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HA, Bao [US/US]; 208 Dandelion Lane, San Ramon, California 94583 (US). TRANIER, Jean-Pierre [FR/FR]; 15 sentier des Jardins, F-94240 L hay-les-roses (FR).

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(71) Applicant (for all designated States except US): L'AIR LIQUIDE-SOCIETE ANONYME POUR L'ETUDE ET L'EXPLOITATION DES PROCEDES GEORGES CLAUDE [FR/FR]; 75 Quai d'Orsay, F-75321 Paris Cedex 07 (FR).

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(72) Inventors; and

(75) Inventors/Applicants (for US only): DARDE, Arthur [FR/FR]; 32 boulevard Saint-Marcel, F-75005 Paris (FR).

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(54) Title: PROCESS AND APPARATUS FOR THE SEPARATION OF A GASEOUS MIXTURE

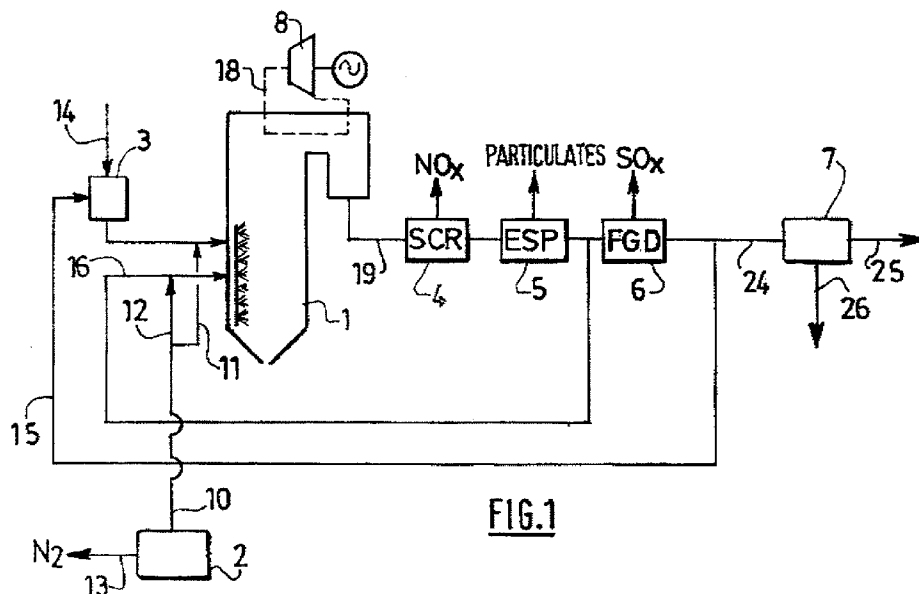


FIG.1

(57) Abstract: A process for separating carbon dioxide from a fluid containing carbon dioxide, NO₂, and at least one of oxygen, argon, and nitrogen comprises the steps of separating at least part of the fluid into a carbon dioxide enriched stream, a carbon dioxide depleted stream comprising CO₂ and at least one of oxygen, argon, and nitrogen and a NO₂ enriched stream and recycling said NO₂ enriched stream upstream of the separation step.

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PROCESS AND APPARATUS FOR THE SEPARATION OF A GASEOUS MIXTURE

Technical Field

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The present invention relates to a process and apparatus for the separation of gaseous mixture containing carbon dioxide as main component. It relates in particular to processes and apparatus for purifying carbon dioxide, for example coming from combustion of a carbon containing fuel, such as takes place in an oxycombustion fossil fuel or biomass power plant.

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Background Art

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The combustion of carbon containing fuels (biomass, waste, fossil fuels such as coal, lignite, hydrocarbons,...) produces CO₂ and gases, such as SO₂, SO₃, NO_x, which pollute the atmosphere and are major contributors to the greenhouse effect especially CO₂. These emissions of CO₂ are concentrated in four main sectors: power generation, industrial processes, transportation, and residential and commercial buildings. The main application of CO₂ capture is likely to be in power generation and large energy consuming industries, particularly cement, iron and steel and chemical production and oil refining. Capturing CO₂ directly from small and mobile sources in the transportation and domestic and commercial buildings sectors is expected to be significantly more difficult and expensive. Most of the emissions of CO₂ to the atmosphere from the electricity generation and industrial sectors are currently in the form of flue gas from combustion, in which the CO₂ concentration is typically 4-14% by volume, although CO₂ is produced at high concentrations by a few industrial processes. In principle, flue gas could be stored, to avoid emissions of CO₂ to the atmosphere it would have to be compressed to a pressure of typically more than 100 bar abs and this would consume an excessive amount of energy. Also, the high volume of the flue gas

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would mean that storage reservoirs would be filled quickly. For these reasons it is preferable to produce relatively high purity stream of CO₂ for transport and storage; this process is called CO₂ capture. This carbon dioxide could be used for enhanced oil recovery or just injected in depleted gas and oil fields or in aquifers.

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The present invention is based on application to the power generation sector. Nevertheless, it could also be applied to flue gases coming from other industrial processes with a relatively high purity, above 50% by volume (dry base).

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There are three main techniques for capture of CO₂ in power plants:

- Post-combustion: the flue gas from a power station is scrubbed with a chemical solvent such as an aqueous solution of amines which will remove the CO₂ by absorption.
- Pre-combustion: the fuel together with oxygen is sent to a gasifier where a synthesis gas (main component of the mixture: H₂, CO and CO₂) is produced. CO is then shifted to H₂ and CO₂ ($\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$) and CO₂ is scrubbed by a physical or chemical solvent. A mixture containing essentially H₂ and N₂ is sent to a gas turbine where it is burnt.
- Oxycombustion: in order to increase the carbon dioxide content in the flue gas, the fuel is burnt with a mixture of mainly carbon dioxide and oxygen instead of air. This mixture of oxygen and carbon dioxide is obtained by recycling part of the flue gas rich in carbon dioxide and mixing it with oxygen (typically at 95% purity) coming from a cryogenic air separation unit. The flue gas is then purified in order to remove components like water and oxygen and compressed to a pressure between 100 and 200 bar abs in order to be injected underground (see Figure 1). It should be noted that the recycling of flue gases would not be necessary with high temperature materials for the boiler. However, they do not exist at the time of invention. The recycling of flue gases is not mandatory for the invention disclosed here in.

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EP-A-0503910 describes a process for the recovery of carbon dioxide and other acid gases from flue gases coming from a power plant using the oxycombustion technique

5 A more recent document on the same subject is "Oxy-Combustion Processes for CO₂ Capture from Power Plant', IEA Report No. 2005/9, September 2005.

The purpose of this invention is to improve the solution proposed in this patent both in term of specific energy and/or carbon dioxide recovery and/or carbon
10 dioxide product purity.

Summary of the Invention

According to the present invention, there is provided a process for separating
15 carbon dioxide from a fluid containing carbon dioxide, NO₂ and at least one of oxygen, argon, and nitrogen comprising the steps of:

- 20 i) separating at least part of the fluid into a carbon dioxide enriched stream, a carbon dioxide depleted stream comprising CO₂ and at least one of oxygen, argon and nitrogen and a NO₂ enriched stream;
and
- ii) recycling said NO₂ enriched stream upstream of the separation step.

According to further optional features:

- 25 - the separation step of i) includes:
 - a) separating at least part of the fluid into a carbon dioxide enriched stream, a carbon dioxide depleted stream comprising CO₂ and at least one of oxygen, argon and nitrogen; and
 - 30 b) separating the carbon dioxide enriched stream to form a NO₂ enriched stream and the recycling step ii) consists of

recycling the NO₂ enriched stream upstream of separation phase a);

- the separation phase b) consists of producing the NO₂ enriched stream by distillation;
- 5 - the separation phase b) consists of producing the NO₂ enriched stream by phase separation;
- the separation phase b) consists of producing the NO₂ enriched stream by adsorption;
- the separation step i) includes a) separating the fluid to produce the
10 NO₂enriched stream and an NO₂ depleted stream and b) separating the NO₂ depleted stream to produce a carbon dioxide enriched stream and a carbon dioxide depleted stream;
- the NO₂ enriched stream is removed by sending the fluid to an adsorption unit, removing the NO₂ depleted gas to the adsorption unit, sending a
15 regeneration gas to the adsorption unit and removing the regeneration gas from the adsorption unit as the NO₂ enriched stream;
- the NO₂ enriched stream is recycled to a unit producing the fluid;
- the unit producing the fluid is a combustion zone of a boiler;
- the fluid is compressed in a compressor upstream of separation step i) and
20 the NO₂ enriched stream is recycled upstream of the compressor;
- the NO₂ enriched stream is recycled to a unit for treating the fluid;
- the NO₂ enriched stream reacts with SO₂ in the unit for treating the fluid to form SO₃ and NO;
- the SO₃ subsequently reacts with water to form sulfuric acid;
- 25 - the unit for treating the fluid is a wash column;
- a unit for producing the fluid is a boiler with burners generating more than 500ppm NO_x;
- a unit producing the fluid generates enough NO_x to convert most of the SO₂ contained in the flue gas to sulfuric acid; and

- NO_x produced by an external source, possibly another plant of the same or another kind, is added to the unit producing the fluid and used to oxidize at least part of the SO₂ contained in the flue gas.

5 According to a further aspect of the invention, there is provided an apparatus for separating carbon dioxide from a fluid containing carbon dioxide, NO₂ and at least one of oxygen, argon, and nitrogen comprising:

- i) a separation unit for separating at least part of the fluid into a carbon dioxide enriched stream, a carbon dioxide depleted stream
10 comprising CO₂ and at least one of oxygen, argon and nitrogen and a NO₂ enriched stream
- ii) a conduit for recycling said NO₂ enriched stream upstream of the separation unit

15 According to further optional features:

- the separation unit includes:
 - a) a carbon dioxide separation unit for separating at least part of the fluid into a carbon dioxide enriched stream, a carbon dioxide
20 depleted stream comprising CO₂ and at least one of oxygen, argon, and nitrogen; and
 - b) an NO₂ separation unit for separating the carbon dioxide enriched stream to form a NO₂ enriched stream and wherein the conduit connects the NO₂ separation unit with a point upstream of the carbon dioxide separation unit to permit the NO₂ enriched stream to
25 be sent to that point;
- the NO₂ separation unit comprises at least one distillation column;
- the NO₂ separation unit comprises at least one phase separator;
- the NO₂ separation unit comprises at least one distillation column and at least one phase separator;
- 30 - the NO₂ separation unit comprises at least one adsorption unit;

- the separation unit includes a) an NO₂ separation unit for separating the fluid to produce the NO₂ enriched stream and an NO₂ depleted stream and b) a carbon dioxide separation unit for separating the NO₂ depleted stream to produce a carbon dioxide enriched stream and a carbon dioxide depleted stream and the conduit connects the NO₂ separation unit with a point upstream of the carbon dioxide separation unit to permit the NO₂ enriched stream to be sent to that point;
- the apparatus comprises an adsorption unit, a conduit for sending the fluid to the adsorption unit, a conduit for removing the NO₂ depleted gas from the adsorption unit, a conduit for sending a regeneration gas to the adsorption unit and a conduit for removing the regeneration gas from the adsorption unit as the NO₂ enriched stream;
- the apparatus comprises a unit producing the fluid and wherein the conduit for recycling the NO₂ enriched stream is connected to the unit producing the fluid;
- the unit producing the fluid is a combustion zone of a boiler;
- the NO₂ enriched stream is recycled to a unit for treating the fluid;
- the unit for treating the fluid is a compressor upstream of separation unit and comprising a conduit for sending the fluid to the compressor and wherein the conduit for recycling the NO₂ enriched stream is connected upstream of the compressor; and
- the unit for treating the fluid is a wash column.

Detailed Description of the Invention

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The invention will now be described in further detail with reference to the figures of which Figures 1 and 3 show apparatuses according the invention, in varying degrees of detail, going from Figure 1 which is the least detailed to Figure 3 which is the most detailed. Figures 4 and 5 show heat exchange diagrams for the prior art and one of the exchangers of Figure 3 respectively.

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Figure 1 is a schematic view of an oxycombustion plant. Air separation unit **2** produces an oxygen stream **10** at a typical purity of 95-98 mol. % and a waste nitrogen stream **13**. Oxygen stream **10** is split into two sub streams **11** and **12**. The primary flue gas recycle stream **15** passes through coal mills **3** where coal **14** is pulverized. Substream **11** is mixed with the recycle stream downstream of the coal mills **3** and the mixture is introduced in the burners of the boiler **1**. Substream **12** is mixed with secondary flue gas recycle stream **16** which provides the additional ballast to the burners to maintain temperatures within the furnace at acceptable levels. Water stream(s) is introduced in the boiler **1** in order to produce steam stream(s) **18** which is expanded in steam turbine **8**. Flue gas stream **19** rich in CO₂, typically containing more than 70 mol. % on a dry basis, goes through several treatments to remove some impurities. Unit **4** is NO_x removing system like selective catalyst reduction. Unit **5** is a dust removal system such as electrostatic precipitator and/or baghouse filters. Unit **6** is a desulfurization system to remove SO₂ and/or SO₃. Units **4** and **6** may not be necessary depending on the CO₂ product specification. Flue gas stream **24** is then introduced in a compression and purification unit **7** in order to produce a high CO₂ purity stream **25** which will be sequestrable and a waste stream **26**.

Figure 2 is a schematic view of a compression and purification unit which could be used as unit **7** in Figure 1. Flue gas stream **110** (corresponding to stream **24** of Figure 1) enters a low pressure pretreatment unit **101** where it is prepared for compression unit **102**. This unit could include, for example, among other steps:

- a dust removal step in a wet scrubber and/or a dry process either dynamic, such as pulse-jet cartridges or static, such as pockets and cartridges;
- a (further) desulfurization step in a wet scrubber with water and/or soda ash or caustic soda injection; and
- a cooling step in order to minimize the flow through water condensation and the power of compression unit both due to flow and temperature reduction.

Waste stream(s) **111** could consist of condensed water, dust and dissolved species like H_2SO_4 , HNO_3 , Na_2SO_4 , CaSO_4 , Na_2CO_3 , CaCO ...

Compression unit **102** compresses stream **112** from a pressure close to atmospheric pressure to a high pressure typically between 15 and 60 bar abs, preferably around 30 bar abs. This compression could be done in several stages with intermediate cooling. In this case, some condensate(s) **113** could be produced. Heat of compression could also be recovered in these intermediate cooling step, for example to preheat boiler feed water. Hot stream **114** leaves the compression unit **102** and enters a high pressure pretreatment unit **103**. This unit at least includes:

- one or several cooling step(s) in order to decrease the temperature and decrease the water content; and
- a drying step to remove most of the water, for example by adsorption.

and could include (non-exhaustive list):

- a high pressure washing column for cooling and/or purification; and
- a mercury removal step.

Effluents from this unit are gaseous stream **115** (regeneration stream of the drying step) and could be liquid stream(s) **116/117** (from the cooling step and/or the high pressure washing column).

The stream **114** may contain NO_2 . In this case, it is sometimes preferable to remove the NO_2 by adsorption upstream of the unit **104**. In this case, the stream **114** may be treated by adsorption and the regeneration gas used to regenerate the adsorbent is removed having a content enriched in NO_2 with respect to that of stream **114**. The gaseous stream **115** may be recycled at least in part upstream of the compression unit **102**, upstream of the pretreatment unit **101** or to the boiler **1** of the combustion unit.

Below 158° C., NO₂ is in equilibrium with its polymer/dimer N₂O₄. The lower the temperature, the higher the concentration of N₂O₄ compared to NO₂. In this document, the word NO₂ is used to mean not only NO₂ but also its polymer/dimer N₂O₄ in equilibrium.

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Unit **104** is a low temperature purification unit. In this case, low temperature means a minimum temperature in the process cycle for the purification of the flue gas below 0° C. and preferably below -20° C. as close as possible to the triple point temperature of pure CO₂ at -56.6° C. In this unit, stream **118** is cooled down and partially condensed in one (or several steps). One (or several) liquid phase stream(s) enriched in CO₂ is (are) recovered, expanded and vaporized in order to have a product enriched in CO₂ **119**. One (or several) non-condensable high pressure stream(s) **120** is (are) recovered and could be expanded in an expander.

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CO₂ enriched product **119** is further compressed in compression unit **105**. In unit **106** compressed stream **121** is condensed and could be further compressed by a pump in order to be delivered at high pressure (typically 100 to 200 bar abs) as stream **122** to a pipeline to be transported to the sequestration site.

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Figure 3 shows a low temperature purification unit that could be used as unit **104** in Figure 2. At least one process according to the invention operates within such a unit.

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Stream **118** comprising flue gas at around 30 bar and at a temperature of between 15° C. and 43° C. is filtered in **3** to form stream **5**. Stream **118** contains mainly carbon dioxide as well as NO₂, oxygen, argon and nitrogen. It may be produced by unit **103** directly at the high pressure or may be brought up to the high pressure using optional compressor **2** shown in dashed lines. Stream **5** cools in heat exchange line **9** and is partially condensed. Part **7** of stream **5** may not be cooled in the heat exchange but is mixed with the rest of stream **5** downstream of the

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heat exchange line to vary its temperature. The partially condensed stream is sent to first phase separator **11** and separated into gaseous phase **13** and liquid phase **17**. The gaseous phase **13** is divided in two to form stream **15** and stream **21**. Stream **21** is used to reboil column **43** in exchanger **25** and is then sent to a second phase separator **22**. Stream **15** by-passes the reboilers in order to control the reboiling duty.

Liquid stream **17** from the first phase separator **11** is expanded in valve **19** and liquid stream **29** is expanded in valve **31**, both streams being then sent to the top of column **43**. Column **43** serves principally to remove the incondensable components (oxygen, nitrogen, and argon) from the feed stream.

A carbon dioxide depleted stream **33** is removed from the top of column **43** and sent to compressor **35**. The compressed stream **37** is then recycled to stream **5**.

A carbon dioxide enriched or rich stream **67** is removed from the bottom of column **43** and divided in two. One part **69** is pumped by pump **71** to form stream **85**, further pumped in pump **87** and then removed from the system. Stream **85** corresponds to stream **25** of Figure 1. The rest **73** provides the frigorific balance.

It is desirable to provide means for removing NO_2 from the fluid **118** to be separated. In general this involves separating at least part of the fluid **118** into a carbon dioxide enriched stream, a carbon dioxide depleted stream comprising CO_2 and at least one of oxygen, argon, and nitrogen and a NO_2 enriched stream, and recycling the NO_2 enriched stream upstream of the separation step.

The incondensable removal step (removing mainly O_2 and/or N_2 and/or Ar) may take place before or after the NO_2 removal step.

Several types of NO₂ removal step may be envisaged, involving distillation and/or phase separation and/or adsorption. The adsorption step may be carried out on a product of the CO₂ separation step or the fluid itself before separation.

5 In Figure 3, after stream **69** is removed, the rest of the carbon dioxide enriched stream **73** is vaporized in heat exchange line **9** and sent to NO₂ removal column **105**.

This column may have a top condenser and a bottom reboiler, as shown, the feed
10 being sent to an intermediate point. Alternatively, there need be no bottom reboiler, in which case the feed is sent to the bottom of the column. An NO₂ depleted stream **79** is removed from the column and sent back to the heat exchange line. This stream is further warmed, compressed in compressors **75**, **77**, sent to heat exchanger **65**, removed therefrom as stream **78**, cooled in
15 exchangers **81**, **83** and mixed with stream **69** to form stream **85**. Exchanger **81** may be used to preheat boiler feed water. Exchanger **83** is cooled using a refrigerant stream **185** which may be R134a, ammonia, water, water mixed with glycol or any other suitable fluid. The warmed fluid is designated as **187**. An NO₂ enriched stream **84** is removed from the bottom of the column **105**. This stream
20 **84** is then recycled to a point upstream of filter **3**.

Alternatively or additionally the separation phase may consist of producing the NO₂ enriched stream by adsorption of the NO₂ contained in stream **67** in adsorption unit **68**.

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In either case, at least part of the NO₂ enriched stream may be recycled to a unit producing the fluid, such as the combustion zone of a boiler **1**, as seen previously for stream **115**. It should be noted that recycling NO_x in the combustion zone does not increase the NO_x content in the flue gas. In other words, recycling NO_x
30 to the combustion zone eliminates NO_x.

Additionally or alternatively at least part of the NO₂ enriched stream may be recycled to a unit for treating the fluid.

5 For example the NO₂ enriched stream may be recycled upstream of the compressor **2** (if present) or one of units **101**, **102**.

10 In addition, low-NO_x burners (with NO_x content in the flue gas in the range of 150-500 ppm volume) may not be required anymore. To convert SO₂ to sulfuric acid, it is desirable to have an excess of NO₂. As SO₂ content in the flue gas is in general higher than 500 ppm (typically several thousands ppm), it is now better to have burners which generate high amounts of NO_x (typically also several thousands ppm). Those burners will be more compact (no need for stage combustion) and more heat efficient (higher heat input for a given volume). Therefore, the furnace could be more compact and thus less costly.

15 NO₂ is recycled because in the low pressure flue gas coming from the boiler, the NO_x are essentially under the NO form which does not react with SO₂. It is only by compressing the flue gas and cooling it, that the oxidation of NO to form NO₂ ($2\text{NO} + \text{O}_2 \leftrightarrow \text{NO}_2$) occurs. This reaction has very low kinetics at atmospheric pressure. The kinetics are tremendously improved by high pressure and to a lower extent by low temperature.

25 If there is not enough NO_x from the boiler to oxidize the SO_x from the same flue gas, it is an option to introduce NO_x, being mostly NO₂, into the flue gas at low pressure from an external source, upstream of the low pressure scrubbing column. Part of the NO_x will be recirculated in the process via the separation in the low temperature section. Part of the NO_x must be reintroduced continuously or from time to time because of NO_x losses in condensate purges.

It may be advantageous to recycle at least part of the NO₂ enriched stream to a wash column, such as that of pretreatment unit **103**. In this case, the NO₂ may be converted to nitric acid in the wash column and subsequently removed from the system.

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In a wash column where SO₂ is present in the flue gas, the recycled NO₂ enriched stream will react with SO₂ to form NO and SO₃ that will immediately turn to H₂SO₄ with water and be removed in the water drain. Therefore, if enough NO₂ is present in the recycled stream, it is a means to remove SO_x from the flue gas and to avoid the injection of reactants like soda ash or caustic soda or even a classical flue gas desulphurization.

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Top gas **32** from the second phase separator **22** is cooled in heat exchanger **55** and sent to third phase separator **133**. Part of the liquid from the phase separator **133** is sent to the column **43** and the rest as the intermediate purity stream **45** is divided in two streams **47**, **141**. Stream **47** is vaporized in heat exchanger **55** and sent to the top of column **43** or mixed with stream **33**.

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Stream **141** is expanded in a valve, warmed in heat exchangers **55**, **9**, compressed in compressor **59**, cooled as stream **91** in heat exchanger **60**, and mixed with compressed stream **5**. The valve used to expand stream **141** could be replaced by a liquid expander.

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The top gas from the third phase separator **133** is cooled in heat exchanger **55**, optionally after compression by compressor **134** and sent to a fourth phase separator **143**. The carbon dioxide lean top gas **157** from fourth phase separator **143** is warmed in heat exchanger **55**, then in heat exchanger **9** as stream **157**, warmed in exchanger **65** and expanded as stream **23** in expander **63**, coupled to compressor **35**. The carbon dioxide lean top gas **157** contains between 30 and 45% carbon dioxide and between 30 and 45% nitrogen. It also contains

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substantial amounts of oxygen and argon. The bottom liquid **51** from phase separator **143** is sent to the column with stream **47**.

The stream expanded in expander **63** is mixed with stream **115** which does not pass through the expander and then warmed in **89**. Part **97** of the warmed stream is expanded in expander **61** and sent as stream **99, 101** to the atmosphere.

The optional compressor **2** may be powered by one of expanders **61, 63**.

Expander **61** is coupled to compressor **59** in the figure.

Molar fractions in % (example) for O₂, N₂, Ar, CO₂

FLUIDS / Components	118	33	67	84	157	141	78
O ₂	2.5	4.8	0	0	13.3	2.3	0
N ₂	7.8	11	0	0	43.8	0.1	0
Ar	1.9	4.9	0	0	9.5	2.6	0
CO ₂	87.8	79.3	99.95	99	33.4	95	100
NO _x	250 ppm	50 ppm	500 ppm	1	5 ppm	500 ppm	0

Table 1

Figure 4 shows a heat exchange diagram for heat exchange between a vaporizing high purity carbon dioxide stream and a cooling and condensing feed stream as known from the prior art.

Figure 5 shows a heat exchange diagram for heat exchange between an intermediate purity carbon dioxide stream and a cooling and condensing feed stream as observed in exchanger **55** of Figure 3.

Claims

1. A process for separating carbon dioxide from a fluid containing carbon dioxide, NO₂ and at least one of oxygen, argon, and nitrogen comprising the steps of:
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- i) separating at least part of the fluid into a carbon dioxide enriched stream, a carbon dioxide depleted stream comprising CO₂ and at least one of oxygen, argon and nitrogen and a NO₂ enriched stream; and
 - 10 ii) recycling said NO₂ enriched stream upstream of the separation step
2. The process of claim 1, wherein the separation step of i) includes:
- 15 a) separating at least part of the fluid into a carbon dioxide enriched stream, a carbon dioxide depleted stream comprising CO₂ and at least one of oxygen, argon and nitrogen and
 - b) separating the carbon dioxide enriched stream to form a NO₂ enriched stream and the recycling step ii) consists of recycling the NO₂ enriched stream upstream of separation phase a).
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3. The process of claim 2, wherein the separation phase b) consists of producing the NO₂ enriched stream by distillation.
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4. The process of claim 2, wherein the separation phase b) consists of producing the NO₂ enriched stream by phase separation.
5. The process of claim 2, wherein the separation phase b) consists of producing the NO₂ enriched stream by adsorption.
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6. The process of any preceding claim, wherein the separation step i) includes a) separating the fluid to produce the NO₂ enriched stream and an NO₂ depleted stream and b) separating the NO₂ depleted stream to produce a carbon dioxide enriched stream and a carbon dioxide depleted stream.

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7. The process of claim 6, wherein the NO₂ enriched stream is removed by sending the fluid to an adsorption unit, removing the NO₂ depleted gas to the adsorption unit, sending a regeneration gas to the adsorption unit and removing the regeneration gas from the adsorption unit as the NO₂ enriched stream.

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8. The process of any preceding claim, wherein the NO₂ enriched stream is recycled to a unit producing the fluid.

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9. The process of claim 8, wherein the unit producing the fluid is a combustion zone of a boiler.

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10. The process of any preceding claim, wherein the fluid is compressed in a compressor upstream of separation step i) and the NO₂ enriched stream is recycled upstream of the compressor.

11. The process of any preceding claim, wherein the NO₂ enriched stream is recycled to a unit for treating the fluid.

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12. The process of claim 11, wherein the NO₂ enriched stream reacts with SO₂ in the unit for treating the fluid to form SO₃ and NO.

13. The process of claim 12, wherein the SO₃ subsequently reacts with water to form sulfuric acid.

14. The process of claim 11, wherein the unit for treating the fluid is a wash column.

5 15. The process of any preceding claim, wherein a unit for producing the fluid is a boiler with burners generating more than 500ppm NO_x.

10 16. The process of any preceding claim, wherein a unit producing the fluid generates enough NO_x to convert most of the SO₂ contained in the flue gas to sulfuric acid.

17. The process of any preceding claim, wherein NO_x produced by an external source is added to the unit producing the fluid and used to oxidize at least part of the SO₂ contained in the flue gas.

15 18. An apparatus for separating carbon dioxide from a fluid containing carbon dioxide, NO₂ and at least one of oxygen, argon, and nitrogen comprising:
i) a separation unit for separating at least part of the fluid into a carbon dioxide enriched stream, a carbon dioxide depleted stream comprising CO₂ and at least one of oxygen, argon and nitrogen and a NO₂ enriched stream; and
20 ii) a conduit for recycling said NO₂ enriched stream upstream of the separation unit.

25 19. The apparatus of claim 18, wherein the separation unit includes:
a) a carbon dioxide separation unit for separating at least part of the fluid into a carbon dioxide enriched stream, a carbon dioxide depleted stream comprising CO₂ and at least one of oxygen, argon and nitrogen; and
30 b) an NO₂ separation unit for separating the carbon dioxide enriched stream to form a NO₂ enriched stream; and

wherein the conduit connects the NO₂ separation unit with a point upstream of the carbon dioxide separation unit to permit the NO₂ enriched stream to be sent to that point .

5 20. The apparatus of claim 18, wherein the NO₂ separation unit comprises at least one distillation column.

 21. The apparatus of claim 18, wherein the NO₂ separation unit comprises at least one phase separator.

10

 22. The apparatus of claim 18, wherein the NO₂ separation unit comprises at least one distillation column and at least one phase separator.

15

 23. The apparatus of claim 18, wherein the NO₂ separation unit comprises at least one adsorption unit.

20

 24. The apparatus of claim 18, wherein the separation unit includes:
 a) an NO₂ separation unit for separating the fluid to produce the NO₂ enriched stream and an NO₂ depleted stream; and
 b) a carbon dioxide separation unit for separating the NO₂ depleted stream to produce a carbon dioxide enriched stream and a carbon dioxide depleted stream and the conduit connects the NO₂ separation unit with a point upstream of the carbon dioxide separation unit to permit the NO₂ enriched stream to be sent to that point.

25

 25. The apparatus of claim 18 comprises an adsorption unit, a conduit for sending the fluid to the adsorption unit, a conduit for removing the NO₂ depleted gas from the adsorption unit, a conduit for sending a regeneration gas to

the adsorption unit and a conduit for removing the regeneration gas from the adsorption unit as the NO₂ enriched stream.

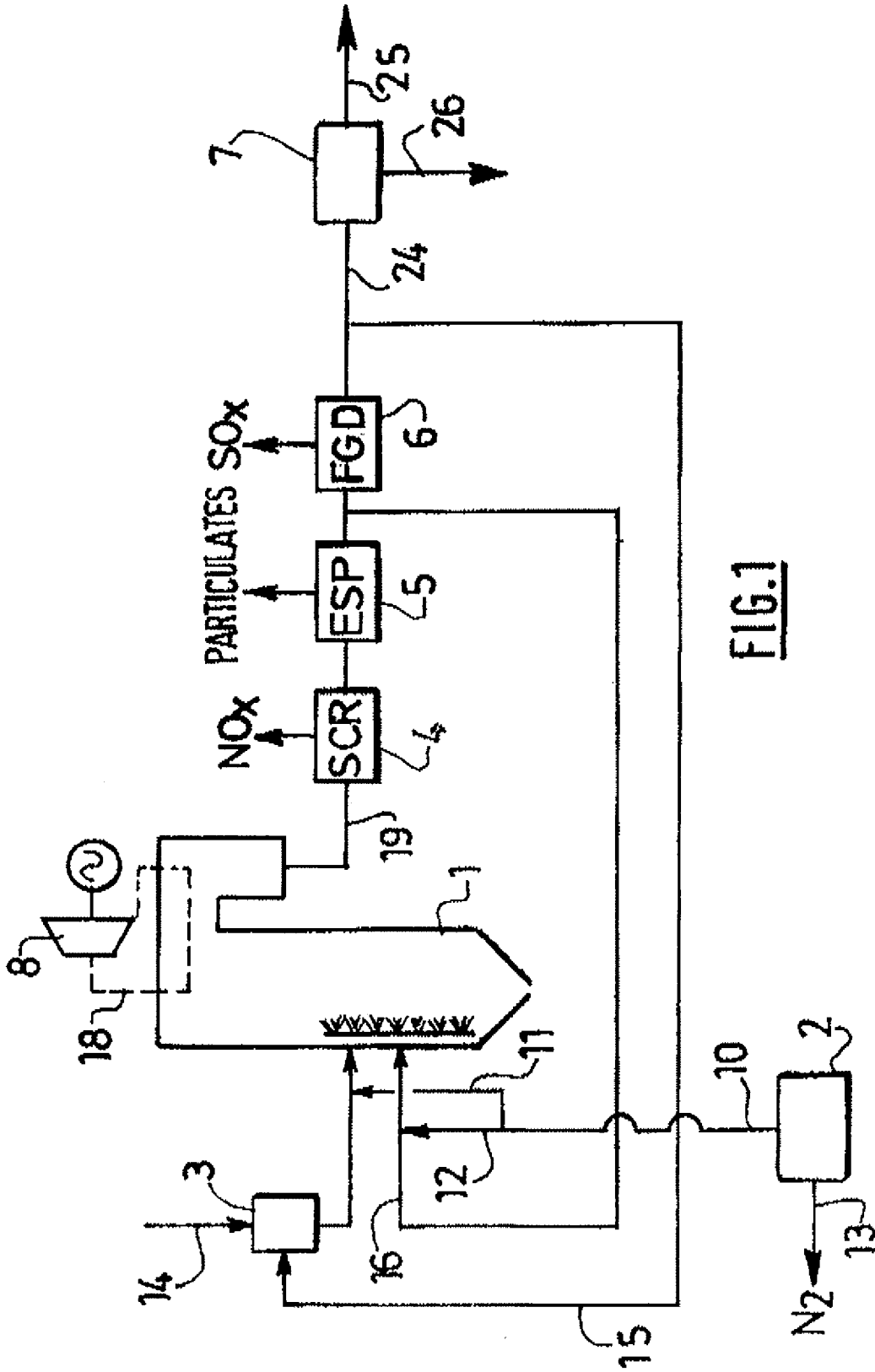
26. The apparatus of claim 18 comprising a unit producing the fluid and
5 wherein the conduit for recycling the NO₂ enriched stream is connected to the unit producing the fluid.

27. The apparatus of claim 26, wherein the unit producing the fluid is a
10 combustion zone of a boiler.

28. The apparatus of any of claims 18 to 25, wherein the NO₂ enriched
stream is recycled to a unit for treating the fluid.

29. The apparatus of claim 28, wherein the unit for treating the fluid is a
15 compressor upstream of separation unit and comprising a conduit for sending the fluid to the compressor and wherein the conduit for recycling the NO₂ enriched stream is connected upstream of the compressor.

30. The apparatus of claim 28, wherein the unit for treating the fluid is a
20 wash column.



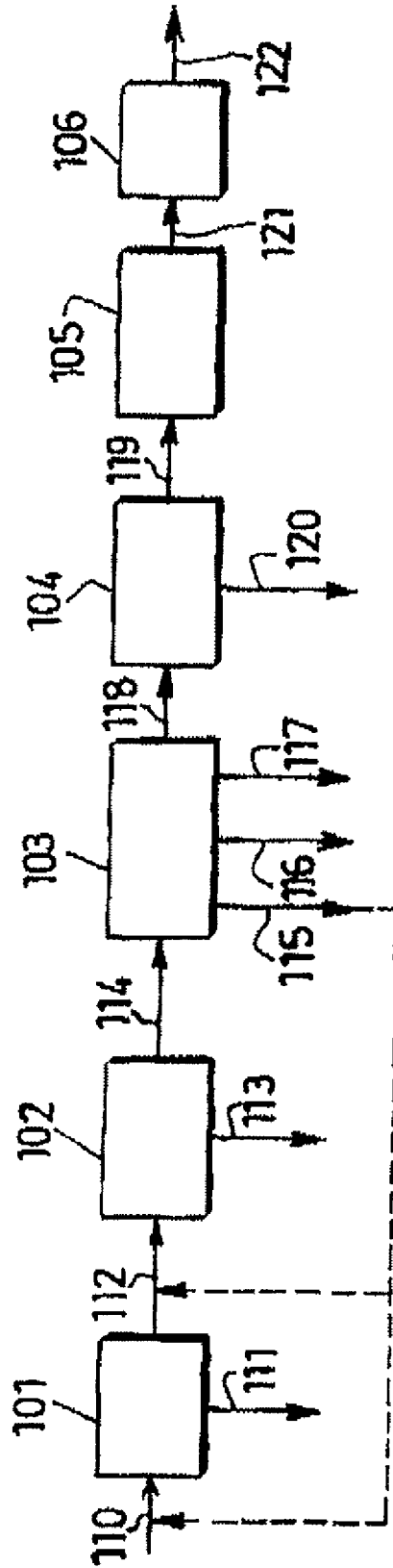


FIG. 2

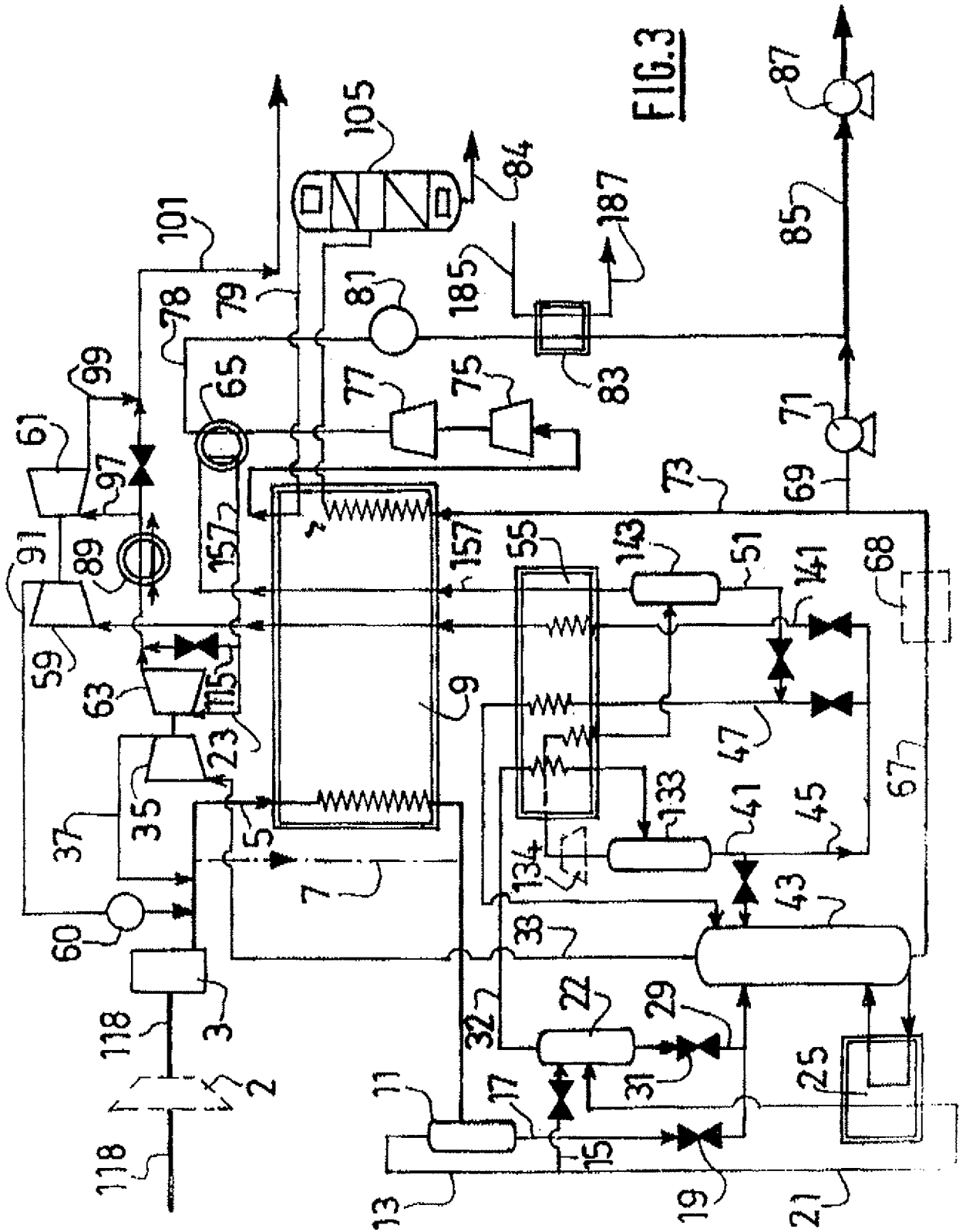


FIG. 3

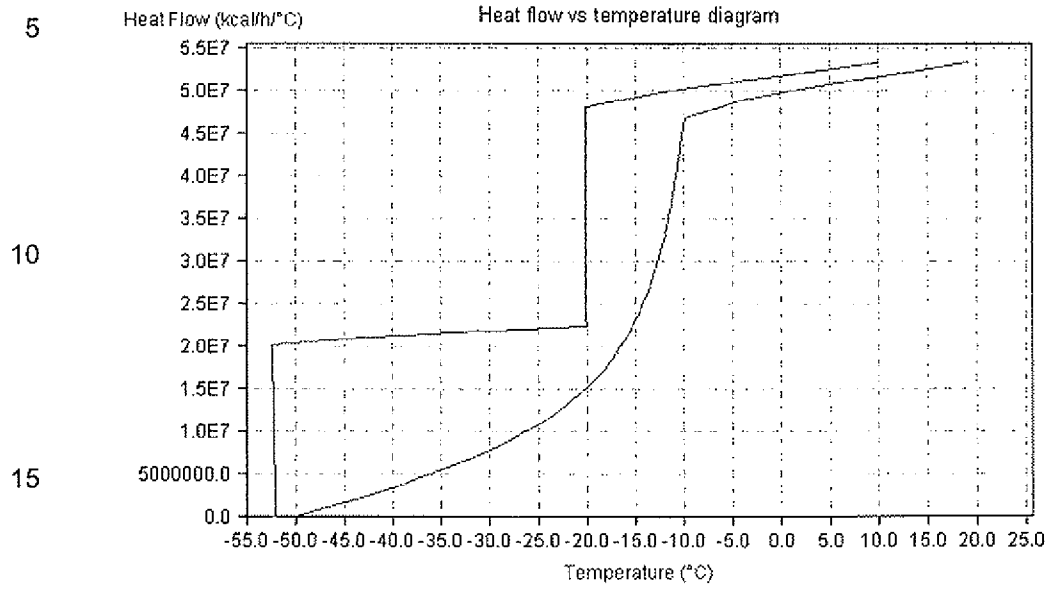


FIG. 4

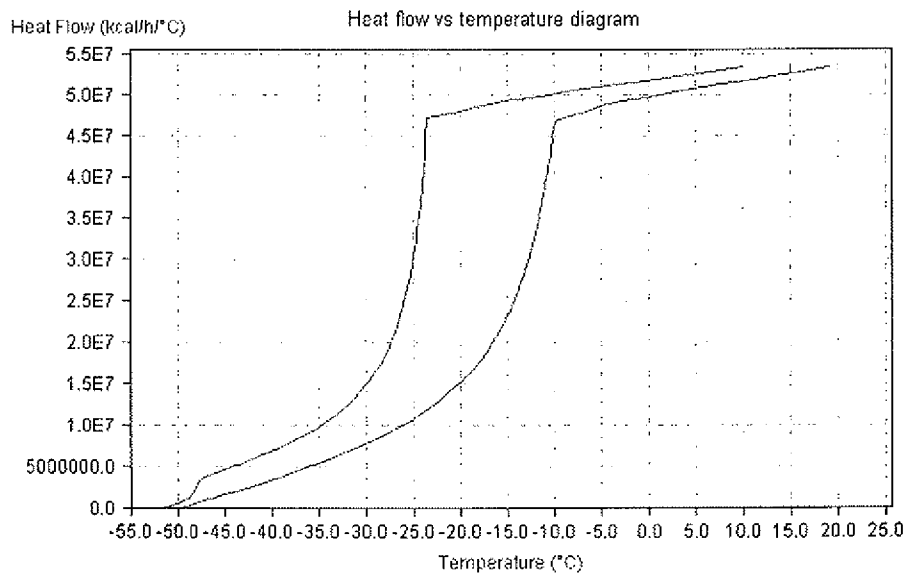


FIG. 5