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(54) Title: CROSS-LINKED RUBBERY POLYURETHANE-ETHER MEMBRANES FOR SEPARATIONS

(57) Abstract: Cross-linked rubbery polyurethane-ether polymeric membranes are made from cross-linked rubbery polyurethane-ether polymers that are synthesized from a diisocyanate-terminated polyether and a tetrol with four hydroxyl functional groups. The hydroxyl groups on the tetrol react with the isocyanate groups on the diisocyanate-terminated polyether to form urethane bonds. The cross-linked rubbery polyurethane-ether polymeric membrane selectively permeate condensable vapors such as C3 to C35 hydrocarbons, aromatics, water vapor, carbon dioxide, and hydrogen sulfide and rejects methane and ethane. The cross-linked rubbery polyurethane-ether polymeric membrane have high permeance for condensable vapors, high selectivity for condensable vapors over methane and ethane, and high resistance to liquid chemicals.



WO 2015/065617 A1

CROSS-LINKED RUBBERY POLYURETHANE-ETHER
MEMBRANES FOR SEPARATIONS

PRIORITY CLAIM OF EARLIER NATIONAL APPLICATION

[0001] This application claims priority to U.S. Application No. 14/066,248 filed
5 October 29, 2013.

BACKGROUND OF THE INVENTION

[0002] In the past 30-35 years, the state of the art of polymer membrane-based gas separation processes has evolved rapidly. Membrane-based technologies have advantages of both low capital cost and high-energy efficiency compared to conventional separation
10 methods. Membrane gas separation is of special interest to petroleum producers and refiners, chemical companies, and industrial gas suppliers. Several applications have achieved commercial success, including carbon dioxide removal from natural gas and from biogas and enhanced oil recovery, and also in hydrogen removal from nitrogen, methane, and argon in ammonia purge gas streams.

15 [0003] However, it was demonstrated in practice that the membrane performance can deteriorate very quickly without the use of a pretreatment system. The major reason for the loss of membrane performance is heavy hydrocarbon liquid condensation on the membrane surface. Condensation can be prevented by providing a sufficient dew point margin for operation, based on the calculated dew point of the membrane product gas. UOP's
20 MemGuard™ system, a pretreatment regenerable adsorbent system that uses molecular sieves, was developed to remove water as well as heavy hydrocarbons ranging from C₆ to C₃₅ from the natural gas stream, hence, to lower the dew point of the stream. The selective removal of heavy hydrocarbons by a pretreatment system can significantly improve the performance of the membranes.

25 [0004] Although these pretreatment systems can effectively remove heavy hydrocarbons from natural gas streams to control the dew point of natural gas, the cost is very high. Some commercial membrane projects showed that the cost of the pretreatment system was as high as 10 to 40% of the total cost (pretreatment system and membrane system) depending on the feed composition. Reduction of the pretreatment system cost or total elimination of the
30 pretreatment system would significantly reduce the membrane system cost for natural gas

upgrading. On the other hand, in recent years, more and more membrane systems have been applied to large offshore natural gas upgrading projects. For offshore projects, the footprint is a big constraint. Hence, reduction of footprint is very important for offshore projects. The footprint of the pretreatment system is also very high at more than 10-50% of the footprint of the whole membrane system. Therefore, the removal of the pretreatment system from the membrane system will remarkably reduce the cost and footprint of the membrane system especially for offshore natural gas applications such as floating production storage and offloading vessel (FPSO) applications.

[0005] Conditioned natural gas has been used as fuel gas in gas engines and turbines in the hydrocarbon processing industry particularly for offshore platforms and remote locations and will be used in future floating liquefied natural gas (FLNG) and FPSO applications. To improve the reliability and reduce unscheduled downtime of the equipment that is used for fuel gas conditioning, a simple fuel gas conditioning technology is required. Rubbery polymeric membranes that can selectively and efficiently permeate heavy hydrocarbons and other contaminants such as CO₂, H₂S, and water vapor will allow conditioning of fuel gas.

[0006] A rubbery polymeric membrane that can selectively permeate condensable heavy hydrocarbon vapors such as C₃+ hydrocarbons and can reject non-condensable gases such as methane can also be used for natural gas liquid (NGL) recovery.

[0007] A legacy Grace rubbery polyurea/urethane membrane (S-Brane) has been used for aromatic/non-aromatic separations. However, the treating capacity (flux) is not high enough for most aromatic separation applications.

[0008] The present invention describes a new cross-linked rubbery polyurethane-ether polymeric membrane, a method of making the membrane, and the use of such a novel membrane.

SUMMARY OF THE INVENTION

[0009] The present invention involves a cross-linked rubbery polyurethane-ether polymeric membrane, a method of making the membrane, and the use of such a novel membrane system for NGL recovery, fuel gas conditioning, natural gas pre-treatment, sulfur removal from fluidized catalytic cracking (FCC) and other naphtha streams, as well as aromatic separations such as aromatic/n-paraffin separation and xylene separation.

[0010] The cross-linked rubbery polyurethane-ether polymeric membrane described in the current invention comprises a cross-linked rubbery polyurethane-ether polymer synthesized from a diisocyanate-terminated polyether and a rigid cross-linking agent comprising four or more hydroxyl functional groups. The use of the rigid cross-linking agent comprising four or more hydroxyl functional groups for the synthesis of cross-linked rubbery polyurethane-ether polymer in the present invention results in the formation of cross-linked polymer structure. The hydroxyl groups on the rigid cross-linking agent react with the isocyanate groups on the diisocyanate-terminated polyether to form urethane bonds.

[0011] The cross-linked rubbery polyurethane-ether polymeric membrane described in the current invention selectively permeates condensable vapors such as C₃ to C₃₅ hydrocarbons, aromatics, water vapor, carbon dioxide, and hydrogen sulfide and rejects methane and ethane. Fluid streams, including gases and liquids, can be treated for separation of higher hydrocarbons from natural gas. These membranes can also be used for separation of aromatic hydrocarbon streams. The cross-linked rubbery polyurethane-ether polymeric membrane described in the current invention has high permeance for condensable vapors, high selectivity for condensable vapors over methane and ethane, and high resistance to liquid chemicals.

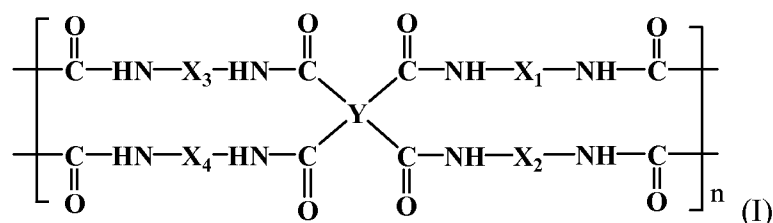
DETAILED DESCRIPTION OF THE INVENTION

[0012] The present invention involves a novel cross-linked rubbery polyurethane-ether polymeric membrane, a method of making the membrane, and the use of such a novel membrane system for NGL recovery, fuel gas conditioning, natural gas pre-treatment, sulfur removal from fluidized catalytic cracking (FCC) streams and other naphtha streams, as well as aromatic separations such as aromatic/n-paraffin separation and xylene separation.

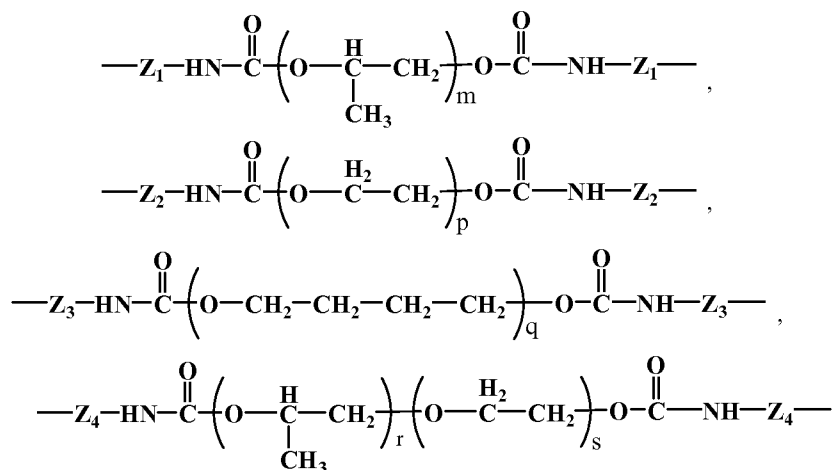
[0013] The cross-linked rubbery polyurethane-ether polymeric membrane described in the current invention comprises a cross-linked rubbery polyurethane-ether polymer synthesized from a diisocyanate-terminated polyether and a rigid cross-linking agent comprising four or more hydroxyl functional groups. The use of the rigid cross-linking agent comprising four or more hydroxyl functional groups for the synthesis of cross-linked rubbery polyurethane-ether polymer in the present invention results in the formation of cross-linked polymer structure. The hydroxyl groups on the rigid cross-linking agent react with the isocyanate groups on the diisocyanate-terminated polyether to form urethane bonds.

[0014] The cross-linked rubbery polyurethane-ether polymeric membrane described in the current invention selectively permeates condensable vapors such as C₃ to C₃₅ hydrocarbons, aromatics, water vapor, carbon dioxide, and hydrogen sulfide and rejects methane and ethane. The cross-linked rubbery polyurethane-ether polymeric membrane described in the current invention has high permeance for condensable vapors, high selectivity for condensable vapors over methane and ethane, and high resistance to liquid chemicals.

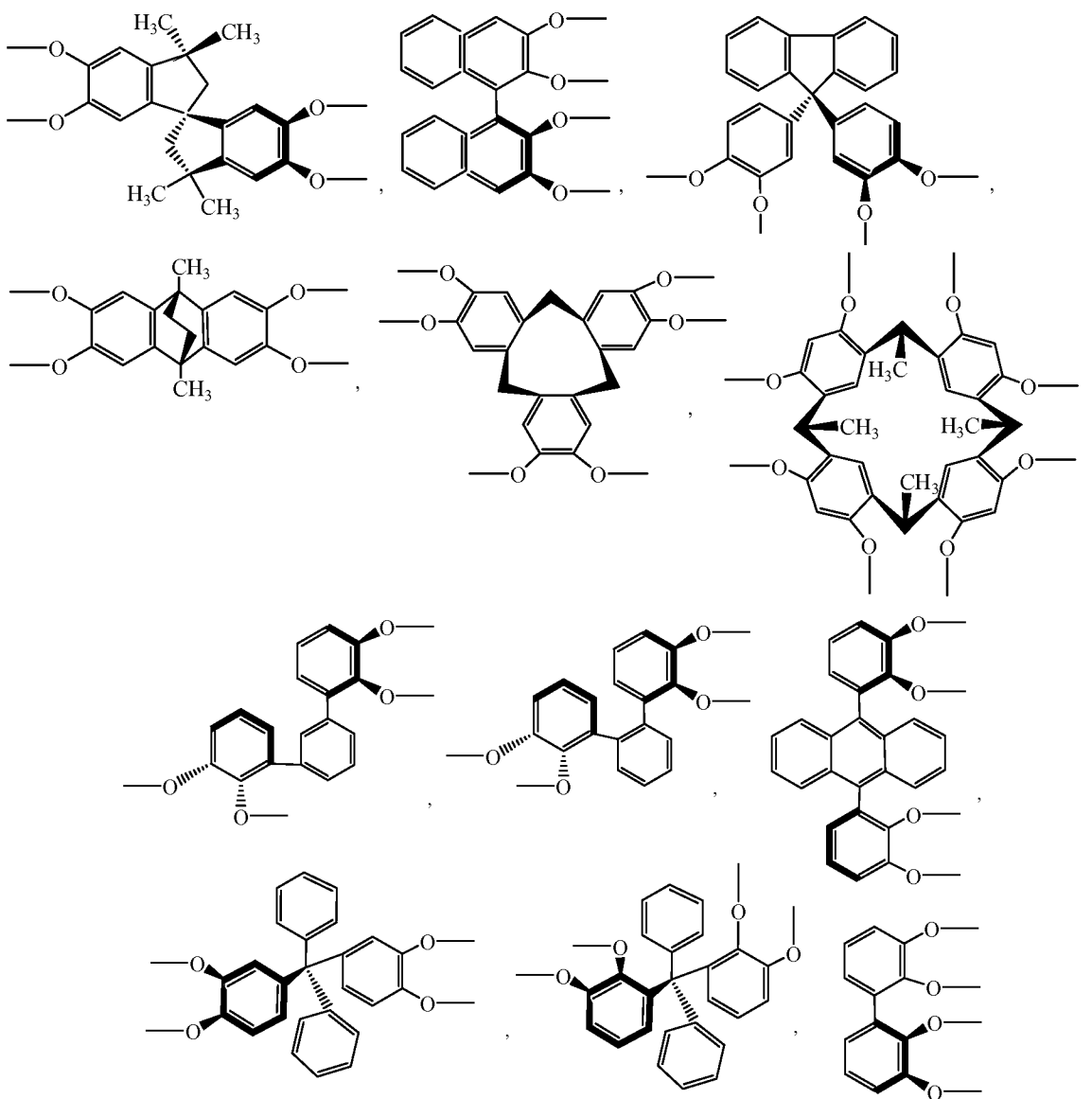
[0015] The cross-linked rubbery polyurethane-ether polymeric membrane described in the current invention comprises a cross-linked rubbery polyurethane-ether polymer with a plurality of repeating units of a formula (I), wherein said formula (I) is:



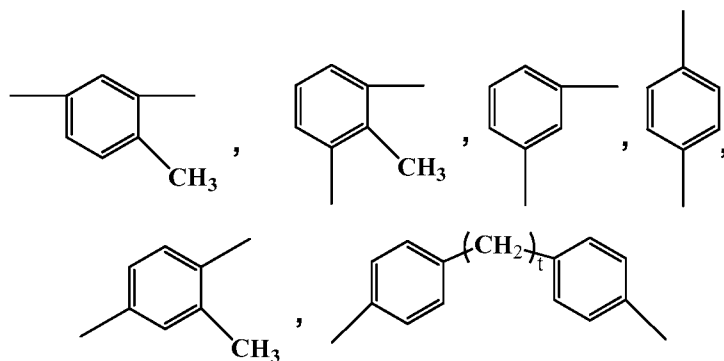
wherein X₁, X₂, X₃, and X₄ are selected from the group consisting of



and mixtures thereof, respectively; X₁, X₂, X₃, and X₄ are the same or different from each other; wherein Y is selected from the group consisting of

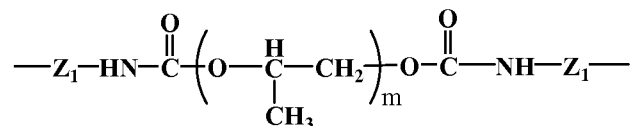


and mixtures thereof; wherein Z_1 , Z_2 , Z_3 , and Z_4 are selected from the group consisting of

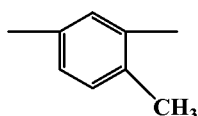


- 5 and mixtures thereof, respectively; Z_1 , Z_2 , Z_3 , and Z_4 are the same or different from each other and t is 0 to 4; wherein n , m , p , q , r , and s are independent integers from 2 to 500.

It is preferred that X_1 , X_2 , X_3 , and X_4 of formula (I) are the same and have the chemical structure of:

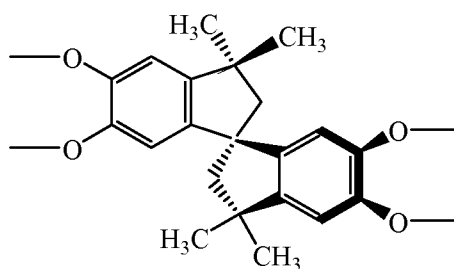


It is preferred that Z_1 of X_1 , X_2 , X_3 , and X_4 of formula (I) is:



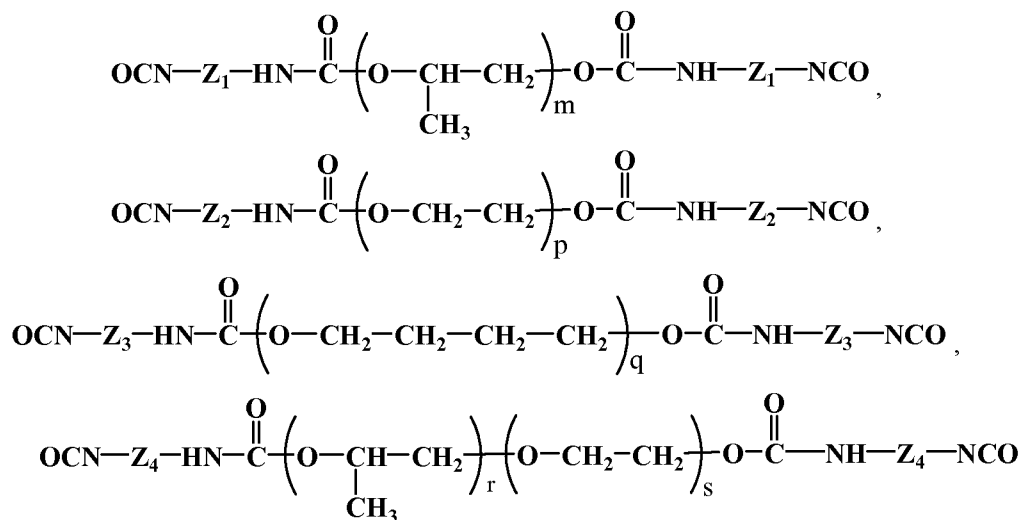
5

It is preferred that Y of formula (I) is:

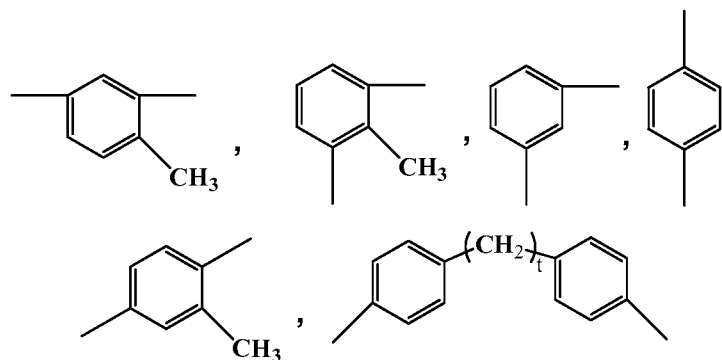


[0016] The cross-linked rubbery polyurethane-ether membrane in the present invention is prepared by: 1) dissolving a diisocyanate-terminated polyether and a rigid cross-linking agent comprising four or more hydroxyl functional groups in a solvent to form a homogeneous solution; 2) heating the solution at a temperature of 30° to 100°C for 0.5 to 12 hours to form a polyurethane-ether prepolymer; 3) Coating a layer of the polyurethane-ether prepolymer solution on a relatively porous membrane support (e.g., a support made from inorganic ceramic material or a support made from a polymer); 4) heating the coated membrane at a temperature of 30° to 100°C for 0.5 to 12 hours to provide a thin selective layer comprising the cross-linked rubbery polyurethane-ether material on the membrane support. In some cases, a second layer of the cross-linked rubbery polyurethane-ether is added after step 4) by repeating steps 3) and 4).

[0017] The diisocyanate-terminated polyether used for the synthesis of the cross-linked rubbery polyurethane-ether polymer in the current invention is selected from the group consisting of

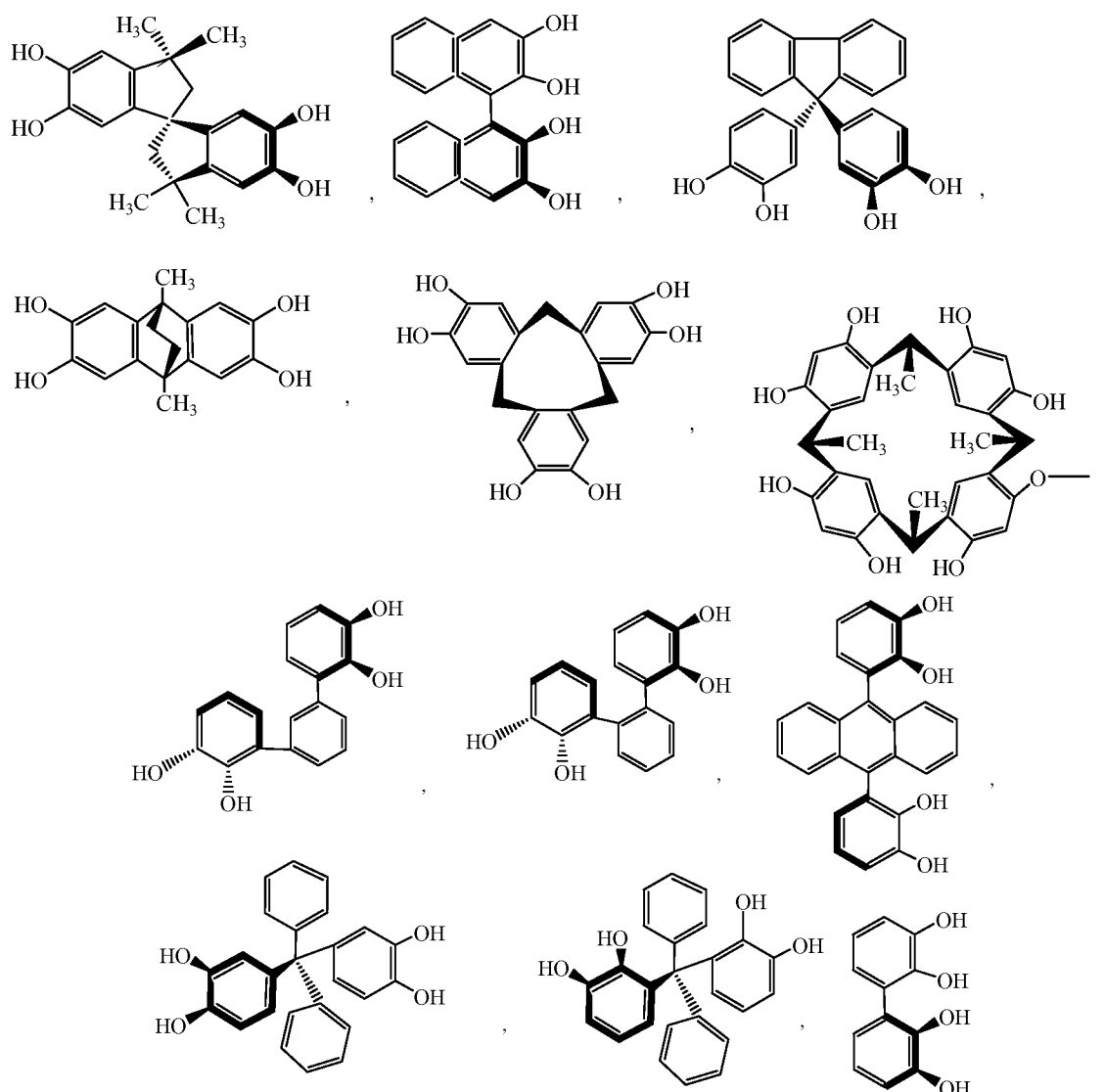


5 and mixtures thereof; wherein Z_1 , Z_2 , Z_3 , and Z_4 are selected from the group consisting of



and mixtures thereof, respectively; Z_1 , Z_2 , Z_3 , and Z_4 are the same or different from each other and t is 0 to 4; wherein m , p , q , r , and s are independent integers from 2 to 500.

10 [0018] The rigid cross-linking agent comprising four or more hydroxyl functional groups used for the synthesis of the cross-linked rubbery polyurethane-ether polymer in the current invention is selected from the group consisting of



and mixtures thereof.

[0019] The solvents used for dissolving the diisocyanate-terminated polyether and the
 5 rigid cross-linking agent comprising four or more hydroxyl functional groups are chosen
 primarily for their ability to completely dissolve the diisocyanate-terminated polyether and
 the rigid cross-linking agent comprising four or more hydroxyl functional groups and for ease
 of solvent removal in the membrane formation steps. Other considerations in the selection of
 solvents include low toxicity, low corrosive activity, low environmental hazard potential,
 10 availability and cost. Representative solvents for use in this invention include, but are not
 limited to, N-methylpyrrolidone (NMP), N,N-dimethyl acetamide (DMAC), methylene
 chloride, tetrahydrofuran (THF), acetone, N,N-dimethylformamide (DMF), dimethyl
 sulfoxide (DMSO), toluene, dioxanes, 1,3-dioxolane, mixtures thereof, and mixtures thereof.
 Other solvents as known to those skilled in the art may also be used.

[0020] The cross-linked rubbery polyurethane-ether membrane in the present invention can be fabricated into any convenient form such as sheet, disk, tube, or hollow fiber. These cross-linked rubbery polyurethane-ether membranes can also be fabricated into thin film composite membranes incorporating a selective thin cross-linked rubbery polyurethane-ether layer and a porous supporting layer comprising a polymer material or an inorganic material.

[0021] The present invention involves the use of a novel membrane system for natural gas upgrading. This membrane system includes a first-stage cross-linked rubbery polyurethane-ether polymeric membrane described in the present invention to selectively remove hydrocarbons from C_3 to C_{35} to control the dew point of natural gas, and a second-stage membrane to selectively remove CO_2 from natural gas. The new membrane system described in the current invention eliminates the use of high cost and high footprint membrane pretreatment systems. The membrane system described in the current invention does not require an inter-stage compressor. This is because the natural gas with controlled dew point comes out from the retentate side of the first cross-linked rubbery polyurethane-ether polymeric membrane at high pressure and is directly introduced to the second membrane as a high pressure feed. Therefore, the membrane system significantly reduces the footprint and cost of the membrane system for natural gas upgrading compared to the current commercially available membrane systems that include a non-membrane-related pretreatment system. The membranes most commonly used for commercial natural gas upgrading applications such as cellulose acetate and polyimide are glassy polymers. These membranes, however, cannot be used to control the dew point of natural gas because they are more selectively permeable for CH_4 than for hydrocarbons from C_3 to C_{35} . Pretreatment system is necessary when using these commercial glassy polymer membranes for natural gas upgrading. The membrane used as the second-stage membrane in the new membrane system described in the current invention has higher CO_2/CH_4 selectivity than the first-stage cross-linked rubbery polyurethane-ether polymeric membrane described in the present invention for natural gas upgrading. Preferably the membrane materials for the second-stage membrane in the new membrane system described in the current invention have CO_2/CH_4 selectivity of 10 or higher at $50^\circ C$ under 6.89 MPa (1000 psig) feed gas pressure and with 10% CO_2 and 90% CH_4 in the feed gas. The membrane materials for the second-stage membrane in the new membrane system described in the current invention can be selected from, but is not limited to, polyacrylonitrile, polysulfones; sulfonated polysulfones; polyetherimides such as Ultem;

cellulosic polymers, such as cellulose acetate and cellulose triacetate; polyamides; polyimides such as Matrimid and P84 or P84HT; polyamide/imides; polyketones, polyether ketones; poly(arylene oxides) such as poly(phenylene oxide) and poly(xylene oxide); poly(esteramide-diisocyanate); polyurethanes; polyesters (including polyarylates), such as poly(ethylene terephthalate), poly(alkyl methacrylates), poly(acrylates), and poly(phenylene terephthalate); polysulfides; polymers from monomers having alpha-olefinic unsaturation in addition to those polymers previously listed including poly(ethylene), poly(propylene), poly(butene-1), poly(4-methyl pentene-1), polyvinyls, e.g., poly(vinyl chloride), poly(vinyl fluoride), poly(vinylidene chloride), poly(vinylidene fluoride), poly(vinyl alcohol), poly(vinyl esters) such as poly(vinyl acetate) and poly(vinyl propionate), poly(vinyl pyridines), poly(vinyl pyrrolidones), poly(vinyl ethers), poly(vinyl ketones), poly(vinyl aldehydes) such as poly(vinyl formal) and poly(vinyl butyral), poly(vinyl amides), poly(vinyl amines), poly(vinyl urethanes), poly(vinyl ureas), poly(vinyl phosphates), and poly(vinyl sulfates); polyallyls; poly(benzobenzimidazole); polyhydrazides; polyoxadiazoles; polytriazoles; poly(benzimidazole); polycarbodiimides; polyphosphazines.

[0022] Some preferred polymers used for the preparation of the second-stage membrane in the new membrane system described in the current invention include, but are not limited to, polysulfones; sulfonated polysulfones; polyetherimides such as Ultem; cellulosic polymers such as cellulose acetate and cellulose triacetate; polyamides; polyimides such as P84 and poly(3,3',4,4'-benzophenone tetracarboxylic dianhydride-pyromellitic dianhydride-3,3',5,5'-tetramethyl-4,4'-methylenedianiline) (poly(BTDA-PMDA-TMMDA)); polyamide/imides; polyketones; polyether ketones; and polyacrylonitrile.

[0023] The cross-linked rubbery polyurethane-ether polymeric membrane described in the current invention can also be used for NGL recovery from natural gas. The cross-linked rubbery polyurethane-ether polymeric membrane described in the current invention selectively permeates condensable vapors such as C₃ to C₃₅ hydrocarbons and aromatics, therefore, it can separate C₃+ hydrocarbons from methane and ethane to recover NGL.

[0024] The cross-linked rubbery polyurethane-ether polymeric membrane described in the current invention can also be used for fuel gas conditioning. Conditioning natural gas has been used as fuel gas in gas engines and turbines in the hydrocarbon processing industry particularly for offshore platforms and remote locations and FLNG and FPSO applications. The cross-linked rubbery polyurethane-ether polymeric membrane described in the

current invention has shown high permeance and high selectivity for C₃+ hydrocarbons over methane that will allow conditioning of fuel gas.

EXAMPLES

[0025] The following examples are provided to illustrate one or more preferred
5 embodiments of the invention, but are not limited embodiments thereof. Numerous variations can be made to the following examples that lie within the scope of the invention.

EXAMPLE 1

Preparation of cross-linked polyurethane-propylene glycerol membrane

[0026] 15.0 g of poly(propylene glycol) toluene 2,4-diisocyanate terminated was
10 dissolved in 30 g of anhydrous DMF solvent under stirring to form a homogeneous solution. 1.1 g of 3,3,3',3'-tetramethyl-1,1''-spirobisindane-5,5',6,6'-tetrol was added to the solution under stirring. The solution was mixed for 1 hour at 60°C to form a homogeneous solution. The solution was degassed for 1 hour and then cast onto the surface of a clean glass plate. The DMF solvent was evaporated at 50°C for 12 hours. The resulting membrane was
15 detached from the glass plate and further dried at 120°C for 24 hours in vacuum to form cross-linked polyurethane-propylene glycerol dense film membrane.

EXAMPLE 2

Evaluation of separation performance of cross-linked polyurethane-propylene glycerol membrane

[0027] The following Table shows the pure-gas permeabilities and selectivities of the
20 cross-linked polyurethane-propylene glycerol membrane. The permeabilities (P_A) and selectivities ($\alpha_{A/B}$) of the cross-linked polyurethane-propylene glycerol membrane for CH₄, CO₂, propane (C₃H₈), and n-butane (n-C₄H₁₀) were measured by pure gas measurements at 50°C. It can be seen from the Table that the cross-linked polyurethane-propylene glycerol
25 membrane has >200 Barrers of CO₂ permeability, which is much higher than traditional polymer membranes such as CA, Matrimid polyimide, and Ultem polyetherimide membranes. Different from these traditional polymer membranes which are more permeable to small gases, such as CH₄, than to large, condensable organic vapors, such as C₃H₈ and n-

C₄H₁₀, the results in the Table have shown that the cross-linked polyurethane-propylene glycerol membrane is much more permeable to large, condensable organic vapors, such as C₃H₈ and n-C₄H₁₀, than to small, permanent gases, such as CH₄. Therefore, the cross-linked polyurethane-propylene glycerol membrane can be used to selectively remove water and hydrocarbons from C₃ to C₃₅ to control the dew point of natural gas for natural gas processing. The high pressure retentate from the cross-linked polyurethane-propylene glycerol membrane mainly comprises CH₄, CO₂, and trace amount of ethane and propane, and some other components.

TABLE
Pure-Gas Permeation Test Results of Cross-Linked
Polyurethane-Propylene Glycerol Membrane

Gas	Permeability (Barrer)	Selectivity (gas/CH ₄)
CH ₄ ^a	33.7	---
CO ₂ ^a	222.1	6.5
Propane (C ₃ H ₈) ^a	205.5	6.1
n-butane (n-C ₄ H ₁₀) ^b	343.3	10.2

^a Tested at 50°C and 791 kPa (100 psig);

^b Tested at 50°C and 170 kPa (10 psig);

1 Barrer = 10⁻¹⁰ cm³(STP).cm/cm².sec.cmHg.

EXAMPLE 3

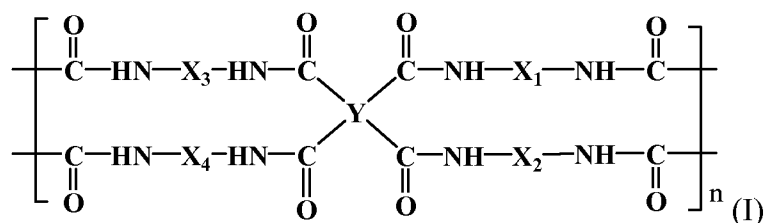
Preparation of cross-linked polyurethane-propylene glycerol thin film composite membrane

[0028] 6.0 g of poly(propylene glycol) toluene 2,4-diisocyanate terminated was dissolved in 155 g of 1,3-dioxolane solvent under stirring to form a homogeneous solution. 0.44 g of 3,3,3',3'-tetramethyl-1,1''-spirobisindane-5,5',6,6'-tetrol was added to the solution under stirring. The solution was mixed for 1 h at 60°C to form a homogeneous solution. The solution was degassed for 1 h. The resulting solution was coated onto the surface of a porous polyacrylonitrile (PAN) ultrafiltration membrane substrate via dip coating or knife casting. The solvent was evaporated to form a continuous film. The polyurethane-propylene glycerol thin film composite membrane was then heated at 100°C for 1 h in an oven to form the cross-linked polyurethane-propylene glycerol/PAN thin film composite membrane.

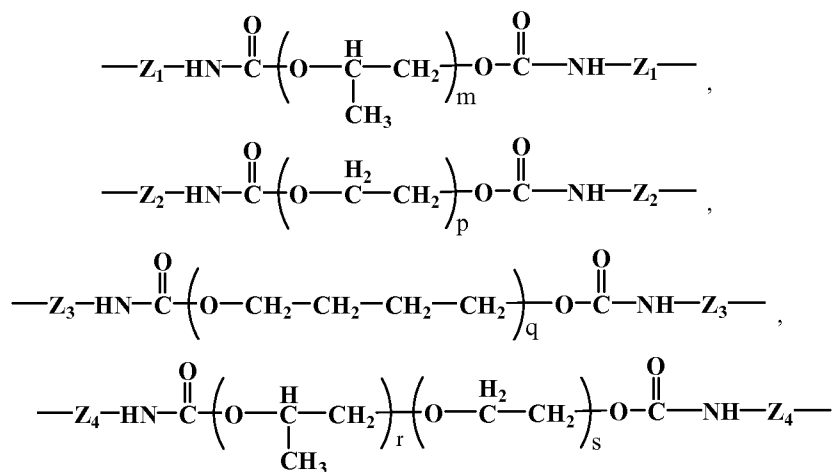
SPECIFIC EMBODIMENTS

[0029] While the following is described in conjunction with specific embodiments, it will be understood that this description is intended to illustrate and not limit the scope of the preceding description and the appended claims.

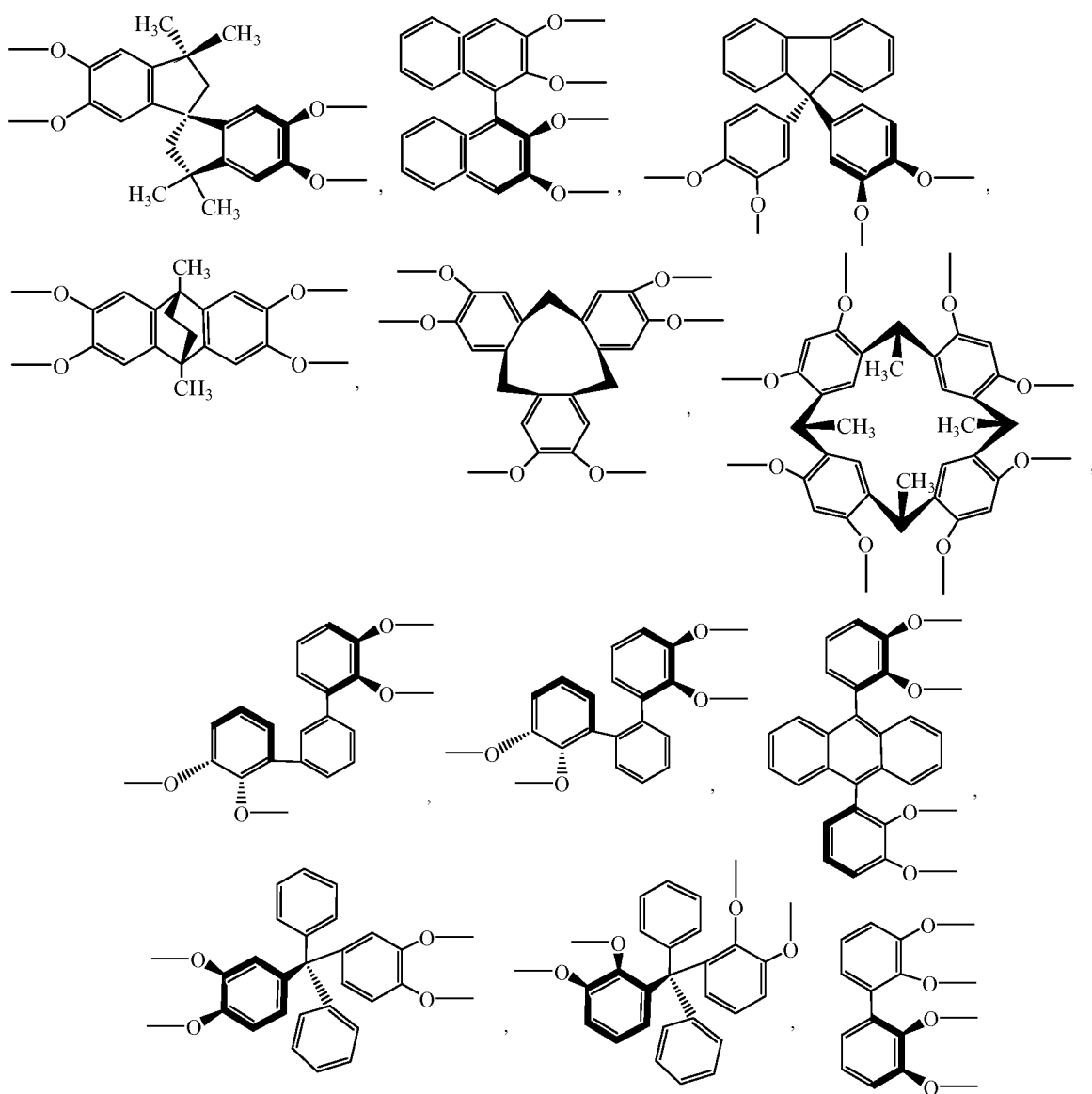
- 5 [0030] In a first embodiment, the invention involves a cross-linked rubbery polyurethane-ether polymeric membrane comprising a cross-linked rubbery polyurethane-ether polymer with a plurality of repeating units of a formula (I), wherein formula (I) is represented by a structure comprising:



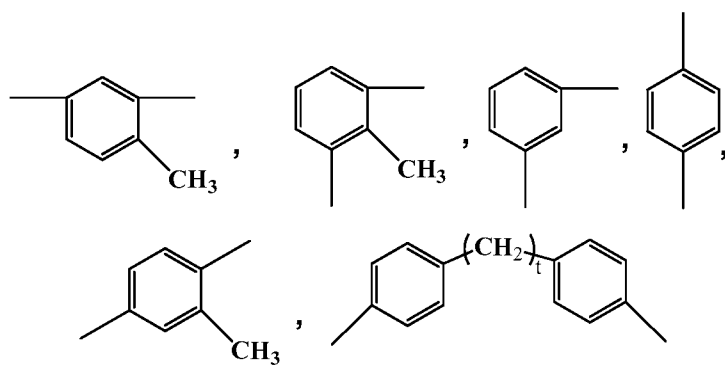
- 10 wherein X₁, X₂, X₃, and X₄ are selected from the group consisting of



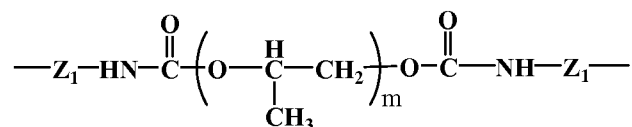
and mixtures thereof, respectively; X₁, X₂, X₃, and X₄ are the same or different from each other; wherein Y is selected from the group consisting of



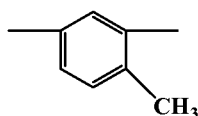
and mixtures thereof; wherein Z_1 , Z_2 , Z_3 , and Z_4 are selected from the group consisting of



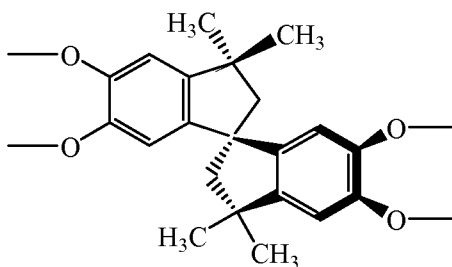
and mixtures thereof, respectively; Z_1 , Z_2 , Z_3 , and Z_4 are the same or different from each other and t is 0 to 4; and wherein n , m , p , q , r , and s are independent integers from 2 to 500. X_1 , X_2 , X_3 , and X_4 of formula (I) may be the same and have a chemical structure comprising:



5 Z_1 of X_1 , X_2 , X_3 , and X_4 of formula (I) may be represented by



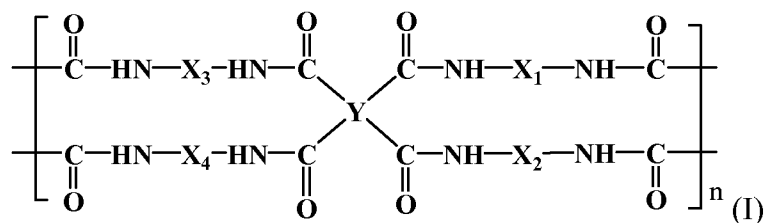
Y of formula (I) may be



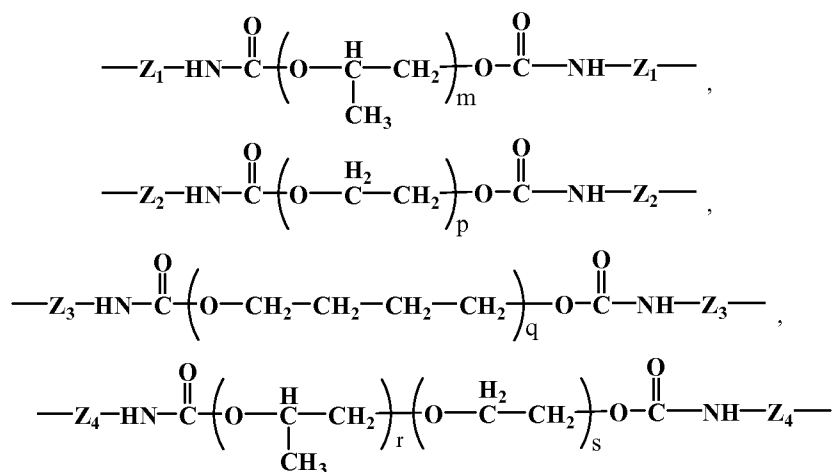
[0031] In a second embodiment, the invention involves a process of making a cross-linked rubbery polyurethane-ether membrane comprising dissolving a diisocyanate-terminated polyether and a rigid cross-linking agent comprising four or more hydroxyl functional groups in a solvent to form a homogeneous solution; 2) then heating the homogenous solution at a temperature of 30° to 100°C for 0.5 to 12 hours to form a polyurethane-ether prepolymer solution; 3) coating a layer of the polyurethane-ether prepolymer solution on a porous membrane support; and 4) heating the coated membrane at a temperature of 30° to 100°C for 0.5 to 12 hours to provide a thin selective layer comprising a cross-linked rubbery polyurethane-ether material on the porous membrane support. The porous membrane support prepared in the process may comprise an inorganic ceramic material or a polymer. There may be at least one additional layer of the cross-linked rubbery polyurethane-ether material added to the porous membrane support. The cross-linked rubbery polyurethane-ether membrane may be fabricated into an appropriate configuration such as a

sheet, disk, tube or hollow fiber. The cross-linked rubbery polyurethane-ether membranes may also be fabricated into a thin film composite membrane incorporating a selective thin cross-linked rubbery polyurethane-ether layer and a porous supporting layer comprising a polymer material or an inorganic material. In the process, the cross-linked rubbery

- 5 polyurethane-ether polymeric membrane comprises a cross-linked rubbery polyurethane-ether polymer with a plurality of repeating units of a formula (I), wherein said formula (I) is represented by a structure comprising:

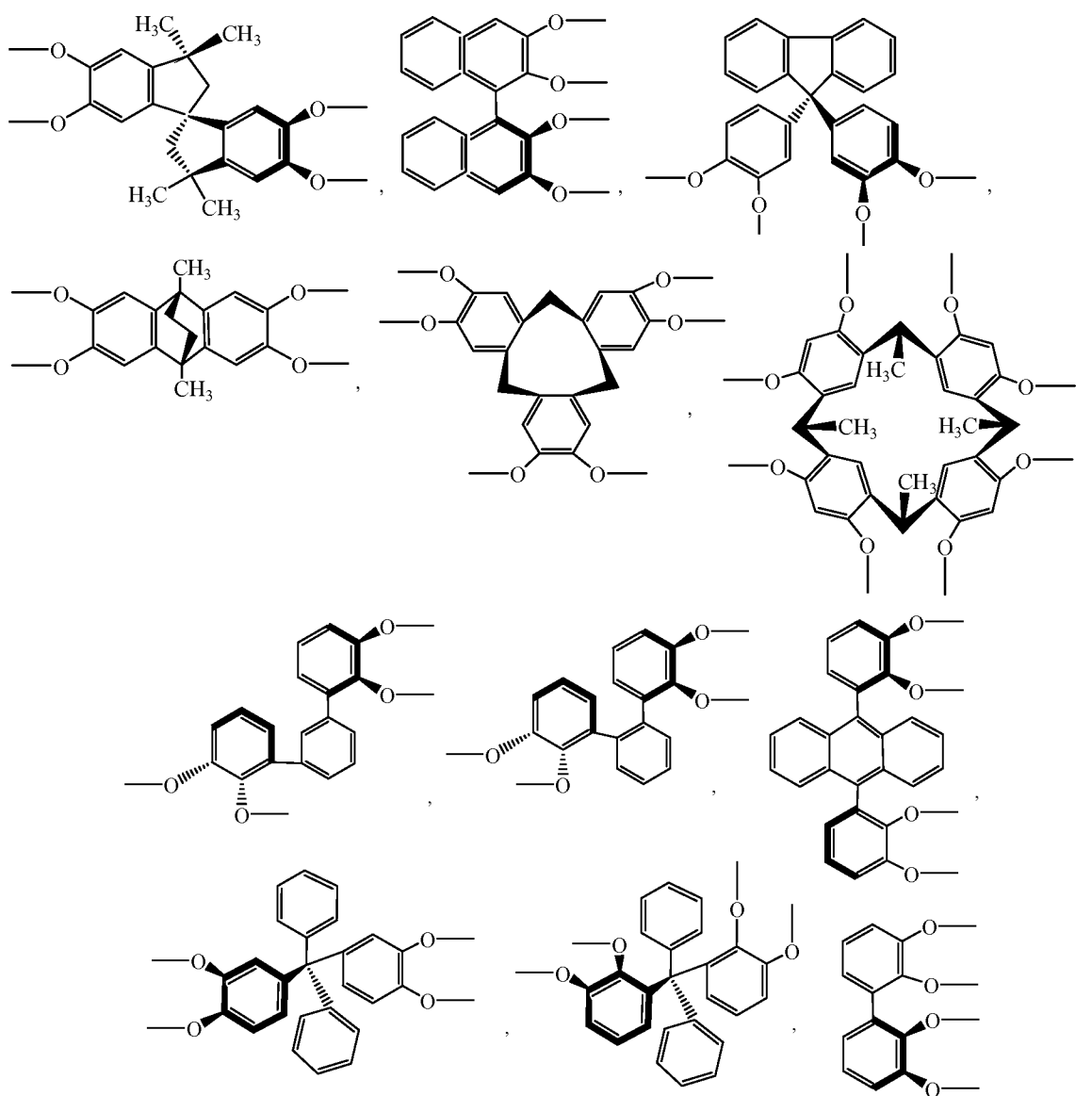


wherein X_1 , X_2 , X_3 , and X_4 are selected from the group consisting of

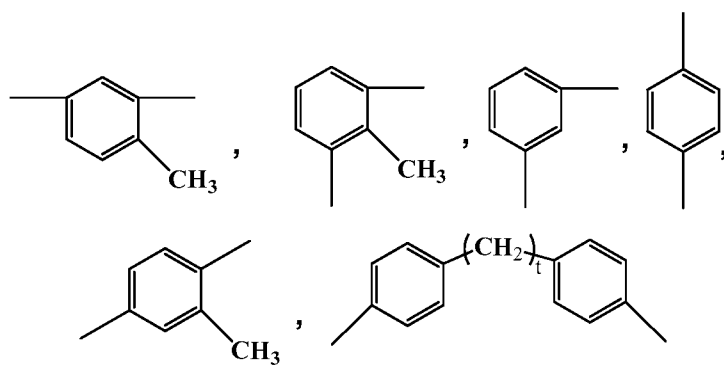


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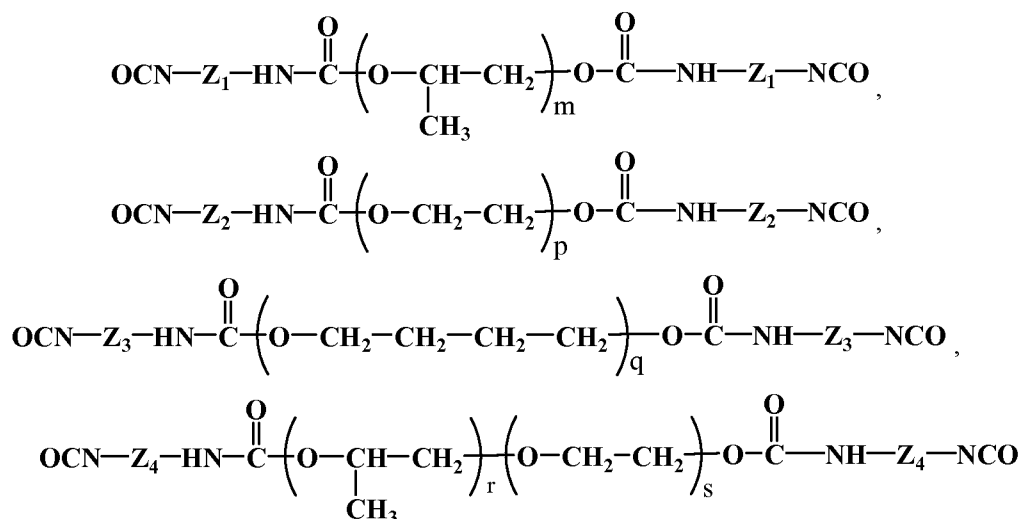
and mixtures thereof, respectively; X_1 , X_2 , X_3 , and X_4 are the same or different from each other; wherein Y is selected from the group consisting of



and mixtures thereof; wherein Z_1 , Z_2 , Z_3 , and Z_4 are selected from the group consisting of

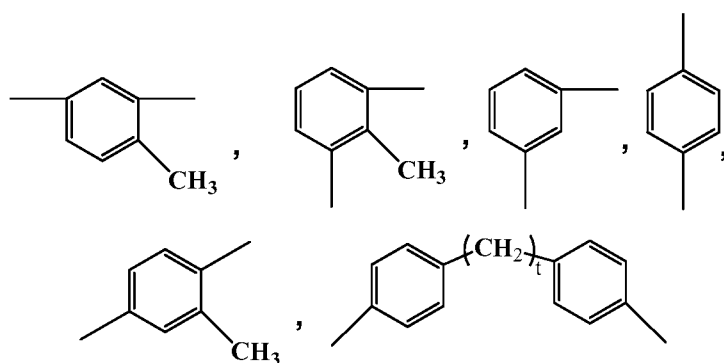


and mixtures thereof, respectively; Z_1 , Z_2 , Z_3 , and Z_4 are the same or different from each other and t is 0 to 4; and wherein n , m , p , q , r , and s are independent integers from 2 to 500. In an embodiment of the process the diisocyanate-terminated polyether is selected from the group consisting of



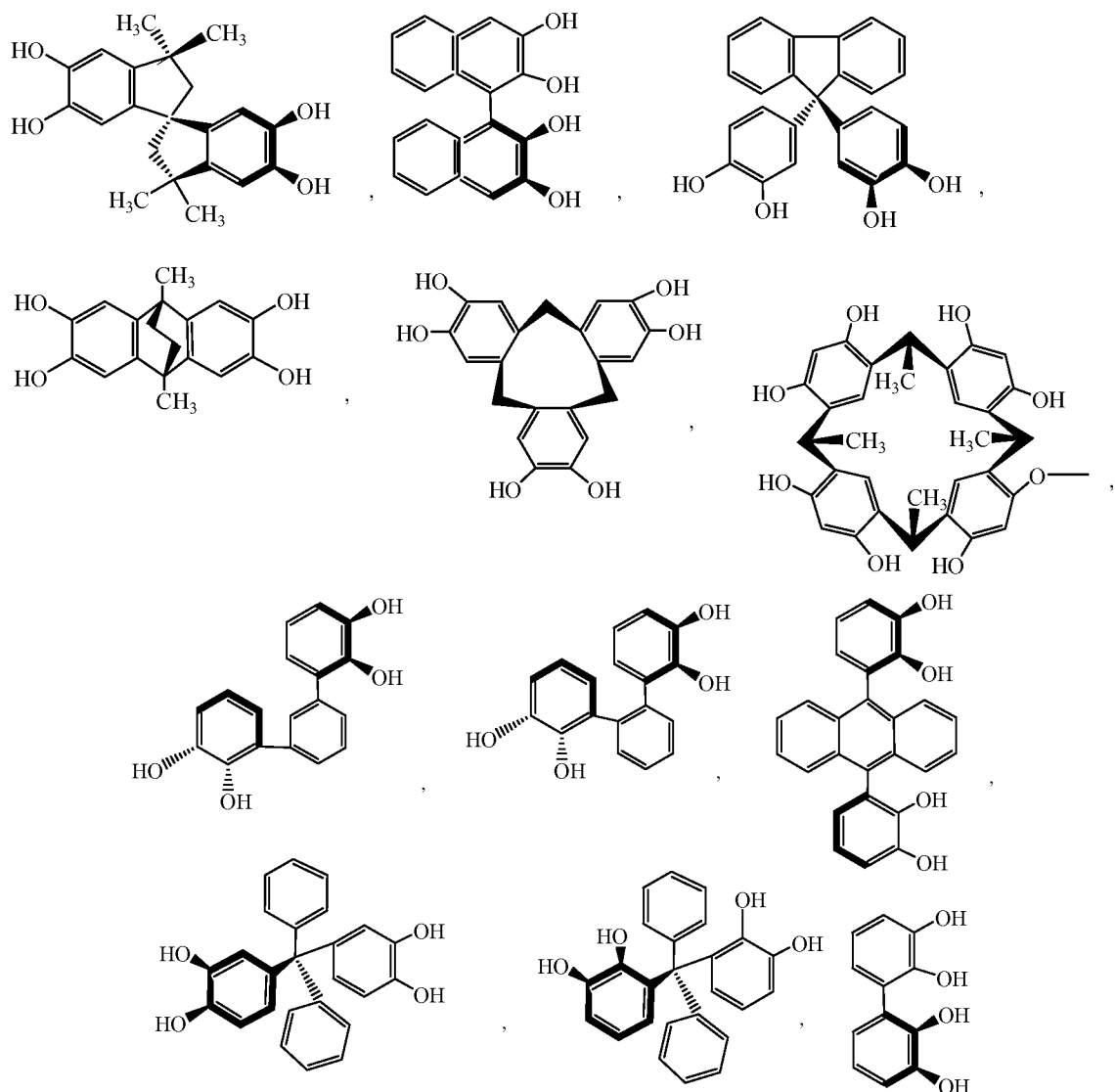
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and mixtures thereof; wherein Z_1 , Z_2 , Z_3 , and Z_4 are selected from the group consisting of



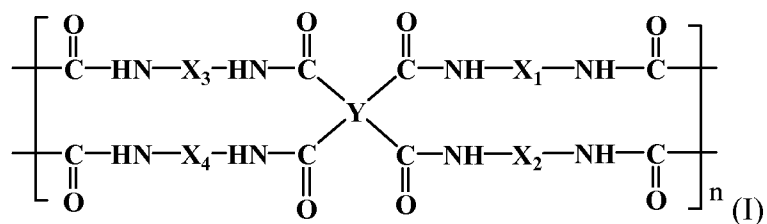
and mixtures thereof, respectively; Z_1 , Z_2 , Z_3 , and Z_4 are the same or different from each other and t is 0 to 4; wherein m , p , q , r , and s are independent integers from 2 to 500. In an embodiment of the process of the invention, the rigid cross-linking agent comprises four or more hydroxyl functional groups is selected from the group consisting of

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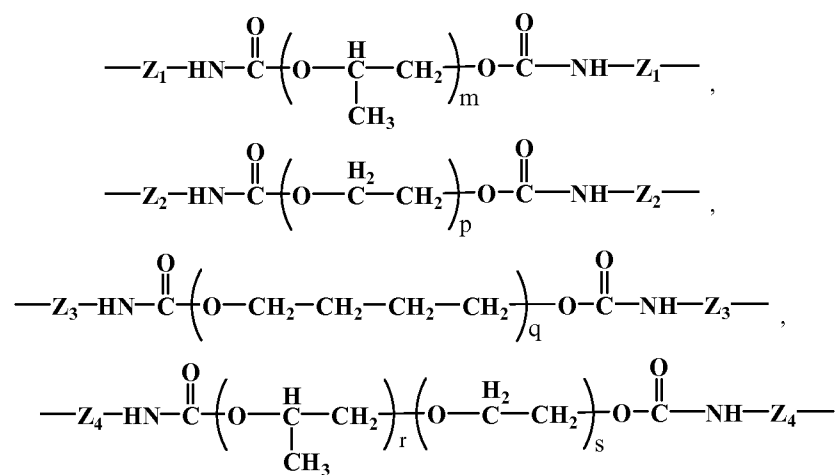


and mixtures thereof.

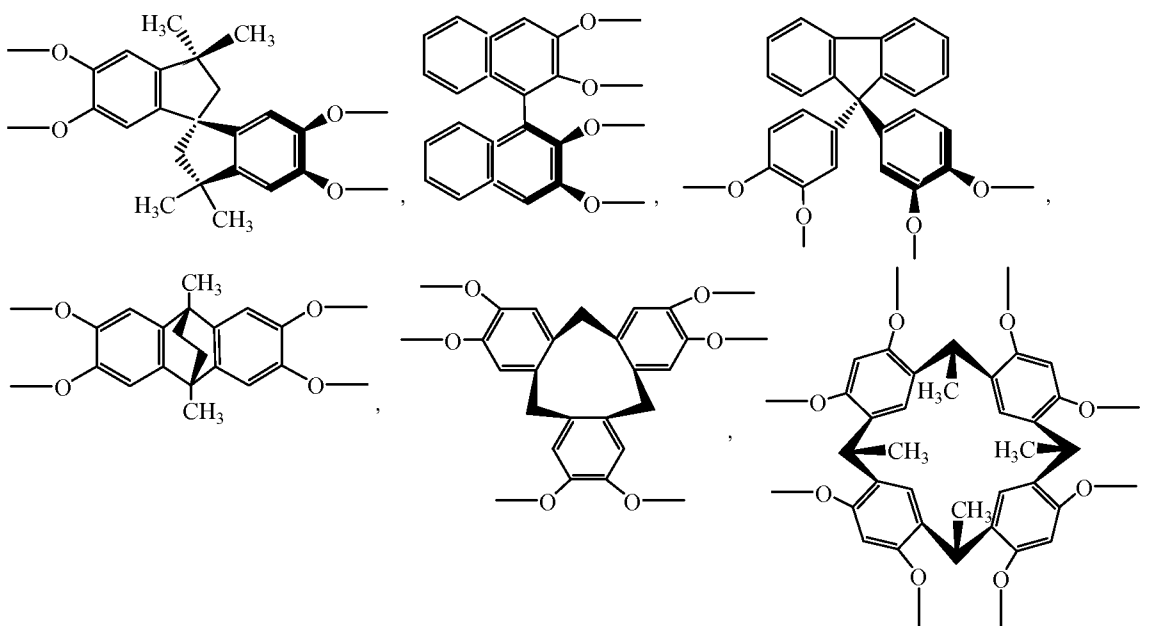
[0032] In a third embodiment, the invention comprises a process for treating a fluid stream comprising contacting the fluid stream with a cross-linked rubbery polyurethane-ether polymer membrane having a plurality of repeating units of a formula (I), wherein said formula (I) is represented by a structure comprising:

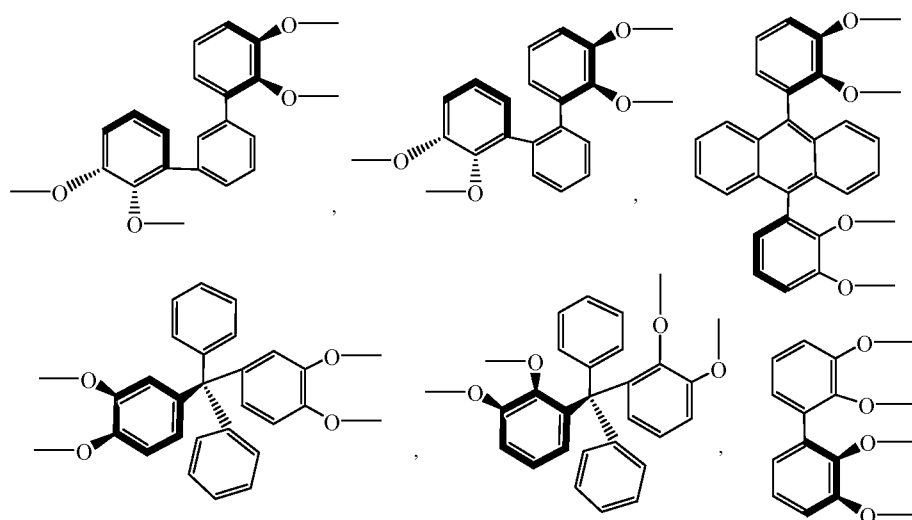


wherein X_1 , X_2 , X_3 , and X_4 are selected from the group consisting of

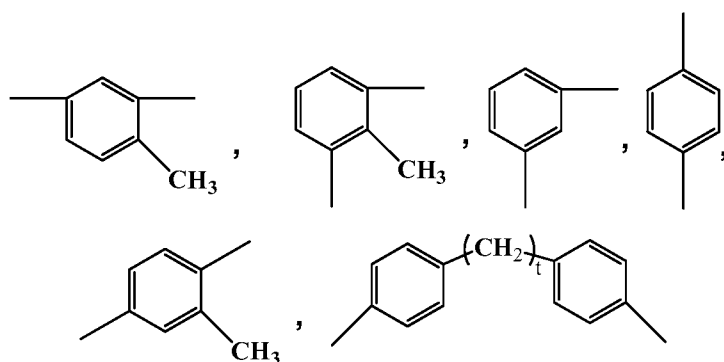


and mixtures thereof, respectively; X_1 , X_2 , X_3 , and X_4 are the same or different from each other; wherein Y is selected from the group consisting of





and mixtures thereof; wherein $Z_1, Z_2, Z_3,$ and Z_4 are selected from the group consisting of



and mixtures thereof, respectively; $Z_1, Z_2, Z_3,$ and Z_4 are the same or different from each

other and t is 0 to 4; and wherein $n, m, p, q, r,$ and s are independent integers from 2 to 500 to

produce a permeate stream and a retentate stream. The process for treating a fluid includes a

process for removing C_3 to C_{35} hydrocarbons from natural gas. In an embodiment of the

invention, a dew point of the natural gas stream is controlled within specified limits. In an

embodiment of the invention, carbon dioxide is removed from the natural gas stream. In an

embodiment of the invention, the permeate stream comprises propane, n-butane and other

heavy hydrocarbons and said retentate stream comprises methane and ethane. In an

embodiment of the invention, the fluid stream comprises a mixture of aromatic compounds.

In an embodiment of the invention, the fluid stream is first sent through the cross-linked

rubbery polyurethane-ether polymeric membrane and then is sent through a second

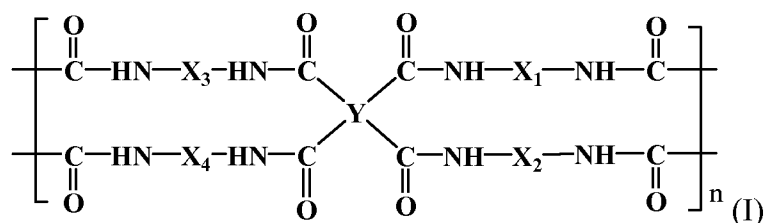
membrane. The second membrane may include a polymer selected from the group consisting

of polysulfone, cellulose acetate, cellulose triacetate, polyamide, polyimide, polyketone,

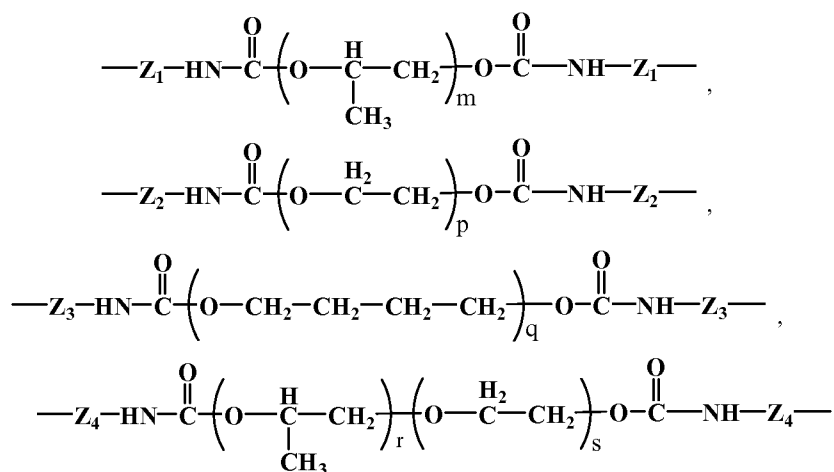
polyether ketone, and polyacrylonitrile. In some embodiments of the invention, the second membrane has higher CO₂/CH₄ selectivity than the cross-linked rubbery polyurethane-ether polymeric membrane.

CLAIMS:

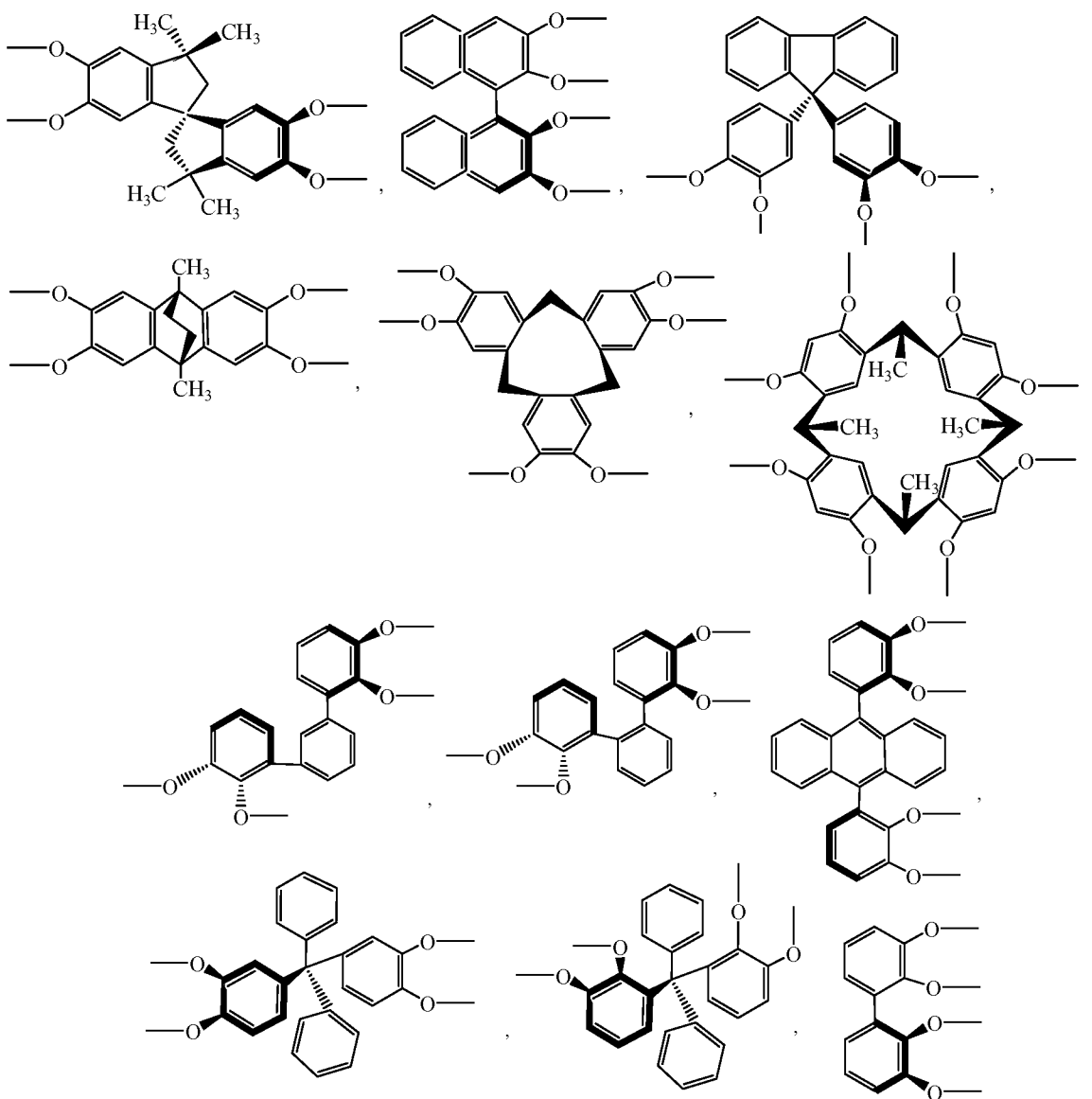
1. A cross-linked rubbery polyurethane-ether polymeric membrane comprising a cross-linked rubbery polyurethane-ether polymer with a plurality of repeating units of a formula (I), wherein said formula (I) is represented by a structure comprising:



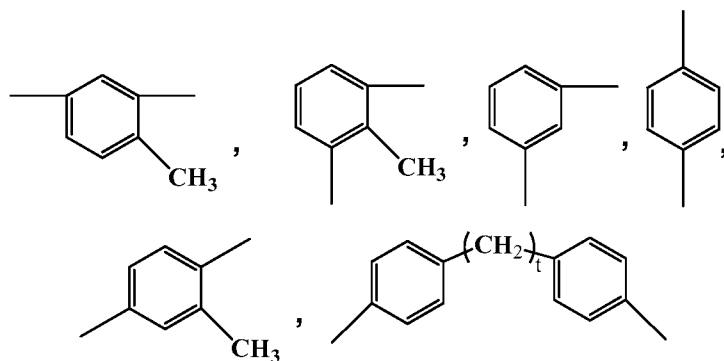
wherein X_1 , X_2 , X_3 , and X_4 are selected from the group consisting of



and mixtures thereof, respectively; X_1 , X_2 , X_3 , and X_4 are the same or different from each other; wherein Y is selected from the group consisting of

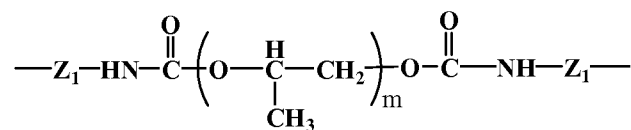


and mixtures thereof; wherein Z_1 , Z_2 , Z_3 , and Z_4 are selected from the group consisting of

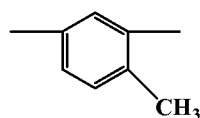


- 5 and mixtures thereof, respectively; Z_1 , Z_2 , Z_3 , and Z_4 are the same or different from each other and t is 0 to 4; and wherein n , m , p , q , r , and s are independent integers from 2 to 500.

2. The membrane of claim 1 wherein X_1 , X_2 , X_3 , and X_4 of formula (I) are the same and have a chemical structure comprising:

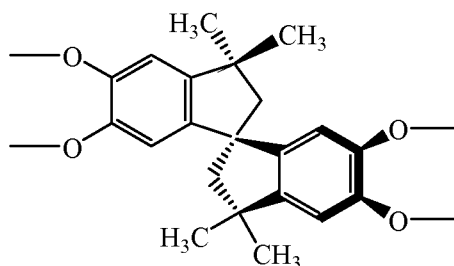


wherein Z_1 of X_1 , X_2 , X_3 , and X_4 of formula (I) is:



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and wherein Y of formula (I) is:



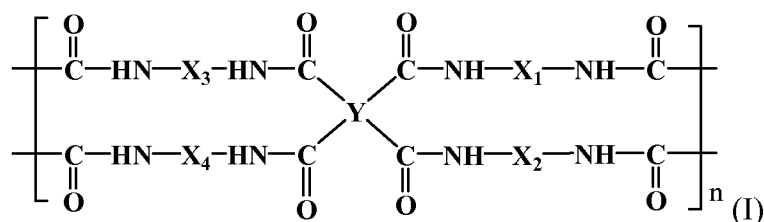
3. A method of making the cross-linked rubbery polyurethane-ether membrane of claim 1 comprising dissolving a diisocyanate-terminated polyether and a rigid cross-linking agent comprising four or more hydroxyl functional groups in a solvent to form a homogeneous solution; 2) then heating the homogenous solution at a temperature of 30° to 100°C for 0.5 to 12 hours to form a polyurethane-ether prepolymer solution; 3) coating a layer of the polyurethane-ether prepolymer solution on a porous membrane support; and 4) heating the coated membrane at a temperature of 30° to 100°C for 0.5 to 12 hours to provide a thin selective layer comprising a cross-linked rubbery polyurethane-ether material on the porous membrane support.

4. The method of claim 3 further comprising fabricating said cross-linked rubbery polyurethane-ether membrane into a sheet, disk, tube or hollow fiber.

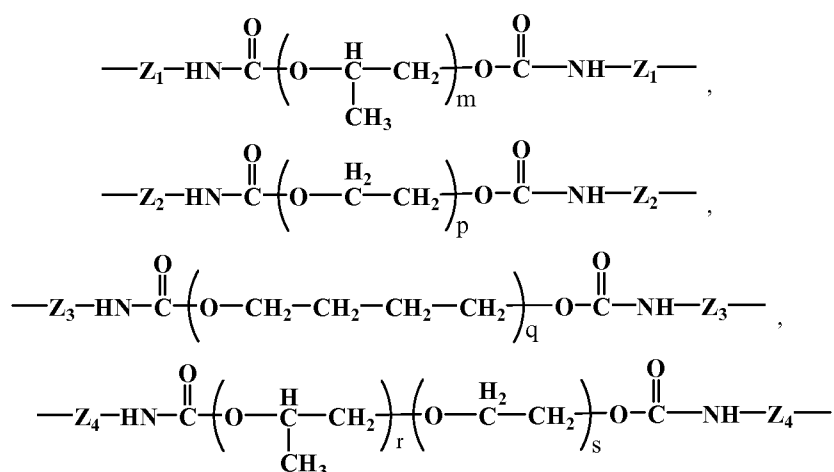
5. The method of claim 3 further comprising fabricating said cross-linked rubbery polyurethane-ether membranes into a thin film composite membrane incorporating a selective

thin cross-linked rubbery polyurethane-ether layer and a porous supporting layer comprising a polymer material or an inorganic material.

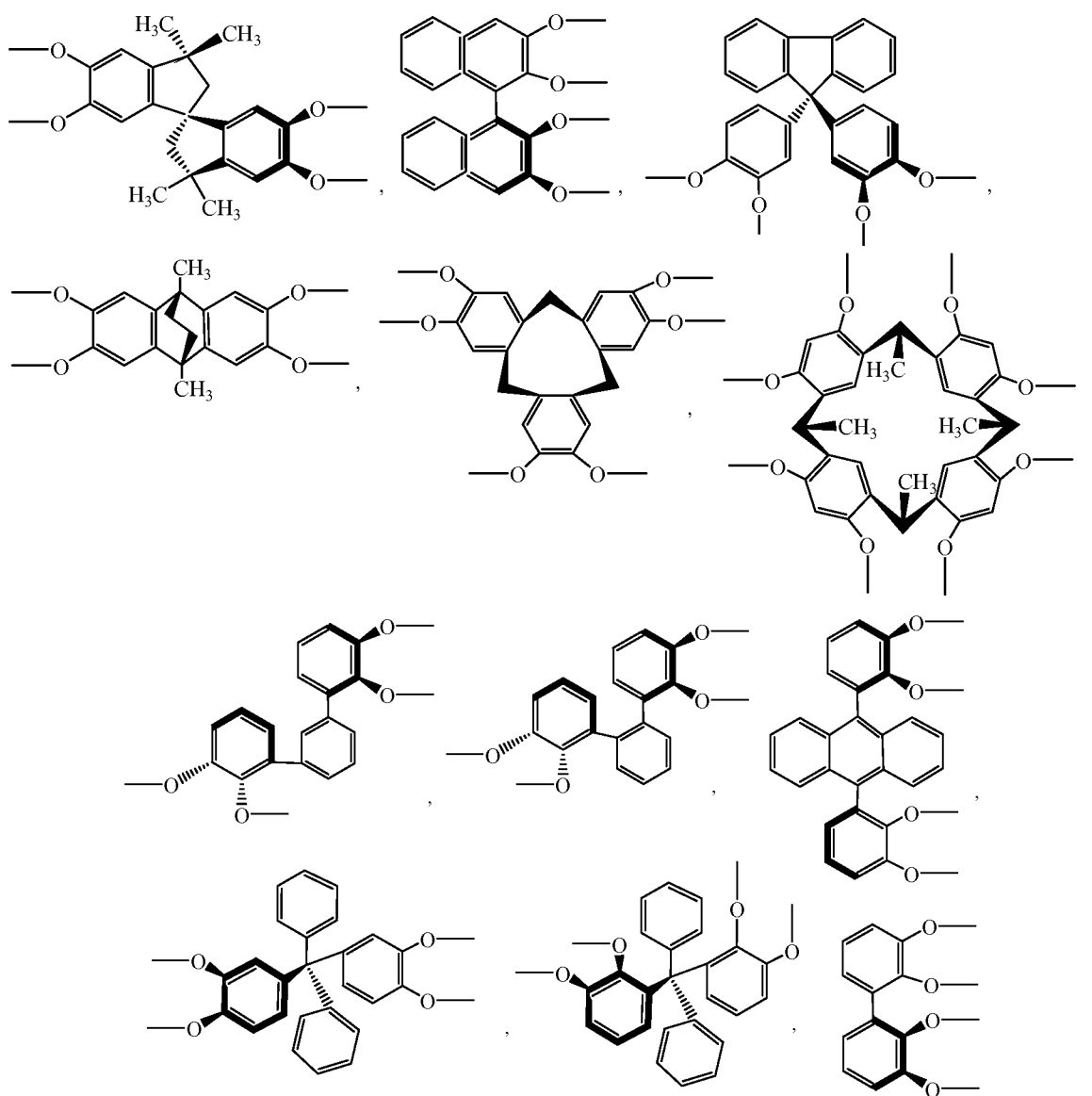
6. A process for treating a fluid stream comprising contacting the fluid stream with a cross-linked rubbery polyurethane-ether polymer membrane having a plurality of repeating units of a formula (I), wherein said formula (I) is represented by a structure comprising:



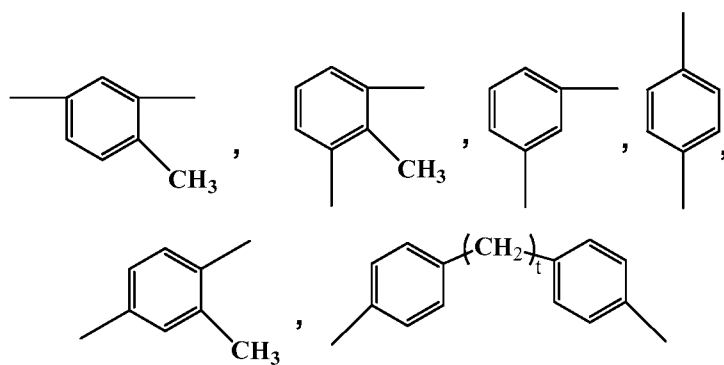
wherein X_1 , X_2 , X_3 , and X_4 are selected from the group consisting of



- and mixtures thereof, respectively; X_1 , X_2 , X_3 , and X_4 are the same or different from each other; wherein Y is selected from the group consisting of



and mixtures thereof; wherein Z_1 , Z_2 , Z_3 , and Z_4 are selected from the group consisting of



and mixtures thereof, respectively; Z_1 , Z_2 , Z_3 , and Z_4 are the same or different from each other and t is 0 to 4; and wherein n , m , p , q , r , and s are independent integers from 2 to 500 to produce a permeate stream and a retentate stream.

5 7. The process of claim 6 wherein said process for treating a fluid comprises removing C_3 to C_{35} hydrocarbons and carbon dioxide from natural gas.

8. The process of claim 7 wherein a dew point of said natural gas stream is controlled within specified limits.

9. The process of claim 6 wherein said permeate stream comprises propane, n-butane and other heavy hydrocarbons and said retentate stream comprises methane and ethane.

10 10. The process of claim 6 wherein said fluid stream is first sent through said cross-linked rubbery polyurethane-ether polymeric membrane and then is sent through a second membrane wherein said second membrane comprises a polymer selected from the group consisting of polysulfone, cellulose acetate, cellulose triacetate, polyamide, polyimide, polyketone, polyether ketone, and polyacrylonitrile.

A. CLASSIFICATION OF SUBJECT MATTER**B01D 71/54(2006.01)i**

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

B01D 71/54; B01D 53/22; C08J 5/20; B01D 69/12; H01M 8/10; C08L 67/00; C08G 18/71; B01D 71/48

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

eKOMPASS(KIPO internal) & Keywords: membrane, polyurethane-ether polymer, diisocyanate-terminated polyether, porous support, coating, heating

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2013-057492 A1 (IMPERIAL INNOVATIONS LIMITED) 25 April 2013 See abstract; claims 1-15, 23, 27; and pages 1, 16-25.	1-10
A	US 2003-0226446 A1 (SIMMONS, J. W.) 11 December 2003 See abstract; and claim 1.	1-10
A	US 2010-0167100 A1 (MOORE, D. R. et al.) 01 July 2010 See abstract; claims 1, 5; and paragraphs [0043], [0064]-[0070], [0076], [0084].	1-10
A	WO 2010-002404 A1 (UOP LLC) 07 January 2010 See abstract; and claims 1-3, 6.	1-10
A	US 2009-0281250 A1 (DESIMONE, J. M. et al.) 12 November 2009 See abstract; and paragraph [0083].	1-10



Further documents are listed in the continuation of Box C.



See patent family annex.

* 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

16 December 2014 (16.12.2014)

Date of mailing of the international search report

16 December 2014 (16.12.2014)

Name and mailing address of the ISA/KR

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2014/056714

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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