

**(12) STANDARD PATENT**  
**(19) AUSTRALIAN PATENT OFFICE**

(11) Application No. **AU 2006264241 B2**

- (54) Title  
**Method for gasifying solid fuel with unified gas purification and gasifier using said method**
- (51) International Patent Classification(s)  
**C10J 3/00** (2006.01)                      **C10J 3/48** (2006.01)  
**B01J 20/04** (2006.01)                      **C10K 1/26** (2006.01)  
**C10J 3/46** (2006.01)                      **C10K 1/30** (2006.01)
- (21) Application No:   **2006264241**                      (22) Date of Filing:   **2006.03.23**
- (87) WIPO No:   **WO07/004342**
- (30) Priority Data
- (31) Number                      (32) Date                      (33) Country  
**2005-195945**                      **2005.07.05**                      **JP**
- (43) Publication Date:                      **2007.01.11**  
(44) Accepted Journal Date:                      **2010.01.21**
- (71) Applicant(s)  
**IHI Corporation**
- (72) Inventor(s)  
**Kyo, Koubun;Murakami, Takahiro;Suda, Toshiyuki;Kusama, Shigeru;Fujimori, Toshiro**
- (74) Agent / Attorney  
**Griffith Hack, Level 3 509 St Kilda Road, Melbourne, VIC, 3004**
- (56) Related Art  
**JP 2001-316680 A**  
**JP 59-184291 A**  
**WO 2002/038706 A1**  
**US 2004/237404 A1**  
**JP 7-54666 A**  
**JP 2003-238973 A**  
**US 4231760 A**  
**US 3115394 A**  
**WO 2001/042132 A1**  
**JP 2002-53876 A**

(19) 世界知的所有権機関  
国際事務局



(43) 国際公開日  
2007年1月11日 (11.01.2007)

PCT

(10) 国際公開番号  
WO 2007/004342 A1

- (51) 国際特許分類:  
C10J 3/00 (2006.01) C10J 3/48 (2006.01)  
B01J 20/04 (2006.01) C10K 1/26 (2006.01)  
C10J 3/46 (2006.01) C10K 1/30 (2006.01)
- (21) 国際出願番号: PCT/JP2006/305785
- (22) 国際出願日: 2006年3月23日 (23.03.2006)
- (25) 国際出願の言語: 日本語
- (26) 国際公開の言語: 日本語
- (30) 優先権データ:  
特願2005-195945 2005年7月5日 (05.07.2005) JP
- (71) 出願人 (米国を除く全ての指定国について): 石川島播磨重工業株式会社 (ISHIKAWAJIMA-HARIMA)

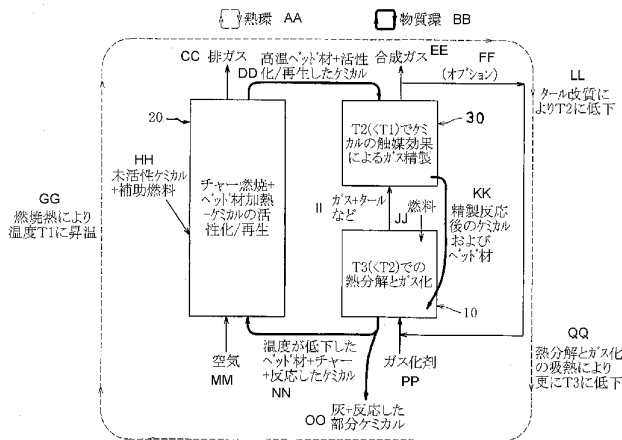
HEAVY INDUSTRIES CO., LTD. [JP/JP]; 〒1358710  
東京都江東区豊洲三丁目1番1号 Tokyo (JP).

- (72) 発明者; および
- (75) 発明者/出願人 (米国についてのみ): 許光文 (KYO, Koubun) [CN/JP]; 〒1358710 東京都江東区豊洲三丁目1番1号 石川島播磨重工業株式会社内 Tokyo (JP). 村上高広 (MURAKAMI, Takahiro) [JP/JP]; 〒1358710 東京都江東区豊洲三丁目1番1号 石川島播磨重工業株式会社内 Tokyo (JP). 須田俊之 (SUDA, Toshiyuki) [JP/JP]; 〒1358710 東京都江東区豊洲三丁目1番1号 石川島播磨重工業株式会社内 Tokyo (JP). 草間滋 (KUSAMA, Shigeru) [JP/JP]; 〒1358710 東京都江東区豊洲三丁目1番1号 石川島播磨重工業株式会社内 Tokyo (JP). 藤森俊郎 (FUJIMORI, Toshiro) [JP/JP]; 〒1358710 東京都江東区豊洲三丁目1番1号 石川島播磨重工業株式会社内 Tokyo (JP).

[続葉有]

(54) Title: METHOD OF SOLID FUEL GASIFICATION INCLUDING GAS PURIFICATION AND GASIFIER EMPLOYING THE METHOD

(54) 発明の名称: ガス精製を統合した固体燃料のガス化方法及び該方法を用いたガス化装置



- 10... PYROLYSIS AND GASIFICATION AT T3 (<T2)
- 20... CHAR COMBUSTION + BED MATERIAL HEATING + CHEMICAL ACTIVATION/REGENERATION
- 30... GAS PURIFICATION BY CATALYTIC EFFECT OF CHEMICAL AT T2 (<T1)
- AA... HEAT CYCLE
- BB... SUBSTANCE CYCLE
- CC... DISCHARGE GAS
- DD... HIGH-TEMPERATURE BED MATERIAL + ACTIVATED/REGENERATED CHEMICAL
- EE... SYNTHESIS GAS
- FF... (OPTION)
- GG... RISING TO TEMPERATURE T1 BY COMBUSTION HEAT
- HH... UNACTIVATED CHEMICAL + AUXILIARY FUEL
- II... GAS + TAR, ETC.
- JJ... FUEL
- KK... CHEMICAL AND BED MATERIAL AFTER PURIFICATION REACTION
- LL... DECLINING TO T2 BY TAR REFORMING
- MM... AIR
- NN... COOLED BED MATERIAL + CHAR + REACTED CHEMICAL
- OO... ACH + PART OF REACTED CHEMICAL
- PP... GASIFYING AGENT
- QQ... FURTHER DECLINING TO T3 BY ENDOTHERM BY PYROLYSIS AND GASIFICATION

(57) Abstract: A method in which the function of causing CO<sub>2</sub> contained in a gas to be absorbed by a chemical to accelerate a gasification reaction is reconciled with the catalytic function of reforming a tar contained in the gas produced by the gasification reaction, and which enables a high gasification efficiency and the production of a clean product gas to be realized. A process of gasification is divided into three phases, i.e., a gasification oven (10) in which pyrolysis and gasification are conducted (pyrolysis/gasification phase; first step), a combustion oven (20) in which char is burnt to obtain a burnt active chemical (char combustion phase; second step), and a gas purification oven (30) in which the gas obtained by the gasification is purified (gasification/gas purification phase; third step). Due to the thermal transfer by a flowable heat carrier and a chemical or the harmony between the chemical reactions of the chemical in the phases, the temperature in the gasification oven (10) and that in the gas purification oven (30) are independently regulated respectively to a low to medium temperature (773-1073°K), which is necessary for CO<sub>2</sub> absorption and gasification, and to a high temperature (1073°K or higher), which is necessary for gas purification.

(57) 要約: ケミカルによってガス中のCO<sub>2</sub>を吸収してガス化反応を促進する作用と当該ガス化反応により生成されたガス化ガス中のタールを改質する触媒作用との両立を図り、高いガス化効率とクリーンな製品ガスの生産を実現可能にする。ガス化の過程を熱分解とガス化で行うガス化炉10(熱分解ガス化フェーズ、第

一工程)、チャーを燃焼させ焼成した活性ケミカルを得る燃焼炉20

[続葉有]

WO 2007/004342 A1



- (74) 代理人: 山田 恒光, 外(YAMADA, Tsunemitsu et al.); 〒1010047 東京都千代田区内神田三丁目5番3号 矢萩第二ビル Tokyo (JP).
- (81) 指定国 (表示のない限り、全ての種類の国内保護が可能): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, KE, KG, KM, KN, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
- (84) 指定国 (表示のない限り、全ての種類の広域保護が可能): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), ユーラシア (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), ヨーロッパ (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- 添付公開書類:  
— 国際調査報告書
- 2文字コード及び他の略語については、定期発行される各PCTガゼットの巻頭に掲載されている「コードと略語のガイダンスノート」を参照。

(チャー燃烧フェーズ、第二工程)及びガス化ガスを精製するガス精製炉30(ガス化ガス精製フェーズ、第三工程)の3つの過程(フェーズ)に分け、流動熱媒体やケミカルによる熱伝達により、また該ケミカルが各フェーズで行う化学反応の調和により、独立して、ガス化炉10をCO<sub>2</sub>の吸収ができるガス化に必要な低中温(773~1073°K)に制御し、ガス精製炉30をガス精製に必要な高温(1073°K以上)に制御する。

## DESCRIPTION

METHOD FOR GASIFYING SOLID FUEL WITH UNIFIED GAS  
PURIFICATION AND GASIFIER USING SAID METHOD

## Technical Field

[0001]

The present invention relates to technique for gasifying solid fuel, and more specifically relates to technique for gasifying solid fuel highly efficiently and more cleanly.

## Background Art

[0002]

Gasification of solid fuel such as coal, biomass or various wastes in a gasification furnace is generally carried out in a high-temperated environment of about 1123°K or more so as to obtain sufficient reaction speed and heat supply to the reaction. In order to attain such high-temperated environment of about 1123°K or more in the gasification furnace, part of the solid fuel itself must be burned.

[0003]

However, such combustion of the solid fuel itself disadvantageously deteriorates gasification efficiency of

the fuel. To carry out the combustion and gasification of the fuel in one and the same reaction space or gasification furnace inevitably causes a large amount of inert gases such as  $\text{CO}_2$  and  $\text{N}_2$  to be admixed in the gasified gas, resulting in lowering in purity and heat quantity of the product gas.

[0004]

Moreover, the gas gasified in the high-temperated environment is rich in CO and  $\text{CO}_2$  and poor in  $\text{H}_2$ ; in order to produce  $\text{H}_2$ -enriched product gas required, for example, for a synthesizing process of GTL (Gas to Liquid), the high-temperated gasified gas must be cooled to independently carry out CO shift reaction and removal of  $\text{CO}_2$ .

[0005]

A conventionally known method for concurrently removing CO during gasification of solid fuel is to absorb  $\text{CO}_2$  in gasified gas in a gasification furnace, using a chemical such as CaO-based oxide; however, in a high-temperated environment of 1123°K or more, there is a restriction in terms of chemical equilibrium that absorption of  $\text{CO}_2$  requires the gasification furnace to be in a high pressure environment of 20 atm or more (see, for example, Patent References 1 and 2).

[0006]

The gasification technique at such high pressure can be utilized practically only in large-scaled energy/fuel producing systems of several hundreds MW from a viewpoint of cost or other restrictions; in other various low-capacity systems such as a dispersed hydrogen fuel cell power and synthesis system, it has been desired that production of H<sub>2</sub>-enriched product gas be carried out through gasification at low or preferably normal pressure.

[0007]

Thus, it is conceivable that a gasification process with enabled high efficiency at low or medium temperature and at low pressure is indispensable for application to various energy-scale energy/fuel production systems including the above-mentioned GTL or in order to construct next-generation, highly effective electric generating systems.

[0008]

More specifically, if gasification at low or medium temperature were put into practice, there would be no need of burning the solid fuel itself; instead, for example, various industrial waste heats such as heat of exhaust gas from a gas turbine may be utilized as heat source for gasification with expectation for high efficiency of the gasification. There would be no need of a high pressure environment; instead, for example even at a normal

pressure, CO<sub>2</sub> in the gasified gas may be satisfactorily absorbed by oxide chemical such as CaO, providing that it is at low or medium temperature.

[0009]

With respect to a method for gasifying fuel through combustion of solid fuel itself (usual partial oxidation method, other method of not using a gasifying agent or auto-thermal gasification method, or other method of using a gasifying agent such as steam or CO<sub>2</sub>), known is twin-circulating-fluidized-bed-type gasification technique (see, for example, Patent References 3 and 4) wherein inert gas such as CO<sub>2</sub> generated by combustion and N<sub>2</sub> fed through supply of air for combustion are prevented from being admixed in the gasified gas in such a manner that the solid fuel is gasified in the gasification furnace, the gasified char being burned in a combustion furnace separate from the gasification furnace, heat fluid medium being circulated between these gasification and combustion furnaces to transfer heat from the combustion furnace to the gasification furnace.

[0010]

In such gasification method with fuel gasification separate from char combustion and in order to absorb CO<sub>2</sub> in gasified gas to produce H<sub>2</sub>-enriched product gas, there has been developed, in Europe, a gasification method called

AER (Absorption Enhanced Reforming) wherein heat medium circulated between the combustion and gasification furnaces is added with CaO chemical (see Non-patent Reference 1). In the AER method, circulating fluidized bed is used; biomass is gasified in a gasification furnace adjacent to a downcomer in an environment of 873-973°K and at normal pressure, CO<sub>2</sub> being absorbed by CaO chemical to obtain gasified gas with high H<sub>2</sub> content and to accelerate the gasifying reaction, CaCO<sub>3</sub> thus generated being regenerated into CaO in a riser combustion furnace and being circulated to the gasification furnace together with the fluid heat medium.

[Patent Reference 1] US4231760

[Patent Reference 2] JP2004-59816A

[Patent Reference 3] US4568362

[Patent Reference 4] AT405937B

[Non-Patent Reference 1] <http://www.aer-gas.de>

Summary of the Invention

Problems to be Solved by the Invention

[0011]

In the existing gasification methods with separate combustion (char) and gasification (fuel), the gasification reaction is either at high temperature of 1123°K or more (Patent References 3 and 4) or at low or

medium temperature of 973°K or so (AER).

[0012]

The gasification at the low or medium temperature inevitably generates tar in large quantity. Although CaO is used as catalyst for reformation of tar in the above-mentioned AER, temperature as high as 1123°K or more is required for CaO to exhibit sufficient catalytic function to tar, as is generally known in the art.

Disadvantageously, in low-temperature environment of 873-973°K as in AER, tar is not sufficiently reformed, i.e., the gasified gas is not sufficiently purified. Thus, it is predicted that the gasified gas obtained in the above-mentioned AER actually contains tar in large quantity.

[0013]

On the other hand, in the case of the gasification reaction temperature of 1123°K or more, CaO-based chemical indeed exhibits sufficient catalytic function for reformation of tar in the gasified gas; however, at such high temperature, CO<sub>2</sub> cannot be sufficiently absorbed by CaO. As mentioned above, in order to bring about absorption of CO<sub>2</sub>, the operation pressure of the gasification furnace must be set to as high as 20 atm or more, which causes problems that gasification in high-pressure environment is costly and that application of gasification technique is restricted.

[0014]

Thus, in fact, a catalytic function of reforming tar in gasified gas through chemical such as CaO is not compatible with a function of absorbing CO<sub>2</sub> in gas to accelerate gasifying reaction.

[0015]

An aim of the invention is to address the above problem, to make it possible that a function of absorbing CO<sub>2</sub> in gas by chemical to accelerate gasifying reaction is compatible with a catalytic function of reforming tar in gasified gas generated by the gasifying reaction, to provide a gasification method of solid fuel with unified gas purification with enabled high gasification efficiency and production of clean produced gas as well as a gasifier using said method, or to at least provide the public with a useful alternative.

#### Means or Measures for Solving the Problems

[0016]

According to a first aspect of the invention, the invention is directed to a method for gasifying solid fuel with unified gas purification, wherein it comprises a first process of feeding solid fuel and a gasifying agent to a reactor of pyrolysis gasification phase where said

solid fuel is pyrolyzed in contact with heat medium to generate char gasified by said gasifying agent, CO<sub>2</sub> in gasified gas generated by said pyrolysis and gasification being absorbed by active chemical at a reaction temperature of said pyrolysis gasification phase, said active chemical having at least CO<sub>2</sub> absorbing function and catalytic function of tar reformation, a second process of feeding residual char not gasified in said reactor of pyrolysis gasification phase, the heat medium low-temperated through contribution to the pyrolysis and gasification of said solid fuel, the low-active chemical less-activated through reaction with said CO<sub>2</sub> and newly added inactive chemical to a reactor of char combustion phase where said char is burned by an oxidizing agent to bring about combustion heat with which said low-temperated heat medium is heated, said low-active and inactive chemicals are calcined to be re-activated and activated, respectively; and a third process of feeding the heat medium heated in said reactor of char combustion phase and the active chemical activated as well as said gasified gas from said reactor of pyrolysis gasification phase to a reactor of gasified gas purification phase where said active chemical functions as catalyst to reform tar in said gasified gas at a reaction temperature of said

gasified gas purification phase and absorbs  $H_2S$  and  $HCl$  in said gasified gas to purify said gasified gas, the active chemical having contributed mainly as catalyst to purifying said gasified gas being circulated together with the heat medium to said reactor of pyrolysis gasification phase, said heat medium low-temperated by reforming tar in the gasified gas in the reactor of gasified gas purification phase in the third process and said active chemical being supplied to the reactor of pyrolysis gasification phase in the first process to absorb  $CO_2$  in the gasified gas.

[0017]

Thus, in the reactor of char combustion phase, the heat medium is heated and the low-active and newly added inactive chemicals are calcined to generate the active chemical (second process), these high-temperated heat medium and active chemical being fed to the reactor of gasified gas purification phase where, at the high reaction temperature of the gasified gas purification phase, tar in the gasified gas is satisfactorily reformed with the active chemical functioning as catalyst, and  $H_2S$  and  $HCl$  in the gasified gas are satisfactorily absorbed by the active chemical (third process). Then, the chemical having reformed the heat medium and tar and having

absorbed  $H_2S$  and  $HCl$  is circulated to the reactor of pyrolysis gasification phase while it possesses absorption activity of  $CO_2$ ; in the reactor of pyrolysis gasification phase,  $CO_2$  in gasified gas generated by the pyrolysis and gasification of the solid fuel is satisfactorily absorbed by the chemical at the low or medium reaction temperature of the pyrolysis gasification phase (first process).

[0018]

In the first process, the reaction temperature in the reactor of pyrolysis gasification phase for said pyrolysis

gasification phase is controlled to 773-1073°K in harmony at least with the absorption reaction of CO<sub>2</sub> in the gasified gas by the active chemical.

Thus, the reaction temperature of the pyrolysis and gasification phase in said reactor of pyrolysis gasification phase is in harmony for example with the absorption reaction of CO<sub>2</sub> in the gasified gas by the active chemical so that it is maintained to the low or medium temperature of 773-1073°K at which CO<sub>2</sub> in the gasified gas can be satisfactorily absorbed by the active chemical, so that even if the reactor of pyrolysis gasification phase is substantially at normal pressure, CO<sub>2</sub> in the gasified gas generated by gasification is reliably absorbed by the active chemical.

[0019]

In the second process, the reaction temperature in said reactor of char combustion phase can be controlled to 1073°K or more in harmony at least with re-activation and activation reactions of the low-active and inactive chemicals, respectively.

Thus, the reaction temperature in the reactor of char combustion phase is in harmony with the re-activation and activation reactions of the low-active and inactive chemicals, respectively, and is maintained to high temperature of 1073°K or more so that the heat medium and

active chemical are made sufficiently high-temperated and the active chemical is sufficiently activated.

[0020]

In the third process, the reaction temperature in said reactor of gasified gas purification phase for said gasified gas purification phase can be controlled to the temperature of 1073°K or more in harmony at least with sufficient exhibition of the catalytic function of the active chemical to the tar reforming reaction, which is lower than the reaction temperature in the reactor of char combustion phase and higher than the reaction temperature in the reactor of pyrolysis gasification phase for the pyrolysis gasification phase.

Thus, the reaction temperature in the reactor of gasified gas purification phase for the gasified gas purification phase is in harmony for example with exhibition of the catalytic function of the active chemical to the tar reforming reaction so that it is maintained to high temperature of 1073°K or more at which tar in the gasified gas can be satisfactorily reformed by the active chemical; the tar in the gasified gas is reliably reformed by the active chemical and at the same time H<sub>2</sub>S, HCl and the like are satisfactorily removed. In this case, owing to the more or less endotherm in the tar reforming reaction in the gasified gas purification phase,

the high reaction temperature in said phase is somewhat lowered than the reaction temperature in the char combustion phase, i.e., the temperature of the particles and active chemical heated in the char combustion phase, but is reliably higher than the low or medium reaction temperature in the reactor of phase for the pyrolysis gasification phase.

[0021]

The inactive chemical may be mineral which has, as its base, metal carbonate or hydroxide.

When the inactive chemical is mineral such as  $\text{Ca}(\text{OH})_2$  which has, as its base, metal carbonate such as  $\text{CaCO}_3$  or hydroxide, then the activated active chemical such as  $\text{CaO}$  can satisfactorily absorb  $\text{CO}_2$  in the gasified gas in the reactor of pyrolysis gasification phase and at the low or mediate reaction temperature of said phase; and in the reactor of gasified gas purification phase, it can suitably function as catalyst to satisfactorily reform the tar in the gasified gas at high reaction temperature of the phase.

[0022]

According to a second aspect of the invention, the invention is directed to a gasifier for solid fuel with unified gas purification comprising a reactor of pyrolysis

gasification phase fed with the solid fuel and a gasifying agent, said solid fuel being pyrolyzed in contact with heat medium to generate char gasified by said gasifying agent, CO<sub>2</sub> in gasified gas generated by said pyrolysis and gasification being absorbed by active chemical at a reaction temperature of the pyrolysis and gasification, said active chemical having at least CO<sub>2</sub> absorbing function and catalytic function of tar reformation, a reactor of char combustion phase fed with residual char not gasified in said reactor of pyrolysis gasification phase, the heat medium low-temperated through contribution to the pyrolysis and gasification of said solid fuel, the low-active chemical less-activated through reaction with said CO<sub>2</sub> and newly added inactive chemical, said char being burned by an oxidizing agent to bring about combustion heat with which said low-temperated heat medium is heated and said low-active and inactive chemicals are calcined to be re-activated and activated, respectively; and a reactor of gasified gas purification phase fed with the heat medium heated in said reactor of char combustion phase, the activated active chemical and said gasified gas from said reactor of pyrolysis gasification phase, said active chemical functioning as catalyst to reform tar in said gasified gas at a tar reforming reaction temperature

and absorbing H<sub>2</sub>S and HCl in said gasified gas to purify said gasified gas, the active chemical having contributed mainly as catalyst to purifying said gasified gas being circulated together with the heat medium low-temperated by reforming action of the tar to said reactor of pyrolysis gasification phase.

[0023]

Thus, in the reactor of char combustion phase, the heat medium is heated and the low-active and newly added inactive chemicals are calcined to generate active chemical, so that these high-temperated heat medium and active chemical are fed to the reactor of gasified gas purification phase where tar in the gasified gas is satisfactorily reformed with the active chemical functioning as catalyst at high reaction temperature required for tar reformation and H<sub>2</sub>S and HCl in the gasified gas are satisfactorily absorbed by the active chemical. Then, the chemical having reformed the tar and absorbed H<sub>2</sub>S and HCl is circulated together with the heat medium to the reactor of pyrolysis gasification phase while possessing the absorption activity of CO<sub>2</sub>, and in the reactor of pyrolysis gasification phase, CO<sub>2</sub> in the gasified gas generated by the pyrolysis and gasification of the solid fuel is satisfactorily absorbed by the

chemical at the low or medium reaction temperature of the  
pyrolysis gasification required for absorption of CO<sub>2</sub>.

[0024]

The reaction temperature of the pyrolysis  
gasification in the reactor of pyrolysis gasification

phase can be controlled to 773-1073°K in harmony at least with the absorption reaction of CO<sub>2</sub> in the gasified gas by the active chemical.

Thus, the reaction temperature of the pyrolysis gasification in the reactor of pyrolysis gasification phase is in harmony for example with the absorption reaction of CO<sub>2</sub> in the gasified gas by the active chemical, so that it is maintained to the low or medium temperature of 773-1073°K at which CO<sub>2</sub> in the gasified gas can be satisfactorily absorbed by the active chemical. As a result, even if the reactor of pyrolysis gasification phase is substantially at the normal pressure, CO<sub>2</sub> in the gasified gas generated by the gasification is reliably absorbed by the active chemical.

[0025]

The reaction temperature in the reactor of char combustion phase can be controlled to 1073°K or more in harmony at least with the re-activation and activation reactions of the low-active and inactive chemicals, respectively.

Thus, the reaction temperature in the reactor of char combustion phase is in harmony for example with the re-activation and activation reactions of the low-active and inactive chemicals, respectively, so that it is maintained to 1073°K or more. As a result, the heat medium and active

chemical are sufficiently high-temperated and the active chemical is sufficiently activated.

[0026]

The reaction temperature for tar reformation in the reactor of gasified gas purification phase can be controlled to the temperature of 1073°K or more in harmony at least with sufficient exhibition of the catalytic function of the active chemical to the tar reforming reaction, which is lower than the reaction temperature in the reactor of char combustion phase and higher than the reaction temperature in the reactor of pyrolysis gasification phase for the pyrolysis gasification.

Thus, reaction temperature for tar reformation in the reactor of gasified gas purification phase is in harmony for example with exhibition of the catalytic function of the active chemical to the tar reforming reaction, so that it is maintained to the high temperature of 1073°K or more at which tar in the gasified gas can be satisfactorily reformed by the active chemical. As a result, the tar in the gasified gas is reliably reformed and at the same time H<sub>2</sub>S, HCl and the like is satisfactorily removed by the active chemical. In this case, due to the more or less endotherm by the tar reforming reaction in the gasified gas purification phase, the high reaction temperature in the phase is somewhat lower than the reaction temperature

in the char combustion phase, i.e., the temperature of the particles and active chemical heated in the char combustion phase, but is reliably higher than the low or medium reaction temperature for the pyrolysis gasification phase in the reactor of pyrolysis gasification phase.

[0027]

The inactive chemical may be mineral which has, as its base, metal carbonate or hydroxide.

[0028]

Thus, as the inactive chemical is mineral such as  $\text{Ca}(\text{OH})_2$  which has, as its base, metal carbonate such as  $\text{CaCO}_3$  or hydroxide, the activated active chemical such as  $\text{CaO}$  can satisfactorily absorb  $\text{CO}_2$  in the gasified gas in the reactor of pyrolysis gasification phase at the low or medium reaction temperature for the pyrolysis and gasification and can suitably function as catalyst to sufficiently reform the tar in the gasified gas at the high temperature for tar reformation in the reactor of gasified gas purification phase.

[0029]

The reactor of gasified gas purification phase may be larger in horizontal cross sectional area than the reactor of pyrolysis gasification phase.

This prolongs the dwell time of the gasified gas in the reactor of gasified gas purification phase, so that

the gasified gas is sufficiently purified.

[0030]

The reactor of gasified gas purification phase may be arranged integral with the reactor of pyrolysis gasification phase, and the particle passage for circulation of the heat medium and active chemical from the reactor of gasified gas purification phase to the reactor of pyrolysis gasification phase may be arranged inside or outside of the integrated reactor of gasified gas purification phase and reactor of pyrolysis gasification phase.

As a result, the integrated arrangement of the reactor of gasified gas purification phase with the reactor of pyrolysis gasification phase makes the whole of the apparatus compact in size, and the inside or outside arrangement of the particle passage from the reactor of gasified gas purification phase to the reactor of pyrolysis gasification phase stabilizes the circulation of the heat medium and active chemical.

Effects of the Invention

[0031]

According to the method for gasifying solid fuel with unified gas purification in the first aspect of the invention, the whole process of gasifying the solid fuel

is divided into three phases of pyrolysis gasification, char combustion and gasified gas purification. Tar in the gasified gas generated by the pyrolysis gasification of the solid fuel is reformed in the gasified gas purification phase at the high reaction temperature in said phase by the active chemical. The active chemical having contributed as catalyst to reforming the tar is circulated together with the heat medium to the pyrolysis gasification phase where, at the low or medium temperature in said phase,  $\text{CO}_2$  in the gasified gas is absorbed by the same active chemical. Further, in the char combustion phase, the heat medium is heated and the low-active and newly added inactive chemicals are calcined to be activated. As a result, by the active chemical which is circulated,  $\text{CO}_2$  in the gasified gas can be sufficiently absorbed at a proper reaction temperature in the pyrolysis gasification phase and tar in the gasified gas can be sufficiently reformed at a proper reaction temperature in the gasified gas purification phase; and, in the char combustion phase, the low-active and inactive chemicals can be sufficiently activated before contribution to tar reformation.

In short, in the respective phases of pyrolysis gasification, char combustion and gasified gas purification, the reaction temperatures can be

independently controlled for realization of maximum reaction performances, so that the action of accelerating the gasifying reaction through absorption of  $\text{CO}_2$  in the gas by the chemical can be made compatible with the catalytic action of reforming the tar in the gasified gas generated by the gasifying reaction.

Thus, the gasification of the solid fuel can be realized at high efficiency and cleanly to obtain the gasified gas with high quality.

[0032]

In the reactor of pyrolysis gasification phase, in harmony for example with the absorption reaction of  $\text{O}_2$  in the gasified gas by the active chemical, the reaction temperature in said phase can be maintained to the low or medium temperature of  $773\text{--}1073^\circ\text{K}$  at which  $\text{CO}_2$  in the gasified gas can be satisfactorily absorbed by the active chemical, so that even if the reactor of pyrolysis gasification phase is not at high pressure but substantially at normal pressure,  $\text{CO}_2$  in the gasified gas generated by the gasification can be reliably absorbed by the active chemical.

[0033]

In the reactor of char combustion phase, in harmony for example with the re-activation and activation reactions of the low-active and inactive chemicals,

respectively, the reaction temperature can be maintained to high temperature of 1073°K or more, so that the heat medium and active chemical can be sufficiently high-temperated and the active chemical can be sufficiently activated.

[0034]

In the reactor of gasified gas purification phase, in harmony for example with exhibition of the catalytic function of the active chemical to the tar reforming reaction, the reaction temperature in said phase can be maintained to high temperature of 1073°K or more at which tar in the gasified gas can be satisfactorily reformed by the active chemical, so that the tar in the gasified gas can be reliably reformed by the active chemical and at the same time H<sub>2</sub>S, HCl and the like can be satisfactorily removed. In this case, owing to the more or less endotherm of the tar reforming reaction in said phase, the high reaction temperature in said phase is somewhat lower than the reaction temperature in the char combustion phase, i.e., the temperature of the particles and active chemical heated in the char combustion phase, but can be reliably higher than the low or medium reaction temperature in the reactor of pyrolysis gasification phase for said phase.

[0035]

The inactive chemical may be mineral such as Ca(OH)<sub>2</sub>

which has, as its base, metal carbonate such as  $\text{CaCO}_3$  or hydroxide, so that, in the reactor of pyrolysis gasification phase,  $\text{CO}_2$  in the gasified gas can be sufficiently absorbed by the activated active chemical such as  $\text{CaO}$  in the low or medium reaction temperature in said phase, and in the reactor of gasified gas purification phase, the tar in the gasified gas can be sufficiently reformed in the high reaction temperature in said phase.

[0036]

According to the gasifier for solid fuel with unified gas purification in the second aspect of the invention, just like the above-mentioned first aspect, the whole process of gasifying the solid fuel is divided into three phases of pyrolysis gasification, char combustion and gasified gas purification. By the active chemical which is circulated,  $\text{CO}_2$  in the gasified gas can be sufficiently absorbed at a proper reaction temperature in the pyrolysis gasification phase and tar in the gasified gas can be sufficiently reformed at a proper reaction temperature in the gasified gas purification phase; and, in the char combustion phase, the low-active and inactive chemicals can be sufficiently activated before contribution to tar reformation.

In short, in the respective phases of pyrolysis

gasification, char combustion and gasified gas purification, the reaction temperatures can be independently controlled for realization of maximum reaction performances, so that the action of accelerating the gasifying reaction through absorption of  $\text{CO}_2$  in the gas by the chemical can be made compatible with the catalytic action of reforming the tar in the gasified gas generated by the gasifying reaction.

Thus, the gasification of the solid fuel can be realized at high efficiency and cleanly to obtain the gasified gas with high quality.

[0037]

In the reactor of pyrolysis gasification phase, in harmony for example with the absorption reaction of  $\text{CO}_2$  in the gasified gas by the active chemical, the reaction temperature in the pyrolysis gasification can be maintained to the low or medium temperature of 773-1073°K at which  $\text{CO}_2$  in the gasified gas can be satisfactorily absorbed by the active chemical, so that even if the reactor of pyrolysis gasification phase is not high pressure but substantially at normal pressure,  $\text{CO}_2$  in the gasified gas generated by the gasification can be reliably absorbed by the active chemical.

[0038]

In the reactor of char combustion phase, in harmony

for example with the re-activation and activation reactions of the low-active and inactive chemicals, respectively, the reaction temperature can be maintained to high temperature of 1073°K or more, so that the heat medium and the active chemical can be sufficiently high-temperated and the active chemical can be sufficiently activated.

[0039]

In the reactor of gasified gas purification phase, in harmony for example with exhibition of the catalytic function of the active chemical to the tar reforming reaction, the tar reforming reaction temperature can be maintained to high temperature of 1073°K or more at which tar in the gasified gas can be satisfactorily reformed by the active chemical, so that the tar in the gasified gas can be reliably reformed by the active chemical and at the same time H<sub>2</sub>S, HCl and the like can be satisfactorily reformed. In this case, owing to the more or less endotherm of the tar reforming reaction in said phase, the high reaction temperature in said phase is somewhat lower than the reaction temperature in the char combustion phase, i.e., the temperature of the particles and active chemical heated in the char combustion phase, but can be reliably higher than the low or medium reaction temperature in the reactor of pyrolysis gasification phase for said phase.

[0040]

The inactive chemical may be mineral such as  $\text{Ca}(\text{OH})_2$  which has, as its base, metal carbonate such as  $\text{CaCO}_3$  or hydroxide, so that, in the reactor of pyrolysis gasification phase,  $\text{CO}_2$  in the gasified gas can be sufficiently absorbed by the activated active chemical such as  $\text{CaO}$  in the low or medium reaction temperature in said phase, and in the reactor of gasified gas purification phase, the tar in the gasified gas can be sufficiently reformed in the high reaction temperature for tar reformation.

[0041]

The reactor of gasified gas purification phase may be larger in horizontal cross sectional area than the reactor of pyrolysis gasification phase, so that the dwell time of the gasified gas in the reactor of gasified gas purification phase can be prolonged to sufficiently purify the gasified gas.

[0042]

The reactor of gasified gas purification phase may be arranged integral with the reactor of pyrolysis gasification phase, so that the whole of the apparatus can be made compact in size. Moreover, the inside or outside arrangement of the particle passage from the reactor of gasified gas purification phase to the reactor of

pyrolysis gasification phase can stabilize the circulation of the heat medium and active chemical.

#### Brief Description of the Drawings

[0043]

[Fig. 1] A view showing schematic construction of a gasifier for solid fuel with unified gas purification according to a first embodiment of the invention.

[Fig. 2] A diagram schematically showing an operational principle of the method for gasifying solid fuel with unified gas purification according to the invention.

[Fig. 3] A graph showing thermo gravimetric (TG) weight variation of  $\text{CaCO}_3$  when temperature is varied with a lower  $\text{CO}_2$  concentration.

[Fig. 4] A graph showing chemical equilibrium on the basis of pressure and temperature in the chemical reaction of  $\text{CaO}$  with  $\text{CO}_2$ .

[Fig. 5] A graph showing TG weight variation of  $\text{CaO}$  when atmosphere temperature is increased to about  $1000^\circ\text{K}$  at normal pressure and in the presence of lower  $\text{CO}_2$  concentration.

[Fig. 6] A graph showing TG weight variation of  $\text{CaO}$  when atmosphere temperature is increased to about  $1130^\circ\text{K}$  at normal pressure and in the presence of higher  $\text{CO}_2$  concentration.

[Fig. 7] A view showing schematic construction of a gasifier for solid fuel with unified gas purification according to a second embodiment of the invention.

[Fig. 8] A view showing schematic construction of a gasifier for solid fuel with unified gas purification according to a third embodiment of the invention.

[Fig. 9] A view showing schematic construction of a gasifier for solid fuel with unified gas purification according to a fourth embodiment of the invention.

#### Explanation of the Reference Numerals

[0044]

- 10 gasification furnace (reactor of pyrolysis gasification phase)
- 12 fluidized bed
- 14 upper fluidized bed
- 15, 15' and 15" particle pipe (particle passage)
- 20 combustion furnace (reactor of char combustion phase)
- 20a chemical supply pipe (inactive chemical supply means)
- 22 fluidized bed
- 30 gas purification furnace (reactor of gasified gas purification phase)
- 32 fluidized bed
- 40 particle classifier (discharge means)

## Best Mode for Carrying Out the Invention

[0045]

Next, embodiments of the invention will be described in conjunction with accompanying drawings.

[Embodiment 1]

[0046]

First of all, a first embodiment will be described.

Fig. 1 shows schematic construction of a gasifier for solid fuel with unified gas purification according to the first embodiment of the invention. The description will be made in conjunction with Fig. 1.

[0047]

The gasifier using the method for gasifying solid fuel with unified gas purification according to the invention is constructed as a system with an external circulation type fluidized bed, which separately comprises, as shown in Fig. 1, a gasification furnace (reactor of pyrolysis gasification phase) 10, a combustion furnace (reactor of char combustion phase) 20 and a gas purification furnace (reactor of gasified gas purification phase) 30, solid components being circulated through the furnaces 10, 20 and 30 together with fluid heat medium (bed material such as sand).

[0048]

The gasification furnace 10 is a device with a

fluidized bed 12 fed with solid fuel such as coal, biomass or various wastes and with a gasifying agent such as steamer or CO<sub>2</sub> for gasification (including pyrolysis) of the solid fuel through heat of the fluid heat medium heated and high-temperated as mentioned hereinafter. The gasification furnace 10 is communicated at its top with the gas purification furnace 30, so that product gas (produced or gasified gas) gasified in the furnace 10 is fed to the gas purification furnace 30.

[0049]

The gasification furnace 10 is communicated at its side center through a particle classifier 40 with a lower portion of the combustion furnace 20. The particle classifier 40 serves to separate ash of the solid fuel and part of low-active chemical mentioned hereinafter, char generated through the gasification and the low-temperated fluid heat medium and has a function of discharging and discarding the ash of the solid fuel (the ash generated by char combustion in the combustion furnace 20) and part of low-active chemical mentioned hereinafter and a function of feeding the char, the part of the low-active chemical and the fluid heat medium to a lower portion of the combustion furnace 20.

[0050]

The combustion furnace 20 is a device with a

fluidized bed 22 fed with an oxidizing agent (air or O<sub>2</sub>) from below for burning the char fed from the gasification furnace 10 and heating the fluid heat medium into high temperature, the furnace 20 being communicated at its top with a cyclone 50. The cyclone 50 is a device for separating the solid components from the gaseous components and has a function of discharging exhaust gas generated in the combustion furnace 20 into atmosphere and a function of feeding the high-temperature fluid heat medium and solid components entrained in the exhaust gas to the gas purification furnace 30.

[0051]

The combustion furnace 20 is provided with a chemical supply pipe (inactive chemical supply means) 20a which feeds chemical with its inactive state (inactive chemical or chemical agent) such as limestone (CaCO<sub>3</sub>) to the fluidized bed 22.

[0052]

The gas purification furnace 30 is a device for purifying the product gas fed from the gasification furnace 10 and is constructed to be capable of reforming tar in the product gas and absorbing and removing H<sub>2</sub>S, HCl and the like in the product gas.

[0053]

The gas purification furnace 30 is communicated at

its top with a cyclone 55. The cyclone 55 is a device for separating the solid components from the gaseous components just like the cyclone 50 and has a function of feeding the product gas purified in the gas purification furnace 30, for example, as fuel to a gas turbine or the like and a function of returning the solid components entrained in the product gas to the gasification furnace 10.

[0054]

A particle pipage 15 (particle passage) extends from a side center of the gas purification furnace 30 into the gasification furnace 10, whereby particles mainly constituted by the fluid heat medium are fed through the pipage 15 to the furnace 10.

[0055]

The description will be made on mode of operation of the thus constructed gasifier using the gasification method with unified gas purification and the method for purifying gasified gas of solid fuel according to the invention.

[0056]

Fig. 2 schematically shows an operational principle of the method for gasifying solid fuel with unified gas purification according to the invention. The description hereinafter is referred also to the figure. In Fig. 2,

solid arrows conceptually show material circulation of gas, fluid heat medium, chemical and the like and dotted arrows, heat circulation.

[0057]

As mentioned in the above, the combustion furnace 20 is fed with the char from the gasification furnace 10 and with the oxidizing agent, and the char is burned. In this connection, the fluidized bed 22 in the furnace 20 is fed with chemical such as limestone ( $\text{CaCO}_3$ ),  $\text{CaCO}_3$  or the like being heated together with the fluid heat medium by combustion heat of the char. More specifically, the combustion of the char lacks endothermic reaction unlike the gasification of the solid fuel in the gasification furnace 10, so that the temperature in the combustion furnace 20 is satisfactorily increased to high temperature  $T_1$  (for example,  $1073^\circ\text{K}$  or more) in harmony with  $\text{CaCO}_3$  degradation chemical reaction with formula (16) shown in table 1 below. In table 1, plus (+) and minus (-) indicate endothermic and exothermic amounts, respectively, for  $\Delta H_0$ .

[0058]

Table 1

phase	main reactions	$\Delta H_0$ (KJ)	roles
pyrolysis/ gasification (gasification furnace) (973±50°K)	(1) $C_mH_nO_x \rightarrow C + CO + H_2 + CO_2 + \dots$ (2) $C + H_2O \rightarrow CO + H_2O$ (3) $C + CO_2 \rightarrow 2CO$ (4) $CO + H_2O \rightarrow CO_2 + H_2$ (5) $CO_2 + CaO \rightarrow CaCO_3$ (6) $C + 2H_2 \rightarrow CH_4$ (7) $CO + 3H_2 \rightarrow CH_4 + H_2O$ (8) $CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$ (9) $CaO + H_2O \rightarrow Ca(OH)_2$ (10) $H_2S + CaO \rightarrow CaS + H_2O$ (11) $2HCl + CaO \rightarrow CaCl_2 + CO$	$\Delta H_0 > 0$ +131.3 +172.5 -41.2 -170.4 -74.9 -206.2 -165.0 -109.0 $\Delta H_0 < 0$ $\Delta H_0 > 0$	fuel pyrolysis gasification of steam gasification of $CO_2$ CO shift Absorption of $CO_2$ methanation of C methanation of CO methanation of $CO_2$ hydration of chemical absorption of $H_2S$ absorption of HCl
gas purification (gas purifica- tion furnace) (about 1123°K)	(12) $tar + H_2O \rightarrow CO + H_2 + CO_2 + \dots$ (13) $H_2S + CaO \rightarrow CaS + H_2O$ (14) $2HCl + CaO \rightarrow CaCl_2 + H_2O$	$\Delta H_0 > 0$ $\Delta H_0 < 0$ $\Delta H_0 > 0$	reformation of tar absorption of $H_2S$ absorption of HCl
combustion of char (≥1123°K)	(15) $C + O_2 \rightarrow CO_2$ (16) $CaCO_3 \rightarrow CaO + CO_2$ (17) $2CaS + O_2 \rightarrow 2CaO + SO_2$	-393.5 +170.4 $\Delta H_0 > 0$	combustion of char calcining of $CaCO_3$ regeneration of CaS

[0059]

The combustion of the char is carried out differently from the gasification of the solid fuel, so that a  $CO_2$  content in the gasified gas is lower than that in a usual gasification furnace where combustion and gasification coexist; thus,  $CO_2$  concentration in the combustion furnace 20 is suppressed to a value as low as, for example, 10-15 mol % or so whereas that in the usual gasification furnace is 20 mol % or more.

[0060]

Thus, in the combustion furnace 20,  $CaCO_3$  or the like is satisfactorily pyrolyzed at high temperature and with less  $CO_2$  as shown by chemical formula (16) in table 1, resulting in satisfactory calcination of the active chemical such as CaO (second process).

[0061]

Fig. 3 shows weight variation (thermo gravimetric (TG) weight variation) in TG calcination of  $\text{CaCO}_3$  when the temperature is varied with a low  $\text{CO}_2$  concentration. It is seen from the figure that, if  $\text{CO}_2$  concentration is low (for example, 15 mol %),  $\text{CaCO}_3$  starts to be calcined at temperature of  $1050^\circ\text{K}$  or so, whereby  $\text{CaO}$  is satisfactorily calcined as shown by chemical formula (16). The reaction conditions of the  $\text{CO}_2$  concentration being 15 mol % and temperature being  $1050^\circ\text{K}$  or more are just satisfied by atmosphere in the combustion furnace 20.

[0062]

The thus calcined active chemical such as  $\text{CaO}$  is fed together with the high-temperature fluid heat medium via the cyclone 50 to the gas purification furnace 30 which is also fed with product gas gasified in the gasification furnace 10.

[0063]

In the gas purification furnace 30, the product gas gasified in the gasification furnace 10 is purified by the catalytic action of the above-mentioned active chemical such as  $\text{CaO}$ .

[0064]

More specifically, in the gas purification furnace 30, gas purification chemical reactions such as formulae (12)-

(14) shown in Table 1 proceed by heat of the fluid heat medium and active chemical such as CaO. Here, because of less reaction heat, the reaction temperature (reaction temperature in the phase, reaction temperature of reformation of tar) T2 in the fluidized bed 32 is as high as 1073°K or more and is substantially equal to the temperature of the particles from the cyclone 50, the catalytic function of the active chemical such as CaO to the tar reforming reaction formula (12) being sufficiently exhibited. The more or less endotherm in the tar reforming reaction formula (12) somewhat lowers the temperature of the particles passing through the gas purification furnace 30, so that actually the reaction temperature T2 is somewhat lower than the above-mentioned T1 in the combustion furnace 20.

[0065]

Thus, with the product gas containing tar, dust, H<sub>2</sub>S, HCl and the like, the fluidized bed 32 in the gas purification furnace 30 is maintained to high temperature (>1073°K) necessary to sufficiently exhibit and in harmony with the catalytic function of the active chemical to the tar reforming reaction formula (12), so that CaO or the like sufficiently exhibits the catalytic function to tar and dust (reformation of tar) or exhibit attaching function (attachment of tar and dust) and can clarify them.

Moreover, CaO or the like exhibits oxidation function as oxidizing agent to H<sub>2</sub>S, HCl and the like and can absorb them. As a result, in the gas purification furnace 30, tar, dust, H<sub>2</sub>S, HCl and the like in the product gas are sufficiently removed by CaO or the like, so that the product gas is sufficiently purified (third process).

[0066]

Then, CaO or the like after the purification reaction and used in the purification of the product gas is circulated together with the fluid heat medium via the particle pipe 15 to the gasification furnace 10. CaO or the like jumped together with the product gas out of the gas purification furnace 30 also undergoes the solid-gas separation by the cyclone 55 and is fed to the gasification furnace 10.

[0067]

In the gasification furnace 10, in the presence of heat from the fluid heat medium and CaO or the like, the chemical reactions of formulae (1)-(11) shown in table 1 above proceed through intervention of the CO<sub>2</sub> absorption activity of the chemical such as CaO; fuel pyrolysis and char gasification of formulae (1)-(3), which are highly endothermic reactions, further lowers the temperature of the above-mentioned solid matters (particles) from the gas purification furnace 30 than the above-mentioned reaction

temperature T2. Then, at reaction pressure of as low as 1-5 atm and in harmony with CO<sub>2</sub> absorption reaction (5), for example control of fuel treated amount is carried out to control the reaction temperature in the fluidized bed 12 to the reaction temperature T3 (for example 773-1073°K, more preferably 873-1023°K), i.e., to the low or medium temperature necessary for absorptive chemical reaction of CO<sub>2</sub>.

[0068]

Thus, in the gasification furnace 10, in the environment of low pressure and the required low or medium temperature T3, the solid fuel is gasified and CaO or the like is reacted with CO<sub>2</sub> for sufficient absorption of CO<sub>2</sub>.

[0069]

More specifically, in the chemical reaction of CaO with CO<sub>2</sub>, chemical equilibrium as shown in Fig. 4 exists on the basis of pressure and temperature; if interior of the gasification furnace 10 is at low pressure (for example, 1-5 atm) or even at a normal pressure (1 atm), to maintain the gasification furnace 10 at the low or medium temperature T3 (for example, 873-1023°K) enables CaO to satisfactorily absorb CO<sub>2</sub>, and the reaction in the reaction formula (5) in table 1 can be satisfactorily brought about.

[0070]

Fig. 5 shows weight variation (thermo gravimetric or TG weight variation) of CaO when atmosphere temperature is increased to about 1000°K at normal pressure and in the presence of 10 mol % of CO<sub>2</sub>; and Fig. 6 shows, as comparative example, weight variation (TG weight variation) of CaO when atmosphere temperature is increased to about 1130°K at normal pressure and in the presence of 25 mol % of CO<sub>2</sub>. It is apparent from these figures that the weight of CaO, which does not vary at high temperature of about 1130°K even with high CO<sub>2</sub> partial pressure, is drastically increased at the low or medium temperature of about 1000°K in the case of lower CO<sub>2</sub> partial pressure and that CaO is satisfactorily converted into CaCO<sub>3</sub> in the latter temperature condition.

[0071]

Thus, in the gasification furnace 10, the active chemical such as CaO is satisfactorily reacted with CO<sub>2</sub> in the product gas to absorb CO<sub>2</sub>, and is converted back into inactive chemical such as CaCO<sub>3</sub>, i.e., returned into the original chemical.

[0072]

As CO<sub>2</sub> is removed from the product gas in this manner, combustion heat amount possessed by the product gas is enhanced and H<sub>2</sub> concentration in the product gas is enhanced (H<sub>2</sub>-enrichment). Moreover, absorption of CO<sub>2</sub> by

CaO or the like is thermolysis reaction so that gasifying reaction speed is accelerated. Moreover, such temperature control of the fluidized bed 12 in the gasification furnace 10 contributes to stabilizing heat supply for gasification (including fuel pyrolysis) (first process).

[0073]

When the active chemical such as CaO is reacted with CO<sub>2</sub> into low-active chemical such as CaCO<sub>3</sub>, then part of regenerable CaCO<sub>3</sub> or the like is fed again, together with the char and the fluid heat medium low-temperated by the fuel gasifying reaction, to the combustion furnace 20 and thus is activated again and regenerated, as mentioned above, into CaO or the like.

[0074]

CaS or the like, which is generated when CaO or the like is used for oxidation of H<sub>2</sub>S or the like, or part of the low-active chemical having been reacted in the gasification furnace 10 is separated in the particle classifier 40 and discharged together with ash for disposal.

[0075]

Since such disposal of CaS or the like and partial low-active chemical results in lack of CaO or the like, CaCO<sub>3</sub> or the like corresponding to such lack is replenished (as newly added inactive chemical) in the form

of mineral such as limestone from the chemical supply pipe 20a to the fluidized bed 22 of the combustion furnace 20; thus, CaO or the like is continued to be satisfactorily generated.

[0076]

As mentioned in the above, in the gasifier using the method for gasifying solid fuel with unified gas purification according to the invention, the whole gasification process is divided into three processes or phases: the gasification furnace 10 for fuel pyrolysis and gasification (pyrolysis gasification phase, first process), the combustion furnace 20 for burning the gasified char and for calcining chemical such as  $\text{CaCO}_3$  to obtain active chemical such as CaO (char combustion phase, second process) and the gas purification furnace 30 for purification of the product gas (gasified gas purification phase, third process).

[0077]

Thus, the temperatures of the respective furnaces may be readily controlled independently from each other. Especially in the gas purification furnace 30, owing to heat of the high-temperature fluid heat medium and of the active chemical such as CaO circulated from the combustion furnace 20 and in harmony for example with exhibition of the catalytic function by the active chemical to the tar

reforming reaction, the fluidized bed 32 may be controlled to the reaction temperature T2 (for example, 1073°K or more), i.e., high temperature required for active CaO or the like to sufficiently exhibit the catalytic function to the tar reforming reaction; in the gasification furnace 10, in the presence of heat possessed by the fluid heat medium and CaO or the like circulated from the gas purification furnace 30, for example adjustment of the fuel amount fed to the gasification furnace 10 can be carried out to control the fluidized bed 12, in harmony with CO<sub>2</sub> absorption chemical reaction by CaO, to the reaction temperature T3 (for example, 873-1023°K), i.e., the lower or medium temperature required for absorption chemical reaction of CO<sub>2</sub>.

[0078]

Thus, in the fluidized bed 22 in the combustion furnace 20, the fluid heat medium is heated and CaCO<sub>3</sub> or the like chemical is calcined to generate active chemical such as CaO, these fluid heat medium and CaO or the like are fed to the gas purification furnace 30; in the fluidized bed 32 in the furnace 30, at the predetermined reaction temperature T2, the product gas can be satisfactorily purified with CaO or the like being used as catalyst, so that tar, dust, H<sub>2</sub>S, HCl and the like in the product gas can be satisfactorily removed. Moreover, in

the fluidized bed 12 in the gasification furnace 10, at the predetermined reaction temperature  $T_3$  and at the predetermined low pressure (1-5 atm),  $\text{CO}_2$  in the product gas generated through gasification can be satisfactorily absorbed by active chemical such as  $\text{CaO}$ , so that combustion heat amount possessed by the product gas can be enhanced and  $\text{H}_2$  concentration in the product gas can be enhanced ( $\text{H}_2$ -enrichment) while gasifying reaction speed can be accelerated and further, heat supply for gasification (including fuel pyrolysis) can be stabilized.

[0079]

That is, the action of absorbing  $\text{CO}_2$  in the gas by the chemical to accelerate the gasifying reaction (including fuel pyrolysis) can be compatible with the catalytic action of reforming tar in the product gas generated through the gasifying reaction.

[0080]

Thus, while enhancing the gasification efficiency as a whole, the product gas clean, with high quality and useable for various uses can be obtained.

[0081]

As shown in Fig. 1 as option, part of the purified product gas may be returned to and charged together with the gasifying agent to the gasification furnace 10; then, heat of the product gas may be used for temperature

control in the gasification furnace 10 to further stabilize heat supply for gasification (including fuel pyrolysis).

[0082]

To maintain the temperature in the gasification furnace 10 to the low or medium temperature or predetermined reaction temperature T3 (for example, 873-1023°K) makes it possible to utilize various industrial waste heat (for example, exhaust gas from a gas turbine) as stable heat source for gasification (including fuel pyrolysis), contributing to constructing a highly effective system.

[Embodiment 2]

[0083]

Next, a second embodiment will be described.

Fig. 7 shows schematic construction of a gasifier for solid fuel with unified gas purification according to the second embodiment of the invention. The description will be made in conjunction with Fig. 7. In this connection, explanation is omitted with respect to portions in common with the above-mentioned first embodiment.

[0084]

In the second embodiment, the apparatus comprises a gasification furnace 10 and a gas purification furnace 30 which are vertically connected into an integral unit,

calcined active chemical such as CaO and fluid heat medium being passed into the gasification furnace 10 through a particle pipage (particle passage) 15' arranged in the furnaces 30 and 10.

[0085]

Such integral construction of the gasification furnace 10 with the gas purification furnace 30 can make the whole of the apparatus compact in size and stabilize transfer of the fluid heat medium and active chemical such as CaO to the gasification furnace 10, thereby further stabilizing heat supply for gasification.

[0086]

As shown in Fig. 7 as option and as in the above, part of the product gas purified may be returned to and charged together with the gasifying agent to the gasification furnace 10.

[Embodiment 3]

[0087]

Next, a third embodiment will be described.

Fig. 8 shows schematic construction of a gasifier for solid fuel with unified gas purification according to the third embodiment of the invention. The description will be made in conjunction with Fig. 8. In this connection, explanation is made only on portions different from those in the above-mentioned second embodiment.

[0088]

In the third embodiment, the apparatus comprises a gasification furnace 10 and a gas purification furnace 30 which are integrally constructed, a horizontal cross sectional area of the furnace 30 being larger than that of the furnace 10.

[0089]

Such increased horizontal cross sectional area of the gas purification furnace 30 than that of the gasification furnace 10 prolongs dwell time of the product gas, which is generated in the gasification furnace 10, in the fluidized bed 32 of the gas purification furnace 30, so that the product gas is further satisfactorily purified during its passage through the furnace 30.

[0090]

Thus, tar, dust,  $H_2S$ ,  $HCl$  and the like in the product gas can be further reliably removed in comparison with the above-mentioned second embodiment, thereby further enhancing the purification effect of the product gas.

[0091]

As shown in Fig. 8 as option and as in the above, part of the product gas purified may be returned to and charged together with the gasifying agent to the gasification furnace 10.

[Embodiment 4]

[0092]

Next, a fourth embodiment will be described.

Fig. 9 shows schematic construction of a gasifier for solid fuel with unified gas purification according to the fourth embodiment of the invention. The description will be made in conjunction with Fig. 9. Also in this connection, explanation is made only on portions different from those in the above-mentioned second embodiment.

[0093]

In the fourth embodiment, the apparatus comprises a gasification furnace 10 and a gas purification furnace 30 which are integrally constructed, a particle pipage (particle passage) 15" being provided as outer passage between the furnaces 30 and 10.

[0094]

Such communication between the gas purification furnace 30 and the gasification furnace 10 through the particle pipage 15" or outer passage brings about supply of the active chemical such as CaO and the fluid heat medium from the gas purification furnace 30 via the particle pipage 15" to the gasification furnace 10. At this time, together with these fluid heat medium and active chemical, part of the product gas purified is fed to the particle pipage 15", whereby enhanced is the supply of particles such as the fluid heat medium and active

chemical from the gas purification furnace 30 to the gasification furnace 10.

[0095]

As a result, in comparison with the above-mentioned second embodiment, transfer of the fluid heat medium and active chemical such as CaO to the gasification furnace 10 can be further stabilized and heat supply for gasification can be further stabilized.

[0096]

As shown in Fig. 9 as option and as in the above, part of the product gas purified may be returned to and charged together with the gasifying agent to the gasification furnace 10.

[0097]

The description has been made with respect to the embodiments of the invention. It is to be understood that the invention is not limited to the above embodiments and that various changes and modifications may be made without leaving the scope and spirit of the invention.

[0098]

For example, in the above embodiments, the description has been made with the chemical being limestone ( $\text{CaCO}_3$ ) and the active chemical being CaO; however, the chemical may be mineral such as  $\text{Ca(OH)}_2$  which has, as its basis, metal carbonate such as dolomite ( $\text{CaCO}_3$ ).

(MgCO<sub>3</sub>) or hydroxide; the active chemical may be MgO, CaO, MgO or the like.

[0099]

With the above embodiments, the description has been made with respect to the system having outer circulation type fluidized bed; however, the invention is applicable also to a system with moving bed.

#### Industrial Applicability

[0100]

The invention can be effectively utilized when tar and H<sub>2</sub>S in gasified gas of solid fuel are to be easily and inexpensively removed, using natural mineral and to sufficiently purify the gasified gas.

It is to be understood that, if any prior art publication is referred to herein, such reference does not constitute an admission that the publication forms a part of the common general knowledge in the art, in Australia or any other country.

In the claims which follow and in the preceding description of the invention, except where the context requires otherwise due to express language or necessary implication, the word "comprise" or variations such as "comprises" or "comprising" is used in an inclusive sense,

i.e. to specify the presence of the stated features but not to preclude the presence or addition of further features in various embodiments of the invention.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A method for gasifying solid fuel with unified gas purification comprising:

a first process of feeding solid fuel and a gasifying agent to a reactor of pyrolysis gasification phase where said solid fuel is pyrolyzed in contact with heat medium to generate char which is gasified by said gasifying agent, CO<sub>2</sub> in gasified gas generated by said pyrolysis and gasification being absorbed by active chemical at a reaction temperature of said pyrolysis gasification phase, said active chemical having at least CO<sub>2</sub> absorbing function and catalytic function of tar reformation,

a second process of feeding residual char not gasified in said reactor of pyrolysis gasification phase, the heat medium low-temperated through contribution to the pyrolysis and gasification of said solid fuel, the low-active chemical less-activated through reaction with said CO<sub>2</sub> and newly added inactive chemical to a reactor of char combustion phase where said char is burned by an oxidizing agent to bring about combustion heat with which said low-temperated heat medium is heated, said low-active and inactive chemicals are calcined to be re-activated and activated, respectively, and

a third process of feeding the heat medium heated in said reactor of char combustion phase, the active chemical activated and said gasified gas from said reactor of pyrolysis gasification phase to a reactor of gasified gas purification phase where said active chemical functions as catalyst to reform tar in said gasified gas at a reaction temperature of said gasified gas purification phase and absorbs  $H_2S$  and  $HCl$  in said gasified gas to purify said gasified gas, the active chemical having contributed mainly as catalyst to purifying said gasified gas being circulated together with the heat medium to said reactor of pyrolysis gasification phase,

said heat medium low-temperated by reforming tar in the gasified gas in the reactor of gasified gas purification phase in the third process and said active chemical being supplied to the reactor of pyrolysis gasification phase in the first process to absorb  $CO_2$  in the gasified gas.

2. A method for gasifying solid fuel with unified gas purification as claimed in claim 1, wherein, in said first process, the reaction temperature in said reactor of pyrolysis gasification phase for said pyrolysis gasification phase is controlled to  $773-1073^{\circ}K$  in harmony

at least with the absorption reaction of  $\text{CO}_2$  in said gasified gas by said active chemical.

3. A method for gasifying solid fuel with unified gas purification as claimed in claim 1 or claim 2, wherein, in said second process, the reaction temperature in said reactor of char combustion phase is controlled to  $1073^\circ\text{K}$  or more in harmony at least with the re-activation and activation reactions of said low-active and inactive chemicals, respectively.

4. A method for gasifying solid fuel with unified gas purification as claimed in any one of claims 1-3, wherein, in said third process, the reaction temperature in said reactor of gasified gas purification phase for said gasified gas purification phase is controlled to temperature of  $1073^\circ\text{K}$  or more in harmony at least with sufficient exhibition of the catalytic function by said active chemical to said tar reforming reaction, which is lower than the reaction temperature in said reactor of char combustion phase and is higher than the reaction temperature in said reactor of pyrolysis gasification phase for said pyrolysis gasification phase.

5. A method for gasifying solid fuel with unified gas purification as claimed in any one of claims 1-4, wherein the inactive chemical is mineral which has, as its base, metal carbonate or hydroxide.

6. A gasifier for solid fuel with unified gas purification comprising:

a reactor of pyrolysis gasification phase fed with the solid fuel and a gasifying agent, said solid fuel being pyrolyzed in contact with heat medium to generate char gasified by said gasifying agent, CO<sub>2</sub> in gasified gas generated by the pyrolysis and gasification being absorbed by active chemical at a reaction temperature of the pyrolysis and gasification, said active chemical having at least CO<sub>2</sub> absorbing function and catalytic function of tar reformation,

a reactor of char combustion phase fed with residual char not gasified in said reactor of pyrolysis gasification phase, the heat medium low-temperated through contribution to the pyrolysis and gasification of said solid fuel, the low-active chemical less-activated through reaction with said CO<sub>2</sub> and newly added inactive chemical, said char being burned by an oxidizing agent to bring about combustion heat with which said low-

temperatured heat medium is heated and said low-active and inactive chemicals are calcined to be re-activated and activated, respectively, and

a reactor of gasified gas purification phase fed with the heat medium heated in said reactor of char combustion phase, the activated active chemical and said gasified gas from said reactor of pyrolysis gasification phase, said active chemical functioning as catalyst to reform tar in said gasified gas at a tar reforming reaction temperature and absorbing  $H_2S$  and  $HCl$  in said gasified gas to purify said gasified gas, the active chemical having contributed mainly as catalyst to purifying said gasified gas being circulated together with the heat medium low-temperatured by reforming action of the tar to said reactor of pyrolysis gasification phase.

7. A gasifier for solid fuel with unified gas purification as claimed in claim 6, wherein the reaction temperature of said pyrolysis and gasification in said reactor of pyrolysis gasification phase is controlled to  $773-1073^{\circ}K$  in harmony with at least the absorption reaction of  $CO_2$  in said gasified gas.

8. A gasifier for solid fuel with unified gas

purification as claimed in claim 6 or claim 7, wherein the reaction temperature in said reactor of char combustion phase is controlled to 1073°K or more in harmony with at least the re-activation and activation reactions of said low-active and inactive chemicals, respectively.

9. A gasifier for solid fuel with unified gas purification as claimed in any one of claims 6-8, wherein the reaction temperature for said tar reformation in said reactor of gasified gas purification phase is controlled to temperature of 1073°3K or more in harmony at least with sufficient exhibition of the catalytic function by said active chemical to said tar reforming reaction, which is lower than the reaction temperature in said reactor of char combustion phase and is higher than the reaction temperature of said pyrolysis and gasification in said reactor of pyrolysis gasification phase.

10. A gasifier for solid fuel with unified gas purification as claimed in any one of claims 6-9, wherein the inactive chemical is mineral which has, at its base, metal carbonate or hydroxide.

11. A gasifier for solid fuel with unified gas

purification as claimed in any one of claims 6-10, wherein said reactor of gasified gas purification phase is larger in horizontal sectional area than said reactor of pyrolysis gasification phase.

12. A gasifier for solid fuel with unified gas purification as claimed in any one of claims 6-11, wherein said reactor of gasified gas purification phase and said reactor of pyrolysis gasification phase are integrally arranged,

a particle passage being arranged inside or outside of said integrated reactor of gasified gas purification phase and reactor of pyrolysis gasification phase so as to circulate said heat medium and active chemical from said reactor of gasified gas purification phase to said reactor of pyrolysis gasification phase.

13. A method for gasifying solid fuel with unified gas purification substantially as herein described with reference to the accompanying drawings.

14. A gasifier for solid fuel with unified gas purification substantially as herein described with reference to the accompanying drawings.

FIG. 1

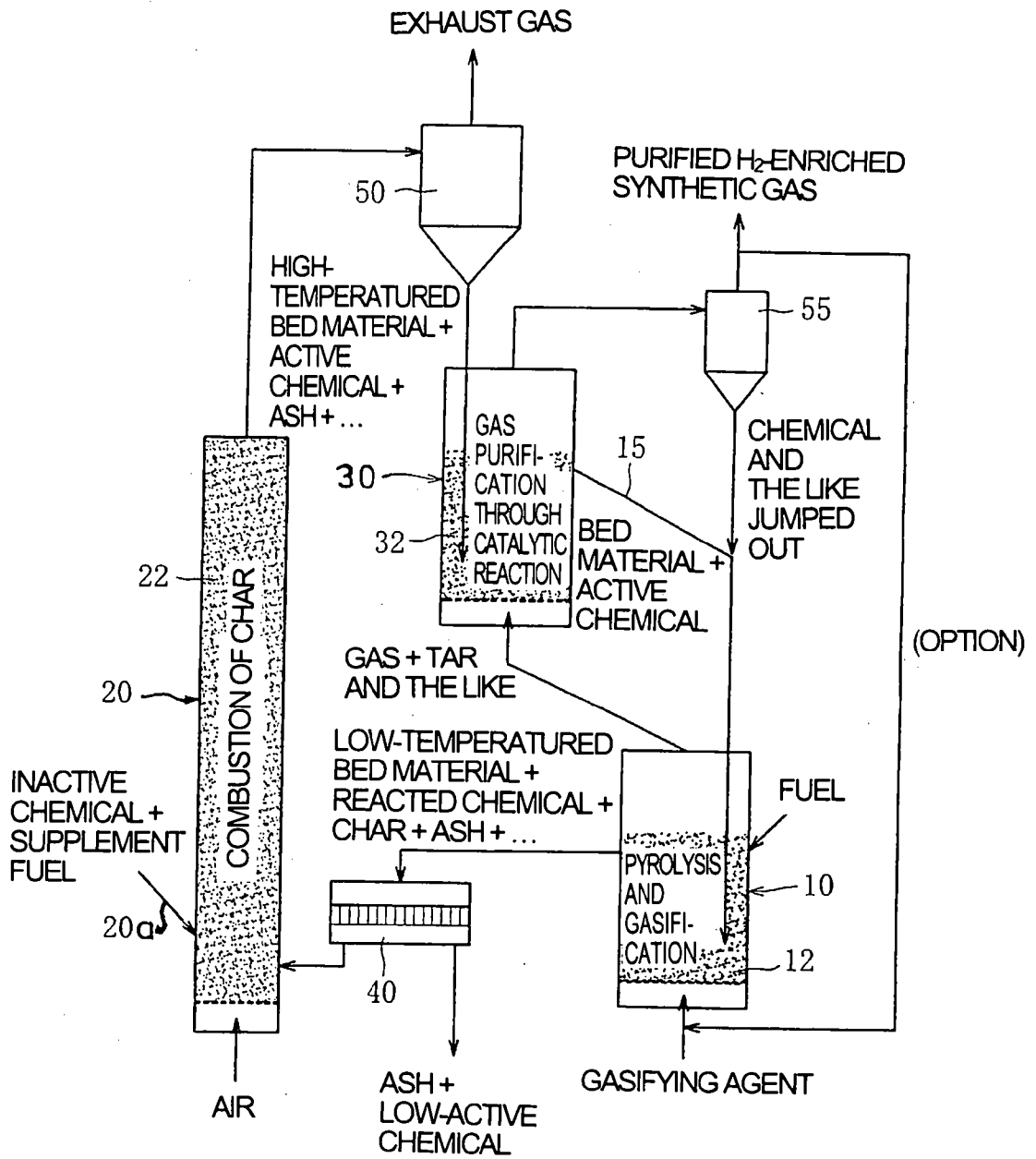


FIG. 2

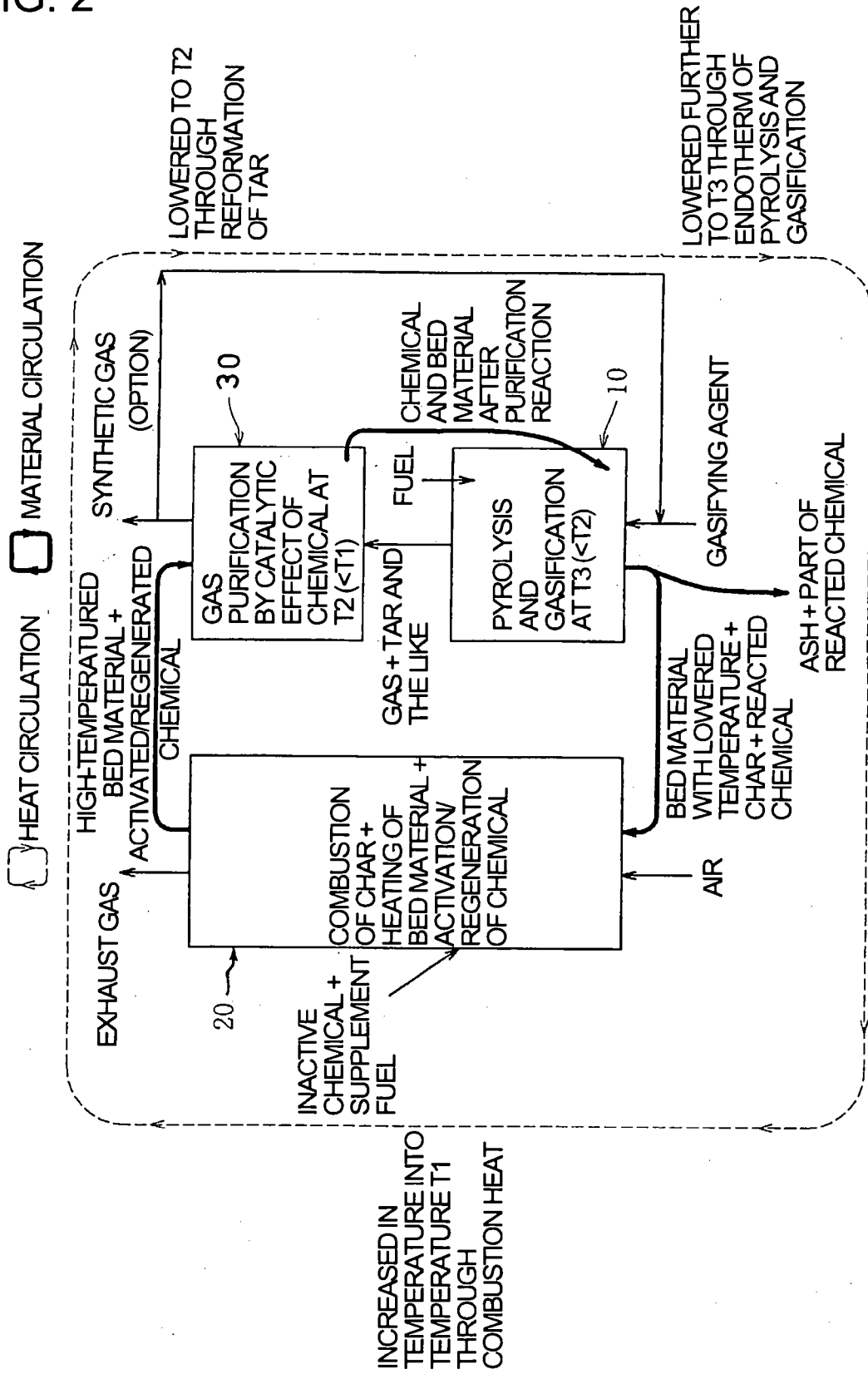


FIG. 3

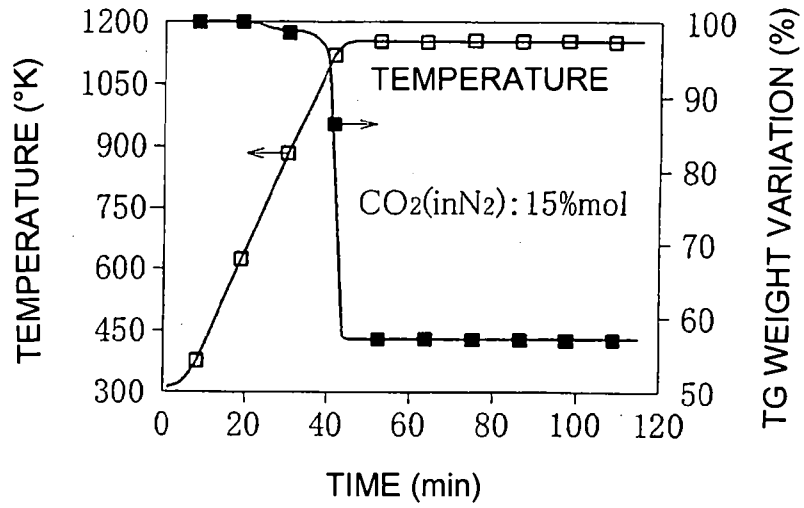


FIG. 4

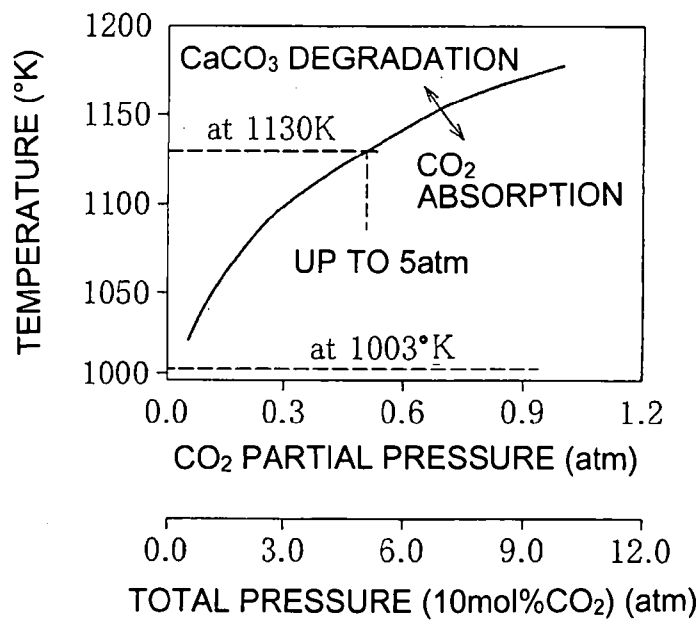


FIG. 5

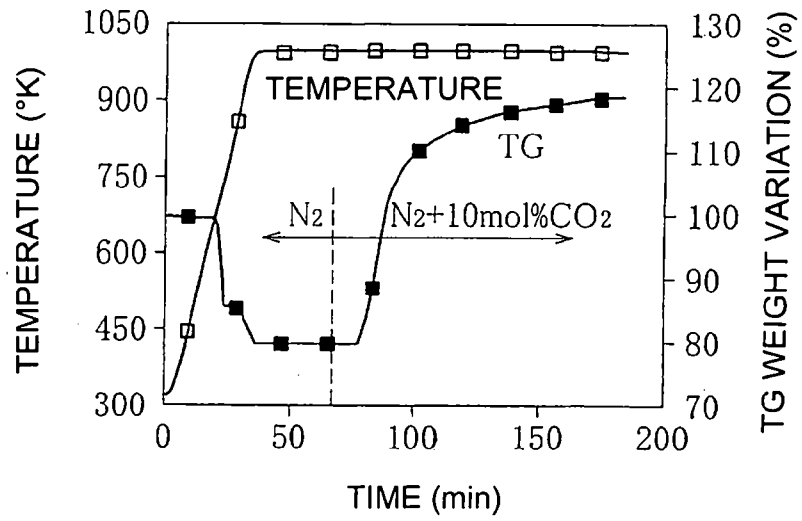


FIG. 6

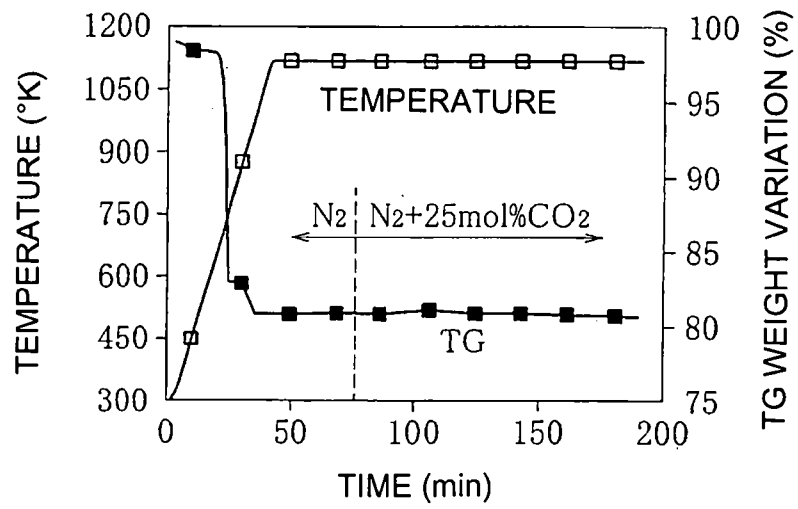


FIG. 7

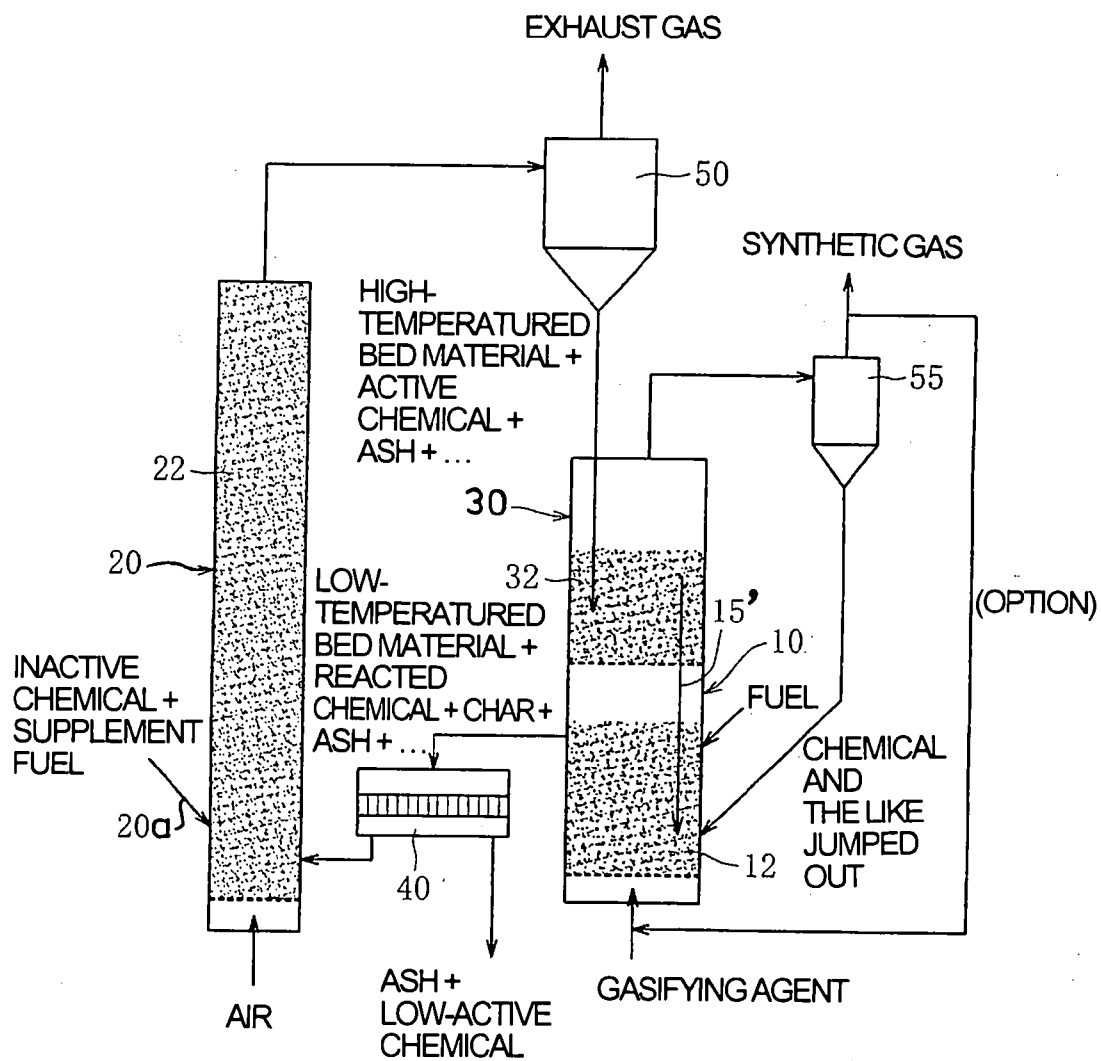


FIG. 8

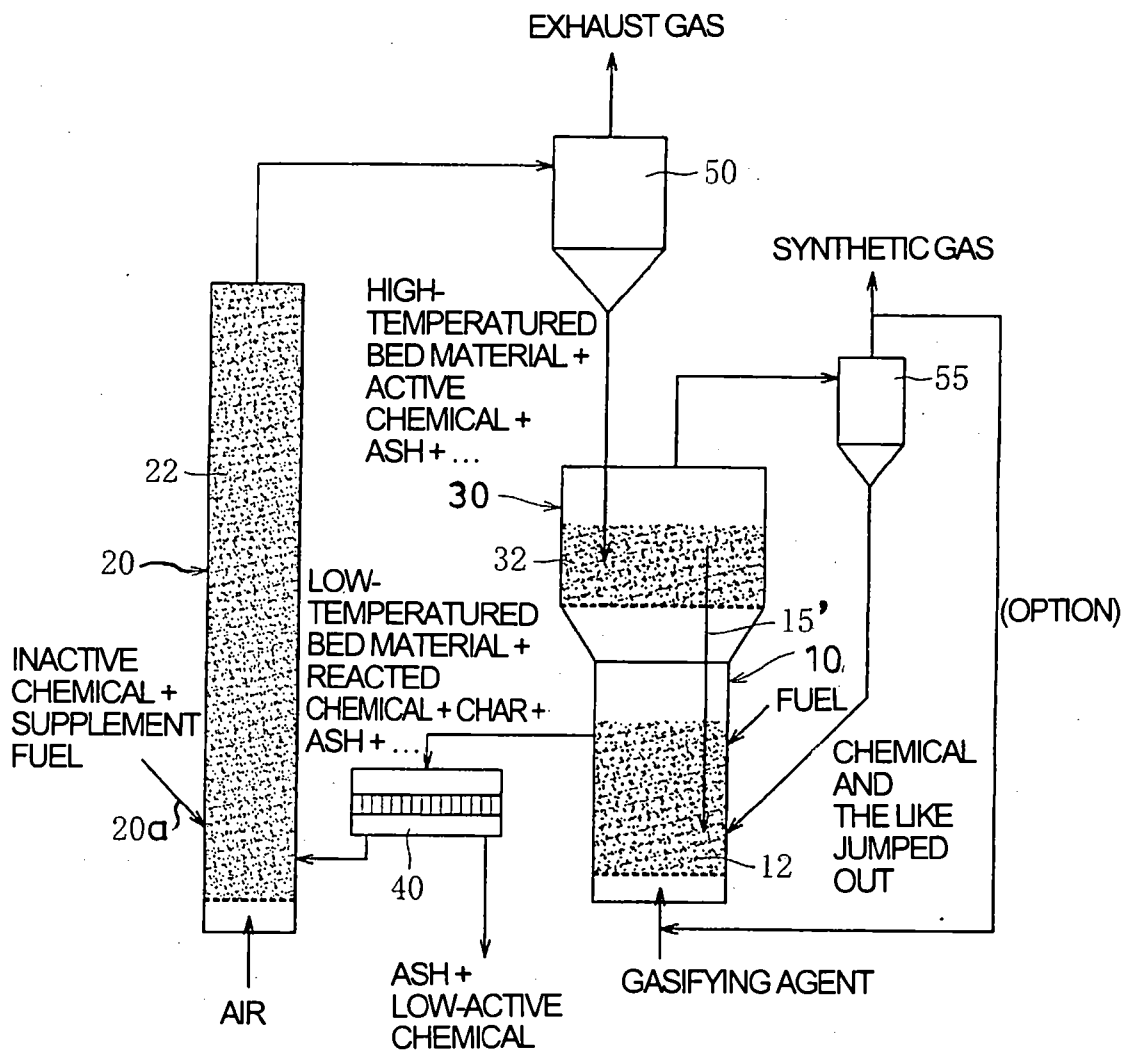


FIG. 9

