

DESCRIPTION

PROCESS FOR PRODUCING ACETIC ACID AND AMMONIA

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TECHNICAL FIELD

[0001] The present invention relates to a process for producing a carboxylic acid (such as acetic acid) and ammonia independently (or for co-producing a carboxylic acid and ammonia or for producing a carboxylic acid (such as acetic acid) and ammonia in parallel).

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BACKGROUND ART

[0002] Ammonia is obtained by a reaction of hydrogen and nitrogen, and in the reaction, a synthetic gas is usually employed as a hydrogen source. The synthetic gas comprises carbon monoxide in addition to hydrogen. The carbon monoxide in the synthetic gas and water are allowed to react with each other (such a reaction is generally called a water gas shift reaction), and the hydrogen generated (or

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produced) by the reaction is used for an ammonia production. The shift reaction mentioned above produces a large amount of the hydrogen available for the ammonia production but also a large amount of carbon dioxide as a by-product.

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[0003] On the other hand, acetic acid is generally obtained by a reaction of carbon monoxide and methanol, and the reaction also usually employs a synthetic gas as a carbon monoxide source. Although the hydrogen in the synthetic

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gas is unnecessary in this reaction, the hydrogen in the synthetic gas is used for the syntheses of methanol, dimethyl ether, or the like. These syntheses also need carbon monoxide. Therefore, a process using the synthetic gas more efficiently is required.

[0004] An attempt to improve use efficiency of synthetic gas has been suggested. WO 01/32594 (Patent Document 1) discloses a process for producing a reaction product (such as acetic acid) from carbon monoxide and methanol. The process comprises the steps of (1) producing a synthetic gas containing hydrogen, carbon monoxide, and carbon dioxide from a hydrocarbon such as a natural gas; and (2) converting the hydrogen and carbon monoxide in the synthetic gas into methanol. This document further discloses the following:

part or all of the synthetic gas is separated into a carbon dioxide-rich gas stream, a carbon monoxide-rich gas stream, and a hydrogen-rich gas stream; the carbon dioxide-rich gas stream is recycled for a production of the synthetic gas; and the hydrogen-rich gas stream is used for a synthesis of ammonia. That is, although this document suggests that the process for co-producing (producing) acetic acid and ammonia (in parallel), the process produces methanol as a raw material of acetic acid and acetic acid from the same synthetic gas after all. This means that the process does not pay attention to the carbon dioxide as a by-product produced by a shift reaction for an ammonia production as mentioned above but uses the carbon dioxide contained in

a small amount in the synthetic gas for synthesizing a synthetic gas, the amount of the carbon dioxide recycled to the synthetic gas is limited. Moreover, for the synthesis of methanol, the process uses the natural gas as a raw material of the synthetic gas having a large hydrogen content. Thus, a large-scale or additional separation apparatus or device for separating a large amount of hydrogen is necessary in the subsequent step(s). Further, this process does not efficiently use oxygen separated from air as a nitrogen source for the synthesis of ammonia.

RELATED ART DOCUMENTS

PATENT DOCUMENTS

[0005] [Patent Document 1] WO 01/32594 (Claims and Drawings)

DISCLOSURE OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0006] Therefore, it is an object of the present invention to provide an efficient process for producing a carboxylic acid (such as acetic acid) and ammonia independently.

[0007] Another object of the present invention is to provide a process for producing a carboxylic acid and ammonia independently while having a less amount of the generated carbon dioxide.

[0008] It is a further object of the present invention to provide a process for producing a carboxylic acid and

ammonia independently while the process requires a less amount of a carbonaceous material (such as a coal) to be used for a raw material of a synthetic gas.

[0009] Another object of the present invention is to
5 provide a process for producing a carboxylic acid and ammonia independently while efficiently using oxygen separated from air as a nitrogen source for an ammonia production.

[0010] An even further object of the present invention is to provide a process for producing a carboxylic acid
10 and ammonia independently while controlling the amounts of the produced carboxylic acid and the produced ammonia (or the proportion of the produced carboxylic acid relative to the produced ammonia).

15 MEANS TO SOLVE THE PROBLEMS

[0011] The inventor of the present invention made extensive studies and finally found that each of the following processes (1) and (2) produces a carboxylic acid and ammonia independently and efficiently. Firstly, the process (1)
20 comprises a carboxylic acid (e.g., acetic acid) production step using the carbon monoxide separated from a synthetic gas (A) (a synthetic gas derived from an oil, a coal, a natural gas, or the like, particularly, a synthetic gas derived from a coal); and an ammonia production step using
25 the hydrogen separated from the synthetic gas (A) and the hydrogen obtained from a shift reaction of a synthetic gas (B) which is the same as or different from the synthetic

gas (A). (In particular, the synthetic gases (A) and (B) are the same.) Secondly, the process (2) comprises a carboxylic acid (e.g., acetic acid) production step using the carbon monoxide separated from a synthetic gas (A) having
5 a molar ratio of carbon monoxide relative to hydrogen of approximately 1; and an ammonia production step using the hydrogen separated from the synthetic gas (A). In particular, the process (1) allows the efficient production of the carboxylic acid and ammonia independently with
10 controlling the ratio thereof. Moreover, the inventor of the present invention found that, in terms of the amounts of the produced carboxylic acid and the produced ammonia, the amounts of the generated carbon dioxide and a carbonaceous material (e.g., a coal) to be used as a raw
15 material of the synthetic gas in each of the processes (1) and (2) are less than those obtained by conducting separately a process for producing a carboxylic acid with a use of a synthetic gas derived from a coal and a process for producing ammonia with a use of a synthetic gas derived therefrom.

20 [0012] That is, a first production process (process (1)) of the present invention is a process for producing a carboxylic acid and ammonia independently or concurrently. The process (1) comprises the steps of: (a) separating carbon monoxide and hydrogen independently from a synthetic gas
25 (A); (b) producing hydrogen by subjecting a synthetic gas (B) to a shift reaction; (c) producing a carboxylic acid from an alcohol and the carbon monoxide separated from the

synthetic gas (A) (or supplying the carbon monoxide separated from the synthetic gas (A) for producing a carboxylic acid, i.e., in the carboxylic acid production step (c) the carbon monoxide separated from the synthetic gas (A) is used); and (d) producing ammonia from nitrogen, the hydrogen separated from the synthetic gas (A), and the hydrogen obtained by the shift reaction step (b) (or supplying the hydrogen separated from the synthetic gas (A) and the hydrogen obtained by the shift reaction step (b) for producing ammonia, i.e., in the ammonia production step (d) the hydrogen separated from the synthetic gas (A) and the hydrogen obtained by the shift reaction step (b) are used). In this process, the synthetic gas (A) is not particularly limited to a specific one and may be, e.g., a synthetic gas derived from such as an oil, a coal, or a natural gas.

[0013] Moreover, a second production process (process (2)) of the present invention is a process for producing a carboxylic acid and ammonia independently or simultaneously. The process (2) comprises the steps of: (e) separating carbon monoxide and hydrogen independently separated from a synthetic gas (A) having a ratio (molar ratio) of carbon monoxide relative to hydrogen (the former relative to the latter) of 1/0.4 to 1/1.5; (f) producing the carboxylic acid from an alcohol and the carbon monoxide separated from the synthetic gas (A) (or supplying the carbon monoxide separated from the synthetic gas (A) for producing a

carboxylic acid, i.e., in the carboxylic acid production step (f) the carbon monoxide separated from the synthetic gas (A) is used); and (g) producing ammonia from nitrogen and the hydrogen separated from the synthetic gas (A)(or
5 supplying the hydrogen separated from the synthetic gas (A) for producing ammonia, i.e., in the ammonia production step (g) the hydrogen separated from the synthetic gas (A) is used).

[0014] Such a process (the process (1) or (2)) may further
10 comprise a step of (i) producing a synthetic gas by a gasification of a carbonaceous material (or a hydrocarbon source, e.g., a coal). The synthetic gas produced in the synthetic gas production step may be used as a synthetic gas (A). Moreover, this process may further comprise a step
15 of (h) separating nitrogen and oxygen independently from air. The oxygen separated from the oxygen/nitrogen separation step (h) may be used for the gasification of a carbonaceous material (e.g., a coal), and the nitrogen separated from the oxygen/nitrogen separation step (h) may
20 be used in the ammonia production step (d) or (g). An incorporation of such an oxygen/nitrogen separation step (h) into a series of the steps can efficiently use the oxygen separated from air as a nitrogen source for the ammonia production step (d) or (g). Therefore, the process
25 advantageously achieves energy-efficiency.

[0015] In the process (2), similarly the process (1), the ammonia production step (g) may use the hydrogen separated

from the synthetic gas (A) and the hydrogen obtained by a shift reaction of a synthetic gas (a synthetic gas (B) which is different from the synthetic gas (A)). That is, the process (2) may further comprise a shift reaction step of (j) producing hydrogen by subjecting the synthetic gas (B) to a shift reaction, and the ammonia production step (g) may use the hydrogen separated from the synthetic gas (A) and the hydrogen obtained by the shift reaction step (j). Incidentally, in the processes (1) and (2), "the hydrogen obtained by the shift reaction (step)" means a mixed gas of the hydrogen originally contained in the synthetic gas (B) and the hydrogen produced by the shift reaction. The use of such a shift reaction allows the parallel production of the carboxylic acid and ammonia (or the co-production of the carboxylic acid and ammonia) while controlling the amount of the produced ammonia. Therefore, the process of the present invention produces the carboxylic acid and ammonia independently at desirable rates while having a less amount (emission) of the produced carbon dioxide (and a less amount of the coal to be used).

[0016] In particular, in the processes (1) and (2), the synthetic gas (A) and the synthetic gas (B) may be produced in the same synthetic gas production step. That is, the synthetic gas produced in the synthetic gas production step may be separated (divided) into the synthetic gas (A) and the synthetic gas (B), and the synthetic gas (A) and the synthetic gas (B) may respectively be supplied into the

carbon monoxide/hydrogen separation step and the shift reaction step. The use of the same synthetic gas production step can simplify the process and control the amounts of the produced carboxylic acid and the produced ammonia.

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EFFECTS OF THE INVENTION

[0017] Since the process (including the processes (1) and (2)) of the present invention uses a shift reaction of a synthetic gas or a specific synthetic gas having a small
10 ratio of hydrogen (particularly a synthetic gas derived from a coal), a carboxylic acid (e.g., acetic acid) and ammonia are independently and efficiently produced. In terms of the amounts of the produced carboxylic acid and the produced ammonia, the process (including the processes
15 (1) and (2)) of the present invention has less amounts of the generated carbon dioxide and a carbonaceous material (e.g., a coal) to be used as a raw material of the synthetic gas than those obtained by conducting separately a process for producing the carboxylic acid and a process for producing
20 ammonia from each synthetic gas. Moreover, the process of the present invention produces the carboxylic acid and ammonia independently while efficiently using the oxygen separated from air as a nitrogen source for the ammonia production. Therefore, the process of the present
25 invention is highly advantageous from an environmental, industrial, and economical view point. Further, in the process (including the processes (1) and (2)) of the present

invention, the use of the shift reaction allows the production of a carboxylic acid and ammonia with controlling the amounts thereof the produced carboxylic acid and the produced ammonia (the proportion of the produced carboxylic acid relative to the produced ammonia). Such a use of the shift reaction controls the amounts thereof regardless of a change in a ratio of carbon monoxide relative to hydrogen in the carbonaceous material.

10 BRIEF DESCRIPTION OF DRAWINGS

[0018] [Fig. 1]

Fig. 1 is a flow diagram explaining an example of the production process (or production apparatus) of the present invention.

15 [Fig. 2]

Fig. 2 is a flow diagram explaining another example of the production process (or production apparatus) of the present invention.

20 DETAILED DESCRIPTION OF THE INVENTION

[0019] Hereinafter, with reference to the attached drawings according to need, the present invention will be illustrated in more detail. Fig. 1 is a flow diagram for explaining an example of the production process (or production apparatus) of the present invention. Fig. 2 is a flow diagram for explaining another example of the production process (or production apparatus) of the present

invention. The example of Fig. 1 represents a process (or apparatus) for producing a carboxylic acid by allowing the carbon monoxide separated from a synthetic gas derived from a coal to react with an alcohol or a derivative thereof; and a process (or apparatus) for producing ammonia by using the hydrogen separated from the synthetic gas.

[0020] The production process (or apparatus) comprises an oxygen/nitrogen separation unit 1 for separating oxygen and nitrogen independently from air; a synthetic gas production unit 2 for producing a synthetic gas (A) by a gasification of a coal with a use of the oxygen separated in the unit 1; a carbon monoxide/hydrogen separation unit 3 for separating carbon monoxide and hydrogen independently from the synthetic gas (A) produced in the unit 2; a carboxylic acid production unit 4 for producing a carboxylic acid from an alcohol and the carbon monoxide separated in the unit 3; and an ammonia production unit 5 for producing ammonia from the hydrogen separated in the unit 3 and the nitrogen separated in the unit 1.

[0021] Moreover, the production process (or apparatus) further comprises various lines for supplying each component to the corresponding unit. That is, the production process (or apparatus) further comprises the following lines: an oxygen supply line 1A for supplying the oxygen separated in the oxygen/nitrogen separation unit 1 to the synthetic gas production unit 2; a nitrogen supply line 1B for supplying the nitrogen separated in the oxygen/nitrogen separation

unit 1 to the ammonia production unit 5; a synthetic gas supply line 2A for supplying the synthetic gas produced in the synthetic gas production unit 2 as the synthetic gas (A) to the carbon monoxide/hydrogen separation unit 3; a carbon monoxide supply line 3A for supplying the carbon monoxide separated in the separation unit 3 to the carboxylic acid production unit 4; and a hydrogen supply line 3B for supplying the hydrogen separated in the separation unit 3 to the ammonia production unit 5.

10 [0022] First, in the synthetic gas production unit 2, a coal is subjected to a gasification to produce the synthetic gas (A). In this example, using the oxygen separated in the oxygen/nitrogen separation unit 1, the coal is subjected to a partial oxidation for the gasification. The
15 gasification of the coal is usually conducted at a high temperature and under a high pressure. Incidentally, a separation method or process in the oxygen/nitrogen separation unit 1 may include a conventional manner, for example, a method for separating oxygen and nitrogen
20 independently from air as a compressed oxygen and a compressed nitrogen. Specifically, the unit 1 may comprise an air compressor, a compressor for oxygen, a compressor for nitrogen, or the like.

[0023] The gasification of the coal may be conducted using
25 water (a steam) in addition to the oxygen. For example, a slurry of the coal and water may be subjected to a partial oxidation with oxygen. This partial oxidation is preferred

since the process uses the oxygen separated from air as a nitrogen source for the ammonia production. Incidentally, since a synthetic gas production process or step using a natural gas or the like can not usually employ the oxygen
5 separated from air as a nitrogen source, the separated oxygen remains useless.

[0024] It is enough for the synthetic gas production unit 2 to comprise a reactor for the gasification of the coal. The synthetic gas production unit 2 may further comprise
10 a heat recover (or recollecting) apparatus (a cooling apparatus) for recovering heat from (cooling) the generated synthetic gas. Moreover, according to need, the heat recovered from the synthetic gas may be supplied to (the) other steps or units to use the heat for (the) other steps
15 or reactions.

[0025] The synthetic gas produced in the synthetic gas production unit 1 is a gas derived from a coal and has a relatively small ratio of hydrogen (H_2) relative to carbon monoxide (CO) compared with a synthetic gas derived from
20 a natural gas or other gases. For example, in the synthetic gas (synthetic gas (A)), the proportion (molar ratio) of carbon monoxide relative to hydrogen (the former/the latter) is about 1/0.4 to 1/1.5, preferably about 1/0.5 to 1/1.2, and more preferably about 1/0.6 to 1/1 (e.g., about 1/0.65
25 to 1/0.9). In the present invention, the use of such a synthetic gas reduces an amount of the hydrogen to be separated in the carbon monoxide/hydrogen separation unit

(or carbon monoxide/hydrogen separation step). Therefore, the present invention not only has a less amount of the generated carbon dioxide but also allows a scale-down of a separation apparatus.

5 [0026] The synthetic gas usually comprises other components in addition to carbon monoxide and hydrogen. The other components include, for example, water, carbon dioxide, a hydrocarbon (e.g., methane), and hydrogen sulfide. Although the amounts of such other components are smaller
10 than those of carbon monoxide and hydrogen, the other components sometimes have adverse affects on the subsequent steps (e.g., serving as catalytic poisons). For that reason, it is basically preferred that the synthetic gas be free from the other components. However, it is often difficult
15 to produce the synthetic gas without generating such other components as by-products. Therefore, the other components may be separated from the synthetic gas in a separation step or the like as needed. In particular, the proportion of the carbon dioxide contained in the synthetic
20 gas (A) is, for example, about 0 to 0.6 mol, for example, about 0.01 to 0.5 mol (e.g., about 0.1 to 0.5 mol and preferably about 0.25 to 0.45 mol), and more preferably about 0.3 to 0.4 mol (e.g., about 0.33 to 0.38 mol) relative to 1 mol of the carbon monoxide contained in the synthetic
25 gas (A).

[0027] The synthetic gas produced in the synthetic gas production unit 2 is supplied to the separation unit 3 as

the synthetic gas (A) via the synthetic gas supply line 2A. In the separation unit 3, carbon monoxide and hydrogen are independently separated from the synthetic gas. The separation method in the unit 3 may include a conventional
5 method (e.g., a membrane separation method, a cryogenic separation or low-temperature separation, and PSA (pressure swing adsorption) method). In a relatively large scale separation, a cryogenic separation may preferably be used. The separation of these components from the synthetic gas
10 (A) is conducted in any order. That is, after separating hydrogen from the synthetic gas (A), carbon monoxide may be separated from the gas after separating hydrogen from the synthetic gas (A) or the other way around.

[0028] Moreover, as mentioned above, the synthetic gas
15 (or the gas after separating hydrogen from the synthetic gas) comprises the other gases (or gaseous component) in addition to carbon monoxide. In particular, an acid (or acidic) gas (such as carbon dioxide or hydrogen sulfide) has sometimes an adverse affect on the subsequent step(s),
20 especially, the ammonia production step. For that reason, it is preferred that the other components be more completely removed from the separated carbon monoxide and/or hydrogen. Therefore, the separation and removal of these components may be conducted in the separation unit 3 (carbon
25 monoxide/hydrogen separation step) or in a removal unit connected to (or disposed on) an upper stream side of the separation unit. In general, before separating carbon

monoxide and hydrogen independently from the synthetic gas, the acid gas or the like is often removed from the synthetic gas. In the illustrated examples, the separation unit 3 (the unit comprising the acid gas removal unit) separates and removes a representative gas (i.e., carbon dioxide) from the synthetic gas (often, prior to separating carbon monoxide and hydrogen independently from each other or from the synthetic gas). Incidentally, in the illustrated examples, a gas such as hydrogen sulfide is not shown.

10 [0029] The carbon monoxide and hydrogen independently separated in the separation unit 3 are respectively supplied to the carboxylic acid production unit 4 via the line 3A and the ammonia production unit 5 via the line 3B. Since, in the ammonia production, carbon monoxide and/or carbon dioxide serves as a component severely inhibiting the reaction, carbon monoxide and/or carbon dioxide is necessary to be removed from the synthetic gas more completely. Therefore, if necessary, the hydrogen (gas) separated in the separation unit 3 (or separation step) may further be subjected to a conventional method such as a methanator treatment (treatment for converting carbon monoxide into methane) to separate carbon monoxide and/or carbon dioxide and the above hydrogen thoroughly from each other, and then the separated hydrogen may be supplied to the ammonia

25 production unit 5 (not shown in Figures).

[0030] In the carboxylic acid production unit 4 the carboxylic acid is produced, and in the ammonia production

unit 5 ammonia is produced. Such a production apparatus or production process co-produces acetic acid and ammonia independently (or produces acetic acid and ammonia in parallel with each other) while having a less amount of the generated carbon dioxide. For illustrating the reduction in the amount of the generated carbon dioxide and the amount of the coal to be used in the production apparatus or production process of the present invention, a model case in which the amounts of the produced acetic acid and the produced ammonia are respectively 500,000 ton/year is assumed.

[0031] For producing acetic acid at a rate of 500,000 ton/year, the present invention requires a coal as a raw material, for example, at a rate 35 ton/h. The synthetic gas (A) obtained by a gasification of the coal contains CO produced at a rate of $28,000 \text{ Nm}^3/\text{h}$, H_2 produced at a rate of $23,000 \text{ Nm}^3/\text{h}$, and CO_2 produced at a rate of $12,000 \text{ Nm}^3/\text{h}$ (i.e., the molar ratio ($\text{CO}/\text{H}_2/\text{CO}_2$) is $1/0.85/0.49$).

Incidentally, the ratio of the components is calculated assuming that the gasification of the coal is conducted by a coal slurry method. Then, assuming that 100% of the hydrogen contained in the synthetic gas is separated from the synthetic gas (A) and the separated hydrogen is used for the ammonia production, ammonia is produced at a rate of 95,000 ton/year; and as mentioned above, carbon dioxide is generated at a rate of $12,000 \text{ Nm}^3/\text{h}$.

[0032] On the other hand, assuming that a production of

acetic acid at the same rate as above with a use of a coal slurry method and a production of ammonia at the same rate as above therewith are independently conducted, the amount of the generated CO₂ and the amount of the coal to be used are calculated as follows. The acetic acid production at a rate of 500,000 ton/year generates CO₂ at a rate of 12,000 Nm³/h as mentioned above. Moreover, in order to produce ammonia at a rate of 95,000 ton/year, a coal is required at a rate of 15.0 ton/h if all carbon monoxide is used to produce hydrogen by the shift reaction of a synthetic gas (i.e., the coal produces, as the synthetic gas, CO at a rate of 13,000 Nm³/h, H₂ at a rate of 11,000 Nm³/h, and CO₂ at a rate of 5,600 Nm³/h). Accordingly, in the ammonia production, carbon dioxide is produced at a rate of 18,600 Nm³/h (the total of the carbon dioxide produced at a rate of 5,600 Nm³/h in the production of the synthetic gas and the carbon dioxide produced at a rate of 13,000 Nm³/h by the shift reaction).

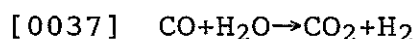
[0033] That is, in the model case in which the amounts of the produced acetic acid and the produced ammonia are respectively 500,000 ton/year and 95,000 ton/year, the amount of the coal to be used can be reduced at a rate of 15 ton/h, and the amount of the generated carbon dioxide can be reduced at a rate of 6,600 Nm³/h.

[0034] The example shown in Fig. 2 represents an apparatus (or process) for producing a carboxylic acid by allowing the carbon monoxide separated from a synthetic gas to react

with an alcohol; and an apparatus (or process) for producing ammonia by using the hydrogen separated from the synthetic gas and the hydrogen obtained by a shift reaction of the synthetic gas.

- 5 [0035] The production process (or apparatus) in this Figure is the same as the production apparatus (or process) shown in Fig. 1 except that the production process further comprises a synthetic gas supply line 2B, a shift reaction unit 10, and a hydrogen supply line 10A. The synthetic gas
10 supply line 2B is used for supplying the synthetic gas produced in the synthetic gas production unit 2 as a synthetic gas (B), which is or to be separated from the synthetic gas (A), to the shift reaction unit. The shift reaction unit 10 is used for producing hydrogen by the shift reaction
15 of the synthetic gas (B) supplied via the line 2B. The hydrogen supply line 10A is used for supplying the hydrogen obtained in the shift reaction unit 10 to the ammonia production unit 5. In the example shown in Fig. 2, in the synthetic gas production unit 2, the synthetic gas is
20 produced using the coal. However, since the example shown in Fig. 2 can use the shift reaction, it is not necessarily to use a synthetic gas derived from a coal as well as a synthetic gas having a relatively small ratio of hydrogen (H_2) relative to carbon monoxide (CO).
- 25 [0036] That is, in this example, the synthetic gas produced in the synthetic gas production unit 2 (or production step) is separated into the synthetic gas (A) and the synthetic

gas (B), and the shift reaction of this synthetic gas (B) controls the amount of the hydrogen to be supplied to the ammonia production unit (production step). Specifically, to the ammonia production unit 5, the hydrogen separated from the synthetic gas (A) and the hydrogen separated from the shift reaction unit 10 after the shift reaction are supplied. The use of such a shift reaction can reduce the amount of the generated carbon dioxide while controlling the proportion of the amount of the produced carboxylic acid and the amount of the produced ammonia. Incidentally, the shift reaction is represented by the following formula.



It is enough for the shift reaction unit 10 to comprise a synthetic gas shift reaction apparatus (reactor). The shift reaction unit 10 usually comprises an apparatus (step) for conducting the shift reaction of the synthetic gas (B); separating hydrogen (including the hydrogen originally contained in the synthetic gas and the hydrogen generated by the shift reaction) from the gas after the shift reaction; and supplying the hydrogen to the line 10A. In other words, since the gas obtained the shift reaction contains the other components mentioned above, particularly, a large amount of carbon dioxide as a by-product of the shift reaction, an apparatus (step) for separating hydrogen from the gas is additionally required. The separation method of hydrogen may include, e.g., the same separation method as mentioned above, Rectisol process, and a

methanator method.

[0038] The production apparatus or production process shown in Fig. 2 produces acetic acid and ammonia while controlling the amounts of the produced acetic acid and the produced ammonia. The amounts of the produced acetic acid and the produced ammonia in the example in Fig. 1 particularly are limited by the proportion of carbon monoxide relative to oxygen in the synthetic gas derived from the coal. Therefore, it is difficult for the example in Fig. 1 to produce a large amount of ammonia. Contrarily, in the example shown in Fig. 2, in addition to the controlling the amounts of the produced acetic acid and the produced ammonia, it is possible to increase the amount of the produced ammonia. Moreover, the amount of the produced ammonia can be controlled in view of balancing the amounts of the produced ammonia and the produced acetic acid with each other; and the emission of carbon dioxide and the amount of the coal to be used can be reduced. Additionally, if the balance of supply and demand of hydrocarbon sources fluctuates, controlling the proportion of CO relative to H₂ allows the process to produce acetic acid and ammonia independently stably.

[0039] For illustrating the reduction in the amount of the generated carbon dioxide and the amount of the coal to be used in the production apparatus or production process in Fig. 2, a model case in which the amounts of the produced acetic acid and the produced ammonia are respectively

500,000 ton/year and 500,000 ton/year is assumed. In this model case, the production process or production apparatus in Fig. 2 requires a coal as a raw material, for example, at a rate of 100 ton/h.

5 [0040] That is, 35 ton/h of 100 ton/h of the coal is used for producing a synthetic gas (A). The obtained synthetic gas (A) contains CO produced at a rate of $28,000 \text{ Nm}^3/\text{h}$, H_2 produced at a rate of $23,000 \text{ Nm}^3/\text{h}$, and CO_2 produced at a rate of $12,000 \text{ Nm}^3/\text{h}$ (i.e., the molar ratio ($\text{CO}/\text{H}_2/\text{CO}_2$) is 1/0.85/0.49) as mentioned above. Incidentally, the ratio of the components is calculated assuming the gasification of the coal is conducted by a coal slurry method.

[0041] The residual coal, i.e., 65 ton/h of the coal, is used for producing a synthetic gas (B). The obtained
15 synthetic gas (B) contains CO produced at a rate of $54,000 \text{ Nm}^3/\text{h}$, H_2 produced at a rate of $46,000 \text{ Nm}^3/\text{h}$, and CO_2 produced at a rate of $24,000 \text{ Nm}^3/\text{h}$.

[0042] Then, by a shift reaction of all CO in the synthetic gas (B), hydrogen and carbon dioxide are generated at the
20 rates which are the same as that of CO, i.e., $54,000 \text{ Nm}^3/\text{h}$. Further, a use of all the resulting hydrogen for the ammonia production can give ammonia at a rate of 500,000 ton/year.

[0043] On the other hand, assuming that a production of acetic acid at the same rate as above with a use of a coal
25 slurry method and a production of ammonia at the same rate as above therewith are independently conducted, the amount of the generated CO_2 and the amount of the coal to be used

are calculated as follows. In order to produce acetic acid at a rate of 500,000 ton/year, a coal is required at a rate of 35 ton/h as mentioned above. In the acetic acid production, CO_2 is generated at a rate of $12,000 \text{ Nm}^3/\text{h}$.
5 Moreover, in order to produce ammonia at a rate of 500,000 ton/year, a coal is required at a rate of 80 ton/h if all carbon monoxide is used to produce hydrogen by the shift reaction of a synthetic gas (i.e., the coal produces, as the synthetic gas, CO at a rate of $67,000 \text{ Nm}^3/\text{h}$, H_2 at a
10 rate of $57,000 \text{ Nm}^3/\text{h}$, and CO_2 at a rate of $30,000 \text{ Nm}^3/\text{h}$). Accordingly, in the ammonia production, carbon dioxide is produced at a rate of $97,000 \text{ Nm}^3/\text{h}$ (the total of the carbon dioxide produced at a rate of $30,000 \text{ Nm}^3/\text{h}$ in the production of the synthetic gas and the carbon dioxide produced at
15 a rate of $67,000 \text{ Nm}^3/\text{h}$ by the shift reaction).

[0044] Summing up, in the model case in which the amounts of the produced acetic acid and the produced ammonia are respectively 500,000 ton/year and 500,000 ton/year, the amount of the coal to be used can be reduced at a rate of
20 15 ton/h, and the amount of the generated carbon dioxide can be reduced at a rate of $19,000 \text{ Nm}^3/\text{h}$.

[0045] In the process or apparatus of the present invention, the synthetic gas is usually obtained by reforming a carbonaceous material. The carbonaceous material may be
25 selected according to the process (1) or (2). In the process (1), the carbonaceous material of the synthetic gas is not limited to a coal and may be an oil, a natural gas or the

like. Moreover, in the process (1), the proportion of carbon
monoxide relative to hydrogen is not necessarily limited
to the above range since the shift reaction is used. The
proportion (molar ratio) of carbon monoxide relative to
5 hydrogen may be about 1/0.2 to 1/4, preferably about 1/0.4
to 1/3.5, and more preferably about 1/0.6 to 1/3. In
particular, the process (1) may use a synthetic gas
(synthetic gas derived from a coal) containing carbon
monoxide and hydrogen in the specific range as in the example
10 in Fig. 2. Further, in the process (1), the proportion of
carbon dioxide in the synthetic gas has the same range as
mentioned above.

[0046] Moreover, in the process (2), as long as the
synthetic gas having a small proportion of hydrogen can
15 be obtained, the carbonaceous material is not limited to
the coal. That is, although it is not necessarily to use
a synthetic gas derived from the coal as the synthetic gas,
the coal may usually be employed as the preferred
carbonaceous material.

20 [0047] In the processes (1) and (2), the coal may be any
one of an anthracite coal, a bituminous coal, a subbituminous
coal, a brown coal, and the like.

[0048] The reforming method may suitably be selected
according to the kinds of the carbonaceous material. For
25 example, the gasification of the coal is not particularly
limited to a specific one. Specifically, the coal slurry
gasification process or method may include GE method or

the like; and a coal dry feed gasification process may include Shell method, SFGT (Siemens Fuel Gasification Technology), or the like. Although in the examples in Figs. 1 and 2 oxygen is used for the gasification, it is not necessary to employ a gasification process using oxygen. However, in view of the capacity of the gasification apparatus or in order to produce carbon monoxide as a product in the subsequent step(s), oxygen is usually employed as an oxidizing agent. [0049] The temperature of the gasification of the coal may be, for example, about 1,300 to 1,500°C and preferably about 1,350 to 1,450°C. Moreover, the pressure of the gasification of the coal may usually be selected from the range of not more than 10 MPa according to the purpose of use of the generated gas (synthetic gas). For example, the pressure of the gasification of the coal may be about 4 to 10 MPa. The coal gasification may be conducted in the absence of a catalyst or in the presence of a suitable catalyst according to the gasification method. The gasification process using water and oxygen may be conducted in the absence of a catalyst.

[0050] As mentioned above, often, the separation and removal of the other components, particularly the acid gas, are preferably conducted in the carbon monoxide/hydrogen separation unit (or separation step) or the shift reaction unit (or shift reaction step). These components may be separated and removed from the synthetic gas itself or the carbon monoxide and/or hydrogen separated from the synthetic

gas. Alternatively, the components may be separated and removed from the synthetic gas and then from the carbon monoxide and/or hydrogen separated from the synthetic gas. The separation and removal method or process may include
5 a conventional method. For example, a removal method used for an acid gas may include a conventional method such as Rectisol process. Incidentally, hydrogen sulfide may further be separated as a sulfur source from the separated acid gas.

10 [0051] In the example in Fig. 2, the synthetic gas (B) used in the shift reaction unit (or shift reaction step) is a synthetic gas obtained through the synthetic gas production step through which the synthetic gas (A) is also produced. However, as long as the synthetic gas (B) is
15 different from the synthetic gas (A), the synthetic gas (B) may be obtained through a step different from the one producing the synthetic gas (A) (e.g., a gas derived from a coal and a gas derived from a component other than a coal (such as an oil or a natural gas)). Moreover, the ratio
20 of each component (e.g., carbon monoxide, hydrogen, and carbon dioxide) in the synthetic gases (A) and (B) may be the same or different. In particular, when the synthetic gas (B) is obtained through the step producing the synthetic gas (A) as in the example in Fig. 2, the process and apparatus
25 are advantageously simplified. Incidentally, in the example in Fig. 2, the compositions of the synthetic gases (A) and (B) are the same.

[0052] In the shift reaction unit (or shift reaction step), the condition of the shift reaction is not particularly limited to a specific one and may be a conventional condition. The shift reaction temperature may be, for example, about
5 200 to 600°C, preferably about 250 to 550°C, and more preferably about 300 to 500°C. Additionally, the shift reaction may be conducted in the presence of a shift reaction catalyst (e.g., an iron/chromium-based catalyst).

[0053] The heat of the mixed gas obtained by the shift
10 reaction may be recovered (or the mixed gas may be cooled) according to need. The recovered heat may be supplied to the other steps or units according to need to use the supplied heat for a heating reaction in the other steps.

[0054] Each of the lines may comprise a control means (such
15 as a flow control means) for controlling the amount of each of the components to be supplied (e.g., the synthetic gas, carbon monoxide, hydrogen, oxygen, and nitrogen).

[0055] In the carboxylic acid production step (or
production unit), the alcohol is not particularly limited
20 to a specific one and may include, for example, an aliphatic alcohol [e.g., an alkanol (e.g., a C₁₋₁₀alkanol such as methanol, ethanol, propanol, isopropanol, butanol, or pentanol) and a cycloalkanol (e.g., a C₄₋₁₀cycloalkanol such as cyclopentanol, cyclohexanol, cycloheptanol, or
25 cyclooctanol)], a phenol compound (e.g., a hydroxyC₆₋₁₀arene such as phenol), and an aromatic aliphatic (or araliphatic) alcohol (e.g., a

hydroxyC₁₋₄alkylC₆₋₁₀arene such as benzyl alcohol or phenethyl alcohol). Representative examples of the alcohol include an aliphatic monool (e.g., a C₁₋₄alkanol such as methanol), particularly methanol.

5 [0056] In the carboxylic acid production step, the condition of the reaction of carbon monoxide and the alcohol is not particularly limited to a specific one, and the conventional condition and apparatus may be used. The carboxylic acid may usually be produced in a liquid phase
10 reaction system. For example, in the reaction system of the carboxylic acid production step, the pressure (or partial pressure) of carbon monoxide may be, for example, about 200 to 3,000 kPa (e.g., about 400 to 1,500 kPa), and preferably about 500 to 1,000 kPa. Moreover, the reaction
15 temperature may be, for example, about 100 to 300°C and preferably about 150 to 250°C (e.g., about 170 to 220°C). The reaction pressure may be about 1,000 to 5,000 kPa (e.g., about 1,500 to 4,000 kPa).

[0057] Additionally, the reaction of carbon monoxide and
20 the alcohol may be conducted in the presence of a catalyst. The catalyst may include a conventional carbonylation catalyst, e.g., a transition metal catalyst (such as a rhodium catalyst, an iridium catalyst, a platinum catalyst, a palladium catalyst, a copper catalyst, or a nickel
25 catalyst). The concentration of the catalyst in the liquid phase reaction system may be, for example, about 5 to 10,000 ppm, and preferably about 10 to 5,000 ppm in terms of weight.

Moreover, the catalyst may be used in combination with a co-catalyst or a reaction accelerator. The co-catalyst or the reaction accelerator may include a metal halide (e.g., an alkali metal halide such as lithium iodide, potassium iodide, sodium iodide, or lithium bromide), a hydrogen halide (e.g., hydrogen iodide and hydrogen bromide), a hydrocarbon halide (e.g., a haloC₁₋₄alkane such as methyl iodide or methyl bromide), and others. The carboxylic acid (e.g., acetic acid) produced in the carboxylic acid production step may be purified and collected by a conventional manner.

[0058] For the carboxylic acid production step (or production unit), the conventional manner (e.g., Japanese Patent No. 3244385 and Japanese Patent Application Laid-Open No. 2002-255890) may be referred.

[0059] In the ammonia production step (or production unit), the condition of the reaction of hydrogen and nitrogen is not particularly limited to a specific one. The conventional condition and apparatus may be used. For example, the reaction temperature may be, e.g., about 300 to 700°C and preferably about 350 to 650°C (e.g., about 400 to 600°C). The reaction pressure may optionally be selected according to a manner (such as a low-pressure method, a middle-pressure method, or a high-pressure method) and may be, for example, about 5 to 50 MPa (e.g., about 10 to 30 MPa).

[0060] The reaction of hydrogen and nitrogen may be

conducted in the presence of a catalyst. The catalyst may include a conventional catalyst, for example, a transition metal catalyst, e.g., an iron-based catalyst (such as triiron tetraoxide) and a ruthenium-based catalyst (such as a Ru/C-containing catalyst). Moreover, the above catalyst may be used in combination with a co-catalyst. The co-catalyst may include, for example, an alkali metal or alkaline earth metal oxide (such as potassium oxide, magnesium oxide, or calcium oxide), an aluminium compound (such as an alumina), and a silicon compound (such as silicon dioxide). The ammonia produced in the ammonia production step may be purified and collected by a conventional method.

INDUSTRIAL APPLICABILITY

[0061] The production process or production apparatus of the present invention produces a carboxylic acid (such as acetic acid) and ammonia independently efficiently from a synthetic gas (particularly, a synthetic gas derived from an inexpensive coal as a raw material). Moreover, since the amount of the generated carbon dioxide and the amount of the carbonaceous material (particularly a coal) to be used are reduced, the production process or production apparatus of the present invention are environmentally, industrially, economically advantageous. Additionally, since the amounts of the generated carbon monoxide and the generated hydrogen are controlled, the carboxylic acid and ammonia are produced at desired production rates.

DISCRIPTION OF REFERENCE NUMERALS

- [0062] 1. Oxygen/nitrogen separation unit
2. Synthetic gas production unit
- 5 3. Carbon monoxide/hydrogen separation unit
4. Carboxylic acid production unit
5. Ammonia production unit
- 1A. Oxygen supply line
- 1B. Nitrogen supply line
- 10 2A, 2B. Synthetic gas supply line
- 3A. Carbon monoxide supply line
- 3B. Hydrogen supply line
10. Shift reaction unit
- 10A. Hydrogen supply line

CLAIMS

[Claim 1] A process for producing a carboxylic acid and ammonia independently, comprising the steps of

5 (a) separating carbon monoxide and hydrogen independently from a synthetic gas (A);

(b) producing hydrogen by subjecting a synthetic gas (B) to a shift reaction;

(c) producing the carboxylic acid from an alcohol
10 and the carbon monoxide separated from the synthetic gas (A); and

(d) producing ammonia from nitrogen, the hydrogen separated from the synthetic gas (A), and the hydrogen obtained by the shift reaction step (b).

15 [Claim 2] A process for producing a carboxylic acid and ammonia independently, comprising the steps of

(e) separating carbon monoxide and hydrogen independently from a synthetic gas (A) having a molar ratio of carbon monoxide relative to hydrogen of 1/0.4 to 1/1.5;

20 (f) producing the carboxylic acid from an alcohol and the carbon monoxide separated from the synthetic gas (A); and

(g) producing ammonia from nitrogen and the hydrogen separated from the synthetic gas (A).

25 [Claim 3] A process according to claim 1 or 2, further comprising the steps of

(h) separating nitrogen and oxygen independently

from air; and

(i) producing a synthetic gas by a gasification of a coal;

wherein the oxygen separated in the oxygen/nitrogen separation step (h) is used for the gasification of the coal, the nitrogen separated in the oxygen/nitrogen separation step (h) is used in the ammonia production step, and the synthetic gas produced in the synthetic gas production step (i) is used as the synthetic gas (A).

[Claim 4] A process according to claim 2, further comprising the step of

(j) producing hydrogen by subjecting a synthetic gas (B) to a shift reaction,

wherein in the ammonia production step (g), the hydrogen separated from the synthetic gas (A) and the hydrogen obtained by the shift reaction step (j) are used.

[Claim 5] A process according to claim 1 or 4, wherein the synthetic gas (A) and the synthetic gas (B) are produced in the same synthetic gas production step.