

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
16 February 2006 (16.02.2006)

PCT

(10) International Publication Number
WO 2006/017801 A2

(51) International Patent Classification: Not classified

(21) International Application Number:
PCT/US2005/028030

(22) International Filing Date: 5 August 2005 (05.08.2005)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/599,111 5 August 2004 (05.08.2004) US

(71) Applicant and

(72) Inventor: **KRIECH, Anthony, J.** [US/US]; 9029 Shetland Lane, Indianapolis, IN 46278 (US).

(74) Agent: **GZYBOWSKI, Michael, S.**; Butzel Long, 350 South Main Street, Suite 300, Ann Arbor, MI 28104 (US).

(81) Designated States (*unless otherwise indicated, for every kind of national protection available*): 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, JP, KE, KG, KM, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, 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) Designated States (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (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).

Published:

— *without international search report and to be republished upon receipt of that report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: REDUCTION OF NO_x IN COMBUSTION FLUE GAS

(57) Abstract: A method of decreasing the concentration of nitrogen oxides in flue gases emitted into the atmosphere from combustion systems that burn carbonaceous materials which involves pretreating carbonaceous material particles with vanadium, titanium and ammonia. In the case of coal particles, vanadium, titanium dioxide and ammonium acetate are used to coat the coal particles. The vanadium and titanium dioxide are applied as substantially uniform coatings on the surfaces of the coal particles by incorporating the vanadium and titanium dioxide in emulsions or suspensions.



WO 2006/017801 A2

REDUCTION OF NO_x IN COMBUSTION FLUE GASRelated Applications

The present invention is based on United States Provisional Patent Application Serial No. 60/599,111, filed August 5, 2004, and claims priority to United States Provisional Patent Application Serial No. 60/599,111 under 35 U.S.C. §120.

Technical Field

The present invention relates to a method of reducing nitrogen oxide emissions in combustion systems. More specifically, the present invention is directed to a method of decreasing the concentration of nitrogen oxides in flue gases emitted into the atmosphere from combustion systems that burn carbonaceous materials.

Background Art

Nitrogen oxides are major air pollutants emitted by boilers, furnaces, and other combustion sources that burn carbonaceous materials. Nitrogen oxides include nitric oxide (NO), nitrogen dioxide (NO₂), and nitrous oxide (N₂O). Total NO+NO₂ concentration is usually referred to as NO_x. Combustion sources produce nitrogen oxides mainly in the form of NO. Some NO₂ and N₂O are also formed, but their concentrations are typically less than 5% of the

NO concentration, which is generally in the range of about 200-1000 ppm. Nitrogen oxides are the subject of growing concern because they are toxic compounds, and are precursors to acid rain and photochemical smog. Nitrous oxide also contributes to the greenhouse effect.

Combustion modifications such as low NO_x burners (LNB) and overfire air (OFA) injection provide only modest NO_x control, reducing NO_x concentrations by about 30-50%. For greater NO_x control, Selective Catalytic Reduction (SCR), reburning, Advanced Reburning (AR), or Selective Non-Catalytic Reduction (SNCR) can be used in conjunction with low NO_x burners and overfire air injection, or they can be installed as stand-alone systems.

Currently, SCR is the commercial technology with the highest NO_x control efficiency. With SCR, NO_x is reduced by reactions with nitrogenous reducing agents (N-agents) such as ammonia, urea, etc., on the surface of a catalyst. The SCR systems are typically positioned at a temperature of about 700°F in the exhaust stream. Although SCR can achieve 80% NO_x reduction, it is far from an ideal solution for NO_x control because the size of the catalyst bed can be quite large and expensive to implement. In addition, catalyst deactivation techniques typically limit the catalyst life for coal-fired applications and the spent catalysts are toxic and pose disposal problems.

The reduction of NO_x can proceed without a catalyst at higher temperatures using SNCR processes. SNCR processes involve the use of N-agents that form NH₂ radicals which react with NO. Under ideal laboratory conditions, SNCR is very effective; however, in practical, full-scale installations, the non-uniformity of the temperature profile, difficulties of mixing the N-agent across the full combustor cross section, limited residence time for reactions, and ammonia slip (unreacted N-agent) limit the effectiveness of SNCR.

Thermal DeNO_x processes are known in which ammonia is injected into combustion flue

gases containing NO and oxygen at temperatures between about 1,500 and 2,000°F. In such processes, a series of chemical reactions occur and NO is converted to molecular nitrogen. The reaction is believed to start with formation of NH_2 radicals by reaction of ammonia with OH, O or H atoms.

It is also known to add urea to combustion flue gases. The urea is rapidly thermally decomposed into NH_3 and HNCO and the HNCO reacts with radicals to form NH_2 or NCO. As in Thermal DeNO_x processes, NH_2 radicals can remove NO or the NCO radicals can remove NO to form N_2 and then CO and N_2O molecules are oxidized by OH and H, respectively.

An alternative to controlling NO_x emissions by SCR or SNCR processes is reburning. Reburning is a method of controlling NO_x emissions that involves fuel staging. The main portion of the fuel (80-90%) is fired through conventional burners with a normal amount of air (about 10% excess) in a main combustion zone. The combustion process forms a definite amount of NO_x. Then, in a second stage, the rest of the fuel (the reburning fuel) is added at temperatures of about 2,000-2,600°F into the secondary combustion zone, called the reburning zone, to maintain a fuel-rich environment. In this reducing atmosphere both NO_x formation and NO_x removal reactions occur. Experimental results indicate that in a specific range of conditions (equivalence ratio in the reburning zone, temperature and residence time in the reburning zone), the NO_x concentrations can typically be reduced by about 50-70%. In a third stage, air is injected (overfire air, or OFA) to complete combustion of the fuel. Addition of the reburning fuel leads to the rapid oxidation of a portion of the fuel by oxygen to form CO and hydrogen.

Advanced Reburning (AR) is a process that integrates reburning and SNCR. In an AR process, an N-agent is injected along with the OFA, and the reburning system is adjusted to optimize NO_x reduction by the N-agent. By adjusting the reburning fuel injection rate to achieve

near stoichiometric conditions (instead of the fuel rich conditions normally used for reburning), the CO level is controlled and the temperature window for effective SNCR chemistry is considerably broadened. With AR, the NO_x reduction achieved from the N-agent injection is increased.

The present invention provides a method of reducing NO_x emissions in combustion systems that burn carbonaceous materials which involves the chemical pretreatment of the carbonaceous materials.

Disclosure of the Invention

According to various features, characteristics and embodiments of the present invention which will become apparent as the description thereof proceeds, the present invention provides a method of reducing NO_x emissions in combustion systems that burn carbonaceous materials which method involves the steps of:

- a) providing a source of carbonaceous material particles;
- b) substantially uniformly distributing vanadium on the surfaces of the carbonaceous material particles;
- c) substantially uniformly distributing a source of titanium on the surfaces of the carbonaceous material particles;
- d) distributing a source of ammonia on the surfaces of the carbonaceous material particles; and
- e) combusting the carbonaceous material particles treated in steps b), c) and d) in a combustor.

The present invention further provides carbonaceous material which is treated so as to reduce NO_x emissions when combusted in a combustor, the carbonaceous material includes:

particles of carbonaceous material in which the surfaces of the individual particles are substantially uniformly coated with vanadium and a source of titanium.

Brief Description of Drawings

The present invention will be described with reference to the attached drawings which are given as non-limiting examples only, in which:

Figure 1 is a flowchart of one embodiment of the method according to the present invention.

Figure 2 is a flowchart of another embodiment of the method according to the present invention.

Figure 3 is a flowchart of another embodiment of the method according to the present invention.

Best Mode for Carrying out the Invention

The present invention is directed to a method of reducing NO_x emissions in combustion systems that burn carbonaceous materials which involves the chemical pretreatment of the carbonaceous materials. The method is particularly suitable for treating coal used in furnaces in the power production industry, but is equally applicable for treating other carbonaceous materials used in other combustion systems. Examples of carbonaceous materials include coal, coal fines, coke, coke breeze, coke fines, revert materials and mixtures thereof. The treated carbonaceous

materials of the present invention can be produced in the form of individual particles, agglomerated particles, pelletized or briquetted materials, or any convenient form that can be fed into a combustion system such as a furnace, boiler, etc.

According to the present invention, the carbonaceous material is treated with vanadium, titanium and ammonia. The treatment involves preparing a suitable slurry or suspension or emulsion or solution of the vanadium, titanium and ammonia, separately or in combination, and applying the suspension or emulsion or solution to the carbonaceous material particles so that at least the vanadium and titanium are uniformly distributed on the surfaces of the particles. After treatment, the treated carbonaceous material particles can be pelletized or briquetted, if desired, and otherwise stored or used immediately. According to further embodiments of the present invention, the vanadium, titanium and ammonia can be used in combination with conventional coal binders and coal binder compositions and agglomerating compositions, including the emulsion disclosed in U.S. Patent No. 6,530,966 to Kriech et al.

The use of the vanadium and titanium according to the present invention is different than NO_x reduction methods such as SCR that reduce NO_x after the NO_x is formed. In the present method, the vanadium and titanium work as NO_x is formed rather than after NO_x is formed. This is in part accomplished by providing the vanadium and titanium close to the reductant, i.e. by uniformly distributing the vanadium and titanium on the carbonaceous material particles. This uniform distribution of the vanadium and titanium can be accomplished by incorporating the vanadium and titanium into suitable emulsions, slurries, suspensions, solutions, etc. and physically applying, i.e. coating, the carbonaceous material particles with the emulsions, suspensions, solutions, etc. using any suitable mixer, blender, mill, contacting apparatus, etc.

The amount of vanadium used can be from about 0.01 to about 20 parts per million (ppm) or greater. In the case of coal used in power plants, the amount of vanadium can be from about 0.01 to about 20 ppm, but can be greater than 20 ppm.

The titanium can be provided as a suspension of TiO_2 in water in an amount of from about 0.01 to about 0.2 wt. % of the carbonaceous material.

The ammonia can be provided in any suitable form including ammonia, urea, ammonium sulfate, hydrazine, ammonium bisulfite, ammonium bisulfate, ammonium formate, ammonium carbonate, ammonium bicarbonate, biuret, triuret, ammeline, and mixtures thereof. A particular source of ammonia that has been determined to be useful for purposes of the present invention is ammonium acetate because ammonium acetate is easy to disperse and does not have an objectionable odor. The source of ammonia should be added so that there is one molecule of ammonia for every molecule of NO_x that is anticipated to be produced. In the case of using ammonium acetate from about 0.05 to about 0.6 wt.% of ammonium acetate was used based upon the weight of the carbonaceous material.

Figure 1 is a flowchart of one embodiment of a method according to the present invention. In the method illustrated in Fig. 1 the carbonaceous material 1, e.g. coal is first contacted with vanadium 2 in mixer/blender 3. Thereafter, the carbonaceous material is contacted with a source of titanium 4 in mixer/blender 5. Thereafter, the carbonaceous material is contacted with a source of ammonia 6 in mixer/blender 7. After treatment, the treated carbonaceous material is fed into combustor 8 (or stored and later fed into combustor 8).

The mixers/blenders used in the treating process can be any conventional type of mixer, blender, mill, contacting apparatus, etc. that is capable of uniformly distributing the treating

components, i.e. the vanadium, titanium and ammonia, on the surface of the carbonaceous material particles.

The combustor 8 in Fig. 1 can be a furnace, boiler, or any combustion system in which carbonaceous materials such as coal is combusted. Examples of combustors include power plant furnaces, steel production furnaces, heat treatment furnaces, industrial boiler furnaces, and other carbonaceous fired furnaces, including those of steam powered vessels.

In the case of using coal as a carbonaceous material, about 0.01 to about 20 ppm of vanadium (per parts of coal) were added to an emulsion that was formed by emulsifying a distillable liquid petroleum hydrocarbon with a surfactant and about 25-75 wt. % water (based on the emulsion). The emulsion, which is described in U.S. Patent No. 6,530,966 to Kriech et al., was provided to mixer/blender 3 in a suitable amount to coat the surface of the individual coal particles.

In the same process of treating coal, about 0.01 to about 0.2 wt. % of titanium dioxide (TiO_2) (per weight of coal) was added to water to form a slurry which was provided to mixer/blender 5. The amount of water was sufficient to coat the surface of the individual coal particles with the TiO_2 .

In the same process of treating coal, about 0.05 to about 0.6 wt.% ammonium acetate was mixed in water. This mixture was provided to mixer/blender 7 in an amount sufficient to coat the surface of the individual coal particles. The amount of ammonia used was calculated to match the amount of NO_x which was anticipated to be produced. One molecule of ammonia is needed to each molecule of NO_x produced.

Figure 2 is a flowchart of another embodiment of the method according to the present invention. In Fig. 2 The titanium 2 and ammonia 6 are combined together, e.g. in a suspension

or slurry with carbonaceous material particles 1 in mixer/blender 7' after the carbonaceous material particles with vanadium 2 in mixer/blender 3.

Figure 3 is a flowchart of another embodiment of the method of the present invention. In Fig. 3 the vanadium 2 and titanium 4 are combined together, e.g. in an emulsion with the carbonaceous material particles 1 in mixer/blender 3' prior to contacting the carbonaceous material particles with ammonia 6 in mixer/blender 8.

In general, both the vanadium and titanium should be in intimate contact with the surface of the carbonaceous material particles. Accordingly, the process illustrated in Fig. 3 first contacts the carbonaceous material particles with the vanadium and titanium before contacting the carbonaceous material particles with the ammonia. In further embodiments of the present invention, the vanadium, titanium and ammonia could be combined together in an emulsion or suspension and applied to the carbonaceous material particles.

As noted above, the treated carbonaceous materials can be used (combusted) immediately after treatment. Alternatively, the treated carbonaceous material can be stored or pelletized or briquetted or formed into agglomerates using any conventional techniques, including the use of binders.

Features and characteristics of the present invention are exemplified in the following non-limiting example.

Example

In this example a batch of eastern Kentucky mined coal with a BTU/lb of 12,500 was treated with vanadium, titanium and ammonia according to the present invention. 1000 tons of the ¾" x 0 size coal was stockpiled for this example. An emulsion was prepared using a #6 Fuel

Oil which contained 160 mg/kg of vanadium. This #6 Fuel Oil emulsion was spray mixed through a pugmill with the coal at a 1.5% by weight of #6 emulsion on the coal so as to produce a 8.5 mg/kg (parts per million) concentration of vanadium on the coal.

Next, a titanium dioxide suspension of 50% weight titanium in water was prepared and mixed at 0.2% by weight (0.1% TiO₂ on coal) through the pugmill with the previously treated coal.

Subsequently a solution of ammonium acetate in water was prepared by mixing 50% by weight ammonium acetate with water. This mixture was combined through the pugmill with the previously treated coal at 0.6% by weight (0.3% by weight of ammonium acetate).

The finished mixture (treated coal) was then combusted in a power plant. The power plant's NOx emissions were monitored during the combustion of the treated coal. The test results found that NOx emissions dropped by 21% during the test burn from 0.313 lbs of NOx/million BTU's to 0.247 lbs/million BTU's.

This reduction in NOx emissions is significant and the process is easily adaptable for use in conjunction with boilers, furnaces, and other combustion sources that burn carbonaceous materials.

The present method of decreasing the concentration of nitrogen oxides in flue gases emitted into the atmosphere from combustion systems that burn carbonaceous materials does not require the installation of auxiliary treatment equipment to existing combustors. Moreover, the equipment needed to pretreat the carbonaceous materials is relatively inexpensive and easy to operate.

Although the present invention has been described with reference to particular means, materials and embodiments from the foregoing description, one skilled in the art can easily

ascertain the essential characteristics of the present invention and various changes and modifications can be made to adapt the various uses and characteristics without departing from the spirit and scope of the present invention as described above and set forth in the attached claims.

WHAT IS CLAIMED IS:

1. A method of reducing NO_x emissions in combustion systems that burn carbonaceous materials which method comprises the steps of:
 - a) providing a source of carbonaceous material particles;
 - b) substantially uniformly distributing vanadium on the surfaces of the carbonaceous material particles;
 - c) substantially uniformly distributing a source of titanium on the surfaces of the carbonaceous material particles;
 - d) distributing a source of ammonia on the surfaces of the carbonaceous material particles; and
 - e) combusting the carbonaceous material particles treated in steps b), c) and d) in a combustor.
2. A method of reducing NO_x emissions in combustion systems that burn carbonaceous materials according to claim 1, wherein steps b) and c) are combined in a single step in which the titanium and ammonia are combined together and distributed on the surfaces of the carbonaceous material particles.
3. A method of reducing NO_x emissions in combustion systems that burn carbonaceous materials according to claim 1, wherein at least one of the vanadium, source of

titanium and source of ammonia is incorporated into at least one of an emulsion, slurry, suspension and solution prior to being distributed onto the surfaces on the carbonaceous material.

4. A method of reducing NO_x emissions in combustion systems that burn carbonaceous materials according to claim 1, wherein the carbonaceous material comprises at least one of coal, coal fines, coke, coke breeze, coke fines, revert materials and mixtures thereof.

5. A method of reducing NO_x emissions in combustion systems that burn carbonaceous materials according to claim 4, wherein the carbonaceous material is coal.

6. A method of reducing NO_x emissions in combustion systems that burn carbonaceous materials according to claim 1, wherein the amount of vanadium incorporated is from about 0.01 to about 20 ppm of carbonaceous material.

7. A method of reducing NO_x emissions in combustion systems that burn carbonaceous materials according to claim 5, wherein the amount of vanadium incorporated is from about 0.01 to about 20 ppm of carbonaceous material.

8. A method of reducing NO_x emissions in combustion systems that burn carbonaceous materials according to claim 5, wherein the source of titanium comprises titanium dioxide.

9. A method of reducing NO_x emissions in combustion systems that burn carbonaceous materials according to claim 8, wherein the amount of titanium dioxide incorporated is from about 0.01 to about 0.2 wt. % of the carbonaceous material.

10. A method of reducing NO_x emissions in combustion systems that burn carbonaceous materials according to claim 5, wherein the source of ammonia comprises ammonium acetate.

11. A method of reducing NO_x emissions in combustion systems that burn carbonaceous materials according to claim 10, wherein the amount of ammonium acetate incorporated is from about 0.05 to about 0.6 wt.% of the carbonaceous material.

12. A method of reducing NO_x emissions in combustion systems that burn carbonaceous materials according to claim 1, wherein the combustor comprises a furnace.

13. A method of reducing NO_x emissions in combustion systems that burn carbonaceous materials according to claim 1, wherein the combustor comprises a boiler.

14. A carbonaceous material which is treated so as to reduce NO_x emissions when combusted in a combustor, said carbonaceous material comprising:

particles of carbonaceous material in which the surfaces of the individual particles are substantially uniformly coated with vanadium and a source of titanium.

15. A carbonaceous material according to claim 14, where the particles of carbonaceous material are further coated with a source of ammonia.
16. A carbonaceous material according to claim 14, wherein the particles of carbonaceous material comprises coal particles.
17. A carbonaceous material according to claim 14, wherein the amount of vanadium coated on the carbonaceous material particles is from about 0.01 to about 20 ppm based on the carbonaceous material.
18. A carbonaceous material according to claim 14, wherein the source of titanium comprises titanium dioxide.
19. A carbonaceous material according to claim 18, wherein the amount of titanium dioxide coated on the carbonaceous material particles is from about 0.01 to about 0.2 wt. % based on the carbonaceous material.
20. A carbonaceous material according to claim 14, wherein a sufficient amount of ammonia is coated on the carbonaceous material particles so as to provide one molecule of ammonia for each molecule of NO_x that will be produced during combustion of the carbonaceous material.

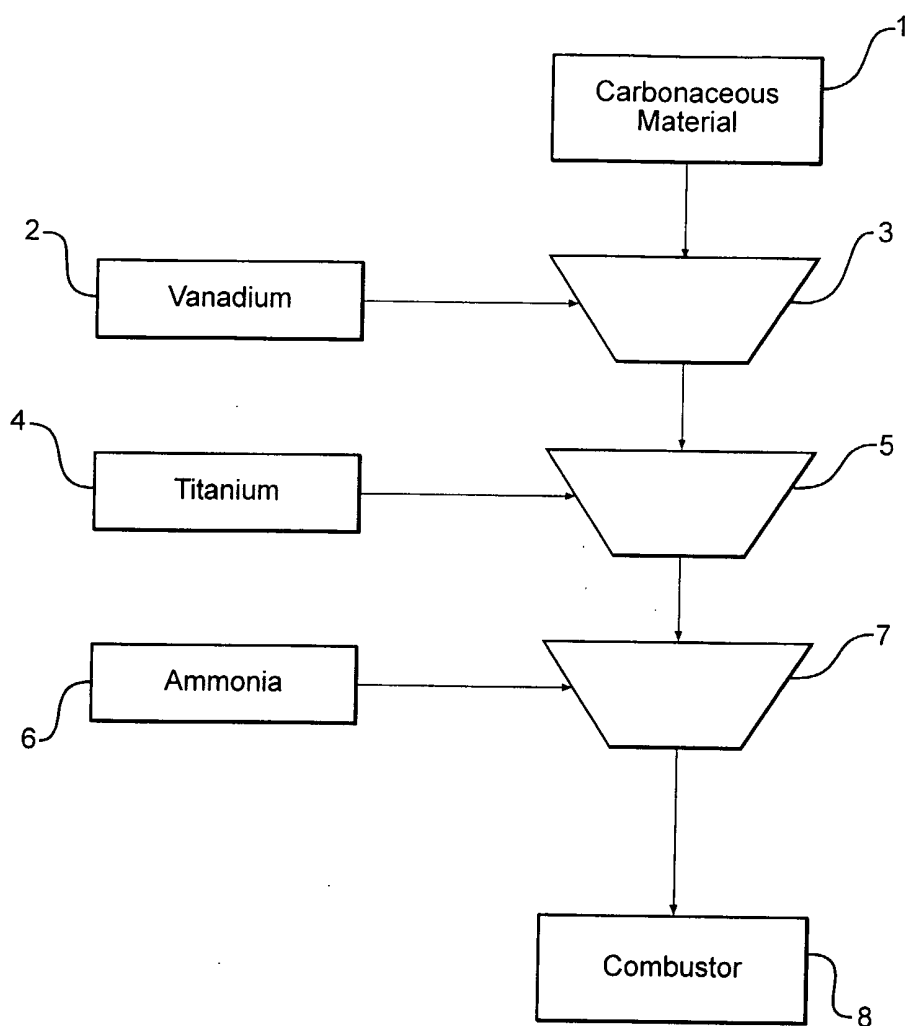


FIG - 1

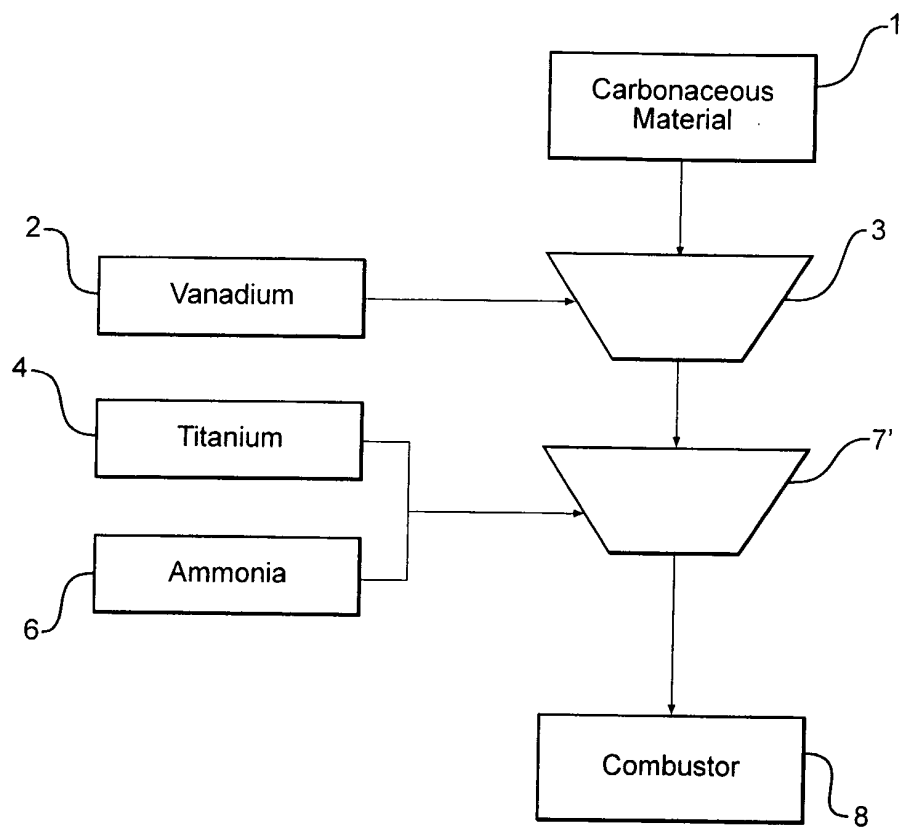


FIG - 2

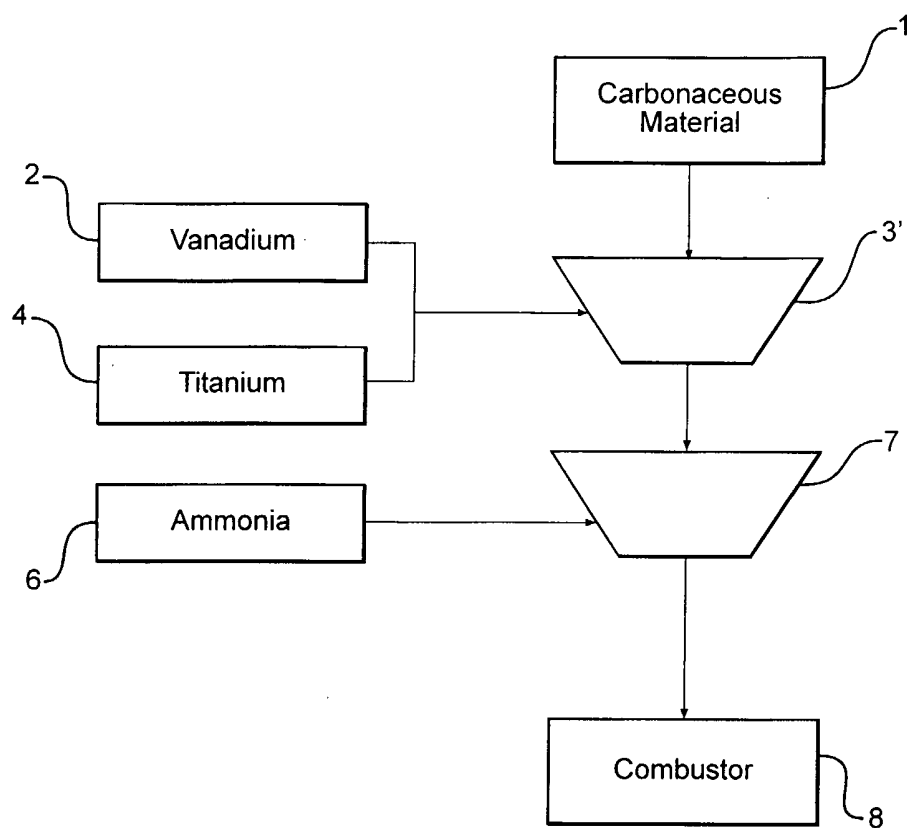


FIG - 3