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PROCESS FOR CONVERTING HYDROCARBON FEEDSTOCKS WITH
ELECTROLYTIC RECOVERY OF HALOGEN

FIELD OF THE INVENTION

[0001] The present invention is directed to a process for converting natural gas and other hydrocarbon feedstocks into higher-value products, such as fuel-grade hydrocarbons, methanol, and aromatic compounds.

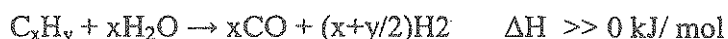
BACKGROUND OF THE INVENTION

[0002] U.S. Patent Application No. 11/703,358 ("the '358 application."), entitled "Continuous Process for Converting Natural Gas to Liquid Hydrocarbons", filed February 5, 2007, based on U.S. Provisional Application No. 60/765,115, filed February 3, 2006, describes a continuous process for reacting molecular halogen with a hydrocarbon feedstock to produce higher hydrocarbons. In one embodiment, the process includes the steps of alkane halogenation, "reproportionation" of polyhalogenated compounds to increase the amount of monohalides that are formed, oligomerization (C-C coupling) of alkyl halides to form higher carbon number products, separation of products from hydrogen halide, continuous regeneration of halogen, and recovery of molecular halogen from water. Hydrohalic acid (e.g., HBr) is separated from liquid hydrocarbons in a liquid-liquid phase splitter, and then converted into molecular halogen (e.g., bromine) by reaction with a source of oxygen in the presence of a metal oxide catalyst. The '358 application is incorporated by reference herein in its entirety.

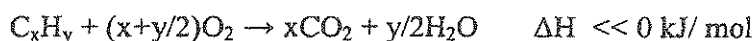
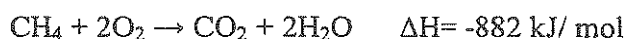
[0003] The '358 application represents a significant advance in the art of C-H bond activation and industrial processes for converting a hydrocarbon feedstock into higher value products. The present invention builds on the '358 application by employing electrolysis to regenerate molecular halogen (e.g., Br₂, Cl₂) from hydrohalic acid (e.g., HBr, HCl).

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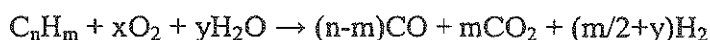
[0004] Electrolysis of aqueous solutions to produce hydrogen and oxygen is a known way of producing hydrogen with electrical energy. Similarly, halogens have been produced by electrolysis of halide brines or metal halide vapor. Conventional hydrogen production relies on reforming of hydrocarbons with water (steam) to produce carbon monoxide and molecular hydrogen:



[0005] The energetically unfavorable reforming reaction can be compared to the exothermic complete oxidation of hydrocarbons in oxygen to produce the low-energy products water and carbon dioxide:



[0006] Typically, the reforming process is coupled with complete oxidation to provide energy to drive the otherwise endothermic reaction. The resulting overall reaction produces both carbon oxides and hydrogen and can be operated nearly isoergically:



[0007] Alternatively, hydrogen can be produced by dissociation of water:



[0008] Although energetically unfavorable, the reaction can be driven by electrolysis using 2×10^5 Coulombs per gram-mole H_2 . Water is the source of both the hydrogen and the oxygen, and the high activation energy for oxygen production requires over potentials of approximately 1.6 Volts and a stoichiometric current. In practice, the electrical energy required is approximately 300 kJ/mol H_2 .

[0009] In halogen production by electrolysis of halide salts, e.g. the chloralkali process, halogen (Cl_2) and alkali base (NaOH) are produced from the haloanion and water in an aqueous solution of salt (NaCl). Water is again the source of the hydrogen. Similarly, bromine can be

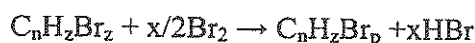
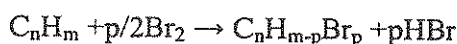
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produced from bromine salts (NaBr). In the latter instance, the production of molecular halogen from the haloanion is energetically and kinetically advantageous compared to oxygen production, requiring a lower over potential (1.1 V versus 1.6V):



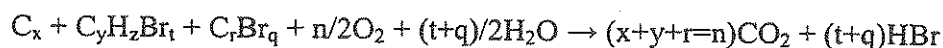
[0010] With 2×10^5 Coulombs per gram-mole H_2 and the required electrical energy reduced significantly (compared to H_2O alone) to approximately 200 kJ/g mol H_2 .

[0011] Many attempts have been made to develop economically viable hydrogen production processes. In principle, hydrocarbons can be directly oxidized electrochemically using oxygen (as in a solid oxide fuel cell) and/or water to produce hydrogen; however this typically leads to complex, difficult to separate intermediates and is not economically useful. Another means of removing hydrogen from hydrocarbons is by stepwise partial oxidation with a halogen, (preferably bromine). The major advantage is that complete oxidation of hydrocarbon to carbon dioxide cannot occur and the hydrogen is transferred to the less stable HBr ($\Delta H_{\text{formation}} = -36$ kJ/ mol), rather than water ($\Delta H_{\text{formation}} = -286$ kJ/ mol):



[0012] Final products after removal of HBr depend on the reaction conditions and may consist of mixtures of coke and brominated and perbrominated hydrocarbons: $\text{C}_x + \text{C}_y\text{H}_z\text{Br}_t + \text{C}_r\text{Br}_q$.

Combustion of these final products in an oxygen atmosphere containing trace water may be used to produce heat and carbon oxides and to convert the residual bromine to HBr:



[0013] Another process for making hydrogen, based on HBr electrolysis, reportedly yields energy savings of about 25% relative to water electrolysis. However, this process requires that bromine produced in electrolysis be converted back to HBr, and this conversion step is a major disadvantage of the HBr electrolysis route to hydrogen. In contrast, the present invention uses the

bromine generated in electrolysis to produce valuable products, rather than simply converting it back to HBr.

SUMMARY

[0014] The present disclosure combines the thermal (non-electrochemical) reactivity of halogens (preferably bromine) with hydrocarbons to produce hydrogen halide (preferably HBr) and reactive alkyl halides or other carbon-containing intermediates that may be converted to subsequent products, more readily than the original hydrocarbon, with the facile electrolysis of hydrogen halides or halide salts to create an overall process with significantly higher efficiency. The use of halogens prevents the total oxidation of the hydrocarbon to carbon dioxide and allows subsequent production of partial oxidation products.

[0014a] In a first aspect, there is provided a continuous process for converting a hydrocarbon feedstock into higher hydrocarbons, comprising:

- (a) reacting molecular halogen with a hydrocarbon feedstock so as to form alkyl halides and hydrogen halide;
- (b) contacting the alkyl halides with a catalyst so as to form higher hydrocarbons and hydrogen halide;
- (c) separating the higher hydrocarbons from the hydrogen halide;
- (d) electrolytically converting the hydrogen halide into hydrogen and molecular halogen; and
- (e) repeating steps (a) through (d) a desired number of times, wherein the molecular halogen in step (d) is used in repeated step (a).

[0014b] In a second aspect, there is provided a continuous process for converting a hydrocarbon feedstock into methanol, comprising:

- (a) reacting molecular halogen with a hydrocarbon feedstock so as to form alkyl halides and hydrogen halide;
- (b) contacting the alkyl halides with aqueous alkali so as to form methanol and alkaline halide;
- (c) separating the methanol from the alkaline halide;
- (d) electrolytically converting the alkaline halide into hydrogen, molecular halogen, and aqueous alkali; and
- (e) repeating steps (a) through (d) a desired number of times, wherein the molecular halogen in step (d) is used in repeated step (a).

[0014c] In a third aspect, there is provided a continuous process for converting a hydrocarbon feedstock into an alkyl amine, comprising:

- (a) reacting molecular halogen with a hydrocarbon feedstock so as to form alkyl halides and hydrogen halide;
- (b) contacting the alkyl halides with aqueous alkali amine so as to form alkyl amines and alkaline halide;
- (c) separating the alkyl amines from the alkaline halide;
- (d) electrolytically converting the alkaline halide into hydrogen and molecular halogen; and
- (e) repeating steps (a) through (d) a desired number of times wherein the molecular halogen in step (d) is used in repeated step (a).

[0014d] In a fourth aspect, there is provided a method comprising:

- (a) reacting molecular halogen with oil or gas pumped from a well at an oil or gas production facility so as to form alkyl halides and hydrogen halide;
- (b) contacting the alkyl halides with a catalyst so as to form higher hydrocarbons and hydrogen halide;
- (c) separating the higher hydrocarbons from hydrogen halide; and
- (d) electrolytically converting the hydrogen halide into hydrogen and molecular halogen using electricity provided by an electrical generator or electrical power supply.

[0014e] In a fifth aspect, there is provided a method comprising:

- (a) reacting molecular halogen with a hydrocarbon feedstock so as to form alkyl halides and hydrogen halide;
- (b) contacting the alkyl halides with aqueous alkali so as to form methanol and alkaline halide;
- (c) separating the methanol from the alkaline halide;
- (d) electrolytically converting the alkaline halide into hydrogen, molecular halogen, and aqueous alkali using electricity provided by an electrical generator or electrical power supply at an oil or gas production facility.

[0014f] In a sixth aspect, there is provided a continuous process for converting coal into coke and hydrogen, comprising:

- (a) reacting crushed coal with molecular halogen so as to form brominated coal intermediates and hydrogen halide;
- (b) reacting the brominated coal intermediates over a catalyst so as to form coke and hydrogen halide;
- (c) separating the coke from the hydrogen halide found in step (a) and/or step (b);
- (d) electrolytically converting the hydrogen halide found in step (a) and/or step (b) into hydrogen and molecular halogen; and
- (e) repeating steps (a) through (d) a desired number of times, wherein the molecular halogen in step (d) is used in repeated step (a).

[0014g] In a seventh aspect, there is provided a continuous process for converting coal or biomass-derived hydrocarbons into polyols, comprising:

- (a) reacting molecular halogen with coal or a biomass-derived hydrocarbon feedstock so as to form alkyl halides and hydrogen halide;
- (b) contacting the alkyl halides with aqueous alkali so as to form polyols and alkaline halide;
- (c) separating the polyols from the alkaline halide;
- (d) electrolytically converting the alkaline halide into hydrogen and molecular halogen; and

(e) repeating steps (a) through (d) a desired number of times, wherein the molecular halogen in step (d) is used in repeated step (a).

[0014h] In an eighth aspect, there is provided a continuous process for converting a hydrocarbon feedstock into higher hydrocarbons, comprising:

- (a) reacting molecular halogen with a hydrocarbon feedstock so as to form alkyl halides and hydrogen halide;
- (b) contacting the alkyl halides with a catalyst so as to form higher hydrocarbons and hydrogen halide;
- (c) separating the higher hydrocarbons from the hydrogen halide;
- (d) electrolytically converting the hydrogen halide into water and molecular halogen in an electrolytic cell or cells equipped with an oxygen depolarized cathode; and

(e) repeating steps (a) through (d) a desired number of times, wherein the molecular halogen in step (d) is used in repeated step (a).

[0014i] In a ninth aspect, there is provided a continuous process for converting a hydrocarbon feedstock into methanol, comprising:

- (a) reacting molecular halogen with a hydrocarbon feedstock so as to form alkyl halides and hydrogen halide;
- (b) contacting the alkyl halides with aqueous alkali so as to form methanol and alkaline halide;
- (c) separating the methanol from the alkaline halide;
- (d) electrolytically converting the alkaline halide into molecular halogen and aqueous alkali in an electrolytic cell or cells equipped with an oxygen depolarized cathode; and

(e) repeating steps (a) through (d) a desired number of times, wherein the molecular halogen in step (d) is used in repeated step (a).

[0015] In one embodiment, a continuous process for converting a hydrocarbon feedstock into one or more higher hydrocarbons comprises: (a) forming alkyl halides by reacting molecular halogen with a hydrocarbon feedstock under process conditions sufficient to form alkyl halides and hydrogen halide, preferably with substantially complete consumption of the molecular halogen; (b) forming higher hydrocarbons and hydrogen halide by contacting the alkyl halides with a first catalyst under process conditions sufficient to form higher hydrocarbons and hydrogen halide; (c) separating the higher hydrocarbons from hydrogen halide; (d) converting the hydrogen halide into hydrogen and molecular halogen electrolytically, thereby allowing the halogen to be reused; and (e) repeating steps (a) through (d) a desired number of times. These steps can be carried out in the order presented or, alternatively, in a different order. Electrolysis is carried out in aqueous media, or in the gas phase. Optionally, the alkyl halides are "reproportionated" by reacting some or all of the alkyl halides with an alkane feed, whereby the fraction of monohalogenated hydrocarbons present is increased. Also, in some embodiments, hydrogen produced in the process is used for power generation.

[0016] In an embodiment, a continuous process for converting a hydrocarbon feedstock into methanol comprises: (a) forming alkyl halides by reacting molecular halogen with a hydrocarbon feedstock under process conditions sufficient to form alkyl halides and hydrogen halide, preferably with substantially complete consumption of the molecular halogen; (b) forming methanol and alkaline halide by contacting the alkyl halides with aqueous alkali under process conditions sufficient to form methanol and alkaline halide; (c) separating the methanol from the alkaline halide; (d) converting the alkaline halide into hydrogen, or molecular halogen, and aqueous alkali electrolytically, thereby allowing the halogen and the alkali to be reused; and (e) repeating steps (a) through (d) a desired number of times. These steps can be carried out in the order presented or, alternatively, in a different order. Optionally, the polyhalogenated hydrocarbons are "reproportionated" by reacting some or all of the alkyl halides with an alkane feed, whereby the fraction of monohalogenated hydrocarbons present is increased.

[0017] The production of methanol by this process requires that the reaction of alkyl halides with aqueous alkali be carried out under alkaline conditions. However, the electrolysis process yields alkali and acid in stoichiometrically equivalent amounts. Hence, simply recombining all of the alkali with all of the acid would result in a neutral solution. The process described herein provides for disproportionation of the acid and base such that more than sufficient alkali is available to react with the alkyl bromides to achieve alkaline conditions. The acid removed in the disproportionation step is later recombined with the excess alkali after methanol and other products have been formed and separated.

[0018] In some embodiments it may be necessary to maintain the anolyte in acidic condition, which may require a small amount of acid to be added. The separation of a portion of the acid can be accomplished by a liquid phase process or, alternatively, by the use of a regenerable solid reactant or adsorbent. Acid can also be provided from an external source, either from on-site or

off-site generation. Alternatively, an overall excess of acid can be achieved by removal of a small amount of alkali from the system.

[0019] In an embodiment, a continuous process for converting a hydrocarbon feedstock into an alkyl amine comprises: (a) forming alkyl halides by reacting molecular halogen with a hydrocarbon feedstock under process conditions sufficient to form alkyl halides (e.g., ethyl bromide) and hydrogen halide, preferably with substantially complete consumption of the molecular halogen; (b) forming alkyl amines and alkaline halide by contacting the alkyl halides with ammonia or aqueous ammonia under process conditions sufficient to form alkyl amines and alkaline halide; (c) separating the alkyl amines from the alkaline halide; (d) converting the alkaline halide into hydrogen and molecular halogen electrolytically, thereby allowing the halogen to be reused; and (e) repeating steps (a) through (d) a desired number of times. These steps can be carried out in the order presented or, alternatively, in a different order. Optionally, the alkyl halides are "reproportionated" by reacting some or all of the alkyl halides with an alkane feed, whereby the fraction of monohalogenated hydrocarbons present is increased.

[0020] In an embodiment, a continuous process for converting coal into coke and hydrogen is provided and comprises the steps of (a) forming brominated coal intermediates and hydrogen halide by reacting crushed coal with molecular halogen under process conditions sufficient to brominate and dissociate significant elements of the coal skeleton, thereby forming a mixture of brominated coal intermediates (e.g., polybrominated hydrocarbons); (b) forming coke and hydrogen halide by reacting the brominated coal intermediates over a catalyst under process conditions sufficient to form coke and hydrogen halide; (c) separating the coke from the hydrogen halide; (d) converting hydrogen halide formed in step (a) and/or step (b) into hydrogen and molecular halogen electrolytically, thereby allowing the halogen to be reused; and (e) repeating steps (a) through (d) a desired number of times. These steps can be carried out in the order presented or, alternatively, in a different order. The coke that is produced can be used to generate

electrical power for the process (via combustion, steam generation, and production of electricity), or collected and sold.

[0021] In an embodiment, a continuous process for converting coal or biomass-derived hydrocarbons into polyols and hydrogen is provided and comprises: (a) forming alkyl halides by reacting molecular halogen with coal or a biomass-derived hydrocarbon feedstock under process conditions sufficient to form alkyl halides and hydrogen halide, preferably with substantially complete consumption of the molecular halogen; (b) forming polyols and alkaline halide by contacting the alkyl halides with aqueous alkali under process conditions sufficient to form polyols and alkaline halide; (c) separating the polyols from the alkaline halide; (d) converting the alkaline halide into hydrogen and molecular halogen electrolytically, thereby allowing the halogen to be reused; and (e) repeating steps (a) through (d) a desired number of times. These steps can be carried out in the order presented or, alternatively, in a different order. Optionally, the alkyl halides are "reproportionated" by reacting some or all of the alkyl halides with an alkane feed, whereby the fraction of monohalogenated hydrocarbons present is increased.

[0022] In an important variation of the present disclosure, an oxygen-depolarized electrode is used in the electrolyzer, and electrolysis of hydrogen halide yields molecular halogen and water, and electrolysis of alkaline halide yields molecular halogen and alkaline hydroxide, rather than hydrogen. This variation has the advantage of greatly reducing the power requirements of the electrolytic cell(s). An improved electrolytic cell, having an oxygen-depolarized electrode is also provided as yet another embodiment of the present disclosure.

[0023] A number of elements are common to various embodiments of the present disclosure, including: (1) halogenation of a hydrocarbon feedstock in the presence of molecular halogen to produce hydrogen halide and an oxidized carbon-containing product; (2) further reaction of the oxidized carbon products to produce final products; (3) separation of carbon-containing products from bromine-containing components; (4) electrolysis of the remaining halogen-containing components (e.g.,

HBr, NaBr) to form halogen and hydrogen in an electrolytic cell (or, alternatively, use of an oxygen-depolarized electrode to yield halogen and water, or halogen and alkaline hydroxide, instead of hydrogen). Hydrogen that is produced can be used to power one or more process components, or compressed and sold.

[0024] The present conventional commercial process for utilizing methane, coal, and other hydrocarbons yields syngas ($\text{CO} + \text{H}_2$), which can be converted to higher value products, such as methanol and linear alkanes. The intermediate syngas is extremely expensive to form, and the nearly fully oxidized carbon must be reduced to form useful products. When compared to the conventional syngas process, the present disclosure is superior in many respects and has at least the following advantages:

- Use of alkyl halide intermediates to produce higher value products, including fuels and higher value chemicals.
- Lower operating pressure (e.g., $\sim 1\text{-}5\text{atm}$ vs. $\sim 80\text{atm}$).
- Lower peak operating temperature (e.g., $\sim 50^\circ\text{C}$ vs. $\sim 1,000^\circ\text{C}$).
- No need for pure oxygen
- No fired reformer, and thus greater safety when used on offshore platforms.
- Simple reactor design vs. complex syngas-to-methanol converter.
- No catalyst necessary vs. catalysts required for reforming and for syngas conversion.
- Fewer by-products and thus simpler methanol purification operations.
- No steam supply for reforming is needed.
- Hydrogen is produced on a separate electrode as a relatively pure product.
- The reaction is pushed to completion in the final step by the removal of products from the reaction vessel.

[0025] According to the present disclosure, molecular halogen used to form alkyl halides is recovered as hydrogen halide and recycled to the electrolytic cell, and the alkyl halides are converted to

higher value products. Examples include the conversion of methyl bromide over a zeolite catalyst to aromatic chemicals and HBr, and conversion of mono alkyl bromides (e.g. ethyl bromide) over a catalyst to olefins (e.g. ethylene) and HBr. Alternatively, the alkyl halides are readily converted to oxygenates, such as alcohols, ethers, and aldehydes. Examples include the conversion of methyl bromide in an aqueous solution of NaOH to methanol and NaBr, and the conversion of dibromomethane in NaOH to ethylene glycol and NaBr. In still another embodiment, the alkyl halides are readily converted to amines. Examples include the conversion of bromobenzene in an aqueous solution of ammonia to phenol and aniline, and the conversion of ethyl bromide in ammonia to ethylamine and NaBr.

[0026] The present disclosure finds particular utility when it is used on-site at an oil or gas production facility, such as an offshore oil or gas rig, or at a wellhead located on land. The continuous processes described herein can be utilized in conjunction with the production of oil and/or gas, using electricity generated on-site to power the electrolytic cell(s).

BRIEF DESCRIPTION OF THE DRAWINGS

[0027] Various features, embodiments, and advantages of the invention will become better understood when considered in view of the detailed description, and by referring to the appended drawings, wherein:

[0028] FIG. 1 is a schematic diagram of a continuous process for converting a hydrocarbon feedstock into higher hydrocarbons according to one embodiment of the invention;

[0029] FIG. 2 is a schematic diagram of a continuous process for converting a hydrocarbon feedstock into higher hydrocarbons according to another embodiment of the invention;

[0030] FIG. 3 is a schematic diagram of a continuous process for converting a hydrocarbon feedstock into methanol according to one embodiment of the invention, in which a membrane-type electrolytic cell is used to regenerate molecular bromine;

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[0031] FIG. 4 is a schematic diagram of a continuous process for converting a hydrocarbon feedstock into methanol according to another embodiment of the invention, in which a diaphragm-type electrolytic cell is used to generate molecular bromine;

[0032] FIG. 5 is a schematic diagram of a continuous process for converting a hydrocarbon feedstock into higher hydrocarbons in which an oxygen-depolarized cathode is provided, according to one embodiment of the invention;

[0033] FIG. 6. is a schematic illustration of an electrolytic cell according to one embodiment of the invention;

[0034] FIG. 7 is a schematic illustration of a continuous process for converting coal into coke and hydrogen, according to one embodiment of the invention;

[0035] FIG. 8 is a schematic illustration of a process for converting coal or biomass into polyols and hydrogen, according to one embodiment of the invention;

[0036] FIG. 9 is a chart illustrating product selectivity for bromination of methane according to one embodiment of the invention;

[0037] FIG. 10 is a chart illustrating product selectivity for coupling of methyl bromide according to one embodiment of the invention; and

[0038] FIG. 11 is a chart illustrating product selectivity for coupling of methyl bromide according to another embodiment of the invention.

DETAILED DESCRIPTION OF THE INVENTION

[0039] The present invention provides a chemical process for converting hydrocarbon feedstocks into higher value products, such as fuel-grade hydrocarbons, methanol, aromatics, amines, coke, and polyols, using molecular halogen to activate C-H bonds in the feedstock and electrolysis to convert hydrohalic acid (hydrogen halide) or halide salts (e.g., sodium bromide) formed in the process back into molecular halogen. Nonlimiting examples of hydrocarbon

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feedstocks appropriate for use in the present invention include alkanes, e.g., methane, ethane, propane, and even larger alkanes; olefins; natural gas and other mixtures of hydrocarbons; biomass-derived hydrocarbons; and coal. Certain oil refinery processes yield light hydrocarbon streams (so-called "light-ends"), typically a mixture of C₁-C₃ hydrocarbons, which can be used with or without added methane as the hydrocarbon feedstock. With the exception of coal, in most cases the feedstock will be primarily aliphatic in nature.

[0040] The hydrocarbon feedstock is converted into higher products by reaction with molecular halogen, as described below. Bromine (Br₂) and chlorine (Cl₂) are preferred, with bromine being most preferred, in part because the over potential required to convert Br⁻ to Br₂ is significantly lower than that required to convert Cl⁻ to Cl₂ (1.09V for Br⁻ vs. 1.36V for Cl⁻). It is contemplated that fluorine and iodine can be used, though not necessarily with equivalent results. Some of the problems associated with fluorine can likely be addressed by using dilute streams of fluorine (e.g., fluorine gas carried by helium nitrogen, or other diluent). It is expected, however, that more vigorous reaction conditions will be required for alkyl fluorides to couple and form higher hydrocarbons, due to the strength of the fluorine-carbon bond. Similarly, problems associated with iodine (such as the endothermic nature of certain iodine reactions) can likely be addressed by carrying out the halogenation and/or coupling reactions at higher temperatures and/or pressures. In general, the use of bromine or chlorine is preferred, with bromine being most preferred.

[0041] As used herein, the term "higher hydrocarbons" refers to hydrocarbons having a greater number of carbon atoms than one or more components of the hydrocarbon feedstock, as well as olefinic hydrocarbons having the same or a greater number of carbon atoms as one or more components of the hydrocarbon feedstock. For instance, if the feedstock is natural gas -- typically a mixture of light hydrocarbons, predominantly methane, with lesser amounts of ethane, propane and butane, and even smaller amounts of longer chain hydrocarbon such as pentane, hexane, etc. -- the "higher hydrocarbon(s)" produced according to the invention can include a C₂ or higher

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hydrocarbon, such as ethane, propane, butane, C₅+ hydrocarbons, aromatic hydrocarbons, etc., and optionally ethylene, propylene and/or longer olefins. The term "light hydrocarbons" (sometimes abbreviated "LHCs") refers to C₁-C₄ hydrocarbons, e.g., methane, ethane, propane, ethylene, propylene, butanes, and butenes, all of which are normally gasses at room temperature and atmospheric pressure. Fuel grade hydrocarbons typically have 5 or more carbons and are liquids at room temperature.

[0042] Both in this written description and in the claims, when chemical substances are referred to in the plural, singular referents are also included, and vice versa, unless the context clearly dictates otherwise. For example, "alkyl halides" includes one or more alkyl halides, which can be the same (e.g., 100% methyl bromide) or different (e.g., methyl bromide and dibromomethane); "higher hydrocarbons" includes one or more higher hydrocarbons, which can be the same (e.g., 100% octane) or different (e.g., hexane, pentane, and octane).

[0043] FIGS. 1-5 are schematic flow diagrams generally depicting different embodiments of the invention, in which a hydrocarbon feedstock is allowed to react with molecular halogen (e.g., bromine) and converted into one or more higher value products. Referring to FIG. 1, one embodiment of a process for making higher hydrocarbons from natural gas, methane, or other light hydrocarbons is depicted. The feedstock (e.g., natural gas) and molecular bromine are carried by separate lines 1, 2 into a bromination reactor 3 and allowed to react. Products (HBr, alkyl bromides, optionally olefins), and possibly unreacted hydrocarbons, exit the reactor and are carried by a line 4 into a carbon-carbon coupling reactor 5. Optionally, the alkyl bromides are first routed to a separation unit (not shown), where monobrominated hydrocarbons and HBr are separated from polybrominated hydrocarbons, with the latter being carried back to the bromination reactor to undergo "reproportionation" with methane and/or other light hydrocarbons, as described in the '358 application.

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[0044] In the coupling reactor 5, monobromides and possibly other alkyl bromides and olefins react in the presence of a coupling catalyst to form higher hydrocarbons. Nonlimiting examples of coupling catalysts are provided in the '358 application, at ¶¶61-65. The preparation of doped zeolites and their use as carbon-carbon coupling catalysts is described in Patent Publication No. US 2005/0171393 A1, at pages 4-5, which is incorporated by reference herein in its entirety.

[0045] HBr, higher hydrocarbons, and (possibly) unreacted hydrocarbons and alkyl bromides exit the coupling reactor and are carried by a line 6 to a hydrogen bromide absorption unit 7, where hydrocarbon products are separated from HBr via absorption, distillation, and/or some other suitable separation technique. Hydrocarbon products are carried away by a line 8 to a product recovery unit 9, which separates the higher hydrocarbon products from any residual natural gas or other gaseous species, which can be vented through a line 10 or, in the case of natural gas or lower alkanes, recycled and carried back to the bromination reactor. Alternatively, combustible species can be routed to a power generation unit and used to generate heat and/or electricity for the system.

[0046] Aqueous sodium hydroxide or other alkali is carried by a line 11 into the HBr absorption unit, where it neutralizes the HBr, and forms aqueous sodium bromide. The aqueous sodium bromide and minor amounts of hydrocarbon products and other organic species are carried by a line 12 to a separation unit 13, which operates via distillation, liquid-liquid extraction, flash vaporization, or some other suitable method to separate the organic components from the sodium bromide. The organics are either routed away from the system to a separate product cleanup unit or, in the embodiment shown, returned to the HBr absorption unit 7 through a line 14 and ultimately exit the system via line 8.

[0047] Aqueous sodium bromide is carried from the NaBr-organics separation unit 13 by a line 15 to an electrolytic cell 16, having an anode 17, and a cathode 18. An inlet line 19 is provided for the addition of water, additional electrolyte, and/or acid or alkali for pH control. More preferably, a series of electrolytic cells, rather than a single cell, is used as an electrolyzer. As an alternative,

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several series of cells can be connected in parallel. Nonlimiting examples of electrolytic cells include diaphragm, membrane, and mercury cell, which can be mono-polar or di-polar. The exact material flows with respect to make-up water, electrolyte, and other process features will vary with the type of cell used. Aqueous sodium bromide is electrolyzed in the electrolytic cell(s), with bromide ion being oxidized at the anode ($2\text{Br}^- \rightarrow \text{Br}_2 + 2\text{e}^-$) and water being reduced at the cathode ($2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$). Aqueous sodium hydroxide is removed from the electrolyzer and routed to the HBr absorption unit via line 11.

[0048] Bromine and hydrogen produced in the electrolyzer are recovered, with bromine being recycled and used again in the process. Specifically, wet bromine is carried by a line 20 to a dryer 21, and dry bromine is carried by a line 22 to a heater 23, and then by line 2 back into the bromination reactor 3. In instances where the amount of water associated with the bromine is tolerable in bromination and coupling, the dryer may be eliminated. Hydrogen produced at the anode of the electrolytic cell can be off-gassed or, more preferably, collected, compressed, and routed through a line 24 to a power generation unit, such as a fuel cell or hydrogen turbine. Alternatively, hydrogen produced can be recovered for sale or other use. The electrical power that is generated can be used to power various pieces of equipment employed in the continuous process, including the electrolytic cells.

[0049] Exemplary and preferred conditions (e.g., catalysts, pressure, temperature, residence time, etc.) for bromination, C-C coupling, reproporationation, product separation, HBr clean-up, and corrosion-resistant materials are provided in the '358 application at ¶¶39-42 (bromination), 43-50 (reproporationation), 61-65 (C-C coupling), 66-75 (product separation), 82-86(HBr clean-up and halogen recovery), and 87-90 (corrosion-resistant materials), which paragraphs are incorporated herein in their entirety. Anodes, cathodes, electrolytes, and other features of the electrolytic cell(s) are selected based on a number of factors understood by the skilled person, such as throughput, current power levels, and the chemistry of the electrolysis reaction(s). Nonlimiting examples are

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found in U.S. Patent Nos. 4,110,180 (Nidola et al.) and 6,368,490 (Gestermann); Y. Shimizu, N. Miura, N. Yamazoe, *Gas-Phase Electrolysis of Hydrocarbonic Acid Using PTFE-Bonded Electrode*, Int. J. Hydrogen Energy, Vol. 13, No. 6, 345-349 (1988); D. van Velzen, H. Langenkamp, A. Moryoussef, P. Millington, *HBr Electrolysis in the Ispara Mark 13A Flue Gas Desulphurization Process: Electrolysis in a DEM Cell*, J. Applied Electrochemistry, Vol. 20, 60-68 (1990); and S. Motupally, D. Mak, F. Freire, J. Weidner, *Recycling Chlorine from Hydrogen Chloride*, The Electrochemical Society Interface, Fall 1998, 32-36, each of which is incorporated by reference herein in their entirety.

[0050] In one embodiment of the invention, illustrated in FIG. 1, methane is introduced into a plug flow reactor made of the alloy ALCOR, at a rate of 1 mole/second, and molecular bromine is introduced at a rate of 0.50 moles/second with a total residence time of a 60 seconds at 425°C. The major hydrocarbon products include methyl bromide (85%) and dibromomethane (14%), and 0.50 moles/s of HBr is produced. The methane conversion is 46%. The products are carried by a line 4 into a coupling reactor 5, which is a packed bed reactor containing a transition metal (e.g., Mn) ion-exchanged alumina-supported ZSM5 zeolite coupling catalyst at 425°C. In the coupling reactor 5, a distribution of higher hydrocarbons is formed, as determined by the space time of the reactor. In this example, 10 seconds is preferred to produce products that are in the gasoline range. HBr, higher hydrocarbons, and (trace) unreacted alkyl bromides exit the coupling reactor and are carried by a line 6 to a hydrogen bromide separation unit 7, where HBr is partially separated by distillation. Aqueous sodium hydroxide is introduced and allowed to react at 150°C, forming sodium bromide and alcohols from the HBr and unreacted alkyl bromides. The aqueous and organic species are carried by a line 12 to a separation unit 13, which operates via distillation to separate the organic components from the sodium bromide. Aqueous sodium bromide is carried from the NaBr-organics separation unit 13 by line 15 to an electrolytic cell 16, having an anode 17, and a cathode 18. An inlet line 19 is provided for the addition of water, additional electrolyte, and the pH

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adjusted to be less than 2 by addition of acid. Electrolysis is performed in a membrane cell type. Aqueous sodium bromide is electrolyzed in the electrolytic cell, with bromide ion being oxidized at the anode ($2\text{Br}^- \rightarrow \text{Br}_2 + 2\text{e}^-$) and water being reduced at the cathode ($2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$). Aqueous sodium hydroxide is removed from the electrolyzer and routed to the HBr absorption unit via line 11. Bromine and hydrogen are produced in the electrolyzer.

[0051] Referring to FIG. 2, an alternate embodiment for converting natural gas, methane, or other hydrocarbon feedstocks into higher hydrocarbons, such as fuel grade hydrocarbons and aromatic compounds, is depicted. In this embodiment, electrolysis takes place in a non-alkaline medium. Products from the coupling reactor (i.e., higher hydrocarbons and HBr) are carried by a line 6 to an HBr absorption unit 7, where hydrocarbon products are separated from HBr. After residual organic components are removed from the HBr in a separation unit 13, rich aqueous HBr is carried by a line 15 to the electrolytic cell 16. Make-up water, electrolyte, or acid/base for pH control, if needed, is provided by a line 19. The aqueous HBr is electrolyzed, forming molecular bromine and hydrogen. As Br_2 is evolved and removed from the electrolyzer, the concentration of HBr in the electrolyzer drops. The resulting lean aqueous HBr, along with some bromine (Br_2) entrained or dissolved therein, is carried by a line 25 to a bromine stripper 26, which separates bromine (Br_2) from lean aqueous HBr via distillation or some other suitable separation operation. The lean aqueous HBr is carried back to the HBr absorption unit by a line 27. Wet bromine is carried by a line 28 to the dryer 21, where it is dried.

[0052] In another embodiment of this aspect of the invention (not shown), natural gas, methane, or another hydrocarbon feedstock is converted into higher hydrocarbons, and halogen (e.g., Br_2) is recovered by gas phase electrolysis of hydrogen halide (e.g., HBr). Products from the coupling reactor (i.e., higher hydrocarbons and HBr) are carried by a line to an HBr absorption unit, where hydrocarbon products are separated from HBr. After residual organic components are removed from the HBr in a separation unit, gaseous HBr is carried by a line to the electrolytic cell.

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The gaseous HBr is electrolyzed, forming molecular bromine and hydrogen. Wet bromine is carried by a line to the dryer, where it is dried. Optionally, if dry HBr is fed to the electrolysis
5 cells, the dryer can be eliminated.

[0053] FIG. 3 depicts one embodiment of another aspect of the invention, in which natural gas, methane, or another hydrocarbon feedstock is converted into methanol via the intermediate, methyl bromide. Natural gas and gaseous bromine are carried by separate lines 201 and 202 into a bromination reactor 203 and allowed to react. The products (e.g., methyl bromide and HBr), and
10 possibly unreacted hydrocarbons, are carried by a line 204 through a heat exchanger 205, which lowers their temperature. If necessary, the gasses are further cooled by passing through a cooler 206. A portion of the gasses 206 are carried by a line 207 to an HBr absorber 208. The remainder by-passes the HBr absorber and are carried by a line 209 directly to the reactor/absorber 210. The split proportions are determined by the acid/base disproportionation needed to achieve the proper
15 pH in the reactor absorber.

[0054] Water, optionally pre-treated in, e.g., a reverse osmosis unit 211 to minimize salt content, is provided to the methanol reactor 210 via line 212. In addition, a separate line 213 carries water to the HBr absorber 208.

[0055] HBr solution formed in the HBr absorber 208 is sent via a line 214 to a stripper 215
20 (where organics are separated by stripping or other means) and then sent to the reactor/absorber 210 via a line 216. Gasses from the HBr absorber join the by-passed stream from the cooler 206 and are carried by a line 209 to the reactor/absorber 210. HBr solution from the stripper 215 is carried by a line 217 to an HBr holding tank 218.

[0056] Aqueous sodium hydroxide (e.g., 5-30 wt %) is provided to the methanol reactor 210
25 by a line 219. A weak NaBr/water solution is also delivered to the methanol reactor 210 by a line 220.

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[0057] In the methanol formation reactor, methyl bromide reacts with water in the presence of strong base (sodium hydroxide), and methanol is formed, along with possible byproducts such as formaldehyde or formic acid. A liquid stream containing methanol, by-products, aqueous sodium bromide, and aqueous sodium hydroxide is carried away from the reactor via a line 221, to a stripper 222. A portion of the bottom liquid from the reactor/absorber 210 is circulated via a line 223 through a cooler 224 to control temperature in the reactor/absorber 210.

[0058] The stripper 222 is equipped with a reboiler 225 and, optionally, a partial reflux. Aqueous sodium bromide and sodium hydroxide are removed with most of the water as the "bottoms" stream of the stripper. The vapor exiting the top of the stripper is carried by a line 226 to another distillation unit 227 equipped with a reboiler 228 and a condenser 229. In the distillation unit 227, by-products are separated from methanol, and the methanol is removed from the distillation unit 227 via a line 230, through a cooler 231, to a storage tank 232. The vapor from the distillation unit 227 (which contains by-products) is carried via a line 233 through the condenser 229 and then through a line 234 to a by-product storage tank 235. Optionally, depending on the particular by-products produced and their boiling points, methanol may be taken as a distillate while by-products are recovered as bottoms.

[0059] The effluent stream removed from the distillation unit 222 and reboiler 225 contains water and aqueous sodium bromide and sodium hydroxide. This is carried away from the distillation unit via a line 236 and cooled by passing through a cooler 237 before being delivered to a sodium bromide holding tank 238. It is desirable to lower the pH of this salt solution. This is accomplished by metering the delivery of aqueous HBr from the hydrogen bromide holding tank 218 via a line 239 to a pH control device 240 coupled to the sodium bromide holding tank 238.

[0060] With the pH of the sodium bromide in the holding tank 238 brought to the desired level (e.g., slightly acidic), aqueous sodium bromide is removed from the tank and carried via a line 241 through a filter 242, and delivered to an electrolytic cell 243, having an anode 244 and a cathode

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245. The filter is provided to protect the membranes in the electrolytic cells. Preferably, a series of electrolytic cells, rather than a single cell, is used as an electrolyzer.

[0061] Aqueous sodium bromide is electrolyzed in the electrolytic cell(s), with bromide ion being oxidized at the anode ($2\text{Br}^- \rightarrow \text{Br}_2 + 2\text{e}^-$) and water being reduced at the cathode ($2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$). This results in the formation of sodium hydroxide, which is carried away from the electrolyzer as an aqueous solution via line 246 to a holding tank 247. The sodium hydroxide solution is then routed to the methanol reactor 210 via a line 219.

[0062] Molecular bromine is removed from the electrolyzer via a line 248 to a compressor 249, and then to a dryer 250. The bromine is returned to the bromination reactor 203 by passing it through a heat exchanger 205 and, if necessary, a heater 251. Molecular bromine that is dissolved in the anolyte is also removed from the electrolytic cell(s) 243 by carrying the anolyte from the cell(s) via a line 252 to a stripper 253, where bromine is removed by stripping with natural gas (supplied via a line 254) or by other means. The molecular bromine is carried by a line 255 to the compressor 249, dryer 250, etc., before being returned to the bromination reactor as described above.

[0063] Hydrogen generated in the electrolyzer is removed by a line 256, compressed in a compressor 257 and, optionally, routed to a power generation unit 258. Residual methane or other inert gasses can be removed from the methanol formation reactor via a line 259. The methane or natural gas can be routed to the power generation unit 258 to augment power generation. Additional natural gas or methane can be supplied to the unit via a line 260 if needed.

[0064] In a laboratory implementation of elements of the process depicted in FIG. 3, methane is reacted with gaseous bromine at 450°C in a glass tube bromination reactor, with a space time is a 60 seconds. The products are methyl bromide, HBr, and dibromomethane with a methane conversion of 75%. In the methanol formation reactor, the methyl bromide, HBr, and dibromomethane, react with water in the presence of sodium hydroxide to form methanol and

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formaldehyde (from the dibromomethane). It is further demonstrated that the formaldehyde is disproportionated to methanol and formic acid. Hence, overall, the products are methanol and formic acid.

[0065] The process shown in FIG. 3 employs membrane-type electrolytic cells, rather than diaphragm-type cells. In a membrane cell, sodium ions with only a small amount of water flow to the cathode compartment. In contrast, in a diaphragm-type cell, both sodium ions and water proceed into the cathode compartment. In an alternate embodiment of the invention shown in FIG. 4, diaphragm cells are used, resulting in continuous depletion of the anolyte with respect to NaBr. To replenish the NaBr, depleted anolyte is taken through a line 252 to a bromine stripper 253 where bromine is removed and carried to a compressor 249 and then a dryer 250. NaBr solution from the stripper 253 is carried by a line 270 to the NaBr holding tank 238, where it combines with a richer NaBr solution. Other features of the process are similar to those in FIG. 3.

[0066] In another aspect of the invention, molecular halogen is recovered by electrolysis using a non-hydrogen producing cathode, i.e., an oxygen depolarized cathode, which significantly reduces the power consumption by producing water instead of hydrogen. FIG. 5 depicts one embodiment of this aspect of the invention, in this case involving the production of higher hydrocarbons. The flow diagram is similar to that shown in FIG. 1, with the differences noted below.

[0067] Bromine and natural gas, methane, or another light hydrocarbon are caused to react in a bromination reactor 303, and followed by a coupling reactor 305. The organics and HBr are separated in an HBr absorption unit 307. Aqueous sodium bromide is carried via line 315 to an electrolytic cell 316 equipped with an anode 317, oxygen depolarized cathode 318, and an oxygen inlet manifold or line 324. Optionally, additional water or electrolyte or pH control chemicals are carried into the cell via a line 319.

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[0068] Molecular bromine is generated at the anode ($2\text{Br}^- \rightarrow \text{Br}_2 + 2\text{e}^-$), and the wet bromine is carried via a line 320 to a dryer 321, through a heater 323, and then routed back to the bromination reactor 303. At the cathode, oxygen is electrolytically reduced in the presence of water ($\frac{1}{2}\text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{OH}^-$), and hydroxyl ions are carried away as aqueous sodium hydroxide, via line 311, to the HBr absorption unit 307.

[0069] The invention also provides an improved electrolytic cell for converting halides into molecular halogen, one embodiment of which is shown in FIG. 6. The cell 400 includes a gas supply manifold 401, through which oxygen gas, air, or oxygen-enriched air can be introduced; a gas diffusion cathode 402, which is permeable to oxygen (or an oxygen-containing gas); a cation exchange membrane 403; a cathode electrolyte chamber 404 disposed between the cation exchange membrane and the gas diffusion cathode; an anode electrolyte chamber 405; and an anode 406, extending into the anode electrolyte chamber. When operating under basic (alkaline) conditions, water is introduced into the cathode electrolyte chamber through a port 407, and aqueous sodium hydroxide is removed from the chamber via another port 408. Similarly, aqueous sodium bromide is introduced into the anode electrolyte chamber through a port 409, and molecular bromine is carried away from the anode electrolyte chamber via a line 410. The anode and cathode can be connected to an electrical power supply (not shown), which may include equipment for converting AC to DC current (e.g. mechanical rectifier, motor-generator set, semiconductor rectifier, synchronous converter, etc.) and other components.

[0070] In operation, water is introduced into the cathode electrolyte chamber through the water inlet port 407, and aqueous sodium bromide is introduced into the anode electrolyte chamber 405 through port 409. Oxygen flow through the gas supply manifold 401 is commenced and the power to the cell is turned on. Sodium bromide is reduced at the anode, bromine gas is evolved and carried away by line 410, and sodium ions are carried through the cation exchange membrane into the cathode electrolyte chamber. At the cathode, oxygen is electrolytically reduced to hydroxyl ion

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in the presence of water. Aqueous sodium hydroxide exits the cathode electrolyte chamber through port 408.

5 [0071] The electrolytic cell described herein can be used in conjunction with various processes, including the embodiments presented above. It is particularly advantageous when power consumption is an issue, and where it is desirable not to form hydrogen (for example, where the risk of fire warrants extra precautions, such as on an offshore drilling rig).

10 [0072] Although the invention can be used in a variety of industrial settings, particular value is realized where a continuous process as described herein for making, e.g., higher hydrocarbons or methanol, is carried out at an offshore oil rig or drilling platform, or at a facility located onshore in a remote location. Part of the utility lies in the conversion of a difficult to transport material (e.g., natural gas) into a more easily transported liquid material, such as higher hydrocarbons or methanol. Another utility resides in the use of the production facility's existing electrical
15 generation capacity, such as an electrical generator or other power supply.

[0073] According to one embodiment of this aspect of the invention, an improved production facility where oil or gas is pumped from a well and thereby extracted from the earth is provided, the facility having an electrical generator or other electrical power supply, the improvement comprising: (a) forming alkyl halides by reacting molecular halogen with oil or gas pumped from
20 the well, under process conditions sufficient to form alkyl halides and hydrogen halide, optionally with substantially complete consumption of the molecular halogen; (b) forming higher hydrocarbons and hydrogen halide by contacting the alkyl halides with a first catalyst under process conditions sufficient to form higher hydrocarbons and hydrogen halide; (c) separating the higher hydrocarbons from hydrogen halide; and (d) converting the hydrogen halide into hydrogen
25 and molecular halogen electrolytically, using electricity provided by the electrical generator or electrical power supply, thereby allowing the halogen to be reused.

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[0074] In another embodiment, an improved production facility where oil or gas is pumped from a well and thereby extracted from the earth is provided, the facility having an electrical generator or other electrical power supply, the improvement comprising: (a) forming alkyl halides by reacting molecular halogen with a hydrocarbon feedstock under process conditions sufficient to form alkyl halides and hydrogen halide, optionally with substantially complete consumption of the molecular halogen; (b) forming methanol and alkaline halide by contacting the alkyl halides with aqueous alkali under process conditions sufficient to form methanol and alkaline halide; (c) separating the methanol from the alkaline halide; (d) converting the alkaline halide into hydrogen, molecular halogen, and aqueous alkali electrolytically, using electricity provided by the electrical generator or electrical power supply, thereby allowing the halogen and the alkali to be reused.

[0075] In another aspect of the invention, the general approach described above, including the steps of halogenation, product formation, product separation, and electrolytic regeneration of halogen is used to make alkyl amines. Thus, in one embodiment, natural gas, methane, or another aliphatic hydrocarbon feedstock is converted into alkyl amines via intermediate alkyl bromides. The feedstock and gaseous bromine are carried by separate lines into a bromination reactor and allowed to react. The bromination products (e.g., methyl bromide and HBr), and possibly unreacted hydrocarbons, are carried by a line through a heat exchanger, which lowers their temperature. The alkyl bromides are then carried by a line to an amination reactor. Ammonia or aqueous ammonia is also provided to the amination reactor by a separate line. The alkyl bromide and ammonia are allowed to react under process conditions sufficient to form alkyl amines (e.g., RN_2) and sodium bromide, which are then separated in a manner analogous to that described above with respect to the production of methanol. Aqueous sodium bromide is carried by a line to an electrolytic cell or cells, where it is converted into hydrogen and molecular bromine electrolytically, thereby allowing the bromine to be reused in the next cycle.

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[0076] Referring now to FIGS. 7 and 8, two other aspects of the invention are presented, in which coal is converted to higher value coke, or coal or biomass is converted into higher value polyols (poly-alcohols), and the halogen used in the process is regenerated electrolytically. In the embodiments shown in FIG. 7, crushed coal is allowed to react with molecular bromine at elevated temperature, forming coke, HBr, and brominated coal intermediates (" C_xBr_n "). The brominated coal intermediates are converted into coke by allowing them to contact a catalyst, thereby forming additional hydrogen bromide. The coke and hydrogen bromide are then separated, and the hydrogen bromide is then carried by a line to an electrolytic cell or cells, similar to that described above, thereby allowing molecular bromine to be regenerated and reused.

[0077] FIG. 8 depicts a similar process in which coal or biomass-derived hydrocarbons are brominated, thereby forming alkyl bromines or alkyl bromides and HBr, which are then processed in a manner analogous to that described above, e.g., the alkyl bromides and HBr are at least partially separated and the alkyl bromides are allowed to react with alkali, (e.g., sodium hydroxide), thereby forming sodium bromide, water, and poly-alcohols (" $C_xH_{y-q}(OH)_q$ "). The poly-alcohols are separated from sodium bromide, and the aqueous sodium bromide is carried by a line to an electrolytic cell or cells, where molecular bromine is regenerated and subsequently separated and reused.

[0078] The following nonlimiting examples illustrate various embodiments or features of the invention, including methane bromination, C-C coupling to form higher hydrocarbons, e.g., light olefins and aromatics (benzene, toluene, xylenes ("BTX")), hydrolysis of methyl bromide to methanol, hydrolysis of dibromomethane to methanol and formaldehyde, and subsequent disproportionation to formic acid.

[0079] Example 1 Bromination of Methane

Methane (11 sccm, 1.0atm) was combined with nitrogen (15 sccm, 1.0atm) at room temperature via a mixing tee and passed through an 18°C bubbler full of bromine. The $CH_4/N_2/Br_2$

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mixture was passed into a preheated glass tube (inside diameter 2.29 cm, length, 30.48 cm, filled with glass beads) at 500°C, where bromination of methane took place with a residence time of 60 seconds, producing primarily bromomethane, dibromomethane and HBr:



As products left the reactor, they were collected by a series of traps containing 4M NaOH, which neutralized the HBr and hexadecane (containing octadecane as an internal standard) to dissolve as much of the hydrocarbon products as possible. Volatile components like methane were collected in a gas bag after the HBr/hydrocarbon traps.

After the bromination reaction, the coke or carbonaceous deposits were burned off in a flow of heated air (5sccm) at 500°C for 4 hours, and the CO₂ was captured with a saturated barium hydroxide solution as barium carbonate. All products were quantified by GC. The amount of coke was determined based on the CO₂ evolution from decoking. The results are summarized in FIG. 9.

Example 2 CH₃Br Coupling to Light Olefins

2.27g of a 5% Mg-doped ZSM-5 (CBV8014) zeolite was loaded in a tubular quartz reactor (1.0cm ID), which was preheated to 400°C before the reaction. CH₃Br, diluted by N₂, was pumped into the reactor at a flow rate of 24μl/min for CH₃Br, controlled by a micro liquid pump, and 93.3ml/min for N₂. The CH₃Br coupling reaction took place over the catalyst bed with a residence time of 0.5sec and a CH₃Br partial pressure of 0.1 based on this flow rate setting.

After one hour of reaction, the products left the reactor and were collected by a series of traps containing 4M NaOH, which neutralized the HBr and hexadecane (containing octadecane as an internal standard) to dissolve as much of the hydrocarbon products as possible. Volatile components like methane and light olefins were collected in a gas bag after the HBr/hydrocarbon traps.

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After the coupling reaction, the coke or carbonaceous deposits were burned off in a flow of heated air (5sccm) at 500°C for 4hours, and the CO₂ was captured with a saturated barium hydroxide solution as barium carbonate. All products were quantified by GC. The amount of coke was determined based on the CO₂ evolution from decoking. The results are summarized in FIG. 10.

Even at such a short residence time, CH₃Br conversion reached 97.7%. Among the coupling products, C₃H₆ and C₂H₄ are the major products, and the sum of them contributed to 50% of carbon recovery. BTX, other hydrocarbons, bromohydrocarbons and a tiny amount of coke made up the balance of the converted carbon.

Example 3 CH₃Br Coupling to BTX

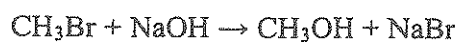
Pellets of Mn ion exchanged ZSM-5 zeolite (CBV3024, 6 cm in length) were loaded in a tubular quartz reactor (ID, 1.0cm), which was preheated to 425°C before the reaction. CH₃Br, diluted by N₂, was pumped into the reactor at a flow rate of 18μl/min for CH₃Br, controlled by a micro liquid pump, and 7.8ml/min for N₂. The CH₃Br coupling reaction took place over the catalyst bed with a residence time of 5.0 sec and a CH₃Br partial pressure of 0.5 based on this flow rate setting.

After one hour of reaction, the products left the reactor and were collected by a series of traps containing 4M NaOH, which neutralized the HBr and hexadecane (containing octadecane as an internal standard) to dissolve as much of the hydrocarbon products as possible. Volatile components like methane and light olefins were collected in a gas bag after the HBr/hydrocarbon traps.

After the coupling reaction, the coke or carbonaceous deposits were burned off in a flow of heated air (5sccm) at 500°C for 4hours, and the CO₂ was captured with a saturated barium hydroxide solution as barium carbonate. All products were quantified by GC. The amount of coke was determined based on the CO₂ evolution from decoking. The results are summarized in FIG. 8.

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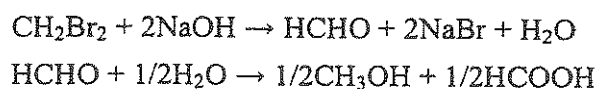
With this BTX maximum operation mode, CH₃Br can be converted completely. BTX yield reached 35.9%. Other hydrocarbons, aromatics, bromohydrocarbons, and coke contributed to the carbon recovery of 51.4%, 4.8%, 1.0%, and 6.9% respectively. Propane is a major components of the "other hydrocarbons," and can be sent back for reproporationation followed by further coupling to boost the overall BTX yield even higher.

Example 4 Caustic Hydrolysis of Bromomethane to Methanol

In a 30ml stainless steel VCR reactor equipped with a stir bar, 13.2g 1M sodium hydroxide aqueous solution (13.2mmol) and 1.3g bromomethane (12.6mmol) were added in sequence. The reactor was gently purged with nitrogen to remove the upper air before closing the cap. The closed reactor was placed in an aluminum heating block preheated to 150°C and the reaction started simultaneously. The reaction was run for 2 hours at this temperature with stirring.

After stopping the reaction, the reactor was placed in an ice-water bath for a start time to cool the products inside. After opening the reactor, the reaction liquid was transferred to a vessel and diluted by cold water. The vessel was connected with a gas bag used to collect the un-reacted bromomethane, if any. The reaction liquid was weighed and the product concentrations were analyzed with a GC-FID, in which an aqueous injection applicable capillary column was installed.

The gas product analysis shows that there was no bromomethane remaining, indicating that bromomethane was converted completely. Based on the concentration measurements for the liquid product, the methanol yield including tiny amount of dimethyl ether, was calculated to be 96%.

Example 5 Caustic Hydrolysis of Dibromomethane to Formaldehyde Followed by Disproportionation to Methanol and Formic Acid

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5 Caustic hydrolysis of dibromomethane was carried out according to the same procedure as in Example 5, with the exception that a high NaOH/CH₂Br₂ ratio (2.26) was employed. After collecting the reaction liquid, a sufficient quantity of concentrated hydrogen chloride solution was added to neutralize the extra sodium hydroxide and acidify sodium formate. Methanol and formic acid were observed to be the only products, indicating that hydrolysis to methanol and formaldehyde was followed by complete disproportionation of formaldehyde to (additional) methanol and formic acid. The GC analysis shows that the conversion of dibromomethane reached 99.9%; while the yields of methanol and formic acid reached 48.5% and 47.4% respectively.

10 Examples 4 and 5 demonstrate that bromomethane can be completely hydrolyzed to methanol, and dibromomethane can be completely hydrolyzed to methanol and formic acid, under mild caustic conditions. The results are summarized in Table 1.

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Table 1
Caustic Hydrolysis of CH_3Br and CH_2Br_2 and
Subsequent Disproportionation of HCHO

	Starting from	
	CH_3Br	CH_2Br_2
NaOH/ CH_3Br or CH_2Br_2	1.05	2.17
Temperature ($^{\circ}\text{C}$)	150	150
Reaction time (hr)	2	2
Conversion (%)	100.0	99.9
CH_3OH yield (%)	96.0	48.5
HCOOH yield (%)		47.4

[0080] The invention has been described with reference to various representative and preferred embodiments, but is not limited thereto. Other modifications and equivalent arrangements, apparent to a skilled person upon consideration of this disclosure, are also included within the scope of the invention.

[0081] As one example, molecular bromine can also be removed from the electrolytic cell(s) using a concurrent extraction technique, wherein an inert organic solvent, such as chloroform, carbon tetrachloride, ether, etc. is used. The solvent is introduced on one side of a cell; bromine partitions between the aqueous and organic phases; and bromine-laden solvent is withdrawn from another side of the cell. Bromine can then be separated from the solvent by distillation or another suitable technique and then returned to the system for reuse. Partitioning is favored by bromine's significantly enhanced solubility in solvents such as chloroform and carbon tetrachloride, as compared to water. Extraction in this way serves a dual purpose: it separates Br_2 from other forms of bromine that may be present (e.g., Br^- , OBr^- , which are insoluble in the organic phase); and it allows bromine to be concentrated and easily separated from the organic phase (e.g., by

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distillation). An optimal pH for extraction (as well as for separation of bromine by heating
bromine-containing aqueous solutions in a gas flow) is pH 3.5--the pH at which the concentration
5 of molecular bromine (Br_2) is at its highest, as compared to other bromine species.

[0082] As another example of modifications to the process disclosed herein, various pumps,
valves, heaters, coolers, heat exchangers, control units, power supplies, and equipment in addition
or in the alternative to that shown in the figures can be employed to optimize the processes. In
addition, other features and embodiments, such as described in the '358 application and elsewhere,
10 can be utilized in the practice of the present invention. The invention is limited only by the
accompanying claims and their equivalents.

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WHAT IS CLAIMED IS:

1. A continuous process for converting a hydrocarbon feedstock into higher hydrocarbons, comprising:
 - (a) reacting molecular halogen with a hydrocarbon feedstock so as to form alkyl halides and hydrogen halide;
 - (b) contacting the alkyl halides with a catalyst so as to form higher hydrocarbons and hydrogen halide;
 - (c) separating the higher hydrocarbons from the hydrogen halide;
 - (d) electrolytically converting the hydrogen halide into hydrogen and molecular halogen; and
 - (e) repeating steps (a) through (d) a desired number of times, wherein the molecular halogen in step (d) is used in repeated step (a).
2. A continuous process as recited in claim 1, wherein the hydrocarbon feedstock comprises natural gas.
3. A continuous process as recited in claim 1, wherein the hydrocarbon feedstock comprises methane.
4. A continuous process as recited in claim 1, wherein step (d) is carried out in aqueous media.
5. A continuous process as recited in claim 1, wherein step (d) is carried out in the gas phase.
6. A continuous process as recited in claim 1, wherein the higher hydrocarbons comprise fuel grade hydrocarbons and/or aromatic hydrocarbons.
7. A continuous process as recited in claim 6, wherein the aromatic hydrocarbons comprise benzene, toluene, and xylenes.
8. A continuous process for converting a hydrocarbon feedstock into methanol, comprising:

(a) reacting molecular halogen with a hydrocarbon feedstock so as to form alkyl halides and hydrogen halide;

(b) contacting the alkyl halides with aqueous alkali so as to form methanol and alkaline halide;

(c) separating the methanol from the alkaline halide;

(d) electrolytically converting the alkaline halide into hydrogen, molecular halogen, and aqueous alkali; and

(e) repeating steps (a) through (d) a desired number of times, wherein the molecular halogen in step (d) is used in repeated step (a).

9. A continuous process as recited in claim 8, wherein the hydrocarbon feedstock comprises natural gas.

10. A continuous process as recited in claim 8, wherein the hydrocarbon feedstock comprises methane.

11. A continuous process as recited in claim 8, wherein step (d) is carried out in aqueous media.

12. A continuous process as recited in claim 8, wherein step (d) is carried out in the gas phase.

13. A continuous process for converting a hydrocarbon feedstock into an alkyl amine, comprising:

(a) reacting molecular halogen with a hydrocarbon feedstock so as to form alkyl halides and hydrogen halide;

(b) contacting the alkyl halides with aqueous alkali amine so as to form alkyl amines and alkaline halide;

(c) separating the alkyl amines from the alkaline halide;

(d) electrolytically converting the alkaline halide into hydrogen and molecular halogen; and

(e) repeating steps (a) through (d) a desired number of times wherein the molecular halogen in step (d) is used in repeated step (a).

14. A continuous process as recited in claim 13, wherein the aqueous alkaline amine comprises NaNH_2 .

15. A continuous process as recited in claim 13, wherein the alkyl halides comprise ethyl bromide and the aqueous alkaline amine comprises NaNH_2 .

16. A method comprising:

(a) reacting molecular halogen with oil or gas pumped from a well at an oil or gas production facility so as to form alkyl halides and hydrogen halide;

(b) contacting the alkyl halides with a catalyst so as to form higher hydrocarbons and hydrogen halide;

(c) separating the higher hydrocarbons from hydrogen halide; and

(d) electrolytically converting the hydrogen halide into hydrogen and molecular halogen using electricity provided by an electrical generator or electrical power supply.

17. The method as recited in claim 16, wherein the oil or gas production facility is located offshore.

18. A method comprising:

(a) reacting molecular halogen with a hydrocarbon feedstock so as to form alkyl halides and hydrogen halide;

(b) contacting the alkyl halides with aqueous alkali so as to form methanol and alkaline halide;

- (c) separating the methanol from the alkaline halide;
 - (d) electrolytically converting the alkaline halide into hydrogen, molecular halogen, and aqueous alkali using electricity provided by an electrical generator or electrical power supply at an oil or gas production facility.
19. The method as recited in claim 18, wherein the oil or gas production facility is located offshore.
20. A continuous process for converting coal into coke and hydrogen, comprising:
- (a) reacting crushed coal with molecular halogen so as to form brominated coal intermediates and hydrogen halide;
 - (b) reacting the brominated coal intermediates over a catalyst so as to form coke and hydrogen halide;
 - (c) separating the coke from the hydrogen halide found in step (a) and/or step (b);
 - (d) electrolytically converting the hydrogen halide found in step (a) and/or step (b) into hydrogen and molecular halogen; and
 - (e) repeating steps (a) through (d) a desired number of times, wherein the molecular halogen in step (d) is used in repeated step (a).
21. A continuous process for converting coal or biomass-derived hydrocarbons into polyols, comprising:
- (a) reacting molecular halogen with coal or a biomass-derived hydrocarbon feedstock so as to form alkyl halides and hydrogen halide;
 - (b) contacting the alkyl halides with aqueous alkali so as to form polyols and alkaline halide;
 - (c) separating the polyols from the alkaline halide;
 - (d) electrolytically converting the alkaline halide into hydrogen and molecular halogen; and

(e) repeating steps (a) through (d) a desired number of times, wherein the molecular halogen in step (d) is used in repeated step (a).

22. A continuous process for converting a hydrocarbon feedstock into higher hydrocarbons, comprising:

(a) reacting molecular halogen with a hydrocarbon feedstock so as to form alkyl halides and hydrogen halide;

(b) contacting the alkyl halides with a catalyst so as to form higher hydrocarbons and hydrogen halide;

(c) separating the higher hydrocarbons from the hydrogen halide;

(d) electrolytically converting the hydrogen halide into water and molecular halogen in an electrolytic cell or cells equipped with an oxygen depolarized cathode; and

(e) repeating steps (a) through (d) a desired number of times, wherein the molecular halogen in step (d) is used in repeated step (a).

23. A continuous process for converting a hydrocarbon feedstock into methanol, comprising:

(a) reacting molecular halogen with a hydrocarbon feedstock so as to form alkyl halides and hydrogen halide;

(b) contacting the alkyl halides with aqueous alkali so as to form methanol and alkaline halide;

(c) separating the methanol from the alkaline halide;

(d) electrolytically converting the alkaline halide into molecular halogen and aqueous alkali in an electrolytic cell or cells equipped with an oxygen depolarized cathode; and

(e) repeating steps (a) through (d) a desired number of times, wherein the molecular halogen in step (d) is used in repeated step (a).

24. A continuous process as recited in claim 1, wherein step (d) comprises electrolytically converting the hydrogen halide into hydrogen and molecular halogen with an electrolytic cell, the electrolytic cell comprising:

- a gas supply manifold through which oxygen gas, air, or oxygen-enriched air can be introduced;
- a gas diffusion cathode, which is permeable to oxygen or an oxygen-containing gas;
- a cation exchange membrane;
- a cathode electrolyte chamber disposed between the cation exchange membrane and the gas diffusion cathode;
- an anode electrolyte chamber; and
- an anode extending into the anode electrolyte chamber.

25. A continuous process as recited in claim 8, wherein step (d) comprises electrolytically converting the alkaline halide into hydrogen, molecular halogen, and aqueous alkali with an electrolytic cell, the electrolytic cell comprising:

- a gas supply manifold through which oxygen gas, air, or oxygen-enriched air can be introduced;
- a gas diffusion cathode, which is permeable to oxygen or an oxygen-containing gas;
- a cation exchange membrane;
- a cathode electrolyte chamber disposed between the cation exchange membrane and the gas diffusion cathode;
- an anode electrolyte chamber; and
- an anode extending into the anode electrolyte chamber.

26. A continuous process as recited in claim 13, wherein step (d) comprises electrolytically converting the alkaline halide into hydrogen and molecular halogen with an electrolytic cell, the electrolytic cell comprising:

- a gas supply manifold through which oxygen gas, air, or oxygen-enriched air can be introduced;
- a gas diffusion cathode, which is permeable to oxygen or an oxygen-containing gas;
- a cation exchange membrane;
- a cathode electrolyte chamber disposed between the cation exchange membrane and the gas diffusion cathode;

an anode electrolyte chamber; and

an anode extending into the anode electrolyte chamber.

27. The method as recited in claim 16, wherein step (d) comprises electrolytically converting the hydrogen halide into hydrogen and molecular halogen with an electrolytic cell, the electrolytic cell comprising:

a gas supply manifold through which oxygen gas, air, or oxygen-enriched air can be introduced;

a gas diffusion cathode, which is permeable to oxygen or an oxygen-containing gas;

a cation exchange membrane;

a cathode electrolyte chamber disposed between the cation exchange membrane and the gas diffusion cathode;

an anode electrolyte chamber; and

an anode extending into the anode electrolyte chamber.

28. The method as recited in claim 18, wherein step (d) comprises electrolytically converting the hydrogen halide into hydrogen and molecular halogen with an electrolytic cell, the electrolytic cell comprising:

a gas supply manifold through which oxygen gas, air, or oxygen-enriched air can be introduced;

a gas diffusion cathode, which is permeable to oxygen or an oxygen-containing gas;

a cation exchange membrane;

a cathode electrolyte chamber disposed between the cation exchange membrane and the gas diffusion cathode;

an anode electrolyte chamber; and

an anode extending into the anode electrolyte chamber.

29. A continuous process as recited in claim 20, wherein step (d) comprises electrolytically converting the hydrogen halide found in step (a) and/or step (b) into hydrogen and molecular halogen with an electrolytic cell, the electrolytic cell comprising:

a gas supply manifold through which oxygen gas, air, or oxygen-enriched air can be introduced;

a gas diffusion cathode, which is permeable to oxygen or an oxygen-containing gas;

a cation exchange membrane;

a cathode electrolyte chamber disposed between the cation exchange membrane and the gas diffusion cathode;

an anode electrolyte chamber; and

an anode extending into the anode electrolyte chamber.

30. A continuous process as recited in claim 21, wherein step (d) comprises electrolytically converting the alkaline halide into hydrogen and molecular halogen with an electrolytic cell, the electrolytic cell comprising:

a gas supply manifold through which oxygen gas, air, or oxygen-enriched air can be introduced;

a gas diffusion cathode, which is permeable to oxygen or an oxygen-containing gas;

a cation exchange membrane;

a cathode electrolyte chamber disposed between the cation exchange membrane and the gas diffusion cathode;

an anode electrolyte chamber; and

an anode extending into the anode electrolyte chamber.

31. A continuous process as recited in claim 22, wherein the electrolytic cell comprises:

a gas supply manifold through which oxygen gas, air, or oxygen-enriched air can be introduced;

a gas diffusion cathode, which is permeable to oxygen or an oxygen-containing gas;

a cation exchange membrane;

a cathode electrolyte chamber disposed between the cation exchange membrane and the gas diffusion cathode;

an anode electrolyte chamber; and

an anode extending into the anode electrolyte chamber.

32. A continuous process as recited in claim 23, wherein the electrolytic cell comprises:

- a gas supply manifold through which oxygen gas, air, or oxygen-enriched air can be introduced;

- a gas diffusion cathode, which is permeable to oxygen or an oxygen-containing gas;

- a cation exchange membrane;

- a cathode electrolyte chamber disposed between the cation exchange membrane and the gas diffusion cathode;

- an anode electrolyte chamber; and

- an anode extending into the anode electrolyte chamber.