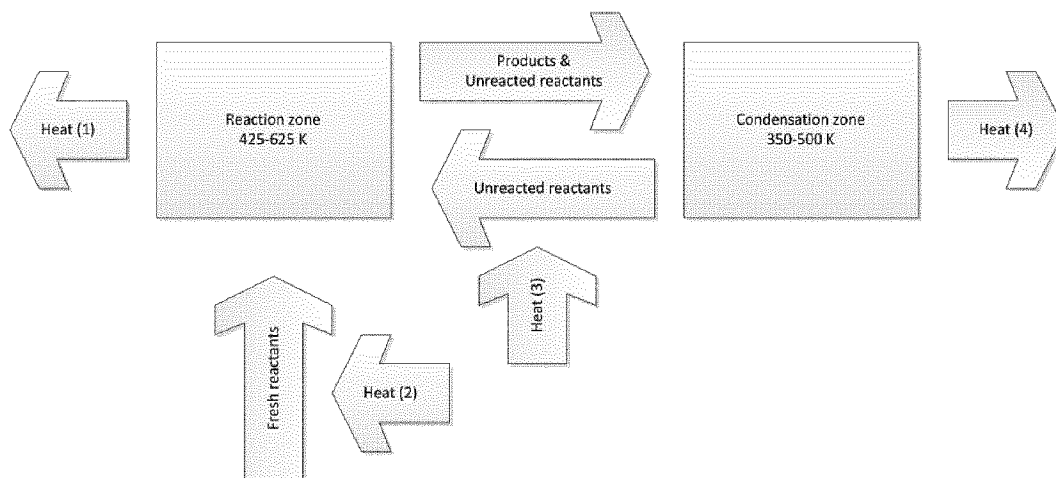




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(72) Inventeurs/Inventors:
O'CONNOR, PAUL, NL;
ROESTENBERG, TIMO, NL;
MARINIC, SASA, NL
(73) Propriétaire/Owner:
CLIMEWORKS AG, CH
(74) Agent: BERESKIN & PARR LLP/S.E.N.C.R.L.,S.R.L.

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(54) Title: ENERGY INTEGRATED CARBON DIOXIDE CONVERSION PROCESS



(57) Abrégé/Abstract:

An energy integrated process is disclosed for the conversion of carbon dioxide to a liquid product. The conversion reaction is exothermic. The heat of reaction and the heat of condensation of the reaction product or products are used as energy input in a carbon dioxide enrichment step. The enrichment step produces a feed gas for the conversion reaction.

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(71) Applicant: ANTECY B.V. [NL/NL]; Hogebrinkerweg
15E, NL-3871 KM Hoevelaken (NL).

(72) Inventors: O'CONNOR, Paul; Hogebrinkerweg 9, NL-
3871 KM Hoevelaken (NL). ROESTENBERG, Timo;
David Wijnveldtweg 1, NL-7425 AC Deventer (NL).
MARINIC, Saša; Speenkruid 6, NL-3892 AC Zeewolde
(NL).

(74) Agents: DERKS, Wilhelmus et al.; P.O. Box 94361, Rem-
brandt Tower, 31st floor, Amstelplein 1, NL-1096 HA Am-
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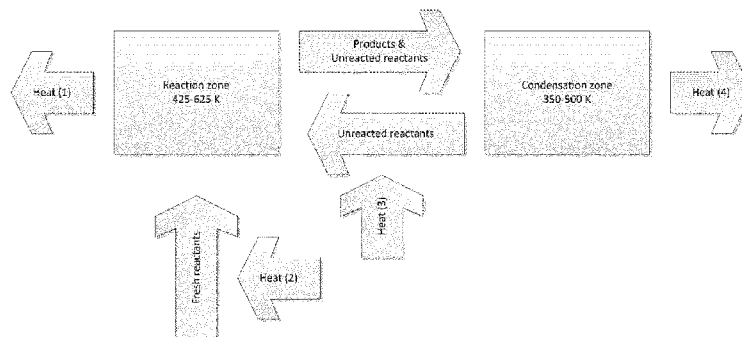
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(54) Title: ENERGY INTEGRATED CARBON DIOXIDE CONVERSION PROCESS

Figure 1



(57) Abstract: An energy integrated process is disclosed for the conversion of carbon dioxide to a liquid product. The conversion reaction is exothermic. The heat of reaction and the heat of condensation of the reaction product or products are used as energy input in a carbon dioxide enrichment step. The enrichment step produces a feed gas for the conversion reaction.

ENERGY INTEGRATED CARBON DIOXIDE CONVERSION PROCESS

BACKGROUND OF THE INVENTION

1. Field of the Invention

[0001] The invention relates generally to a process for converting carbon dioxide in an exothermic reaction, and more specifically to such process whereby energy released in the exothermic reaction is used in a preceding carbon dioxide enrichment step.

2. Description of the Related Art

[0002] Prior art processes for converting carbon dioxide to liquid products, such as methanol, are known. Such processes require feed gases having high carbon dioxide content. For this reason such processes generally are integrated with industrial plants that produce gases having high carbon dioxide content, such as power plants, refineries, and the like. Such gases typically contain contaminants, such as SO_x, that are corrosive and act as poisons to carbon dioxide conversion catalysts. The feed gases therefore need to be purified before they can be used in the carbon dioxide conversion process.

[0003] Carbon dioxide conversion processes, such as the conversion to methanol, are strongly exothermic. Thermal energy must continuously be withdrawn from the carbon dioxide conversion reactor. To avoid energy waste and thermal pollution of the environment, carbon dioxide conversion plants need to be operated in conjunction with other industrial processes having a net energy demand, so that heat generated by the carbon dioxide conversion process can be put to good economic use.

[0004] Thus, there is a need for a carbon dioxide conversion process that is sufficiently energy balanced to be operated in stand-alone fashion. There is a further need for a carbon dioxide conversion process that can use feedstock gases that have relatively low carbon dioxide concentration, such as ambient air.

BRIEF SUMMARY OF THE INVENTION

[0005] The present invention addresses these problems by providing an energy integrated CO₂ conversion process comprising the steps of:

- a. a CO₂ enrichment step whereby the CO₂ concentration of a feed gas is increased, said enrichment step requiring an energy input;

b. a CO₂ conversion step whereby CO₂ is converted to a liquid product, said conversion step producing an energy output;

whereby the energy output is used to at least partially offset the energy input.

BRIEF DESCRIPTION OF THE DRAWINGS

[0005b] FIG. 1 is a schematic representation of an embodiment of the process according to the invention.

[0005c] FIG. 2 schematically depicts an embodiment of the process according to the invention in which the reaction zone and the condensation zone are at the same or close to the same temperature.

DETAILED DESCRIPTION OF THE INVENTION

[0006] The following is a detailed description of the invention.

Definitions

[0007] In its broadest aspect the present invention relates to an energy integrated CO₂ conversion process comprising the steps of:

a. a CO₂ enrichment step whereby the CO₂ concentration of a feed gas is increased, said enrichment step requiring an energy input;

b. a CO₂ conversion step whereby CO₂ is converted to a liquid product, said conversion step producing an energy output;

whereby the energy output is used to at least partially offset the energy input.

[0008] An important aspect of the process of the present invention is the use of a feed gas having low carbon dioxide concentration. In general, any feed gas having a carbon dioxide concentration of less than 50% v/v is suitable for the process. However, the economic advantages of the process are most pronounced when feed gases having much lower carbon dioxide concentrations are used. The process is suitable for use of ambient air as a feed gas. Ambient air currently has a carbon dioxide concentration of

about 400 ppm. As ambient air is abundantly available, and substantially free of corrosive contaminants, ambient air is a preferred feed gas for the process of the present invention.

[0009] The process comprises a carbon dioxide enrichment step, whereby the carbon dioxide concentration of the feed gas is increased. The carbon dioxide enrichment step requires an energy input.

[0010] Examples of carbon dioxide enrichment processes include processes whereby the feed gas is contacted with an absorbent material capable of absorbing carbon dioxide. In a desorption step, absorbed carbon dioxide is released from the absorbent material in a form that is purified relative to the feed gas. Such processes require energy input for contacting the feed gas with the absorbent material, for example using a compressor to force the feed gas through a bed of absorbent material. It will be understood that, the lower the carbon dioxide concentration of the feed gas, the larger the volume of feed gas that must be contacted with the absorbent, and the larger the energy input required.

[0011] The desorption step may involve heating the absorbent material, flushing the absorbent material with a flushing gas, applying vacuum to the absorbent material, or a combination of these measures. Whatever method is employed for desorbing carbon dioxide from the absorbent material, energy input will unavoidably be required.

[0012] The absorbent material can be any absorbent material for carbon dioxide known in the art. Examples include amines, alkali metal and earth alkaline salts, oxides and hydroxides, and the like. It has been found that salts that absorb carbon dioxide under formation of a bicarbonate are particularly suitable. Sodium and potassium salts, in particular potassium salts, are particularly preferred, in particular sodium and potassium carbonates and hydrates thereof. Highly preferred absorbent materials are disclosed in more detail in published patent application PCT/EP 2013/065070.

[0013] Swing processes have been found to be particularly suitable for enrichment of carbon dioxide-containing feed gases. Examples include temperature swing processes,

pressure swing processes, moisture swing processes, and processes using combinations thereof. A preferred method and apparatus, optionally using water vapor as a flushing gas, is disclosed in published patent application PCT/EP 2013/065074.

[0014] The feed gas enriched in carbon dioxide is used in a subsequent carbon dioxide conversion reaction. Particularly preferred for use in the process of the invention is the conversion of carbon dioxide to methanol. A suitable example of this conversion is the thermo-catalytic conversion. Various catalysts have been proposed for this reaction, for example Cu/ZnO/Al₂O₃. See, for example, a discussion of the history of the industrial use of this reaction in J.G. van Bennekom et al., Chem. Eng. Sci. 87 (2013) 204-208.

[0015] The conversion reaction:



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is exothermic, and produces 141 kJ/mole. In addition the process generally includes condensation of the reaction products (methanol and water), which produces 28 kJ mole of methanol, and 39 kJ/mole of water, for a total of 67 kJ/mole of converted CO₂.

[0016] In an embodiment condensation of methanol takes place in the conversion reactor. This can be accomplished by carrying out the reaction at a relatively high pressure (e.g., 25-175 bar), and by providing one or more condensation zones inside the reactor. The condensation zone or zones are kept at a lower temperature than the reaction zone or zones inside the reactor. For example, the reaction zone or zones may be kept at a temperature in the range of 475K to 575K, and the condensation zones at a temperature in the range of 350K to 400K. It will be understood that the temperature of the condensation zone or zones must be low enough to achieve condensation of methanol. If the reactor pressure is at the high end of the range, for example 175 bar, the temperature of the condensation zone can be kept relatively high, for example 400K. If the reactor pressure is at the low end of the range, for example 25 bar, the condensation zone must be kept at a lower temperature, for example 350K in order to cause condensation of the methanol.

[0017] Carrying out condensation of methanol inside the reactor has the important advantage of causing an equilibrium shift. In effect, condensation of methanol causes this reaction product to be withdrawn from the reaction mixture, which shifts the equilibrium of reaction (1) to the right hand side.

[0018] In an alternate embodiment unreacted reactants and reaction products are withdrawn from the conversion reactor as a gaseous mixture. The reaction products are separated from this mixture by condensation in a separate vessel. The unreacted reactants are recycled to the conversion reactor.

[0019] The integrated process of the invention comprises various heating and cooling steps. For example, step a. may be carried out at temperatures in the range of 250K to 450K. Step a. may involve a temperature swing over a range of 60K to 150K, preferably from 60K to 99K. Step b. may be carried out at a temperature in the range of, for example, 425K to 550K. In general, increasing the temperature of reactants, reaction products and equipment requires an energy input; decreasing the temperature of reactants, reaction products and equipment produces an energy output. The process of the invention aims at capturing the energy outputs as much as possible, and applying them to the required energy inputs.

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[0020] Key to successful operation of the process of the invention is the significant energy output of step b. It should be noted that step b. is the conversion of CO₂ to a liquid reaction product, that is, its energy output comprises the heat of reaction of the conversion, and the heat of condensation of the reaction products. Accordingly, step b. may produce from 100kJ to 200kJ per mole of converted CO₂.

DESCRIPTION OF ILLUSTRATIVE EMBODIMENTS/EXAMPLES

[0021] The following is a description of certain embodiments of the invention, given by way of example only.

Example 1

[0022] Figure 1 is a schematic representation of an embodiment of the process. The reaction zone and the condensation zone are operated at a relatively low pressure, for example in the range of 25 to 100 bar. The reaction zone and the condensation zone are kept at significantly different temperatures. The reaction zone may be at 425K to 625K; the condensation zone at 350K to 500K. Figure 1 also represents embodiments in which the condensation is carried out in a separate vessel.

[0023] It will be understood that Figure 1 captures only step b. of the process. The various energy flows are as follows. Heat (1) is the heat of reaction. Heat (2) is the energy required to raise the temperature of the reactants from ambient to the reaction temperature. In many cases carbon dioxide produced in step a. may have a temperature significantly above ambient temperature, so that Heat (2) in those cases is less than is calculated in this example.

[0024] Unreacted reactants are recycled from the condensation zone to the reaction zone. Heat (3) represents the energy input required for raising the temperature of the unreacted reactants from the condensation zone temperature to the reaction zone temperature. Heat (4) is the energy output resulting from cooling the reactants and reaction products from the reaction zone temperature to the condensation zone temperature, and the heat of condensation of the reaction products.

[0025] The energy balance has been calculated for a reaction zone temperature of 525K and a condensation zone temperature of 375K. The conversion is assumed to be 20% per pass.

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This means that for every mole CO₂ in the fresh reactant stream there are 4 moles of CO₂ in the stream of unreacted reactants. For every mole of CO₂ in the fresh reactant stream there are 3 moles of H₂ in the fresh reactant stream, and 12 moles of H₂ in the stream of unreacted reactants.

[0026] The heat balance calculations are summarized in Table 1

Flow	Contributor	Energy (per mole CO ₂ converted)	Total
Heat (1)	Reaction heat	141 kJ @525K	141 kJ @525K
Heat (2)	Heat capacity CO ₂ , 1 mole , 293 → 525K	-9.5 kJ @525K	-37 kJ @525K
	Heat capacity H ₂ , 3 mole, 293 → 525K	-27 kJ @525K	
Heat (3)	Heat capacity CO ₂ , 4 mole, 375 → 525K	-25 kJ @525K	-95 kJ @525K
	Heat capacity H ₂ , 12 mole, 375 → 525K	-70 kJ @525K	
Heat (4)	Heat capacity CO ₂ , 4 mole, 525 → 375K	25 kJ @375K	176 kJ @375K
	Heat capacity H ₂ , 12 mole, 525 → 375K	70 kJ @375K	
	Heat capacity CH ₃ OH, 1 mole, 525 → 375K	9.2 kJ @375K	
	Heat capacity H ₂ O, 1 mole, 525 → 375K	5.4 kJ @375K	
	Condensation heat CH ₃ OH, 1 mole	28 kJ @375K	
	Condensation heat H ₂ O, 1 mole	39 kJ @375K	

[0027] In Table 1, positive values represent energy outputs, and negative values represent energy inputs. The net energy output of step b. in this example is 141-37-95+176=185kJ per mole of converted CO₂.

Step a. may be a temperature swing absorption/desorption process, whereby CO₂ is absorbed from ambient air by potassium sesquihydrate on an active carbon support. Absorption of CO₂ involves conversion of the potassium carbonate to potassium bicarbonate, and desorption requires the reverse reaction. The heat of reaction is 41kJ/mole. The heat capacity of the active carbon support is 900 J/kg*K. The absorption capacity of the absorbent material, which according to literature data is between 1 and 2.5 mole of CO₂ per kg, is for the purpose of this calculation assumed to be 1 mole/kg. If the available heat energy from step b. is 185

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kJ/mole, the achievable temperature swing is $(185-41)/0.9=160\text{K}$. This is more than sufficient for an absorption/desorption swing process.

Example 2

[0028] Figure 2 schematically depicts an embodiment of the process in which the reaction zone and the condensation zone are at the same (or close to the same) temperature, for example in the range of from 425K to 625K. To accomplish methanol condensation at the reaction temperature, a relatively high pressure is required, for example >150 bar.

[0029] Heat (A) is the energy input required for raising the temperature of the reactants from ambient temperature to the reaction temperature. Heat (B) is the energy output resulting from the conversion reaction and the condensation of the reaction products.

[0030] The energy balance has been calculated for a reaction temperature of 525K. The one-pass conversion is assumed to be 100% (due to the equilibrium shift resulting from the *in situ* condensation of methanol). The energy calculations are summarized in Table 2.

Table 2

Flow	Contributor	Energy (per mole CO ₂ converted)	Total
Heat (A)	Heat capacity CO ₂ , 1 mole, 293 → 525K	-9.5 kJ @525K	-37 kJ @525K
	Heat capacity H ₂ , 3 mole, 293 → 525K	-27 kJ @525K	
Heat (B)	Reaction heat	141 kJ @525K	208 kJ @525K
	Condensation heat CH ₃ OH, 1 mole	28 kJ @375K	
	Condensation heat H ₂ O, 1 mole	39 kJ @375K	

[0031] In this embodiment step b. produces $(208-37)=171\text{kJ/mole}$ of converted CO₂. As in Example 1, the energy produced by step b. is more than the energy required for step a.

[0032] Thus, the invention has been described by reference to certain embodiments discussed above. It will be recognized that these embodiments are susceptible to various modifications and alternative forms well known to those of skill in the art.

[0033] Many modifications in addition to those described above may be made to the structures and techniques described herein without departing from the spirit and scope of the

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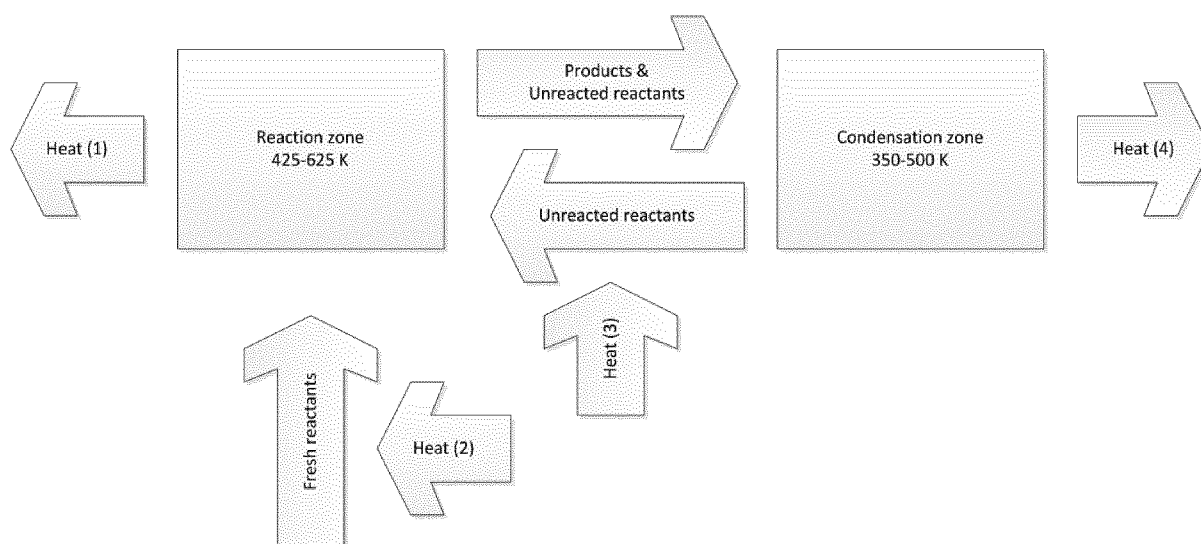
invention. Accordingly, although specific embodiments have been described, these are examples only and are not limiting upon the scope of the invention.

WHAT IS CLAIMED IS:

1. An energy integrated CO₂ conversion process comprising the steps of
 - a. a CO₂ enrichment step whereby the CO₂ concentration of a feed gas is increased, said enrichment step requiring an energy input, wherein said feed gas is ambient air;
 - b. a CO₂ conversion step whereby CO₂ is converted to a liquid product, said conversion step producing an energy output;whereby the energy output is used to at least partially offset the energy input wherein step a. comprises use of an absorbent comprising an alkali metal salt or an alkaline earth salt wherein step a. is operated at temperatures in a range of from 250K to 450K and wherein step b. is carried out in a reactor, and equilibrium shift is accomplished by condensing liquid product inside the reactor.
2. The process of claim 1, wherein step a. comprises a swing absorption/desorption process.
3. The process of claim 2, wherein the swing process comprises a temperature swing, a pressure swing, a moisture swing, or a combination thereof.
4. The process of any one of claims 1 to 3, wherein the absorbent comprises a salt of sodium or potassium.
5. The process of claim 4, wherein the absorbent comprises potassium carbonate or a hydrate thereof.
6. The process of any one of claims 1 to 5, wherein step b. comprises conversion of CO₂ to methanol.
7. The process of claim 6 wherein step b. comprises a thermo-catalytic conversion of CO₂ to methanol.
8. The process of any one of claims 1 to 7, wherein the reactor comprises at least one reaction zone and at least one methanol condensation zone, the reaction zone or zones having a higher temperature than the methanol condensation zone or zones.

9. The process of claim 8, wherein the reaction zone or zones have substantially the same pressure as the condensation zone or zones.
10. The process of any one of claims 1 to 9, wherein step a. comprises a temperature swing of 60K to 150K.
11. The process of claim 10, wherein step a. comprises a temperature swing of 60K to 99K.
12. The process of any one of claims 1 to 11, wherein step b. is operated at temperatures in a range of from 425K to 550K.
13. The process of any one of claims 1 to 12, wherein step b. produces from 100 kJ to 200 kJ per mole of converted CO₂.
14. An energy integrated CO₂ conversion process comprising the steps of
 - a. a CO₂ enrichment step whereby the CO₂ concentration of a feed gas is increased, said enrichment step requiring an energy input, wherein said feed gas is ambient air;
 - b. a CO₂ conversion step whereby CO₂ is converted to a liquid product, said conversion step producing an energy output;whereby the energy output is used to at least partially offset the energy input wherein step a. comprises use of an absorbent comprising an alkali metal salt or an alkaline earth salt wherein step a. is operated at temperature in a range of from 250K to 450K and step b. produces from 100 kJ to 200 kJ per mole of converted CO₂.
15. The process of claim 14, wherein step a. comprises a swing absorption/desorption process.
16. The process of claim 15, wherein the swing process comprises a temperature swing, a pressure swing, a moisture swing, or a combination thereof.
17. The process of any one of claims 14 to 16, wherein the absorbent comprises a salt of sodium or potassium.
18. The process of claim 17, wherein the absorbent comprises potassium carbonate or a hydrate thereof.
19. The process of any one of claims 14 to 18, wherein step b. comprises conversion of CO₂ to methanol.

20. The process of claim 19 wherein step b. comprises a thermo-catalytic conversion of CO₂ to methanol.
21. The process of any one of claims 19 or 20, wherein step b. is carried out in a reactor, and equilibrium shift is accomplished by condensing methanol inside the reactor.
22. The process of claim 21, wherein the reactor comprises at least one reaction zone and at least one methanol condensation zone, the reaction zone or zones having a higher temperature than the methanol condensation zone or zones.
23. The process of claim 22, wherein the reaction zone or zones have substantially the same pressure as the condensation zone or zones.
24. The process of any one of claims 14 to 23, wherein step a. comprises a temperature swing of 60K to 150K.
25. The process of claim 24, wherein step a. comprises a temperature swing of 60K to 99K.
26. The process of any one of claims 14 to 25, wherein step b. is operated at temperatures in a range of from 425K to 550K.

Figure 1**Figure 2**