to about 105°C, and 1.2 to about 6% by weight benzene).

[0023] The light olefin-containing fraction is recovered, and the benzene-containing naphtha fraction is contacted with a membrane. The membrane selected for use is benzene selective, and therefore should have a sufficient flux and selectivity to separate from the naphtha a benzene-enriched permeate fraction and a benzene deficient naphtha retentate fraction, said benzene-enriched permeate fraction being enriched in benzene compared to the retentate. One then recovers the benzene deficient naphtha retentate fraction, and routes the benzene-enriched permeate fraction for further processing.

[0024] In operating such a process, one has at its disposal a method of producing light olefins and low benzene-containing naphtha in a catalytic cracking unit when the unit's conditions are selected to enhance light olefin yield in the catalytic cracking unit, e.g., conditions such as type and composition of catalyst, temperature, catalyst to oil ratio, pressure, steam dilution and/or space velocity.

[0025] Being able to remove benzene in this fashion allows a refiner to maximize its light olefin yield from a FCC product stream. When the unit is utilizing pentasil zeolite for its olefin production, the stream can contain propylene in the range of 6 to about 20% by weight propylene based on the weight of the feedstock to the FCC unit.

[0026] Accordingly, aromatic selective membranes that preferentially remove benzene from gasoline feedstocks, provide for simultaneous increased yield of light olefins, e.g., propylene, from an FCC unit while still producing a large fraction of gasoline with less than 1% benzene

levels, and preferably less than 0.6%. Pervaporation with an aromatic selective membrane is a preferred process for removing benzene.

[0027] Catalysts and process conditions can moreover be adjusted in an FCC unit to increase the yield of C3 and C4 light olefins to greater than 20 weight % from a lights stripping tower. Even though such a process leaves a naphtha fraction that can contain more than 1% benzene, the membrane step of the invention splits the gasoline fraction into a major fraction, the retentate, with less than 1% benzene, and a minor fraction, the permeate, containing greater than 1% benzene. The major retentate fraction can be directly used in the gasoline pool, while the minor permeate fraction is sent for further processing in the refinery.

## **DETAILED DESCRIPTION OF THE INVENTION**

### **Catalytic Cracking Processes**

[0028] The catalytic cracking process of this invention is preferably a FCC process. Catalysts used in FCC processes are in particle form, usually have an average particle size in the range of 20 to 200 microns, and circulate between a cracking reactor and a catalyst regenerator. In the reactor, hydrocarbon feed contacts hot, regenerated catalyst that vaporizes and cracks the feed. A FCC unit can be operated under a range of conditions, wherein the reaction temperatures range from about 400° to 700°C with regeneration occurring at temperatures of from about 500° to 900°C. The particular conditions depend on the petroleum feedstock being treated, the product streams desired and other conditions well known to refiners. For example, lighter feedstock can be cracked at lower temperatures. The catalyst (i.e., inventory) is circulated through the unit in a continuous manner between catalytic cracking reaction and regeneration while maintaining the equilibrium catalyst in the reactor. The invention can be employed in a FCC unit under conventional cracking conditions. Typical conditions found in a FCC unit are listed below.

Temperature, °C	500-535
Cat./Oil	5 to 10
Pressure, atmospheres	1 to 4
Steam Dilution, wt% of feed	1 to 5
WHSV, hr <sup>-1</sup>	125-200

[0029] Certain embodiments of the invention will utilize conditions that are somewhat more severe. These more severe processes include those known as Deep Catalytic Cracking (DCC), Catalytic Pyrolysis Process (CPP), and Ultra Catalytic Cracking (UCC). Illustrative conditions for the more severe processes are listed in the table below.

	<u>DCC</u>	<u>CPP</u>	<u>UCC</u>
Temperature, °C	505-575	560-650	550-570
Cat./Oil	9 to 15	15-25	18 to 22
Pressure, atmospheres	0.7 to 1.5	0.8	1 to 4
Steam Dilution, wt% of feed	10 to 30	30 to 50	20 to 35
WHSV*	0.2-20	---	50 to 80

\*weight hourly space velocity ( $\text{hr}^{-1}$ )

[0030] Those of ordinary skill in the art are familiar as to when such processes can be used with the invention. When the invention is used with such processes, certain modifications to the invention may be required, e.g., activity and attrition may require alteration of the catalyst, in order to optimize the catalyst composition's effectiveness in those processes. Such modifications are known to those skilled in the art. For example, when using increased amounts of pentasil zeolites such as ZSM5, the FCC unit can be operated under conventional FCC conditions listed in the first column of the table above to enhance light olefin yields.

[0031] The cracking reaction deposits carbonaceous hydrocarbons or coke on the catalyst, thereby deactivating it. The cracked products are separated from the coked catalyst. The coked catalyst is stripped of volatiles, usually with steam, in a catalyst stripper and then regenerated. The catalyst regenerator burns coke from the catalyst with oxygen containing gas, usually air, to restore catalyst activity and heat catalyst to, e.g., 500°C to 900°C, usually 600°C to 750°C. The hot regenerated catalyst recycles to the cracking reactor to crack more fresh feed. Flue gas from the regenerator may be treated to remove particulates or convert CO, and then discharged into the atmosphere. The FCC process, and its development, is described in the Fluid Catalytic Cracking Report, Amos A. Avidan, Michael Edwards and Hartley Owen, in the Jan. 8, 1990 edition of the Oil & Gas Journal.

[0032] A variety of hydrocarbon feedstocks can be cracked in the FCC unit to produce light olefins and gasoline. Typical feedstocks include in whole or in part, a gas oil (e.g., light,



medium, or heavy gas oil) having an initial boiling point above about 120°C [250°F], a 50% point of at least about 315°C [600°F], and an end point up to about 850°C [1562°F]. The feedstock may also include deep cut gas oil, vacuum gas oil, coker gas oil, thermal oil, residual oil, cycle stock, whole top crude, tar sand oil, shale oil, synthetic fuel, heavy hydrocarbon fractions derived from the destructive hydrogenation of coal, tar, pitches, asphalts, hydrotreated feedstocks derived from any of the foregoing, and the like. As will be recognized, the distillation of higher boiling petroleum fractions above about 400°C must be carried out under vacuum in order to avoid thermal cracking. The boiling temperatures utilized herein are expressed in terms of convenience of the boiling point corrected to atmospheric pressure. Even high metal content resids or deeper cut gas oils having an end point of up to about 850°C can be cracked.

**[0033]** Y-type zeolites are typically used in FCC processes to produce gasoline. These zeolites include zeolite Y (U.S. Pat. No. 3,130,007); ultrastable Y zeolite (USY) (U.S. Pat. No. 3,449,070); rare earth exchanged Y (REY) (U.S. Pat. No. 4,415,438); rare earth exchanged USY (REUSY); dealuminated Y (DeAlY) (U.S. Pat. No. 3,442,792; U.S. Pat. No. 4,331,694); and ultrahydrophobic Y (UHPY) (U.S. Pat. No. 4,401,556). These zeolites are large-pore molecular sieves having pore sizes greater than about 7 Angstroms. In current commercial practice most cracking catalysts contain these zeolites.

**[0034]** Metal cation exchanged zeolites, e.g., MgUSY, ZnUSY and MnUSY zeolites, can also be employed and are formed by using exchange solutions containing the metal salts of Mg, Zn or Mn or mixtures thereof in the same manner with respect to the formation of REUSY except that a salt of magnesium, zinc or manganese is used in lieu of the rare-earth metal salt used to form REUSY. The content and manufacture of these catalysts are well known in the art.

**[0035]** The amount of Y-type zeolite in the catalyst composition for use in the invention should be sufficient to produce molecules in the gasoline naphtha range. In general, zeolite Y will be present in amounts ranging from 1 to 99% by weight of the catalyst. Catalysts comprising about 12 to about 60% by weight Y-type zeolite are more typical, with specific amounts depending on amount of activity desired. The amount of Y-type zeolite typically is such that the total amount of Y-type zeolite and the pentasil described below comprises at least about 35% by weight of the total catalyst composition.

**[0036]** As indicated above, adding pentasil zeolites to the catalyst inventory is one method of operating a FCC unit to enhance light olefin yield in accordance with this invention. These

catalysts are well known and are commonly called additive catalysts. The pentasil zeolites suitable for this invention include those zeolite structures having a five-membered ring. In preferred embodiments, the catalyst composition of this invention comprises one or more pentasils having an X-ray diffraction pattern of ZSM-5 or ZSM-11. Suitable pentasils include those described in U.S. Patent 5,380,690, the contents of which are incorporated by reference. Commercially available synthetic shape selective zeolites are also suitable.

[0037] The preferred pentasil zeolites generally have a Constraint Index of 1-12. Details of the Constraint Index test are provided in *J. Catalysis*, 67, 218-222 (1981) and in U.S. Pat. No. 4,711,710, both of which are incorporated herein by reference. Such pentasils are exemplified by intermediate pore zeolites, e.g., those zeolites having pore sizes of from about 4 to about 7 Angstroms. ZSM-5 (U.S. Pat. No. 3,702,886 and Re.29,948) and ZSM-11 (U.S. Pat. No. 3,709,979) are preferred. Methods for preparing these synthetic pentasils are well known in the art. The preferred embodiments of pentasil have relatively low silica to alumina ratios, e.g., less than 100:1, preferably less than 50:1. A preferred embodiment of this invention has a silica to alumina ratio less than 30:1. The pentasil may also be exchanged with metal cations. Suitable metals include those metal dopants described in US 2004/011029, the contents of which are incorporated by reference. Briefly these metals can be alkaline earth metals, transition metals, rare earth metals, phosphorus, boron, noble metals and combinations thereof. Catalysts comprising ZSM-5 pentasils are commercially available from W.R. Grace & Co.-Conn. and sold as Olefins Ultra®, Olefins Extra®, and OlefinsMax® brand catalysts. Olefins Ultra® HZ additive is particularly suitable for use in this invention.

[0038] Use of these additive catalysts in combination with the macroporous zeolite Y catalysts to enhance light olefins yield is known, and can be used in this invention in accordance with techniques and under conditions known in the art. For example, refiners can add pentasil containing catalysts as additive catalysts to their FCC units, with 10-80 wt %, typically 12 to 35 wt % , and more typically 25 to 50wt.%, pentasil zeolite in an amorphous support. In this instance, the pentasil is added as particles that are separate from the particles containing the conventional large pore zeolite catalysts. These additives are manufactured to have physical properties that allow them to circulate between the reaction zone and regeneration zone with the large pore zeolite cracking catalyst. Using pentasil in a separate additive allows a refiner to retain the ability to use the myriad types of commercially available large pore zeolite cracking

catalyst available today, and allows a refiner to switch between focusing production on gasoline and production of light olefins.

[0039] Regardless of the pentasil zeolite content in the additive particle, the amount of pentasil zeolite crystal in the total inventory of catalyst should be in a quantity sufficient to enhance olefin yields of the FCC unit compared to when such catalyst are not present, or only low concentrations (e.g., 1% by weight or less) are present, e.g., to enhance octane. A "pentasil zeolite crystal" is meant to refer to crystalline pentasil zeolite in the neat form. The selected pentasil zeolite crystal content, preferably ZSM-5, will preferably be in the range of 2 to about 20% by weight of the catalyst to be used with this invention. The amount of the pentasil crystal can be calculated from a catalyst particle containing support and/or matrix utilizing x-ray diffraction techniques known to those skilled in the art.

[0040] High pentasil zeolite content catalyst particles will be preferable in this invention in order to obtain the crystal amount in the aforementioned range. Utilizing the high content particles should avoid dilution of the gasoline cracking activity of the zeolite Y. Such high pentasil zeolite content catalysts are known and described in US Patent 6,916,757, the contents of which are incorporated by reference.

[0041] These catalyst additives can be used under a wide range of conditions in the FCC unit, with light olefins yields depending on the conditions used. Temperature severity, i.e., higher temperatures, in combination with use of pentasil zeolites such as ZSM5 will typically result in enhanced light olefins yields, but frequently also mean lowered gasoline yields with increasing benzene content.

[0042] A particularly suitable pentasil zeolite catalyst for use in a FCC unit to enhance olefin yields from a FCC unit is described in WO 2006/050487, and US 2008/0093263, the contents of which are incorporated by reference. Briefly, this catalyst is formulated with a Y-type zeolite to contain pentasil zeolite in a range of about 10% to about 50%, and a pentasil zeolite to Y-type zeolite ratio of at least 0.25. The ratio of pentasil zeolite to Y type zeolite for this catalyst should in general be no more than about 3.0. Typical embodiments of the invention comprise about 10% to about 30% by weight pentasil zeolite, and more typically 10 to about 20% by weight. The amount of pentasil zeolite in this catalyst is generally such that the amount of pentasil zeolite and Y-type zeolite described above is at least 35% by weight of the total catalyst composition.

[0043] Another suitable pentasil zeolite catalyst for use in this invention is one containing at least 1% by weight iron oxide based on the weight of the particles containing the pentasil zeolite. Such catalysts are described in WO 2007/005075, the contents of which are incorporated by reference. These iron oxide-containing pentasil zeolites typically comprise 1 to 10% by weight iron oxide, and the iron in that amount is outside the framework of the pentasil framework, e.g., iron present in the pentasil particles' matrix, as opposed to that present in the pentasil's silica alumina framework. WO 2007/005075 describes methods of preparing these type of pentasil catalysts, and how such catalysts can be incorporated into the catalyst inventory of a FCC unit. These catalysts are particularly designed to enhance the olefin yield of the FCC unit, and this invention would have particular utility with a FCC unit whose catalyst inventory contains such catalysts.

[0044] The invention is also suitable for use with an FCC unit whose catalyst inventory comprises an iron-based catalyst such as that described in US Patent Application 2006-0011513, wherein the pentasil catalyst comprises a metal phosphate binder, especially those catalysts that comprise an iron phosphate binder.

[0045] As mentioned above, light olefins yields in a FCC unit are also enhanced utilizing more severe operations such as DCC, UCC, and CPP listed in the table above. These methods employ the same catalysts typically used in FCC, but in amounts and ratios tailored to the particular conditions selected. A range of conditions for each of these operations is provided in the table above. These processes and catalysts used therein are known in the art. See Chapin et al., "Deep Catalytic Cracking, Maximize Olefin Production", *Presented at 1994 NPRA Annual Meeting*, San Antonio, Texas, March 20-22, 1994 (DCC); Meng et al., "Production of Light Olefins by Catalytic Pyrolysis of Heavy Oil", *Petroleum Science and Technology* Vol. 24, pages 413-422, 2006 (CPP); and US Patent 5,846,402 (UCC).

[0046] It is also envisioned that the invention can utilize units conducting a process known and licensed by Kellogg Brown and Root as the Superflex process. In such an embodiment, the Superflex process is by design operated to enhance light olefin yields when directly processing light naphtha feeds, and the product from the unit would then otherwise be processed in accordance with the teachings herein.

[0047] The hydrocarbon effluent or product from the FCC unit varies and depends not only on the feedstock, but also the conditions in the unit. A hydrocarbon stream processed under

typical FCC conditions, as well as those processed in accordance with the invention will result in product having specifications illustrated in the examples below.

[0048] The product from the FCC unit is then routed to a fractionation column for further processing according to this invention. When the FCC unit is operated to enhance the light olefin yield in the FCC product, the light olefins will comprise 6 to about 20% propylene based on the weight of the feed to the FCC unit. Table 2 in the aforementioned NPRA presentation regarding DCC processes for maximizing propylene yields is illustrative of the FCC unit product specifications, e.g., about an 8% propylene yield from an FCC unit operated to maximize C<sub>3</sub> olefins. FCC product, e.g., about 7% propylene yield, obtained under more conventional conditions are illustrated in Table 3 of "Reformulated Gasoline: The Role of Current and Future FCC Catalysts", Young et al. presented at the 1991 NPRA Annual Meeting, March 17-19, 1991, San Antonio, Texas.

#### Fractionation

[0049] The FCC product is separated into various fractions depending on the final product targets for the refinery. For the purposes of this invention, the fractionation column, e.g., also known as the FCC Main Column, separates the FCC product into at least a light olefin-containing fraction and a naphtha fraction. The light olefin-containing fraction generally comprises C<sub>4</sub> or lower saturated and/or unsaturated fractions. The column or fractionator can be those known in the art. See Fluid Catalytic Cracking Handbook-Design, Operation, and Troubleshooting of FCC Facility, Sadeghbiegi, pp. 18-21 (1995) Conditions for running these columns vary depending on the number of fractions desired. A refiner running a FCC unit will typically fractionate the FCC product into a light olefin fraction, gasoline naphtha fraction, light cycle oil (LCO) fraction, and heavy cycle or bottoms fraction.

[0050] Light olefin fractions comprising C<sub>4</sub> or lower saturated and/or unsaturated fractions are typically distilled off as "wet gas". Wet gas fractions are generally considered those fractions having a boiling point of 50°C or lower. These fractions are typically recovered in a compressor apparatus and processed/distilled into the individual light olefins flashed from the column.

[0051] The gasoline naphtha fraction generally comprises C<sub>5</sub> to C<sub>12</sub> hydrocarbons. For purposes of this invention, the terms "naphtha" and "gasoline naphtha" are used interchangeably herein to indicate hydrocarbon streams found in refinery operations that have a boiling range

between about 50°C to about 220°C. The naphtha fractions contain various amounts of olefinic, aromatic, and non-aromatic, e.g., aliphatic, hydrocarbon compounds and are primarily differentiated by the following boiling ranges. Light naphthas have a boiling point ranging from 50°C to about 105°C. Intermediate (mid) naphtha has a boiling point ranging from 105°C to about 160°C. Heavy cat naphtha has a boiling point ranging from about 160°C to about 220°C.

[0052] Benzene has a boiling point of 80°C and significant portions of the benzene content in the FCC product will distill with the naphtha fraction. The naphtha fraction of product from a FCC unit operating to produce enhanced olefin yields can comprise 0.6 to about 3% by weight benzene, and frequently above 1% benzene.

[0053] If the FCC product is separated into the light, intermediate and heavy cat naphtha fractions, significant amounts of benzene will flash with the light cat naphtha, i.e., the 50 to 105°C fraction. A light cat naphtha from a FCC unit operating to produce enhanced olefin yields can comprise 1.2 to about 6% by weight benzene, and frequently above 2% benzene. Such benzene concentrations can be found in light cat naphtha produced in units in which pentasil zeolite, e.g., ZSM5, crystal comprises 2 to 20% by weight of the catalyst inventory.

[0054] Without being held to a particular theory, it is believed that when processes of higher severity are utilized to produce more light olefins in a FCC unit, dealkylation of aromatic side chain, cyclization, and dehydrogenation reactions occur to create a greater concentration of benzene. Processes relying on pentasil zeolites to produce light olefins, on the other hand, cracks molecules to olefin molecules that are removed from the naphtha fraction, thereby resulting in a stream with higher benzene concentrations. In other words, the pentasil catalyst removes molecules from the naphtha stream that would otherwise dilute the presence of benzene.

[0055] The benzene-containing naphtha fraction, e.g., full range or light, is collected from the column and then routed to a membrane for further processing according to the invention. See Figure 1. The remaining fractions coming off the column, e.g., LCO and HCO, represent, respectively, hydrocarbon fractions in the C<sub>12</sub> – C<sub>22</sub> range and the C<sub>22</sub> and higher range. It is envisioned that these fractions will not typically require further processing according to this invention. These latter streams are frequently collected and routed for separate processing, or, e.g., recycle through the FCC unit.

### Membrane Separation

[0056] Membranes useful in the present invention are those membranes having a sufficient flux and selectivity to permeate at least benzene in the presence of hydrocarbons containing multiple aromatic-compounds, e.g., benzene-containing gasoline naphtha. Any aromatic selective membrane can be used. Favorable membranes are chosen on the basis of high productivity which is the combination of high flux and good aromatics selectivity, and on the ability to withstand hot operating temperatures typically in the range of 80 to 120 °C. Benzene is highly permeable across aromatic selective membranes. When you compare the transport rate of benzene across a benzene selective membrane against transport rates for compounds of C<sub>5</sub> and above in the feedstock, the relative rate of benzene removal is the fastest, thereby making this invention rather efficient, and at the same time preserving the valuable gasoline fractions in the retentate. Moreover, the membrane systems can be designed to handle large-scale feed streams, e.g., on the order of 34,000 barrels/day, thereby offering potential economies of scale to the refiner utilizing this invention.

[0057] The membrane will typically have a benzene enrichment factor of greater than 1.5, preferably greater than 2, even more preferably from about 2 to about 20, most preferably from about 2.5 to 15. Preferably, the membranes have an asymmetric structure, which may be defined as an entity composed of a dense ultra-thin top "skin" layer over a thicker porous substructure of a same or different material. Typically, the asymmetric membrane is supported on a suitable porous backing or support material.

[0058] In one embodiment of the invention, the membrane is a polyimide membrane prepared from a Matrimid<sup>®</sup> 5218 or a Lenzing polyimide polymer as described in U.S. Patent 6,180,008, the contents of which are incorporated herein by reference.

[0059] In another embodiment of the invention, the membrane is one having a siloxane-based polymer as part of the active separation layer, e.g., coated onto a microporous or ultrafiltration support layer. Examples of membrane structure incorporating polysiloxane functionality are found in U.S. Patent No. 4,781,733; U.S. Patent 4,243,701; U.S. Patent No. 4,230,463; U.S. Patent No. 4,493,714; U.S. Patent No. 5,265,734; U.S. Patent No. 5,286,280; and U.S. Patent No. 5,733,663; said references being herein incorporated by reference.

[0060] In still another embodiment of the invention, the membrane is an aromatic polyurea/urethane membrane as disclosed in U.S. Patent 4,962,271, incorporated herein by reference. Such polyurea/urethane membranes are characterized as possessing a urea index of at least 20 %, but less than 100%, an aromatic carbon content of at least 15 mole %, a functional group density of at least about 10 per 1000 grams of polymer, and a C=O/NH ratio of less than about 8.

[0061] The polyimide, polyurea-urethane, and polysiloxane based membranes described above are particularly useful when separating benzene from gasoline (e.g., light cat naphtha) produced in a unit whose catalysts comprise pentasil zeolite crystal, e.g., ZSM-5, in a range of 2 to about 20% by weight. As mentioned earlier, light cat naphthas produced from such catalysts can comprise 1.2 to 6.0 weight percent benzene.

[0062] The membranes can be used in any convenient form such as sheets, tubes or hollow fibers. Sheets can be used to fabricate spiral wound modules familiar to those skilled in the art. Alternatively, sheets can be used to fabricate a flat stack permeator comprising a multitude of membrane layers alternately separated by feed-retentate spacers and permeate spacers. This device is described in U.S. Patent No. 5,104,532, herein incorporated by reference.

[0063] Tubes can be used in the form of multi-leaf modules wherein each tube is flattened and placed in parallel with other flattened tubes. Internally each tube contains a spacer. Adjacent pairs of flattened tubes are separated by layers of spacer material. The flattened tubes with positioned spacer material are fitted into a pressure resistant housing equipped with fluid entrance and exit means. The ends of the tubes are clamped to create separate interior and exterior zones relative to the tubes in the housing. Apparatus of this type is described and claimed in U.S. Patent No. 4,761,229, herein incorporated by reference.

[0064] Hollow fibers can be employed in bundled arrays potted at either end to form tube sheets and fitted into a pressure vessel thereby isolating the insides of the tubes from the outsides of the tubes. Apparatus of this type are known in the art. A modification of the standard design involves dividing the hollow fiber bundle into separate zones by use of baffles, which redirect fluid flow on the tube side of the bundle and prevent fluid channeling and polarization on the tube side. This modification is disclosed in U.S. Patent No. 5,169,530, herein incorporated by reference.



[0065] Multiple separation elements, be they spirally wound, plate and frame, tubular, or hollow fiber elements can be employed either in series or in parallel. U.S. Patent No. 5,238,563, herein incorporated by reference, discloses a multiple-element housing wherein the elements are grouped in parallel with a feed/retentate zone defined by a space enclosed by two tube sheets arranged at the same end of the element.

[0066] Selective membrane separation of the benzene-containing gasoline, e.g., whether it is the full range gasoline or light cat naphtha, into permeate and retentate is conducted under pervaporation or perstraction conditions. Preferably, the process is conducted under pervaporation conditions.

[0067] The pervaporation process typically relies on vacuum on the permeate side to evaporate or otherwise remove the permeate from the surface to the membrane and maintain the concentration gradient driving force which drives the separation process. The feed is in the liquid and/or gas state. When in the gas state the process can be described as vapor permeation. The maximum temperature employed in pervaporation will be that necessary to vaporize the components in the feed which one desires to selectively permeate through the membrane, while still being below the temperature at which the membrane is physically damaged. Pervaporation can be performed at a temperature of from about 25°C to 200°C and higher, the maximum temperature being that temperature at which the membrane is physically damaged. The feed pressure into a membrane unit is usually in the range of 1 to 20 atmospheres and the unit operated under vacuum in the range of 0.1 to 300 millimeter of mercury. It is preferred that the pervaporation process be operated as a single stage operation to reduce capital costs. Alternatively to a vacuum, a sweep gas can be used on the permeate side to remove the product. In this mode the permeate side would be at atmospheric pressure.

[0068] In a perstraction process, the permeate molecules in the feed diffuse into the membrane film, migrate through the film and reemerge on the permeate side under the influence of a concentration gradient. A sweep flow of liquid is used on the permeate side of the membrane to maintain the concentration gradient driving force. The perstraction process is described in U.S. Patent No. 4,962,271, herein incorporated by reference.

[0069] Whether pervaporation or perstraction, the selected membrane process can easily be adjusted to various products of the FCC unit by changing feed flow rates or operating temperatures. This invention therefore provides additional process control variables to help the

refinery increase yields, and still have a process that handles the benzene-containing naphtha streams.

[0070] Very significant reductions of benzene in the naphtha are achievable by the selective membranes according to this invention. Generally, the retentate, also referred to herein as the benzene deficient retentate will have less than 1% benzene and as low as 100 ppm, depending on the benzene concentration in the naphtha, membrane separation conditions, etc. The invention preferably reduces gasoline benzene such that the retentate contains less than 0.6% by weight benzene. Generally, sufficient benzene reduction is readily achievable in the retentate while substantially or significantly maintaining the level of gasoline naphtha molecules in the retentate. The retentate stream is then routed to the refiner's gasoline pool where other refinery streams are combined to form gasoline product.

[0071] The benzene enriched permeate is routed to the refinery's BTX unit (benzene, toluene, and xylene) for collection and appropriate processing, use and/or disposal. The permeate from this invention will commonly have benzene (and toluene) in amounts ranging from 1 to 10% by weight benzene. Depending on the refinery, the high benzene enriched permeate can be routed to processes that further concentrate the stream to a substantially pure benzene for use in chemical operations, or the permeate can be further processed to become a feedstock in reforming or alkylation processes.

[0072] Increased efficiency of the invention may be attained by fractionating the benzene-containing naphtha (full range or light) in a depentanizer distillation column prior to the membrane unit for separating benzene from the naphtha fraction. Depending on the membrane selected, C<sub>5</sub> olefins in the gasoline stream will usually remain in the retentate, but these olefins can also concentrate in the permeate. Treating the naphtha stream removes the C<sub>5</sub> olefins from the permeate, and therefore, concentrates benzene in the feedstock being directed to the membrane. Overall this should reduce the stage cut requirement. The C<sub>5</sub>'s have been cut out, and higher benzene concentrations are removed at a faster absolute rate than when lower concentrations of benzene are present. The costs of condensing permeate without C<sub>5</sub>'s will also be reduced. The C<sub>5</sub> olefins recovered from the depentanizer can then be further processed for another refinery need, or returned to the retentate stream prior to processing to the gasoline pool. Depentanizers columns are known in the art. The column to be used in this embodiment of the

invention can be run to flash fractions at the column's top at 50°C, and bottom fractions at a temperature in the range of 150 to 200°C.

[0073] To further illustrate the present invention and the advantages thereof, the following specific examples are given. The examples are given for illustrative purposes only and are not meant to be a limitation on the claims appended hereto. It should be understood that the invention is not limited to the specific details set forth in the examples.

[0074] All parts and percentages in the examples, as well as the remainder of the specification, which refers to solid compositions or concentrations, are by weight unless otherwise specified. However, all parts and percentages in the examples as well as the remainder of the specification referring to gas compositions are molar or by volume unless otherwise specified.

[0075] Further, any range of numbers recited in the specification or claims, such as that representing a particular set of properties, units of measure, conditions, physical states or percentages, is intended to literally incorporate expressly herein by reference or otherwise, any number falling within such range, including any subset of numbers within any range so recited.

#### Example 1

[0076] A benzene selective polyurea/urethane membrane (M1) was made in a two-step coating process. A solution was made that consists of 1.05 to 1 mole ratio of toluene diisocyanate terminated polyethylene adipate and 4,4'-methylenebis(2,6-diethylaniline) at 4.0% solids in dioxane. This is allowed to react overnight for 16 hours to generate a polyurea/urethane solution. A polyacrylonitrile ultrafiltration substrate was dip coated with the resulting solution. The coated substrate was then transferred to a ventilated oven at 100 °C to dry and cure. In a second step, a separate solution of toluene diisocyanate terminated polyethylene adipate and 4,4'-methylenebis(2,6-diethylaniline) was prepared, but this time at 2.65% solids in dioxane. This was allowed to react overnight for 16 hours to generate a polyurea/urethane solution. This solution was then dip coated onto the earlier coated substrate, which had been allowed to age 7 days. The newly coated substrate was again transferred to a ventilated oven at 100 °C. The finished membrane was dry and durable.

[0077] Properties for the polymeric separation layer of M1 was calculated using the methodology of Feimer et al. (US 4,879,044). Calculated was an aromatic index = 17.56, a urea index = 50, the sum of (C=O + NH)/1000 g = 12.64, and C=O/NH value = 5.34.

#### Example 2

[0078] A second benzene selective membrane (M2) was made in a two-step coating process similar to that described in Example 1. A solution was made of 1.05 to 1 mole ratio of toluene diisocyanate terminated polyethylene adipate and 4,4'-methylenebis(2,6-diethylaniline) at 2.65% solids in dioxane. This was allowed to react overnight for 16 hours to generate a polyurea/urethane solution. The same polyacrylonitrile ultrafiltration substrate mentioned above was dip coated and then transferred to a ventilated oven at 100 °C to dry and cure. The coated substrate was coated a second time with the same coating above, after the first coating aged for 7 days. The finished membrane was dry and durable.

[0079] M2 was another polyurea/urethane membrane with more aromatic content and higher functional group density. Calculated was an aromatic index = 29.63, a urea index = 50, the sum of (C=O + NH)/1000 g = 12.97, and C=O/NH value = 2.33.

#### Example 3

[0080] An FCC feedstock, having 25.5 API gravity, 11.94 K-Factor, 0.68% Conradson Carbon, and 0.12 wt% Nitrogen was treated in a Davison Circulating Riser at 1010°F reactor temperature, 25 psig reactor pressure and 1300°F regenerator temperature, using a catalyst blend of 80% Ultima and 20% Olefin Ultra. Propylene yield was 8.37 weight % on the fresh feed basis. The light C3 and C4 compounds were separated from naphtha by a distillation column, operating with a bottom temperature of 90°F and the top temperature of 12°F. The recovered naphtha contained 1.1 wt% benzene.

[0081] The benzene selective membranes M1 and M2 were used to further treat this naphtha in a pervaporation system at consisting of a feed reservoir, circulation pump, flow meters, a test cell containing a membrane sample located inside an oven, permeate collection vessels, and a vacuum pump. The permeate traps are cooled in liquid nitrogen [-195°C]. The feed stream was the FCC naphtha stripped of C3 and C4 compounds. A membrane trial was run for each membrane M1 and M2 in the pervaporation unit at 120 °C and full vacuum to reduce the

benzene levels in this naphtha. A pressure regulator allowed the naphtha to be pressurized to 80 psi and remain as liquid phase while hot. The vacuum pump generates a vacuum of less than 10 torr on the permeate side of the membrane.

[0082] Each permeate sample was collected for 1-2 hours. Collecting multiple permeate samples generates a large stage cut. The retentate was continuously returned to the feed reservoir for recycle over the membrane. The retentate samples were collected at the start of each fraction of permeate collection along with one final sample at the end of the run.

[0083] Concentrations of hydrocarbons (weight %) were determined for both retentates and permeates using standard GC methods.

[0084] Results are shown on the graph (Figure 2) where stage cut refers to the fraction of feed removed as permeate. M1 produced retentate with less than 0.6% benzene at 25% stage cut. M2, a more selective membrane, generated less than 0.6% benzene by 21% stage cut.

**WHAT IS CLAIMED IS:**

1. A catalytic cracking process comprising:
  - a. introducing a hydrocarbon feedstock into a reaction zone of a catalytic cracking unit which feedstock is characterized as having: an initial boiling point from about 120°C with end points up to about 850°C;
  - b. catalytically cracking said feedstock in said reaction zone employing a cracking catalyst, temperature, catalyst-to-oil ratio, pressure, steam dilution and space velocity such that an olefin yield from the unit is enhanced to produce a product comprising olefin, naphtha and benzene, wherein the product comprises about 6 to about 20% propylene based on the weight of the hydrocarbon feedstock introduced in step a. above;
  - c. fractionating the product into at least a light olefin-containing fraction, and a benzene-containing naphtha fraction;
  - d. recovering the light olefin-containing fraction;
  - e. contacting the benzene-containing naphtha fraction with a membrane having a sufficient flux and selectivity to separate a benzene-enriched permeate fraction and a benzene-deficient naphtha retentate fraction, said benzene-enriched permeate fraction being enriched in benzene compared to the retentate;
  - f. recovering the benzene-deficient naphtha retentate fraction; and
  - g. routing the benzene-enriched permeate fraction for further processing.

2. A catalytic cracking process according to claim 1, wherein the cracking catalyst in step b. comprises a pentasil zeolite crystal content in the range of 2 to about 20% by weight of the catalyst.
3. A catalytic cracking process according to claim 1, wherein the cracking catalyst in step b. comprises a catalyst additive comprising ZSM5 in the range of 10 to about 80% by weight of the catalyst additive.
4. A catalytic cracking process according to claim 1, wherein the benzene-containing naphtha fraction in step c. comprises 0.6 to about 3% by weight benzene.
5. A catalytic cracking process according to claim 1, wherein the benzene-containing naphtha fraction in step c. is light cat naphtha having a boiling point in the range of 50 to 105°C, and comprises 1.2 to about 6% by weight benzene.
6. A catalytic cracking process according to claim 2, wherein the benzene-containing naphtha fraction in step c. is light cat naphtha having a boiling point in the range of 50 to 105°C, and comprises 1.2 to about 6% by weight benzene.
7. A catalytic cracking process according to claim 1, wherein the process is a deep catalytic cracking process, and the conditions in the reaction zone of step a. are as follows:

Temperature, °C	505-575
Cat./Oil	9 to 15
Pressure, atmospheres	0.7 to 1.5
Steam Dilution, wt% of feed	10 to 30
WHSV, hr <sup>-1</sup>	0.2-20.

Pentasil crystal content, % by 10-75  
weight catalyst

8. A catalytic cracking process according to claim 1, wherein the membrane in step e. comprises a member selected from the group consisting of polyimide, polyurea-urethane, polysiloxane and combinations thereof.
9. A catalytic cracking process according to claim 2, wherein the membrane in step e. comprises a member selected from the group consisting of polyimide, polyurea-urethane, polysiloxane and combinations thereof.
10. A catalytic cracking process according to claim 5, wherein the membrane in step e. comprises a member selected from the group consisting of polyimide, polyurea-urethane, polysiloxane and combinations thereof.
11. A catalytic cracking process according to claim 1, where in the benzene-containing naphtha fraction is contacted with the membrane under pervaporation conditions.
12. A catalytic cracking process according to claim 1, wherein the benzene-deficient naphtha retentate comprises less than 1% by weight to about 100 ppm benzene.
13. A catalytic cracking process according to claim 1, wherein the benzene-deficient naphtha retentate comprises less than 0.6% by weight to about 100 ppm benzene.
14. A catalytic cracking process according to claim 1, wherein the benzene-enriched permeate comprises 1 to about 10% by weight benzene.
15. A catalytic cracking process according to claim 1 further comprising fractionating the benzene-containing naphtha fraction from step c. to remove C<sub>5</sub> fractions prior to contacting the benzene-containing naphtha fraction with a membrane in accordance with step e.



16. A method of producing light olefins and low benzene-containing naphtha in a catalytic cracking unit from a hydrocarbon feedstock, the method comprising:
- a. selecting catalyst, temperature, catalyst to oil ratio, pressure, steam dilution and/or space velocity to enhance olefin yield in the catalytic cracking unit;
  - b. contacting the feedstock with cracking catalyst in the unit, thereby producing a product comprising olefin, naphtha and benzene;
  - c. fractionating the product into at least a light olefin-containing fraction, and a benzene-containing naphtha fraction;
  - d. recovering the light olefin-containing fraction;
  - e. contacting the benzene-containing naphtha fraction with a membrane having a sufficient flux and selectivity to separate a benzene-enriched permeate fraction and a benzene deficient naphtha retentate fraction, said benzene-enriched permeate fraction being enriched in benzene compared to the retentate;
  - f. recovering the benzene deficient naphtha retentate fraction; and
  - g. routing the benzene-enriched permeate fraction for further processing.
17. A method according to claim 16, wherein the benzene-containing naphtha fraction in step c. has a boiling point in the range of 50°C to about 220°C, and the fraction comprises 0.6 to about 3% by weight benzene.
18. A method according to claim 16, wherein the benzene-containing naphtha fraction in step c. has a boiling point in the range of 50°C to about 105°C, and the fraction comprises 1.2 to about 6% by weight benzene.

19. A method according to claim 16, wherein the product from step b. comprises 6 to about 20% by weight propylene based on the weight of the feedstock in step a.
20. A method according to claim 16, wherein the membrane in step e. comprises a member selected from the group consisting of polyimide, polyurea-urethane, polysiloxane and combinations thereof.
21. A method according to claim 16 wherein the benzene-containing naphtha fraction is contacted with the membrane under pervaporation conditions.
22. A method according to claim 16, wherein the benzene-deficient naphtha retentate comprises less than 1% by weight to about 100 ppm benzene.
23. A method according to claim 16, wherein the benzene-deficient naphtha retentate comprises less than 0.6% by weight to about 100 ppm benzene.
24. A method according to claim 18, wherein the benzene-deficient naphtha retentate comprises less than 1% by weight to about 100 ppm benzene.
25. A method according to claim 19, wherein the benzene-deficient naphtha retentate comprises less than 1% by weight to about 100 ppm benzene.
26. A method according to claim 16, wherein the feedstock is contacted with a catalyst comprising ZSM5.
27. A method according to claim 16, wherein the feedstock in step b. is contacted with a catalyst comprising 2 to about 20% by weight pentasil crystal.
28. A method according to claim 19, wherein the feedstock in step a. is contacted with a catalyst comprising 2 to about 20% by weight pentasil crystal.

29. A method according to claim 27, wherein the pentasil is ZSM-5.
30. A method according to claim 28, wherein the pentasil is ZSM-5.
31. A method according to claim 16, wherein the cracking catalyst in step b. comprises a catalyst additive comprising ZSM5 in the range of 10 to about 80% by weight of the catalyst additive.
32. A method according to claim 19, wherein the cracking catalyst in step b. comprises a catalyst additive comprising ZSM5 in the range of 10 to about 80% by weight of the catalyst additive.

FIG. 1

Overall process scheme

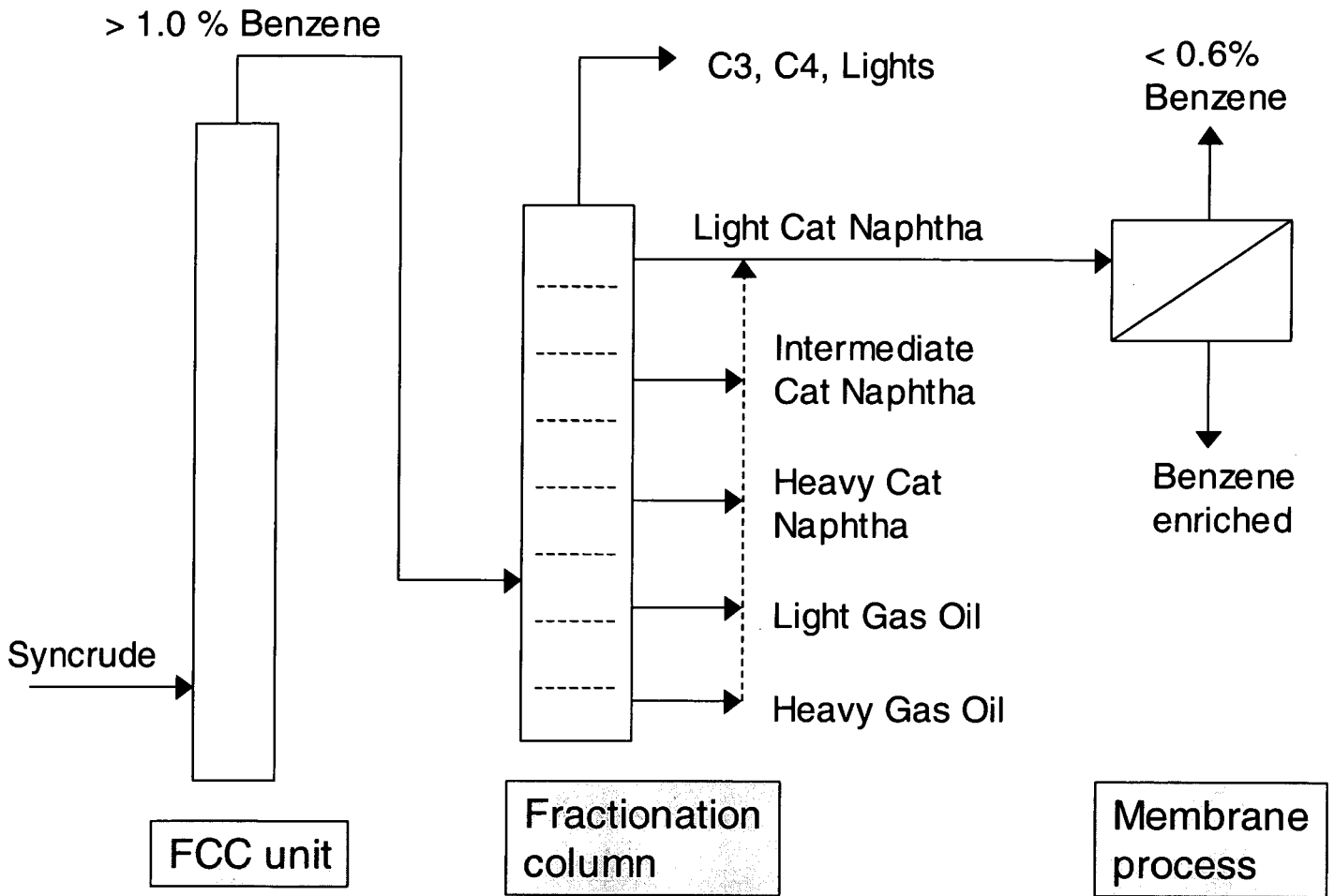
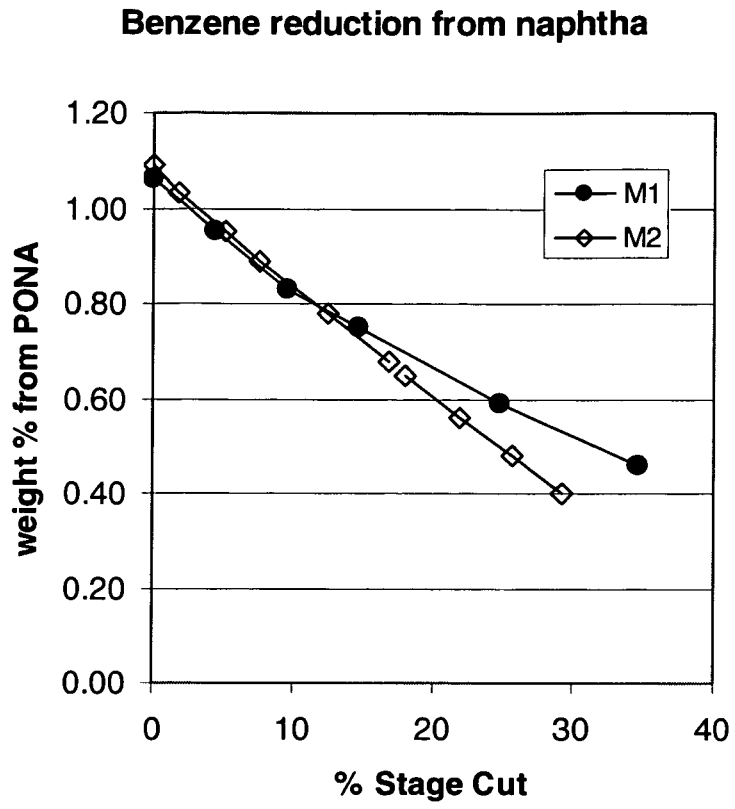


FIG. 2



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 09/05095

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> IPC(8) - B01J 29/00, C10G 11/00 (2009.01) USPC - 208/120.01, 208/113, 208/114 According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) USPC: 208/120.01, 208/113, 208/114 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched USPC: 208/120.01, 208/113, 208/114 and all USPC classes (text search - see terms below) Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) PubWEST(USPT,PGPB,EPAB,JPAB); Google; Google Scholar Search Terms: FCC, fluidized catalytic cracking, propylene, olefin, benzene, pentasil, ZSM5, membrane, permeate, retentate, distillation, fractionation, naphtha, benzol, coal oil, coal naphtha, cyclohexatriene, reduce, lower, eliminate, ppm, weight percent, abate, lessen.		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2006/0260981 A1 (GOSLING) 23 November 2006 (23.11.2006), para [0001], [0010], [0013], [0014], [0016], [0017], [0024], [0028]-[0030], [0042], [0055], Table 2	1-32
Y	US 5,914,435 A (STREICHER et al.) 22 June 1999 (22.06.1999), col 1, ln 65-66, col 2, ln 59, 60, 62, 63, col 3, ln 6, 7, 18-22, 24, 25, 37, 51, 52, 63, 64, col 4, ln 1, 5-17, 25, 26, 45	1-32
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/>		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 29 October 2009 (29.10.2009)		Date of mailing of the international search report <b>06 NOV 2009</b>
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201		Authorized officer: Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774