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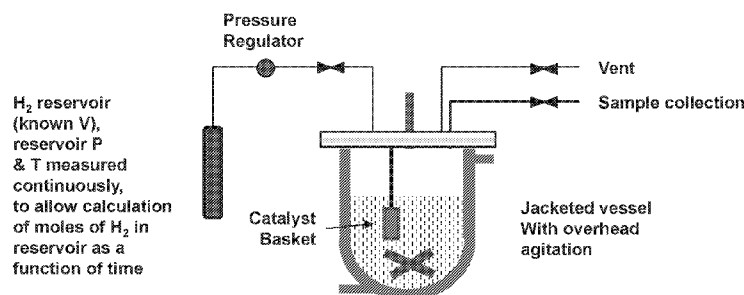
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[Continued on next page]

(54) Title: REGENERATION OF ACIDIC IONIC LIQUID WITHOUT ADDITION OF A HYDROGENATION CATALYST

Figure 1



(57) Abstract: We provide a process for regenerating a spent acidic ionic liquid, comprising contacting the spent acidic ionic liquid with hydrogen and without an addition of a hydrogenation catalyst; wherein a conjunct polymer content is decreased in the spent acidic ionic liquid to produce regenerated acidic ionic liquid. We also provide a process for making an alkylate gasoline blending component, comprising: a) alkylating a mixture of isoparaffins and olefins using an acidic ionic liquid and an alkyl halide or a hydrogen halide, wherein a conjunct polymer accumulates in a spent acidic ionic liquid; and b) feeding the spent acidic ionic liquid and a hydrogen, and without an addition of a hydrogenation catalyst, to a regeneration reactor operated under selected hydrogenation conditions to produce a regenerated acidic ionic liquid that is used for the alkylating, wherein the conjunct polymer in the regenerated acidic ionic liquid is decreased by at least 50 wt%.



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5 REGENERATION OF ACIDIC IONIC LIQUID WITHOUT ADDITION OF A HYDROGENATION CATALYST

TECHNICAL FIELD

This application is directed to a process for regenerating a spent acidic ionic liquid without the addition of a hydrogenation catalyst. This application is also directed to a process for making an alkylate gasoline blending component including feeding a spent acidic ionic liquid and hydrogen to a regeneration reactor, without the addition of any solid hydrogenation catalyst to the regeneration reactor.

BACKGROUND

Improved processes are needed for regenerating spent acidic ionic liquids. Earlier processes have required significant quantities of hydrogenation catalysts to perform the hydro-regeneration. Hydrogenation catalysts need to be periodically replaced and/or regenerated, and they can be costly to purchase, handle, and dispose of.

SUMMARY

This application provides a process for regenerating a spent acidic ionic liquid, comprising contacting the spent acidic ionic liquid with hydrogen and without an addition of a hydrogenation catalyst; wherein a content of a conjunct polymer is decreased in the spent acidic ionic liquid to produce a regenerated acidic ionic liquid.

This application also provides a process for making an alkylate gasoline blending component, comprising:

- a. alkylating a mixture of one or more C₄-C₇ isoparaffins and one or more C₂-C₆ olefins in a presence of an acidic ionic liquid and an alkyl halide or a hydrogen halide, to produce the alkylate gasoline blending component, wherein a conjunct polymer is accumulated in a spent acidic ionic liquid;
- b. feeding the spent acidic ionic liquid and a hydrogen, and without the addition of a hydrogenation catalyst, to a regeneration reactor operated under hydrogenation conditions including a temperature from 100 °C to 350 °C and a pressure from 50 to 5000 psig (446 to 34600 kpa) , wherein a content of the conjunct polymer is decreased by at least 50 wt% in the spent acidic ionic

5 liquid and the spent acidic ionic liquid becomes a regenerated acidic ionic liquid that is used as a catalyst for the alkylating.

The present invention may suitably comprise, consist of, or consist essentially of, the elements in the claims, as described herein.

10 BRIEF DESCRIPTION OF THE DRAWINGS

FIGURE 1 is a schematic diagram of the experimental apparatus used in Examples 2 and 4-7 in this disclosure.

FIGURE 2 is a graph of the moles of hydrogen consumed/g of ionic liquid, and conjunct polymer content, plotted vs. the reaction time from the Example 2 in this disclosure.

15 FIGURE 3 is a graph of the moles of hydrogen consumed/g of ionic liquid, and conjunct polymer content, plotted vs. the reaction time from the Example 3 in this disclosure

FIGURE 4 is a graph of the moles of hydrogen consumed/g of ionic liquid, and conjunct polymer content, plotted vs. the reaction time from the two sets of experiments described in Example 5 of this disclosure.

20 FIGURE 5 is a graph of the moles of hydrogen consumed/g of ionic liquid vs. the reaction time in the three sets of experiments described in Example 7 of this disclosure.

FIGURE 6 is a graph of the wt% conjunct polymer content vs. the reaction time in the three sets of experiments described in Example 7 of this disclosure.

25 FIGURE 7 is a schematic diagram of the experimental apparatus used in Example 8 in this disclosure.

FIGURE 8 is a graph showing the impact of the mode of hydrogen introduction on conjunct polymer content over time, and includes results from Example 2 and Example 8.

FIGURE 9 is a drawing of one example of a segmented reactor for regenerating a spent acidic ionic liquid.

30 GLOSSARY

“Acidic ionic liquid” refers to materials consisting entirely of ions, that can donate a proton or accept an electron pair in reactions, and that are liquid below 100°C.

“Spent” refers to a less active catalytic material that has been contaminated during use, typically with conjunct polymer.

5 “Addition” refers to a purposeful step of adding a different material, e.g., a hydrogenation catalyst, to a vessel used for the contacting.

“Bubble column reactor” refers to an apparatus used for gas-liquid reactions in which the gas, in the form of bubbles, comes in contact with the liquid while moving in the liquid column and providing a driving force for mixing. In a bubble column reactor the liquid is the
10 continuous phase and the gas is the dispersed phase.

“Hydrogenation” refers to a chemical reaction between molecular hydrogen (H₂) and another compound or element to reduce or saturate organic compounds. For example, hydrogenation reduces double and triple bonds in hydrocarbons.

“Hydrogenation catalyst” refers to a metal-containing material that catalyzes hydrogenation
15 of organic compounds.

“Periodic Table” refers to the version of the IUPAC Periodic Table of the Elements dated June 22, 2007, and the numbering scheme for the Periodic Table Groups is as described in Chemical And Engineering News, 63(5), 27 (1985).

“Conjunct polymer” refers to poly-unsaturated cyclic, polycyclic, and acyclic molecules
20 formed by concurrent acid-catalyzed reactions including, among others, polymerization, alkylation, cyclization, and hydride transfer reactions. Conjunct polymers contain double and conjugated double bonds in intricate structures containing a combination of cyclic and acyclic skeletons. Examples of conjunct polymers are described by Miron et al. (Journal of Chemical And Engineering Data, 1963) and Pines (Pines, H., The Chemistry of Catalytic Hydrocarbon
25 Conversions, Wiley, 1981, p. 39ff).

“Hydrocracking” refers to a process in which hydrogenation and dehydrogenation accompanies the cracking/fragmentation of hydrocarbons, e.g., converting heavier hydrocarbons into lighter hydrocarbons, or converting aromatics and/or cycloparaffins(naphthenes) into non-cyclic branched paraffins.

30 “Noble metal” refers to a metal that is resistant to corrosion and oxidation in moist air (unlike most base metals). Examples of noble metals are ruthenium, rhodium, palladium, silver, osmium, iridium, platinum, and gold.

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“Plug flow reactor” refers to a reactor with one or more continuous flowing systems of cylindrical geometry.

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DETAILED DESCRIPTION

Hydrogenation is known to be an effective method used to regenerate spent acidic ionic liquids, but the processes known previously all required the addition of a hydrogenation catalyst to reduce a conjunct polymer in the spent acidic ionic liquid.

15 Hydrogenation Catalysts:

In conventional hydrogenation processes, significant quantities of hydrogenation catalysts are added, along with H₂, to the organic compounds to be reduced or saturated. The amount of the hydrogenation catalyst that is required to be added depends to a large extent on the metals present in the hydrogenation catalyst, but typically the hydrogenation catalyst is added in amounts greater than 5 wt% of the organic compounds being treated. The amount of the metal that needed to be used in the past for the effective hydrogenation of a spent acidic ionic liquid was added in excess to the concentration of the conjunct polymers present in the spent catalyst. Platinum, palladium, rhodium, and ruthenium can form highly active hydrogenation catalysts, which can operate at lower temperatures and lower pressures of H₂ compared to other metals. Non-precious metal hydrogenation catalysts, especially those based on nickel (such as Raney-nickel and Urushibara-nickel) have also been developed as economical alternatives, but they are often less active and require higher temperatures. The Raney-nickel catalyzed hydrogenations also require high pressures.

Conventional hydrogenation catalysts can comprise at least one metal selected from the group consisting of elements from Group 6 and Groups 8 through 10 of the Periodic Table. Hydrogenation catalysts can comprise at least one Group 6 metal and at least one metal selected from Groups 8 through 10 of the Periodic Table. For example, the metal can be selected from the group consisting of nickel (Ni), palladium (Pd), platinum (Pt), cobalt (Co), iron (Fe), chromium (Cr), molybdenum (Mo), tungsten (W), and mixtures thereof. Exemplary mixtures of metals that have been used in hydrogenation catalysts include Ni/Mo/W, Ni/Mo, Ni/W, Co/Mo, Co/W, Co/W/Mo, Ni/Co/W/Mo, and Pt/Pd. Exemplary metal combinations used in hydrogenation catalysts include Ni/Mo/W, Ni/Mo, Ni/W, Co/Mo,

5 Co/W, Co/W/Mo and Ni/Co/W/Mo. Hydrogenation catalysts can be heterogenous or homogeneous. Heterogenous hydrogenation catalysts are in a different phase from the unsaturated organic compounds to be reduced or saturated. Typical examples of heterogeneous hydrogenation catalysts involve a solid catalyst with the unsaturated organic compounds being either liquids or gases. The unsaturated organic compounds are
10 chemisorbed onto the heterogeneous hydrogenation catalyst, and hydrogen forms surface hydrides from which hydrogen can be transferred to the chemisorbed unsaturated organic compounds. Heterogeneous hydrogenation catalysts can be affected by their supports, i.e. the material upon which the heterogeneous hydrogenation catalyst is bound.

Homogeneous hydrogenation catalysts dissolve in the solvent that contains the
15 unsaturated organic compounds to be reduced or saturated. Illustrative homogeneous hydrogenation catalysts include the rhodium-based compound known as Wilkinson's catalyst and the iridium-based Crabtree's catalyst.

Unlike earlier known processes used for regenerating acidic ionic liquids by hydrogenation, the process for regenerating a spent acidic ionic liquid described herein is
20 done without the addition of a hydrogenation catalyst. Only the spent acidic ionic liquid is contacted with the hydrogen, and the conjunct polymer is reduced sufficiently to produce a regenerated acidic ionic liquid.

In one embodiment, no drying or reducing of the spent acidic ionic liquid is done before the contacting.

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Contacting Conditions:

The conditions used for the contacting include a temperature less than 400 °C (752 °F). In one embodiment, the temperature is from 100 °C (212 °F) to 350 °C (662 °F).

The conditions used for the contacting include sufficient mixing to contact the spent
30 acidic ionic liquid with hydrogen to produce the regenerated acidic ionic liquid. The sufficient mixing can be done using any equipment in the vessel that provides effective mixing, such as agitating, baffling, stirring, shaking, bubbling, vortexing, whisking or any other methods (or combinations thereof) known to produce the sufficient mixing. Examples of equipment that can be used to provide effective mixing include baffles, paddles, agitators,
35 stirrers, nozzles, screens, filters, vibrators, vortex mixers, gas injectors, dispersers, spargers, and combinations thereof. In one embodiment, the contacting occurs in a vessel with an agitation rate of 50 to 2500 rpm.

5 The conditions for the contacting include an adequate supply of hydrogen to produce the regenerated acidic ionic liquid. In one embodiment, the contacting occurs in a vessel fed with hydrogen gas and the vessel having a pressure greater than 300 kpa. In one embodiment, the contacting occurs in a vessel under a pressure of 50 to 5000 psig (446 to 34600 kpa). Other ranges of pressure in the vessel during the contacting that can be used
10 include 200 to 4000 psig (1480 to 27700 kpa), or 400 to 3000 psig (2860 to 20800 kpa).

 The regenerated acidic ionic liquid can be produced over a wide range of times, depending on the contacting conditions used. In one embodiment, the contacting time is greater than 1 hour. In one embodiment, the contacting time is from 2 to 50 hours. In one embodiment, when the apparatus used for performing the contacting is a segmented reactor,
15 the contacting time can be greater than 5 minutes, such as from five minutes to 50 hours, or from five minutes to 10 hours.

 In one embodiment, paraffinic light gases are formed during the contacting. These light gases can be entirely non-olefinic, and may comprise C₂-C₄ alkanes, such as ethane, propane, i-butane, and n-butane.

20 In one embodiment, an extracted conjunct polymer naphtha having between 5 and 30 carbon atoms can be produced by the contacting. In one embodiment, the extracted conjunct polymer naphtha has a final boiling point less than 246 °C (475 °F), a Bromine Number of 5 or less, and at least 30 wt% naphthenes. In one embodiment, the extracted conjunct polymer naphtha has at least 60 wt% carbon numbers in a range of C₅ through C₁₀. Extracted conjunct
25 polymer naphthas made by contacting a spent acidic ionic liquid and hydrogen with the addition of a solid noble metal hydrogenation catalyst are disclosed in US8704018. In one embodiment, the extracted conjunct polymer naphtha is mixed with an effluent from an alkylation reactor to make a blended alkylate gasoline.

 In one embodiment, no solids are added or formed in a vessel used for the contacting.

30 In one embodiment, hydrogen chloride is formed during the contacting. The hydrogen chloride can be dissolved into the spent acidic ionic liquid. In one embodiment, the acidity of the spent acidic ionic liquid can be modulated by an amount of hydrogen chloride in the vessel used for the contacting. In one embodiment, the amount of the hydrogen chloride in the spent acidic ionic liquid is maintained at a level that increases a rate of
35 decrease of the content of the conjunct polymer.

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Acidic Ionic Liquids:

Acidic ionic liquids can be used as catalysts for various types of hydrocarbon conversions. Also, the regenerated acidic ionic liquid can also be effective for catalyzing a hydrocarbon conversion. Examples of these hydrocarbon conversions include: an alkylation, a polymerization, a dimerization, an oligomerization, an acylation, a hydrocracking, a metathesis, a copolymerization, an isomerization, a carbonylation, a hydroformylation, a dehalogenation, a dehydration, a disproportionation, a transalkylation, and combinations thereof. In one embodiment, the hydrocarbon conversion is alkylation of paraffins with olefins. In another embodiment, the hydrocarbon conversion is alkylation of aromatics. Examples of ionic liquid catalysts and their use for alkylation of paraffins with olefins are taught, for example, in U.S. Patent Numbers 7,432,408 and 7,432,409, 7,285,698, and U.S. Patent Application Number 12/184069, filed July 31, 2008. In one embodiment, the acidic ionic liquid is a composite ionic liquid catalyst, wherein the cations come from a hydrohalide of an alkyl-containing amine or pyridine, and the anions are composite coordinate anions coming from two or more metal compounds. In another embodiment the conversion of a hydrocarbon is alkylation of paraffins, alkylation of aromatics, or combinations thereof.

The most common acidic ionic liquids are those prepared from organic-based cations and inorganic or organic anions. Ionic liquid catalysts are used in a wide variety of reactions, including Friedel-Crafts reactions.

The acidic ionic liquid is composed of at least two components which form a complex. The acidic ionic liquid comprises a first component and a second component. The first component of the acidic ionic liquid will typically comprise a Lewis acid compound selected from components such as Lewis acid compounds of Group 13 metals, including aluminum halides, alkyl aluminum dihalides, gallium halide, and alkyl gallium halide (see the Periodic Table, which defines the elements that are Group 13 metals). Other Lewis acid compounds besides those of Group 13 metals may also be used. In one embodiment the first component is aluminum halide or alkyl aluminum dihalide. For example, aluminum trichloride (AlCl_3) may be used as the first component for preparing the ionic liquid catalyst. In one embodiment, the alkyl aluminum dihalides that can be used can have the general formula $\text{Al}_2\text{X}_4\text{R}_2$, where each X represents a halogen, selected for example from chlorine and bromine, each R represents a hydrocarbyl group comprising 1 to 12 atoms of carbon, aromatic or aliphatic, with a branched or a linear chain. Examples of alkyl aluminum

5 dihalides include dichloromethylaluminum, dibromomethylaluminum, dichloroethylaluminum, dibromoethylaluminum, dichloro n-hexylaluminum, dichloroisobutylaluminum, either used separately or combined.

The second component making up the acidic ionic liquid is an organic salt or mixture of salts. These salts may be characterized by the general formula Q^+A^- , wherein Q^+ is an ammonium, phosphonium, boronium, oxonium, iodonium, or sulfonium cation and A^- is a negatively charged ion such as Cl^- , Br^- , ClO_4^- , NO_3^- , BF_4^- , BCl_4^- , PF_6^- , SbF_6^- , $AlCl_4^-$, $Al_2Cl_7^-$, $Al_3Cl_{10}^-$, $GaCl_4^-$, $Ga_2Cl_7^-$, $Ga_3Cl_{10}^-$, AsF_6^- , TaF_6^- , $CuCl_2^-$, $FeCl_3^-$, $AlBr_4^-$, $Al_2Br_7^-$, $Al_3Br_{10}^-$, $SO_3CF_3^-$, and 3-sulfurtrioxyphenyl. In one embodiment the second component is selected from those having quaternary ammonium halides containing one or more alkyl

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15 moieties having from about 1 to about 9 carbon atoms, such as, for example, trimethylammonium hydrochloride, methyltributylammonium, 1-butyl pyridinium, or alkyl substituted imidazolium halides, such as for example, 1-ethyl-3-methyl-imidazolium chloride.

In one embodiment, the acidic ionic liquid comprises a monovalent cation selected from the group consisting of a pyridinium ion, an imidazolium ion, a pyridazinium ion, a pyrazolium ion, an imidazolinium ion, a imidazolidinium ion, an ammonium ion, a phosphonium ion, and mixtures thereof. Examples of possible cations (Q^+) include a butylethylimidazolium cation [beim], a butylmethylimidazolium cation [bmim], butyldimethylimidazolium cation [bmmim], decaethylimidazolium cation [dceim], a

20
25 decamethylimidazolium cation [dcmim], a diethylimidazolium cation [eeim], dimethylimidazolium cation [mmim], an ethyl-2,4-dimethylimidazolium cation [e-2,4-mmim], an ethyldimethylimidazolium cation [emmim], an ethylimidazolium cation [eim], an ethylmethylimidazolium [emim] cation, an ethylpropylimidazolium cation [epim], an ethoxyethylmethylimidazolium cation [etO-emim], an ethoxydimethylimidazolium cation [etO-mmim], a hexadecylmethylimidazolium cation [hexadmim], a heptylmethylimidazolium cation [hpmim], a hexaethylimidazolium cation [hxeim], a hexamethylimidazolium cation [hxmim], a hexadimethylimidazolium cation [hxmmim], a methoxyethylmethylimidazolium cation [meO-emim], a methoxypropylmethylimidazolium cation [meO-prmim], a

30
35 methylimidazolium cation [mim], dimethylimidazolium cation [mmim], a methylnonylimidazolium cation [nmim], a methylpropylimidazolium cation [mpim], an octadecylmethylimidazolium cation [octadmim], a hydroxyethylmethylimidazolium cation [OH-emim], a hydroxyloctylmethylimidazolium cation [OH-omim], a

5 hydroxylpropylmethylimidazolium cation [OH-prmim], an octylmethylimidazolium cation [omim], an octyldimethylimidazolium cation [ommim], a phenylethylmethylimidazolium cation [ph-emim], a phenylmethylimidazolium cation [ph-mim], a phenyldimethylimidazolium cation [ph-mmim], a pentylmethylimidazolium cation [pnmim], a propylmethylimidazolium cation [prmim], a 1-butyl-2-methylpyridinium cation[1-b-2-mpy], 1-butyl-3-methylpyridinium cation[1-b-3-mpy], a butylmethylpyridinium [bmpy] 10 cation, a 1-butyl-4-dimethylacetylpyridinium cation [1-b-4-DMApy], a 1-butyl-4-methylpyridinium cation[1-b-4-mpy], a 1-ethyl-2-methylpyridinium cation[1-e-2-mpy], a 1-ethyl-3-methylpyridinium cation[1-e-3-mpy], a 1-ethyl-4-dimethylacetylpyridinium cation[1-e-4-DMApy], a 1-ethyl-4-methylpyridinium cation[1-e-4-mpy], a 1-hexyl-4dimethylacetylpyridinium cation[1-hx-4-DMApy], a 1-hexyl-4-methylpyridinium cation[1-hx-4-mpy], a 1-octyl-3-methylpyridinium cation[1-o-3-mpy], a 1-octyl-4-methylpyridinium cation[1-o-4-mpy], a 1-propyl-3-methylpyridinium cation[1-pr-3-mpy], a 1-propyl-4-methylpyridinium cation[1-pr-4-mpy], a butylpyridinium cation [bpy], an ethylpyridinium cation [epy], a heptylpyridinium cation [hppy], a hexylpyridinium cation [hxy], a 20 hydroxypropylpyridinium cation [OH-prpy], an octylpyridinium cation [opy], a pentylpyridinium cation [pnpy], a propylpyridinium cation [prpy], a butylmethylpyrrolidinium cation [bmpyr], a butylpyrrolidinium cation [bpyr], a hexylmethylpyrrolidinium cation [hxmpyr], a hexylpyrrolidinium cation [hxyr], an octylmethylpyrrolidinium cation [ompyr], an octylpyrrolidinium cation [opyr], a propylmethylpyrrolidinium cation [prmpyr], a butylammonium cation [b-N], a tributylammonium cation [bbb-N], a tetrabutylammonium cation [bbbb-N], a butylethyldimethylammonium cation [bemm-N], a butyltrimethylammonium cation [bmmm-N], a N,N,N-trimethylethanolammonium cation [choline], an ethylammonium cation [e-N], a diethylammonium cation [ee-N], a tetraethylammonium cation [eeee-N], a 25 tetraheptylammonium cation [hphphph-N], a tetrahexylammonium cation [hxxhxx-N], a methylammonium cation [m-N], a dimethylammonium cation [mm-N], a tetramethylammonium cation [mmmm-N], an ammonium cation [N], a butyldimethylethanolammonium cation [OHe-bmm-N], a dimethylethanolammonium cation [OHe-mm-N], an ethanolammonium cation [OHe—N], an ethyldimethylethanolammonium cation [OHe-emm-N], a tetrapentylammonium cation [pnpnpnpn-N], a tetrapropylammonium cation [prprprpr-N], a tetrabutylphosphonium cation [bbbb-P], a tributylloctylphosphonium cation [bbbo-P], or combinations thereof.

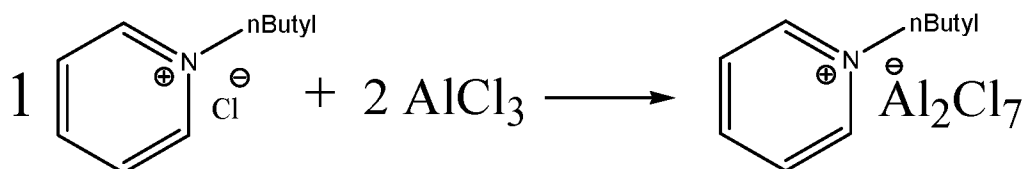
5 In one embodiment, the second component is selected from those having quaternary phosphonium halides containing one or more alkyl moieties having from 1 to 12 carbon atoms, such as, for example, trialkylphosphonium hydrochloride, tetraalkylphosphonium chlorides, and methyltrialkylphosphonium halide.

10 In one embodiment, the acidic ionic liquid comprises an unsubstituted or partly alkylated ammonium ion.

In one embodiment, the acidic ionic liquid is chloroaluminate or a bromoaluminate. In one embodiment the acidic ionic liquid is a quaternary ammonium chloroaluminate ionic liquid having the general formula $RR'R''NH^+Al_2Cl_7^-$, wherein R, R', and R'' are alkyl groups containing 1 to 12 carbons. Examples of quaternary ammonium chloroaluminate 15 ionic liquids are an N-alkyl-pyridinium chloroaluminate, an N-alkyl-alkylpyridinium chloroaluminate, a pyridinium hydrogen chloroaluminate, an alkyl pyridinium hydrogen chloroaluminate, a di alkyl- imidazolium chloroaluminate, a tetra-alkyl-ammonium chloroaluminate, a tri-alkyl-ammonium hydrogen chloroaluminate, or a mixture thereof.

20 The presence of the first component should give the acidic ionic liquid a Lewis or Franklin acidic character. Generally, the greater the mole ratio of the first component to the second component, the greater is the acidity of the acidic ionic liquid.

For example, a typical reaction mixture to prepare n-butyl pyridinium chloroaluminate ionic liquid is shown below:



30 In one embodiment, the acidic ionic liquid is used as a catalyst for a hydrocarbon conversion and the hydrocarbon conversion utilizes a co-catalyst to provide enhanced or improved catalytic activity. In one embodiment, the hydrocarbon conversion is alkylating a mixture of one or more C₄-C₇ isoparaffins and one or more C₂-C₆ olefins in a presence of an acidic ionic liquid and an alkyl halide or a hydrogen halide to produce an alkylate gasoline 35 blending component. The alkyl halide or the hydrogen halide can be co-catalysts for the hydrocarbon conversion. A co-catalyst can comprise, for example, anhydrous HCl or organic chloride (see, e.g., U.S. Pat. Nos. 7,495,144 to Elomari, and 7,531,707 to Harris et al.) When

5 organic chloride is used as the co-catalyst with the acidic ionic liquid, HCl may be formed *in situ* in the apparatus either during the hydrocarbon conversion process or during post-processing of the output of the hydrocarbon conversion. In one embodiment, the hydrocarbon conversion is conducted in the presence of a hydrogen halide, e.g., HCl.

The alkyl halides that may be used include alkyl bromides, alkyl chlorides and alkyl
10 iodides. A variety of alkyl halides may be used, but alkyl halide derivatives of the hydrocarbons that comprise the feed streams to the hydrocarbon conversion (e.g., isoparaffins or the olefins for alkylating) can be preferable. Such alkyl halides include but are not limited to isopentyl halides, isobutyl halides, tertiary butyl halides, n-butyl halides, propyl halides and ethyl halides. Alkyl chloride versions of these alkyl halides are preferable when
15 chloroaluminate ionic liquids are used. Other alkyl chlorides or alkyl halides having from 1 to 8 carbon atoms may be also used. The alkyl halides may be used alone or in combination.

When used, the alkyl halide or hydrogen halide are used in catalytic amounts. In one embodiment, the amounts of the alkyl halides or hydrogen halide should be kept at low concentrations and not exceed the molar concentration of the AlCl_3 in the acidic ionic liquid.
20 For example, the amounts of the alkyl halides or hydrogen halide used may range from 0.05 mol %-100 mol % of the Lewis acid AlCl_3 in the acidic ionic liquid in order to keep the acidity of the acidic ionic liquid catalyst at the desired performing capacity.

Spent Acidic Ionic Liquid:

25 Spent acidic ionic liquid can be made by using the acidic ionic liquid to perform the hydrocarbon conversion. Over time, the acidic ionic liquid accumulates impurities and becomes less active and selective for performing the desired hydrocarbon conversion. One of the impurities that accumulates in the acidic ionic liquid is conjunct polymer. The conjunct polymer deactivates the acidic ionic liquid by weakening the acid strength of the acidic ionic
30 liquid. Complexation of the conjunct polymer with the acidic ionic liquid can deplete the concentration of the Lewis acid in the acidic ionic liquid. As more conjunct polymers accumulate in the acidic ionic liquid the acidic ionic liquid becomes weaker for performing the desired catalysis. In one embodiment, the spent acidic ionic liquid comprises greater than 3 wt% of the conjunct polymer. For example, the spent acidic ionic liquid can have from
35 greater than 3 wt% to 30 wt% conjunct polymer.

The spent acidic ionic liquid can also comprise corrosion metals. The corrosion metals can leach from the metal materials that the acidic ionic liquid contacts. Examples of

metal materials used for vessels and equipment handling acidic ionic liquids are steel, titanium, nickel-copper alloys, and nickel-based super alloys. Examples of some of these metal materials include Inconel® alloys, Incoloy® alloys, Monel® 400 alloy, and Hastelloy® alloys. The compositions of some of these specific alloys are summarized in Table 1. Inconel® and Incoloy® are trademarks of Special Metals Corporation.

Table 1

Nickel-Copper Alloy Chemical Composition Ranges (all values in weight percent):

Alloy	UNS #	Ni	Cu	Fe	Mn	Si	S	C
Monel® 400	N04400	63.0 min	28-34	2.50 max	2.0 max	0.024 max	0.50 max	0.30 max

Monel® is a trademark of Special Metals.

Table 2

Nickel Based Super Alloy Elemental Composition Ranges (all values in weight percent):

Hastelloy®	UNS #	Ni	Cr	Mo	Fe	W	Co
C-276	N10276	Balance	14.5-16.5	15-17	4-7	3-4.5	2.5 max
C-22	N06022	Balance	20-22.5	12.5-14.5	2-6	2.5-3.5	2.5 max
B2	N10665	Balance	1.0 max	26-30	2.0 max	-	1.0 max

Hastelloy®	UNS #	Mn	C	P	Si	S	V
C-276	N10276	1.0 max	0.01 max	0.04 max	0.08 max	0.03 max	0.35 max
C-22	N06022	0.50 max	0.01 max	0.02 max	0.08 max	0.02 max	0.35 max
B2	N10665	1.0 max	0.02 max	0.04 max	0.10 max	0.03 max	-

Hastelloy® is a trademark of Haynes International, Inc.

In one embodiment, the spent ionic liquid comprises from 100 wppm to 50,000 wppm corrosion metals. In one embodiment, the spent ionic liquid comprises less than 10,000 wppm corrosion metals. In one embodiment, the spent ionic liquid comprises from 10 to 2,500 wppm nickel, wherein the nickel is a corrosion metal.

In one embodiment, the spent acidic ionic liquid catalyst comprises a metal halide. Without being bound by theory, it is possible that a homogeneous metal halide complex forms *in situ* in the spent acidic ionic liquid catalyst, and that this complex functions as a homogeneous hydrogenation catalyst. In one embodiment, the homogeneous metal halide complex comprises nickel.

5 Regenerated Acidic Ionic Liquid:

After the contacting, the content of the conjunct polymer in the spent acidic ionic liquid is decreased enough such that the acidic ionic liquid is regenerated. In one embodiment, the content of the conjunct polymer in the regenerated acidic ionic liquid is 30 wt% to 100 wt% of the amount of the conjunct polymer in the spent acidic ionic liquid. In one embodiment, the conjunct polymer in the regenerated acidic ionic liquid is decreased by at least 50 wt%. In one embodiment the regenerated acidic ionic liquid comprises from 0 to 5 wt% conjunct polymer. In one embodiment, the regenerated acidic ionic liquid comprises less than 1.5 wt% of the conjunct polymer.

15 Feeds for the Hydrocarbon Conversion:

In one embodiment, the feed to the hydrocarbon conversion comprises at least one olefin and at least one isoparaffin. For example, the feed can comprise a mixture of at least one mostly linear olefin from C₂ to about C₃₀. In another embodiment, the feed can comprise at least 50% of a single alpha olefin species. In one embodiment, the olefin feed comprises at least one isomerized olefin.

In one embodiment, the feed to an alkylation reactor comprises one or more C₄-C₇ isoparaffins and one or more C₂-C₆ olefins, and the process produces an alkylate gasoline blending component.

In one embodiment, the feed to the hydrocarbon conversion comprises isobutane. Isopentanes, isohexanes, isoheptanes, and other higher isoparaffins up to about C₃₀ are also useable in the process and apparatuses disclosed herein. Mixtures of light isoparaffins can also be used in the present invention. Mixtures such as C₃-C₄, C₃-C₅, or C₄-C₅ isoparaffins can also be used and may be advantaged because of reduced separation costs. The feed to the hydrocarbon conversion can also contain diluents such as normal paraffins. This can be a cost savings by reducing the cost of separating isoparaffins from close boiling paraffins. In one embodiment, the normal paraffins will tend to be unreactive diluents in the hydrocarbon conversion.

Reuse of a Previously Used Hydrogenation Vessel:

In one embodiment, a vessel previously containing a solid hydrogenation catalyst is emptied of the solid hydrogenation catalyst and reused for the contacting. Even without the

5 solid hydrogenation catalyst in the vessel, the hydrogenation is effective for regenerating the spent acidic ionic liquid catalyst.

Apparatus:

10 In one embodiment, we provide an apparatus that is used for performing the processes disclosed herein. The apparatus can comprise a vessel comprising an inlet for introducing the hydrogen, a second inlet for introducing the spent acidic ionic liquid, equipment that provides mixing of the hydrogen and the spent acidic ionic liquid, a vent, no parts used for separately adding a hydrogenation catalyst, and an outlet for removing the regenerated acidic ionic liquid. In one embodiment, the vessel is a stirred tank reactor where efficient mixing of 15 hydrogen and the spent acidic ionic liquid catalyst is achieved. In one embodiment, the vessel can comprise an internal particulate filter, having no hydrogenation activity, which provides some or all of the mixing and can be used for improving dispersion and/or adsorbing any contaminants from the spent acidic ionic liquid. Examples of vessels that could use an internal particulate filter in this manner could include flow-through open tubes, plug-flow 20 reactors, or bubble columns. One example of a suitable particulate filter is a Crystaphase CatTrap® internal particulate filter. In one embodiment, the internal particulate filter is a reticulated ceramic which comes in large discs (1.5" to 2" diameter). These discs can have the ability to filter and store particles inside the discs. Because the large external pathways in the discs stay open, there is no pressure drop build up as the material filters.

25 In one embodiment, the hydrogen halide in an offgas from the apparatus used for performing the contacting can be monitored. In one embodiment, a level of dissolved hydrogen halide in the spent ionic liquid catalyst can be adjusted to optimize the hydrogenation and hydrocracking in the apparatus used for performing the contacting. The level of dissolved hydrogen halide can be adjusted by increasing an amount of hydrogen 30 halide or alkyl halide co-catalyst used for the hydrocarbon conversion, by increasing a back pressure in the apparatus used for performing the contacting, or by feeding hydrogen halide or alkyl halide to the apparatus during the contacting. Back pressure refers to a pressure opposed to the desired flows of the liquid and/or gas in the apparatus. The amount of back pressure can be adjusted by valves, a back-pressure regulator, or other obstructions, and also 35 by adjusting a size of the piping in the outlet, or installing and adjusting vents in the segmented reactor.

5 In one embodiment, the apparatus that is used for performing the contacting is a segmented reactor with partitions along an axis of the segmented reactor that create segments, wherein each segment functions as a bubble column reactor.

10 Segmented Reactor

 The segmented reactor comprises no solid hydrogenation catalyst and provides no addition of a solid hydrogenation catalyst. The segmented reactor comprises a gas inlet for feeding a gas feed comprising, a liquid inlet for feeding a spent acidic ionic liquid, and partitions along an axis of the reactor that create segments, wherein each segments functions
15 as a bubble column reactor. Additionally, the segmented reactor comprises an outlet from which a regenerated acidic ionic liquid flows out of the reactor. One example of a segmented reactor is shown in Fig. 9. In one embodiment, the number of segments in the segmented reactor can vary from two to twenty.

 The axis of the segmented reactor can be in any direction, as long as there is sufficient
20 mixing and the process conditions are conducive to the regeneration. In one embodiment, the axis is vertical.

 The inlets and outlets are placed strategically on the segmented reactor to provide sufficient mixing and process conditions that are conducive to the regeneration. In one embodiment, the gas inlet and liquid inlet are adjacent to each other. In one embodiment the
25 gas inlet and liquid inlet are on an opposing side of the segmented reactor, to the outlet that elutes the regenerated acidic ionic liquid. In one embodiment, the gas inlet is on a lower portion of one or more segments in the reactor. In one embodiment, the outlet is on an upper portion of one or more segments. In one embodiment, the gas inlet and the liquid inlet are at the bottom of the segmented reactor and the outlet is above the bottom of the segmented
30 reactor. In one embodiment, the outlet is at the top of the segmented reactor. In one embodiment, the gas feed and the spent acidic ionic liquid flow directionally through the segmented reactor, and do not flow back from a subsequent segment to an earlier segment in the segmented reactor. In one embodiment, the gas feed and the spent acidic ionic liquid flow upwardly through the segmented reactor, and do not flow back from an upper segment
35 to a lower segment in the segmented reactor.

 In an embodiment, one purpose of the segments in the segmented reactor is to induce back mixing of a liquid phase comprising the spent acidic ionic liquid. The gas feed

5 comprising hydrogen flows continuously through the reactor such that the reactor operates as a plug flow reactor. In one embodiment, the partitions in the segmented reactor provide an overall plug flow pattern in the reactor such that both the spent acidic ionic liquid and the gas feed flow continuously through the reactor without back mixing into an earlier segment.

10 In one embodiment, the gas inlet is designed to introduce a gas feed stream uniformly into the cross-section of a reactor column to enable an optimum gas exchange with the spent acidic ionic liquid. In one embodiment, the gas inlet that feeds the gas feed comprising the hydrogen is a perforated plate, or a plate with many small holes drilled into it, which allows gas bubbles to flow easily through the perforations. In one embodiment, the gas inlet used for feeding the gas feed comprising the hydrogen is a gas sparger. In one embodiment, the gas
15 sparger distributes the gas feed stream via many cross-linked pipes arranged in such a way that it uniformly injects gas bubbles from many small holes drilled on the cross-linked pipes into an entire flow cross-section of the segmented reactor. In another embodiment, the gas inlet for feeding the gas feed comprising the hydrogen is a porous medium. Porous media can introduce gases into liquids through many tiny pores, creating bubbles far smaller and
20 more numerous than with typical sparging methods. In one embodiment, the gas inlet can produce gas bubbles with a mean diameter less than 20 mm, such as from 0.1 mm to 10 mm.

In one embodiment, the gas feed rate can be adjusted and controlled. The gas feed rate should be adequate to provide sufficient mixing and mass transfer between the gas bubbles and the liquid phase in the segmented reactor. In one embodiment, the gas feed rate
25 and a column diameter of the segmented reactor are designed to have a superficial gas velocity (defined as the gas flow rate under the reactor conditions divided by the cross-sectional area of the reactor column) of 0.01 cm/s to 5 cm/s.

The liquid inlet for feeding the spent acidic ionic liquid is designed to give adequate flow and mixing with the gas feed comprising hydrogen. Examples of suitable liquid inlets
30 include tubing, piping, drilled piping, nozzles, nipples, and others. In one embodiment the mass flow ratio of a liquid feed to a gas feed in the segmented reactor is 1-100. In another embodiment, the mass flow ratio of a liquid feed to a gas feed in the segmented reactor is 10-50.

In one embodiment the segmented reactor additionally comprises a diluent inlet for
35 introducing a hydrocarbon solvent. In another embodiment, the liquid inlet for feeding a spent acidic ionic liquid is designed to feed a mixture of the spent acidic ionic liquid and a hydrocarbon solvent. Some examples of hydrocarbon solvents that can be used in the

5 segmented reactor include normal paraffins, isobutane, alkylate gasoline, isomerized olefin, and mixtures thereof. The use of certain types of hydrocarbon extraction solvents during hydro-regeneration of acidic ionic liquids is described in US Pat. Pub. No. US20140039231A1.

10 The segmented reactor comprises partitions along an axis of the segmented reactor that create segments within the reactor. Examples of partitions include screens, perforated plates, particulate filtration media, and combinations thereof. In one embodiment, the partitions are perforated plates. In one embodiment, the partitions comprise openings and the openings provide high gas-liquid velocity. For example, the high gas-liquid velocity in the segmented reactor can be from 1 to 100 cm/s.

15 In one embodiment, the openings in the partitions in the segmented reactor allow gas and liquid flow only upward from a lower segment to an upper segment, such that the overall segmented reactor operates as a plug flow reactor. A plug flow reactor (PFR) is a type of chemical reactor where the influent is pumped into the direction of flow within the length of the reactor. Chemical reactions occur along the length of the PFR and the reaction rate varies
20 along the reactor axis.

In one embodiment, the partitions along the axis of the segmented reactor distribute gas bubbles evenly across the cross-section of the reactor column within each segment in the segmented reactor. This feature is shown in Fig. 1. In one embodiment, the partitions along the axis of the segmented reactor are the only internals in the segmented reactor.

25 In one embodiment, the partitions along the axis of the segmented reactor have openings that are at least 0.1 cm in diameter, or big enough to avoid being plugged up by solid impurities in the reactor system. In another embodiment, the partitions along the axis of the segmented reactor have openings that are at most 5 cm in diameter, or small enough, to create a high enough pressure drop across the partition to prevent gas and/or liquid flow back
30 from an upper segment to a lower segment. In one embodiment, the partitions have openings that are 0.5 to 2.5 cm in diameter. In one embodiment, the partitions comprise perforated plates having many holes of diameter 0.5 to 2.5 cm. The number of holes in the partitions can vary between the different partitions or be the same in one or more of the partitions. In one embodiment, the number of openings in the partitions can vary from 3-1000.

35 In one embodiment, particulate filter media having no hydrogenation activity can be added to the top of one or more of the partitions for improving dispersion and/or adsorbing any contaminants from the spent acidic ionic liquid. One example of a suitable particulate

5 filter medium is a Crystaphase CatTrap® internal particulate filter media. In one embodiment, the internal particulate filter medium comprises a reticulated ceramic which comes in large discs (1.5" to 2" diameter). These discs can have the ability to filter and store particles inside the discs, while the large dimensions of the discs keep the material from filtering externally. Because the large external pathways stay open, there is no pressure drop
10 build up as the material filters. Apparatuses including appropriately designed internal particulate filter systems can require less space than traditional grading systems and can provide the additional benefit of no pressure drop over the length of the segmented reactor. In a further embodiment, a layer of 2.5 cm to 15 cm thick Crystaphase CatTrap® or similar internal particulate filter media can be added to the partition of one or more, or all, of the
15 segments in the segmented reactor. In one embodiment, the particulate filter medium can have a pore size from 0.001 to 0.25 cm, or greater than 0.005 cm.

In one embodiment, the partitions are inserted into a conventional bubble column reactor. Conventional bubble column reactors are those previously designed or constructed for known chemical reactions, such as wet oxidation or algae bio-reactions. Conventional
20 bubble column reactors have vertically arranged cylindrical columns where the gas inlet is at the bottom of the reactor and the liquid can flow through the reactor in parallel flow or counter-current to the flow of the gas in the reactor.

In one embodiment, the segmented reactor additionally comprises a vent at the top of the segmented reactor that collects paraffinic light gases that are formed during a contacting
25 of the hydrogen and the spent acidic ionic liquid. Examples of paraffinic light gases include methane, ethane, propane, butanes, and pentanes. These light gases can be entirely non-olefinic, and may comprise C₂-C₄ alkanes, such as ethane, propane, i-butane, and n-butane. In one embodiment, at least a portion of the paraffinic light gases are formed by the hydrocracking in the segmented reactor.

30 In one embodiment, the segmented reactor additionally comprises a level control valve or a lateral effluent outlet, which maintains a steady level of a liquid in the segmented reactor. A guard bed vessel containing adsorbent material with appropriate pore size can be added before the segmented reactor to minimize contaminants going into the segmented reactor.

35 In one embodiment, the segmented reactor is sized, designed, or positioned within a process unit, such that the temperature is maintained below 380 °C. In one embodiment, the temperature in the segmented reactor is maintained from 100 °C to 350 °C to provide optimal

5 conditions for producing the regenerated acidic ionic liquid. For example, the segmented reactor can comprise a temperature controller than maintains the temperature in the segmented reactor from 100 °C to 350 °C. The relatively low operating temperature in the segmented reactor can significantly reduce corrosion compared to earlier reactors used to perform hydro-regeneration of spent acidic ionic liquids.

10 In one embodiment, the segmented reactor is designed and operated to maintain a pressure in the segmented reactor in a range that is optimal for regenerating the acidic ionic liquid. In one embodiment, the pressure in the segmented reactor is greater than 300 kpa. In one embodiment, the segmented reactor additionally comprises a pressure controller than maintains the pressure in the segmented reactor from 50 to 5000 psig (446 to 34600 kpa).

15 Other ranges of pressure in the segmented reactor can be 200 to 4000 psig (1480 to 27700 kpa, or 400 to 3000 psig (2860 to 20800 kpa).

In one embodiment, the segmented reactor additionally comprises a fluid connection between the outlet from which the regenerated acidic ionic liquid flows out of the reactor and an alkylation reactor outlet, wherein an extracted conjunct polymer naphtha produced in the segmented reactor is mixed with an alkylate gasoline made in an alkylation reactor, to make a blended alkylate gasoline.

20 In one embodiment, the segmented reactor additionally comprises a recycle loop that feeds the regenerated acidic ionic liquid back to a hydrocarbon conversion reactor that produced the spent acidic ionic liquid. Examples of hydrocarbon conversion reactors that can produce spent acidic ionic liquids are those that perform an alkylation, a polymerization, a dimerization, an oligomerization, an acylation, a hydrocracking, a metathesis, a copolymerization, an isomerization, a carbonylation, a hydroformylation, a dehalogenation, a dehydration, a disproportionation, a transalkylation, and combinations thereof.

30 EXAMPLES

Example 1: Spent Acidic Ionic Liquid Catalyst

A sample of spent acidic ionic liquid catalyst was obtained from an alkylation process unit producing alkylate gasoline blending component. The spent acidic ionic liquid catalyst comprised n-butyl pyridinium chloroaluminate ionic liquid, conjunct polymer, and additional elements. The additional elements included dissolved metals, some as metal halides. The additional elements were dissolved and were not a colloidal

5 suspension of solids. The dissolved metals were formed by the corrosion of Monel piping in the alkylation process unit. This sample of spent acidic ionic liquid catalyst had the following properties:

Table 3: Spent Acidic Ionic Liquid from Alkylation Reactor

Conjunct Polymer Content, wt%	4.10
Elemental Analyses, wppm	
Chromium	298
Copper	3520
Iron	2060
Manganese	158
Nickel	1820
Sulfur	255

The method used to measure the conjunct polymer content was vibrational infrared spectroscopy, as described in US Patent Publication No. US20120296145A1.

To perform the elemental analyses, the samples were prepared using a Milestone Ethos Plus™ closed vessel microwave digestion system according to ASTM D4309-12, “Standard Practice for Sample Digestion Using Closed Vessel Microwave Heating Technique for the Determination of Total Metals in Water”. The digested solutions were then analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES) according to ASTM D7260-12, “Standard Practice for Optimization, Calibration, and Validation of Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) for Elemental Analysis of Petroleum Products and Lubricants”.

The spent acidic ionic liquid catalyst sample was examined under a scanning electron microscope (SEM) using a Mylar sample cell that kept the spent acidic ionic liquid sample in an anhydrous atmosphere. Using a back scattering technique, the presence of particles containing corrosion metal elements was searched and no solid metal particles containing heavy metals (Ni, Fe, and Cu) were observed.

5 **Example 2:** Hydro-regeneration in the Absence of Added Catalyst and With Vessel
Drying and Hydrogen Pre-treatment

 An empty 1.2 liter jacketed HASTELLOY® C-22 vessel, equipped with a
HASTELLOY C-22 temperature sensor, HASTELLOY C-22 catalyst basket, and
HASTELLOY C-22 gassing agitator, were heated to 176.7 °C (350 °F) under a flow of
10 190 cc/min. of nitrogen and held at that temperature for 15 hours to dry the vessel.
HASTELLOY is a registered trademark of Haynes International, Inc. The apparatus
used for this example is shown in Fig. 1. The flow of nitrogen was stopped, and
hydrogen gas was introduced into the vessel at 190 cc/min. The vessel was
subsequently pressurized with hydrogen at 400 psig (2860 kpa) and held at this same
15 temperature and pressure for seven hours. The vessel was then cooled to room
temperature, depressurized, and hydrogen was purged from the vessel by pressurizing
the vessel with nitrogen to 400 psig (2860 kpa), depressurizing, and repeating this
pressurization/depressurization sequence twice.

 510 g of the spent acidic ionic liquid catalyst described in Example 1 was
20 charged to the vessel by nitrogen pressure transfer from a glass bottle. No catalyst was
added to the catalyst basket. The vessel was purged with nitrogen by pressuring the
vessel with nitrogen to 400 psig (2860 kpa), depressurizing, and repeating this
pressurization/depressurization sequence twice. About 50 psig (446 kpa) of nitrogen
was applied, and the vessel was heated to 180 °C (356 °F) over two hours while
25 agitating at 400 rpm. When the target 180 °C (356 °F) temperature was reached, a
sample was taken from the vessel and analyzed for conjunct polymer content. The
conjunct polymer content was 4.26 wt%, which was close to the 4.10 wt% in the spent
acidic ionic liquid catalyst that was analyzed prior to charging it to the vessel. The
agitation was stopped, and hydrogen was exchanged for the nitrogen in the headspace
30 of the vessel by depressurizing the vessel, pressurizing with hydrogen to 400 psig (2860
kpa), depressurizing, and repeating the pressurization/depressurization cycle twice.
The vessel was then pressurized to a 400 psig (2860 kpa) reaction pressure with
hydrogen. The agitator was started at 700 rpm to obtain a well-defined time for the
start of reaction. Reaction progress was monitored two ways: (a) by measuring the
35 hydrogen consumption, calculated from the pressure change of the reservoir feeding the
vessel, and (b) by analyzing samples taken directly from the vessel using vibrational
infrared spectroscopy.

5 The data from this run is shown in Fig. 2. The hydrogen consumption profile flattened about 20 hours after the start of reaction, and the conjunct polymer content decreased from 4.26 wt% to about 1 wt% over the same time period. The correlation of the hydrogen consumption profile with the decrease in conjunct polymer content showed that the decrease in the conjunct polymer content occurred due to a
10 combination of hydrogenation and hydrocracking. Hydrogenations are catalyzed by metals (see page 4) whereas hydrocracking typically requires a bifunctional metal catalyst comprising a hydrogenation function and an acidic function, typically from an acidic support or perhaps an acidic solvent. One novel and remarkable feature of this example was the occurrence of hydrogenation and hydrocracking in the complete
15 absence of any added hydrocracking or hydrogenation catalyst. In theory, the catalytic hydrogenation activity can be attributed in part to the dissolved corrosion metals, which originated from either corrosion of Monel piping in the alkylation unit and which were present in a concentration exceeding 1000 ppm (see Example 1) or from corrosion of the Hastelloy vessel wall and inserts.

20
Example 3: Lab-Prepared Spent Acidic Ionic Liquid

A lab-prepared spent acidic ionic liquid catalyst comprising n-butyl pyridinium chloroaluminate ionic liquid, conjunct polymer, and without significant amounts of additional elements, was prepared as follows. 272 g of t-butyl chloride was added to a
25 glass flask containing about 1358 g fresh n-butyl pyridinium chloroaluminate ionic liquid and 100 ml n-heptane. The mixture was stirred in the glass flask while immersed in an ice bath for 1.5 hours, then removed from the ice bath and stirred for an additional hour. The as-prepared reaction product in the glass flask had 6.9 wt% conjunct polymer, and it was diluted with fresh n-butyl pyridinium chloroaluminate ionic liquid
30 to a level of 4.4 wt% conjunct polymer. This sample of lab-prepared spent acidic ionic liquid catalyst had the following properties:

5

Table 4: Lab-Prepared Spent Acidic Ionic Liquid

Conjunct Polymer Content, wt%	4.4
Elemental Analyses, wppm	
Chromium	<2.9
Iron	<23
Molybdenum	<5.7
Nickel	<2.9
Sulfur	<29

One key feature of this lab-prepared conjunct polymer was its low metal content (< 10 wppm), which was in sharp contrast to the spent acidic ionic liquid from the alkylation plant (Table 3). This lab-prepared conjunct polymer with a low metal content was well suited to investigate the impact of dissolved metals on decreasing the content of the conjunct polymer, or conjunct polymer removal.

Example 4: Hydro-regeneration in the Absence of Added Catalyst and Without Vessel Drying and Hydrogen Pre-treatment

15

The empty 1.2 liter jacketed HASTELLOY® C-22 vessel described in Example 2 was charged with 510 g sample of the lab-prepared spent acidic ionic liquid described in Example 3. No hydrogenation catalyst was added to the catalyst basket. In this example, vessel drying and hydrogen pre-treatment were not carried out. The lab-prepared spent acidic ionic liquid in the vessel was heated to 180 °C (356 °F) over 1.8 hours, the vessel headspace was exchanged with hydrogen, and the reaction started as described for Example 2.

The data from this experiment is shown in Fig. 3. Hydrogen consumption was again correlated with conjunct polymer decrease, similar to the findings in Example 2. The conjunct polymer content decreased from 4.4 wt% to about 0 wt% (less than detectable) in less than 20 hours of reaction time. No solids formation occurred in the vessel. This example demonstrated that the hydro-regeneration of the spent acidic ionic liquid catalyst was conducted in the absence of an added hydrogenation catalyst, and even without drying or hydrogen pre-treatment. No solids were added or formed in the vessel used for the contacting.

More significantly, the decrease in the content of conjunct polymer by hydrogenation/hydrocracking occurred with a much lower level of corrosion metals present in the feed. Despite the occurrence of some corrosion in the vessel (as evidenced, for example, by the increase in nickel from 33 wppm at the reaction start to 376 wppm at the reaction end), the conjunct polymer removal occurred even though the corrosion metals content was more than an order of magnitude lower than in Example 1. The impact of corrosion metals on conjunct polymer removal is evidently weak,

Table 5: Metal Leaching in Lab-Prepared Spent Acidic Ionic Liquid Catalyst

	Freshly Prepared	After Heating, Before Hydrogen Introduction	After 22.4 Hours Contact with Hydrogen
Conjunct Polymer Content, wt%	4.4	4.9	0
Elemental Analyses, wppm			
Chromium	<2.9	18.4	154.0
Iron	<23	44.8	94.5
Molybdenum	<5.7	17.6	64.5
Nickel	<2.9	33.3	376.0
Sulfur	<29	<25	<21

Example 5: Hydro-regeneration in the Absence of Added Catalyst, Without Vessel Drying and Hydrogen Pre-treatment, and With Minimal Exposure to Metal Surfaces

The experiment described in Example 4 was repeated, but with a glass sleeve placed in the vessel to minimize exposure of the spent acidic ionic liquid catalyst to metal surfaces. The catalyst basket was removed before starting this experiment, and a pitched-blade impeller with a solid shaft was used instead of the hollow shaft gassing agitator used in Examples 1 and 3. The aforementioned changes decreased the metal surface area exposed to the ionic liquid by 85%, thus decreasing exposure of metal surfaces to the acidic ionic liquid significantly. As shown in Figure 4, the impact of significantly smaller metal exposure to the acidic ionic liquid did not impact the rate of

5 decrease in content of the conjunct polymer significantly. As expected, the dissolved metals content in the reaction mixture was much lower due to the smaller metal exposure; for example, the nickel content ranged from 17 to 140 wppm over the length of the reaction vs. 33-376 wppm in Example 4.

This example thus indicated that a lower metals content in the acidic ionic liquid at the start of reaction had no significant impact on the rate of decrease of the conjunct polymer content for the same acidic ionic liquid. It indicated further that the impact of corrosion metals concentration in the acidic ionic liquid on the rate of decrease of the conjunct polymer content was weak, or negligible.

15 **Example 6:** Composition of Headspace Gas

Another regeneration experiment was conducted in a manner similar to that described in Example 4, but at a 230 °C (446 °F) reaction temperature. The headspace gas composition was analyzed using an on-line gas chromatograph (GC), connected to the same line as used for the vent.

20 Table 6: GC Analysis of Headspace Gas

Component	Area %
Methane	4.92
Ethane	9.24
Propane	30.22
i-Butane	29.06
n-Butane	17.36
i-Pentane	6.71
n-Pentane	1.83

The GC analysis of the headspace gas revealed that only alkanes were formed. While not being bound by theory, the findings that the headspace gas comprised only alkanes and that no olefins were formed was consistent with the expected product distribution obtained by catalytic hydrocracking. In catalytic hydrocracking, initially formed olefins due to cracking are thought to be hydrogenated to give paraffins.

Even at the highest temperature used (namely, 230°C), no light olefinic components (typically formed in thermal cracking) were detected.

5 **Example 7:** Impact of Pressure on Conjunct Polymer Decrease Rate

The experiment described in Example 2 was repeated at two other operating pressures of 200 psig, and 800 psig. The results of these experiments were compared to results at 400 psig (Example 1) in Figures 4 and 5. The data showed a strong impact of pressure on the rate of decrease of the conjunct polymer, with the higher reactor
10 pressure or H₂ partial pressure causing a significantly higher rate of conjunct polymer removal. The 800 psig data showed that a 1 wt% level of conjunct polymer was achieved in about 10 hours at 180 °C (356 °F). One advantage to operating at higher pressures and at a more moderate temperature is that corrosion rates of the vessel used for the hydrogenation can be lower. The strong impact of the reactor pressure seen in
15 this example was also consistent with the theory that the decrease in the content of the conjunct polymer in the acidic ionic liquid occurred by hydrogenation and hydrocracking.

Example 8: Impact of Dissolved Hydrogen Chloride in Acidic Ionic Liquid

20 The apparatus shown in Figure 1 was modified as indicated in Figure 7 to allow introduction of hydrogen by a flow-through method, thus allowing for continuous removal of light components during the reaction. A procedure similar to that given in Examples 2, 4, 5, and 7 was used, except that hydrogen gas was introduced via a mass flow controller and the reactor pressure was controlled using a back-pressure regulator. Hydrogen chloride content in
25 the offgas was monitored by measuring the pH of the absorbing water solution as a function of time using a pH probe immersed in this solution.

As conversion of conjunct polymer is known to produce hydrogen chloride, which could impact the acidic character of acidic ionic liquid, it was desired to evaluate the impact of hydrogen chloride on conjunct polymer removal. The data in Figure 8 compared this
30 Example 8 experiment with that from Example 2 and indicated that the decrease in the content of the conjunct polymer in the acidic ionic liquid was slower when hydrogen chloride was continuously removed from the reaction mixture.

This example indicated that modulation of the acidity of the acidic ionic liquid by dissolved hydrogen chloride can be an important parameter in conjunct polymer removal in
35 the absence of a hydrogenation/hydrocracking catalyst.

Our examples above have shown that the conjunct polymer content in a spent acidic ionic liquid catalyst can be decreased effectively by hydrogenating and

5 hydrocracking in the complete absence of a solid hydrogenation catalyst. In the absence of a solid hydrogenation catalyst, the conjunct polymer was hydrocracked to lighter molecules that were fully saturated. The reactor pressure and/or H₂ partial pressure of the reactor, and dissolved HCl content in the acidic ionic liquid, were both important factors affecting the rate of decrease (hydrocracking reaction rate) of the
10 conjunct polymer. While we do not want to be bound by theory, it appears that the acidic functionality to perform the hydrocracking came from the acidic ionic liquid. Upon hydrocracking of the conjunct polymer, olefinic reaction intermediates were created. The olefinic reaction intermediates were hydrogenated with the H₂ gas present in the reactor. The source of the hydrogenation functionality in this catalytic reaction
15 was not clear, but appeared to be related to the acidic ionic liquid (organo-aluminum halide) and the hydrogen chloride. The dissolved corrosion metals in the acidic ionic liquids may have contributed to the hydrogenation and production of fully saturated light hydrocarbons, however the contribution of these dissolved corrosion metals was not significant.

20 The transitional term "comprising", which is synonymous with "including," "containing," or "characterized by," is inclusive or open-ended and does not exclude additional, unrecited elements or method steps. The transitional phrase "consisting of" excludes any element, step, or ingredient not specified in the claim. The transitional phrase "consisting essentially of" limits the scope of a claim to the specified materials or steps "and those that do not materially
25 affect the basic and novel characteristic(s)" of the claimed invention.

For the purposes of this specification and appended claims, unless otherwise indicated, all numbers expressing quantities, percentages or proportions, and other numerical values used in the specification and claims, are to be understood as being modified in all instances by the term "about." Furthermore, all ranges disclosed herein are inclusive of the endpoints
30 and are independently combinable. Whenever a numerical range with a lower limit and an upper limit are disclosed, any number falling within the range is also specifically disclosed. Unless otherwise specified, all percentages are in weight percent.

Any term, abbreviation or shorthand not defined is understood to have the ordinary meaning used by a person skilled in the art at the time the application is filed. The singular
35 forms "a," "an," and "the," include plural references unless expressly and unequivocally limited to one instance.

5 All of the publications, patents and patent applications cited in this application are herein incorporated by reference in their entirety to the same extent as if the disclosure of each individual publication, patent application or patent was specifically and individually indicated to be incorporated by reference in its entirety.

10 This written description uses examples to disclose the invention, including the best mode, and also to enable any person skilled in the art to make and use the invention. Many modifications of the exemplary embodiments of the invention disclosed above will readily occur to those skilled in the art. Accordingly, the invention is to be construed as including all structure and methods that fall within the scope of the appended claims. Unless otherwise specified, the recitation of a genus of elements, materials or other components, from which an
15 individual component or mixture of components can be selected, is intended to include all possible sub-generic combinations of the listed components and mixtures thereof.

The invention illustratively disclosed herein suitably may be practiced in the absence of any element which is not specifically disclosed herein.

5

IT IS CLAIMED:

1. A process for regenerating a spent acidic ionic liquid, comprising contacting the spent acidic ionic liquid with a hydrogen and without an addition of a hydrogenation catalyst; wherein a content of a conjunct polymer is decreased in the spent acidic ionic liquid to produce a regenerated acidic ionic liquid.
2. The process of claim 1, wherein the contacting occurs at a temperature from 100 °C to 350 °C.
3. The process of claim 1, wherein the contacting occurs in a vessel with an agitation rate of 50 to 2500 rpm.
4. The process of claim 1, wherein the contacting occurs in a vessel under a pressure of 50 to 5000 psig (446 to 34600 kpa).
5. The process of claim 1, wherein the contacting occurs in a segmented reactor comprising multiple segments, wherein each of the multiple segments functions as a bubble column reactor.
6. The process of claim 1, wherein a contacting time is from 2 to 50 hours.
7. The process of claim 1, wherein the spent acidic ionic liquid comprises greater than 3 wt% of the conjunct polymer and the regenerated acidic ionic liquid comprises less than 1.5 wt% of the conjunct polymer.
8. The process of claim 1, wherein the spent acidic ionic liquid comprises less than 10,000 wppm corrosion metals.
9. The process of claim 1, wherein the regenerated acidic ionic liquid is effective for catalyzing a hydrocarbon conversion selected from the group consisting of an alkylation, a polymerization, a dimerization, an oligomerization, an acylation, a hydrocracking, a metathesis, a copolymerization, an isomerization, a carbonylation, a hydroformylation, a dehalogenation, a dehydration, a disproportionation, a transalkylation, and combinations thereof.

- 5 10. The process of claim 1, wherein paraffinic light gases are formed during the contacting.
11. The process of claim 1, wherein an extracted conjunct polymer naphtha, having between 5 and 30 carbon atoms, is produced by the contacting.
12. The process of claim 1, wherein no drying or reducing of the spent acidic ionic liquid
10 is done before the contacting.
13. The process of claim 1, wherein no solids are added or formed in a vessel used for the contacting.
14. The process of claim 1, wherein a vessel previously containing a solid hydrogenation catalyst is emptied of the solid hydrogenation catalyst and reused for the contacting.
- 15 15. An apparatus that is used for performing the process of claim 1, comprising: a vessel comprising an inlet for introducing the hydrogen, a second inlet for introducing the spent acidic ionic liquid, an equipment that provides mixing of the hydrogen and the spent acidic ionic liquid, a vent, no separately added hydrogenation catalyst, and an outlet for removing the regenerated acidic ionic liquid.
- 20 16. The apparatus of claim 15, additionally comprising a particulate filter having no hydrogenation activity in the vessel.
17. The apparatus of claim 15, wherein the equipment that provides the mixing is a segmented reactor with partitions along an axis of the segmented reactor that create segments, wherein each segment functions as a bubble column reactor.
- 25 18. The apparatus of claim 15, additionally comprising a back-pressure regulator that maintains an amount of a hydrogen chloride in the spent acidic ionic liquid at a level that increases a rate of decrease of the content of the conjunct polymer.
19. The process of claim 1, additionally comprising:
- 30 a. alkylating a mixture of one or more C₄-C₇ isoparaffins and one or more C₂-C₆ olefins to produce an alkylate gasoline blending component, wherein the conjunct

- 5 polymer is accumulated in a spent acidic ionic liquid that was used for the alkylating;
- b. feeding the spent acidic ionic liquid and the hydrogen to a regeneration reactor operated under hydrogenation conditions including a temperature from 100 °C to 350 °C and a pressure from 50 to 5000 psig (446 to 34600 kpa) , wherein the
- 10 content of the conjunct polymer is decreased by at least 50 wt% in the spent acidic ionic liquid and the spent acidic ionic liquid becomes a regenerated acidic ionic liquid that is used as a catalyst for the alkylating.
20. The process of claim 1 or claim 19, wherein an amount of a hydrogen chloride in the spent acidic ionic liquid is maintained at a level that increases a rate of
- 15 decrease of the content of the conjunct polymer.

Figure 1

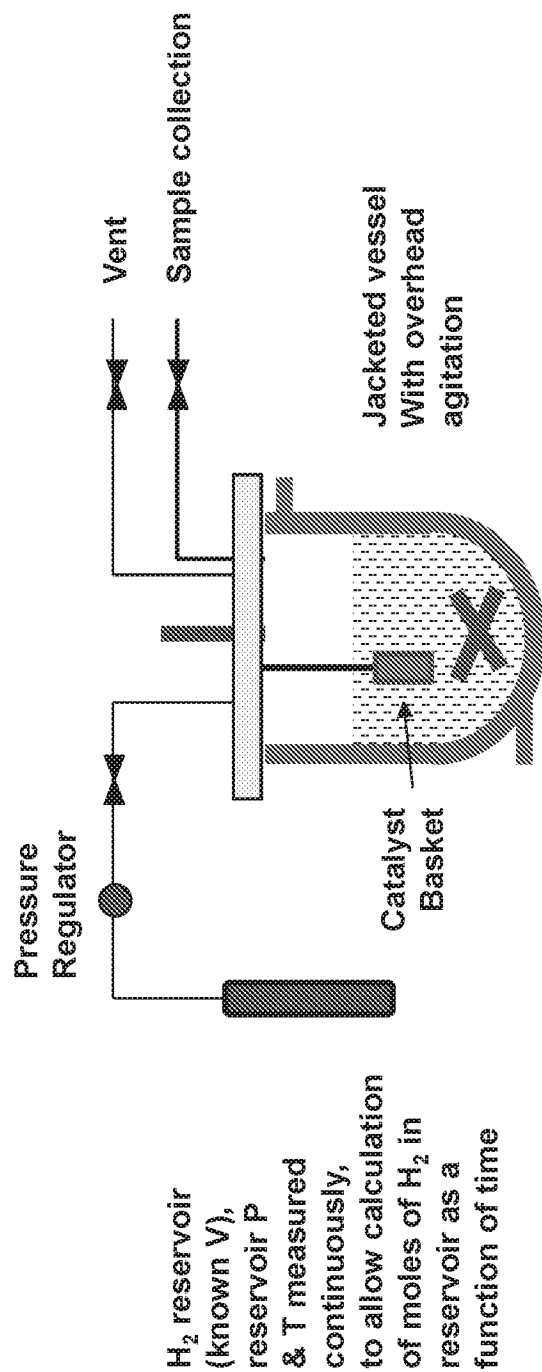


Figure 2

Example 2: 180°C, 400 psig, no catalyst

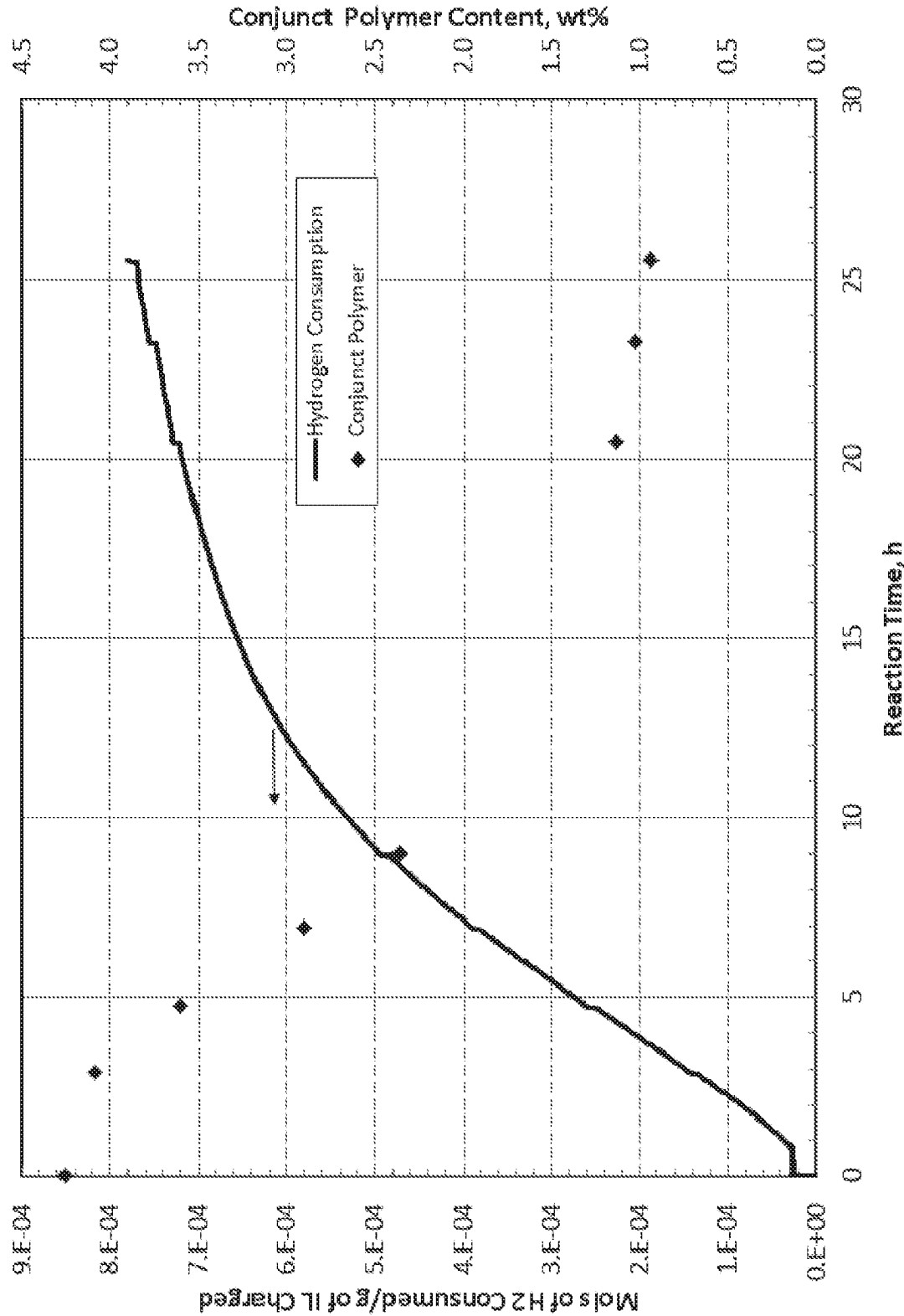


Figure 3

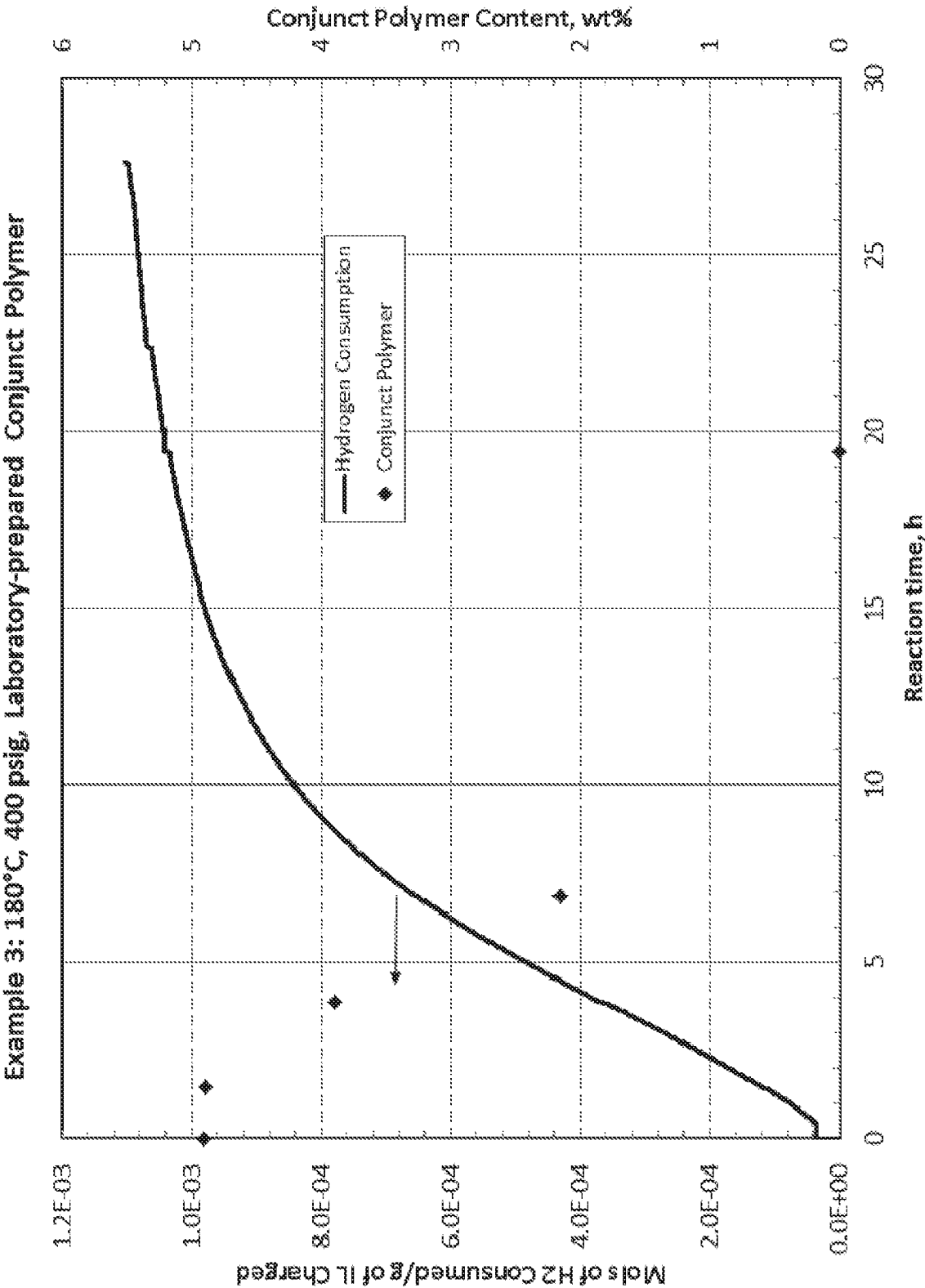


Figure 4

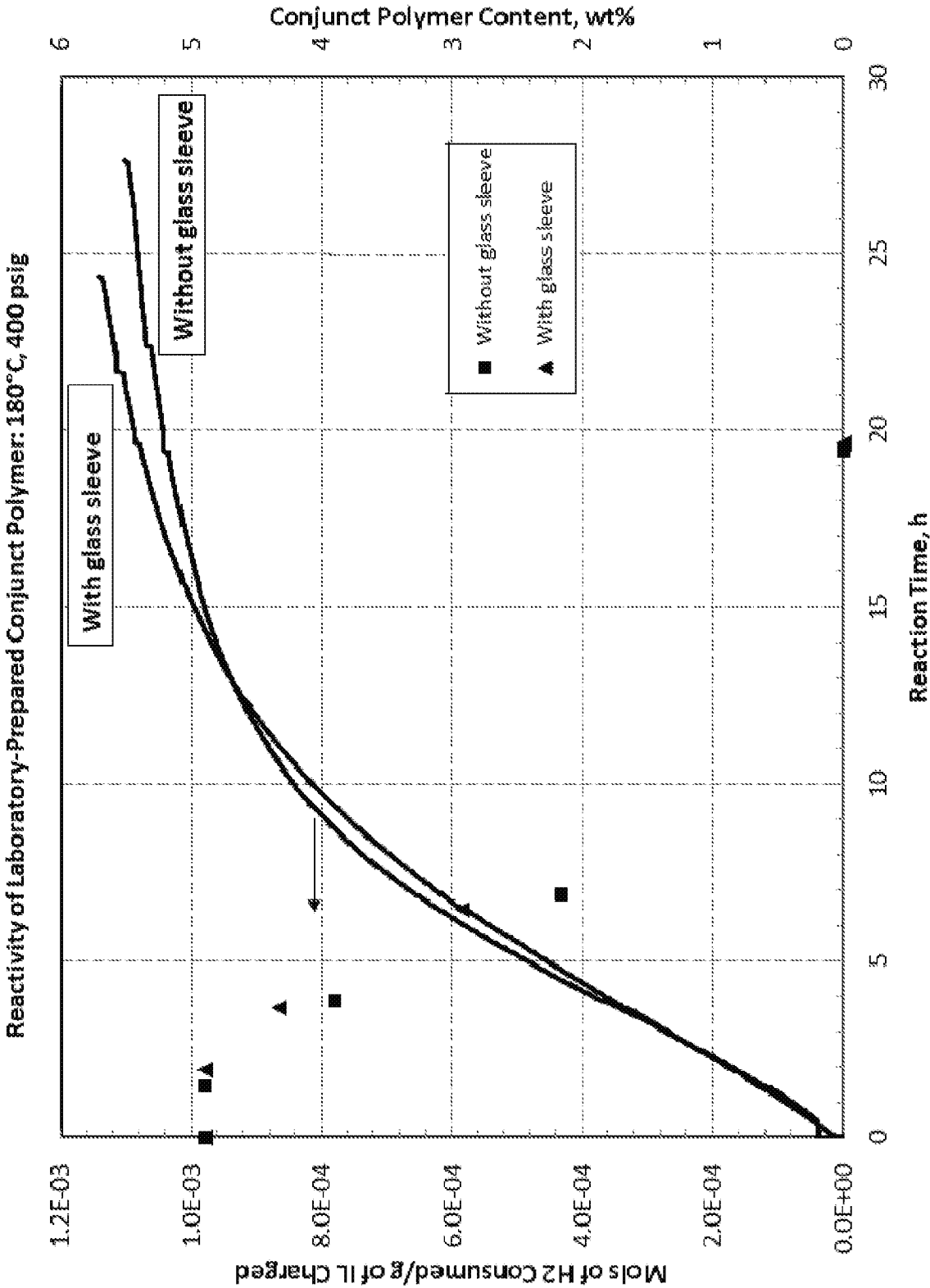


Figure 5

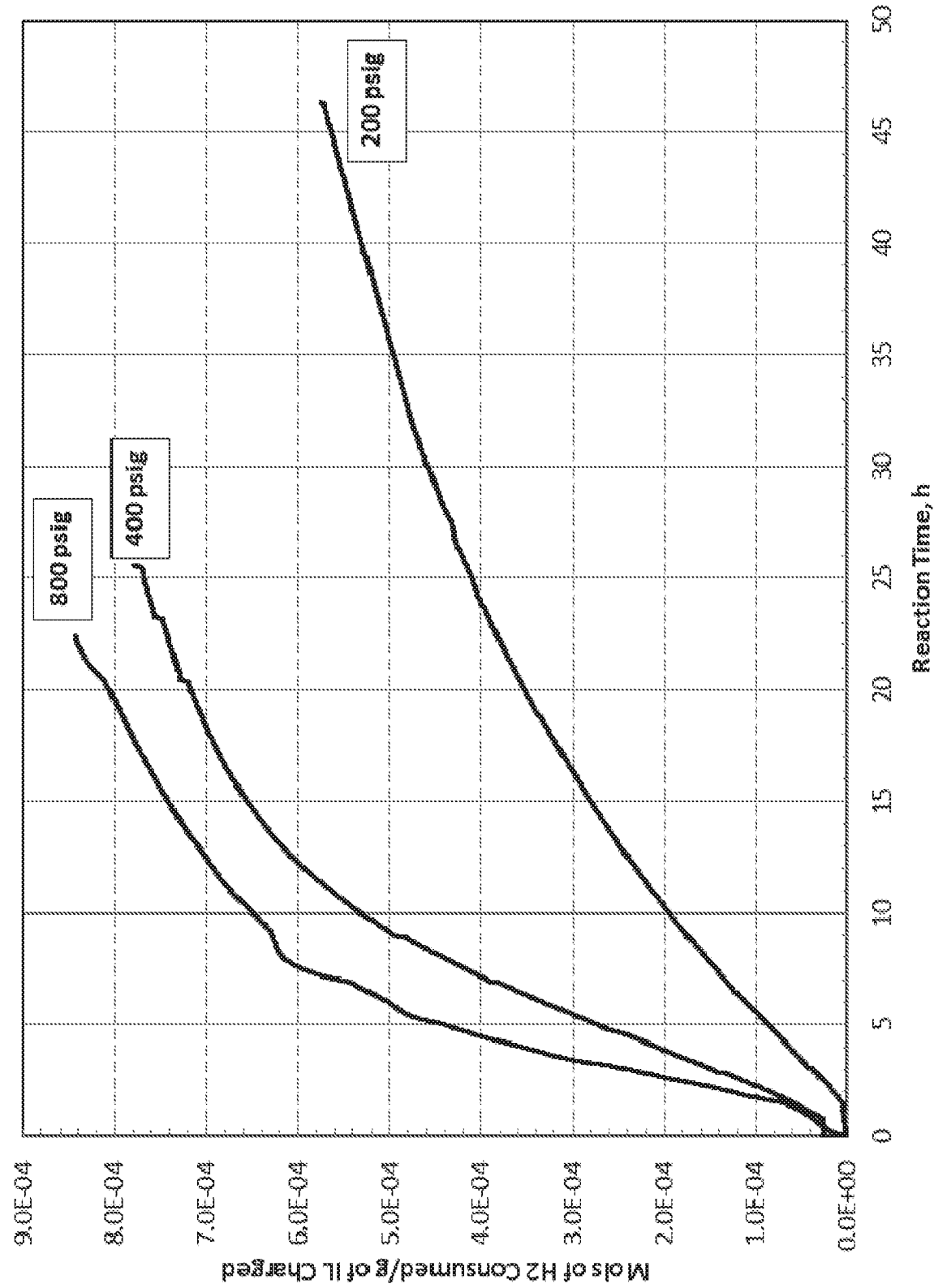


Figure 6

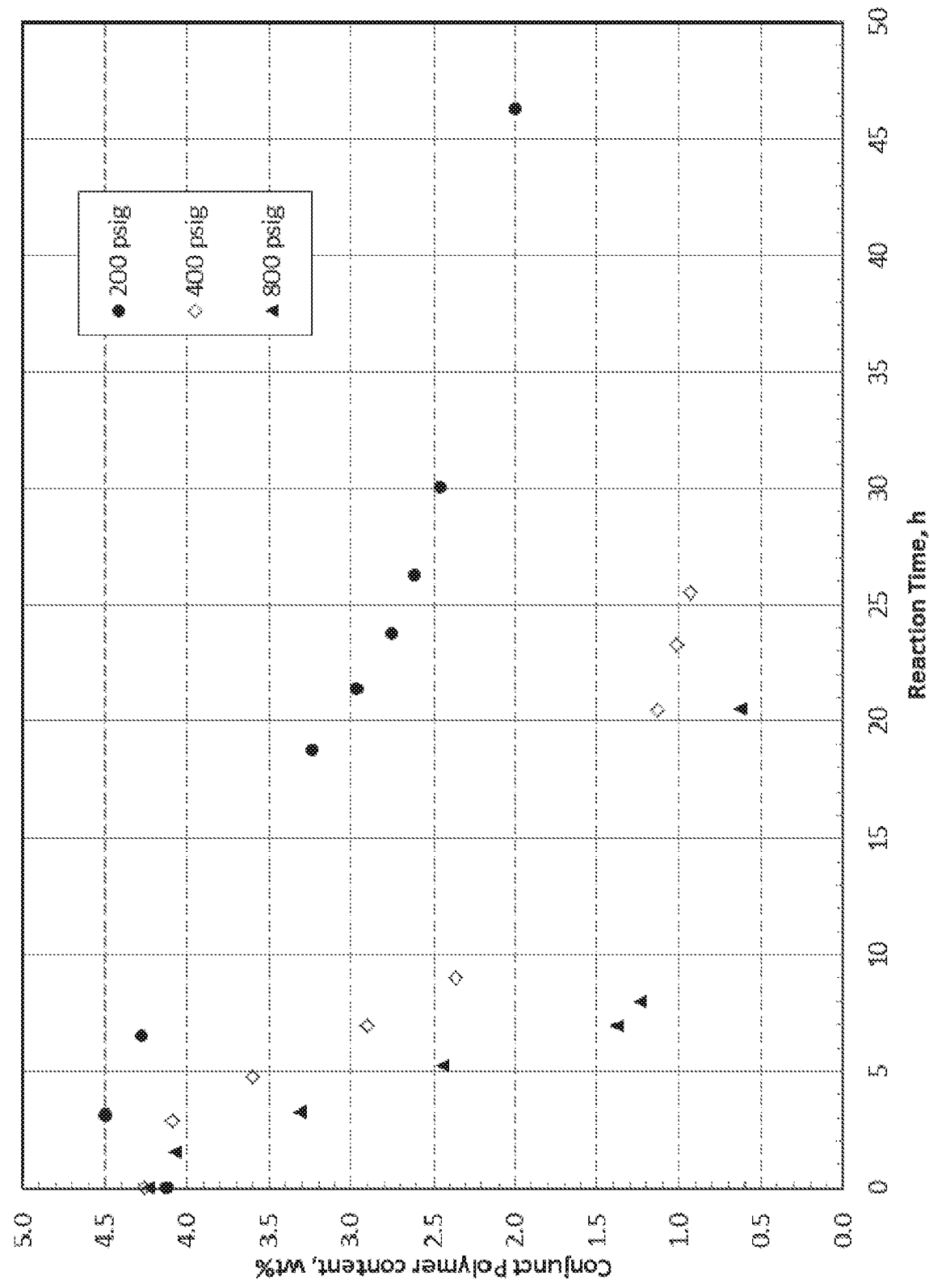


Figure 7

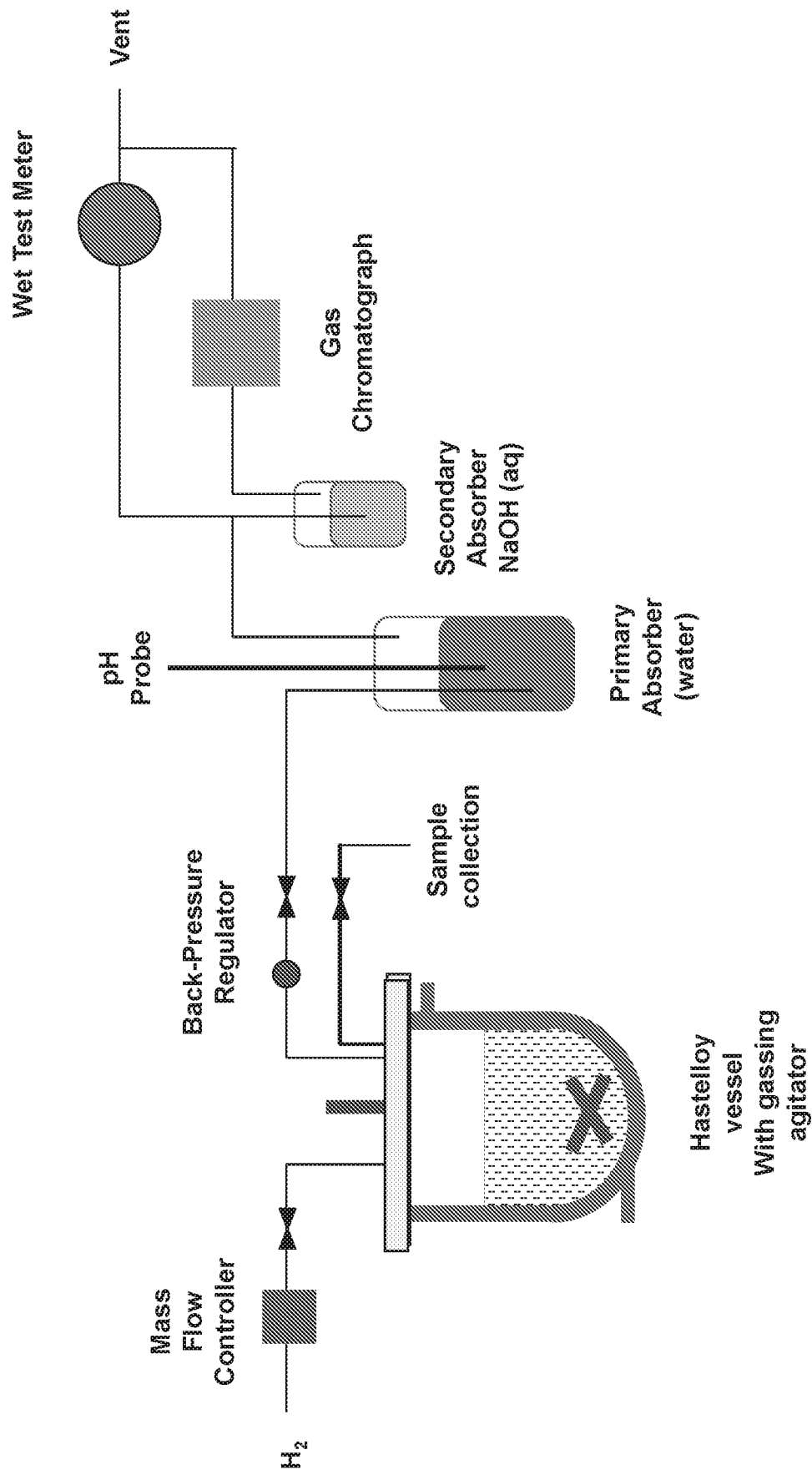
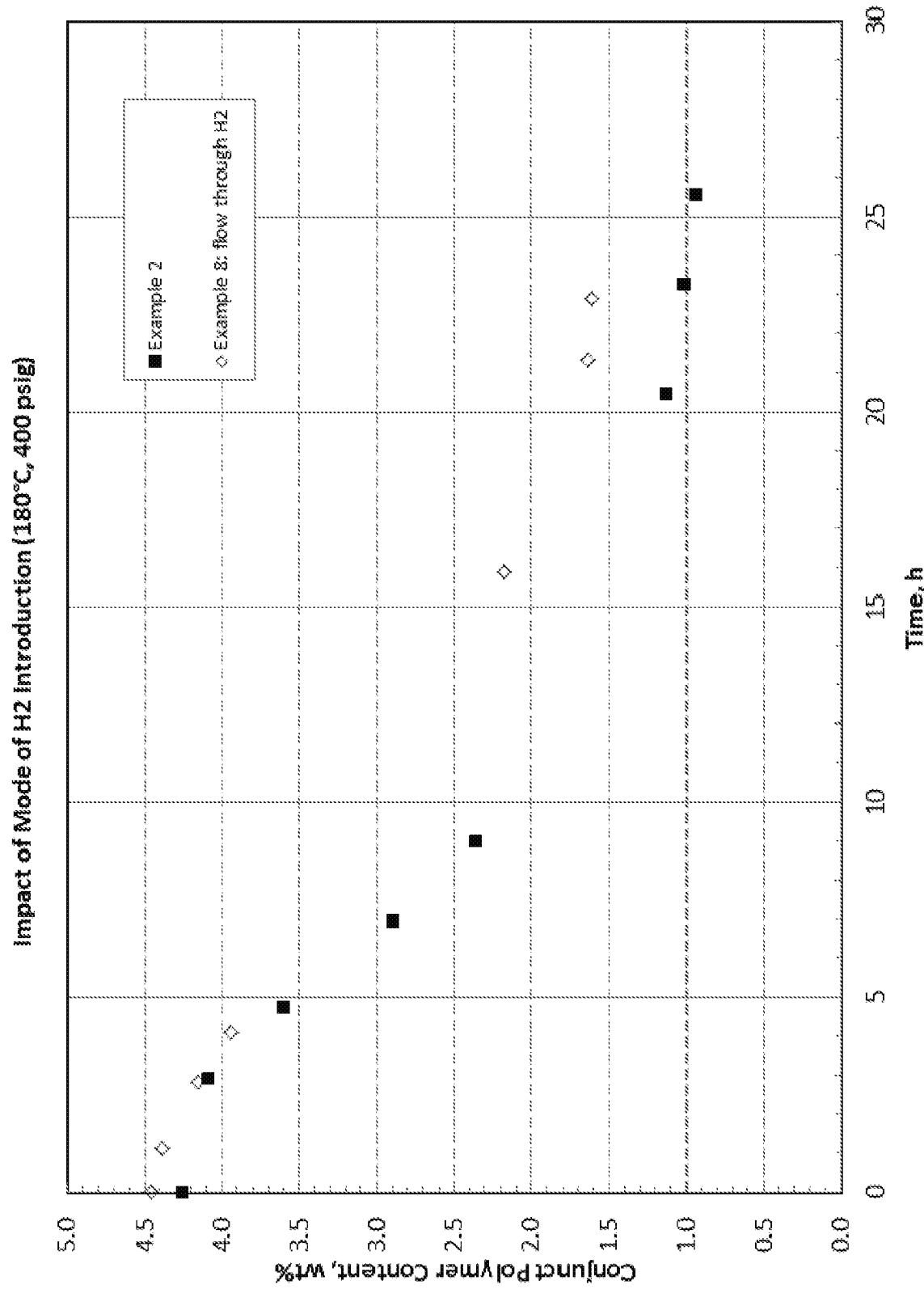
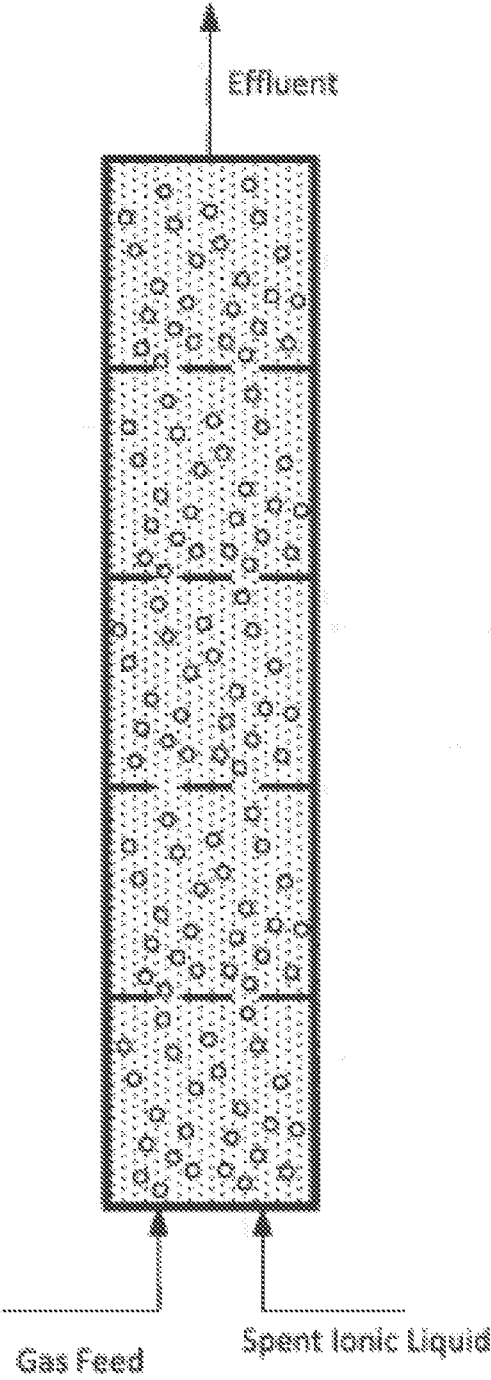


Figure 8





INTERNATIONAL SEARCH REPORT

International application No
PCT/US2017/013858

A. CLASSIFICATION OF SUBJECT MATTER

INV. C10G45/58 C07C2/62 B01J31/02 C10G29/20 C10G67/02
C10G50/00 C10G69/12 C10G3/00 C07C2/56 C07C2/68
B01J38/10 B01J8/22

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)

C10G C07C B01J

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

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

EP0-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2007/249486 A1 (ELOMARI SALEH [US] ET AL) 25 October 2007 (2007-10-25) paragraphs [0029], [0031], [0041], [0050] examples 5, 13, 14 -----	1-20
A	US 2014/039230 A1 (TIMKEN HYE KYUNG CHO [US] ET AL) 6 February 2014 (2014-02-06) paragraphs [0061], [0062], [0063] example 2 -----	19,20
A	GB 1 416 194 A (SCHERING AG [DE]) 3 December 1975 (1975-12-03) page 1, lines 23-30, 54-57 page 2, lines 10-14 figure 1 claim 1 -----	15-18



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

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"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

11 April 2017

Date of mailing of the international search report

25/04/2017

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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