PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : B01D 53/86

A1

(11) International Publication Number: WO 96/18453

(43) International Publication Date: 20 June 1996 (20.06.96)

(21) International Application Number: PCT/US95/15477

(22) International Filing Date: 1 December 1995 (01.12.95)

(30) Priority Data:
08/356,666 15 December 1994 (15.12.94) US

(71) Applicant: COMBUSTION ENGINEERING, INC. [US/US]; 1000 Prospect Hill Road, Windsor, CT 06095 (US).

(72) Inventors: GURVICH, Boris; 41 Clifford Drive, West Hartford, CT 06107 (US). PALKES, Mark; 57 Butler Drive, Glastonbury, CT 06033 (US). WESNOR, James, D.; 5557 Surrey Lane, Birmingham, AL 35242 (US).

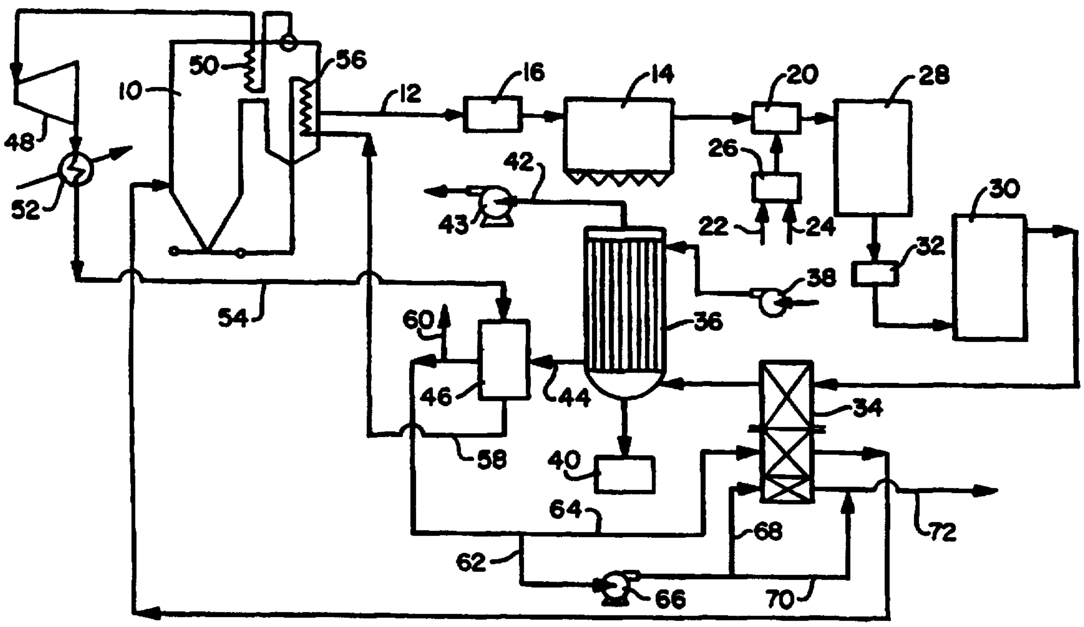
(74) Agents: FOURNIER, Arthur, E., Jr. et al.; Combustion Engineering, Inc., PPS Patent Services, 1000 Prospect Hill Road, Windsor, CT 06095 (US).

(81) Designated States: CZ, FI, HU, KZ, NO, PL, RO, RU, SI, SK, UA, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published

With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: AIR POLLUTION CONTROL AND HEAT RECOVERY SYSTEM



(57) Abstract

A coal fired power plant includes the catalytic reduction of NO_x in the flue gas and the catalytic oxidation of SO_2 to SO_3 followed by the hydration of the SO_3 to H_2SO_4 vapor and then the condensation to H_2SO_4 liquid. The condensation takes place in a wet sulfuric acid condenser (36) by heat exchange with incoming combustion air. A portion of the heat picked up by that combustion air is used to provide a portion of the heat for the condensate from the steam turbine (48). The combustion air is then fed to an air preheater (34) and to the steam generator (10) as primary and secondary combustion air.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria
AU	Australia
BB	Barbados
BE	Belgium
BF	Burkina Faso
BG	Bulgaria
BJ	Benin
BR	Brazil
BY	Belarus
CA	Canada
CF	Central African Republic
CG	Congo
CH	Switzerland
CI	Côte d'Ivoire
CM	Cameroon
CN	China
CS	Czechoslovakia
CZ	Czech Republic
DE	Germany
DK	Denmark
ES	Spain
FI	Finland
FR	France
GA	Gabon
GB	United Kingdom
GE	Georgia
GN	Guinea
GR	Greece
HU	Hungary
IE	Ireland
IT	Italy
JP	Japan
KE	Kenya
KG	Kyrgystan
KP	Democratic People's Republic of Korea
KR	Republic of Korea
KZ	Kazakhstan
LI	Liechtenstein
LK	Sri Lanka
LU	Luxembourg
LV	Latvia
MC	Monaco
MD	Republic of Moldova
MG	Madagascar
ML	Mali
MN	Mongolia
MR	Mauritania
MW	Malawi
NE	Niger
NL	Netherlands
NO	Norway
NZ	New Zealand
PL	Poland
PT	Portugal
RO	Romania
RU	Russian Federation
SD	Sudan
SE	Sweden
SI	Slovenia
SK	Slovakia
SN	Senegal
TD	Chad
TG	Togo
TJ	Tajikistan
TT	Trinidad and Tobago
UA	Ukraine
US	United States of America
UZ	Uzbekistan
VN	Viet Nam

Air Pollution Control And Heat Recovery System

The present invention relates to an air pollution control process and system for the removal of nitrogen and sulfur oxides from power plant flue gas streams and particularly to the heat exchange and heat recovery within the air pollution control process.

Background of Invention

The current global emphasis on environmental protection and pollution abatement has fostered the development of a number of new technologies and processes focused on pollution control in the power production industry. Some of these new technologies represent significant improvements over the previous technologies in the areas of increased pollutant removal efficiencies, reduced reagent requirements, reduced waste streams and reduced operating costs.

One such system is comprised of a selective catalytic reduction (SCR) for the control of nitrogen oxides (NO_x) and sulfuric acid production for sulfur oxide (SO_2) removal. This system results in high efficiency NO_x and SO_2 removal, minimal particulate emissions and no liquid or solid waste production. The system basically begins with some sort of particulate removal apparatus such as an electrostatic precipitator or appropriate filtering equipment. This is followed by a NO_x reduction system which involves the selective catalytic reduction of the NO_x to molecular nitrogen and water by reaction with ammonia (NH_3) and oxygen. Following the selective catalytic reduction of the NO_x, the process catalytically converts sulfur dioxide (SO_2) to sulfur trioxide (SO_3). The SO_3-containing flue gas stream is then cooled in a wet sulfuric acid condenser, by heat exchange with an air stream, to produce a concentrated sulfuric acid by-product stream. The cleaned flue gas is then ready for release to the atmosphere.

This process generates a considerable amount of recoverable heat in several ways. All of the reactions which take place with respect to NO_x and SO_2 removal are exothermic and increase the temperature of the flue gas. These include the reaction of NO_x and NH_3, SO_2 oxidation, SO_3 hydration to form sulfuric acid fume and condensation of the sulfuric acid. These heats of reaction plus any support heat which may have been added are recovered in the wet sulfuric acid condenser by cooling air. This heated air stream has typically been used for combustion air. A small percentage of the hot air has been used for system auxiliaries, such as ammonia evaporation and dilution, any support burner combustion air required and coal milling. However, the amount of air that is required for cooling in the wet sulfuric acid condenser is usually equal to or greater than the amount required for combustion and auxiliary purposes and/or is often at a higher temperature than desired for either the combustion air preheater or the primary air to the coal pulverizers.

Summary of the Invention

The objective of the present invention is to provide a system and process for more effectively utilizing the available heat within an air pollution control system for a coal fired power plant. More particularly, the invention relates to a system and process wherein the flue gas SO_2 is converted to SO_3 and then hydrated and condensed to sulfuric acid by heat exchange with cooling air. A portion of the heat picked up by that cooling air is used to provide heat to the condensate from the steam turbine system as a part of the feedwater train and the cooling air is then fed to the air preheater as the combustion air for the coal fired steam generator.

Brief Description of the Drawings

Figure 1 is a flow diagram of one embodiment of the present invention wherein the NO_x reactor precedes the combustion air preheater.

Figure 2 is a flow diagram of another embodiment wherein the NO_x reactor follows the combustion air preheater.

Description of the Preferred Embodiment

The present invention applies to an air pollution control system which includes the catalytic reduction of NO_x and the catalytic oxidation of SO_2 to SO_3 followed by the hydration of the SO_3 to H_2SO_4. It then involves the condensation of the H_2SO_4 by cooling with air to produce concentrated sulfuric acid and a heated air stream. The process flow details of this system can be varied within the confines of the present invention and two such variations are shown in Figures 1 and 2 of the drawings.

Figure 1 relates to the system variation wherein the hot flue gas from the steam generator is processed in the NO_x and SO_2 reactors before going to the combustion air preheater, while Figure 2 illustrates a process variation wherein the hot flue gas is first cooled in the conventional combustion air preheater.

In the scheme shown in Figure 1, the coal fired steam generator 10 generates a flue gas containing some quantity of NO_x and SO_x, as well as particulate material. Most of the NO_x is in the form of NO with only a small amount of NO_2. The SO_x is mostly in the form of SO_2 with only small quantities of SO_3. This flue gas is passed through duct 12 to the particulate collection device 14 which may be any desired device for the conditions such as an electrostatic precipitator, a high temperature bag filter or any other suitable filter. During start-up of the system, it is usually necessary to provide auxiliary heat to the flue gas at 16.

The flue gas with the particulates removed is fed to the ammonia/flue gas mixing unit 20. The ammonia and air necessary for the catalytic reduction of NO_x are fed at 22 and 24 respectively into the ammonia/air mixing unit 26 and then the ammonia/air mixture is fed to the mixing unit 20. The amounts of ammonia and air (O_2) that are added are determined by the reaction:

$$NO + NH_3 + 0.25O_2 \rightleftharpoons N_2 + 1.5H_2O$$

Any small amounts of NO_2 are similarly reduced. In prior art selective catalytic reduction systems, the molar ratio of NH_3 to NO_x was limited to 1.0. This was necessary to limit unreacted NH_3 which might result in ammonium sulfate and bisulfate scaling in lower temperature areas downstream. However, in the present invention with the SO_2 oxidizer, small quantities of unreacted NH_3 are permissible since it is also oxidized. This allows stoichiometric ratios in excess of 1.0 and consequently higher NO_x removal efficiencies. The ammonium salting will not occur between the NO_x reactor and SO_2 reactor because the temperature is above the dew point. Even so, the excess NH_3 must be controlled and minimized since the oxidation of the excess NH_3 produces NO_x.

The ammonia/flue gas mixture from the mixing unit 20 in the temperature range of 340 to 400°C and preferably at 370°C (700°F), is then fed into the selective catalytic reactor 28 containing the NO_x reduction catalyst in which the above reaction is carried out. Preferably, this catalyst is a monolithic titanium dioxide based catalyst such as the Haldor Topsoe DNX catalyst. The NO_x reduction process produces about 13.7 MJ/kg NO (5,880 BTU/lb. NO) of heat.

From the selective catalytic reactor 28, the flue gas goes to the SO_2 reactor 30. The flue gas temperature to this reactor is in the range of 370 to 430°C and preferably 410°C (770°F). Therefore, it may be necessary to add heat to the flue gas at 32 such as by a natural gas trim burner. In this reactor 30, a conventional sulfuric acid catalyst oxidizes the SO_2 to SO_3 according to the reaction:

$$SO_2 + 0.5\ O_2 \rightleftharpoons SO_3$$

This reaction produces about 1.5 MJ/kg SO_2 (660 BTU/lb. SO_2) of heat. As previously indicated, the sulfuric acid catalyst oxidizes any excess NH_3 and also oxidizes most of the CO and remaining hydrocarbons present in the flue gas stream.

The flue gas leaving the SO_2 reactor 30 is at a temperature of about 370 to 430°C and is next passed to the hot side of the gas-to-air heat exchanger 34 where heat is transferred to the incoming combustion air. The flue gas temperature is dropped about 170°C (300°F) to the range of 260 to 290°C and the SO_3 is hydrated to sulfuric acid vapor with the attendant release of about 1.6 MJ/kg SO_3 (688 BTU/lb. SO_2). The cold end of the heat transfer surface in the heat exchanger 34 may need to be protected against corrosion due to presence of the sulfuric acid vapor. From the heat exchanger 34, the flue gas containing the sulfuric acid vapor is fed to the wet sulfuric acid tower 36 which uses ambient air supplied by the forced draft fan 38 as the cooling medium. As an example, this tower is preferably a tube and shell falling film condenser with the cooling air on the shell side and with borosilicate glass tubes used to convey and cool the flue gas to about 100°C (212°F) at the outlet. Virtually complete condensation and capture of the sulfuric acid at concentrations of 94 to 97 wt. % is possible. This condensation is also exothermic and releases about 1.1 MJ/kg SO_2 (460 BTU/lb. SO_2). The condensed sulfuric acid product is funneled through a trough at the bottom to the acid storage tank 40. The cleaned flue gas is discharged at 42 to the atmosphere through the induced draft fan 43.

The wet sulfuric acid condenser has, in effect, collected the heat released from the reactions in the selective catalytic reactor 28, the SO2 converter 30, the hydration of SO_3, the condensation of H_2SO_4, the trim burner 32, the booster fan compression and the overall decrease in flue gas temperature.

The heated air 44 from the wet sulfuric acid condenser 36 is at about 200°C (400°F). The quantity of air required for the wet sulfuric acid tower may be greater than that required for combustion air and/or may be at a temperature higher than needed. In order to achieve the optimum heat recovery within the entire system encompassed by the coal fired power plant, this air should be cooled before it is passed to the boiler air preheater as combustion air. In the present invention, the hot air from the wet sulfuric acid condenser 36 is passed to condensate heat exchanger 46 which is any suitable type of gas-to-liquid heat exchanger.

In a conventional power plant, the condensate from the plant's low pressure turbine is passed through a series of condensate heaters which reheat the condensate from the low pressure turbine which is then passed back to the boiler's economizer. In Figure 1, this is shown for illustration purposes by only a single turbine 48 connected to the superheater 50 of the steam generator. The condensate from the turbine 48 goes to the condensate heater 52 and then through line 54 to the condensate heat exchanger 46 of the present invention. The condensate heat exchanger 46 of the present invention, depending on the steam turbine heat balance, would be installed in parallel or in series with a plurality of these conventional condensate heaters 52. The reheated condensate is passed back to the economizer 56 in line 58. The condensate heat exchanger of the present invention replaces the heat duty of probably one or more of the conventional coal fired power plant's condensate heaters. Since those conventional condensate heaters normally used the turbine extraction steam for the heat source, the steam turbine is now capable of producing an additional power source, and this extraction steam is no longer needed. The air, upon exiting the air-to-condensate heat exchanger 46, proceeds to the heat exchanger 34 where heat is transferred from the flue gas to the combustion air. This heat exchanger 34 may be of any desired type, such as a tubular or rotary regenerative air preheater, or a no-leakage heat pipe heat exchanger. In a conventional power plant, the combustion air is preheated only in the flue gas-to-air heat exchanger. The air preheating duty in the present invention is first partially accomplished in the condenser 36, and then completed in the heat exchanger 34. As a result, the heat exchanger 34 is smaller then it would be for the conventional power plant. The combustion air from the heat exchanger 46 is split into primary combustion air 62 and secondary combustion air 64. The primary combustion air 62 passes through the primary air booster fan 66 passing through a section of the heat exchanger 34 and another portion 70 by-passing the heat exchanger 34 as tempering air to control the temperature of the air 72 which is fed to the coal pulverizer. The other portion of the combustion 64 is heated in the air preheater 34 and fed to the boiler as secondary combustion air. Also, if there is any excess air needed for the wet sulfuric acid condenser 36 above that needed for combustion air, the excess air can be used for firing natural gas in the trim burner 32, and/or in other heat recovery applications, or merely be vented at 60.

Figure 2 of the drawings shows the present invention as applied when the flue gas from the boiler is first cooled in the combustion air preheater which is now designated 134. The cooled flue gas from the air preheater goes to the same type of start-up burner 16 and electrostatic precipitator 14 or other particulate removal system. Since the flue gas is at a significantly lower temperature at this point than in the version of the invention shown in Figure 1, it is possible to use lower temperature particulate removal equipment such as bag house filters. From the precipitator, the flue gas goes to a gas-to-gas heat exchanger 136. Since the flue gas has been cooled in the air preheater

134, it is necessary to reheat this flue gas up to the temperature necessary for the selective catalytic reduction, 340 to 400°C, which is done in the gas-to-gas heat exchanger 136. From that point, the flue gas follows the same process steps as in Figure 1 through the ammonia/flue gas mixing unit 20, the selective catalytic reactor 28, the trim heater 32 and the SO_2 reactor 30. The treated flue gas then goes to the gas-to-gas heat exchanger 136 where heat is transferred from the exiting flue gas to the entering flue gas. The flue gas temperature is dropped to the range of 260 to 290°C and the SO_3 is hydrated to sulfuric acid vapor just as in the heat exchanger 34 in Figure 1. The flue gas containing the sulfuric acid vapor then goes to the wet sulfuric acid condenser 36 which is operated in the same manner as in the Figure 1 embodiment to condense the sulfuric acid and produce heated combustion air.

The heated combustion air 44 from the wet sulfuric acid condenser 36 now goes to the condensate heat exchanger 46 which also operates just as in the Figure 1 embodiment. The combustion air from the condensate heat exchanger proceeds to the combustion air preheater 134 where heat is transferred from the flue gas to the combustion air. Once again, if there is any excess air needed for the wet sulfuric acid condenser 36 above that needed for combustion air, the excess air can be used for firing natural gas in the trim burner 32, and/or in other heat recovery applications, or merely be vented at 60. Also, the combustion air is split between primary and secondary combustion air and a portion of the primary air can by-pass the air preheater as tempering air for the coal pulverizers.

We Claim:

1. In an air pollution control system for the flue gas from a coal fired power plant, wherein said power plant includes a steam generator, a source of condensed steam from said steam generator and means for feeding condensed steam back to said steam generator, said air pollution control system including means for catalytically reducing NO_x in said flue gas to N_2 and H_2O, means for oxidizing SO_2 in said flue gas to SO_3, means for hydrating said SO_3 to H_2SO_4 vapor in said flue gas and condenser means for condensing said H_2SO_4 vapor from said flue gas to liquid H_2SO_4, said condenser means consisting of an air cooled heat exchanger and means for conducting a source of combustion air through said air cooled heat exchanger whereby heat is transferred from said flue gas to said combustion air and H_2SO_4 vapor is condensed; the improvement comprising condensate heat exchange means, means for passing said condensed steam and said heated combustion air from said condenser means in heat exchange contact in said condensate heat exchange means whereby said condensed steam is heated and said heated combustion air is cooled, and means for further heating said combustion air from said condensate heat exchanger and means for feeding said further heated combustion air to said steam generator as combustion air.

2. An air pollution control system as recited in claim 1, wherein said source of condensed steam is a steam turbine and said means for further heating said combustion air comprises an air preheater for transferring heat from said flue gas to said combustion air.

3. An air pollution control system as recited in claim 2, wherein said air preheater comprises a rotary regenerative air preheater.

4. A coal fired power plant system comprising:

a steam generator for producing steam and flue gas containing NO_x and SO_2;

a steam turbine;

means for feeding said steam through said steam turbine thereby producing condensed steam;

a selective catalytic reduction reactor and means for feeding said flue gas from said steam generator to said selective catalytic reactor wherein said NO_x in said flue gas is reduced to N_2 and H_2O;

means for oxidizing SO_2 in said flue gas to SO_3;

means for hydrating said SO_3 to H_2SO_4 vapor;

means for condensing said H_2SO_4 vapor from said flue gas to form liquid H_2SO_4 consisting of means for transferring heat from said flue gas to a combustion air stream and condensing said H_2SO_4 vapor;

condensate heat exchange means for feeding said condensed steam and said combustion air stream from said means for condensing said H_2SO_4 vapor to said condensate heat exchange means for transfer of heat from said combustion air stream to said condensed steam;

means for further heating said combustion air stream from said condensate heat exchanger comprising means for transferring heat from said flue gas to said combustion air stream; and

means for feeding said combustion air from said means for further heating to said steam generator as combustion air.

5. A process for removing NO_x and sulfur oxides from the flue gas stream from a coal fired steam generator and for heating condensed steam from said steam generator comprising the steps of:

a. catalytically reducing said NO_x with a reductant to produce N_2 and H_2O;

b. oxidizing SO_2 in said flue gas to SO_3;

c. hydrating said SO_3 in said flue gas to H_2SO_4 vapor;

d. passing said flue gas containing said H_2SO_4 vapor into heat exchange contact with a combustion air stream whereby said H_2SO_4 vapor is condensed and said combustion air stream is heated;

e. passing said heated combustion air stream into heat exchange contact with said condensed steam whereby said condensed steam is heated and said combustion air stream is cooled;

f. passing said cooled combustion air stream into heat exchange contact with said flue gas stream whereby said combustion air stream is further heated and said flue gas stream is cooled;

g. passing said heated condensed steam back to said steam generator; and

h. passing said further heated combustion air stream to said steam generator as combustion air.

6. A process as recited in claim 5, wherein said step (f) of passing said cooled combustion air stream into heat exchange contact with said flue gas stream comprises heat exchange contact with said flue gas stream prior to said catalytic reduction of NO_x and further including reheating said flue gas stream prior to said catalytic reduction of NO_x by

heat exchange contact with said flue gas stream after SO_2 oxidation and prior to H_2SO_4 vapor condensation.

7. A process as recited in claim 5, wherein said step (f) of passing said cooled combustion air stream into heat exchange contact with said flue gas stream comprises heat exchange contact with said flue gas stream after said SO_2 oxidation and prior to said H_2SO_4 vapor condensation.

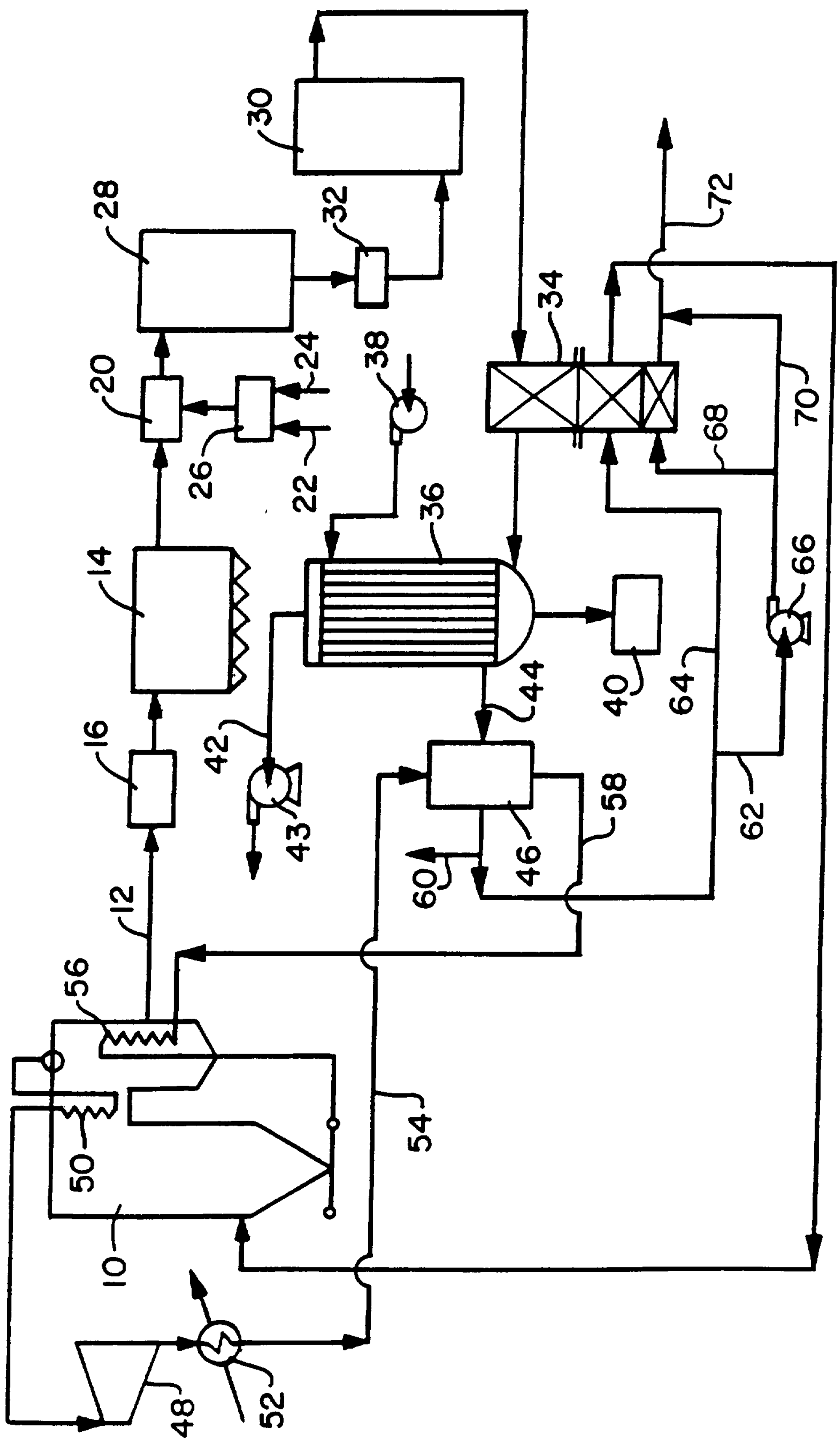

10
12
14
16
20
22
24
26
28
30
32
34
36
38
40
42
43
44
46
48
50
52
54
56
58
60
62
64
66
68
70
72

Fig. 1

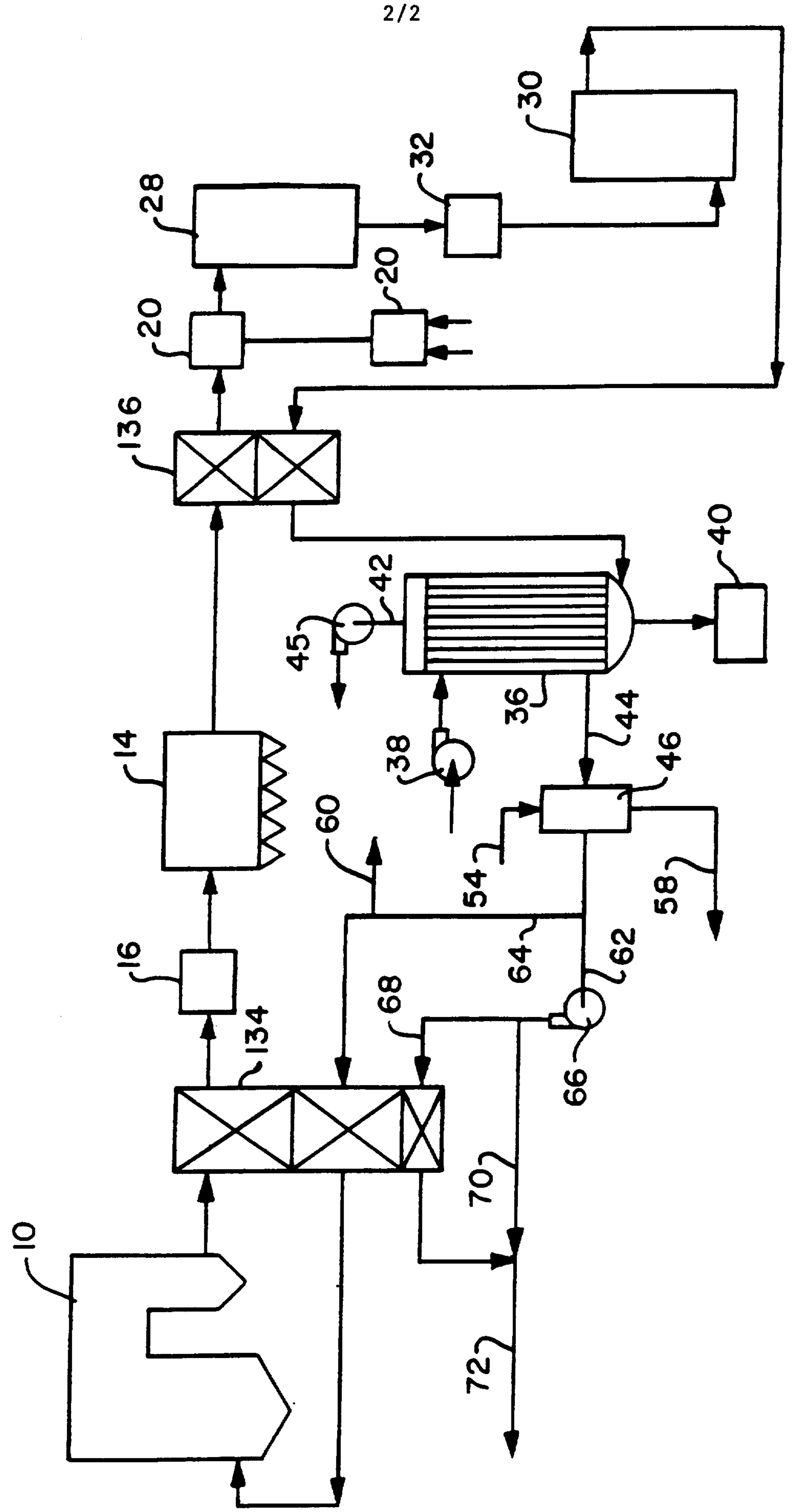

10
134
16
14
136
20
20
28
32
30
40
42
45
36
38
44
46
54
58
60
64
62
66
68
70
72

Fig. 2

INTERNATIONAL SEARCH REPORT

Inte   onal Application No
PCT/US 95/15477

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B01D53/86

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 622 106 (DEGUSSA) 2 November 1994 ---	
A	EP,A,0 254 362 (METALLGESELLSCHAFT) 27 January 1988 -----	

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
"&" document member of the same patent family

1

Date of the actual completion of the international search	Date of mailing of the international search report
29 March 1996	17-04-1996

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Bogaerts, M

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 95/15477

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-622106	02-11-94	DE-C- 4313897	02-03-95
		CA-A- 2122321	29-10-94
		JP-A- 6319955	22-11-94
EP-A-254362	27-01-88	DE-A- 3624462	28-01-88
		JP-A- 63039614	20-02-88
		US-A- 4842835	27-06-89