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(54) **Integrated process for synthesizing alcohols and ethers from alkanes**

Integriertes Verfahren zur Synthese von Alkoholen und Ethern aus Alkanen

Procédé intégré de synthèse d' alcools et d' éthers à partir d' alcanes

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**US-A- 5 243 098 US-B1- 6 403 840**

• **OLAH, GEORGE A. ET AL: "Antimony pentafluoride/graphite catalyzed oxidative conversion of methyl halides with copper oxides (or copper/oxygen) to dimethyl ether" JOURNAL OF ORGANIC CHEMISTRY , 55(14), 4289-93 CODEN: JOCEAH; ISSN: 0022-3263, 1990, XP002283993**

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**Description****TECHNICAL FIELD**

5 **[0001]** This invention relates generally to the synthesis of alcohols and ethers from alkanes, and more particularly to a method of manufacturing methanol and dimethyl ether from methane.

**BACKGROUND OF THE INVENTION**

10 **[0002]** Methane has previously been converted to methanol by the halogenation of methane followed by hydrolysis of the methyl halide to form methanol. For example, gaseous chlorine has been used to chlorinate methane to form chlorinated methane, principally methyl chloride, together with other chlorides, i.e., dichloromethane, trichloromethane and carbon tetrachloride. Alternatively, methane has been subjected to oxychlorination with oxygen and hydrochloric acid to form the foregoing compounds. The chlorinated methanes produced are hydrolyzed in the vapor phase to produce  
15 methanol, formaldehyde, formic acid and by-products, including carbon dioxide and hydrochloric acid, depending on the chlorination selectivity. Hydrochloric acid is produced or used in the halogenation of methane by either method and must be recovered, dehydrated by azeotropic distillation and recycled. Corrosion and other problems involved with the handling of chlorine and hydrochloric acid are substantial.

**[0003]** U.S. Patent No. 3,172,915 granted to Borkowski, et al. is directed to a process for converting methane to methanol. Borkowski discloses the chlorination of methane using ferric chloride at high temperatures to produce chloromethanes and hydrogen chloride. The process requires temperatures in the range of 220-800°C., more preferably 250-450°C., and long residence times, e.g., more than one hour. Further, the process is hindered by the production of a mixture of chlorination products, e.g., chloromethane, dichloromethane, trichloromethane and carbon tetrachloride, which must be separated before hydrolysis to methanol. Other disadvantages result from the energy required to dry the  
25 ferric chloride and from the corrosion and handling problems inherent with hydrochloric acid.

**[0004]** U.S. Patent No. 5,243,098 granted to Miller discloses another method for converting methane to methanol. In the Miller process the reaction of methane with cupric chloride produces chloromethane and hydrochloric acid. These intermediates are then reacted with steam and a catalyst containing magnesium oxide to produce methanol and magnesium chloride. Magnesium oxide is regenerated by treatment of the magnesium chloride by-product with air or oxygen. Cupric chloride is regenerated by treatment of the cuprous chloride by-product with air and hydrochloric acid. While these reactions proceed at favorable rates, attrition of the solid reactants, i.e., cupric and magnesium oxide, is significant. Special filters and processes are required to recover and regenerate the reactants in the required particle size. Miller also suggests cupric bromide and magnesium zeolite as alternative reactants. Because of the attrition of the reactants, difficulties associated with the handling of solids, and the special filters and processes required to regenerate the reactants, the Miller process has proven unsatisfactory. U.S. Pat. No. 5,334,777, also granted to Miller, discloses a nearly  
35 identical process for converting ethene to ethylene glycol.

**[0005]** U.S. Patent No. 5,998,679 granted to Jorge Miller, discloses a process for converting alkanes and alkenes to the corresponding lower alkanols and diols. In the method of the invention, a gaseous halogen (bromine) is produced by decomposing a metal halide in a liquid having a melting point below and a boiling point above the decomposition temperature of the metal halide. The preferred liquid is molten hydrated ferric chloride maintained at a temperature between about 37-280°C. The lower alkane or alkene is halogenated in a gas phase reaction with the halogen. The resulting alkyl halide or alkyl dihalide is contacted with a metal hydroxide, preferably an aqueous solution of ferric hydroxide, to regenerate the metal halide and produce the corresponding lower alkanol or diol. Problems with this process include low monohalogenation selectivity, and corrosiveness of the hydrated ferric halides, which may present a containment problem if the process is run at 280°C, where high pressures of steam are required to maintain ferric halide hydration. Finally, the process produces a great deal of water and HCl or HBr, all of which are difficult to separate on a large scale from the desired product methanol.

**[0006]** Published international patent application WO 00/07718, naming Giuseppe Bellussi, Carlo Peregò, and Laura Zanibelli as inventors, discloses a method for directly converting methane and oxygen to methanol over a metal halide/metal oxide catalyst. This is not a catalyst in the true sense of the word, however, because the reaction involves transfer of halide from a metal halide via reaction with methane to a different metal oxide producing the metal halide and methanol downstream. Eventually the halide is leached and the catalyst loses activity.

**[0007]** Olah et al. (George A. Olah, et al. J. Am. Chem. Soc. 1985, 107, 7097-7105) discloses a method for converting methane to methanol via methyl halides (CH<sub>3</sub>Br and CH<sub>3</sub>Cl), which are then hydrolyzed to prepare methanol. In the process, CH<sub>3</sub>Br and CH<sub>3</sub>Cl are hydrolyzed over catalysts with excess steam generating a methanol, water, and HCl or HBr mixture. The separation of methanol (about 2% by mole) from HCl or HBr and water on an industry scale (2000 tons per day) requires an enormous amount of energy and generates a great deal of aqueous HCl or HBr waste. Aqueous HCl and HBr are very corrosive as well.

## SUMMARY OF THE INVENTION

**[0008]** The present invention comprises a process wherein bromine or a bromine containing compound is used as an intermediate to convert alkanes to alcohols, ethers, or olefins by reaction with oxygen or air. While the process can be used to convert a variety of alkanes, including methane, ethane, propane, butane, isobutane, pentanes, hexanes, cyclohexane, etc. to their respective alcohols, ethers, or olefins, the conversion of methane to methanol and dimethyl ether is illustrative.

**[0009]** Methane reacts with bromine over a catalyst to form  $\text{CH}_3\text{Br}$  and  $\text{HBr}$ .  $\text{CH}_3\text{Br}$  and  $\text{HBr}$  react with a metal oxide to form a variable mixture of dimethyl ether (DME), water and methanol, and the metal bromide. The metal oxide and molecular bromine are regenerated by reaction of the metal bromide with air and/or oxygen. The regenerated bromine is recycled to react with methane while the regenerated metal oxide is used to convert more methyl bromide to methanol and DME, completing the reaction cycle.

**[0010]** The process can be easily carried out in a riser reactor. Compared to the current industrial two step process, in which methane and steam are first converted to  $\text{CO}$  and  $\text{H}_2$  at  $800^\circ\text{C}$  followed by conversion to methanol over a  $\text{Zn-Cu-Al-O}$  catalyst at approximately 70-150 atmospheres, the process of the present invention operates at roughly atmospheric pressure and relatively low temperatures, thereby providing a safe and efficient process for methanol production.

**[0011]** The present invention operates with solid/gas mixtures at atmospheric pressure. In the process, the hydrogen halide is gaseous, and therefore not as corrosive as when aqueous at high temperatures. The reaction of  $\text{Br}_2$  with an alkane can reach more than 90% selectivity with high conversion to alkane-monobromide. The main side products, alkane dibromides such as  $\text{CH}_2\text{Br}_2$ , can be converted back to the monobromides by reaction with an alkane over another catalyst. Very few by-products are produced.

**[0012]** In the process most of the Br atoms are trapped in the solid state, making the system less corrosive. Another advantage is that DME and alcohol ( $\text{CH}_3\text{OH}$ ) are not produced as a mixture with excess water. By controlling reaction conditions, almost pure DME and/or methanol is obtained directly so that it is not necessary to separate  $\text{CH}_3\text{OH}$  from water. Finally, in the present process, methane and oxygen do not come into direct contact, resulting in improved safety.

## BRIEF DESCRIPTION OF THE DRAWING

**[0013]** A more complete understanding of the present invention may be had by reference to the following Detailed Description when taken in connection with the accompanying Drawing, wherein:

FIGURE 1 is a schematic illustration of a method of and apparatus for synthesizing ethers and/or alcohols from alkanes comprising an embodiment of the invention.

## DETAILED DESCRIPTION

**[0014]** Alkanes (methane, ethane, propane, butane, isobutane, pentanes, hexanes, cyclohexane, etc.) react with molecular bromine over a metal oxide catalyst selected from all possible metal oxide compounds and mixtures thereof to form alkylbromides. For  $\text{CH}_4$  (although the process may be applied to higher alkanes as well), the process of the present invention can convert more than 50%  $\text{CH}_4$  to  $\text{CH}_3\text{Br}$  and  $\text{HBr}$ , with selectivity higher than 90%. Most of the by-product is  $\text{CH}_2\text{Br}_2$  (with trace amounts of  $\text{CHBr}_3$ , and  $\text{CBr}_4$ )(+ 2  $\text{HBr}$ ), which can be catalytically reconverted to  $\text{CH}_3\text{Br}$  by reacting  $\text{CH}_2\text{Br}_2$  with  $\text{CH}_4$ .

**[0015]** A method and apparatus for synthesizing alcohols and ethers from alkanes using bromine comprising a first embodiment of the invention is provided. In the operation of the method and apparatus, bromine is received from a suitable source through a first line and is directed to a bromine storage container. For example, bromine is easily manufactured from bromide, which is readily available from sea water.

**[0016]** As is well known, bromine is a liquid at room temperature. Liquid bromine from the storage container is directed through a second line to a bromine vaporizer wherein the bromine is converted from the liquid phase to the gas phase. From the vaporizer the gaseous bromine is directed through a third line to a reactor.

**[0017]** Methane from a suitable source is directed to the reactor, which contains a bromination catalyst, through a fourth line. Within the reactor the methane and the gaseous bromine are mixed together and the temperature of the mixture is raised to between  $20^\circ\text{C}$  and  $600^\circ\text{C}$ , thereby converting the methane and the bromine to methyl bromide ( $\text{CH}_3\text{Br}$ ) and hydrogen bromide ( $\text{HBr}$ ).

**[0018]** From the reactor, the  $\text{CH}_3\text{Br}$ , the  $\text{HBr}$ , any unreacted methane and by products  $\text{CH}_2\text{Br}_2$ ,  $\text{CHBr}_3$ , and  $\text{CBr}_4$  are directed to a first condenser. The by products  $\text{CH}_2\text{Br}_2$ ,  $\text{CHBr}_3$ , and  $\text{CBr}_4$ , now in the liquid state, are sent to a first converter with methane from the fourth line. In the first converter, methane reacts with the by products  $\text{CH}_2\text{Br}_2$ ,  $\text{CHBr}_3$ , and  $\text{CBr}_4$  to form  $\text{CH}_3\text{Br}$ . The newly formed  $\text{CH}_3\text{Br}$  and any unreacted  $\text{CH}_2\text{Br}_2$ ,  $\text{CHBr}_3$ ,  $\text{CBr}_4$  and/or methane are sent to the first condenser. From the first condenser, the gas phase methane,  $\text{HBr}$ , and  $\text{CH}_3\text{Br}$  are sent to a second converter.

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In the second converter HBr and CH<sub>3</sub>Br react with metal oxide to form CH<sub>3</sub>OCH<sub>3</sub>, CH<sub>3</sub>OH, and H<sub>2</sub>O, which are sent to a first separator along with unreacted methane and CH<sub>3</sub>Br. In the first separator, methanol and dimethyl ether are separated as products. CH<sub>3</sub>Br is sent back to the second converter. Methane is sent back to the bromination reactor. In the second converter, the original metal oxide has been converted to metal bromide after reaction. The metal bromide is sent to a third converter to react with oxygen (from source ) to regenerate bromine and metal oxide. The regenerated metal oxide is sent back to the second converter, while the bromine and unreacted oxygen are sent to a second condenser, then to a second separator. The liquid bromine is sent to the storage container, while oxygen is sent to the third converter.

[0019] There is also provided a method of and apparatus for synthesizing alcohols and ethers from alkanes comprising a second embodiment of the invention. Methane and bromine are directed to a heated vaporizer where they are heated to form a gas mixture. The gas mixture is passed into a bromination reactor, containing a bromination catalyst, if desired. After the reaction, the mixture is directed to a condenser. The liquid phase contains by products CH<sub>2</sub>Br<sub>2</sub>, CHBr<sub>3</sub>, and CBr<sub>4</sub>, while the gas phase contains bromomethane, HBr, and unreacted methane.

[0020] The liquid by products CH<sub>2</sub>Br<sub>2</sub>, CHBr<sub>3</sub>, and CBr<sub>4</sub> are sent to a first converter where they react with methane to form bromomethane. After reaction the mixture is sent to the condenser, where any remaining byproducts can once again be cycled to the bromination reactor.

[0021] The gas phase mixture from condenser is passed through a second converter, where HBr reacts with metal oxide to form metal bromide and water. The metal bromide is sent to a regenerator to regenerate metal oxide. From the second converter, the water, bromomethane, and methane are separated. Methane is recycled to the first converter and the vaporizer. Bromomethane is sent to a first reactor. Water is sent to a second reactor.

[0022] In the first reactor, bromomethane reacts with metal oxide to generate dimethyl ether (DME) and metal bromide. Metal bromide is sent to the regenerator. The mixture of bromomethane and DME from the first reactor is sent to a first separator. Bromomethane from the first separator is recycled to the first reactor, while DME is obtained as a product or directed to the second reactor.

[0023] In the second reactor, DME reacts with water, e.g., from the first separator, over a suitable catalyst to form methanol.

[0024] In the regenerator, metal bromide from the second converter and the first reactor reacts with air or oxygen to regenerate metal oxide and bromine. After regeneration, metal oxide is sent to the second converter and the first reactor, while bromine is sent to the vaporizer. If air is used as the source of oxygen, nitrogen can be continuously purged from the system through a second separator.

[0025] A method and apparatus 120 for converting methane to dimethyl ether and/or methanol comprising a third embodiment of the invention is illustrated in Figure 1. Liquid bromine is stored in a bromine storage container 122 and is directed therefrom through a line 124 through a bromine vaporizer 126. From the bromine vaporizer 126 the bromine vapor passes through a line 128 to a primary reactor 130 which also receives methane from a suitable source through a line 132.

[0026] Within the primary reactor 130, the bromine and methane react over a solid catalyst, if desired, to form CH<sub>3</sub>Br, CH<sub>2</sub>Br<sub>2</sub>, CHBr<sub>3</sub>, CBr<sub>4</sub> and HBr. The reaction products together with any unreacted methane are directed to a condenser separator 134 through a line 136. The condenser separator 134 directs CH<sub>3</sub>Br, CH<sub>2</sub>Br<sub>2</sub>, CHBr<sub>3</sub>, and CBr<sub>4</sub> to a separation (distillation) apparatus 138 through a line 140. The separation (distillation) apparatus 138 directs CH<sub>2</sub>Br<sub>2</sub>, CHBr<sub>3</sub>, and CBr<sub>4</sub> to a secondary reactor 142 through a line 144. The secondary reactor 142 also receives methane from a suitable source through a line 146.

[0027] The secondary reactor 142 converts the CH<sub>2</sub>Br<sub>2</sub>, CHBr<sub>3</sub>, and CBr<sub>4</sub> received through the line 144 to CH<sub>3</sub>Br. CH<sub>3</sub>Br and excess methane are directed from the secondary reactor 142 to the line 136 through a line 148.

[0028] The condenser separator 134 also directs CH<sub>3</sub>Br and HBr to an HBr converter 150 through a line 152. The HBr converter 150 is filled with a metal oxide. Within the HBr converter 150 the metal oxide and the HBr react to form metal bromide and water. The water and the unreacted methane are directed from the HBr converter 150 to a condenser separator 154 through a line 156. The water is recovered from the condenser separator 154 through an outlet 158, while the unreacted methane is directed through a line 160 to a blower 162 and from the blower 162 through a line 164 to the line 132.

[0029] Metal bromide formed during operation of the HBr converter 150 is directed to a bromide to oxide converter (regenerator) 166 through a line 168. The bromide to oxide converter 166 receives air or oxygen through a line 170 and functions to convert the metal bromide back to metal oxide. The metal oxide is returned to the HBr converter 150 through a line 172.

[0030] Operation of the bromide to oxide converter 166 also produces bromine. Bromine and excess air or oxygen are directed through a line 174 to a blower 176, and from the blower 176 to a condenser separator 178. Operation of the condenser separator 178 produces liquid bromine which is directed to the bromine storage container 122 through a line 180. Excess air and/or oxygen is recovered from the condenser separator 178 through an outlet 182 and is directed therefrom through a blower 184 and a line 186 to the line 170.

[0031] The separation (distillation) apparatus 138 directs CH<sub>3</sub>Br to an oxide to bromide converter 188 through a line

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190. The oxide to bromide converter 188 is filled with a metal oxide, which may be the same metal oxide that is utilized in the operation of the HBr converter 150. Operation of the oxide to bromide converter 188 produces dimethyl ether, which together with unreacted bromomethane is directed through a line 192, a compressor 194, and a line 196 to a condenser separator 198. From the condenser separator 198 dimethyl ether may be recovered as a final product at an outlet 200. The bromomethane is sent back to the converter 188. Alternatively, the dimethyl ether may be directed to a methanol reactor 202, which receives water through an inlet 204. The dimethyl ether and the water react in the methanol reactor 202 to form methanol, which is recovered at an outlet 206.

[0032] Operation of the oxide to bromide converter 188 converts the metal oxide contained therein to metal bromide, which is directed to the bromide to oxide converter 166 through a line 208. Operation of the bromide to oxide converter 166 converts the metal bromide to the original metal oxide, which is returned to the oxide to bromide converter 188 through a line 210.

### EXAMPLES

#### Reaction 1:

##### **Catalyst preparation**

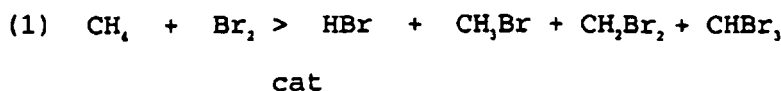
[0033]  $\text{Nb}_2\text{O}_5$  (0.8000g) was mixed with 0.500ml 96(w)%  $\text{H}_2\text{SO}_4$ , then the mixture was heated at 110°C for 4 hours. The temperature increased to 500°C within 6 hours, and kept at 500°C for 4 hours. Catalyst C1 was obtained.

##### **Testing**

Reaction conditions:

[0034] The catalyst was tested at a methane flow of 1.5ml/minute and  $\text{Br}_2$  flow of 0.07ml/hour. The reaction temperature was 400°C. The reaction was carried out in a microreactor system. After 6 hours on line reaction, the reaction effluent was analyzed by a GC/MS. A methane conversion of 24%(mol) with 95%  $\text{CH}_3\text{Br}$  was obtained.

[0035] Summarizing the overall process in Reaction 1:



#### Reaction 2:

##### **Metal oxide preparation**

##### **Zr solution preparation**

[0036]  $\text{Zr}(\text{OCH}_2\text{CH}_2\text{CH}_3)_4$  (70(w)% in isopropanol, 112.6 ml) was dissolved into acetic acid (275 ml) under stirring. After stirring for 10 minutes, the solution was diluted by water to make a total volume of 500 ml. A solution with a Zr concentration of 0.5M was obtained.

##### **Preparation of M1**

[0037]  $\text{Cu}(\text{NO}_3)_2$  (0.5M, 7.200ml) solution was added into  $\text{BaBr}_2$  (0.5M, 0.800 ml). A clear solution was obtained. To this solution, Zr solution (0.5M) as prepared above was added under stirring. After stirring a few seconds, a gel was obtained. The gel was dried at 110°C for 4 hours, then heated to 500°C within 6 hours, and kept at 500°C for 4 hours. M1 was obtained. The metal oxide mixture was tested at a  $\text{CH}_3\text{Br}$  flow of 1.0 ml/minute at 230°C. In the first half hour, the average  $\text{CH}_3\text{Br}$  conversion is 65%, and the average dimethyl ether selectivity is 90.5%.

##### **Catalyst preparation**

[0038]  $\text{ZrO}_2$  (2.0000g) was mixed with  $\text{H}_2\text{SO}_4$  (3.000 ml, 96(w)%), then the mixture was heated at 110°C for 4 hours. The temperature increased to 500°C within 6 hours, and kept at 500°C for 4 hours. Catalyst C2 was obtained.

**Preparation of M2**

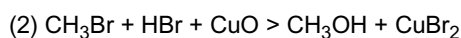
**[0039]** Cu(NO<sub>3</sub>)<sub>2</sub> (0.5M, 40.000 ml) solution was added into Zr solution (0.5M, 30.000 ml as prepared above). After stirring a few seconds, a gel was obtained. The gel was dried at 110°C for 4 hours, then heated to 500°C within 6 hours, and calcined at 500°C for 4 hours. M2 was obtained.

**Testing**

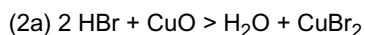
**[0040]** The catalyst C2 (2.0000g) was loaded in the first reactor (R1). A trap was loaded 2.0000g M2 in the oxide form. A second reactor (R2) was also loaded with M2 in the oxide form(0.8500g).

**[0041]** Reactants methane and bromine were fed into the first reactor (methane flow of 1.5 ml/minute, Br<sub>2</sub> flow of 0.07 ml/hour). The reaction temperature was 390°C. After the reaction in R1 (stabilized by online reaction for more than 8 hours), the products generated in R1 were passed through the trap and HBr was removed. Following removal of HBr, a mixture of methane and CH<sub>3</sub>Br (containing 20% mol of CH<sub>3</sub>Br) was obtained. This gas mixture was directly fed into R2 at 220°C. In the first one hour, an average CH<sub>3</sub>Br conversion of 91% with an average dimethyl ether selectivity of 75% was obtained.

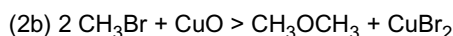
**[0042]** Summarizing the overall process in Reaction 2:



**[0043]** Possible variations of Reaction 2:

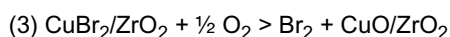


(reaction occurring in the trap)

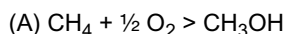
**Reaction 3:**

**[0044]** The solid CuBr<sub>2</sub>/ZrO<sub>2</sub> is transferred from Reactor 2 to Reactor 3 and treated with O<sub>2</sub> at 300°C to yield Br<sub>2</sub> and CuO/ZrO<sub>2</sub> in 100% yield and conversion. This reaction may be run at space velocity 100 h<sup>-1</sup>.

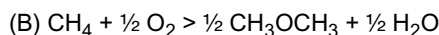
**[0045]** Summarizing the overall process in Reaction 3:



**[0046]** Overall:



**[0047]** Possible variation:



**[0048]** It will therefore be understood that the method of the present invention operates on a continuous or batch basis to convert alkanes to alcohols and ethers. The method of the present invention operates at relatively low temperatures and at low pressures and is therefore economical for manufacture and use. The bromine, which is utilized in the method of the present invention, is continuously recycled. The metal oxide catalyst, which is utilized in the process is continuously refreshed.

**[0049]** Although preferred embodiments of the invention have been illustrated in the accompanying Drawing and described in the foregoing Detailed Description, it will be understood that the invention is not limited to the embodiments disclosed but is capable of numerous rearrangements, modifications, and substitutions of parts and elements without departing from the scope of the invention, but staying within the scope of protection as defined by the claims.

## Claims

1. A method for synthesizing alcohols and/or ethers from alkanes comprising:

5 providing a quantity of an alkane selected from the group consisting of methane, ethane, propane, butane, and isobutane; providing a quantity of bromine; mixing the alkane and the bromine and thereby forming an alkyl bromide and hydrogen bromide; reacting the alkyl bromide and the hydrogen bromide with a metal oxide and thereby forming alcohol and/or ether and a metal bromide; oxidizing the metal bromide to form the original metal oxide and bromine; recycling the metal oxide; and recycling the bromine.

- 10 2. The method according to claim 1 wherein the step of mixing the alkane and the bromine is carried out at a temperature of between 20° C and 600° C.

- 15 3. The method according to claim 1 wherein the step of reacting the alkane with the bromine to form the alkyl bromide and hydrogen bromide and the step of contacting the alkyl bromide with metal oxides are carried out continuously.

- 20 4. The method according to claim 1 wherein the step of reacting the alkane with the bromine to form the alkyl bromide and hydrogen bromide and the step of contacting the alkyl bromide and the hydrogen bromide with metal oxides are carried out in a batch reaction.

- 25 5. The method according to claim 1 wherein the step of oxidizing the metal bromide to form the original metal oxide and bromine, the step of recycling the metal oxide, and the step of recycling the bromine are carried out continuously.

- 30 6. The method according to claim 1 wherein the step of oxidizing the metal bromide to form the original metal oxide and bromine, the step of recycling the metal oxide, and the step of recycling the bromine are carried out in a batch reaction.

- 35 7. A method according to claim 1, wherein the alkane is methane and the alcohol is methanol comprising:

40 providing a quantity of methane; providing a quantity of bromine; reacting the methane with the bromine and thereby forming methyl bromide and hydrogen bromide; reacting the methyl bromide and the hydrogen bromide with a metal oxide catalyst and thereby forming methanol and a metal bromide; oxidizing the metal bromide to form the original metal oxide and bromine; recycling the metal oxide; and recycling the bromine.

- 45 8. The method according to claim 7 wherein the step of mixing the methane and the bromine is carried out at a methane to bromine ratio from 1:10 to 100:1 (by mole).

- 50 9. The method according to claim 7 wherein the step of mixing the methane and the bromine is carried out at a methane to bromine ratio from 1:1 to 10:1 (by mole).

- 55 10. The method according to claim 7 wherein the step of mixing the methane and the bromine is carried out at a methane to bromine ratio from 1:1 to 5:1 (by mole).

11. The method according to claim 7 wherein the step of mixing the methane and the bromine is carried out at a temperature of between 20° C and 600° C.

12. The method according to claim 7 wherein the step of mixing the methane and the bromine to form the methyl bromide and hydrogen bromide and the step of contacting the methyl bromide and the hydrogen bromide with a metal oxide are carried out continuously.

13. The method according to claim 7 wherein the step of mixing the methane and the bromine to form the methyl bromide and hydrogen bromide and the step of contacting the methyl bromide and the hydrogen bromide with a metal oxide are carried out in a batch reaction.

14. The method according to claim 7 wherein the step of oxidizing the metal bromide to form the original metal oxide catalyst and bromine, the step of recycling the metal oxide, and the step of recycling the bromine are carried out continuously.

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15. The method according to claim 7 wherein the step of oxidizing the metal bromide to form the original metal oxide and bromine, the step of recycling the metal oxide, and the step of recycling the bromine are carried out in a batch reaction.
- 5 16. A method according to claim 1, wherein an ether is synthesised from an alkane comprising:  
providing a quantity of an alkane selected from the group consisting of methane and ethane; providing a quantity of bromine; mixing the alkane and the bromine and thereby forming an alkyl bromide and hydrogen bromide;  
10 reacting the alkyl bromide with a metal oxide and thereby forming an ether and a metal bromide;  
oxidizing the metal bromide to form the original metal oxide catalyst and  
bromine; recycling the metal oxide catalyst; and recycling the bromine.
17. The method according to claim 16 wherein the step of mixing the alkane and the bromine is carried out at an alkane to bromine mol ratio between 1:10 to 100:1.
- 15 18. The method according to claim 16 wherein the step of mixing the alkane and the bromine is carried out at an alkane to bromine mol ratio between 1:5 to 50:1.
19. The method according to claim 16 wherein the step of mixing the alkane and the bromine is carried out at an alkane to bromine mol ratio between 1:2 to 10:1.
- 20 20. The method according to claim 16 wherein the step of mixing the alkane and the bromine is carried out at a temperature of between 20° C and 600° C.
- 25 21. The method according to claim 16 wherein the step of mixing the alkane and the bromine to form the alkyl bromide and hydrogen bromide and the step of contacting the alkyl bromide and the hydrogen bromide with a metal oxide are carried out continuously.
22. The method according to claim 16 wherein the step of mixing the alkane and the bromine to form the alkyl bromide and hydrogen bromide and the step of contacting the alkyl bromide and the hydrogen bromide with a metal oxide are carried out in a batch reaction.
- 30 23. The method according to claim 16 wherein the step of oxidizing the metal bromide to form the original metal oxide and bromine, the step of recycling the metal oxide catalyst, and the step of recycling the bromine are carried out continuously.
- 35 24. The method according to claim 16 wherein the step of oxidizing the metal bromide to form the original metal oxide and bromine, the step of recycling the metal oxide, and the step of recycling the bromine are carried out in batch reactions.
- 40 25. A method according to claim 1, wherein methane is converted into dimethyl ether comprising:  
providing a quantity of methane; providing a quantity of bromine; mixing the methane and the bromine and thereby forming methyl bromide and hydrogen bromide; trapping the HBr by metal oxide; reacting the methyl bromide with a metal oxide and thereby forming dimethyl ether and a metal bromide; oxidizing the metal bromide to form the original metal oxide and bromine; recycling the metal oxide; and recycling the bromine.
- 45 26. The method according to claim 25 wherein the step of mixing the methane and the bromine is carried out at a methane to bromine mol ratio between 1:10 to 100:1.
- 50 27. The method according to claim 25 wherein the step of mixing the methane and the bromine is carried out at a methane to bromine mol ratio between 1:5 to 50:1.
28. The method according to claim 25 wherein the step of mixing the methane and the bromine is carried out at a methane to bromine mol ratio between 1:2 to 10:1.
- 55 29. The method according to claim 25 wherein the step of mixing the methane and the bromine is carried out at a temperature of between 20° C and 600° C.



30. The method according to claim 25 wherein the step of mixing the methane and the bromine to form the methyl bromide and hydrogen bromide, the step of trapping HBr by metal oxide, and the step of contacting the methyl bromide with metal oxides is carried out continuously.

5 31. The method according to claim 25 wherein the step of oxidizing the metal bromide to form the original metal oxide and bromine, the step of recycling the metal oxide, and the step of re cycling the bromine are carried out continuously.

### Patentansprüche

- 10 1. Verfahren zur Synthese von Alkoholen und/oder Ethern aus Alkanen, umfassend:
- Bereitstellen einer Menge eines Alkans, das ausgewählt ist aus der Gruppe, bestehend aus Methan, Ethan,  
15 Propan, Butan und Isobutan; Bereitstellen einer Menge Brom;  
Mischen des Alkans und des Broms und dadurch Bilden von einem Alkylbromid und  
Bromwasserstoff; Umsetzen des Alkylbromids und des Bromwasserstoffs mit einem Metalloxid und dadurch  
Bilden von Alkohol und/oder Ether und einem Metallbromid;  
Oxidieren des Metallbromids, um das ursprüngliche Metalloxid und Brom zu bilden;  
20 Rückführen des Metalloxids; und Rückführen des Broms.
2. Verfahren nach Anspruch 1, wobei der Schritt des Mischens des Alkans und des Broms bei einer Temperatur von  
zwischen 20°C und 600°C durchgeführt wird.
3. Verfahren nach Anspruch 1, wobei der Schritt des Umsetzens des Alkans mit dem Brom, um das Alkylbromid und  
25 Bromwasserstoff zu bilden, und der Schritt des Inkontaktbringens des Alkylbromids mit Metalloxiden kontinuierlich  
durchgeführt werden.
4. Verfahren nach Anspruch 1, wobei der Schritt des Umsetzens des Alkans mit dem Brom, um das Alkylbromid und  
Bromwasserstoff zu bilden, und der Schritt des Inkontaktbringens des Alkylbromids und des Bromwasserstoffs mit  
30 Metalloxiden in einer diskontinuierlichen Reaktion durchgeführt werden.
5. Verfahren nach Anspruch 1, wobei der Schritt des Oxidierens des Metallbromids, um das ursprüngliche Metalloxid  
und Brom zu bilden, der Schritt des Rückführens des Metalloxids und der Schritt des Rückführens des Broms  
kontinuierlich durchgeführt werden.
- 35 6. Verfahren nach Anspruch 1, wobei der Schritt des Oxidierens des Metallbromids, um das ursprüngliche Metalloxid  
und Brom zu bilden, der Schritt des Rückführens des Metalloxids und der Schritt des Rückführens des Broms in  
einer diskontinuierlichen Reaktion durchgeführt werden.
- 40 7. Verfahren nach Anspruch 1, wobei das Alkan Methan ist und der Alkohol Methanol ist, umfassend:
- Bereitstellen einer Menge Methan; Bereitstellen einer Menge Brom; Umsetzen des Methans mit dem Brom und  
dadurch Bilden von Methylbromid und Bromwasserstoff;  
45 Umsetzen des Methylbromids und des Bromwasserstoffs mit einem Metalloxid-Katalysator und dadurch Bilden  
von Methanol und einem Metallbromid; Oxidieren des Metallbromids, um das ursprüngliche Metalloxid und  
Brom zu bilden; Rückführen des Metalloxids; und Rückführen des Broms.
8. Verfahren nach Anspruch 7, wobei der Schritt des Mischens des Methans und des Broms bei einem Methan-zu-  
Brom-Verhältnis von 1:10 bis 100:1 (molbezogen) durchgeführt wird.
- 50 9. Verfahren nach Anspruch 7, wobei der Schritt des Mischens des Methans und des Broms bei einem Methan-zu-  
Brom-Verhältnis von 1:1 bis 10:1 (molbezogen) durchgeführt wird.
10. Verfahren nach Anspruch 7, wobei der Schritt des Mischens des Methans und des Broms bei einem Methan-zu-  
55 Brom-Verhältnis von 1:1 bis 5:1 (molbezogen) durchgeführt wird.
11. Verfahren nach Anspruch 7, wobei der Schritt des Mischens des Methans und des Broms bei einer Temperatur von  
zwischen 20°C und 600°C durchgeführt wird.

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12. Verfahren nach Anspruch 7, wobei der Schritt des Mischens des Methans und des Broms, um das Methylbromid und Bromwasserstoff zu bilden, und der Schritt des Inkontaktbringens des Methylbromids und des Bromwasserstoffs mit einem Metalloxid kontinuierlich durchgeführt werden.
- 5 13. Verfahren nach Anspruch 7, wobei der Schritt des Mischens des Methans und des Broms, um das Methylbromid und Bromwasserstoff zu bilden, und der Schritt des Inkontaktbringens des Methylbromids und des Bromwasserstoffs mit einem Metalloxid diskontinuierlich durchgeführt werden.
- 10 14. Verfahren nach Anspruch 7, wobei der Schritt des Oxidierens des Metallbromids, um den ursprünglichen Metalloxid-Katalysator und Brom zu bilden, der Schritt des Rückführens des Metalloxids und der Schritt des Rückführens des Broms kontinuierlich durchgeführt werden.
- 15 15. Verfahren nach Anspruch 7, wobei der Schritt des Oxidierens des Metallbromids, um das ursprüngliche Metalloxid und Brom zu bilden, der Schritt des Rückführens des Metalloxids und der Schritt des Rückführens des Broms diskontinuierlich durchgeführt werden.
- 20 16. Verfahren nach Anspruch 1, wobei ein Ether aus einem Alkan synthetisiert wird, umfassend:  
Bereitstellen einer Menge eines Alkans, das ausgewählt ist aus der Gruppe, bestehend aus Methan und Ethan;  
Bereitstellen einer Menge Brom; Mischen des Alkans und des Broms und dadurch Bilden von einem Alkylbromid und Bromwasserstoff; Umsetzen des Alkylbromids mit einem Metalloxid und dadurch Bilden eines Ethers und eines Metallbromids; Oxidieren des Metallbromids, um den ursprünglichen Metalloxid-Katalysator und Brom zu bilden; Rückführen des Metalloxid-Katalysators; und  
Rückführen des Broms.
- 25 17. Verfahren nach Anspruch 16, wobei der Schritt des Mischens des Alkans und des Broms bei einem Alkan-zu-Brom-Molverhältnis zwischen 1:10 bis 100:1 durchgeführt wird.
- 30 18. Verfahren nach Anspruch 16, wobei der Schritt des Mischens des Alkans und des Broms bei einem Alkan-zu-Brom-Molverhältnis zwischen 1:5 bis 50:1 durchgeführt wird.
- 35 19. Verfahren nach Anspruch 16, wobei der Schritt des Mischens des Alkans und des Broms bei einem Alkan-zu-Brom-Molverhältnis zwischen 1:2 bis 10:1 durchgeführt wird.
- 40 20. Verfahren nach Anspruch 16, wobei der Schritt des Mischens des Alkans und des Broms bei einer Temperatur von zwischen 20°C und 600°C durchgeführt wird.
- 45 21. Verfahren nach Anspruch 16, wobei der Schritt des Mischens des Alkans und des Broms, um das Alkylbromid und Bromwasserstoff zu bilden, und der Schritt des Inkontaktbringens des Alkylbromids und des Bromwasserstoffs mit einem Metalloxid kontinuierlich durchgeführt werden.
- 50 22. Verfahren nach Anspruch 16, wobei der Schritt des Mischens des Alkans und des Broms, um das Alkylbromid und Bromwasserstoff zu bilden, und der Schritt des Inkontaktbringens des Alkylbromids und des Bromwasserstoffs mit einem Metalloxid diskontinuierlich durchgeführt werden.
- 55 23. Verfahren nach Anspruch 16, wobei der Schritt des Oxidierens des Metallbromids, um das ursprüngliche Metalloxid und Brom zu bilden, der Schritt des Rückführens des Metalloxid-Katalysators und der Schritt des Rückführens des Broms kontinuierlich durchgeführt werden.
24. Verfahren nach Anspruch 16, wobei der Schritt des Oxidierens des Metallbromids, um das ursprüngliche Metalloxid und Brom zu bilden, der Schritt des Rückführens des Metalloxids und der Schritt des Rückführens des Broms diskontinuierlich durchgeführt werden.
25. Verfahren nach Anspruch 1, wobei Methan in Dimethylether umgewandelt wird, umfassend:  
Bereitstellen einer Menge Methan; Bereitstellen einer Menge Brom; Mischen des Methans und des Broms und dadurch Bilden von Methylbromid und Bromwasserstoff;  
Einfangen des HBr durch Metalloxid; Umsetzen des Methylbromids mit einem Metalloxid und dadurch Bilden

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von Dimethylether und einem Metallbromid;  
Oxidieren des Metallbromids, um das ursprünglichen Metalloxid und Brom zu bilden;  
Rückführen des Metalloxids; und Rückführen des Broms.

- 5     **26.** Verfahren nach Anspruch 25, wobei der Schritt des Mischens des Methans und des Broms bei einem Methan-zu-Brom-Molverhältnis zwischen 1:10 bis 100:1 durchgeführt wird.
- 27.** Verfahren nach Anspruch 25, wobei der Schritt des Mischens des Methans und des Broms bei einem Methan-zu-Brom-Molverhältnis zwischen 1:5 bis 50:1 durchgeführt wird.
- 10     **28.** Verfahren nach Anspruch 25, wobei der Schritt des Mischens des Methans und des Broms bei einem Methan-zu-Brom-Molverhältnis zwischen 1:2 bis 10:1 durchgeführt wird.
- 29.** Verfahren nach Anspruch 25, wobei der Schritt des Mischens des Methans und des Broms bei einer Temperatur von zwischen 20°C und 600°C durchgeführt wird.
- 30.** Verfahren nach Anspruch 25, wobei der Schritt des Mischens des Methans und des Broms, um das Methylbromid und Bromwasserstoff zu bilden, der Schritt des Einfangens von HBr durch Metalloxid und der Schritt des Inkontaktbringens des Methylbromids mit Metalloxiden kontinuierlich durchgeführt wird.
- 20     **31.** Verfahren nach Anspruch 25, wobei der Schritt des Oxidierens des Metallbromids, um das ursprüngliche Metalloxid und Brom zu bilden, der Schritt des Rückführens des Metalloxids und der Schritt des Rückführens des Broms kontinuierlich durchgeführt werden.

25

### Revendications

1. Procédé de synthèse d'alcools et/ou d'éthers à partir d'alcane comprenant :
- 30           la fourniture d'une quantité d'un alcane sélectionné dans le groupe constitué par le méthane, l'éthane, le propane, le butane et l'isobutane ; la fourniture d'une quantité de brome ; le mélange de l'alcane et du brome et ainsi la formation de bromure d'alkyle et de bromure d'hydrogène ; la réaction du bromure d'alkyle et du bromure d'hydrogène avec un oxyde de métal et ainsi la formation d'un alcool et/ou d'un éther et d'un bromure de métal ; l'oxydation du bromure de métal pour former l'oxyde de métal et le bromure d'origine ; le recyclage de l'oxyde de métal et le recyclage du brome.
- 35
2. Procédé selon la revendication 1, dans lequel l'étape de mélange de l'alcane et du brome est réalisée à une température entre 20°C et 600°C.
- 40
3. Procédé selon la revendication 1, dans lequel l'étape de réaction de l'alcane avec le brome pour former le bromure d'alkyle et le bromure d'hydrogène et l'étape de mise en contact du bromure d'alkyle avec des oxydes de métaux sont réalisées en continu.
- 45
4. Procédé selon la revendication 1, dans lequel l'étape de réaction de l'alcane avec le brome pour former le bromure d'alkyle et le bromure d'hydrogène et l'étape de mise en contact du bromure d'alkyle et du bromure d'hydrogène avec des oxydes de métaux sont réalisées dans une réaction discontinue.
- 50
5. Procédé selon la revendication 1, dans lequel l'étape d'oxydation du bromure de métal pour former l'oxyde de métal et le brome d'origine, l'étape de recyclage de l'oxyde de métal et l'étape de recyclage du brome sont réalisées en continu.
- 55
6. Procédé selon la revendication 1, dans lequel l'étape d'oxydation du bromure de métal pour former l'oxyde de métal et le brome d'origine, l'étape de recyclage de l'oxyde de métal et l'étape de recyclage du brome sont réalisées dans une réaction discontinue.
7. Procédé selon la revendication 1, dans lequel l'alcane est le méthane et l'alcool est le méthanol, comprenant :
- la fourniture d'une quantité de méthane ; la fourniture d'une quantité de brome ; la réaction du méthane avec

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le brome et ainsi la formation de bromure de méthyle et de bromure d'hydrogène ; la réaction du bromure de méthyle et du bromure d'hydrogène avec un catalyseur d'oxyde de métal et ainsi la formation de méthanol et d'un bromure de métal ;

l'oxydation du bromure de métal pour former l'oxyde de métal et le bromure d'origine ; le recyclage de l'oxyde de métal et le recyclage du brome.

- 5
8. Procédé selon la revendication 7, dans lequel l'étape de mélange du méthane et du brome est réalisée selon un rapport entre le méthane et le brome de 1:10 à 100:1 (en moles).
- 10
9. Procédé selon la revendication 7, dans lequel l'étape de mélange du méthane et du brome est réalisée selon un rapport entre le méthane et le brome de 1:1 à 10:1 (en moles).
10. Procédé selon la revendication 7, dans lequel l'étape de mélange du méthane et du brome est réalisée selon un rapport entre le méthane et le brome de 1:1 à 5:1 (en moles).
- 15
11. Procédé selon la revendication 7, dans lequel l'étape de mélange du méthane et du brome est réalisée à une température entre 20°C et 600°C.
12. Procédé selon la revendication 7, dans lequel l'étape de mélange du méthane et du brome pour former le bromure de méthyle et le bromure d'hydrogène et l'étape de mise en contact du bromure de méthyle et du bromure d'hydrogène avec un oxyde de métal sont réalisées en continu.
- 20
13. Procédé selon la revendication 7, dans lequel l'étape de mélange du méthane et du brome pour former le bromure de méthyle et le bromure d'hydrogène et l'étape de mise en contact du bromure de méthyle et du bromure d'hydrogène avec un oxyde de métal sont réalisées dans une réaction discontinue.
- 25
14. Procédé selon la revendication 7, dans lequel l'étape d'oxydation du bromure de métal pour former le catalyseur d'oxyde de métal et le brome d'origine, l'étape de recyclage de l'oxyde de métal et l'étape de recyclage du brome sont réalisées en continu.
- 30
15. Procédé selon la revendication 7, dans lequel l'étape d'oxydation du bromure de métal pour former le catalyseur d'oxyde de métal et le brome d'origine, l'étape de recyclage de l'oxyde de métal et l'étape de recyclage du brome sont réalisées dans une réaction discontinue.
- 35
16. Procédé selon la revendication 1, dans lequel un éther est synthétisé à partir d'un alcane, comprenant :
- la fourniture d'une quantité d'un alcane sélectionné dans le groupe constitué par le méthane et l'éthane ; la fourniture d'une quantité de brome ; le mélange de l'alcane et du brome et ainsi la formation de bromure d'alkyle et de bromure d'hydrogène ; la réaction du bromure d'alkyle avec un oxyde de métal et ainsi la formation d'un éther et d'un bromure de métal ; l'oxydation du bromure de métal pour former le catalyseur d'oxyde de métal et le brome d'origine ; le recyclage du catalyseur d'oxyde de métal et le recyclage du brome.
- 40
17. Procédé selon la revendication 16, dans lequel l'étape de mélange de l'alcane et du brome est réalisée selon un rapport molaire entre l'alcane et le brome entre 1:10 et 100:1.
- 45
18. Procédé selon la revendication 16, dans lequel l'étape de mélange de l'alcane et du brome est réalisée selon un rapport molaire entre l'alcane et le brome entre 1:5 et 50:1.
19. Procédé selon la revendication 16, dans lequel l'étape de mélange de l'alcane et du brome est réalisée selon un rapport molaire entre l'alcane et le brome entre 1:2 et 10:1.
- 50
20. Procédé selon la revendication 16, dans lequel l'étape de mélange de l'alcane et du brome est réalisée à une température entre 20°C et 600°C.
- 55
21. Procédé selon la revendication 16, dans lequel l'étape de mélange de l'alcane et du brome pour former le bromure d'alkyle et le bromure d'hydrogène et l'étape de mise en contact du bromure d'alkyle et du bromure d'hydrogène avec un oxyde de métal sont réalisées en continu.

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22. Procédé selon la revendication 16, dans lequel l'étape de mélange de l'alcane et du brome pour former le bromure d'alkyle et le bromure d'hydrogène et l'étape de mise en contact du bromure d'alkyle et du bromure d'hydrogène avec un oxyde de métal sont réalisées dans une réaction discontinue.
- 5 23. Procédé selon la revendication 16, dans lequel l'étape d'oxydation du bromure de métal pour former l'oxyde de métal et le brome d'origine, l'étape de recyclage du catalyseur d'oxyde de métal et l'étape de recyclage du brome sont réalisées en continu.
- 10 24. Procédé selon la revendication 16, dans lequel l'étape d'oxydation du bromure de métal pour former l'oxyde de métal et le brome d'origine, l'étape de recyclage de l'oxyde de métal et l'étape de recyclage du brome sont réalisées dans des réactions discontinues.
- 15 25. Procédé selon la revendication 1, dans lequel le méthane est converti en éther diméthylque, comprenant :
- la fourniture d'une quantité de méthane ; la fourniture d'une quantité de brome ; le mélange du méthane et du brome et ainsi la formation de bromure de méthyle et de bromure d'hydrogène ; le piégeage de HBr par l'oxyde de métal ; la réaction du bromure de méthyle avec un oxyde de métal et ainsi la formation d'éther diméthylque et d'un bromure de métal ;  
l'oxydation du bromure de métal pour former l'oxyde de métal et le brome d'origine ; le recyclage de l'oxyde de métal et le recyclage du brome.
- 20 26. Procédé selon la revendication 25, dans lequel l'étape de mélange du méthane et du brome est réalisée selon un rapport molaire entre le méthane et le brome entre 1:10 et 100:1.
- 25 27. Procédé selon la revendication 25, dans lequel l'étape de mélange du méthane et du brome est réalisée selon un rapport molaire entre le méthane et le brome entre 1:5 et 50:1.
- 30 28. Procédé selon la revendication 25, dans lequel l'étape de mélange du méthane et du brome est réalisée selon un rapport molaire entre le méthane et le brome entre 1:2 et 10:1.
- 35 29. Procédé selon la revendication 25, dans lequel l'étape de mélange du méthane et du brome est réalisée à une température entre 20°C et 600°C.
- 40 30. Procédé selon la revendication 25, dans lequel l'étape de mélange du méthane et du brome pour former le bromure de méthyle et le bromure d'hydrogène, l'étape de piégeage de HBr par un oxyde de métal et l'étape de mise en contact du bromure de méthyle avec des oxydes de métaux sont réalisées en continu.
- 45 31. Procédé selon la revendication 25, dans lequel l'étape d'oxydation du bromure de métal pour former l'oxyde de métal et le brome d'origine, l'étape de recyclage de l'oxyde de métal et l'étape de recyclage du brome sont réalisées en continu.
- 50
- 55

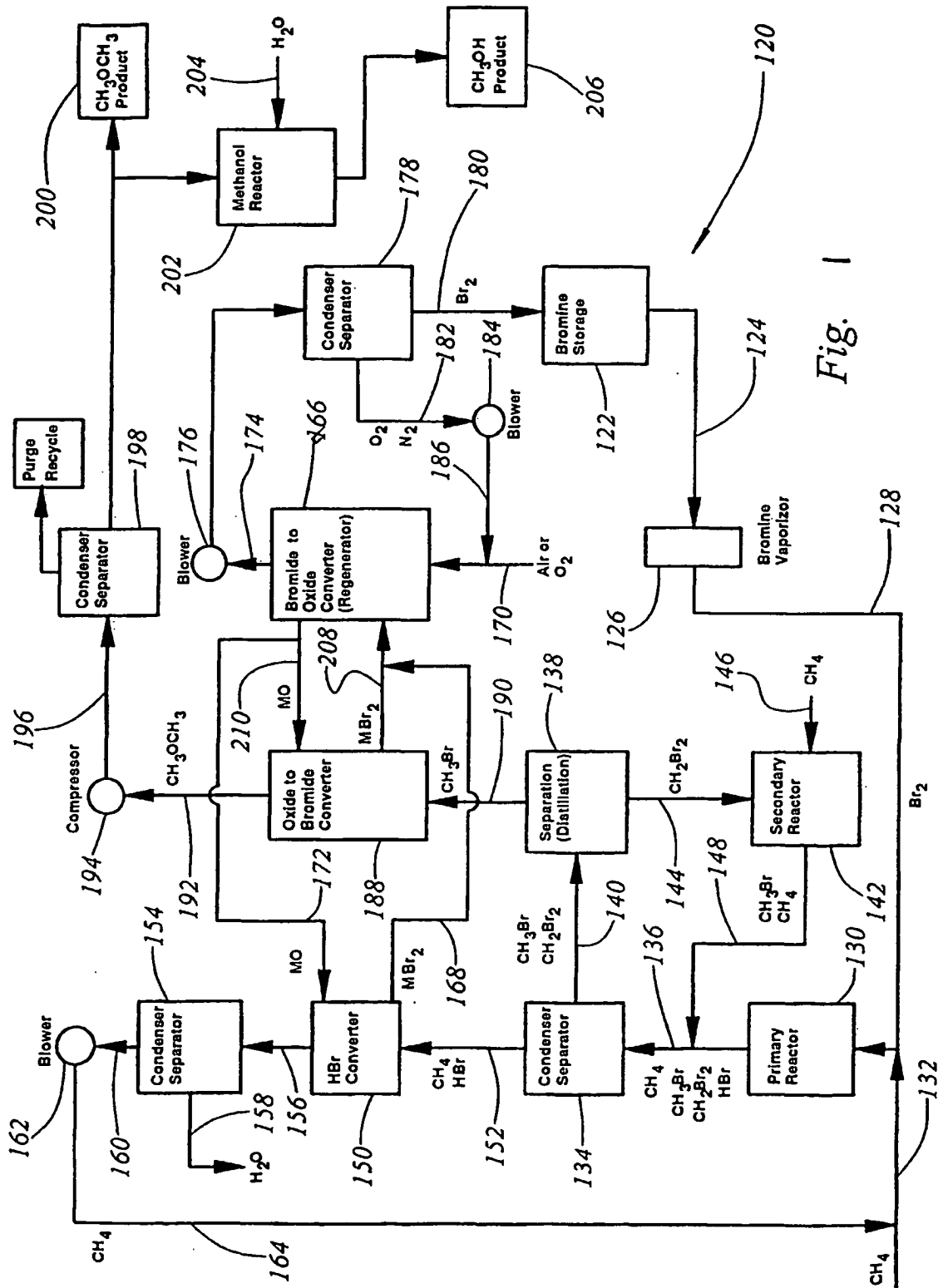


Fig. 1

**REFERENCES CITED IN THE DESCRIPTION**

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