

PROCESS FOR PRODUCTION OF PARAXYLENE

This invention relates to a process and a chemical plant for the production of paraxylene. In particular the process and chemical plant utilise molecular sieve
5 membranes for enhanced paraxylene production.

In the petrochemical production chain one of the most important streams is the C₆ to C₈ aromatics stream which is a source of raw materials for high value downstream products. From this stream, benzene, toluene and the C₈
10 aromatics which are particularly valuable may be obtained. The C₈ aromatics are orthoxylene, metaxylene, paraxylene and ethylbenzene. Paraxylene is often the most desirable of the xylenes; however because the boiling points of ethylbenzene, ortho-, meta- and paraxylene (hereinafter collectively referred to as "C₈ aromatics") are close, they are difficult to separate by fractional
15 distillation. As a consequence various alternative methods of separating paraxylene from C₈ aromatics have been developed. The most common of such methods are fractional crystallisation which utilises the difference in freezing points between ethylbenzene, ortho-, meta- and paraxylene, and selective adsorption which commonly utilises zeolite materials to selectively
20 adsorb paraxylene from C₈ aromatics streams; the adsorbed paraxylene is recovered after desorbing from the zeolite. When either of these processes are used paraxylene can be recovered in high yields from the C₈ aromatics stream. The resulting filtrate from the crystallisation process or the raffinate from the adsorption process are depleted in paraxylene and contain relatively
25 high proportions of ethylbenzene, ortho-, and metaxylene. These streams are typically subjected to further processing downstream of the crystallisation or adsorption process.

Typically one of the additional downstream processes is an isomerisation
30 process which is used to increase the proportion of paraxylene in paraxylene depleted streams from such processes as fractional crystallisation or selective adsorption before recycle of this stream back to the fractional crystallisation process or selective adsorption process usually via intermediate additional process steps as part of a xylenes loop. The xylenes, which are predominately
35 ortho- and metaxylene, may be contacted with an isomerisation catalyst under appropriate temperature and pressure which results in the conversion of some

of the ortho- and metaxylene to paraxylene. It is also usually necessary to convert some of the ethylbenzene to prevent it from building up to high concentrations as a consequence of recycle through the xylenes loop. A catalyst may be selected to enable conversion of ethylbenzene to benzene, and/or to orthoxylene through a C₈ naphthene intermediate and/or to C₁₀ aromatics and benzene via transalkylation. It may be that the catalyst for conversion of ethylbenzene to orthoxylene is also a xylenes isomerisation catalyst in which case the orthoxylene from the ethylbenzene is converted to an equilibrium mixture of xylenes.

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Prior art processes for making paraxylene have typically included combinations of isomerisation with fractional crystallisation and/or adsorption separation. The problem with this combination is that despite improvements in catalyst performance the isomerisation technology is only able to produce equilibrium or near-equilibrium mixtures of xylenes and may also be relatively inefficient for the conversion of ethylbenzene to benzene or xylenes. The consequence of this is that big recycles of the xylenes stream back through these processes are needed to ensure the conversion of the C₈ aromatics stream to paraxylene is maximised with or without the additional recovery if desired of orthoxylene and/or metaxylene. There is a need therefore for improved processes and chemical plants for the production of paraxylene from C₈ aromatics streams, which in particular address the problems associated with large recycles and/or low ethylbenzene conversions.

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Molecular sieve membranes, such as for example zeolite membranes, have been described in the prior art, for example in US 4,699,892, US 5,100,596, EP 0481658, EP 0481659, EP 0481660, WO 92/13631, WO 93/00155, WO 94/01209, and WO 94/25151. However the prior art does not describe how to use such membranes in actual C₈ aromatics processing in the petrochemical cycle nor does the prior art describe how to use such membranes in combination with existing processes to significantly enhance their paraxylene production capability.

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The present invention is therefore directed to a chemical plant and process which offers an improvement over the prior art for the recovery of paraxylene from streams which comprise C₈ aromatics. The present invention resides in

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the specific application of a molecular sieve membrane unit and process in a paraxylene or paraxylene with orthoxylene and/or metaxylene recovery process. This invention utilises molecular sieve membranes, in particular zeolite membranes, to continuously separate paraxylene and/or ethylbenzene from xylenes, or to isomerise ortho- and metaxylene to paraxylene and/or ethylbenzene to xylenes and simultaneously or subsequently separate paraxylene from the xylenes mixture. The use of a molecular sieve membrane unit and process in for example a process for paraxylene recovery provides for a significant improvement in paraxylene production when compared to conventional paraxylene recovery processes.

Accordingly the present invention provides a process for recovering paraxylene from a feed stream comprising paraxylene and at least one other isomer of xylene, ethylbenzene, or mixtures thereof which process comprises:

(a) recovering by means of a paraxylene separation process in a paraxylene recovery unit a portion of said paraxylene from at least a portion of said feed stream to produce a first stream having a reduced paraxylene content compared to the feed stream and comprising at least a portion of said one or other isomers of xylene, said ethylbenzene, or mixtures thereof;

(b) passing at least a portion of said first stream directly or indirectly to a molecular sieve membrane unit comprising a molecular sieve membrane under such conditions that the permeate withdrawn through the molecular sieve membrane and from the molecular sieve membrane unit is enriched in paraxylene when compared to the portion of the first stream fed to the molecular sieve membrane unit and

(c) recovering paraxylene from the permeate.

Preferably step (c) is achieved by feeding the permeate back to the paraxylene separation process as part of a xylenes recovery loop.

Preferably under step (b) there is present in the molecular sieve unit an isomerisation catalyst under isomerisation conditions.

Preferably there is an additional step between (a) and (b) wherein at least a portion of said first stream is subjected to an isomerisation process in an isomerisation unit to produce an isomerate having an enriched paraxylene content compared to that of the first stream and it is at least a portion of this
5 isomerate stream which is passed to the molecular sieve membrane unit. Most preferably the permeate withdrawn from the molecular sieve membrane unit is enriched in paraxylene compared to the equilibrium concentration of paraxylene in a xylenes equilibrium mixture.

10 The present invention further provides a plant for processing hydrocarbon streams comprising paraxylene which plant comprises;

(a) a paraxylene separation unit , and

15 (b) a molecular sieve membrane unit comprising a molecular sieve membrane.

Preferably the paraxylene recovery plant comprises an isomerisation unit located between the paraxylene recovery unit and molecular sieve membrane unit. The preferred arrangement of units in the plant is in the form of a recycle
20 loop. Preferably the molecular sieve membrane unit further comprises an isomerisation catalyst.

The molecular sieve membrane unit apart from comprising a molecular sieve membrane may comprise additional features which are necessary to operate
25 the membrane unit in the chosen application. Such additional features will depend to some extent on the exact nature of the chosen application and the modality of operation of the molecular sieve membrane unit.

In separation processes molecular sieve membranes especially zeolite
30 membranes can be operated in a variety of modes depending on the phase (i.e. gas or liquid), composition and pressure of the feed. Two of these modes of operation are pervaporation and perstraction. In the pervaporation mode, the feed is in the liquid phase and molecules permeating through the membrane are transported in the gas phase from the permeate side. In the
35 perstraction mode molecules permeating the molecular sieve membrane are transported away from the permeate side by a flowing sweep stream. The

flowing sweep stream can be in either the liquid or gas phase. When the feed and sweep streams are both in the gas phase, the mode of operation is referred to as gas phase perstraction. The present invention applies to these as well as other possible modes of operating a molecular sieve membrane in a separation process. The preferred mode of operation is gas phase perstraction.

Molecular sieve membranes may also be used in a catalytic membrane reactor. A catalytic membrane reactor comprises, in addition to the molecular sieve membrane, a catalyst within the membrane or catalyst proximate to the membrane or both, or the membrane may itself be catalytically active. A catalytic membrane with a catalyst proximate to the membrane is referred to as a permselective wall membrane reactor.

In the case where the molecular sieve membrane unit is being used in the gas phase perstraction of paraxylene the molecular sieve membrane unit may comprise additional features for the application of a sweep stream to the permeate side of the membrane, for the application of a purge stream to the retentate side of the membrane, means of providing and maintaining a pressure differential across the membrane, heating means for the unit, means for pre-heating sweep and/or purge streams and means for the separation of sweep and/or purge streams from permeate and retentate streams respectively. Examples of such means are described in Figure 6 and the description thereof. When the molecular sieve unit is being used in conjunction with an isomerisation unit some or all of these additional features may be shared with such a unit. Some of the features may also be shared with other additional upstream or down stream process units. The exact nature and amount of sharing will in part be dependant on economic factors which make it sensible to utilise the additional feature for both parts of the process e.g. stream heaters, heat exchangers and compressors etc. Ideally the molecular sieve membrane is incorporated within a module as described below for inclusion in the molecular sieve membrane unit.

When the molecular sieve membrane unit comprises a molecular sieve membrane or a permselective wall membrane reactor, and is used in conjunction with an isomerisation unit, and is located down stream of the

isomerisation unit it may be advantageous to maintain the molecular sieve membrane unit at a lower temperature than that of the isomerisation unit. This will depend on the operating temperature of the isomerisation catalyst and the temperature limitations and temperature related performance characteristics of the membrane unit used. If these are such to require or make desirable lower operation temperature for the molecular sieve membrane unit then membrane unit catalyst life and/or membrane performance may be optimised.

The paraxylene recovery unit uses separation technology to produce a paraxylene enriched stream and a paraxylene depleted stream. Such separation technology includes for example the known processes of fractional crystallisation, or selective adsorption using for example molecular sieve adsorbers. The paraxylene recovery unit may therefore be a fractional crystallisation unit which utilises the difference in freezing points between ethylbenzene, ortho-, meta- and paraxylene or it may be a selective adsorption unit which commonly utilises zeolite materials to selectively adsorb paraxylene from C₈ aromatics streams; the adsorbed paraxylene is recovered after desorbing from the zeolite. The paraxylene recovery unit may also be a combination of such separation units, or may incorporate other less commonly used techniques such as fractional distillation.

Fractional crystallisation units are well known in the art and are described for example in US Patent 4 120 911. Commercially available processes include the crystallisation Isofining process, direct contact CO₂ crystallisers, scraped drum crystallisers, and continuous countercurrent crystallisation processes. The crystalliser may operate for example in the manner described in Machell et. al. US 3 662 013. Commercial fractional crystallisation processes typically recover about 60% to 68% of the paraxylene from the feed to the paraxylene recovery unit when this feed is an equilibrium or near equilibrium mixture of xylenes and ethylbenzene. The reason for this is that they are limited by the formation of a eutectic between paraxylene and metaxylene. However the actual recovery depends on the composition of the feed with higher recoveries possible when the paraxylene content of the feed is higher than the xylenes equilibrium content.

Selective adsorption units are also well known in the art and are described for example in US 3 706 812, US 3 732 325, US 4 886 929, and references cited therein, the disclosures of which are hereby incorporated by reference.

Commercially available processes include UOP PAREXTM, and IFP-Chevron
5 ELUXYLTM processes. Commercial molecular sieve selective adsorption processes may recover higher levels of paraxylene than fractional crystallisation processes; typically they recover over 90% or more typically over 95% of the paraxylene from the feed to the paraxylene recovery unit.

10 The paraxylene recovery unit produces a paraxylene enriched stream that usually comprises over 99% and may even be as high as 99.9 % paraxylene. The exact amount depends on the process used and the design and operating conditions of the specific plant. The balance in this stream being
15 ethylbenzene, ortho-, and metaxylene, toluene, and C₉ aromatics, paraffin's, naphthenes and possibly small amounts of other materials. The paraxylene recovery also produces a paraxylene depleted stream containing the balance of ethylbenzene, ortho-, and metaxylene, toluene, C₉ aromatics, paraffins, etc. along with any paraxylene fed to the paraxylene recovery unit that is not
20 removed in the paraxylene rich stream. It is this paraxylene depleted stream which is then fed to the isomerisation unit and/or molecular sieve membrane unit in the process of the present invention.

A C₈ aromatics stream may be used as the feed stream for the paraxylene separation process. Such a stream may come from a variety of sources in the
25 petrochemical plant. One possible source is from naphtha reforming. Examples of such processes include Exxon POWERFORMINGTM, UOP PlatformingTM, IFP AromizingTM. Another possible source is pyrolysis gasoline from steam cracking processes although this is likely to be a minor source of such streams. A further possible source is the UOP Cyclar process
30 for conversion of C₃/C₄ hydrocarbon streams to aromatics (see for example US5,258,563, the disclosure of which is hereby incorporated by reference). A further possible source is from toluene disproportionation and/or C₉ aromatics transalkylation. Examples of such processes include UOP TATORAYTM, TORAY TAC9TM, Mobil Selective Toluene DisproportionationTM (MSTDTM),
35 Mobil Toluene DisproportionationTM (MTDP), IFP Xylenes PLUSTM and FINA

T2BXTM. There are other possible sources of feed which comprise C₈ aromatics. The source of such C₈ aromatic streams for the process of the present invention is not critical and may be a single stream or may be a combination of streams from any of the above processes.

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The isomerisation unit may be any of the well known units in the art such as those described in US 4 236 996, US 4 163 028, US 4 188 282, US 4 224 141, US 4 218 573, US 4 236 996, US 4 899 011, US 3 856 872 and Re. 30,157, the disclosures of which are hereby incorporated by reference.

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The isomerisation catalyst may be any of the well known catalysts for isomerisation units in the art. There are primarily two types of catalyst system which are used in isomerisation units. The choice of catalyst has an impact on the overall yield and structure of the aromatics complex and also on the plant design and economics. The first type of catalyst is designed to convert ethylbenzene to xylenes and to isomerise the paraxylene depleted feed stock to a near equilibrium xylene composition. This type of catalyst system is generally the choice for aromatics producers whose objective is to maximise para and ortho-xylene production from a fixed quantity of feed stock. A second catalyst system is also designed to isomerise the paraxylene depleted feed stock; however rather than converting ethylbenzene to xylenes, this catalyst system dealkylates the ethylbenzene to produce benzene. This catalyst system is often employed when the benzene requirements are high relative to ortho and paraxylene production or when feed stock availability is not a limiting factor.

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Examples of processes and catalyst systems which include the capability of converting ethylbenzene to benzene are the Mobil MHTI (Mobil High Temperature Isomerisation) process and catalyst (see for example US 3 856 871 and US 4 638 105, the disclosures of which are hereby incorporated by reference), the Mobil MHAI (Mobil High Activity Isomerisation) process and catalyst, the AMOCO AMSAC process and catalyst and the UOP ISOMARTM I-100 process and catalyst.

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Examples of processes and catalyst systems which include the capability of converting ethylbenzene to xylenes are the IFP/ENGELHARD Octafining and

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Octafining II processes and catalyst, and the UOP ISOMARTM I-9 process and catalyst. Other processes include catalysts capable of converting ethylbenzene to C₁₀ aromatics.

- 5 Isomerisation units typically use a zeolite type catalyst. Isomerisation catalysts known to promote conversion of ortho- and metaxylene to paraxylene include metal promoted molecular sieves such as for example Pt Promoted ZSM-5, Pt promoted Mordenite and metal promoted borosilicates etc. Commercial examples are Mobil MHA1 and ISOMARTM I-9 catalyst.

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The isomerisation reactor is arranged and effective to isomerise ortho- and metaxylene to paraxylene at these conditions and also advantageously to convert ethylbenzene to benzene and/or xylenes. The term "arranged and effective" is used in this application to denote the conditions in a process unit as described in this specification, such as the temperatures, pressures, space velocities, reaction time, other reactants, and any other process conditions necessary to achieve the desired reaction, conversion or separation that is the normal function of that process unit.

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- 20 Operating temperatures of the isomerisation unit are typically in the range of 200°C to 500°C and pressures in the range of 1.5 to 35 atm gauge. The weight hourly space velocity (WHSV) based on hydrocarbon feed typically ranges from 0.5 to 20. Most isomerisation catalyst systems require a source of hydrogen which can be introduced to the isomerisation reactor to promote the isomerisation reaction that converts ortho- and metaxylene to paraxylene, to assist in the conversion of ethylbenzene to benzene and or xylenes and assists also in the prevention of coking of the isomerisation catalyst.

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- Even if an isomerisation catalyst is used which does not require hydrogen it is preferred that hydrogen is present in the process of the present invention when the molecular sieve membrane is a zeolite membrane and the zeolite membrane is susceptible to flux decay.

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- It has been discovered that operating molecular sieve membranes and molecular sieve membrane composites in the presence of hydrogen substantially reduces flux decay. Stated differently, it has been discovered that

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in separation processes an amount of hydrogen can be added in order to maintain transport flux at a predetermined acceptable level. Flux decay reduction is achieved when hydrogen is present in the feed stream, the permeate, or the optional sweep stream when present, or in any combination of feed stream, permeate, and optional sweep stream. When molecular sieve membranes and molecular sieve membrane composites are operated without the presence of hydrogen while using a hydrocarbon feed, the flux through the membrane is observed to decay in an approximately exponential fashion with time.

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In the absence of hydrogen, permeate flux, F , through the molecular sieve membrane at any particular time, t , can be approximately determined from the flux at some arbitrary earlier time, F_0 by the use of a rate constant, K , according to the following relationship:

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$$F = F_0 e^{-Kt}.$$

The units of flux used herein are $\text{Kg/M}^2\text{-day}$. This relationship describes an exponential decay of flux with time. Using this relationship, a lifetime for the flux, τ , can be defined as the length of time for the permeate flux to decay to $1/e$ of its original value. τ can be calculated from the relationship

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$$\tau = 1/K.$$

Similarly, a flux half life, $t_{1/2}$, is defined as the time in which the initial flux decays to half its original value. The half life is determined from the relationship

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$$t_{1/2} = \tau (\ln 1/2).$$

The rate of flux decay, K , increases with operating temperature and depends on the molecular composition of the feed stock and membrane composition. This approximately exponential decay of flux with time is especially troublesome during high temperature separation processes with hydrocarbon feeds. It is especially advantageous to operate the separation process at high temperatures because the diffusion coefficients of typical permeates increases

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with temperature. Additionally, in the case of membranes used as components in a catalytic membrane reactor, high temperatures may be required because many catalytic processes operate only at high temperatures. However, the half life for the flux decreases dramatically as the operating temperature is
5 increased.

An example where transport flux reduction would be especially troublesome is the separation of paraxylene permeate from a feed stream comprising a mixture of xylenes and ethylbenzene. Transport flux decay would quickly
10 reduce paraxylene yield in the preferred separation temperature range of 170°C to 500 °C, and flux decay has been routinely observed with permselective molecular sieve membranes and molecular sieve membrane composites fabricated on alumina and steel supports. MFI zeolite membranes and MFI zeolite membrane composites that were permselective for paraxylene
15 were found to have a flux half life at 225 °C of 10 to 10000 times less than at room temperature when operated with an argon sweep removing the paraxylene permeate from a mixed A8 aromatic feed. However, while separating xylenes at 300 °C, first with an inert sweep gas such as argon or nitrogen and then adding hydrogen to the sweep, transport flux was increased
20 and remained stable when hydrogen was present, whereas it decayed when hydrogen was absent.

While the flux decay prevention and remediation through the presence of hydrogen may be observed in all cases where the feedstream is derived from
25 hydrocarbons, the rate of change of transport flux in time depends on separation and separation/catalysis process conditions such as temperature, pressure, trans-membrane pressure drop or differential, and space velocity. The rate of change also will depend on feed composition, membrane and membrane composite composition and structure, hydrogen partial pressure,
30 the ratio of the amount of hydrogen present to the amount of feed, and other similar parameters.

The exact rate of flux decay varies with choice of membrane and also increased slightly with feed pressure. Feed pressure of the mixed A8 aromatic
35 feed (xylenes and ethylbenzene) varied from 1 atmosphere to 15 atmospheres in these experiments and sweep pressure was maintained equal to or 2 to 10

atmospheres below the feed pressure. At temperatures approaching ~400 °C the half life of the flux was in general less than ~2 days when hydrogen was not present during paraxylene separations. This rapid rate of flux decay is a problem for any practical higher temperature application of molecular sieve
5 membranes. Higher temperature operation is desirable because permselective transport increases with temperature. For example, in a preferred embodiment such as paraxylene separation the invention is practised at temperatures above 225 °C and preferably at temperatures above 300 °C.

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Reductions in flux decay occur when the separation is conducted in the presence of hydrogen in an amount of at least about 0.1 mole percent of the total molecules in the feed and sweep. At temperatures greater than 225 °C at least 1 mole percent hydrogen must be present, although further reductions in
15 flux decay will be observed when there is at least 10 mole percent hydrogen in the total number of molecules in the feed and sweep. At temperatures greater than 300 °C at least 20 mole percent hydrogen should be in the total number of molecules in the feed and sweep although further reductions in flux decay will be observed when about 30 to about 60 mole percent hydrogen is present. In
20 the preferred embodiment of the present invention in which an isomerisation catalyst is used in combination with a molecular sieve membrane to provide enhanced production of paraxylene the hydrogen content of the feed and sweep must be sufficient to ensure optimum catalyst performance. When considering the hydrogen requirements for both flux decay and for catalyst
25 performance the level of hydrogen used is dictated by the most critical of these factors. For example if a catalyst is used which does not require hydrogen then the hydrogen requirements for flux decay prevail however if the catalyst requires a particularly high level of hydrogen e.g. 75 mole percent or even 90 mole percent, then the hydrogen requirements for the catalyst performance are
30 likely to meet the hydrogen requirements for prevention of flux decay.

The addition of hydrogen to separation and combinations of separation and catalytic reactions reduces flux decay in cases where hydrogen is not present in sufficient quantity initially. Hydrogen can be added to either the feed or
35 sweep if one is employed in the process. However, it should be noted that hydrogen readily diffuses through molecular sieve membranes, and therefore

contacts both faces of the molecular sieve membrane regardless of whether it is introduced on the feed stream or permeate side of the membrane.

When gas phase perstraction is used in conjunction with an isomerisation catalyst for the production of paraxylene it is important to ensure the correct operation of the molecular sieve membrane unit in respect of the hydrogen to oil ratio which is maintained in the region of the isomerisation catalyst.

It has been found that, for operation of a molecular sieve membrane unit under conditions of high pressure differential between the upstream and downstream sides of the membrane, sufficient hydrogen may not be maintained at the upstream side of the membrane, where the isomerisation catalyst is located, to ensure that the hydrogen to oil ratio is at least that required for the particular catalyst used. The exact ratio of hydrogen to oil required will depend on a number of factors including the nature of the isomerisation catalyst.

It has been found that under these conditions of operation the maximum allowable pressure differential can be determined from the following equation:

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$$\frac{P_2}{P_1 K} = \frac{[R_0 - R_1(1-f) + f] R_1}{(R_1 + 1)[R_0 - R_1(1-f)]}$$

where:

25	P ₁	=	absolute (not gauge) upstream pressure.
	P ₂	=	absolute (not gauge) downstream pressure.
	K	=	hydrogen partial pressure driving force factor normally in the range 1 to 1.1.
	R ₀	=	initial overall H ₂ /oil ratio including the feed and sweep.
30	R ₁	=	minimum allowable hydrogen/oil ratio on upstream side of membrane, which is dependent on the catalyst to be used.
	f	=	fraction of hydrocarbon that ends up on downstream side of the membrane.

In principle this relationship is based on the assumption that the hydrogen partial pressure upstream of the membrane approximately equals the hydrogen partial pressure downstream of the membrane. The underlying assumption is that hydrogen moves more easily through the membrane than the other components present in the feed or permeate. For a desired upstream pressure or downstream pressure or hydrogen to oil ratio, this expression will give you the maximum pressure differential which is permissible in order to maintain the hydrogen to oil ratio at least, at the desired level on the upstream side of the membrane.

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The K factor is a minor correction because, based on computer modelling, it is expected that for paraxylene separation from an equilibrium or near equilibrium mixture of xylenes containing ethylbenzene there will in fact be a small difference in the partial pressures of hydrogen on the upstream and downstream sides of the membrane to provide a driving force for hydrogen to move across the membrane. The K factor will depend on the membrane and conditions of operation of the unit is expected to be in the range of 1.0 to 1.1 and most likely within the range 1.0 to 1.03.

20 The above relationship may be illustrated for a zeolite membrane which has a relative permeability of paraxylene to ethylbenzene of 5, a relative permeability of paraxylene to (metaxylene+ortho-xylene) of 10 and a relative permeability of hydrogen to paraxylene of 10 as shown in Figures 7 and 8.

25 Figure 7 shows the allowable pressure drops under the condition where the minimum allowable value for $R_1 = 1$ with various values of R_0 and for $f=1, 0.9$ and 0.8 .

30 Figure 8 shows the allowable pressure drops under the conditions where the minimum allowable value for $R_1=2$ with various values of R_0 and for $f=1, 0.9$ and 0.8 .

The relationship illustrates a number of points. Firstly, for a given desired R_1 , there is a point where you achieve diminishing returns by adding additional hydrogen to the system to try to increase the allowable pressure differential. The desired cut off point will be arrived at by consideration of economic factors

such as the cost of applying and maintaining high pressure differentials, versus cost of hydrogen, versus the overall recovery at paraxylene from the unit, versus membrane area requirement. Energy consumption increases as total hydrogen and pressure differential increase. However, higher pressure
5 differentials improve paraxylene recovery and reduce required membrane area.

Secondly, when comparing Figure 7 and Figure 8 one can see that as R_1 increases from 1 to 2 (dependent on catalyst) there is less flexibility of operation in respect of the pressure differential which may be used to maintain
10 the R_1 target.

In one aspect of the present invention the molecular sieve membrane unit is used to selectively separate paraxylene or a mixture of paraxylene and ethylbenzene from a stream which comprises ethylbenzene and an equilibrium
15 or near equilibrium mixture of xylenes. In this aspect the molecular sieve membrane unit may be located downstream of an isomerisation unit and does not have an isomerisation catalyst in combination with the membrane.

In a further and most preferred aspect of the present invention, a molecular
20 sieve membrane unit utilises an isomerisation catalyst as described above in combination with the membrane to isomerise ortho- and metaxylene to paraxylene in co-operation with the selective separation function of the membrane and may also include the catalytic conversion of ethylbenzene to benzene or xylenes. In this aspect of the present invention the molecular sieve
25 membrane may itself be rendered catalytically active for the isomerisation reaction or more preferably an appropriate isomerisation catalyst as described above may be located proximate to the membrane. By proximate to the membrane is meant that the catalyst is arranged and effective to isomerise the ortho- and/or metaxylene and/or convert ethylbenzene in the material in the
30 molecular sieve membrane unit, but on the upstream side of the molecular sieve membrane, to produce paraxylene. The exact amount of paraxylene which is required to be produced by the isomerisation process in the molecular sieve membrane unit depends in part on the properties of the molecular sieve membrane used. If the membrane for example has high flux and/or high
35 selectivity for paraxylene then it may be possible or even desirable for the isomerisation reaction to produce and maintain paraxylene at a non-equilibrium

concentration compared to its concentration in an equilibrium xylene mixture whilst the membrane selectively removes paraxylene from the upstream material and into the permeate. However the isomerisation catalyst in the molecular sieve membrane unit should ideally be arranged and effective to

5 produce and maintain paraxylene, upstream of the membrane and inside the molecular sieve membrane unit, at 50 % or more, preferably 80 % or more, and most preferably 90 % or more of the paraxylene equilibrium concentration whilst the membrane selectively removes paraxylene from the upstream side of the membrane and into the permeate. Depending on membrane properties it

10 may be desirable and preferable to maintain the paraxylene concentration at or near to equilibrium for xylenes isomerisation whilst the membrane selectively removes paraxylene from the retentate into the permeate. Thus the isomerisation catalyst isomerises the ortho- and metaxylene to paraxylene and the paraxylene selectively permeates through the molecular sieve membrane

15 to be produced as a permeate stream. Ortho- and metaxylene less readily pass through the molecular sieve membrane and tend to stay on the upstream side in the retentate stream where they can be further isomerised or leave the unit in the retentate stream. The permeate stream from molecular sieve membrane unit may be fractionated to remove materials boiling below and

20 above the boiling point of xylenes e.g. benzene, toluene and C9+ aromatics and then transferred to the paraxylene recovery unit. If the molecular sieve membrane unit is particularly efficient at isomerisation and separation there may theoretically be no retentate stream as there would be no paraxylene depleted stream to reject. In practice there will however likely be impurities

25 and heavier aromatic compounds such as C₉ aromatics which remain in the retentate stream and must be purged from the molecular sieve membrane unit for further treatment. Thus in the molecular sieve membrane unit there is a dynamic and coupled process of isomerisation and separation of xylenes. If the catalytic function is also capable of converting ethylbenzene to benzene or

30 xylenes then any ethylbenzene which enters into the retentate stream of the unit is also involved in this dynamic process with the resulting xylenes entering into the xylenes isomerisation reactions or the resulting benzene passing through the membrane into the permeate stream. In this aspect the molecular sieve membrane unit may be downstream of an isomerisation unit or less

35 preferred may be used in place of an isomerisation unit. The preferred combination of an isomerisation reaction process and separation process in the

same unit which is located downstream of a conventional isomerisation unit has been found to be particularly effective in upgrading a typical xylenes loop and debottlenecking the process.

5 The molecular sieve membrane used in the molecular sieve membrane unit may be any molecular sieve material in the form of a permselective membrane which as such has a binary selectivity for paraxylene to orthoxylene or metaxylene of at least 2:1. Examples of such molecular sieve materials include controlled pore amorphous materials such as MCM-41 and zeolite
10 molecular sieves. It is preferred that the molecular sieve membrane is a zeolite membrane. Examples of zeolite membranes which may be used in molecular sieve membrane units for the present invention are described in the following documents. U. S. Patent 5,110,478, the disclosure of which is hereby incorporated by reference, describes the direct synthesis of zeolite
15 membranes. The membranes produced in accordance with the teachings of U.S. Patent 5,110,478 were discussed in "Synthesis and Characterisation of a Pure Zeolite Membrane," J. G. Tsikoyiannis and W. Haag, Zeolites (Vol. 12, p. 126., 1992). Such membranes are free standing and are not affixed or attached as layers to any supports. Zeolite membranes have also been grown
20 on supports. See e.g. "High temperature stainless steel supported zeolite (MFI) membranes: Preparation, Module, Construction and Permeation Experiments," E. R. Geus, H. vanBekkum, J. A. Moulyin, Microporous Materials, Vol. 1, p. 137, 1993; Netherlands Patent Application 91011048; European Patent Application 91309239.1 and U.S. Patent 4,099,692, the disclosures of which are hereby incorporated by reference. Other literature
25 describing supported inorganic crystalline molecular sieve layers includes U.S. Patent No. 4,699,892; J. C. Jansen *et al.*, Proceedings of 9th International Zeolite Conference 1992 (in which lateral and axial orientations of the crystals with respect to the support surface are described), J. Shi *et al.*, Synthesis of
30 Self-supporting Zeolite Films, 15th Annual Meeting of the British Zeolite Association, 1992, Poster Presentation (in which oriented Gmelinite crystal layers are described); and S. Feng *et al.*, Nature, 28th April, 1994, p 834 (which discloses an oriented zeolite X analogue layer), the disclosures of which are hereby incorporated by reference.

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Further examples of zeolite membranes which may be used in molecular sieve membrane units for the present invention are described in the following documents; International Application WO 94/25151, USSN 267760 filed 8th July 1994, PCT US95/08512 (Published as WO96/01682), PCT US95/08514
5 (Published as WO96/01687), PCT US95/08513 (Published as WO96/01686), PCT EP95/02704 (Published as WO96/01683) and WO94/01209, the disclosures of which are hereby incorporated by reference. In our earlier International Application WO 94/25151 we have described a supported inorganic layer comprising optionally contiguous particles of a crystalline
10 molecular sieve, the mean particle size being within the range of from 20 nm to 1 μ m. The support is advantageously porous. When the pores of the support are covered to the extent that they are effectively closed, and the support is continuous, a molecular sieve membrane results; such membranes have the advantage that they may perform catalysis and separation simultaneously if
15 desired. Preferred zeolite membranes are those which are prepared by the Inverted In-Situ-Crystallisation (I-ISC) process. Most preferred zeolite membranes are prepared by using a GEL layer and a Low Alkaline synthesis solution using the Inverted In-Situ-Crystallisation process (GEL-LAI-ISC), or by using a Seeding Layer and a Low-Alkaline-synthesis solution using the
20 Inverted In-Situ Crystallisation (S-LAI-ISC). These processes are described in USSN 267760 filed 8th July 1994, PCT US95/08512, PCT US95/08514, PCT US95/08513 and PCT EP95/02704. Zeolite compositions fabricated using the above described LAI-ISC, GEL-LAI-ISC, or S-LAI-ISC techniques can have dense zeolite layers in which the zeolite crystals are intergrown such that non-
25 selective permeation pathways in these as-synthesised zeolite layers are virtually non-existent.

It is envisaged that the molecular sieve membrane unit will contain at least one zeolite membrane which may or may not be catalytically active. If the
30 membrane is not catalytically active for the desired process a suitable catalyst may be used in combination with the membrane. This catalyst may be located on the upstream side of the membrane or the downstream side of the membrane depending on the process and the nature and purpose of the catalyst. In one embodiment one or more membranes may be arranged with
35 one or more catalysts to provide alternating membrane and catalyst regions in the molecular sieve membrane unit. In this arrangement the feedstream to the

unit may for example pass through a membrane region with the retentate flowing to a catalyst containing region and then through a second membrane region to a second catalyst region. The exact number of membrane and catalyst regions will depend on the nature of the separations and catalyst processes desired. The separation and catalyst process may be substantially the same for each combination of catalyst and membrane or may be different.

It should be understood that two or more molecular sieve membrane units with or without isomerisation catalyst in close proximity to the molecular sieve membrane in each unit may be used in the processes of the present invention. Reference to molecular sieve membrane unit in this specification should also be taken to include embodiments where two or more molecular sieve membrane units may be used in sequence to each other with or without any further intervening processes or process units.

The molecular sieve membrane unit used for example in gas phase perstraction (e.g as illustrated in Figure 6) comprises certain features which are required for operation within a xylenes loop. These features are adequately described under the description of Figure 6.

The zeolite membranes described above may be incorporated into the molecular sieve membrane unit in the form of a module such as that described in WO94/01209 the disclosure of which is incorporated by reference. In the context of the present invention the term module signifies the combination of a molecular sieve membrane which may or may not be deposited on a substrate supported within a housing which has all the means and additional features required to effectively include the membrane into the molecular sieve unit. These additional means and features include valves and pipework which is necessary to attach the module to the other components of the molecular sieve membrane unit. The module may therefore comprise some or all of those features which are required to operate a molecular sieve membrane unit.

The module may comprise a housing preferably made out of metal such as stainless steel which can withstand the temperatures, pressures and chemical environment to which the membrane unit is exposed in operation. The module will contain a membrane element which comprises the molecular sieve

membrane either self-supporting or on a suitable support. It is preferred that, for robustness, the molecular sieve membrane is deposited on a suitable support. Suitable supports are inorganic supports which are able to withstand the operating environment of the molecular sieve membrane unit and include stainless steel and ceramic supports. Examples of suitable supports are provided in the references cited above for zeolite membranes. The exact method of incorporating the membrane element into the module will depend on the nature of the materials in the module housing and element. If the housing is stainless steel one method of incorporation is as described in WO94/01209 the disclosure of which is incorporated by reference. Another possible arrangement is to incorporate a number of membrane elements which comprise zeolite membrane on a porous stainless steel support within a plate and frame arrangement. Such arrangements are well known in the art. If the membrane element comprises a ceramic support for example when it is a ceramic cordierite monolith then it may be required that suitable seals are utilised to incorporate the membrane element into a metal housing. Such seals should be capable of withstanding the operating conditions of the membrane unit and are known in the art. The module will also have means for introducing the feed to the upstream side of the membrane and means for removing the product from the downstream side of the membrane. On the upstream side the module may be engineered to provide a purge for removing retentate. On the downstream side the module may be engineered to provide a sweep gas to remove product from the downstream side of the module. The module may also be engineered to allow temperature control by means of heating and/or cooling. The module may also contain means such as valving and pressure regulators to provide and control the pressure within the module such that there is either no pressure differential across the membrane or preferably so that there is a pressure differential between the upstream and downstream side of the membrane such that the pressure on the upstream side of the membrane is higher. The feed may be introduced to the module such that the pressure on the upstream side of the membrane is at 1 to 35 atm, preferably 10-30 atm and most preferably 15 to 25 atm. The average pressure differential between the upstream and downstream sides of the membrane may be 0 to 35 atm, preferably 2 to 35 atm and most preferably 5 to 15 atm. The pressure differential is expressed as an average as there may be a reduction in the upstream and downstream pressures as you move along a membrane element

- within a module depending on how this is engineered. Also located within the module on the feed side of the membrane is the isomerisation catalyst. The membrane element may be engineered or its arrangement within the module may be such so as to allow counter-current operation between feed and sweep within the module or it may be arranged to allow co-current operation between feed and sweep within the module or it may be arranged for cross-flow operation. Thus the membrane element may comprise a multichannel ceramic monolith support in which some of the channels are utilised for introducing the feed to the element and some of the channels are utilised for introducing the sweep to the element. The feeds may be arranged through the use of appropriate flanges and masking to allow co-current, counter-current or cross-flow operation. When such a multichannel monolith is used the isomerisation catalyst for use in combined isomerisation and separation is located within the feed channels of the monolith. Alternatively the catalyst may be located within the monolithic support but on the feedstream side of the membrane. When desirable the combination of the retentate stream (with or without purge) with the permeate stream (with or without sweep) may take place within the module itself.
- The membrane elements may be included in the module as described in WO94/01209. The membrane elements may also be incorporated into other known designs for membrane separation units such as for example plate and frame membrane modules. Suitable ceramic monolith elements may be constructed according to US 5 221 484, US 5 114 581, US 5 120 576, EP 0 373 215, US 5 108 601, EP 0 396 684, EP 0 310 632 but with the use of a zeolite membrane. Such monolithic tubes may be incorporated into a metal module by the use of techniques known in the art such as for example EP 0 270 051.
- When the process is gas phase perstraction the temperature of the feed into the module possibly may be up to 500 °C. The temperature within the module must be at least 150°C preferably at least 170°C to ensure that there is adequate isomerisation reaction and separation of paraxylene. Preferably the temperature is above 225 °C most preferably above 300°C. Preferably the temperature is 480°C or less most preferably 450°C or less e.g. 435°C.

The molecular sieve membrane unit may be installed downstream of an existing xylenes isomerisation reactor or installed as a replacement of an isomerisation reactor in an existing paraxylene recovery process. The molecular sieve membrane unit may be added to an existing process solely for
5 separation of paraxylene from xylenes, or for both isomerisation and separation. The most preferred option according to the present invention is to have, as part of a xylenes loop, a molecular sieve membrane unit downstream of a xylenes isomerisation unit and for the molecular sieve membrane unit to comprise a molecular sieve membrane and an isomerisation catalyst so that
10 the molecular sieve membrane unit performs both isomerisation of xylenes and selective separation of paraxylene. Preferably it also catalyses conversion of ethylbenzene to xylenes or benzene. If the molecular sieve membrane unit catalyses conversion of ethylbenzene to xylenes or benzene then this may allow less conversion of ethylbenzene in the conventional isomerisation unit
15 with less xylene losses due to the lower operating temperature which would be required in the conventional isomerisation unit. In this case this unit could be a liquid phase isomerisation unit.

The most preferred embodiment of the present invention is the incorporation of
20 a molecular sieve membrane unit comprising isomerisation catalyst into a conventional xylene recovery loop such as that shown in Figure 1 and discussed below. The xylene recovery process is referred to as a "loop" because xylenes not converted to paraxylene are recycled repeatedly to the isomerisation unit that is usually a part of the xylene recovery loop until the
25 xylenes are converted to paraxylene and removed from the loop via the paraxylene separation unit. In such a loop orthoxylene may also be a product which is removed from the loop in the xylene splitter if desired. Orthoxylene can sometimes be generated by the isomerisation unit if the feed to that unit has a less than equilibrium orthoxylene concentration.

30 As indicated above the fresh feed for the xylene recovery loop may come from a variety of sources in the petrochemical cycle. Fresh feed from, for example, a reformer, which is introduced to the xylene recovery loop is usually fractionated before introduction to the paraxylene separation unit to remove
35 materials boiling below the boiling point of xylenes, and may optionally also be fractionated to remove at least part of the material boiling above the boiling

point of xylenes. If lower boiling materials are not removed from the fresh feed, it is introduced to a detoluenizer tower ("DETOL") which removes toluene and lighter materials by distillation. The feed is then introduced to either a xylene rerun tower or splitter. A xylene rerun tower removes C₉+ aromatics from the feed. A xylene splitter tower in addition removes at least part of the orthoxylene for subsequent recovery as orthoxylene product in an orthoxylene rerun tower. The fresh feed in a xylenes loop is combined with a recycle stream which comes from the xylene isomerisation unit or in the present invention from the molecular sieve membrane unit. The overhead stream from the xylene rerun tower or splitter is typically a mixture of compounds which includes 0 to 10 wt% non aromatics, 0 to 5 wt% toluene, 5 to 20 wt% ethylbenzene, 0 to 10 wt% C₈ naphthenes, and 70 to 95 wt% xylenes. The exact composition will depend on the fresh feed and the nature of the catalysts used in the isomerisation unit and in the molecular sieve membrane unit. It should be appreciated that the fresh feed to the xylenes recovery loop could be a combination of two or more feeds such as those discussed above. Thus it could be a combination of a feed from a naphtha reformer with that from a TATORAYTM or MSTDPTM unit.

In the paraxylene recovery process of the present invention additional process units may be present. For example when the process is a xylenes loop there may be present a fractionation unit which may comprise a number of process units after the molecular sieve membrane unit but before the paraxylene separation unit and which are present to remove various products and or impurities from the recycle stream. These additional process units include for example, stabiliser units, DETOL units, clay treaters, xylenes splitters, xylenes re-run towers etc.

It should be understood that in the present description when reference is made to a feed to, or material upstream of, the membrane in a molecular sieve membrane unit being at equilibrium in xylenes, this means that it comprises a mixture of xylenes which are at the typical respective concentrations for an equilibrium mixture of xylenes as known in the art. In the same context by near equilibrium is meant a composition comprising xylenes in which one or more of the xylenes present are at their non-equilibrium concentration with respect to the other xylenes present and includes mixtures where one or more of the

xylene isomers are present at a concentration which is greater than their equilibrium concentration. Ideally in such mixtures the paraxylene should be present at 50 % or more, preferably 80 % or more and most preferably at 90 % or more of the paraxylene equilibrium concentration.

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The exact size of the molecular sieve module will depend in part on the economics of operation of the chemical plant which comprises the module in a molecular sieve membrane unit and will be determined to a large extent on the amount of membrane area required to achieve this economic target. Factors to
10 be taken into account when designing the module are amongst other things the required level of permeation of the feed through the membrane, the relative permeability of the membrane for the desired paraxylene over other components of the feed, the required hydrogen to oil ratio for the isomerisation catalyst present in the molecular sieve membrane unit, the purity of the feed to
15 the unit. This may be illustrated for example in Figure 8 wherein; the feed rate is 500 moles/hr and its composition is 20% paraxylene, 20% ethylbenzene, and 60% meta+ orthoxylene; the overall hydrogen to oil mole ratio is 3:1 with 1/3 of the hydrogen in the sweep; the membrane has a hydrogen/(metaxylene+orthoxylene) relative permeability of 100, an
20 ethylbenzene/(metaxylene+orthoxylene) relative permeability of 2 and a paraxylene/(metaxylene+orthoxylene) relative permeability of 10; and $P1/P2=200/132$ in psi units. Given these constraints the Figure illustrates the relationship between wt% paraxylene in the product and the relative membrane area (with associated catalyst) which is identified as a cumulative membrane
25 area factor required assuming a paraxylene permeability of 1 mole/psi/unit area.

This factor provides an indication of the relative area of membrane required in the module as a function of wt% of paraxylene in the product for a given set of
30 parameters associated with the unit and the membrane itself. Note that at the upper end of the bold line, 100% of the feed has permeated through the membrane. Also illustrated is that if there is a small amount of material which is present in the feed which does not permeate the membrane then there comes a point where additional membrane area is not advantageous. In that
35 case there is never full permeation of the feed through the membrane because the non-permeables partial pressure increases to the point where there is no

partial pressure driving force for paraxylene to permeate across the membrane. As the feed moves through the membrane module, it is depleted in xylenes on the upstream side and equilibrated in xylenes by the isomerisation catalyst there is a danger that the partial pressure driving force for paraxylene diffusion
5 will be reversed and that paraxylene already separated from the feed will move back across the membrane, undesirably reducing the permeate paraxylene concentration. The point at which this will occur for a given feed will be a function of the membrane properties, the feed composition and operating conditions such as temperatures and pressures.

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Other objects and features of the invention are described in the following detailed description wherein reference is made to the accompanying Figures.

Figure 1 shows conventional xylenes loop comprising a paraxylene separation
15 unit, an isomerisation unit and a fractionation unit.

Figure 2 shows a xylene purification loop comprising a paraxylene separation unit, a fractionation unit and utilising a molecular sieve membrane unit with isomerisation catalyst.

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Figure 3 is a xylene purification loop comprising a paraxylene separation unit, a fractionation unit and utilising a molecular sieve membrane unit, with isomerisation catalyst, downstream of an isomerisation unit.

25 Figure 4 shows a xylene purification loop utilising an isomerisation unit upstream of a molecular sieve membrane unit without isomerisation catalyst and used for separating a paraxylene enriched stream that is transferred to a paraxylene recovery unit.

30 Figure 5 shows a xylene purification loop having an isomerisation unit upstream from a molecular sieve membrane unit without isomerisation catalyst and used for separating a paraxylene enriched stream that is then transferred to a xylene splitter.

35 Figure 6 shows a detailed schematic of the molecular sieve membrane unit used in the xylene purification loop described in Figure 3.

Figure 7 Illustrates for a given membrane the allowable pressure drop to maintain minimum upstream hydrogen to oil $R_1=1$.

- 5 Figure 8 Illustrates for a given membrane the allowable pressure drop to maintain minimum upstream hydrogen to oil $R_1=2$.

Figure 9 Illustrates the relationship of wt% PARAXYLENE in the product versus cumulative membrane area factor for a given membrane operated under
10 certain conditions.

In Figure 1 fresh feed containing xylenes is introduced to a xylene splitter 2 through fresh feed line 1. A bottom stream 3 is withdrawn from the xylene splitter 2 containing materials having boiling points above xylenes and possibly
15 containing orthoxylene. An overhead stream 4 is withdrawn from the xylene splitter containing xylenes and ethylbenzene. The overhead stream 4 is fed to paraxylene recovery unit 5. Xylenes are separated in paraxylene recovery unit 5 to yield a paraxylene rich stream 6 and a paraxylene poor stream 7. The paraxylene recovery unit normally uses fractional crystallisation and/or
20 molecular sieve adsorption to separate paraxylene from other stream 4 components. The paraxylene poor stream 7 is then introduced to an isomerisation (ISOM) unit 8 which contains an isomerisation catalyst arranged and effective to promote isomerisation of ortho and metaxylene to paraxylene and the conversion of ethylbenzenes to benzene and/or xylenes or other
25 compounds. The isomerate 9 from the isomerisation unit 8 is then introduced to stabiliser 10. Stabiliser 10 separates five carbon and lighter compounds from stream 9 through differences in boiling points. Five carbon and lighter compounds are withdrawn from stabiliser 10 through line 11 and six carbon and heavier compounds are withdrawn from stabiliser 10 through line 12. The
30 stream in line 12 is introduced to a DETOL unit 13 to remove toluene and lighter compounds through line 14. Xylenes and heavier materials are withdrawn from DETOL unit 13 through line 15 and introduced to xylene splitter 2. Normally fresh feed 2 and the xylenes withdrawn from the DETOL 13 through line 15 are passed through clay treaters which in order to simplify the
35 figures are not shown in Figures 1 to 6. As an alternative to the splitter 2 described in Figure 1 a rerun tower may be used. It is to be understood that

when reference is made to a splitter in this specification that this reference also encompasses the use of a rerun tower in place of the splitter. For the purposes of this application the description "splitter" shall be used when substantial orthoxylene is removed in the bottoms and "rerun" shall be used when it is not.

There are a number of disadvantages associated with this conventional process arrangement for paraxylene recovery. The first is that this combination of process steps requires a significant recycle through the loop in order to remove the maximum possible amounts of paraxylene. This is primarily due to the fact that the isomerisation unit and processes are only able to produce equilibrium or near equilibrium mixture of xylenes for the recycle in the isomerate. A typical concentration of paraxylene in the isomerate from such a unit is 18 to 22 wt%. Another problem is that in most isomerisation processes there are xylenes losses of up to 4% or higher. Thus with repeated recycles this loss of xylenes to undesirable products may be significant. The loop described in this figure has in effect a bottleneck which is associated with the isomerate from the isomerisation unit as this unit is only able to produce an isomerate which comprises paraxylene at or near its equilibrium concentration. This is the maximum amount of paraxylene which is being made available for the recycle.

Figure 2 shows a xylene purification loop according to the present invention. Fresh feed containing xylenes is introduced to a xylene splitter 21 through fresh feed line 20. A bottom stream 22 is withdrawn from xylene splitter 21 containing materials having boiling points above xylenes and possibly containing orthoxylene. An overhead stream 23 is withdrawn from the xylene splitter containing xylenes and ethylbenzene. The overhead stream 23 is fed to paraxylene recovery unit 24. Xylenes are separated in paraxylene recovery unit 24 to yield a paraxylene rich stream 25 and a paraxylene poor stream 26. The paraxylene recovery unit normally uses fractional crystallisation and/or molecular sieve separation to separate paraxylene from other stream 23 components. The paraxylene poor stream 26 is then introduced to molecular sieve membrane unit 27 (which comprises additional features not shown in this Figure but which are as indicated in Figure 6 and description thereof). Molecular sieve membrane unit 27 includes catalyst arranged and effective to promote isomerisation of ortho- and metaxylene to paraxylene and the

conversion of ethylbenzenes to benzene and/or xylenes or other compounds. The molecular sieve membrane also selectively permits permeation of paraxylene through the membrane relative to ortho- and metaxylene. A stream enriched in paraxylene is withdrawn from molecular sieve membrane unit 27 as permeate stream 28. The remaining material in retentate stream 29 should ideally be at equilibrium or near equilibrium in xylenes. The permeate stream 28 and retentate stream 29 may be treated separately (not shown in Figure 2) or combined to form combined feed 30 and introduced to stabiliser 31. Stabiliser 31 separates five carbon and lighter compounds from stream 30 through differences in boiling points. Five carbon and lighter compounds are withdrawn from stabiliser 31 through line 32 and six carbon and heavier compounds are withdrawn from stabiliser 31 through line 33. The stream in line 33 is introduced to a DETOL unit 34 to remove toluene and lighter compounds through line 35. Xylenes and heavier materials are withdrawn from DETOL unit 34 through line 36 and introduced to xylene splitter 21. In addition it is also possible to introduce all or some of the fresh feed directly into the molecular sieve membrane unit 27 as indicated at line 37. This would have the advantage of further increasing the concentration of paraxylene in the paraxylene recovery unit feed, because a higher proportion of that feed would be derived from the molecular sieve membrane unit product rather than from the fresh feed having only an equilibrium or near equilibrium paraxylene concentration. However this approach requires a larger molecular sieve membrane unit, and may require a larger retentate stream to purge heavy aromatics brought in with the fresh feed, so there is an economic optimum for each application regarding how much, if any of the fresh feed to route directly to the molecular sieve membrane unit. For example in a retrofit situation where the paraxylene recovery unit capacity is limiting the plant production rate, it would likely be advantageous to route at least a portion of fresh feed to the molecular sieve membrane unit.

This embodiment of the present invention has a significant advantage over the conventional process as described in Figure 1. The molecular sieve membrane unit produces a permeate with a greater than equilibrium amount of paraxylene and a retentate which has an equilibrium or near equilibrium concentration. The combined products will have a higher paraxylene content than is possible with the conventional isomerisation unit, which is limited by

equilibrium. When those streams are recycled to the paraxylene recovery unit via the xylene splitter the paraxylene concentration is increased there, increasing per pass paraxylene recovery and reducing recycle which is a problem with conventional processes. In this embodiment the molecular sieve
5 membrane unit is required to relatively efficiently isomerise xylenes and convert ethylbenzene and requires a molecular sieve membrane which has selectivity for paraxylene and exhibits acceptable flux through the membrane. Such membranes may be prepared using the LAI-ISC, S-LAI-ISC and GEL-LAI-ISC methods described above.

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The particularly preferred embodiment of the invention is shown in Figure 3. Fresh feed containing xylenes is introduced to xylene splitter 41 through fresh feed line 40. A bottom stream containing 9 carbon and heavier compounds and possibly containing orthoxylene is withdrawn from xylene splitter through
15 line 42. An overhead stream containing xylenes and ethylbenzene is withdrawn from xylene splitter 41 through line 43 and introduced to paraxylene recovery unit 44. Paraxylene is recovered in a paraxylene rich stream 45 while ortho- and metaxylene are recovered in paraxylene poor stream 46. The paraxylene poor stream 46 is introduced to an isomerisation unit 47 which
20 contains an isomerisation catalyst arranged and effective to promote isomerisation of ortho and metaxylene to paraxylene and the conversion of ethylbenzenes to benzene and/or xylenes or other compounds. Isomerised product is withdrawn through line 48 and introduced to molecular sieve membrane unit 50 containing molecular sieve membrane, catalyst that both
25 isomerises ortho- and metaxylene to paraxylene and in which unit there is selective permeation of paraxylene through the molecular sieve membrane relative to ortho- and metaxylene. The molecular sieve membrane unit 50 comprises additional features not shown in this Figure but which are as indicated in Figure 6 and description thereof. It should be noted that in this
30 embodiment the catalyst may be incorporated into the membrane or preferably it may be located on the upstream or inlet side of the membrane but in close proximity to the membrane or, in a less preferred embodiment, the membrane itself may be catalytically active or rendered catalytically active. A stream enriched in paraxylene is withdrawn from molecular sieve membrane unit 50
35 through permeate stream 51. The remaining material leaves in retentate stream 52. Permeate stream 51 and retentate stream 52 may be treated

differently (not shown in Figure 3) or they may be combined in line 53 and introduced to stabiliser 54. Stabiliser 54 separates five carbon and lighter compounds from stream 53 through differences in boiling points. Five carbon and lighter compounds are withdrawn from stabiliser 54 through line 55 and six
5 carbon and heavier compounds are withdrawn from stabiliser 54 through line 56. The stream in line 56 is introduced to a DETOL unit 57 to remove toluene and lighter compounds through line 58. Xylenes and heavier materials are withdrawn from DETOL unit 57 through line 59 and introduced to xylene splitter 41. In addition it is also possible for some or all of the fresh feed to be
10 introduced to the isomerisation unit 47 or to the molecular sieve membrane unit 50 or to both as indicated at lines 60 and/or 61. The reason for using such a split feed has already been discussed above in relation to Figure 2. Diverting fresh feed to either the isomerisation unit via line 60 or the molecular sieve membrane unit via line 61 would have similar benefits in terms of reduced
15 xylene loop recycle. Using line 61 reduces flow through the isomerisation unit versus that required if line 60 is used. However it may still be advantageous to utilise line 60, since then it would combine with the feed in line 46 and could use the same pumps and/or reactor preheating equipment. This may be particularly advantageous if the molecular sieve membrane unit and the
20 isomerisation unit operate under similar conditions where isomerisation unit effluent flows directly to the molecular sieve membrane unit without the need for heating, cooling and/or pressure change. In that situation, stream 53 would typically be cooled by transferring its heat to the isomerisation unit feed to provide at least part of the reactor preheat. Such feed/effluent heat exchange
25 systems usually work at their most efficient when feed and effluent flow rates are approximately the same. The optimum distribution of fresh feed among lines 40, 60 and 61 will vary depending on plant constraints and economic factors, and should be determined for each individual application. Conventional processes without molecular sieve membrane units have little
30 incentive to route fresh feed to isomerisation because the feed normally already contains xylenes in approximately equilibrium proportions so conventional isomerisation would not significantly increase paraxylene concentration to metaxylene and orthoxylene versus that already present.

35 This particularly preferred embodiment not only has significant advantages over the prior art process of Figure 1 but also surprisingly has some significant

advantages over that of Figure 2. The combination of the isomerisation unit and the molecular sieve membrane unit downstream of the isomerisation unit enables the beneficial attributes of both units to be combined for maximum paraxylene production. The embodiment in Figure 2 requires a particularly efficient molecular sieve membrane unit, as the feed to this unit which is derived from the paraxylene recovery unit is significantly depleted in paraxylene. The paraxylene content may be as low as 1% or less with the balance being mainly ortho- and metaxylene, ethylbenzene and minor amounts of other materials. This means that the molecular sieve membrane unit must be able to quickly isomerise this feed to produce the required amount of paraxylene on the upstream side of the membrane which exact concentration of paraxylene depends on the membrane properties and in some case will need to be an equilibrium or near equilibrium mixture of xylenes to achieve maximum efficiency in the process otherwise, the material permeating through the membrane may at least initially have below equilibrium paraxylene concentration which could be worse than that achievable in a conventional isomerisation reactor. Furthermore the molecular sieve membrane unit must also efficiently convert ethylbenzene or this will build up in the xylenes loop. The use of an isomerisation unit in combination with the molecular sieve membrane unit in Figure 3 overcomes these deficiencies with the embodiment of Figure 2. Firstly the isomerate from the isomerisation unit is already enriched in paraxylene and is typically at equilibrium or near equilibrium with respect to xylenes. This means that the molecular sieve membrane unit only has to maintain the isomerate in or near this state to enable the membrane to work efficiently. Secondly because the isomerisation unit has the capability of ethylbenzene conversion, the ability of the molecular sieve membrane unit to destroy ethylbenzene, although desirable is not critical. Typically promoting xylenes equilibrium is easier than destroying ethylbenzene. The negative aspect of xylene losses which normally occur in the isomerisation unit is offset by the greatly reduced recycle needed when using the molecular sieve membrane unit in this embodiment. Also if the molecular sieve membrane unit does have at least some ethylbenzene conversion capability the isomerisation unit does not have to do as much of this conversion. This would allow for the isomerisation unit to be operated under milder conditions which may result in less xylenes loss in the isomerisation unit. Also because there is no need to for the feed to the molecular sieve membrane unit to be brought to equilibrium

in this unit, as is required with some membranes when used in Figure 2 embodiment, it may need significantly less catalyst and be significantly smaller in size compared to the molecular sieve membrane unit which is required for Figure 2. In the particularly preferred embodiment of Figure 3 a membrane
 5 was prepared by the LAI-ISC method and repared with polyimide; this membrane had typical selectivity's (α) for (paraxylene/other C₈ aromatics) of paraxylene/ethylbenzene $\approx$ 2, paraxylene/(metaxylene + orthoxylene) $\approx$ 5 where:

10

$$\alpha = \frac{(\% \text{paraxylene in permeate})/(\% \text{paraxylene in feed})}{(\% \text{others in permeate})/(\% \text{others in feed})}$$

When this membrane is used in combination with an isomerisation catalyst in
 15 the molecular sieve membrane unit, the predicted level by computer modelling of paraxylene in the feed leaving the molecular sieve membrane unit compared to the isomerate leaving the isomerisation unit may surprisingly be as high as 55 wt% compared to 22 wt% (the equilibrium concentration if about 10 wt% non-xylenes are present). This may provide for an overall increase in
 20 paraxylene production in the cycle of 50% or more. Suitable membranes for use in a molecular sieve membrane unit to provide such improved performance are described for example in USSN 267760 filed 8th July 1994, PCT US95/08512, PCT US95/08514, PCT US95/08513 and PCT EP95/02704.

25 Figure 4 shows an embodiment of the invention using a molecular sieve membrane to separate paraxylene from a xylene stream. Fresh feed containing xylenes is introduced to xylene splitter 101 through fresh feed line 100. Compounds boiling above xylenes and possibly including orthoxylene are withdrawn through bottom stream 102 and xylene and lighter boiling
 30 compounds are withdrawn as overhead stream 103. Overhead stream 103 is introduced to isomerisation unit 104 through intermediate line 105. The isomerisation unit 104 converts ortho- and metaxylene to paraxylene and promotes the conversion of ethylbenzenes to benzene and/or xylenes or other compounds. Unconverted ortho- and metaxylene along with paraxylene are
 35 withdrawn from isomerisation unit 104 through line 106 and introduced to stabiliser 107. 5 carbon and lighter boiling compounds are withdrawn from

stabiliser 107 through line 108 with the balance of material withdrawn through line 109 and introduced to DETOL unit 110. Toluene and lighter boiling compounds are withdrawn from DETOL unit 110 through line 111 and xylenes are withdrawn through line 112 and introduced to molecular sieve membrane unit 113. Molecular sieve membrane unit 113 comprises a molecular sieve membrane that is arranged and effective to permit selective permeation of paraxylene relative to ortho- and metaxylene. Most paraxylene is withdrawn through permeate stream 114 and introduced to paraxylene recovery unit 115. Most ortho- and metaxylene are withdrawn from molecular sieve membrane unit 113 through retentate stream 116 and introduced to xylene splitter 101. The paraxylene recovery unit 115 separates paraxylene from ortho-metaxylene. Paraxylene is withdrawn through paraxylene rich stream 117 and the balance of ortho- and metaxylene are withdrawn through paraxylene poor stream 118. Paraxylene poor stream 118 is introduced to isomerisation reactor 104 through line 105. Alternatively all or part of overhead stream 103 may be directed to the molecular sieve membrane unit 113 via line 119 and 112. The optimal routing of stream 103 depends on an economic balance amongst several parameters, namely isomerisation unit per pass xylenes losses and ethylbenzene conversion and the molecular sieve membrane unit's relative selectivity between paraxylene and ethylbenzene. Routing steam 103 to molecular sieve membrane unit 113 has the advantage of avoiding whatever xylenes losses it would have incurred if it had been passed through the isomerisation unit 104. However there is a potential risk in this instance that ethylbenzene will build up in the xylenes loop. For example if molecular sieve membrane unit 113 ensured that all the ethylbenzene was retained in the retentate 116 the ethylbenzene would be retained in the xylenes loop without removal or destruction and would build up indefinitely as additional ethylbenzene is brought into the loop in the fresh feed. However if the selectivity of the molecular sieve membrane in the unit was such that a substantial portion of the ethylbenzene permeated through the membrane and into stream 114 then that portion of the ethylbenzene would pass to the isomerisation unit 104 via lines 115, 118 and 105, where some of it would be converted thus limiting its build up in the xylenes loop. There is also the possibility of an intermediate case where a portion of the stream 103 passes to the molecular sieve membrane unit and the remainder flows to the isomerisation unit. In this case the flow to the isomerisation unit acts as a

purge to prevent the build up of ethylbenzene to unacceptable levels if the amount permeating through the membrane in the membrane unit is insufficient. The optimal balance should be determined for each specific application and will depend on the membrane properties and the properties of the xylenes.

5 isomerisation catalyst amongst others.

Another embodiment of the invention is shown in Figure 5 wherein xylenes are introduced to xylene splitter 201 through fresh feed line 200. Compounds boiling above the boiling point of xylenes and possibly some of the orthoxylene are withdrawn from xylene splitter 201 through bottoms line 202, xylenes and ethylbenzene are withdrawn through overhead stream 203 and introduced to paraxylene recovery unit 204. Paraxylene is withdrawn through paraxylene rich stream 205 and ortho- and metaxylene are withdrawn through paraxylene poor stream 206. Paraxylene poor stream 206 is introduced to an

15 isomerisation unit 207 through line 208. Isomerisation unit 207 isomerises ortho- and metaxylene to paraxylene and promotes the conversion of ethylbenzene to benzene and/or xylenes or other compounds. The isomerate is withdrawn through line 209. The isomerate mixture which contains a near equilibrium mixture of ortho-, meta- and paraxylene is introduced to stabiliser

20 210 through line 209. 5 carbon and lighter compounds are withdrawn through line 211 and heavier boiling compounds are withdrawn through line 212 and introduced to DETOL unit 213. Toluene and lighter boiling compounds are withdrawn through line 214; xylenes and heavier materials are withdrawn from the DETOL unit 213 through line 215. Xylenes and heavier materials in line

25 215 are introduced to molecular sieve membrane unit 216 which comprises a molecular sieve membrane arranged and effective to permit selective permeation of paraxylene there through. Most paraxylene is withdrawn through line 217 and introduced to xylene splitter 201. Ortho- and metaxylene are withdrawn as retentate stream 218 and reintroduced to isomerisation unit

30 207 through line 208. However it will likely be necessary to purge a portion of this stream to xylene splitter 201 via line 219 to avoid an excessive build up of C9+ aromatics as they will tend to stay in the retentate and not be removed in the stabiliser or DETOL units.

35 Figure 6 illustrates one possible arrangement of additional components which may constitute the molecular sieve unit used in the xylenes loop of Figure 3.

Features A to F are the components which make up the molecular sieve membrane unit. Feature D is a membrane module which comprises a membrane element and isomerisation catalyst upstream of the membrane.

5 The feed 600, from the conventional isomerisation unit 601 enters the membrane module (D) with or without additional heating or cooling. A sweep gas is introduced to the membrane module at point 602. This sweep gas is supplied to the unit and held within the unit within a sweep gas recycle loop. This sweep gas recycle loop comprises; a sweep gas compressor (A), a feed/effluent exchanger (B), a sweep gas heater (C), a membrane module (D),
10 re-route to feed/effluent exchanger (B), cooler (E), and high pressure separator (F). The retentate 603 and sweep containing the xylenes permeate product 604 are combined into a stream 605 which passes to the high pressure separator (D) (via the feed/effluent exchanger (B) and cooler (E)) and in which the product stream 606 is removed from the sweep gas (and recycle gas)
15 which is recycled to the sweep gas compressor (A) and back to sweep gas heater (C) via the feed/effluent exchanger (B). The product stream 606 comprises approximately 50 wt% paraxylene. The other features of Figure 6 are common features used in a xylenes loop and need no further explanation.

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CLAIMS

1. A method of processing a hydrocarbon feedstream comprising paraxylene and at least one other isomer of xylene, ethylbenzene, or mixtures thereof which method comprises:
- 5
- (a) recovering by means of a paraxylene separation process in a paraxylene recovery unit a portion of said paraxylene from at least a portion of said feed stream to produce a first stream having a reduced paraxylene content compared to the feed stream and comprising at least
- 10 a portion of said one or other isomers of xylene, said ethylbenzene, or mixtures thereof;
- (b) passing at least a portion of said first stream to a molecular sieve membrane unit comprising a molecular sieve membrane under such conditions that the permeate withdrawn through the molecular sieve membrane and from the molecular sieve membrane unit is enriched in paraxylene when compared to that portion of the first stream fed to the molecular sieve membrane unit .
- 15
2. A method as claimed in claim 1 wherein there is a additional step (c) which comprises recovering paraxylene from the permeate of step (b) by separation of paraxylene from the other components present in the permeate.
- 20
3. A method as claimed in claim 2 wherein the recovery of paraxylene comprises feeding the permeate back to the paraxylene separation process.
- 25
4. A method as claimed in any of claims 1 to 3 wherein the molecular sieve membrane unit further comprises isomerisation catalyst under isomerisation conditions.
- 30
5. A method as claimed in any one of claims 1 to 4 wherein at least a portion of said first stream is subjected to an isomerisation process in an isomerisation unit to produce an isomerate having an enriched
- 35



paraxylene content compared to that of first stream; and at least a portion of the isomerate is passed to the molecular sieve membrane unit.

- 5 6. A method as claimed in claim 1 wherein the permeate withdrawn from the molecular sieve membrane unit is enriched in paraxylene compared to the equilibrium concentration of paraxylene in a xylenes equilibrium mixture.
- 10 7. A method as claimed in claim 1 wherein the paraxylene recovery unit comprises a fractional crystallisation unit.
8. A method as claimed in claim 1 wherein the paraxylene recovery unit comprises an adsorption separation unit.
- 15 9. A method as claimed in claim 1 wherein the paraxylene recovery unit comprises an adsorption separation unit in combination with a fractional crystallisation unit.
- 20 10. A method as claimed in claim 1 wherein the molecular sieve membrane unit isomerises metaxylene and orthoxylene to paraxylene.
11. A method as claimed in claim 1 wherein the molecular sieve membrane unit converts ethylbenzene to benzene and/or xylenes and/or C₁₀ aromatics.
- 25 12. A method as claimed in claim 1 wherein the molecular sieve membrane unit comprises a molecular sieve membrane which is active as an isomerisation catalyst.
- 30 13. A method as claimed in any of claims 1 to 12 wherein the hydrocarbon stream comprises predominately C₈ aromatics.
14. A method as claimed in any of claims 5 to 13 wherein the hydrocarbon feed is additionally or alternatively introduced to the process directly to the isomerisation unit, directly to the molecular sieve membrane unit or both.
- 35



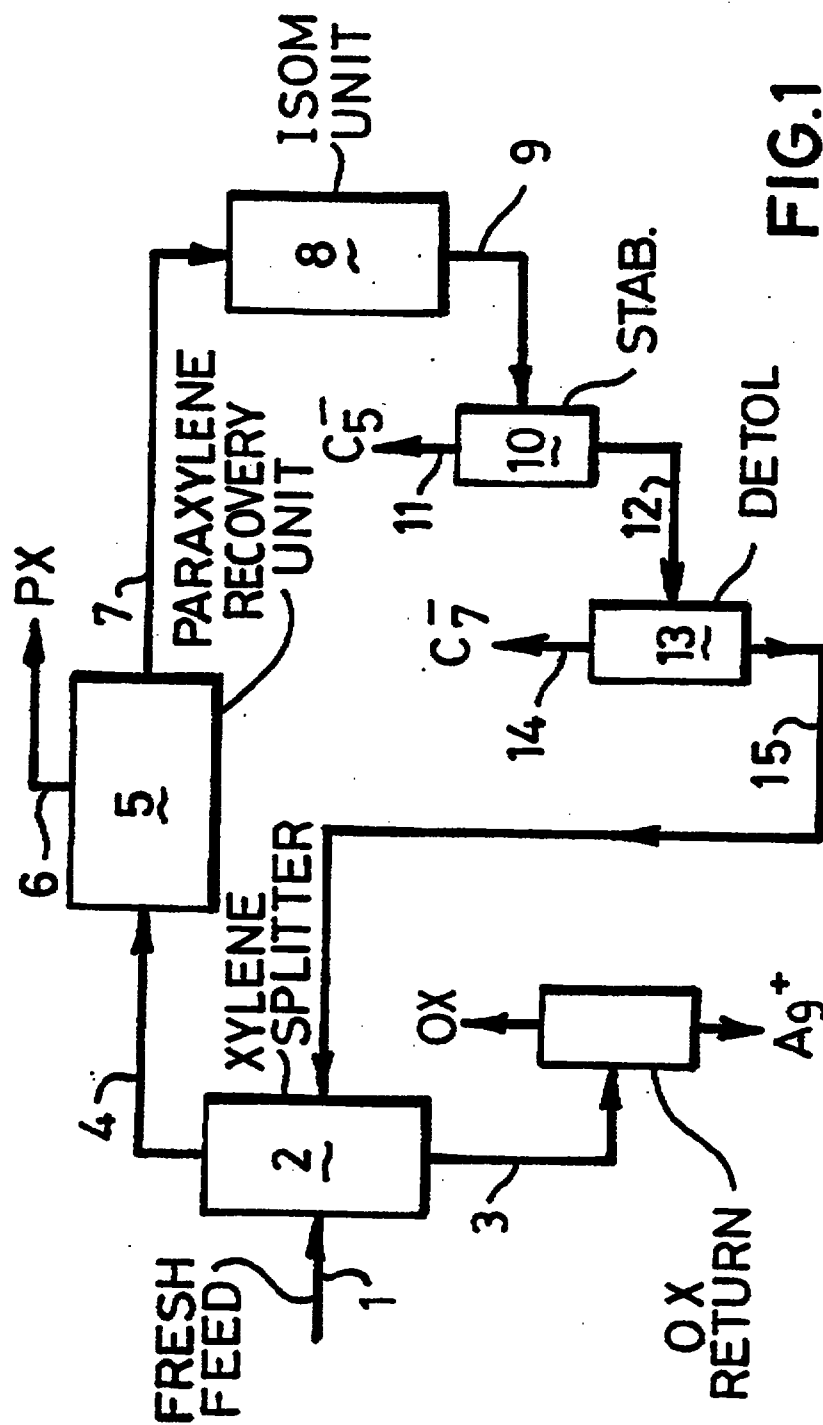


15. A method as claimed in any of claims 1 to 14 wherein there are two or more molecular sieve membrane units with or without isomerisation catalyst arranged sequentially to each other.
- 5
16. A method as claimed in any of claims 1 to 15 wherein the molecular sieve membrane is a zeolite membrane.
17. A plant for processing hydrocarbon streams comprising paraxylene which plant comprises:
- 10
- (a) a paraxylene separation unit , and
- (b) a molecular sieve membrane unit comprising a molecular sieve membrane.
- 15
18. A plant as claimed in claim 17 which further comprises an isomerisation unit.
19. A plant as claimed in claim 17 or 18 which comprises a zeolite membrane which has been prepared by either the LAI-ISC, S-LAI-ISC or GEL-LAI-ISC processes.
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THIS SHEET HAS BEEN
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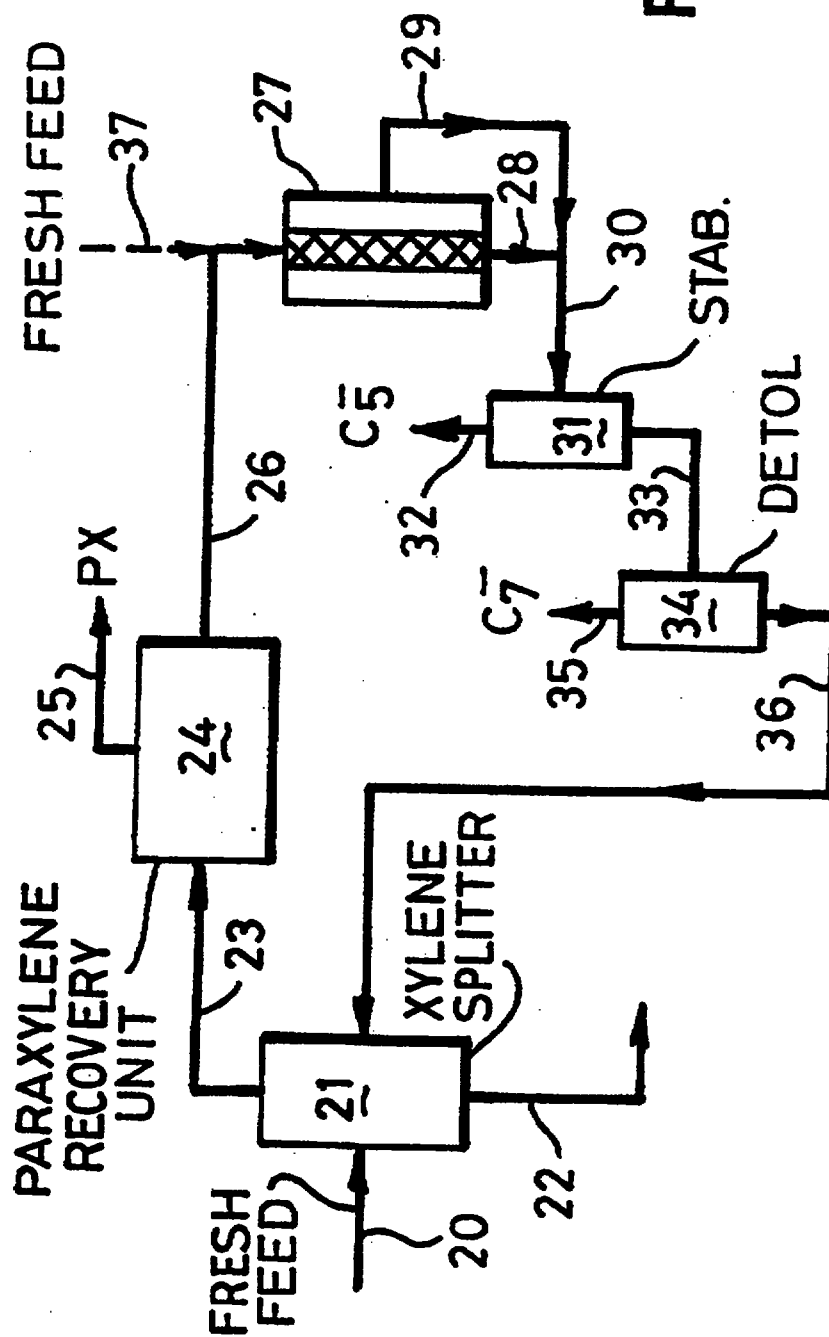
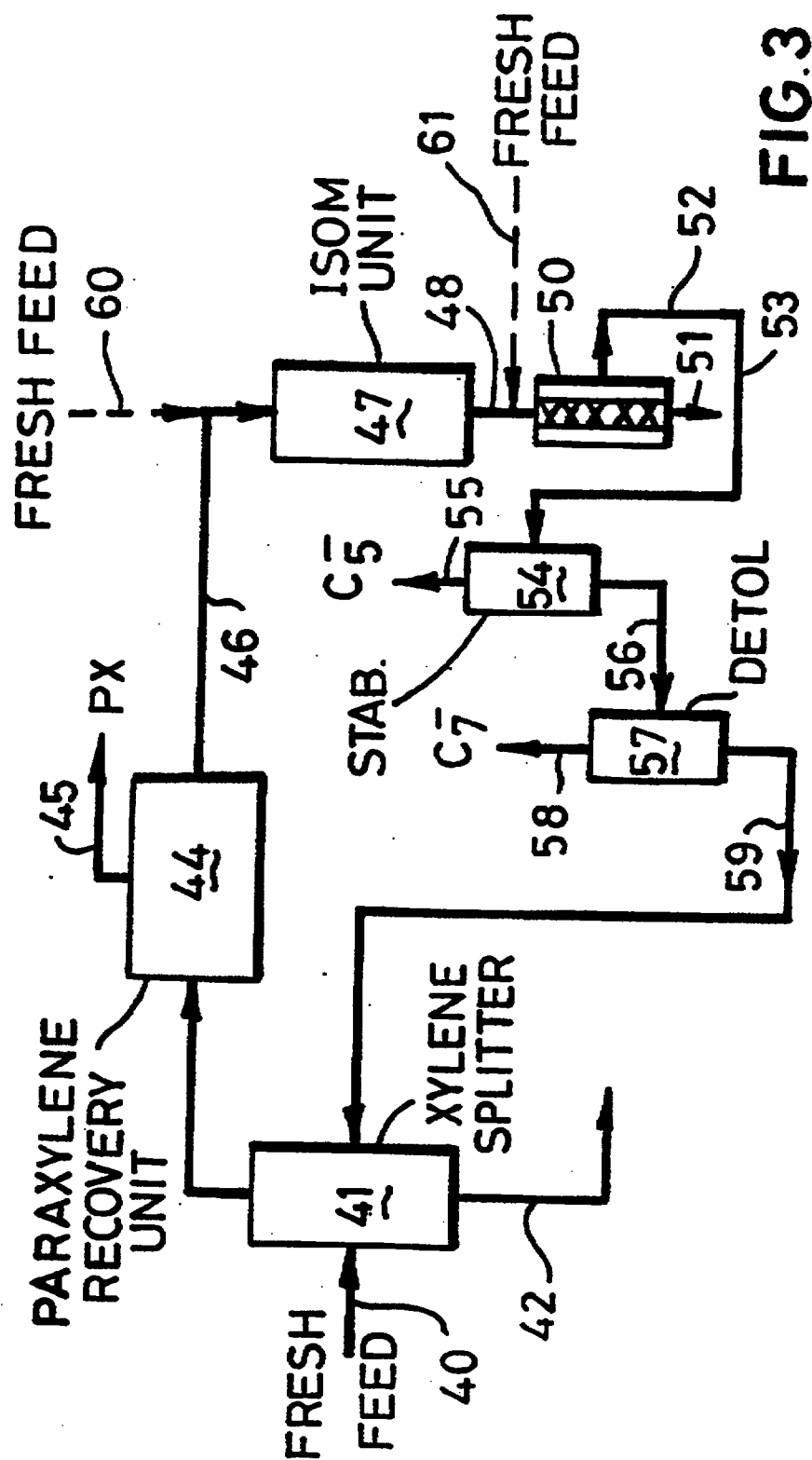


FIG.2



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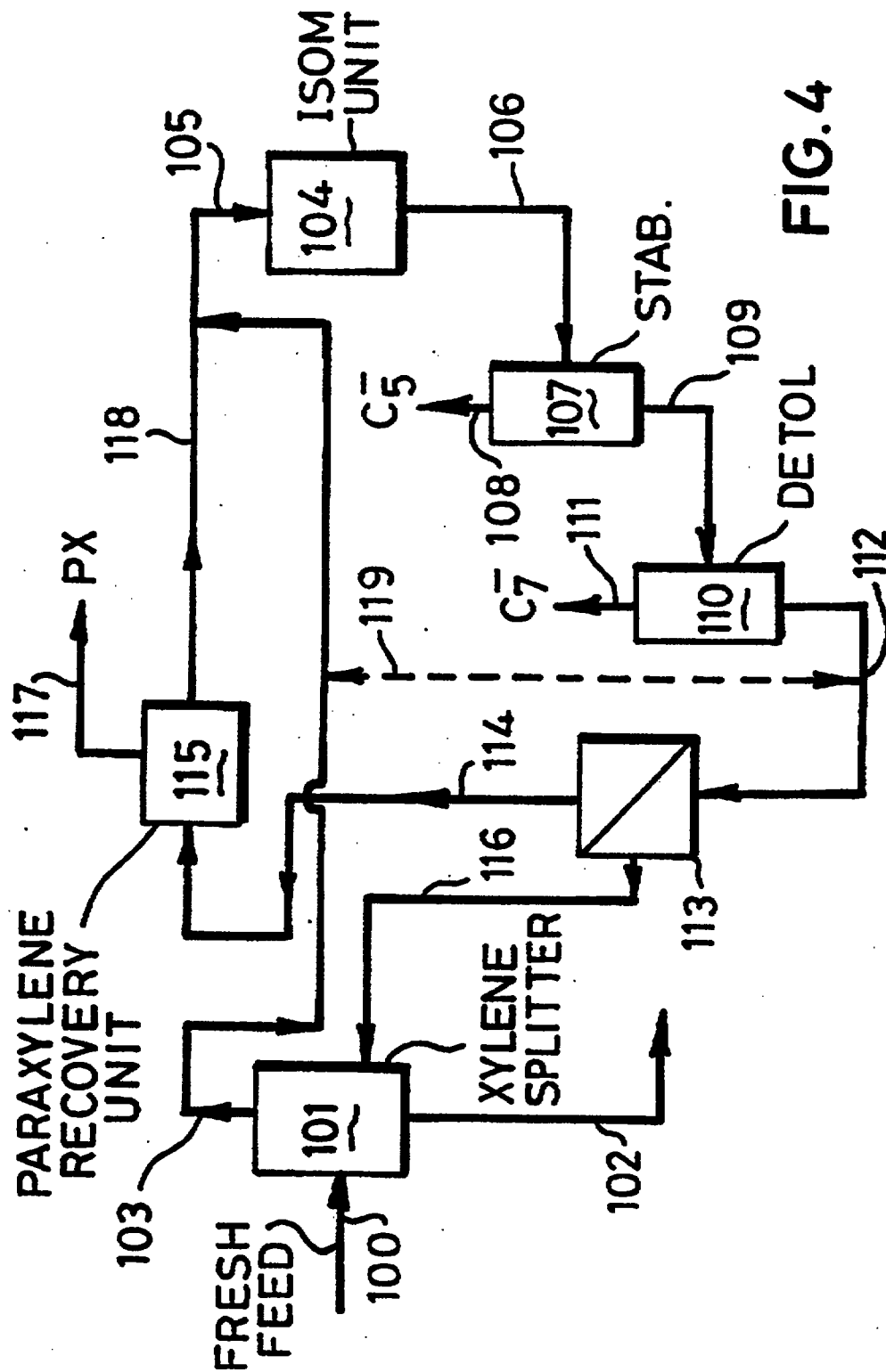


FIG. 4

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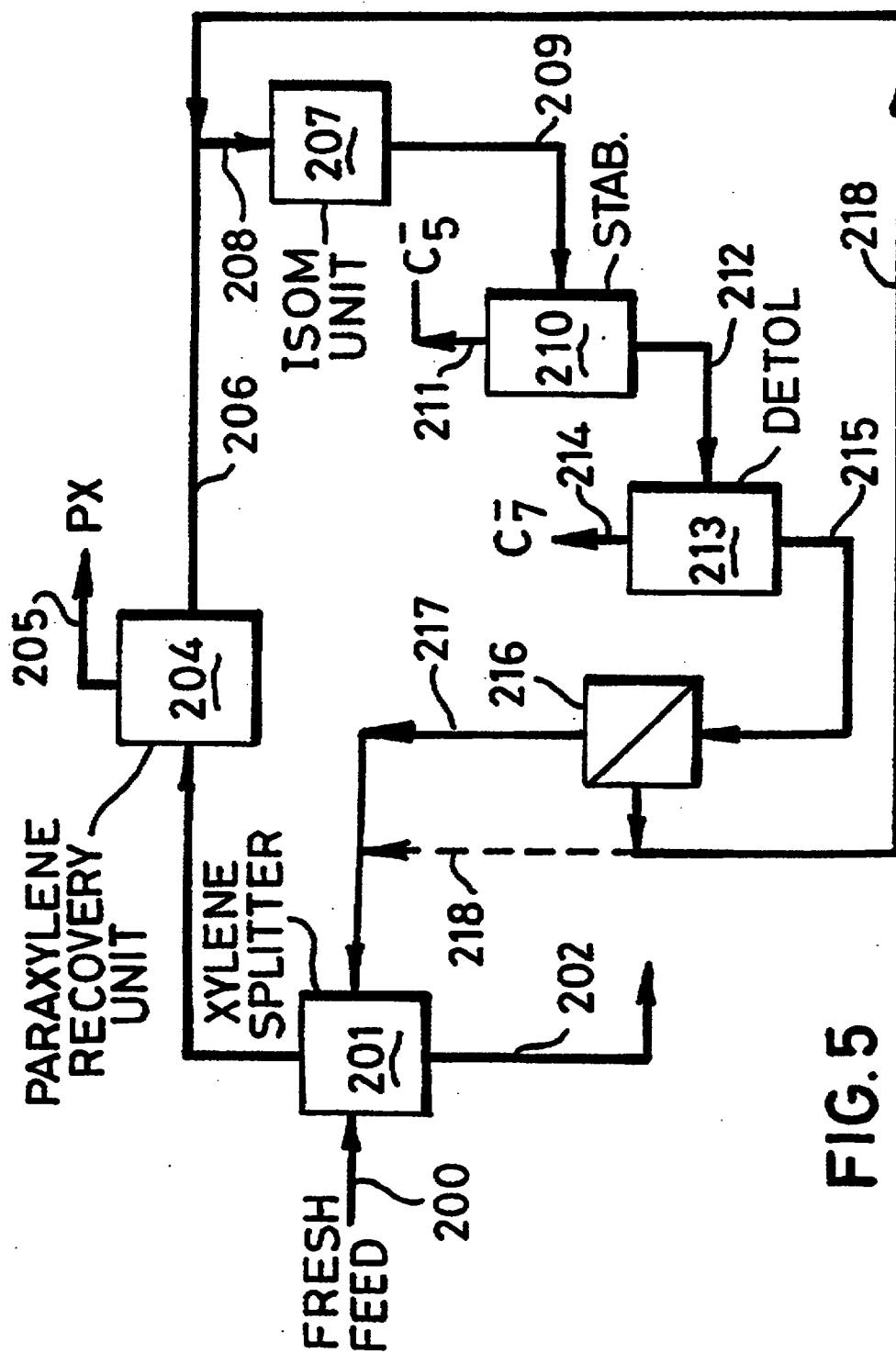
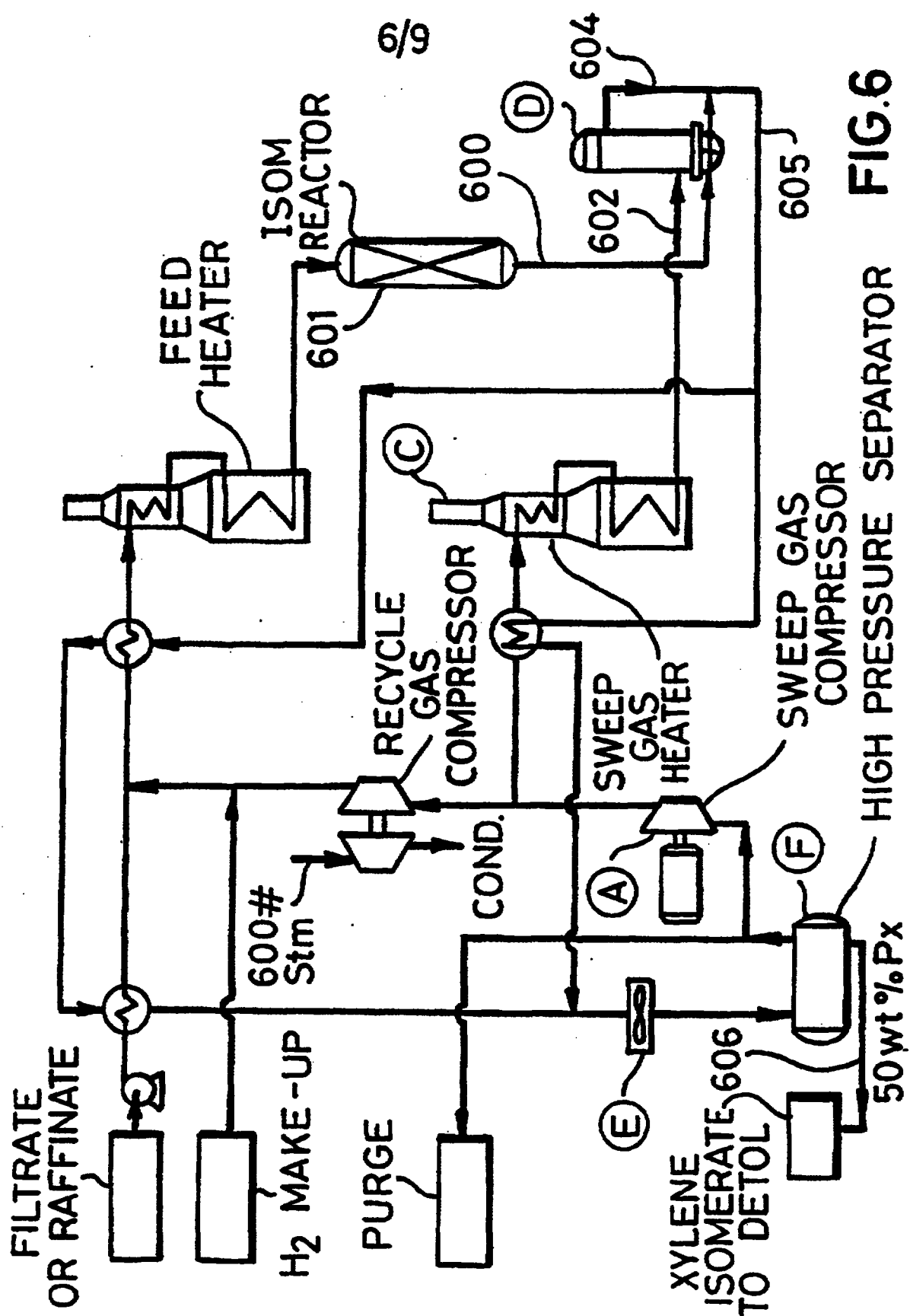
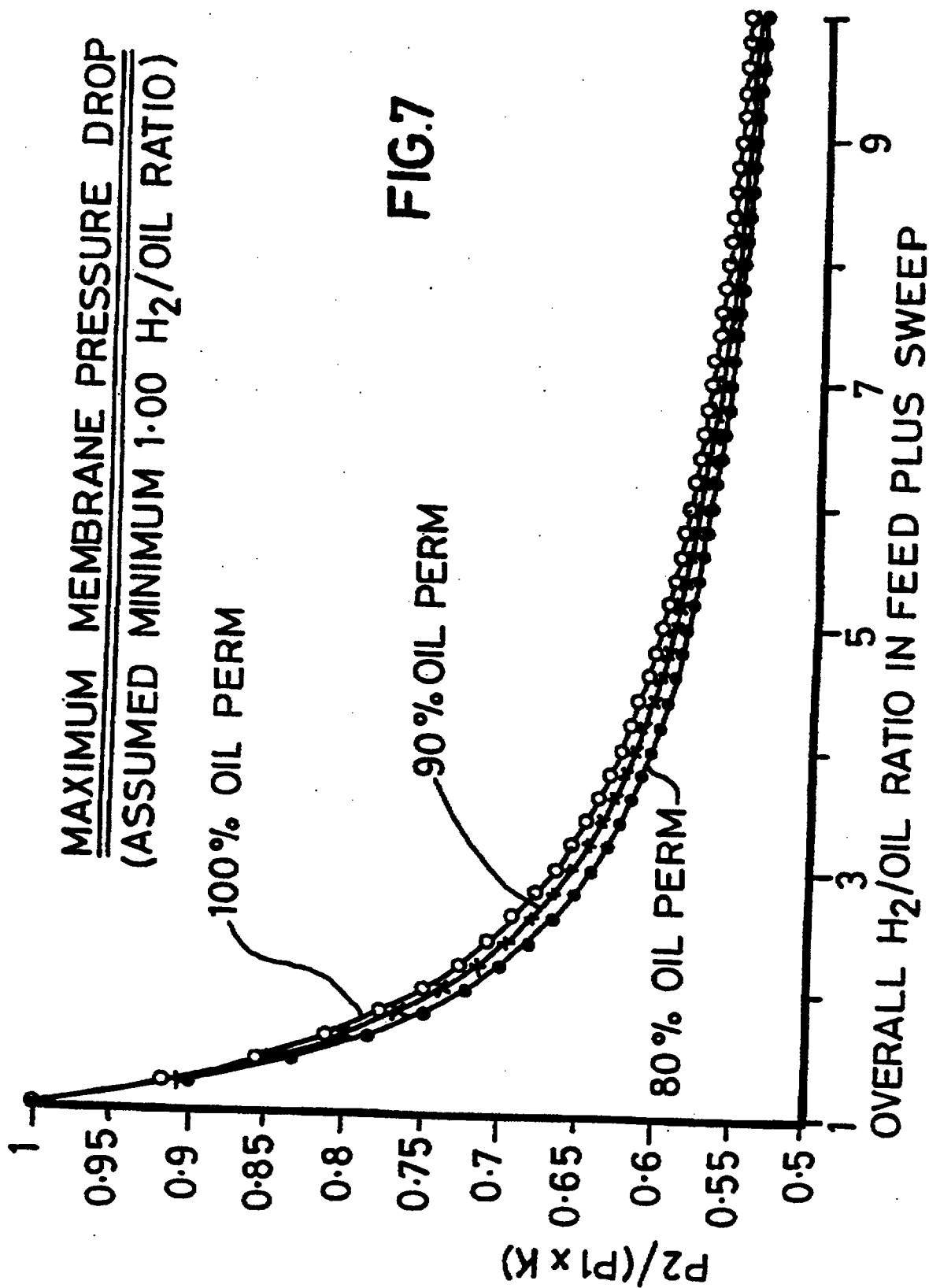
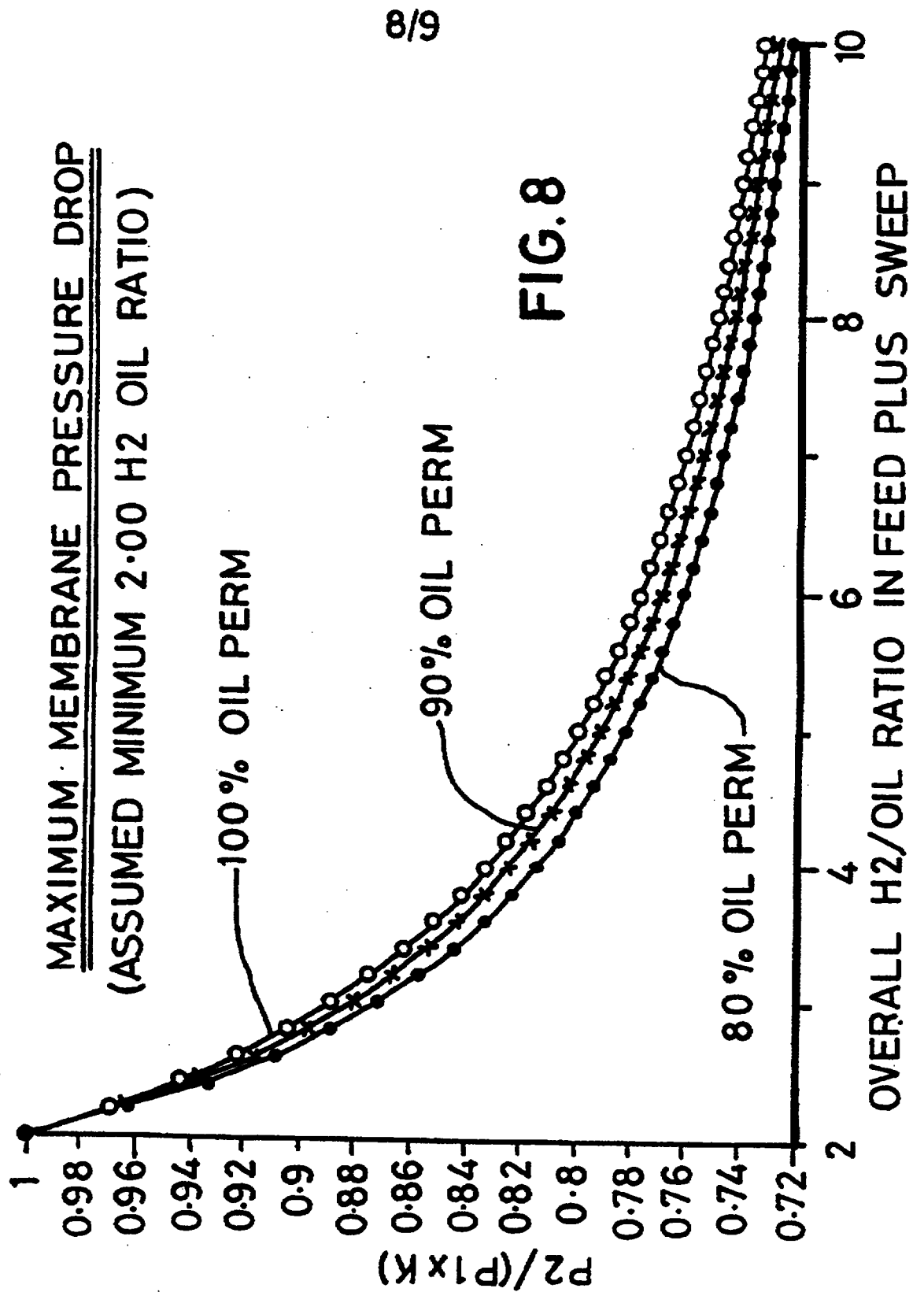


FIG. 5



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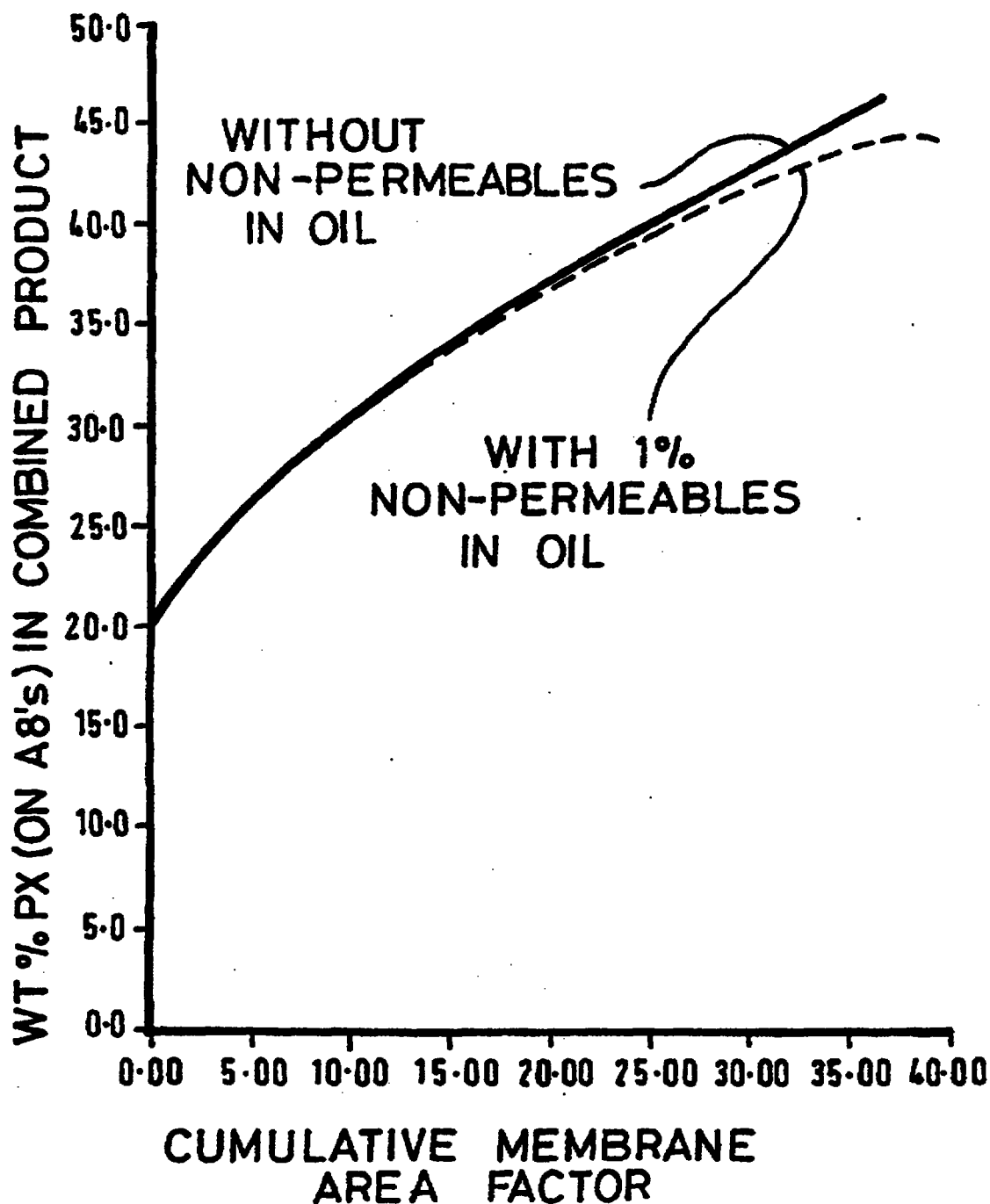




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FIG.9

MEMBRANE XYLENES ISOM (P1/P2=200/132)
3:1 OVERALL H₂/OIL WITH
1/3 H₂ AS SWEEP



AMENDED SHEET

16. A method as claimed in any of claims 1 to 15 wherein the molecular sieve membrane is a zeolite membrane.

17. A plant for processing hydrocarbon streams comprising paraxylene which plant comprises:

(a) a paraxylene separation unit (44), and

(b) a molecular sieve membrane unit (50) comprising a molecular sieve membrane.

18. A plant as claimed in claim 17 which further comprises an isomerisation unit (47).

19 A plant as claimed in claim 17 or 18 which comprises a zeolite membrane which has been prepared by either the LAI-ISC, S-LAI-ISC or GEL-LAI-ISC processes.



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(21) International Application Number: PCT/EP97/00316 (22) International Filing Date: 22 January 1997 (22.01.97) (30) Priority Data: 591,064 25 January 1996 (25.01.96) US (71) Applicants (for all designated States except US): EXXON CHEMICAL LIMITED [GB/GB]; 4600 Parkway, P.O. Box 122, Farham, Hants PO15 7AP (GB). EXXON CHEMICAL PATENTS INC. [US/US]; 1900 East Linden Avenue, Linden, NJ 07036 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): FERRARO, John, Michael [US/US]; 8641 Rainwood Avenue, Baton Rouge, LA 70810 (US). OU, John, Di-Yi [US/US]; 14643 Redwood Bend Trail, Houston, TX 77062 (US). OSMAN, Robert, Michael [US/US]; 15714 Pinewood Cove Drive, Houston, TX 77062 (US). COX, Graeme, Ian [AU/AU]; 18 Ravenswood Court, Doncaster East, VIC 3109 (AU). (74) Agents: WHITE, Nicholas, John et al.; Dibb Lupton Alsop, Fountain Precinct, Balm Green, Sheffield S1 1RZ (GB).		(81) Designated States: AU, BR, CA, CN, IL, JP, KR, MX, RU, SG, UA, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>

(54) Title: PROCESS FOR PRODUCTION OF PARAXYLENE**(57) Abstract**

A feedstream comprising C8 aromatic hydrocarbons is processed as follows: at least a portion of the paraxylene is recovered and the resulting stream, depleted in paraxylene, is passed through a molecular sieve membrane, producing a permeate enriched in paraxylene.