

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property

Organization

International Bureau

(43) International Publication Date

02 March 2023 (02.03.2023)



(10) International Publication Number

WO 2023/025868 A1

(51) International Patent Classification:

C01B 21/26 (2006.01) C01B 21/28 (2006.01)

B01D 53/56 (2006.01) C01B 21/38 (2006.01)

TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

(21) International Application Number:

PCT/EP2022/073638

Declarations under Rule 4.17:

— of inventorship (Rule 4.17(iv))

(22) International Filing Date:

25 August 2022 (25.08.2022)

Published:

— with international search report (Art. 21(3))

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

21193029.2 25 August 2021 (25.08.2021) EP

22150904.5 11 January 2022 (11.01.2022) EP

(71) Applicant: YARA INTERNATIONAL ASA [NO/NO];

Drammensveien 131, 0277 Oslo (NO).

(72) Inventors: VIGELAND, Bent; Nordheimvegen 63, 3714

Skien (NO). ØIEN, Halvor; Hvalenvegen 58, 3943 Pors-

grunn (NO). FAUCONNIER, Peter; Brusselsesteenweg

127, 1850 Grimbergen (BE). DE SMET, Andre; Volkerak

7, 4535 JH Terneuzen (NL).

(74) Agent: DE CLERCQ & PARTNERS; Edgard Gevaert-

dreef 10a, 9830 Sint-Martens-Latem (BE).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM,

AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ,

CA, CH, CL, CN, CO, CR, CU, CV, CZ, DE, DJ, DK, DM,

DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT,

HN, HR, HU, ID, IL, IN, IQ, IR, IS, IT, JM, JO, JP, KE,

KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU,

LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA,

NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO,

RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH,

TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS,

ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH,

GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ,

UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ,

TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK,

EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV,

MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM,

(54) Title: DUAL PRESSURE SYSTEM FOR PRODUCING NITRIC ACID AND METHOD OF OPERATING THEREOF

(57) Abstract: The present disclosure discloses a system for producing nitric acid at reduced power, the system being a standard dual pressure nitric acid plant characterised in that the system further comprises means for splitting a tail gas stream into a first tail gas stream, in fluid communication with an oxygen-rich gas upstream the ammonia mixing unit, and a second tail gas stream, and means for adjusting the amount of tail gas being split into the first tail gas stream and the second tail gas stream, such that an air compressor is not required for operating the nitric acid plant. The present disclosure further relates to a method for operating the system, to the use of the system of the disclosure for performing the method of the disclosure and to a method for revamping a standard dual pressure nitric acid plant into the system of the disclosure.



WO 2023/025868 A1

Dual pressure system for producing nitric acid and method of operating thereof

Field

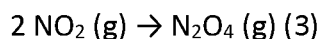
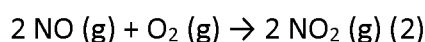
5 The present disclosure relates to the field of nitric acid production in a dual pressure plant.

Introduction

10 Pure nitric acid is a clear, colorless liquid with a strong odor. Nitric acid is produced in large quantities principally by catalytic oxidation of ammonia (Ostwald process). Ammonia is converted to nitric acid in several stages. The ammonia is first oxidized in an ammonia burner on platinum gauzes (commonly called ammonia converter) or cobalt balls, producing nitric oxide (in this disclosure also called nitrogen monoxide (NO)) and water:

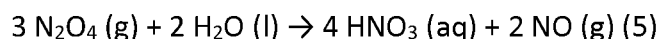
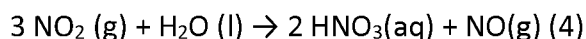


15 The reaction product from (1), nitric oxide, following cooling, is then oxidized to nitrogen dioxide (NO₂) and further to dinitrogen tetroxide N₂O₄ (g) in an oxidation section:



20 Cooling of nitrogen oxide gases is accomplished first through the use of a waste heat recovery system recovering the heat from the conversion of ammonia into nitric oxide, then through the use of a cooler condenser in which condensed nitric acid is separated from nitric oxide, nitrogen dioxide and dinitrogen tetroxide and nitric acid gases, collectively called NO_x gases, and finally by heating the tail gas released at the outlet of the absorption tower in which the NO_x gases are absorbed.

25 By absorption in water, following compression through a NO_x gas compressor, nitrogen dioxide and dinitrogen tetroxide are converted to nitric acid and nitric oxide:



Weak nitric acid which is up to 68 % (azeotrope) is obtained. Through a rectification process the concentration of nitric acid can be increased up to 99 % concentrated nitric acid.
30 The total reaction is given by the following formula:



The main process units in a nitric acid production plant, include an ammonia converter (conversion of ammonia into nitric oxides using oxygen over a suitable catalyst), an oxidation section (conversion of nitric oxide into nitrogen dioxide and nitrogen tetroxide), an absorber unit (for the absorption of NO_x gases into water) and a bleacher unit (removal of unreacted dissolved gases, containing in particular NO_x and gases, from the aqueous nitric acid solution, which give it its typical brownish color).

The process for the production of nitric acid can be differentiated into a mono pressure (single-pressure) and dual pressure (split-pressure) process.

In a dual pressure process, the absorber unit operates at a higher working pressure than the ammonia converter. Modern dual pressure processes feature a low-pressure ammonia converter operating typically at 2 to 6 bara, and a high-pressure absorber unit operating at 9 to 16 bara.

A dual pressure process requires an air compressor to feed low-pressure air (which comprises about 21 vol% of oxygen) to the converter, and a NO_x gas compressor to feed high-pressure NO_x gases to the absorber unit. The working pressure of an air compressor is from 2 to 6 bara, inclusive, and the working pressure of a NO_x gas compressor is from 9 to 16 bara, inclusive.

The drive power for the air compressor typically originates from a tail gas turbine and a steam turbine or a power source such as an electric motor. Accordingly, the compressor train of a dual pressure nitric acid production plant typically comprises an air compressor, a NO_x gas compressor, a tail gas turbine, and a steam turbine or a power source such as an electric motor.

More in detail, referring to Figure 1, a dual pressure plant and process according to the prior art works as follows. Gaseous ammonia **32**, optionally pre-heated in a pre-heater unit (not shown) is mixed with compressed air **34** pressurised to a low pressure using an air compressor **36**, in a mixing apparatus **35**, and the resulting ammonia/oxygen-enriched air mixture **14** is fed to an ammonia converter **37**, operating at a low pressure, where ammonia is oxidized over a suitable catalyst, thus obtaining a LP NO_x gas/steam mixture **15**, comprising water and nitric oxide (NO). The heat of the mixture coming out of the ammonia converter is recovered, after which the NO_x gas/stream mixture is subsequently cooled down in a gas cooler/condenser **38** to temperature where the water condenses, and an aqueous diluted

nitric acid mixture **17** is separated from a gaseous NO_x stream **22**. The gaseous NO_x stream **22** is sent to a NO_x gas compressor **40** wherein its pressure is elevated from a low pressure to a high pressure, being about equal to an absorber unit, **41**, operating pressure, and the pressurized gaseous NO_x stream **24** is sent to the absorber to the absorber unit **41**, commonly called absorption tower. The pressurised NO_x gas stream **24** is further oxidized to further convert the NO to NO₂ and N₂O₄, cooled in an additional gas cooler/condenser **39** and then directed to the absorption tower **41** too. Inside the absorption tower **41**, the pressurized NO_x gas stream **24** reacts with water to produce the tail gas **5** and a stream of raw nitric acid **27** also containing residual NO_x gas, which is fed to a bleacher **62**. The residual NO_x gas in the raw nitric acid stream **27** is then stripped out with a gaseous medium **72** such as an oxygen-containing gas or air, inside the bleacher unit **62** operating at low-pressure; the bleacher unit is generally operated at about the same pressure as the ammonia converter. The drive power for both the air compressor **36** and the NO_x gas compressor **40** originates from a tail gas expander **7** and a steam turbine **51** or a power source such as an electric motor (not shown). The heat generated in the ammonia converter **37** is used for heating the tail gas **5** in the tail gas heat exchanger **43** comprising the heat exchangers **66** and **67**, the tail gas heater being therefore optionally present. The tail gas **5** exchanges heat with the NO_x gas/steam mixture **15** in the heat exchange system **43** and is expanded in the tail gas expander **7**.

The air used for the oxidation of ammonia is commonly denoted as primary air; the air used as stripping medium in the bleacher unit is commonly denoted as secondary air.

According to the prior art, the revamping of the nitric acid production plants to increase its capacity is commonly based on increasing the amount of primary air to the reactor, which leads to a proportional increase of the amount of nitric acid produced.

The increase of the amount of primary air in the reactor entails the installation of a new air compressor or the revamping of the existing one. The increase of the primary air also causes a higher amount of gas to be processed subsequently into the NO_x gas compressor. This entails the further revamping of the NO_x gas compressor or the installation of a new one, and the modification or replacement of the tail gas and/or the steam-turbines and/or the electrical motor. Otherwise, the NO_x gas compressor would easily achieve its process limit, thus becoming the bottleneck of the plant.

However, the revamping has significant drawbacks. First of all, it entails elevated costs for the modification or replacement of the existing equipment, i.e. the air compressor, the NO_x gas compressor and the corresponding turbines and electrical motor. In addition, the revamping of the equipment is also technically demanding leading to long plant downtime.

5 Another problem related to nitric acid production plants is the high amount of energy required in order to operate the air compressor. Consequently, a high amount of energy is required to achieve the targeted nitric acid production throughput.

A goal of the present invention, therefore, is to provide a system and a method for operating the system which allows for the reduction or even suppression of power required
10 to operate the air compressor in a dual nitric acid plant.

Background Prior Art

In CN110540178A (China Chengda Engineering Co Ltd, 2019), process for producing nitric acid is disclosed. Nitric acid is produced by a medium pressure method, which is
15 characterized in that it comprises the following steps: the ammonia oxidation and absorption pressure is 0.5-0.6 MPa; enabling the tail gas leaving the absorption tower to pass through a carbon molecular sieve Temperature Swing Adsorption (TSA) treatment device to reduce the content of nitrogen oxides in the tail gas to be less than 100mg/Nm³; the process air of the air compressor is used as the regeneration desorption gas of the carbon molecular sieve
20 temperature swing adsorption treatment device, and the regeneration desorption gas containing the nitrogen oxide can be returned to the ammonia oxidation reactor for reuse; adding a layer of N₂O decomposition catalyst in the oxidation reactor to reduce the content of N₂O to 50-100 PPM through reaction; the nitric acid bleaching tower is arranged at the bottom of the absorption tower, and the two towers are integrated, so that the process flow
25 is shortened, and the equipment investment is reduced. With regard to the amount of air being compressed by the air compressor, however, the same amount of air is to be compressed as would be in the absence of the TSA unit: in the presence of the TSA unit, the amount of air being compressed is initially split between the TSA unit and the ammonia oxidation reactor directly and, in the end, with the amount of compressed air leaving the TSA
30 unit being directed also to the ammonia oxidation reactor, the total amount of air compressed by the air compressor ends up in the ammonia oxidation reactor.

In WO2018/162150A1 (Casale SA, 13 September 2018) a solution is proposed to overcome the revamping drawbacks. WO2018162150A1 discloses a dual pressure plant for the production of nitric acid comprising a reactor providing a gaseous effluent containing nitrogen oxides, an absorber unit in which nitrogen oxides react with water providing raw nitric acid and, the absorber unit operating at a pressure greater than the pressure of the reactor, a compressor elevating the pressure of the reactor effluent to the absorber unit pressure, the plant also comprising a first HP bleacher unit and a second LP bleacher unit, the first HP bleacher unit stripping with air the NO_x gas from the output stream of the absorber unit, thus providing a partially stripped nitric acid stream and a nitrogen oxides-loaded air stream, the former being fed to the second LP-bleacher unit and the latter being recycled to the oxidation section, upstream of the NO_x gas compressor.

A further air compressor is also provided, which supplies the first HP bleacher unit with air. Hence, energy is required in order to operate a first HP bleacher unit at a high-pressure and then recycle NO_x gases to the delivery side of the NO_x gas compressor.

Therefore, there remains a need for a process and a corresponding plant setup for minimizing or even suppressing the amount of energy required in order to operate the NO_x gas compressor and, preferably, also the air compressor, in order to avoid bottle-necks in the nitric acid production throughput associated with those compressors.

Summary

In one aspect of the disclosure, a production plant for producing nitric acid at reduced power consumption and reduced emissions, comprising, optionally, a source of pressurised air in fluid communication with the production plant, is disclosed. The system comprises:

- a source of an oxygen-rich gas, particularly a source of pressurized oxygen-rich gas, such as a high pressure water electrolyzer;
- a mixing apparatus downstream the source of oxygen-rich gas, for mixing a first oxygen-containing gas with an ammonia gas stream, to produce an ammonia/oxygen-containing gas mixture;
- an ammonia converter, particularly operable at a pressure equal to or higher than P1 and lower than P2, for oxidising ammonia in the ammonia/oxygen-containing gas mixture, to produce a NO_x gas/steam mixture comprising water and nitric oxide;

- a means for regulating the concentration of ammonia and/or of oxygen in the ammonia converter, particularly a means for controlling the flow of the oxygen-rich gas and/or a means for controlling the flow of the ammonia gas stream, for maintaining the oxygen to ammonia molar ratio inside the ammonia converter at a ratio of at least 1.2;
- a first gas cooler/condenser downstream the ammonia converter, to produce an aqueous diluted nitric acid mixture and a gaseous NO_x stream;
- a NO_x gas compressor for compressing the gaseous NO_x stream, to produce a compressed NO_x gas stream at a pressure P₂;
- an absorption tower for absorbing the NO_x gases from the compressed NO_x gas stream in water, to produce a stream of raw nitric acid containing residual NO_x gas, and a tail gas comprising NO_x gases, comprising an absorption tower tail gas outlet for evacuating the tail gas;
- a heat exchange system located upstream the gas cooler/condenser for exchanging heat between the NO_x gas/steam mixture and the tail gas, in particular for heating a tail gas stream with the heat from the NO_x gas/steam coming from the ammonia converter;
- a second gas cooler/condenser for separating and condensing steam from the compressed NO_x gas stream, particularly before the compressed NO_x gas stream is provided to the absorption tower.
- a supply for a second oxygen-containing gas having either (i) a pressure equal to or higher than P₁ and up to P_c, for supplying oxygen downstream the ammonia converter and upstream the NO_x gas compressor, or (ii) a pressure higher than P₂, for supplying oxygen to the compressed NO_x gas stream,
- a means for controlling the flow of the second oxygen-containing gas, such that a tail gas stream contains at least 0.5% by volume oxygen; and
- a first pressure release means, in particular tail gas expander, located downstream the heat exchange system, for expanding a stream of tail gas downstream the absorption tower, to produce a first expanded tail gas at a pressure equal to or higher than P₁ and lower than P₂, wherein the first pressure release means, in particular the tail gas expander, can at least partly power the NO_x gas compressor;

characterised in that the production plant further comprises:

- a means for splitting a tail gas into a first tail gas stream and a second tail gas stream, wherein the first tail gas is in fluid communication with the oxygen-rich gas, particularly wherein the first tail gas stream has a pressure equal to or higher than P1 and up to P2, and wherein the mixing of the oxygen-rich gas and the first tail gas stream provides the first oxygen-containing gas.

The inventors have found that, instead of continuously supplying compressed air provided by an air compressor as primary air to the mixing unit, it is possible to recirculate the first tail gas stream provided by the means for splitting at a pressure P1, particularly when combined with, at the same time, providing oxygen, particularly pressurized oxygen, to the system. Therefore, compressed or pressurized air only has to be supplied in order to start the process, in particular to pressurize the plant or system at startup, but no longer after the production of the tail gas has started. An air compressor is thus not required for operating the nitric acid plant. In this context, an air compressor suitable for pressurizing the plant has a capacity of about 2000 to 19000 m³/h, which is much smaller than an air compressor for operating a prior art nitric acid plant, with a capacity of at least 300000 m³/h. In a dual pressure nitric acid plant, the tail gas has a pressure higher than P1 and, therefore, a first pressure release means, such as a the tail gas expander, can be used to expand a tail gas stream to a pressure P1. In addition, a first oxygen-rich gas having a pressure equal to or higher than P1 and up to P2 and a second oxygen-rich gas having a pressure higher than P2, provide oxygen to the ammonia converter and to the absorption tower, respectively, such that, in the absence of the primary and secondary air provided by the air compressor, the concentration of oxygen in the ammonia converter and in the absorption tower is similar to that in a standard dual pressure nitric acid plant.

In the absence of an air compressor and with the first tail gas stream being recirculated in the system, not only is the power demand of the system reduced, but the NO_x emissions leaving the system are also reduced. Therefore, the size of the treatment unit for treating those NO_x emissions is reduced with respect to the size in the corresponding standard dual pressure nitric acid plant. The system of the present disclosure thus achieves a significant power reduction together with a reduction of the area footprint of the plant and the

simplification of the system, by the removal of the air compressor and reducing the size of the tail gas expander. In addition, the separate supply of the pressurized oxygen or oxygen-rich gas ensures an optimal conversion of ammonia to nitric oxide.

5 In one embodiment according to the production plant of the disclosure, the system further comprises one or more of:

- a steam turbine, wherein the steam turbine can at least partly power the NO_x gas compressor;
- a heat exchanger for exchanging heat between the first expanded tail gas and a colder
10 tail gas stream, wherein the first expanded tail gas exits the heat exchanger particularly at a temperature below 300 °C, and wherein the means for splitting is positioned downstream the heat exchanger and in fluid communication with the first expanded tail gas;
- a De-NO_x treatment unit; and
- 15 • a second pressure release means for expanding the second tail gas stream to atmospheric pressure, to produce a second expanded tail gas.

In one embodiment according to the production plant of the disclosure, the system further comprises a bleacher for bleaching the stream of raw nitric acid-containing residual NO_x gas, to provide a stream of bleached nitric acid, having an inlet for an oxygen-rich bleaching gas,
20 and an outlet for off-gases in fluid communication with any gas stream downstream the ammonia converter and upstream the NO_x gas compressor if the bleacher operates at a pressure equal to or higher than P1 and up to equal to P2, or in fluid communication with any stream downstream the NO_x gas compressor and upstream the absorption tower if the
25 bleacher operates at a pressure higher than P2, such that the supply for the second oxygen containing gas comes at least partly from the off-gases..

In one embodiment according to the production plant of the disclosure, part of the oxygen-rich gas or part of the first oxygen-containing gas or part of the tail gas, is in fluid communication with the inlet of the bleacher, such that the oxygen rich-bleaching gas is at
30 least partly provided by part of the oxygen-rich gas by part of the first oxygen-containing gas or by part of a tail gas stream.

In one embodiment according to the production plant of the disclosure, the system further comprises a stream of a second oxygen-containing gas in direct fluid communication with any tail gas stream, particularly a stream of pressurized oxygen-rich gas in direct fluid communication with any stream of tail gas downstream the absorption tower or upstream the first pressure release means.

In one embodiment according to the production plant of the disclosure, the oxygen-rich gas, the second oxygen-containing gas, the oxygen-rich bleaching gas and the bleacher off-gases are all at least partly provided by a water electrolyser, particularly a high pressure water electrolyser.

In one embodiment according to the production plant of the disclosure, the fluid communication between the source of pressurised air and the system is in direct fluid communication with the oxygen-rich gas.

In one aspect of the disclosure, a method for producing nitric acid at reduced power consumption and reduced emissions, in a production plant according to the production plant of the disclosure, is disclosed. The method comprises the steps of:

prior to step c), providing or preparing an oxygen-rich gas and a first oxygen-containing gas, and providing an ammonia gas stream;

c) supplying the ammonia gas stream and a first oxygen-containing gas to the mixing apparatus, thereby producing the ammonia/oxygen-containing gas mixture;

d) oxidising ammonia in the ammonia/oxygen-containing gas mixture in the ammonia converter, particularly at a pressure equal to or higher than P1 and lower than P2 and at a temperature ranging from 800 to 950 °C, thereby producing the gaseous NO_x gas/steam mixture, comprising water and nitric oxide;

e) cooling the NO_x gas in the gaseous NO_x gas/steam mixture in the heat exchange system and in the first gas/cooler condenser, thereby producing an aqueous diluted nitric acid mixture and a gaseous NO_x stream;

f) compressing the gaseous NO_x stream in the NO_x gas compressor, thereby providing the pressurized NO_x compressed gas stream having a pressure P2;

g) absorbing the pressurized gaseous NO_x stream in the absorption tower, thereby providing the stream of raw nitric acid-containing residual NO_x gas and the tail gas comprising NO_x gases;

h) heating the tail gas in the heat exchange system, with the heat from the NO_x gas/steam mixture coming from the ammonia converter, particularly to a temperature ranging from 150 to 650 °C;

i) cooling the pressurized NO_x gas stream in the second gas cooler/condenser, thereby providing a pressurized NO_x gas stream, particularly having a temperature ranging from 20 to 60 °C; and

j) expanding at least part of the tail gas obtained in step h) in a first pressure release means, thereby providing a first expanded tail gas;

characterised in that the method further comprises the steps of:

k) splitting a tail gas stream with a first means for splitting into a first tail gas stream and a second tail gas stream, and mixing the first tail gas stream with the oxygen-rich gas, thereby providing the first oxygen-containing gas;

m) adjusting the flow of the oxygen-rich gas being mixed in step k) or the flow of the ammonia gas stream, such that the oxygen to ammonia molar ratio at the inlet of the ammonia converter is maintained to a ratio of at least 1.2 or at least 1.25, particularly between 1.2 and 9 or between 1.25 and 9; and

q) adjusting the flow of the oxygen-rich gas at a pressure equal to or higher than P1 and up to P2 upstream the NO_x gas compressor, or at a pressure higher than P2 downstream the NO_x gas compressor, such that the oxygen concentration in a tail gas stream is maintained at a concentration of at least 0.5% by volume;

In one embodiment according to the method of the disclosure, the first tail gas stream, particularly first expanded tail gas stream, mixed in step k) is particularly obtained after step j), and wherein the method further comprises the steps of:

s) particularly before step k), heating up, in the heat exchanger, a tail gas stream that is colder than the first expanded tail gas with the first expanded tail gas, thereby bringing the first expanded tail gas to a temperature below 300°C, in particular before step k), heating up, in the heat exchanger the tail gas obtained in step g) with the first expanded tail gas obtained in step j), thereby bringing the tail gas to be mixed in step k) to a temperature below 300 °C;

t) treating the tail gas stream, particularly obtained in step s, in the De-NO_x treatment unit;

u) expanding the second tail gas stream in the second pressure release means, thereby providing the second expanded tail gas; and

v) recovering at least part of the steam generated in the ammonia converter in the steam turbine.

5 In one embodiment according to the method of the disclosure, the method further comprises the step of:

w) bleaching the stream of raw nitric acid-containing residual NO_x gas in the bleacher, thereby producing the stream of bleached nitric acid.

10 In one embodiment according to the method of the disclosure, the method further comprises the step of:

w1) supplying part of the oxygen-rich or part of the first oxygen-containing gas obtained in step k) or part of the tail gas obtained in step g), to the inlet of the bleacher in step w).

15 In one embodiment according to the method of the disclosure, the method further comprises the step of:

x) supplying a stream of an oxygen-rich gas, particularly as a stream of a pressurized oxygen-rich gas, to a tail gas stream, particularly to a tail gas stream upstream the first pressure release means

20 In one embodiment according to the method of the disclosure, the method further comprises the steps of:

y) operating the water electrolyser, thereby producing oxygen-gas, particularly operating a high pressure water electrolyser, thereby producing pressurized oxygen gas; and

25 z) providing, from the oxygen produced by the water electrolyser in step y), at least part of the oxygen-rich gas, the second oxygen containing gas, the oxygen-rich bleaching gas, and the bleacher off gases.

In one embodiment according to the method of the disclosure, in step a), the pressurised air is supplied in the stream in direct fluid communication with the oxygen-rich gas.

30 In one aspect of the disclosure, the use of the production plant of the disclosure for performing the method of the disclosure, is disclosed.

In one aspect of the disclosure, a method for revamping an (existing) production plant for producing nitric acid, wherein the (existing) production plant comprises:

- an air compressor for providing a compressed air stream;
- 5 • a mixing apparatus, for mixing the compressed air stream with an ammonia gas stream, to produce an ammonia/oxygen-containing gas mixture;
- an ammonia converter operable at a pressure equal to or higher than P1 but lower than P2, for oxidising ammonia in the ammonia/oxygen-containing gas mixture, to produce a NO_x gas/steam mixture, comprising water and nitric oxide;;
- 10 • a first gas cooler/condenser, downstream the ammonia converter, to produce an aqueous diluted nitric acid mixture, and a gaseous NO_x stream;
- a NO_x gas compressor for compressing the gaseous NO_x stream, to produce a pressurized NO_x gas stream at a pressure P2;
- an absorption tower for absorbing the NO_x gases from the pressurized NO_x gas stream
- 15 in water, to produce a stream of raw nitric acid-containing residual NO_x gas and a tail gas comprising NO_x gases;
- a heat exchange system for exchanging heat between the NO_x/gas steam mixture and the tail gas, particularly for heating a tail gas stream with the heat from the NO_x gas/steam mixture from the ammonia converter;
- 20 • a second gas cooler/condenser for separating and condensing steam from the compressed NO_x gas stream between the NO_x compressor and the absorption tower, and
- a tail gas expander for expanding a stream of tail gas downstream the absorption tower, to produce an expanded tail gas at a pressure P1, wherein the tail gas expander
- 25 can at least partly power the NO_x gas compressor

into a production plant according to any one of claims 1 to 8, comprising the steps of:

- introducing a source of pressurised air in fluid communication with the production plant;
- introducing a supply or source of an oxygen-rich gas, such as a high pressure water
- 30 electrolyser, providing part of a first oxygen-containing gas, upstream of and in fluid communication with the mixing apparatus;

- introducing a means for regulating the concentration of ammonia and/or oxygen in the ammonia converter, particularly a means for controlling the flow of the oxygen-rich gas or the flow of the first oxygen-containing gas and/or a means for controlling the flow of the ammonia gas stream, for maintaining the oxygen to ammonia molar ratio inside the ammonia converter at a ratio of at least 1.2 or at least 1.25, particularly between 1.2 and 9 or between 1.25 and 9;
- introducing a supply of a second oxygen-containing gas, having either (i) a pressure equal to or higher than P1 and up to P2 for supplying oxygen upstream the NOx gas compressor, or (ii) a pressure higher than P2, for supplying oxygen to the compressed NOx gas stream, such that a tail gas stream contains at least 0.5% by volume of oxygen;
- introducing means for splitting a stream of tail gas into a first tail gas stream and a second tail gas stream, wherein the first tail gas stream has a pressure equal to or higher than P1 and up to P2, and is in fluid communication with the oxygen-rich gas, which, upon mixing with the oxygen-rich gas provides the first oxygen-containing gas;
- particularly, introducing means for adjusting the amount of tail gas being split into the first tail gas stream and the second tail gas stream; and
- removing the air compressor.

List of Figures

Figure 1: Nitric acid plant according to the prior art.

Figure 2A: An embodiment of a nitric acid plant according to the disclosure, wherein the second oxygen containing gas stream **68** has a pressure equal to or higher than P1 and lower than P2, and is provided upstream the NOx gas compressor.

Figure 2B: An embodiment of a nitric acid plant according to the disclosure, comprising a low pressure bleacher, in particular with a pressure equal to or higher than P1 and up to P2, wherein the bleacher off-gases **77** are provided upstream the NOx gas compressor.

Figure 2C: An embodiment of a nitric acid plant according to the disclosure, wherein the second oxygen containing gas stream **68** has a pressure equal to or higher than P2, and is provided downstream the NOx gas compressor, between the NOx gas compressor and the absorber.

Figure 2D: An embodiment of a nitric acid plant according to the disclosure, comprising a high-pressure bleacher, in particular with a pressure equal to or higher than P2, wherein the bleacher off-gases **77** are provided downstream the NO_x gas compressor, between the NO_x gas compressor and the absorber.

5

Table of numerals

4	air
5	tail gas
6	outlet of nitric acid absorption tower
7	a first pressure release means (tail gas expander)
10	first tail gas stream
14	ammonia/oxygen-containing gas mixture
15	low-pressure NO _x gas/steam mixture
17	aqueous diluted nitric acid mixture
22	gaseous NO _x stream
24	compressed NO _x gas
27	stream of raw nitric acid-containing residual NO _x gas
32	ammonia
34	compressed or pressurized air (prior art)
35	mixing apparatus
36	air compressor
37	ammonia converter operable at a pressure equal to or lower than P1
38	gas cooler/condenser
39	additional gas cooler/condenser
40	NO _x gas compressor, particularly for compressing a gas to a pressure P2 higher than P1
41	absorption tower operable at a pressure P2
43	heat exchange system

50	oxygen-rich gas
51	steam turbine
55	means for splitting the tail gas
56	first oxygen-containing gas
60	second pressure release means
61	pressurised oxygen-rich gas
62	bleacher
63	high-pressure water electrolyser
64	expanded tail gas
65	pressurised air (production plant according to the present disclosure)
66	first heat exchanger of the heat exchange system 43
67	second heat exchanger of the heat exchange system 43
68	second oxygen containing gas
69	second expanded tail gas
70	De-NO _x treatment unit
72	oxygen-rich bleaching gas
73	outlet of the bleacher
74	stream of an oxygen-rich gas in direct fluid communication with a tail gas stream
75	bleached nitric acid
77	off gases from the outlet 73 of the bleacher 62
78	means for pressurising
79	heat exchanger
80	second tail gas stream
83, 84	tail gas stream partly substituting a source of secondary air

Detailed description

Throughout the description and claims of this specification, the words “comprise” and variations thereof mean “including but not limited to”, and they are not intended to (and do

not) exclude other moieties, additives, components, integers or steps. Throughout the description and claims of this disclosure, the singular encompasses the plural unless the context otherwise requires. In particular, where the indefinite article is used, the disclosure is to be understood as contemplating plurality as well as singularity, unless the context requires otherwise.

Features, integers, characteristics, compounds, chemical moieties, or groups described in conjunction with a particular aspect, embodiment or example of the disclosure are to be understood to be applicable to any other aspect, embodiment or example described herein unless incompatible therewith. All of the features disclosed in this disclosure (including the description, claims, abstract and drawing), and/or all of the steps of any method or process so disclosed, may be combined in any combination, except combinations where at least some of such features and/or steps are mutually exclusive. The disclosure is not restricted to the details of any foregoing embodiments. The disclosure extends to any novel one, or any novel combination, of the features disclosed in this disclosure (including the description, claims, abstract and drawing), or to any novel one, or any novel combination, of the steps of any method or process so disclosed.

The enumeration of numeric values by means of ranges of figures comprises all values and fractions in these ranges, as well as the cited end points. The terms "ranging from ... to ..." or "range from ... to ..." or "up to" as used when referring to a range for a measurable value, such as a parameter, an amount, a time period, and the like, is intended to include the limits associated to the range that is disclosed.

Where the term "about" when applied to a particular value or to a range, the value or range is interpreted as being as accurate as the method used to measure it.

As defined herein, an oxygen-rich gas is a gas comprising more than 21 vol% of oxygen, more in particular more than 30 vol%, more than 35 vol%, more than 40 vol%, more than 50 vol%, more than 60 vol%, more than 70 vol%, more than 80 vol%, more than 90 vol%, more than 95 vol%, more than 98 vol% and more than 99 vol%, more in particular 100 vol% of oxygen. Such oxygen-rich gas can, for example, be provided by an air separation unit or a water electrolyser.

As defined herein, a pressurised oxygen-rich gas is a gas having a pressure ranging from 9 to 30 bara, preferably 15 to 30 bara, and comprising more than 21 vol% of oxygen, more in

particular more than 30 vol%, more than 35 vol%, than 40 vol%, more than 50 vol%, more than 60 vol%, more than 70 vol%, more than 80 vol%, more than 90 vol%, more than 95 vol%, more than 98 vol%, and more than 99 vol%, more in particular 100 vol% of oxygen.

As defined herein, air is ambient air having atmospheric pressure.

5 As defined herein, steam are water vapours.

As defined herein, the term “flow” refers to either a volumetric flow or a mass flow.

The present disclosure generally relates to dual pressure methods and systems for producing nitric acid, which typically operates at two pressures, P1 and P2. Typically, P1 ranges from 2 to below 6 bara and P2 ranges from 6 to 16 bara.

10

The present disclosure generally relates to a dual pressure system and method for the production of nitric acid with important gains compared to conventional systems and methods, wherein the conventional primary air and/or secondary air consisting of pressurized air, provided by an air compressor with a typical capacity of at least 300000 m³/h, is replaced

15 by the combination of (i) oxygen gas or an oxygen-rich gas, in particular a pressurized oxygen gas or oxygen-rich gas, such as produced by a high pressure water electrolyzer as further discussed herein; and (ii) a recirculated tail gas stream, thus removing the need for an air compressor to generate compressed primary and/or secondary air. Stated differently, in the system and methods for the production of nitric acid according to the present disclosure:

20 (i) oxygen gas or an oxygen-rich gas, in particular a pressurized oxygen gas or oxygen-rich gas, such as produced by a high-pressure water electrolyzer, is used (a) upon mixing with part of the tail gas stream, to provide a first oxygen-containing gas stream, which is mixed with an ammonia gas stream and subsequently provided to the ammonia converter; and (b) is used to provide a second oxygen-containing gas stream downstream of the ammonia converter, such

25 as a second oxygen-containing gas stream which is mixed with a NO_x containing gas stream downstream of the ammonia converter, such as between the ammonia converter and NO_x compressor or between the NO_x compressor and the absorber, and/or which is used as a stripping gas in a bleacher, wherein, in particular, the oxygen containing bleacher off-gases are subsequently mixed with a NO_x containing gas stream between ammonia converter and

30 absorber; and

(ii) the tail gas exiting the absorber is split in a first tail gas stream and a second tail gas stream, wherein the first tail gas stream is mixed with the oxygen gas or the oxygen-rich gas, in particular the pressurized oxygen or oxygen-rich gas, such as produced by a high pressure water electrolyzer, to provide the first oxygen-containing gas stream; and/or wherein part of the tail gas exiting the absorber may also be mixed with the oxygen gas or oxygen-rich gas, or the first oxygen containing gas, in particular the pressurized oxygen gas or oxygen-rich gas, such as produced by a high-pressure water electrolyzer, to provide the second oxygen containing gas stream.

10 Nitric Acid Production Plant

Reference is made to Figures 2A, 2B, 2C and 2D. In one aspect of the disclosure, a production plant for producing nitric acid at reduced power consumption and reduced emissions, is disclosed. The production plant comprises:

- preferably, a source of pressurised air **65**, particularly for pressurizing the production plant or system during start-up. More in particular, the source of pressurized air is in fluid communication with a system comprising a source or supply of an oxygen rich gas **50**. As defined herein, a source of pressurized air is capable of providing from 2000 to 19000 m³/h of pressurized air;
- a source or supply of an oxygen-rich gas **50**, which provides part of a first oxygen-containing gas;
- a mixing apparatus **35** downstream the source or supply of the oxygen-rich gas **50**, for mixing a first oxygen-containing gas **56** with an ammonia gas stream **32**, to produce an ammonia/oxygen-containing gas mixture **14**;
- an ammonia converter **37**, particularly operable at a pressure equal to or higher than P1 and lower than P2, more particularly operable at a pressure P1, for oxidising ammonia in the ammonia/oxygen-containing gas mixture **14**, to produce a NO_x gas/steam mixture **15**, comprising water and nitric oxide;
- preferably, a means for measuring the oxygen concentration in the first oxygen-containing gas **56**; and preferably, a means for adjusting the supply of the ammonia gas stream **32** to the mixing apparatus **35**; and, preferably, a means for adjusting the concentration of oxygen in the oxygen-containing gas **56** such that the oxygen to ammonia

molar ratio at the inlet of the ammonia converter **37** is at least 1.2 or at least 1.25, particularly between 1.2 and 9, or between 1.25 and 9. The system according to the present disclosure may thus comprise a means for regulating (not shown) the concentration of ammonia and/or oxygen in the ammonia converter **37**, particularly a means for controlling the flow of the oxygen-rich gas **50** and/or a means for controlling the flow of the ammonia gas stream **32**, for maintaining the oxygen to ammonia molar ratio inside the ammonia converter **37** at a ratio of at least 1.2 or at least 1.25; such as between 1.2 and 9, between 1.25 and 9 or between 1.3 and 9;

- preferably, a means for measuring the temperature in the ammonia converter **37**;

- a first gas cooler/condenser **38** downstream the ammonia converter **37**, to produce an aqueous diluted nitric acid mixture **17** and a gaseous NO_x stream **22**;

- a NO_x gas compressor **40** for compressing the gaseous NO_x stream **22**, to produce a compressed NO_x gas stream **24** at a pressure P₂;

- an absorption tower **41** for absorbing the NO_x gases from the compressed NO_x gas stream **24** in water, to produce a stream of raw nitric acid-containing residual NO_x gas **27** and a tail gas **5** comprising NO_x gases, comprising an absorption tower tail gas outlet **6** for evacuating the tail gas **5**;

- preferably, a means for measuring the concentration of oxygen in a tail gas stream downstream the absorption tower **41**;

- a heat exchange system **43** located upstream the first gas cooler/condenser **38** for exchanging heat between the NO_x gas/steam mixture **15** and the tail gas **5**, particularly for heating a tail gas stream with the heat from the NO_x gas/steam mixture **15**;

- a second gas cooler/condenser **39** for separating and condensing steam from the compressed NO_x gas stream **24**, particularly before said stream is provided to the absorption tower, particularly to produce a compressed NO_x gas stream **24** having a temperature ranging from 20 to 60 °C;

- a supply of an oxygen-rich gas **68, 72, 77** having either (a) a pressure equal to or higher than P₁ and up to P₂ (see Figure 2A and 2B), for supplying oxygen downstream the ammonia converter **37** and upstream the NO_x gas compressor **40**, or stated differently between the ammonia converter **37** and the NO_x gas compressor **40**, or (b) a pressure higher than P₂ (see Figure 2C and 2D), for supplying oxygen to the compressed NO_x gas stream **24**, such that a tail

gas stream **5, 10, 64, 69, 80, 83, 84** contains at least 0.5% by volume oxygen. In particular, the system may further comprise a means for controlling the flow of the second oxygen containing gas in order to obtain a tail gas stream **5, 10, 64, 69, 80, 83, 84** containing at least 0.5% by volume oxygen; and

- 5 - a first pressure release means, such as a tail gas expander **7**, located downstream the heat exchange system **43**, for expanding a stream of tail gas, i.e. downstream the absorption tower **41**, to produce a first expanded tail gas **64** at a pressure equal to or higher than P1 and lower than P2, particularly at a pressure P1, wherein the first pressure release means **7** can at least partly power the NO_x gas compressor **40**;

10 The production plant is characterised in that the system further comprises a means for splitting **55** a stream of tail gas (downstream the absorption tower **41**) into a first tail gas stream **10** and a second tail gas stream **80**, wherein the first tail gas stream **10** has a pressure equal to or higher than P1 and up to P2 and is in fluid communication with the oxygen-rich gas **50**, and optionally the compressed air, wherein the mixing of the oxygen-rich
15 gas **50** and the first tail gas stream **10** provides the first oxygen-containing gas **56**. In particular, the production plant may further comprise a means for adjusting the amount of tail gas being split into the first tail gas stream **10** and the second tail gas stream **80**.

Typically, the heat exchange system **43** comprises at least two heat exchangers **66, 67**.
20 The person skilled in the art will realise that it is possible to split a tail gas stream inside the heat exchange system, for example between the heat exchanger **66** and **67**. In particular, the production plant may comprise further heat exchange systems, such that the gaseous NO_x stream **22** or the NO_x compressed gas stream **24** exchange heat with the tail gas **5**.

25 As defined herein, a stream of tail gas, or a tail gas stream, is any gas stream downstream the absorption tower **41**, between the absorption tower **41** and the point of communication between or the point of mixing of between the first tail gas stream **10** and the oxygen-rich gas **50**.

As defined herein, a means for splitting is any means suitable for splitting a tail gas
30 stream, such as to generate a first tail gas stream **10** and a second tail gas stream **80**. In particular, the means for splitting is a T-connection having one inlet and two outlets, such that

a gas flowing through the inlet of the T-connection is split into two gas streams of identical chemical composition. As defined herein, a pressure release means is any suitable means for reducing the pressure of a gas stream, such as a tail gas stream. In particular, the pressure release means may be a gas expander or a gas ejector. A gas ejector provides the benefits of a simplified equipment, wherein mixing of different gas streams is combined with the reduction of the tail gas pressure. For instance, a tail gas stream, processed via the gas ejector, may act as the motive gas, and a second gas fed to the ejector can, for example, be ambient air at a pressure (e.g. atmospheric pressure) lower than the tail gas stream as motive gas. In particular, a tail gas stream may be fed as the motive gas to a gas ejector, and a second gas fed to the ejector is oxygen gas at a pressure lower than the tail gas stream as motive gas. In this context, both the feeding of air or oxygen through the gas ejector contribute to increasing the concentration in the first tail gas stream **10** and/or a further tail gas stream **83, 84** being recycled, thereby reducing the demand on the oxygen-rich gas **50**. In particular, a tail gas stream is fed as the motive gas to the ejector and the second gas fed to the ejector is the NO_x gas/steam mixture **15** or the gaseous NO_x stream **22**.

The person skilled in the art will realise that the means for splitting can be incorporated within the (first) pressure release means, provided that the (first) pressure release means includes at least two outlets for the gas stream being depressurized, in particular one outlet for the first tail gas stream **10** and another outlet for the second tail gas stream **80**.

As defined herein, a means for adjusting the amount of tail gas being split into the first tail gas stream **10** and the second tail gas stream **80**, are any means for controlling the splitting in the means for splitting **55**. In particular, the means for splitting **55** is a T-connection as described above and the means for adjusting may be an orifice or a guide vane or a flow control valve at one or both of the outlets of the T-connection. Even more in particular, the means may be an integrated process control system, in which the temperature in the ammonia converter **37** is determined through a means for measuring the temperature. The temperature in the ammonia converter **37** is then used for controlling a flow control means in the means for splitting **55**, thereby controlling the splitting the tail gas stream, in order for the measured temperature to be maintained in the range 800-950 °C.

As defined herein, a means for adjusting the oxygen concentration is any suitable means for regulating the amount of oxygen to be introduced in the system from a measurement of the oxygen concentration, such as by using a means for measuring the concentration of oxygen. The oxygen concentration can be determined, for example, from a measurement in the gas phase using a process gas analyser. The oxygen concentration can also be determined from computing using the concentration of the oxygen source being introduced in the system, in particular the oxygen concentration of the oxygen rich gas, the flow at which the oxygen source, in particular the oxygen rich gas, is introduced in the system, particularly the flow at which the ammonia gas stream is introduced in the system and the relative flow values of the gases with which the oxygen source is mixed; in particular the relative flow values at which the oxygen rich gas and the ammonia gas stream are mixed. Using the oxygen concentration, the relevant flow of oxygen to be introduced in the system is, in turn, determined and is used in controlling the flow of oxygen, from a gaseous source of oxygen at a pre-determined concentration. Controlling of the flow of gaseous oxygen can, for example, be achieved through flow control valves. In this context, as defined herein, a means for regulating the concentration of ammonia and/or oxygen is any means suitable for achieving a target concentration of ammonia and/or oxygen. In particular, such means are gas flow control means, in particular a flow control valve or an orifice or a guiding vane, for controlling the flow of the oxygen rich gas and/or the ammonia gas stream. In particular, the means is an integrated process control system, in which the concentration of oxygen is measured, and the target flow or relevant flow of oxygen is thereby determined and achieved from controlling the flow of the first oxygen rich gas, from a gaseous source of oxygen at a pre-determined concentration.

The person skilled in the art will determine the optimal concentration of oxygen in the gases entering the ammonia converter **37** and the absorption tower **41**, in order for the catalytic conversion of ammonia to nitric oxide to proceed optimally in the ammonia converter **37** and for the absorption of NO_x gases in the absorption tower **41** to proceed optimally. Further, upon determining the oxygen content exiting the absorption tower **41**, he will also weigh out the benefits of increasing the oxygen content in the absorption tower **41**, against the drawback of a higher gas volume downstream the absorption tower **41**, such as implying equipment, such as heat exchangers, of a larger size, for heating tail gas.

As defined herein, means for measuring the temperature are any means suitable for measuring and indicating the temperature in the ammonia oxidation burner. In particular, the means for measuring the temperature is a thermocouple or a thermometer suitable for measuring and indicating a temperature ranging as high as 1000 °C. More in particular, the means for measuring the temperature is an infrared thermometer for measuring and indicating a temperature ranging as high as 1000 °C.

As defined herein, means for converting steam into power are any means for achieving power from steam. In particular those means are a steam turbine connected to an electric generator.

Considering that a production cycle of a unit or plant comprises a start-up phase, wherein the different processes are initiated; a continuous and essentially constant phase or operation mode, wherein processes operate at a given working load that is usually kept constant during a production cycle; and a shutdown phase, where processes are slowly and safely stopped, the term “during operation” or “during continuous operation” of a unit or plant, in particular of a nitric acid plant, refers to the continuous operation mode wherein the unit or plant produces a product, in particular nitric acid.

The inventors have found that, instead of continuously supplying compressed air provided by an air compressor **36** to the mixing unit **35**, in particular during continuous operation of the nitric acid plant, it is possible to recirculate the first tail gas stream **10** at a pressure P1. Therefore, pressurized air only has to be supplied in order to start the process, i.e. during the start-up phase of the nitric acid plant, in particular to pressurize the system, but no longer after the production of the tail gas **5** has started and an air compressor **36** is not required. The tail gas **5** has a pressure higher than P1 and, therefore, a first pressure release means, such as the tail gas expander **7**, can be used to provide reduce the pressure of the tail gas stream and provide a tail gas stream with pressure P1. In addition, the oxygen-rich gas **50** and the supply of a second oxygen-containing gas **68**, which typically have a pressure equal to or higher than P1 and up to P2 to provide oxygen to the ammonia converter **37** and to the absorption tower **41**, respectively, such that, in the absence of the primary and secondary air provided by the air compressor **36**, the concentration of oxygen in the ammonia converter **37**

and in the absorption tower **41** is similar to and can be controlled to that in a standard dual pressure nitric acid plant.

In the absence of an air compressor **36** and with the tail gas stream **10** being recirculated in the system, not only is the power demand of the system reduced, but the NO_x emissions leaving the system are also reduced. Therefore, the size of the treatment unit for treating those NO_x emissions is reduced with respect to the size in the corresponding standard dual pressure nitric acid plant.

In one embodiment according to the production plant of the disclosure, the system further comprises one or more of:

- a steam turbine **51**, wherein the steam turbine can at least partly power the NO_x gas compressor **40**;
- a heat exchanger **79** for exchanging heat between the first expanded tail gas **64** and a colder tail gas stream, particularly wherein the first expanded tail gas **64** exits the heat exchanger **79** at a temperature below 300°, and wherein the first expanded tail gas **64** downstream the heat exchanger **79** is in direct fluid communication with the means for splitting **55**. Stated differently, the expanded tail gas **64** exchanges heat with the tail gas **5** in the heat exchanger **79** and, particularly exits the heat exchanger **79** at a temperature below 300 °C, wherein the expanded tail gas **64** having exchanged heat with the tail gas **5** is the stream of tail gas splitted by the means for splitting **55** downstream the heat exchanger **79**;
- a De-NO_x treatment unit **70**, particularly located in a tail gas stream downstream the absorption tower **41**; and
- a second pressure release means **60** for expanding the second tail gas stream **80** to atmospheric pressure, to produce a second expanded tail gas **69**. Said pressure release means **60** may be any means suitable for reducing the pressure of the second tail gas stream **80**, in particular by expanding the second tail gas stream **80**. Such means are for example, a pressure release valve or a gas expander.

Advantageously, the means for splitting **55** are located downstream the heat exchange system **43**. Indeed, both the first tail gas stream **10** and the second tail gas stream **80** are then at an optimal temperature. In particular, this means that the first stream of tail gas **10** is at a

temperature below 300 °C, such that the first tail gas stream **10** can be fed to the ammonia converter **37** without the amount of ammonia fed through the stream **32**, having to be adjusted in order to maintain the temperature ranging from 800 to 950 °C in the ammonia converter **37**, the temperature at which the ammonia converter **37** is operable. In addition, the location of the means for splitting **55** at this location confers to the second tail gas stream **80** an optimal temperature for being expanded in the pressure release means **60**, in particular a tail gas expander, such as to provide an optimal of energy which can be used to power the NO_x gas compressor **40**. Further, the presence of a steam turbine **51** allows for the recovery of the heat of the steam produced in the ammonia converter **37** and this recovered heat can be used, at least partly, for powering the tail NO_x gas compressor **40**. Finally, the use of the steam turbine **51** contributes to operating the production plant in an energy-efficient manner.

In particular, the tail gas **5** is heated in a heat exchanger **67** of the heat exchange system **43** and then in the heat exchanger **79** from a temperature ranging from 20 to 250 °C, to a temperature ranging from 100 to 450 °C. Subsequently, the tail gas exiting the heat exchanger **79** is heated in the heat exchange system **43** to a temperature ranging from 200 to 550 °C. The tail gas exiting the heat exchanger **79** then is at an optimal temperature for being treated in the De-NO_x treatment unit **70** and, therefore, the De-NO_x treatment unit **70** is located between the heat exchanger **79** and the heat exchange system **43**. The person skilled in the art will, without any difficulty, select the proper location for the De-NO_x treatment unit **70** such that the operating temperature of the De-NO_x treatment unit **70** is in agreement with the temperature of the corresponding stream of tail gas.

In one embodiment according to the production plant of the disclosure, the system further comprises a bleacher **62** for bleaching the stream of raw nitric acid-containing residual NO_x gas **27**, to provide a stream of bleached nitric acid **75**, wherein the bleacher has an inlet **81** for an oxygen-rich bleaching gas **72**, in particular wherein the inlet **81** is in fluid communication with a high-pressure water electrolyser **63**, and an outlet **73** for the bleacher's off-gases **77**. It is understood that the bleacher **62** further comprises an inlet for the stream of raw nitric acid containing residual NO_x gas and an outlet for bleached nitric acid. The bleaching gases or off-gases **77** are in fluid communication with any gas stream downstream the ammonia converter **37** and upstream the NO_x gas compressor **40** if the bleacher **62** operates at a pressure higher than P1 and up to equal to P2 (Figure 2B), or in fluid communication with

any stream downstream the NO_x gas compressor **40** if the bleacher **62** operates at a pressure equal to or higher than P2 (Figure 2D), such that the supply for or source of the second oxygen-containing gas **68**, **72**, **77** comes at least partly from the off-gases **77**.

When the stream of raw nitric acid containing residual NO_x gas **27** is bleached, the amounts of NO_x gases and nitrous acid HNO₂ in the nitric acid solution are reduced. This in turn results in less brown fumes coming out of the nitric acid solution. In addition, the nitric acid solution provided by the bleacher is of a higher quality, that is purer.

Conveniently, when the stream of raw nitric acid containing residual NO_x gas **27** is bleached, the bleaching gases or off-gases **77** correspond to the second oxygen containing gas (or the oxygen-rich gas supplied by the supply **68**) having a pressure higher than P1 and up to P2 (Figure 2B) or having a pressure higher than P2 (Figure 2D): the supply of the oxygen-rich gas having pressure higher than P1 and up to P2 (Figure 2B) or higher than P2 (Figure 2D), in particular the second oxygen-containing gas, is achieved through the bleacher **62**, as the bleacher off-gases **77**, and no separate source of oxygen is required.

In one embodiment according to the production plant of the disclosure, part of the oxygen-rich gas **50** or part of the first oxygen-containing gas **56** or part of the tail gas **5**, such as part of a tail gas stream **83**, **84**, is in fluid communication with the inlet **81** of the bleacher **62**, such that the oxygen rich-bleaching gas or stripping gas **72** is at least partly provided by part of the oxygen-rich gas **50** or part of the oxygen-containing gas **56** or part of the tail gas **5**, such as part of a tail gas stream **83**, **84**.

If a bleacher **62** is present, as no secondary air is fed by an air compressor (**36** in the standard nitric acid plant) to the bleacher **62**, the bleacher **62** can be conveniently fed by the oxygen-rich gas **50**. Also, once tail gas **5** is produced and recirculated, the first oxygen-containing gas **56** or part of a tail gas stream can be fed to the bleacher **62**: the concentration of NO_x gases in the oxygen-containing gas **56** or the tail gas **5** is sufficiently low that the bleaching in the bleacher **62** remains sufficiently efficient.

In particular, the system further comprises means for pressurising **78** the oxygen-rich gas **50** or the first oxygen-containing gas **56** or the tail gas **5**, when used as a stripping gas in the bleacher, to a pressure equal to or higher than P2, such that the bleacher **62** is a high-pressure bleacher, that is a bleacher operating at a pressure ranging from above 6 bara and

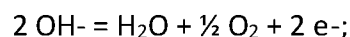
up to 16 bara (Figure 2D). Those means for pressurising **78** can, for example, be a gas compressor.

In one embodiment according to the production plant of the disclosure, the system further comprises a stream of a second oxygen-rich gas **74** in direct fluid communication with any tail gas stream downstream the absorption tower **41**. More in particular, the system further comprises a stream of a pressurized oxygen-rich gas in direct fluid communication with any tail gas stream upstream the first pressure release means **7**.

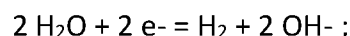
The feeding of a stream of a second oxygen-rich gas **74** allows to reduce the amount of the first oxygen-rich gas **50** having to be provided to the mixing unit **35**. In particular, the stream of the second oxygen-rich gas **74** can be fed downstream the heat exchange **43** and upstream the first pressure release means **7**, which allows more power to be exported from the first pressure release means, e.g. from the tail gas expander **7**.

In one embodiment according to the production plant of the disclosure, the first oxygen-rich gas **50**, the second oxygen containing gas **68**, **72**, **77**, the stream of the second oxygen-rich gas **74**, which is particularly in fluid communication with any stream of tail gas downstream the absorption tower **41**, and the oxygen-rich bleaching gas **72** and the off-gases **77** are all provided at least partly by a water electrolyser **63**, in particular a high-pressure water electrolyser **63**.

A water electrolyser is a device for the electrolysis of water, being the decomposition of water into oxygen and hydrogen gas, due to the passage of an electric current therethrough. This technique can be used to make hydrogen gas, a main component of hydrogen fuel, and oxygen gas. A suitable high-pressure water electrolyser may comprise an anode producing oxygen gas according to the reaction



a cathode, producing hydrogen gas according to the reaction



an electrolyte consisting of an alkaline solution such as potassium hydroxide; and a porous diaphragm separating the anode and the cathode, in order to avoid the mixing of hydrogen gas and oxygen gas that together form an explosive mixture. Alternatively, the anode and the

cathode may be separated by a solid polymer electrolyte such as the fluoropolymer Nafion, where the electrolyte provides the selective transport of protons from the anode to the cathode, as well as the electrical insulation between the anode and the cathode, and avoids the mixing of hydrogen gas and oxygen gas that together form an explosive mixture.

5 The anode and cathode can be made of nickel or steel, or mixtures thereof. Alternatively, for the purpose of enhancing the electrode reactions, the anode and cathode may contain catalysts that can be made of Iridium and Platinum, respectively. The diaphragm of an electrically insulating material is based on, for example, zirconia. The diaphragm has a porosity such that it forms a barrier against transport of hydrogen and oxygen gas bubbles,
10 while containing a continuum of penetrated liquid electrolyte. An anode-diaphragm-cathode assembly constitutes an electrolysis cell. Electrolysis cells are piled in series in stacks that compose the core of an electrolyser. The hydrogen and oxygen production for a given stack volume is proportional to the current density and inversely proportional to the stacking distance. Regardless of stack volume, the hydrogen and oxygen production is proportional to
15 the total current. In addition to the stack, the electrolyser comprises auxiliaries such as a current rectifier, a water demineralization unit, a water pump and a cooling system, a hydrogen purification unit, and instrumentation.

 The electrolyser is operated by applying a voltage corresponding to the standard potential plus the overpotential over each cell. The total voltage depends on the total number
20 of cells of which the electrolyser is comprised. OH⁻ ions generated at the cathode migrate through the electrolyte in the diaphragm to the anode, where they are consumed by the anode reaction. Electrons travel the opposite direction in an external circuit. The electrolyser may be operated at a temperature of 50 to 80 °C, or 60 to 80 °C, and a gas pressure of 2 bara, preferably 9 to 30 bara – as a high pressure water electrolyser, even more preferably 15 to 30
25 bara.

 A high-pressure water electrolyser hence results in the production of pressurised hydrogen at the cathode and pressurised oxygen at the anode, such as having a pressure of 9 to 30 bara, even more preferably a pressure of 15 to 30 bara. What is required to perform high-pressure electrolysis is to pressurize the water used in the electrolysis process. As
30 pressurising water requires less power than pressuring a gas, the use of a high-pressure water

electrolyser results in the production of pressurised oxygen-rich gas at minimized power consumption.

Conveniently, the water electrolyser **63** provides oxygen to all the various points where oxygen needs to be fed. In particular, the supply of oxygen from the electrolyser **63**, is
5 sufficient to provide all of the oxygen of the first oxygen-rich gas, the second oxygen-rich gas **74**, the second oxygen-containing gas **68**, the oxygen-rich bleaching gas **72**, and the off-gases **77**. In this manner, the system is simplified and comprises a single source of oxygen from which different oxygen-containing gas streams can be produced. In particular, oxygen-containing gas streams can be produced at the desired pressure, using standard pressure
10 adjustment means. The use of a high-pressure electrolyser operable at 9 to 30 bara is particularly useful as a source of oxygen gas to be supplied to a bleacher operating at a pressure higher than P2.

Another advantage of the presence of a high-pressure water electrolyser lies in the potential to, in parallel to producing oxygen gas that can be used in the nitric acid production,
15 also produce hydrogen gas. Such hydrogen gas is produced in a green manner, i.e. without the conventional use of natural gas, which results in the production of the greenhouse gas carbon dioxide. The hydrogen gas can then be used in the production of ammonia in an Haber-Bosch process, also conventionally named synthesis gas unit. The high pressure water electrolyser thus enables the integration of the ammonia and nitric acid production processes.

20 In one embodiment according to the production plant of the disclosure, the fluid communication between the source of pressurised air **65**, for pressurizing the system during the startup phase, and the system is in direct fluid communication with the first oxygen-rich gas **50**, particularly having a pressure P1.

25 It is preferred to introduce pressurised air **65** at the start-up in the tail gas stream in direct fluid communication with the oxygen-rich gas **50**. In this manner, upon operating the NOx compressor **40** during the start-up of the system, it is ensured that air flows through the converter **37** when ammonia **32** is being fed to converter **37**, such that there is a sufficient concentration of oxygen to convert ammonia into nitric oxide. Subsequently, the nitric acid
30 process being induced, the tail gas **5** is produced and the first tail gas stream **10** can be recirculated to the mixing unit **35**, upon feeding the oxygen-rich gas **50**.

Method For Producing Nitric Acid

Reference is made to Figures 2A, 2B, 2C and 2D. In one aspect of the disclosure, a method for producing nitric acid at reduced power consumption and reduced emissions, in a production plant according to the production plant of the disclosure, is disclosed. The method comprises the steps of

- a) preferably, pressurizing the system by supplying the pressurised air **65** in the system;
- b) preferably, operating the NO_x gas compressor **40** or the first pressure release means (e.g. tail gas expander) **7** using external power, thereby inducing a pressurised air flow in the system and further pressurizing the system to a pressure P2 downstream the NO_x gas compressor **40**;
- c) supplying the ammonia gas stream **32** and a first oxygen containing gas to the mixing apparatus **35**, thereby producing the ammonia/oxygen-containing gas mixture **14**;
- d) oxidising ammonia in the ammonia/oxygen-containing gas mixture **14** in the ammonia converter **37**, at a pressure equal to or higher than P1 and lower than P2, in particular at a pressure P1, particularly at a temperature ranging from 800 to 950 °C, thereby producing the gaseous NO_x gas/steam mixture **15**, comprising water and nitric oxide;
- e) cooling the NO_x gas in the gaseous NO_x gas/steam mixture **15** in the heat exchange system **43** and in the first gas/cooler condenser **38**, thereby producing an aqueous diluted nitric acid mixture **17** and a gaseous NO_x stream **22**;
- f) compressing the gaseous NO_x stream **22** in the NO_x gas compressor **40**, thereby providing the pressurized NO_x compressed gas stream **24** having a pressure P2;
- g) absorbing the compressed gaseous NO_x stream **24** in the absorption tower **41**, thereby providing the stream of raw nitric acid-containing residual NO_x gas **27** and the tail gas **5** comprising NO_x gases;
- h) heating the tail gas **5** in the heat exchange system **43**, with the heat from the NO_x gas/steam mixture **15** coming from the ammonia converter **37**, particularly to a temperature ranging from 150 to 650 °C;
- i) cooling the compressed NO_x gas stream **24** in a second gas cooler/condenser **39**, thereby providing a compressed NO_x gas stream **24**, particularly having a temperature ranging from 20 to 60 °C; and

j) expanding at least part the tail gas **5** obtained in step h) in a first pressure release means (e.g. a tail gas expander **7**), thereby providing the first expanded tail gas **64**.

The method is characterised in that it further comprises the steps of

k) in particular, splitting a tail gas stream with a first means for splitting **55** into a first tail gas stream **10** and a second tail gas stream **80**, and mixing the first tail gas stream **10** with the (first) oxygen-rich gas **50**, thereby providing the first oxygen-containing gas **56**;

l) optionally, measuring the oxygen concentration in the first oxygen-containing gas **56**;

m) adjusting the flow of the first oxygen-rich gas **50** (e.g. having a pressure P2) being mixed in step k), or the flow of the ammonia gas, such that the oxygen to ammonia molar ratio at the inlet of the ammonia converter **37** is at least 1.2 or 1.25, such as between 1.2 and 9, between 1.25 and 9 or between 1.3 and 9; or stated differently, such as to maintain the oxygen to ammonia molar ratio inside the ammonia converter **37** at a ratio of at least 1.2 or 1.25, such as ranging from 1.2 to 9, from 1.25 to 9 or from 1.3 to 9, particularly if the oxygen concentration measured in step l) is such that the oxygen to ammonia molar ratio in the ammonia converter **37** is less than 1.2 or 1.25;

n) optionally, measuring the temperature in the ammonia converter **37**;

o) optionally, adjusting the gas volume being mixed in step k) or the ammonia gas stream **32** supplied in step d), if the temperature measured in step n) is outside the range of 800-950 °C, such that the temperature in the ammonia converter is maintained in the range of 800-950 °C;

p) optionally, measuring the oxygen concentration in the tail gas **5** downstream the absorption tower **41**;

q) adjusting the flow or supply of the second oxygen-containing gas **68, 72, 77**, particularly at a pressure equal to or higher than P1 and up to P2 upstream the NO_x gas compressor **40**, or at a pressure higher than P2 downstream the NO_x gas compressor **40**, such that the oxygen concentration in a tail gas stream **5, 10, 64, 69, 80, 83, 84** contains at least 0.5% by volume oxygen, particularly if the oxygen concentration measured in step p) is less 0.5% by volume oxygen.

r) in particular, repeating steps c) to q).

Typically, P1 ranges from 2 to 6 bara and P2 ranges from 9 to 16 bara. The person skilled in the art will determine the optimal concentration of oxygen in the gases entering the ammonia converter **37** and the absorption tower **41**, in order for the catalytic conversion of ammonia to nitric oxide to proceed optimally in the ammonia converter **37** and for the absorption of NO_x gases in the absorption tower **41** to proceed optimally. Further, upon determining the oxygen content exiting the absorption tower **41**, he will also weigh out the benefits of increasing the oxygen content in the absorption tower **41**, such as a reduced tower size due to improved absorption, against the drawback of a higher gas volume downstream the absorption tower **41**, which requires equipment, such as heat exchangers, of a larger size, for heating tail gas.

In particular, the gaseous NO_x stream **22** or the NO_x compressed gas stream **24** exchange heat with the tail gas **5**. In particular, the gaseous NO_x stream **22** or the NO_x compressed gas stream **24** exchange heat with the tail gas **5**.

The inventors have found that, instead of continuously supplying compressed air **34** provided by an air compressor **36** to the mixing unit **35**, it is possible to recirculate the first tail gas stream **10** at a pressure P1, in particular during continuous operation of the nitric acid plant. Therefore, compressed or pressurized air only has to be supplied in order to start the process, i.e. during the start-up phase of the nitric acid plant, for pressurizing the system, but no longer after the production of the tail gas **5** has started, during the continuous operation phase or mode of the nitric acid plant, and an air compressor **36** is not required. The tail gas **5** has a pressure higher than P1 and, therefore, a first pressure release means **7**, such as a tail gas expander, can be used to provide a stream of tail gas of pressure P1. In addition, the first oxygen-rich gas **50** and the second oxygen-containing gas **68**, having either a pressure equal to or higher than P1 and up to P2, provide oxygen to the ammonia converter **37** and to the absorption tower **41**, respectively, such that, in the absence of the primary and secondary air provided by the air compressor **36**, the concentration of oxygen in the ammonia converter **37** and in the absorption tower **41** is similar to that in a standard dual pressure nitric acid plant.

In the absence of an air compressor **36** and with the first tail gas stream **10** being recirculated in the system, not only is the power demand of the system reduced: the NO_x emissions leaving the system are also reduced. Therefore, the size of the treatment unit for

treating those NO_x emissions is reduced with respect to the size in the corresponding standard dual pressure nitric acid plant.

In one embodiment according to the method of the disclosure, the first tail gas stream **10** mixed in step k) is obtained after step j), in particular the first expanded tail gas **64** is splitted in step k), and the method further comprises the steps of

s) particularly before step k), heating up, in the heat exchanger **79**, a tail gas stream which is colder than the first expanded tail gas **64** with the first expanded tail gas **64**, thereby bringing the expanded tail gas to be mixed in step k to a temperature below 300°; in particular before

10 step k), heating up, in the heat exchanger, the tail gas **5** obtained in step g) with the first expanded tail gas obtained in step j), thereby bringing the tail gas to be mixed in step k) to a temperature below 300 °C;

t) treating a tail gas stream, particularly the tail gas stream obtained from/heated in step s) in the De-NO_x treatment unit **70**;

15 u) expanding the second tail gas stream **80** in the second pressure release means **60**, thereby providing the second expanded tail gas **69**. The second pressure release means **60** may be any means suitable for reducing the pressure of a gas stream, hence expanding a gas stream, in particular the second tail gas stream **80**. Such means are for example, a pressure release valve or a gas expander; and

20 v) recovering at least part of the steam generated in the ammonia converter **37** in the steam turbine **51**.

Advantageously, the means for splitting **55** are located downstream the heat exchange system **43**. Indeed, both the first tail gas stream **10** and the second tail gas stream **80** are then at an optimal temperature. This means that the first stream of tail gas **10** is at a temperature

25 below 300 °C, such that the first tail gas stream **10** can be fed to the ammonia converter **37** without the amount of ammonia fed through the stream **32**, having to be adjusted in order to maintain the temperature in the ammonia converter, ranging from 800 to 950 °C, the temperature at which the ammonia converter **37** is operable. In addition, the location of the means for splitting **55** at this location confers to the second tail gas stream **80** an optimal

30 temperature for being expanded in the pressure release means **60** such as to provide an optimal of energy which can be used to power the NO_x gas compressor **40**. Further, the

presence of a steam turbine **51** allows for the recovery of the heat of the steam produced in the ammonia converter **37** and this recovered heat can be used, at least partly, for powering the tail NO_x gas compressor **40**. Finally, the use of the steam turbine **51** contributes to operating the production plant in an energy-efficient manner.

5 In particular, the tail gas **5** is heated in the heat exchanger **79**, in particular in a heat exchanger **67** of the heat exchange system **43** and then in the heat exchanger **79**, from a temperature ranging from 20 to 250 °C, to a temperature ranging from 100 to 450 °C. Subsequently, the tail gas exiting the heat exchanger **79** is heated in the heat exchange system **43**, particularly in a heat exchanger **66** of the heat exchange system **43**, to a temperature
10 ranging from 200 to 550 °C. The tail gas exiting the heat exchanger **79** then is at an optimal temperature for being treated in the De-NO_x treatment unit **70** and, therefore, the De-NO_x treatment unit **70** is located between the heat exchanger **79** and the heat exchange system **43**. The person skilled in the art will, without any difficulty, select the proper location for the De-NO_x treatment unit **70** such that the operating temperature of the De-NO_x treatment unit
15 **70** is in agreement with the temperature of the corresponding stream of tail gas.

In one embodiment according to the method of the disclosure, the method further comprises the step of w) bleaching the stream of raw nitric acid-containing residual NO_x gas **27** in the bleacher **62**, thereby producing the stream of bleached nitric acid **75**.

20 When the stream of raw nitric acid containing residual NO_x gas is bleached, the amounts of NO_x gases and nitrous acid HNO₂ in the nitric acid solution are reduced. This in turn results in less brown fumes coming out of the nitric acid solution. In addition, the nitric acid solution provided by the bleacher is of a higher quality, that is purer.

Conveniently, when the stream of raw nitric acid containing residual NO_x gas **27** is
25 bleached, the bleaching gases or off-gases **77** correspond to the second oxygen-containing gas supplied by the corresponding supply or source **68** for an oxygen-rich gas having a pressure higher than P1 and up to P2 (Figure 2B) or higher than P2 (Figure 2D): the supply of the second oxygen-containing gas having pressure higher than P1 and up to P2 (Figure 2B) or higher than P2 (Figure 2D) is the bleacher **62**, in particular the bleacher off-gases **77**, and no separate
30 source of oxygen is required.

In one embodiment according to the method of the disclosure, the method further comprises the step of w1) supplying part of the first oxygen-rich **50** or part of the first oxygen-containing gas **56** obtained in step k) or part of the tail gas stream **5, 83, 84**, such as obtained in step g), to the bleacher **62** in step w).

5 If a bleacher **62** is present, i.e. if such a bleaching step is performed, as no secondary air is fed by an air compressor (**36** in the standard nitric acid plant) to the bleacher **62**, the bleacher **62** can be conveniently fed by the first oxygen-rich gas **50**. Also, once tail gas **5** is produced and recirculated, the first oxygen-containing gas **56** or part of the tail gas stream can be fed to the bleacher **62**: the concentration of NO_x gases in the first oxygen-containing
10 gas **56** or the tail gas **5** is sufficiently low that the bleaching in the bleacher **62** remains sufficiently efficient.

In particular, the system further comprises the step of w2) pressurising the first oxygen-rich gas **50**, part of a tail gas stream, and/or the first oxygen-containing gas **56** to be supplied to the bleacher in the means for pressurising **78**, to a pressure higher than P₂, such
15 that the bleacher **62** is a high-pressure bleacher, that is a bleacher operating at a pressure ranging from above 6 or 9 bara and up to 16 bara (Figure 2D). Those means for pressurising **78** can, for example, be a gas compressor.

In one embodiment according to the method of the disclosure, the method further comprises the step of x) supplying a stream of a second oxygen-rich or oxygen-containing gas
20 **68, 72, 77**, particularly as a stream of a pressurized oxygen-rich gas, to a tail gas stream, particularly to a tail gas stream upstream the first pressure release means **7**. The feeding of a stream of a second oxygen-rich gas **74** allows to reduce the amount of the first oxygen-rich gas **50** having to be provided to the mixing unit **35**. In particular, the stream of a second oxygen-rich gas **74** can be fed downstream the heat exchanger **43** and upstream the first
25 pressure release means **7**, such as a tail gas expander, which allows more power to be exported from the first pressure release means **7**, such as a tail gas expander.

In one embodiment according to the method of the disclosure, the method further comprises the steps of
30 y) operating the water electrolyser **63**, thereby producing oxygen-gas, particularly operating a high-pressure water electrolyzer, thereby producing pressurized oxygen gas; and

z) providing, from the oxygen produced by the water electrolyser **63** in step y), at least part of the (first) oxygen-rich gas **50**, the second oxygen containing gas **68, 72, 77**, the second oxygen-rich gas **74** (particularly in fluid communication with any stream of tail gas downstream the absorption tower **41**), and the oxygen-rich bleaching gas **72** and the off-gases **77**.

5 Conveniently, the water electrolyser **63** provides oxygen to all the various points where oxygen needs to be fed. In particular, the supply of oxygen from the electrolyzer **63** is sufficient to provide all of the oxygen of the first oxygen-rich gas **50**, the second oxygen-rich gas **74**, the second oxygen containing gas **68**, the oxygen-rich bleaching gas **72** and the off-gases **77**. In this manner, the system is simplified and can comprise a single source of oxygen from which
10 different oxygen-containing gas streams can be produced. In particular, different oxygen containing streams can be produced at the desired pressures, using standard pressure adjustment means. The use of a high-pressure electrolyser operable at a pressure of 9 to 30 bara, preferably at a pressure of 15 to 30 bara, is particularly useful as a source of oxygen gas that can be supplied to a bleacher operating at a pressure higher than P2.

15 Another advantage of the presence of a high-pressure water electrolyser lies in the potential to, in parallel to producing oxygen gas that can be used in nitric acid production, also produce hydrogen gas. Such hydrogen gas is produced in a green manner, i.e. without the conventional use of natural gas, which results in the production of the greenhouse gas carbon dioxide. The hydrogen gas can then be used in the production of ammonia in an Haber-Bosch
20 process, also conventionally named synthesis gas unit. The high pressure water electrolyser thus enables the integration of the ammonia and nitric acid production processes. Furthermore, as pressurizing water requires less energy than pressurizing a gas, the use of a high-pressure water electrolyzer results in the production of pressurized oxygen-rich gas at minimized power consumption.

25 In one embodiment according to the method of the disclosure, in step a), the pressurised air **65**, particularly having a pressure P1, is supplied in the stream in direct fluid communication with the oxygen-rich gas **50**, particularly having a pressure P2.

 It is preferred to introduce pressurised air **65** at the start-up in the tail gas stream in direct fluid communication with the oxygen-rich gas **50**. In this manner, upon operating the
30 means for pressurising and the NOx compressor during the start-up of the system, it is ensured that air flows through the converter **37** when ammonia **32** is being fed to converter **37**, such

that there is a sufficient concentration of oxygen to convert ammonia into nitric oxide. Subsequently, the nitric acid process being induced, the tail gas **5** is produced and the first tail gas stream **10** and recirculated to the mixing unit **35**, and mixed with the first oxygen-rich gas **50**.

5

Use Of the Production Plant Of The Disclosure

In one aspect of the disclosure, the use of the production plant of the disclosure for performing the method of the disclosure, is disclosed.

10 Method For Revamping A Nitric Acid Production Plant

In one aspect of the disclosure, a method for revamping a production plant for producing nitric acid, in particular for revamping an existing production plant into a production plant according to the present disclosure is disclosed, wherein the existing system or production plant for producing nitric acid comprises:

- 15 - an air compressor **36** for providing a compressed air stream **34**;
- a mixing apparatus **35**, for mixing the compressed air stream **34** with an ammonia gas stream **32**, to produce an ammonia/oxygen-containing gas mixture **14**;
- preferably, means for adjusting the supply of the ammonia gas stream **32** to the mixing apparatus **35**;
- 20 - an ammonia converter **37**, particularly operable at a pressure equal to or higher than P1 but lower than P2, particularly operable at a pressure P1, for oxidising ammonia in the ammonia/oxygen-containing gas mixture **14**, to produce a NO_x gas/steam mixture **15**, comprising water and nitric oxide;
- preferably, means for measuring the temperature in the ammonia converter **37**;
- 25 - a first gas cooler/condenser **38**, downstream the ammonia converter **37**, to produce an aqueous diluted nitric acid mixture **17** and a gaseous NO_x stream **22**;
- a NO_x gas compressor **40** for compressing the gaseous NO_x stream **22**, to produce a compressed or pressurized NO_x gas stream **24** at a pressure P2;
- an absorption tower **41** for absorbing the NO_x gases from the compressed NO_x gas stream **24** in water, to produce a stream of raw nitric acid-containing residual NO_x gas **27** and

30

a tail gas **5** comprising NO_x gases, comprising an absorption tower tail gas outlet **6** for evacuating the tail gas **5**;

- preferably, means for measuring the concentration of oxygen in the tail gas **5** in a tail gas stream downstream the absorption tower **41**;

5 - a heat exchange system **43** for exchanging heat between the NO_x gas/steam mixture **15** and the tail gas **5**; particularly for heating a tail gas stream with the heat from the NO_x gas/steam mixture from the ammonia converter;

10 - a second gas cooler/condenser **39** for separating and condensing steam from the compressed NO_x gas stream **24** located between the NO_x compressor and the absorption tower, particularly to produce a compressed NO_x gas stream **24** having a temperature ranging from 20 to 60 °C; and

15 - a first pressure release means or tail gas expander **7** located downstream the heat exchange system **43**, for expanding a stream of tail gas downstream the absorption tower **41**, to produce a first expanded tail gas **64**, wherein the first pressure release means or tail gas expander **7** can at least partly power the NO_x gas compressor **40**.

The revamping method comprises the steps of

20 - preferably, introducing a source of pressurised air **65** in fluid communication with the production plant, suitable for pressurizing the production plant during startup, in particular wherein the source of pressurized air is capable of providing from 2000 to 19000 m³/h of pressurized air;

 - introducing a supply or source of an oxygen-rich gas **50**, such as a high-pressure water electrolyzer, providing part of a first oxygen containing gas, upstream of and in fluid communication with the mixing apparatus **35**;

25 - preferably, introducing means for measuring the oxygen concentration in the oxygen-containing gas **56**;

30 - preferably, introducing means for adjusting the concentration of oxygen in the oxygen-containing gas **56** such that the oxygen to ammonia molar ratio at the inlet of the ammonia converter **37** is at least 1.2 or 1.25, particularly between 1.2 and 9 or between 1.25 and 9. More in particular, there may be introduced a means for regulating the concentration of ammonia and/or oxygen in the ammonia converter, particularly a means for controlling the flow of the oxygen-rich gas or the flow of the first oxygen-containing gas and/or a means for

controlling the flow of the ammonia gas stream, for maintaining the oxygen to ammonia molar ratio inside the ammonia converter at a ratio of at least 1.2 or 1.25, particularly between 1.2 and 9, between 1.25 and 9 or between 1.3 and 9;

- in particular, introducing a supply of a second oxygen-containing gas **68, 72, 77**,
5 having either (i) a pressure equal to or higher than P1 and upto P2 for supplying oxygen upstream the NO_x gas compressor, or (ii) a pressure higher than P2, for supplying oxygen to the compressed NO_x gas stream, such that a tail gas stream **5, 10, 62, 69, 80, 83, 84** contains at least 0.5% by volume of oxygen;

- introducing a means for splitting **55** a stream of tail gas downstream the absorption
10 tower **41** into a first tail gas stream **10** and a second tail gas stream **80**, wherein the first tail gas stream is in fluid communication with the first oxygen-rich gas **50**, wherein the mixing of the first tail gas stream and the first oxygen rich gas provides the first oxygen-containing gas;

- particularly introducing a means for adjusting the amount of tail gas being splitted into the first tail gas stream **10** and the second tail gas stream **80**; and

15 - removing the air compressor **36**.

The term "oxygen-rich gas" is used as defined elsewhere herein.

Typically, the heat exchange system **43** comprises at least two heat exchangers **66, 67**.
20 The person skilled in the art will realise that it is possible to split a stream of tail gas inside the heat exchange system, for example between the heat exchanger **66** and **67**. In particular, the production plant both prior to and after revamping comprises further heat exchange systems, such that the gaseous NO_x stream **22** or the NO_x compressed gas stream **24** exchange heat with the tail gas **5**.

25 As defined herein, a stream of tail gas/a tail gas stream is any gas stream downstream the absorption tower, such as located between the absorption tower **41** and the point of communication between or mixing of the first tail gas stream **10** and the (first) oxygen-rich gas **50**.

As defined herein, a means for splitting is any means suitable for splitting a tail gas
30 stream, such as to generate a first tail gas stream **10** and a second tail gas stream **80**. In particular, the means for splitting is a T-connection having one inlet and two outlets, such that

a gas flowing through the inlet of the T-connection is split into two gas streams of identical chemical composition. As defined herein, a pressure release means is any suitable means for reducing the pressure of a gas stream, such as a tail gas stream. In particular, the pressure release means may be a gas expander or a gas ejector. A gas ejector provides the benefits of a simplified equipment, wherein mixing of different gas streams is combined with the reduction of the tail gas pressure. For instance, a tail gas stream, processed via the gas ejector, may act as the motive gas, and a second gas fed to the ejector can, for example, be ambient air at a pressure (e.g. atmospheric pressure) lower than the tail gas stream as motive gas. In particular, a tail gas stream may be fed as the motive gas to a gas ejector, and a second gas fed to the ejector is oxygen gas at a pressure lower than the tail gas stream as motive gas. In this context, both the feeding of air or oxygen through the gas ejector contribute to increasing the concentration in the first tail gas stream **10** and/or a further tail gas stream **83, 84** being recycled, thereby reducing the demand on the oxygen-rich gas **50**. In particular, a tail gas stream is fed as the motive gas to the ejector and the second gas fed to the ejector is the NO_x gas/steam mixture **15** or the gaseous NO_x stream **22**.

The person skilled in the art will realise that the means for splitting can be incorporated within the (first) pressure release means, provided that the (first) pressure release means includes at least two outlets for the gas stream being depressurized, in particular one outlet for the first tail gas stream **10** and another outlet for the second tail gas stream **80**.

As defined herein, a means for adjusting the amount of tail gas being split into the first tail gas stream **10** and the second tail gas stream **80**, are any means for controlling the splitting in the means for splitting **55**. In particular, the means for splitting **55** is a T-connection as described above and the means for adjusting may be an orifice or a guide vane or a flow control valve at one or both of the outlets of the T-connection. Even more in particular, the means may be an integrated process control system, in which the temperature in the ammonia converter **37** is determined through a means for measuring the temperature. The temperature in the ammonia converter **37** is then used for controlling a flow control means in the means for splitting **55**, thereby controlling the splitting the tail gas stream, in order for the measured temperature to be maintained in the range 800-950 °C.

As defined herein, a means for adjusting the oxygen concentration is any suitable means for regulating the amount of oxygen to be introduced in the system from a measurement of the oxygen concentration, such as by using a means for measuring the concentration of oxygen. The oxygen concentration can be determined, for example, from a measurement in the gas phase using a process gas analyser. The oxygen concentration can also be determined from computing using the concentration of the oxygen source being introduced in the system, in particular the oxygen concentration of the oxygen rich gas, the flow at which the oxygen source, in particular the oxygen rich gas, is introduced in the system, particularly the flow at which the ammonia gas stream is introduced in the system and the relative flow values of the gases with which the oxygen source is mixed; in particular the relative flow values at which the oxygen rich gas and the ammonia gas stream are mixed. Using the oxygen concentration, the relevant flow of oxygen to be introduced in the system is, in turn, determined and is used in controlling the flow of oxygen, from a gaseous source of oxygen at a pre-determined concentration. Controlling of the flow of gaseous oxygen can, for example, be achieved through flow control valves. In this context, as defined herein, a means for regulating the concentration of ammonia and/or oxygen is any means suitable for achieving a target concentration of ammonia and/or oxygen. In particular, such means are gas flow control means, in particular a flow control valve or an orifice or a guiding vane, for controlling the flow of the oxygen rich gas and/or the ammonia gas stream. In particular, the means is an integrated process control system, in which the concentration of oxygen is measured, and the target flow or relevant flow of oxygen is thereby determined and achieved from controlling the flow of the first oxygen rich gas, from a gaseous source of oxygen at a pre-determined concentration.

The person skilled in the art will determine the optimal concentration of oxygen in the gases entering the ammonia converter **37** and the absorption tower **41**, in order for the catalytic conversion of ammonia to nitric oxide to proceed optimally in the ammonia converter **37** and for the absorption of NO_x gases in the absorption tower **41** to proceed optimally. Further, upon determining the oxygen content exiting the absorption tower **41**, he will also weigh out the benefits of increasing the oxygen content in the absorption tower **41**, against the drawback of a higher gas volume downstream the absorption tower **41**, which implies equipment, such as heat exchangers, of a larger size, for heating tail gas.

As defined herein, means for measuring the temperature are any means suitable for measuring and indicating the temperature in the ammonia oxidation burner. In particular, the means for measuring the temperature is a thermocouple or a thermometer suitable for measuring and indicating a temperature ranging as high as 1000 °C. More in particular, the means for measuring the temperature is an infrared thermometer for measuring and indicating a temperature ranging as high as 1000 °C.

Examples

1. Recirculation of tail-gas at 99.3%

Reference is made to Figure 2A. Ammonia **32** was mixed with pressurized air **65** in a mixing apparatus **35**. The resulting ammonia/compressed air mixture **14** was fed to an ammonia converter **37**, at a temperature ranging from 800 to 950 °C and operating at a pressure of 5.4 bara. The oxygen to ammonia mola ratio at the inlet of the ammonia converter **37** was at least 1.25. In the ammonia converter **37**, ammonia was oxidized over a mixed platinum/rhodium catalyst, thus obtaining a low-pressure NO_x gas/steam mixture **15**, comprising water and nitric oxide (NO). The heat of the mixture coming out of the ammonia converter was recovered, thereby producing steam that was supplied to a steam turbine **51** and that was also exported to a grid and used for heating the tail gas **5** as will be described below. The NO_x gas/stream mixture was subsequently cooled down in a gas cooler/condenser **38** to a temperature where the water condenses, and an aqueous diluted nitric acid mixture **17** was separated from a gaseous NO_x stream **22**. The aqueous diluted acid mixture **17** was sent to the absorption tower **41**. The gaseous NO_x stream **22** was further oxidized to further convert the NO to NO₂ and N₂O₄. The gaseous NO_x stream **22** then was compressed in the NO_x gas compressor **40** to a pressure of 12 bara, thereby producing the pressurised NO_x gaseous stream **24**. The pressurised NO_x gaseous stream **24** was cooled down in a second gas cooler/condenser **39** and sent to the absorption tower **41** too. Inside the absorption tower **41**, the NO_x gas reacted with water to produce the tail gas **5** and a stream of raw nitric acid also containing residual NO_x gas, which was subsequently fed to a bleacher **62**. The oxygen content in the tail gas **5** was maintained at 3% using the off-gases **77** from a bleacher **62** which were supplied downstream the ammonia converter **37** and upstream the NO_x gas compressor **40**. The tail gas **5** was consecutively heated in a heat exchanger **79**, treated in a De-NO_x unit **70**,

and heated by the gaseous NO_x stream **15** in the heat exchange system **43** to 500 °C, thereby producing a heated tail gas stream. The heated tail gas stream was expanded over a tail gas expander **7**, thereby producing an expanded tail gas **64**. The expanded tail gas **64** was used for heating the tail gas **5** in the heat exchanger **7** and was subsequently splitted, over a T-tube **55**,
5 into a first tail gas stream **10** representing 99.3% of the expanded tail gas **64**, and a second tail gas stream **80**. The first tail gas **10** was then mixed with oxygen-rich gas **50** having a pressure of 7 bara, thereby providing an oxygen-containing gas **56** in the absence of further pressurised air **34** being supplied, such that, during further continuous operation, tail gas **5** was produced, in the absence of an air compressor, heated, expanded and splitted and recirculated to the
10 ammonia converter **37**, together with an oxygen-rich gas **50**. The amount of the oxygen-rich gas **50** fed to the process was controlled in order to ensure that the oxygen to ammonia ratio at the inlet of the ammonia converter **37** was measured and, in case it was lower than 1.25, the amount of the oxygen-rich gas **50** was adjusted, such that the oxygen to ammonia molar ratio at the inlet of the ammonia converter **37** was at least 1.25. The temperature inside the
15 ammonia converter **37** was measured and established to have remained in the range of 800 to 950 °C. The residual 0.7 % of second tail gas stream **80** was sent to an additional tail gas expander **60**. The residual NO_x gas in the raw nitric acid stream **27** was then stripped out with a gaseous medium **72** such as an oxygen-containing gas or air, inside the bleacher unit **62**, operating at about the same pressure as the ammonia converter of 5.4 bara. The drive power
20 for both the air compressor **36** and the NO_x compressor **40** originated from the tail gas expander **7**, the additional tail gas expander **60** and the steam turbine **51**. The net power associated to the NO_x gas compressor **40**, the tail gas expander **7** and the additional tail gas expander **60** was 8 kWh/t 100% HNO₃. This power was produced by the steam turbine **51** or was provided by an electrical motor. The specific steam export amounted to 1100 to 1300
25 kg / t nitric acid.

2. Comparative example: no recirculation of tail-gas

Reference is made to Figure 1. Ammonia **32** was mixed with compressed air **34** in a mixing apparatus **35**. The oxygen to ammonia ratio at the inlet of the ammonia converter **37**
30 was at least 1.25. In the ammonia converter **37**, the ammonia in the mixture of ammonia **32** and compressed air **34** was oxidized, at a pressure of 5.4 bara, over a mixed platinum/rhodium

catalyst, thus obtaining a low-pressure NO_x gas/steam mixture **15**, comprising water and nitric oxide (NO). The heat of the mixture coming out of the ammonia converter was recovered for supplying the steam turbine **51** and was also exported to a grid and used for heating the tail gas **5** as will be described below. The NO_x gas/stream mixture was subsequently cooled down
5 in a gas cooler/condenser **38** to a temperature where the water condenses, and an aqueous diluted nitric acid mixture **17** was separated from a gaseous NO_x stream **22**. Subsequently, the gaseous NO_x stream **22** was consecutively further oxidized to further convert the NO to NO₂ and N₂O₄, cooled down again in another gas cooler/condenser **39**, and then directed to an absorption tower **41**. On the other end, the gaseous NO_x stream **22** was compressed in the
10 NO_x gas compressor **40** to a pressure of 12 bara, thereby producing the pressurised NO_x gaseous stream **24**. The pressurised NO_x gaseous stream **24** was sent to the absorption tower **41** too. Inside the absorption tower **41**, the NO_x gaseous stream **24** reacted with water to produce the tail gas **5** and a stream of raw nitric acid **27** also containing residual NO_x gas, which was fed to a bleacher **62**. The heat from the gaseous NO_x stream **15** was used for
15 heating the tail gas **5** in the heat exchange system **43** to 450 °C. The entire tail gas stream **5** was sent to the tail gas expander **7**. The residual NO_x gas in the raw nitric acid stream **27** was then stripped out with a gaseous medium **72** such as an oxygen-containing gas or air, inside the bleacher unit **62**, operating at 5.4 bara. The drive power for the air compressor **36** and the NO_x compressor **40** originated from the tail gas expander **7** and the steam turbine **51**.
20 This power was produced by the steam turbine **51**. The specific steam export amounted to 600 to 800 kg / t nitric acid.

Claims

1. A production plant for producing nitric acid at reduced power consumption and reduced emissions, comprising:

- a source of an oxygen-rich gas, particularly a source of pressurized oxygen-rich gas, such as a high pressure water electrolyzer;
- a mixing apparatus downstream the source of oxygen-rich gas, for mixing a first oxygen-containing gas with an ammonia gas stream, to produce an ammonia/oxygen-containing gas mixture;
- an ammonia converter, particularly operable at a pressure equal to or higher than P1 and lower than P2, for oxidising ammonia in the ammonia/oxygen-containing gas mixture, to produce a NO_x gas/steam mixture comprising water and nitric oxide
- a means for regulating the concentration of ammonia and/or of oxygen in the ammonia converter, particularly a means for controlling the flow of the oxygen-rich gas and/or a means for controlling the flow of the ammonia gas stream, for maintaining the oxygen to ammonia molar ratio inside the ammonia converter at a ratio of at least 1.2;
- a first gas cooler/condenser downstream the ammonia converter, to produce an aqueous diluted nitric acid mixture and a gaseous NO_x stream;
- a NO_x gas compressor for compressing the gaseous NO_x stream, to produce a compressed NO_x gas stream at a pressure P2;
- an absorption tower for absorbing the NO_x gases from the compressed NO_x gas stream in water, to produce a stream of raw nitric acid containing residual NO_x gas, and a tail gas comprising NO_x gases, comprising an absorption tower tail gas outlet for evacuating the tail gas;
- a heat exchange system located upstream the gas cooler/condenser for exchanging heat between the NO_x gas/steam mixture and the tail gas, in particular for heating a tail gas stream with the heat from the NO_x gas/steam coming from the ammonia converter;
 - a second gas cooler/condenser for separating and condensing steam from the compressed NO_x gas stream, particularly before the compressed NO_x gas stream is provided to the absorption tower;

- a supply for a second oxygen-containing gas having either (i) a pressure equal to or higher than P1 and up to Pc, for supplying oxygen downstream the ammonia converter and upstream the NOx gas compressor, or (ii) a pressure higher than P2, for supplying oxygen to the compressed NOx gas stream,
 - 5 • a means for controlling the flow of the second oxygen-containing gas, such that a tail gas stream contains at least 0.5% by volume oxygen; and
 - a first pressure release means, in particular tail gas expander, located downstream the heat exchange system, for expanding a stream of tail gas downstream the absorption tower, to produce a first expanded tail gas at a pressure equal to or higher than P1 and
10 lower than P2, wherein the first pressure release means, in particular the tail gas expander, can at least partly power the NO_x gas compressor;
- characterised in that the production plant further comprises:
- a means for splitting a tail gas into a first tail gas stream and a second tail gas stream, wherein the first tail gas is in fluid communication with the oxygen-rich gas, particularly
15 wherein the first tail gas stream has a pressure equal to or higher than P1 and up to P2, and wherein the mixing of the oxygen-rich gas and the first tail gas stream provides the first oxygen-containing gas; and

2. A production plant for producing nitric acid according to claim 1, comprising,
20 particularly a source of pressurised air for pressurizing the system, particularly during startup, in fluid communication with a system comprising:

- a source of an oxygen-rich gas, particularly a source of a pressurized oxygen-rich gas, such as a high-pressure water electrolyzer;
- a mixing apparatus downstream the source of the oxygen-rich gas, for mixing a first
25 oxygen-containing gas with an ammonia gas stream, to produce an ammonia/oxygen-containing gas mixture;
- means for measuring the oxygen concentration in the first oxygen-containing gas;
- means for adjusting the concentration of oxygen in the first oxygen-containing gas such that the oxygen to ammonia molar ratio at the inlet of the ammonia converter is
30 at least 1.2 or at least 1.25, particularly is between 1.2 and 9 or 1.25 and 9;
- means for adjusting the supply of the ammonia gas stream to the mixing apparatus;

- an ammonia converter, operable at a pressure P1, for oxidising ammonia in the ammonia/oxygen-containing gas mixture, to produce a NO_x gas/steam mixture, comprising water and nitric oxide;
- means for measuring the temperature in the ammonia converter;
- 5 • a first gas cooler/condenser downstream the ammonia converter, to produce an aqueous diluted nitric acid mixture and a gaseous NO_x stream;
- a NO_x gas compressor for compressing the gaseous NO_x stream, to produce a compressed NO_x gas stream at a pressure P2;
- an absorption tower for absorbing the NO_x gases from the compressed NO_x gas stream
10 in water, to produce a stream of raw nitric acid-containing residual NO_x gas and a tail gas comprising NO_x gases, comprising an absorption tower tail gas outlet for evacuating the tail gas;
- means for measuring the concentration of oxygen in a tail gas stream downstream the absorption tower;
- 15 • a heat exchange system located upstream the gas cooler/condenser for exchanging heat between the NO_x gas/steam mixture and the tail gas;
 - a second additional gas cooler/condenser, for separating and condensing steam from the compressed NO_x gas stream, to produce a compressed NO_x gas stream, particularly having a temperature ranging from 20 to 60 °C;
- 20 • a supply of a second oxygen-containing gas having either (i) a pressure equal to or higher than P1 and up to P2, for supplying oxygen upstream the NO_x gas compressor; or a pressure higher than P2, for supplying oxygen to the compressed NO_x gas stream, such that the tail gas contains at least 0.5% by volume oxygen; and
- 25 • a tail gas expander located downstream the heat exchange system, for expanding a stream of tail gas downstream the absorption tower, to produce a first expanded tail gas at a pressure P1, wherein the tail gas expander can at least partly power the NO_x gas compressor;

characterised in that the system further comprises:

- a means for splitting a stream of tail gas downstream the absorption tower into a first tail gas stream, in fluid communication with the oxygen-rich gas and a second tail gas stream; and
- a means for adjusting the amount of tail gas being splitted into the first tail gas stream and the second tail gas stream.

3. The production plant according to claim 1 or 2, wherein the system further comprises one or more of:

- a steam turbine, wherein the steam turbine can at least partly power the NO_x gas compressor;
- a heat exchanger for exchanging heat between the first expanded tail gas and a colder tail gas stream, wherein the first expanded tail gas exits the heat exchanger particularly at a temperature below 300 °C, and wherein the means for splitting is positioned downstream the heat exchanger and in fluid communication with the first expanded tail gas;
- a De-NO_x treatment unit; and
- a second pressure release means for expanding the second tail gas stream to atmospheric pressure, to produce a second expanded tail gas.

4. The production plant according to any one of claims 1 to 3, further comprising a bleacher for bleaching the stream of raw nitric acid-containing residual NO_x gas, to provide a stream of bleached nitric acid, having an inlet for an oxygen-rich bleaching gas, and an outlet for off-gases in fluid communication with any gas stream downstream the ammonia converter and upstream the NO_x gas compressor if the bleacher operates at a pressure equal to or higher than P₁ and up to equal to P₂, or in fluid communication with any stream downstream the NO_x gas compressor and upstream the absorption tower if the bleacher operates at a pressure higher than P₂, such that the supply for the second oxygen containing gas comes at least partly from the off-gases.

5. The production plant according to claim 4, wherein part of the oxygen-rich gas or part of the first oxygen-containing gas or part of the tail gas, is in fluid communication with the

inlet of the bleacher, such that the oxygen rich-bleaching gas is at least partly provided by part of the oxygen-rich gas by part of the first oxygen-containing gas or by part of a tail gas stream.

6. The production plant according to any one of claims 1 to 5, further comprising a stream of a second oxygen-containing gas in direct fluid communication with any tail gas stream, particularly a stream of pressurized oxygen-rich gas in direct fluid communication with any stream of tail gas downstream the absorption tower or upstream the first pressure release means.
7. The production plant according to any one of claims 1 to 6, wherein the oxygen-rich gas, the second oxygen-containing gas, the oxygen-rich bleaching gas and the bleacher off-gases are all at least partly provided by a water electrolyser, particularly a high pressure water electrolyser.
8. The production plant according to any one of claims 1 to 6, wherein the fluid communication between the source of pressurised air and the system is in direct fluid communication with the oxygen-rich gas.
9. A method for producing nitric acid at reduced power consumption and reduced emissions, in a production plant according to any one of claims 1 to 8, comprising the steps of:
- prior to step c), providing or preparing an oxygen-rich gas and a first oxygen-containing gas, and providing an ammonia gas stream;
- c) supplying the ammonia gas stream and a first oxygen-containing gas to the mixing apparatus, thereby producing the ammonia/oxygen-containing gas mixture;
- d) oxidising ammonia in the ammonia/oxygen-containing gas mixture in the ammonia converter, particularly at a pressure equal to or higher than P1 and lower than P2 and at a temperature ranging from 800 to 950 °C, thereby producing the gaseous NO_x gas/steam mixture, comprising water and nitric oxide;

e) cooling the NO_x gas in the gaseous NO_x gas/steam mixture in the heat exchange system and in the first gas/cooler condenser, thereby producing an aqueous diluted nitric acid mixture and a gaseous NO_x stream;

f) compressing the gaseous NO_x stream in the NO_x gas compressor, thereby providing the pressurized NO_x compressed gas stream having a pressure P2;

g) absorbing the pressurized gaseous NO_x stream in the absorption tower, thereby providing the stream of raw nitric acid-containing residual NO_x gas and the tail gas comprising NO_x gases;

h) heating the tail gas in the heat exchange system, with the heat from the NO_x gas/steam mixture coming from the ammonia converter, particularly to a temperature ranging from 150 to 650 °C;

i) cooling the pressurized NO_x gas stream in the second gas cooler/condenser, thereby providing a pressurized NO_x gas stream, particularly having a temperature ranging from 20 to 60 °C; and

j) expanding at least part of the tail gas obtained in step h) in a first pressure release means, thereby providing a first expanded tail gas;

characterised in that the method further comprises the steps of:

k) splitting a tail gas stream with a first means for splitting into a first tail gas stream and a second tail gas stream, and mixing the first tail gas stream with the oxygen-rich gas, thereby providing the first oxygen-containing gas;

m) adjusting the flow of the oxygen-rich gas being mixed in step k) or the flow of the ammonia gas stream, such that the oxygen to ammonia molar ratio at the inlet of the ammonia converter is maintained to a ratio of at least 1.2 or at least 1.25, particularly between 1.2 and 9 or between 1.25 and 9; and

q) adjusting the flow of the oxygen-rich gas at a pressure equal to or higher than P1 and up to P2 upstream the NO_x gas compressor, or at a pressure higher than P2 downstream the NO_x gas compressor, such that the oxygen concentration in a tail gas stream is maintained at a concentration of at least 0.5% by volume;

10. A method for producing nitric acid at reduced power consumption and reduced emissions according to claim 9, comprising the steps of:

- a) preferably, pressurizing the system by supplying pressurised air in the system;
 - b) preferably, operating the NO_x gas compressor or a first pressure release means, preferably a tail gas expander, using external power, thereby inducing a pressurised air flow in the system and a pressure P2, downstream the NO_x gas compressor;
 - 5 c) supplying the ammonia gas stream and a first oxygen containing gas to the mixing apparatus, thereby producing the ammonia/oxygen-containing gas mixture;
 - d) oxidising ammonia in the ammonia/oxygen-containing gas mixture in the ammonia converter, particularly at a pressure P1 and at a temperature ranging from 800 to 950 °C, thereby producing the gaseous NO_x gas/steam mixture, comprising water and nitric oxide;
 - 10 e) cooling the NO_x gas in the gaseous NO_x gas/steam mixture in the heat exchange system and in the first gas/cooler condenser, thereby producing an aqueous diluted nitric acid mixture and a gaseous NO_x stream;
 - f) compressing the gaseous NO_x stream in the NO_x gas compressor, thereby providing the pressurized NO_x compressed gas stream having a pressure P2;
 - 15 g) absorbing the pressurized gaseous NO_x stream in the absorption tower, thereby providing the stream of raw nitric acid-containing residual NO_x gas and the tail gas comprising NO_x gases;
 - h) heating the tail gas in the heat exchange system, with the heat from the NO_x gas/steam mixture coming from the ammonia converter, particularly to a temperature ranging from 150
 - 20 to 650 °C;
 - i) cooling the pressurized NO_x gas stream in the second gas cooler/condenser, thereby providing a pressurized NO_x gas stream, particularly having a temperature ranging from 20 to 60 °C; and
 - j) expanding the tail gas obtained in step h) in the tail gas expander, thereby providing the first
 - 25 expanded tail gas;
- characterised in that the method further comprises the steps of:
- k) splitting a tail gas stream with a means for splitting into a first tail gas stream and a second tail gas stream and mixing the first tail gas stream with the oxygen-rich gas, thereby providing the oxygen-containing gas;
 - 30 l) measuring the oxygen concentration in the oxygen-containing gas;

m) if the oxygen concentration measured in step l) is such that the oxygen to ammonia molar ratio in the ammonia converter is less than 1.2 or 1.25, adjusting the supply of the oxygen-rich gas, for instance having a pressure P2, and being mixed in step k) or adjusting the supply of the ammonia gas stream in step c), such that the oxygen to ammonia molar ratio at the inlet of the ammonia converter is at least 1.2 or 1.25, preferably between 1.2 and 9 or between 1.25 and 9;

n) measuring the temperature in the ammonia converter;

o) adjusting the volume of the first tail gas stream being mixed in step k) or the ammonia gas stream supplied in step c), if the temperature measured in step n) is outside the range of 800-950 °C, such that the temperature in the ammonia converter is maintained in the range of 800-950 °C;

p) measuring the oxygen concentration in a tail gas downstream the absorption tower;

q) if the oxygen concentration measured in step p) is less 0.5% by volume oxygen, adjusting the supply of the oxygen-rich gas at a pressure equal to or higher than P1 and up to P2 upstream the NO_x gas compressor, or at a pressure higher than P2 downstream the NO_x gas compressor, or adjusting the flow of the second oxygen-containing gas, such that the tail gas contains at least 0.5% by volume oxygen;

r) repeating steps c) to q).

11. The method according to claim 9 or 10, wherein, the first tail gas stream, particularly first expanded tail gas stream, mixed in step k) is particularly obtained after step j), and wherein the method further comprises the steps of:

s) particularly before step k), heating up, in the heat exchanger, a tail gas stream that is colder than the first expanded tail gas with the first expanded tail gas, thereby bringing the first expanded tail gas to a temperature below 300°C, in particular before step k), heating up, in the heat exchanger the tail gas obtained in step g) with the first expanded tail gas obtained in step j), thereby bringing the tail gas to be mixed in step k) to a temperature below 300 °C;

t) treating the tail gas stream, particularly obtained in step s, in the De-NO_x treatment unit;

u) expanding the second tail gas stream in the second pressure release means, thereby providing the second expanded tail gas; and

v) recovering at least part of the steam generated in the ammonia converter in the steam turbine.

12. The method according to any one of claims 9 to 11, further comprising the step of:

5 w) bleaching the stream of raw nitric acid-containing residual NO_x gas in the bleacher, thereby producing the stream of bleached nitric acid.

13. The method according to claim 12, further comprising the step of:

10 w1) supplying part of the oxygen-rich or part of the first oxygen-containing gas obtained in step k) or part of the tail gas obtained in step g), to the inlet of the bleacher in step w).

14. The method according to any one of claims 9 to 13, further comprising the step of:

15 x) supplying a stream of an oxygen-rich gas, particularly as a stream of a pressurized oxygen-rich gas, to a tail gas stream, particularly to a tail gas stream upstream the first pressure release means.

15. The method according to any one of claims 9 to 14, further comprising the steps of:

20 y) operating the water electrolyser, thereby producing oxygen-gas, particularly operating a high pressure water electrolyser, thereby producing pressurized oxygen gas; and
z) providing, from the oxygen produced by the water electrolyser in step y), at least part of the oxygen-rich gas, the second oxygen containing gas, the oxygen-rich bleaching gas, and the bleacher off gases.

25 16. The method according to any of claims 10 to 15, wherein, in step a), the pressurised air is supplied in the stream in direct fluid communication with the oxygen-rich gas.

17. The use of the production plant according to any one of claims 1 to 8 for performing the method according to any one of claims 9 to 16.

30 18. A method for revamping an existing production plant for producing nitric acid, wherein the existing production plant comprises:

- an air compressor for providing a compressed air stream;
- a mixing apparatus, for mixing the compressed air stream with an ammonia gas stream, to produce an ammonia/oxygen-containing gas mixture;
- an ammonia converter operable at a pressure equal to or higher than P1 but lower than P2, for oxidising ammonia in the ammonia/oxygen-containing gas mixture, to produce a NO_x gas/steam mixture, comprising water and nitric oxide;
- a first gas cooler/condenser, downstream the ammonia converter, to produce an aqueous diluted nitric acid mixture, and a gaseous NO_x stream;
- a NO_x gas compressor for compressing the gaseous NO_x stream, to produce a pressurized NO_x gas stream at a pressure P2;
- an absorption tower for absorbing the NO_x gases from the pressurized NO_x gas stream in water, to produce a stream of raw nitric acid-containing residual NO_x gas and a tail gas comprising NO_x gases;
- a heat exchange system for exchanging heat between the NO_x/gas steam mixture and the tail gas, particularly for heating a tail gas stream with the heat from the NO_x gas/steam mixture from the ammonia converter;
- a second gas cooler/condenser for separating and condensing steam from the compressed NO_x gas stream between the NO_x compressor and the absorption tower, and
- a tail gas expander for expanding a stream of tail gas downstream the absorption tower, to produce an expanded tail gas at a pressure P1, wherein the tail gas expander can at least partly power the NO_x gas compressor

into a production plant according to any one of claims 1 to 8, comprising the steps of:

- introducing a source of pressurised air in fluid communication with the production plant;
- introducing a supply or source of an oxygen-rich gas, such as a high pressure water electrolyser, providing part of a first oxygen-containing gas, upstream of and in fluid communication with the mixing apparatus;
- introducing a means for regulating the concentration of ammonia and/or oxygen in the ammonia converter, particularly a means for controlling the flow of the oxygen-rich gas or the flow of the first oxygen-containing gas and/or a means for controlling

the flow of the ammonia gas stream, for maintaining the oxygen to ammonia molar ratio inside the ammonia converter at a ratio of at least 1.2 or at least 1.25, particularly between 1.2 and 9 or between 1.25 and 9;

- introducing a supply of a second oxygen-containing gas, having either (i) a pressure equal to or higher than P1 and upto P2 for supplying oxygen upstream the NOx gas compressor, or (ii) a pressure higher than P2, for supplying oxygen to the compressed NOx gas stream, such that a tail gas stream contains at least 0.5% by volume of oxygen;
- introducing means for splitting a stream of tail gas into a first tail gas stream and a second tail gas stream, wherein the first tail gas stream has a pressure equal to or higher than P1 and upto P2, and is in fluid communication with the oxygen-rich gas, which, upon mixing with the oxygen-rich gas provides the first oxygen-containing gas;
- particularly, introducing means for adjusting the amount of tail gas being split into the first tail gas stream and the second tail gas stream; and
- removing the air compressor.

Figures

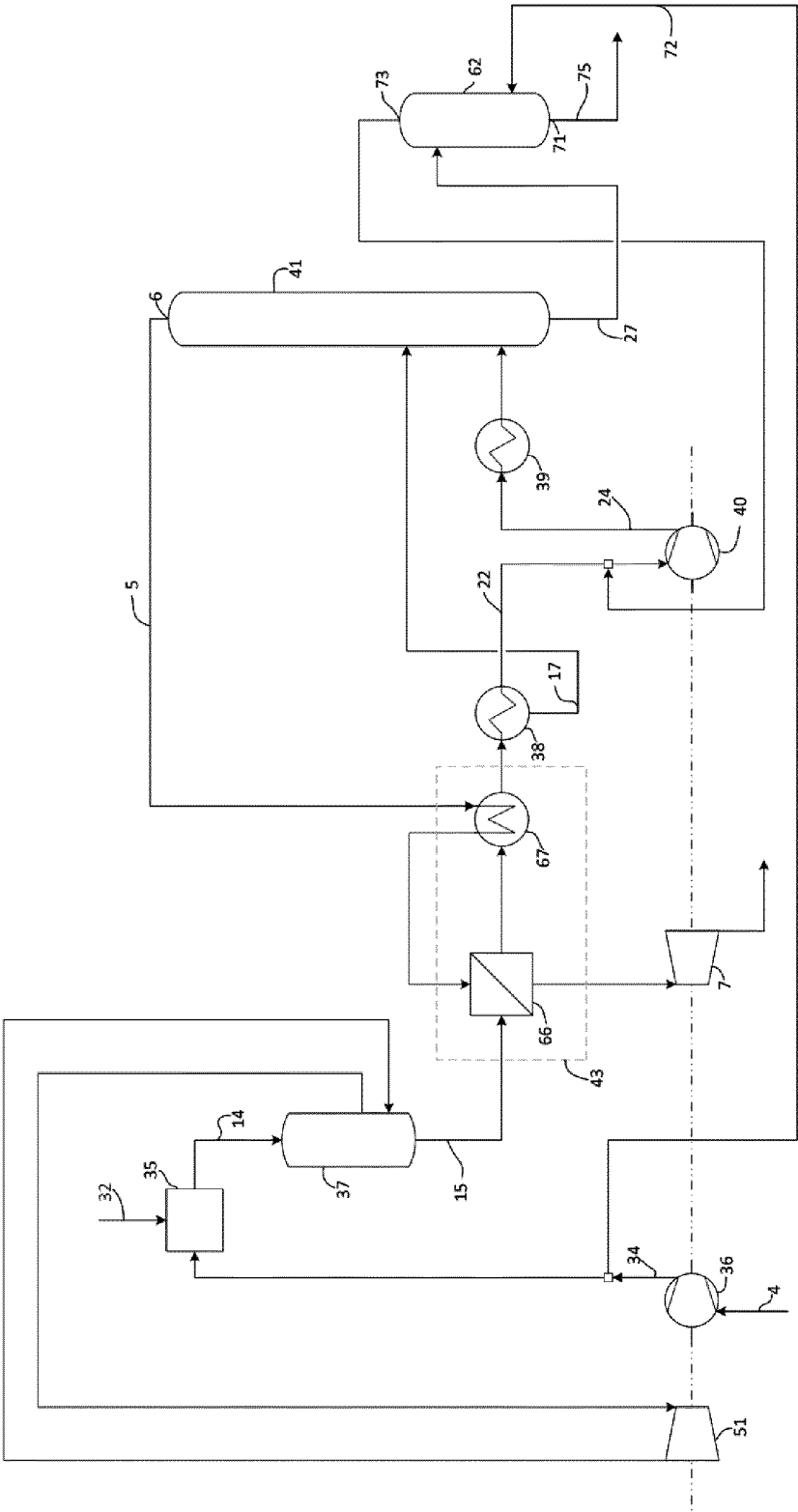


FIGURE 1 (Prior art)

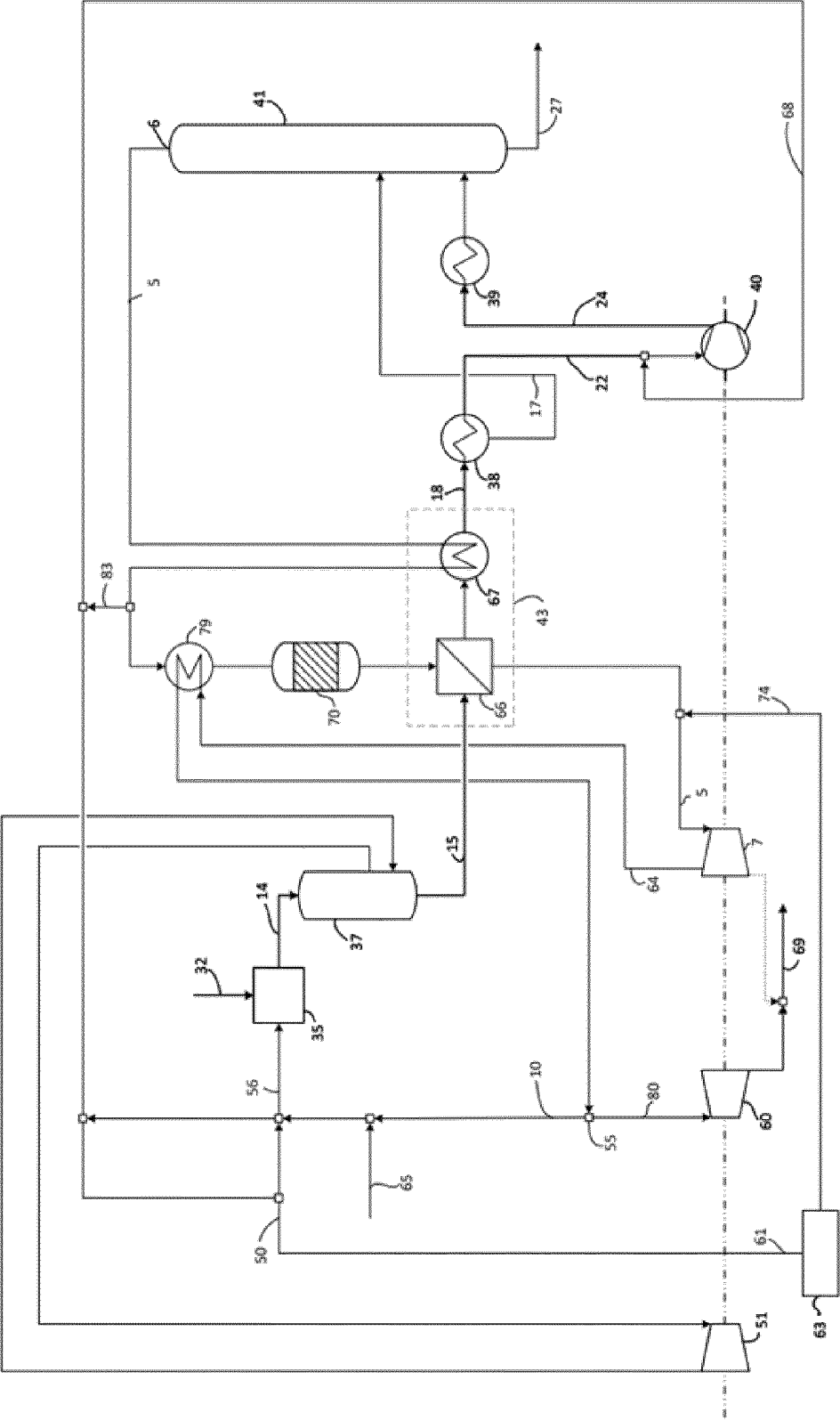


FIGURE 2A

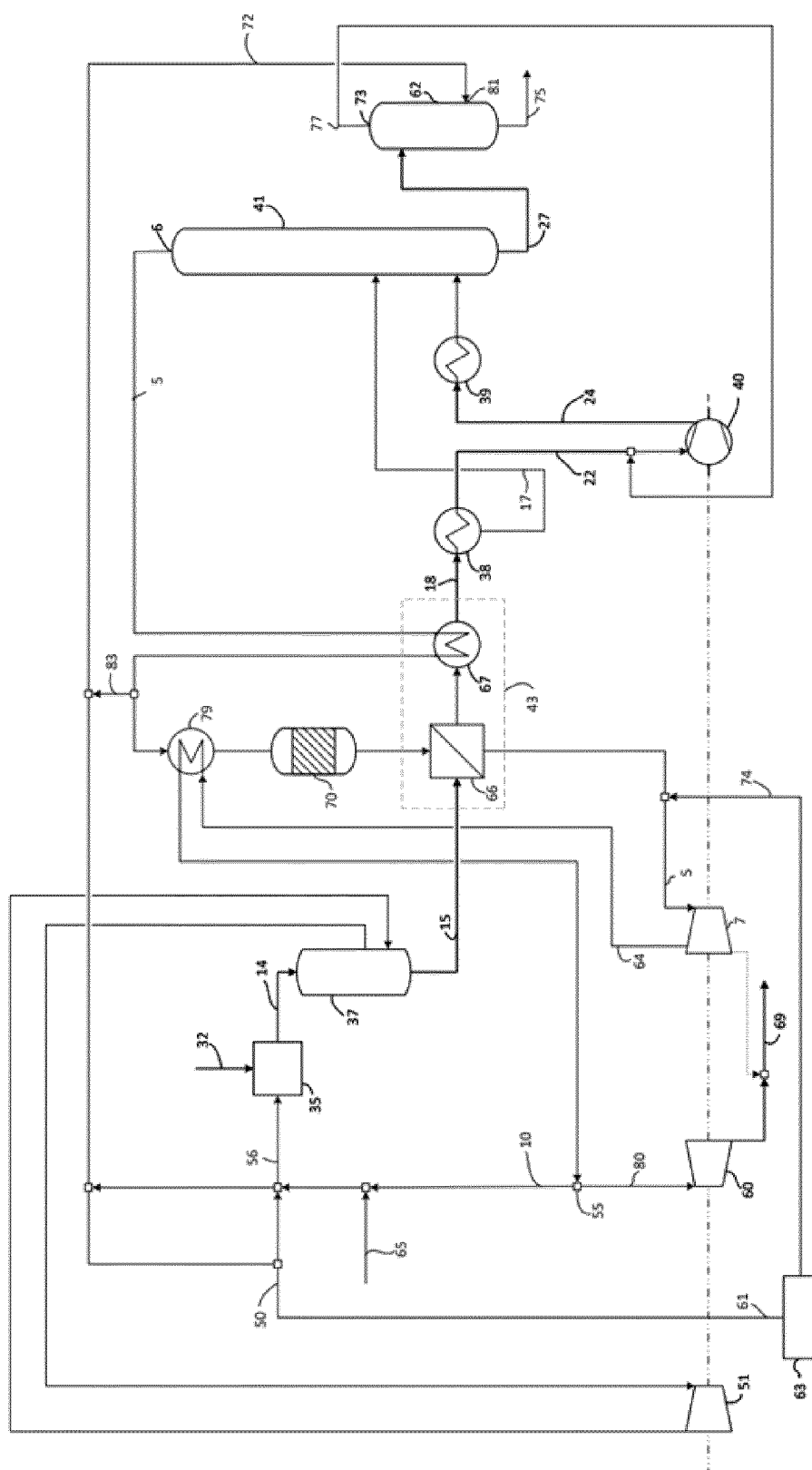


FIGURE 2B

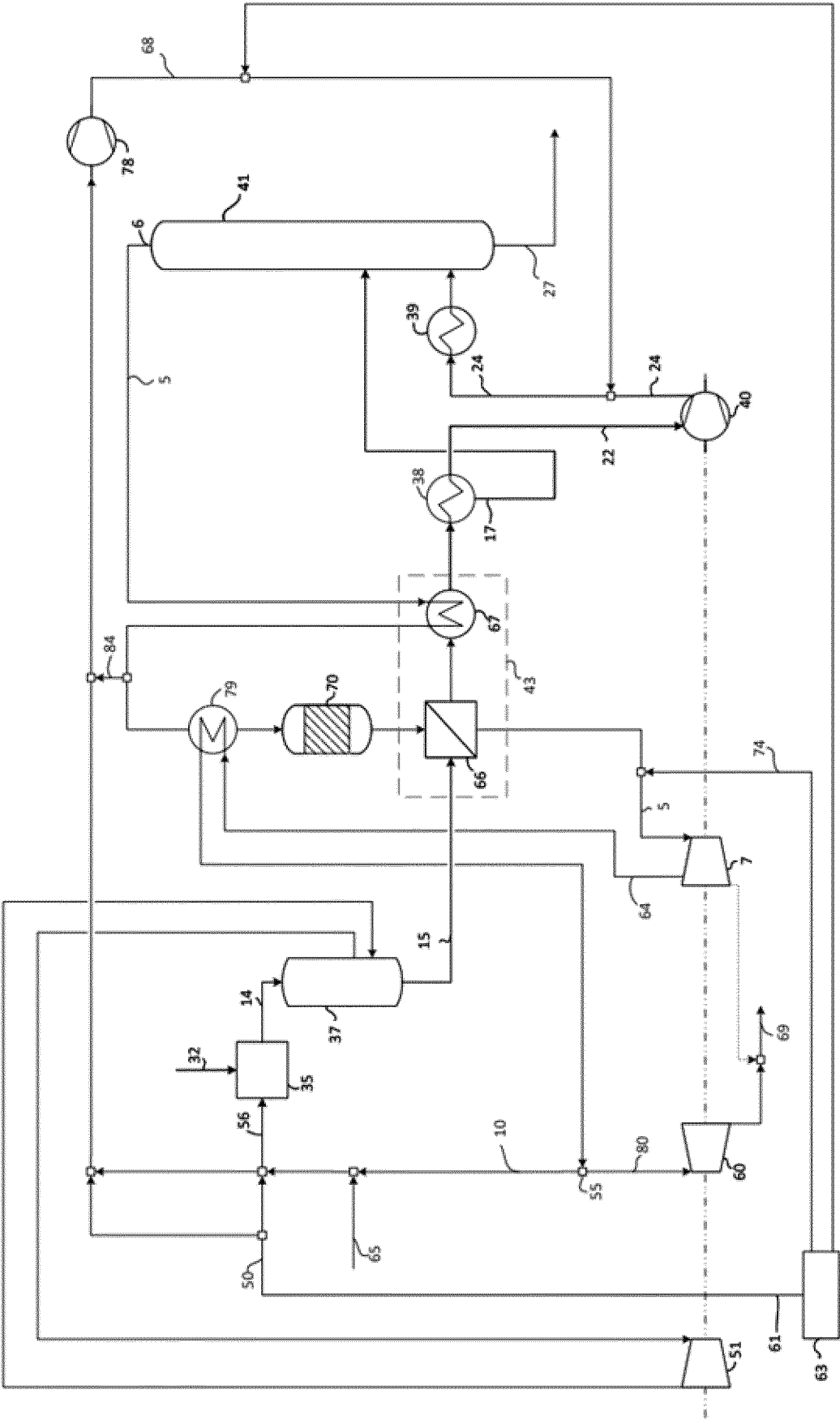


FIGURE 2C

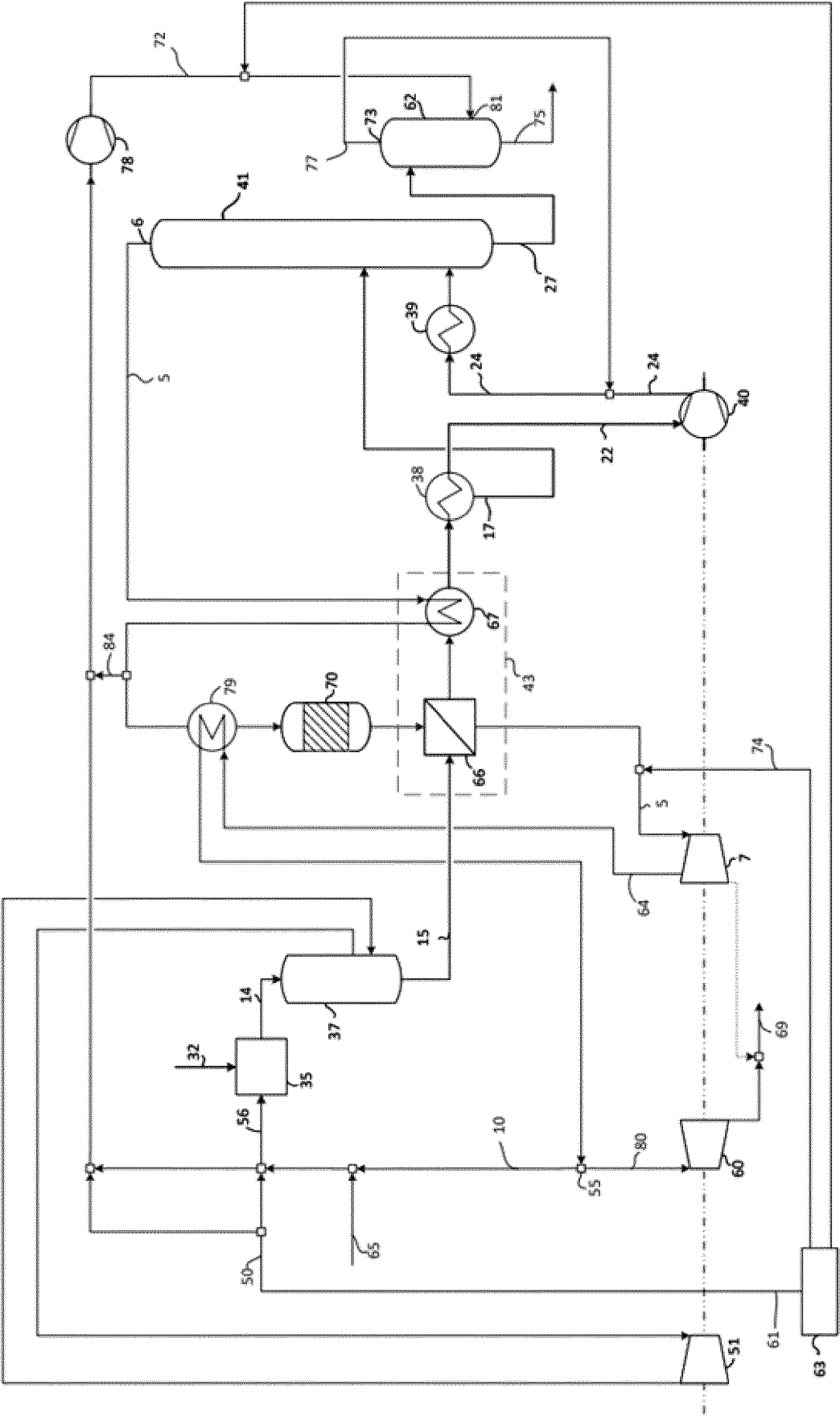


FIGURE 2D

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2022/073638

A. CLASSIFICATION OF SUBJECT MATTER INV. C01B21/26 B01D53/56 C01B21/28 C01B21/38 ADD.		
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) C01B 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 practicable, search terms used) EPO-Internal		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 10 2013 004341 A1 (THYSSENKRUPP UHDE GMBH [DE]) 18 September 2014 (2014-09-18) claims 1-27 paragraphs [0082] - [0104], [0107] - [0111] figures 1,2 -----	1-18
A	US 6 264 910 B1 (MAURER RAINER [DE] ET AL) 24 July 2001 (2001-07-24) claims 1-7 column 5, line 38 - column 6, line 30 figure 1 -----	1-18
A	"Latest nitric acid process design", NITROGEN,, no. 165, 1 January 1987 (1987-01-01), pages 32-40, XP001266113, figure 2 -----	1-16
☐ Further documents are listed in the continuation of Box C. ☒ See patent family 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 application or patent 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		
Date of the actual completion of the international search		Date of mailing of the international search report
28 November 2022		06/12/2022
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Gerwann, Jochen

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2022/073638

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 102013004341 A1	18-09-2014	AU 2014231220 A1	01-10-2015
		BR 112015022805 A2	18-07-2017
		CA 2905560 A1	18-09-2014
		CN 105209382 A	30-12-2015
		DE 102013004341 A1	18-09-2014
		EP 2969937 A1	20-01-2016
		ES 2681599 T3	14-09-2018
		KR 20150128949 A	18-11-2015
		RU 2015140607 A	20-04-2017
		US 2016039674 A1	11-02-2016
		US 2019359486 A1	28-11-2019
		WO 2014139678 A1	18-09-2014

US 6264910 B1	24-07-2001	EP 0945400 A2	29-09-1999
		ES 2177162 T3	01-12-2002
		JP 4469437 B2	26-05-2010
		JP H11314907 A	16-11-1999
		US 6264910 B1	24-07-2001

PATENT COOPERATION TREATY

From the INTERNATIONAL SEARCHING AUTHORITY

PCT

To:

De Clercq & Partners
Edgard Gevaertdreef 10a
9830 Sint-Martens-Latem
BELGIQUE

NOTIFICATION OF TRANSMITTAL OF
THE INTERNATIONAL SEARCH REPORT AND
THE WRITTEN OPINION OF THE INTERNATIONAL
SEARCHING AUTHORITY, OR THE DECLARATION

(PCT Rule 44.1)

Date of mailing (day/month/year) 6 December 2022 (06-12-2022)	
Applicant's or agent's file reference YARA-241-PCT	FOR FURTHER ACTION See paragraphs 1 and 4 below
International application No. PCT/EP2022/073638	International filing date (day/month/year) 25 August 2022 (25-08-2022)
Applicant YARA INTERNATIONAL ASA	

1. ☒ The applicant is hereby notified that the international search report and the written opinion of the International Searching Authority have been established and are transmitted herewith.

Filing of amendments and statement under Article 19:

The applicant is entitled, if he so wishes, to amend the claims of the international application (see Rule 46):

When? The time limit for filing such amendments is normally two months from the date of transmittal of the international search report.

How? Directly to the International Bureau preferably through ePCT, or on paper to:
The International Bureau of WIPO, 34 chemin des Colombettes, 1211 Geneva 20, Switzerland

For more detailed instructions, see the *PCT Applicant's Guide*, International Phase, paragraphs 9.004 - 9.011.

2. ☐ The applicant is hereby notified that no international search report will be established and that the declaration under Article 17(2)(a) to that effect and the written opinion of the International Searching Authority are transmitted herewith.

3. ☐ **With regard to any protest** against payment of (an) additional fee(s) under Rule 40.2, the applicant is notified that:

☐ the protest together with the decision thereon has been transmitted to the International Bureau together with any request to forward the texts of both the protest and the decision thereon to the designated Offices.

☐ no decision has been made yet on the protest; the applicant will be notified as soon as a decision is made.

4. **Reminders**

The applicant may **submit comments on an informal basis on the written opinion of the International Searching Authority** to the International Bureau. These comments will be made available to the public after international publication. The International Bureau will send a copy of such comments to all designated Offices unless an international preliminary examination report has been or is to be established.

Shortly after the expiration of **18 months from the priority date, the international application will be published** by the International Bureau. If the applicant wishes to avoid or postpone publication, a notice of withdrawal of the international application, or of the priority claim, must reach the International Bureau before the completion of the technical preparations for international publication (Rules 90bis.1 and 90bis.3).

Within **19 months** from the priority date, but only in respect of some designated Offices, a demand for international preliminary examination must be filed if the applicant wishes to postpone the entry into the national phase **until 30 months** from the priority date (in some Offices even later); otherwise, the applicant must, **within 20 months** from the priority date, perform the prescribed acts for **entry into the national phase** before those designated Offices. In respect of other designated Offices, the time limit of **30 months** (or later) will apply even if no demand is filed within 19 months. For details about the applicable time limits, Office by Office, see www.wipo.int/pct/en/texts/time_limits.html and the *PCT Applicant's Guide*, National Chapters.

Within **22 months from the priority date, the applicant may request that a supplementary international search be carried out** by a different International Searching Authority that offers this service (Rule 45bis.1). The procedure for requesting supplementary international search is described in the *PCT Applicant's Guide*, International Phase, paragraphs 8.006-8.032.

Name and mailing address of the International Searching Authority  European Patent Office, P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk Tel. (+31-70) 340-2040 Fax: (+31-70) 340-3016	Authorized officer MARCHETTO, Lisa Tel: +49 (0)89 2399-2796
--	---

PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference YARA-241-PCT	FOR FURTHER ACTION see Form PCT/ISA/220 as well as, where applicable, item 5 below.	
International application No. PCT/EP2022/073638	International filing date (<i>day/month/year</i>) 25 August 2022 (25-08-2022)	(Earliest) Priority Date (<i>day/month/year</i>) 25 August 2021 (25-08-2021)
Applicant YARA INTERNATIONAL ASA		

This international search report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This international search report consists of a total of 3 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

1. **Basis of the report**

a. With regard to the **language**, the international search was carried out on the basis of:

- ☒ the international application in the language in which it was filed
☐ a translation of the international application into _____, which is the language of a translation furnished for the purposes of international search (Rules 12.3(a) and 23.1(b))

b. ☐ This international search report has been established taking into account the **rectification of an obvious mistake** authorized by or notified to this Authority under Rule 91 (Rule 43.6bis(a)).

c. ☐ With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, see Box No. I.

2. ☐ **Certain claims were found unsearchable** (See Box No. II)

3. ☐ **Unity of invention is lacking** (see Box No III)

4. With regard to the **title**,

- ☒ the text is approved as submitted by the applicant
☐ the text has been established by this Authority to read as follows:

5. With regard to the **abstract**,

- ☒ the text is approved as submitted by the applicant
☐ the text has been established, according to Rule 38.2, by this Authority as it appears in Box No. IV. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority

6. With regard to the **drawings**,

- a. the figure of the **drawings** to be published with the abstract is Figure No. _____
☐ as suggested by the applicant
☐ as selected by this Authority, because the applicant failed to suggest a figure
☐ as selected by this Authority, because this figure better characterizes the invention
- b. ☒ none of the figures is to be published with the abstract

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2022/073638

A. CLASSIFICATION OF SUBJECT MATTER INV. C01B21/26 B01D53/56 C01B21/28 C01B21/38 ADD.				
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) C01B 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 practicable, search terms used) EPO-Internal				
C. DOCUMENTS CONSIDERED TO BE RELEVANT				
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.		
X	DE 10 2013 004341 A1 (THYSSENKRUPP UHDE GMBH [DE]) 18 September 2014 (2014-09-18) claims 1-27 paragraphs [0082] - [0104], [0107] - [0111] figures 1,2 -----	1-18		
A	US 6 264 910 B1 (MAURER RAINER [DE] ET AL) 24 July 2001 (2001-07-24) claims 1-7 column 5, line 38 - column 6, line 30 figure 1 -----	1-18		
A	"Latest nitric acid process design", NITROGEN,, no. 165, 1 January 1987 (1987-01-01), pages 32-40, XP001266113, figure 2 -----	1-16		
☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.				
* Special categories of cited documents : <table border="0"> <tr> <td> "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent 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 </td> <td> "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 </td> </tr> </table>			"A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent 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
"A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent 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			
Date of the actual completion of the international search		Date of mailing of the international search report		
28 November 2022		06/12/2022		
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Gerwann, Jochen		

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2022/073638

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 102013004341 A1	18-09-2014	AU 2014231220 A1	01-10-2015
		BR 112015022805 A2	18-07-2017
		CA 2905560 A1	18-09-2014
		CN 105209382 A	30-12-2015
		DE 102013004341 A1	18-09-2014
		EP 2969937 A1	20-01-2016
		ES 2681599 T3	14-09-2018
		KR 20150128949 A	18-11-2015
		RU 2015140607 A	20-04-2017
		US 2016039674 A1	11-02-2016
		US 2019359486 A1	28-11-2019
		WO 2014139678 A1	18-09-2014

US 6264910 B1	24-07-2001	EP 0945400 A2	29-09-1999
		ES 2177162 T3	01-12-2002
		JP 4469437 B2	26-05-2010
		JP H11314907 A	16-11-1999
		US 6264910 B1	24-07-2001

PATENT COOPERATION TREATY

From the
INTERNATIONAL SEARCHING AUTHORITY

To:

see form PCT/ISA/220

PCT

WRITTEN OPINION OF THE INTERNATIONAL SEARCHING AUTHORITY (PCT Rule 43bis.1)

Date of mailing
(day/month/year) see form PCT/ISA/210 (second sheet)

Applicant's or agent's file reference
see form PCT/ISA/220

FOR FURTHER ACTION
See paragraph 2 below

International application No.
PCT/EP2022/073638

International filing date (day/month/year)
25.08.2022

Priority date (day/month/year)
25.08.2021

International Patent Classification (IPC) or both national classification and IPC
INV. C01B21/26 B01D53/56 C01B21/28 C01B21/38

Applicant
YARA INTERNATIONAL ASA

1. This opinion contains indications relating to the following items:

- ☒ Box No. I Basis of the opinion
- ☐ Box No. II Priority
- ☐ Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- ☐ Box No. IV Lack of unity of invention
- ☒ Box No. V Reasoned statement under Rule 43bis.1(a)(i) with regard to novelty, inventive step and industrial applicability; citations and explanations supporting such statement
- ☐ Box No. VI Certain documents cited
- ☐ Box No. VII Certain defects in the international application
- ☐ Box No. VIII Certain observations on the international application

2. FURTHER ACTION

If a demand for international preliminary examination is made, this opinion will usually be considered to be a written opinion of the International Preliminary Examining Authority ("IPEA") except that this does not apply where the applicant chooses an Authority other than this one to be the IPEA and the chosen IPEA has notified the International Bureau under Rule 66.1bis(b) that written opinions of this International Searching Authority will not be so considered.

If this opinion is, as provided above, considered to be a written opinion of the IPEA, the applicant is invited to submit to the IPEA a written reply together, where appropriate, with amendments, before the expiration of 3 months from the date of mailing of Form PCT/ISA/220 or before the expiration of 22 months from the priority date, whichever expires later.

For further options, see Form PCT/ISA/220.

Name and mailing address of the ISA:



European Patent Office
D-80298 Munich
Tel. +49 89 2399 - 0
Fax: +49 89 2399 - 4465

Date of completion of
this opinion

see form
PCT/ISA/210

Authorized Officer

Gerwann, Jochen

Telephone No. +49 89 2399-0



Box No. I Basis of the opinion

1. With regard to the **language**, this opinion has been established on the basis of:
 - ☒ the international application in the language in which it was filed.
 - ☐ a translation of the international application into , which is the language of a translation furnished for the purposes of international search (Rules 12.3(a) and 23.1 (b)).
2. ☐ This opinion has been established taking into account the **rectification of an obvious mistake** authorized by or notified to this Authority under Rule 91 (Rule 43bis.1(a))
3. ☐ With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, this opinion has been established on the basis of a sequence listing:
 - a. ☐ forming part of the international application as filed.
 - b. ☐ furnished subsequent to the international filing date for the purposes of international search (Rule 13ter.1(a)),
 - ☐ accompanied by a statement to the effect that the sequence listing does not go beyond the disclosure in the international application as filed.
4. ☐ With regard to any nucleotide and/or amino acid sequence disclosed in the international application, this opinion has been established to the extent that a meaningful opinion could be formed without a WIPO Standard ST.26 compliant sequence listing.
5. Additional comments:

Box No. V Reasoned statement under Rule 43bis.1(a)(i) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes: Claims	<u>1-18</u>
	No: Claims	
Inventive step (IS)	Yes: Claims	
	No: Claims	<u>1-18</u>
Industrial applicability (IA)	Yes: Claims	<u>1-18</u>
	No: Claims	

2. Citations and explanations

see separate sheet

Re Item V

Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

Reference is made to the following documents:

- D1 DE 10 2013 004341 A1 (THYSSENKRUPP UHDE GMBH [DE]) 18 September 2014 (2014-09-18)
- D2 US 6 264 910 B1 (MAURER RAINER [DE] ET AL) 24 July 2001 (2001-07-24)
- D3 "Latest nitric acid process design",
NITROGEN,,
no. 165, 1 January 1987 (1987-01-01), pages 32-40, XP001266113,

- 1 The present application does not meet the criteria of Article 33(1) PCT, because the subject-matter of claims 1-18 does not involve an inventive step in the sense of Article 33(3) PCT.

Document D1 is regarded as being the prior art closest to the subject-matter of claim 1, and discloses a dual-pressure plant for producing HNO₃ (fig. 2). Air (100) is compressed (1) and directed via line (120) together with vaporized NH₃ (2) and O₂ depleted gas mixture (220) into oxidation reactor (3). The gas mixture, entering (3) has a molar ratio of O₂/NH₃ from 1.25 to 1.75. NO_x/H₂O, leaving (3) is first cooled in the heat-exchanger (4) and afterwards directed to the condenser (5), from which non-condensed NO_x leaves via line (140). Diluted HNO₃, leaving (5) is directed to the absorption tower (8) via line (150). NO_x, leaving (5) via (140) is compressed in (7) and directed to (8). HNO₃ is obtained from (8) and leaves via line (160). Tail gas leaves (8) via line (180) and is heated in the heat exchanger (4) and purified in (9). Purified tail gas leaves (9) via line (190) and is split in two streams, wherein one part is directed to the turbine (10) for recovering energy, while the remaining purified tail gas is expanded in (11), before redirected with the compressed air from compressor (1) via line (120) into the reactor (3) (D1: claims 1-27; paragraphs [0082]-[0104], [0107]-[0111]; fig. 1, 2).

The subject-matter of claim 1 therefore differs from this known document D1 in that the plant comprises means for measuring and adjusting different gas concentration.

The subject-matter of claim 1 is therefor novel (Art. 33(2) PCT).

Although no information provided in the present application, the technical effect linked to the differentiating feature can be seen in running the plant under optimized conditions.

The problem to be solved by the present invention may be regarded as to run the plant for preparing HNO₃ und optimized production conditions.

The solution proposed in claim 1 of the present application cannot be considered to involve an inventive step (Article 33(3) PCT):

Using "means" for measuring and adjusting gas concentrations in a modern plant for producing HNO₃ by oxidation of NH₃ is what a skilled person would apply the exercise of inventive skill, in order to solve the problem posed.

Therefore, the subject-matter of claim 1 does not fulfil the requirement of Art. 33(3) PCT.

Dependent claims 2-8 do not appear to contain any additional features which, in combination with the features of any claim to which they refer, meet the requirements of the PCT in respect of novelty and/or inventive step.

Present claim 9 discloses a method for producing HNO₃ in a production plant according to any one of claims 1-8.

With regard to novelty and inventive step, the same arguments apply mutatis mutandis to the subject-matter of independent claim 9 and of dependent claims 10-16.

Present claim 17 discloses a plant according to any one of claims 1-8 for performing the method according to any one of claims 9-16.

With regard to novelty and inventive step, the same arguments appl mutatis mutandis to the subject-matter of independent claim 17.

Present claim 18 discloses a method for revamping a plant for producing HNO₃. With regard to novelty and inventive step, the same arguments appl mutatis mutandis to the subject-matter of independent claim 18.

Information on Search Strategy - Pilot phase (see OJ 2015, A86)

The type of information contained in this sheet may change during the pilot for improving the usefulness of this new service.

Application Number

PCT/EP2022/073638

TITLE: DUAL PRESSURE SYSTEM FOR PRODUCING NITRIC ACID AND METHOD OF OPERATING THEREOF

APPLICANT: YARA INTERNATIONAL ASA

IPC CLASSIFICATION: C01B21/26, B01D53/56, C01B21/28, C01B21/38

EXAMINER: Gerwann, Jochen

CONSULTED DATABASES: NPL

CLASSIFICATION SYMBOLS DEFINING EXTENT OF THE SEARCH:

IPC:

CPC: C01B21/26, B01D53/56, C01B21/28, C01B21/38

FI/F-TERMS:

KEYWORDS OR OTHER ELEMENTS FEATURING THE INVENTION:

dual pressure, HNO₃, pressurized air, redirecting tail gas, turbine

Possible steps after receipt of the international search report (ISR) and written opinion of the International Searching Authority (WO/ISA)

General information

For all international applications, the competent International Searching Authority (**ISA**) will establish an international search report (**ISR**) accompanied by a written opinion of the International Searching Authority (**WO/ISA**). The **WO/ISA** may be responded to by

- filing informal comments with the **International Bureau of WIPO (IB)** (where no demand for international preliminary examination (**demand**) is filed)
- filing amendments under Art. 19 PCT (this can be done whether or not a **demand** is filed)
- filing amendments under Art. 34 PCT and/or formal observations in response to objections raised in the **WO/ISA** (where a **demand** is actually filed)

This document explains these possibilities.

Filing informal comments

After receipt of the **ISR and WO/ISA**, the applicant may file informal comments on the **WO/ISA, directly with the IB** (see International Search and Preliminary Examination Guidelines 2.15). These will be communicated to the designated/elected Offices, together with the International Preliminary Report on Patentability (**IPRP**) at 30 months from the priority date.

Amending claims under Art. 19 PCT

The applicant may file **amended claims** under Art. 19 PCT, **directly with the IB** by the later of the following dates:

- 2 months from the date of mailing of the **ISR** and the **WO/ISA**
- 16 months from the priority date

However, any such amendment received by the **IB** after the expiration of the applicable time limit shall be **considered to have been received on time** by the **IB**, if it reaches it **before** the technical preparations for international publication have been completed (the 15th day prior to the date of publication, see PCT Applicant's Guide, International Phase, 9.013).

For further information, please see Rule 46 PCT as well as form PCT/ISA/220.

Please also note that, when filing amended claims under Art. 19 PCT, such amendments shall be **accompanied by a letter** identifying the amendments made and also the basis for the amendments in the application as originally filed (Rule 46.5(b) PCT). Where a **demand** is filed, failure to comply with this requirement may result in the amendments being ignored in the International Preliminary Examination Report (**IPER**), see Rule 70.2(c-bis) PCT.

Filing a demand for international preliminary examination

In principle, the **WO/ISA** will be considered to be the written opinion of the International Preliminary Examining Authority (**IPEA**). Where the **WO/ISA** issued by the **EPO** as **ISA** gives a positive opinion on the international application and the invention to which it relates, filing a **demand** with the **EPO** as **IPEA** would normally be unnecessary, since a positive IPRP would anyway be established by the **IB** based on the **WO/ISA** (see also further below).

If the applicant wishes to file a **demand** (for example, to allow him to argue his case in international preliminary examination with regard to objections raised in a negative **WO/ISA** before the **IPEA** issues an **IPER**), this must be done before expiration of **3 months after the date of mailing of the ISR and WO/ISA** or **22 months after priority date**, whichever expires later (Rule 54*bis* PCT). Amendments under Art. 34 PCT can be filed with the **IPEA**, normally at the same time as filing the demand (Rule 66.1(b) PCT) or within the time limit set for reply to any written opinion issued during international preliminary examination by the **IPEA**.

If a **demand** is filed at the **EPO** as **IPEA** and no comments/amendments have been received by the time the **EPO** starts drawing up the **IPER** (Rule 66.4*bis* PCT), the **WO/ISA** will be transformed by the **IPEA** into an **IPER** (also called the **IPRP (Chapter II)** which would merely reflect the content of the **WO/ISA** (OJ 10/2011, 532). The **demand** can still be withdrawn (Art. 37 PCT).

Please also note that, when filing amendments under Art. 34 PCT, such amendments shall be accompanied by a letter which identifies the amendments made and also the basis for the amendments in the application as originally filed (Rule 66.8(a) PCT). Failure to comply with this requirement may result in the amendments being ignored in the **IPER (IPRP (Chapter II))**, see Rule 70.2(c-*bis*) PCT.

Filing a request for supplementary international search

The applicant may, with the **IB**, file a request for **supplementary international search** under Rule 45*bis*.1 PCT. The present **ISR** and **WO/ISA** may also be taken into account in the execution of that supplementary international search, provided that these are available to the Authority charged with this task before it starts the supplementary search (Rule 45*bis*.5 PCT).

This kind of request **cannot be filed specifying the ISA** who did the **international search**.

More information on this topic can be found in the **PCT Applicant's Guide**, Chapter 8 (<http://www.wipo.int/pct/en/guide/ip08.html>).

End of the international phase

Where no **demand** is filed, at the end of the international phase, the **IB** will transform the **WO/ISA** into the **IPRP (PCT Chapter I)** (Rule 44*bis* PCT), which will then be transmitted together with possible informal comments to the designated Offices. Where a demand is filed, the **WO/ISA** is not transformed into an **IPRP (Chapter I)** by the **IB**, but rather the **IPEA** will establish an **IPER**, (the **IPER** is the same as the **IPRP (PCT Chapter II)**, see Rule 70.15 PCT).

Bitte beachten Sie, dass angeführte Nichtpatentliteratur (wie z. B. wissenschaftliche oder technische Dokumente) je nach geltendem Recht dem Urheberrechtsschutz und/oder anderen Schutzarten für schriftliche Werke unterliegen könnte. Die Vervielfältigung urheberrechtlich geschützter Texte, ihre Verwendung in anderen elektronischen oder gedruckten Publikationen und ihre Weitergabe an Dritte ist ohne ausdrückliche Zustimmung des Rechtsinhabers nicht gestattet.

Veuillez noter que les ouvrages de la littérature non-brevets qui sont cités, par exemple les documents scientifiques ou techniques, etc., peuvent être protégés par des droits d'auteur et/ou toute autre protection des écrits prévue par les législations applicables. Les textes ainsi protégés ne peuvent être reproduits ni utilisés dans d'autres publications électroniques ou imprimées, ni rediffusés sans l'autorisation expresse du titulaire du droit d'auteur.

Please be aware that cited works of non-patent literature such as scientific or technical documents or the like may be subject to copyright protection and/or any other protection of written works as appropriate based on applicable laws. Copyrighted texts may not be copied or used in other electronic or printed publications or re-distributed without the express permission of the copyright holder.

PCT REQUEST

(Original in Electronic Form)

0	For receiving Office use only	
0-1	International Application No.	
0-2	International Filing Date	
0-3	Name of receiving Office and "PCT International Application"	
0-4	Form PCT/RO/101 PCT Request	
0-4-1	Prepared Using	PCT Online Filing Version 3.51.000.275e MT/FOP 20141031/0.20.5.24
0-5	Petition The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty	
0-6	Receiving Office (specified by the applicant)	European Patent Office (EPO) (RO/EP)
0-7	Applicant's or agent's file reference	YARA-241-PCT
I	Title of Invention	Dual pressure system for producing nitric acid and method of operating thereof
II	Applicant	
II-1	This person is	Applicant only
II-2	Applicant for	All designated States
II-4	Name	Yara International ASA
II-5	Address	Drammensveien 131 0277 Oslo Norway
II-6	State of nationality	NO
II-7	State of residence	NO
III-1	Applicant and/or inventor	
III-1-1	This person is	Inventor only
III-1-3	Inventor for	All designated States
III-1-4	Name (LAST, First)	VIGELAND, Bent
III-1-5	Address	Nordheimvegen 63 3714 Skien Norway
III-2	Applicant and/or inventor	
III-2-1	This person is	Inventor only
III-2-3	Inventor for	All designated States
III-2-4	Name (LAST, First)	ØIEN, Halvor
III-2-5	Address	Hvalenvegen 58 3943 Porsgrunn Norway

PCT REQUEST

(Original in Electronic Form)

III-3	Applicant and/or inventor	
III-3-1	This person is	Inventor only
III-3-3	Inventor for	All designated States
III-3-4	Name (LAST, First)	FAUCONNIER, Peter
III-3-5	Address	Brusselsesteenweg 127 1850 Grimbergen Belgium
III-4	Applicant and/or inventor	
III-4-1	This person is	Inventor only
III-4-3	Inventor for	All designated States
III-4-4	Name (LAST, First)	DE SMET, Andre
III-4-5	Address	Volkerak 7 4535 JH Terneuzen Netherlands
IV-1	Agent or common representative; or address for correspondence	
	The person identified below is hereby/ has been appointed to act on behalf of the applicant(s) before the competent International Authorities as:	Agent
IV-1-1	Name	De Clercq & Partners
IV-1-2	Address	Edgard Gevaertdreef 10a 9830 Sint-Martens-Latem Belgium
IV-1-3	Telephone No.	+3292802340
IV-1-4	Facsimile No.	+3292802345
IV-1-5	e-mail	info@dcp-ip.com
IV-1-6	Agent's registration No.	458
V	DESIGNATIONS	
V-1	The filing of this request constitutes under Rule 4.9(a), the designation of all Contracting States bound by the PCT on the international filing date, for the grant of every kind of protection available and, where applicable, for the grant of both regional and national patents.	
VI-1	Priority claim of earlier regional application	
VI-1-1	Filing date	25 August 2021 (25.08.2021)
VI-1-2	Number	21193029.2
VI-1-3	Regional Office	EP
VI-2	Priority claim of earlier regional application	
VI-2-1	Filing date	11 January 2022 (11.01.2022)
VI-2-2	Number	22150904.5
VI-2-3	Regional Office	EP
VI-3	Priority document request	
	The International Bureau is requested to obtain from a digital library a certified copy of the earlier application(s) identified above as item(s), using, where applicable, the access code(s) indicated:	VI-1 Access code: 885E VI-2 Access code: 5E9B

PCT REQUEST

(Original in Electronic Form)

VI-4	Incorporation by reference : where an element of the international application referred to in Article 11(1)(iii)(d) or (e) or a part of the description, claims or drawings referred to in Rule 20.5(a), or an element or part of the description, claims or drawings referred to in Rule 20.5bis(a) is not otherwise contained in this international application but is completely contained in an earlier application whose priority is claimed on the date on which one or more elements referred to in Article 11(1)(iii) were first received by the receiving Office, that element or part is, subject to confirmation under Rule 20.6, incorporated by reference in this international application for the purposes of Rule 20.6.		
VII-1	International Searching Authority Chosen	European Patent Office (EPO) (ISA/EP)	
VII-2	Request to use results of earlier search; reference to that search		
VII-2-1	Filing date	11 January 2022 (11.01.2022)	
VII-2-2	Application Number	22150904.5	
VII-2-3	Country (or regional Office)	EP	
VII-2-5	Documents are available to the ISA in a form and a manner acceptable to it, and therefore do not need to be submitted by the applicant to the receiving Office, or to the ISA (Rules 12bis1.(c) and (d) and 12bis.2(b)):	A copy of the results of the earlier search A copy of the earlier application A copy of any document cited in the earlier search results	
VIII	Declarations	Number of declarations	
VIII-1	Declaration as to the identity of the inventor	–	
VIII-2	Declaration as to the applicant's entitlement, as at the international filing date, to apply for and be granted a patent	–	
VIII-3	Declaration as to the applicant's entitlement, as at the international filing date, to claim the priority of the earlier application	–	
VIII-4	Declaration of inventorship (only for the purposes of the designation of the United States of America)	–	
VIII-5	Declaration as to non-prejudicial disclosures or exceptions to lack of novelty	–	
IX	Check list	Number of sheets	Electronic file(s) attached
IX-1	Request (including declaration sheets)	4	✓
IX-2	Description	44	✓
IX-3	Claims	11	✓
IX-4	Abstract	1	✓
IX-5	Drawings	5	✓
IX-6a	Sequence listing part of the description (also to be used for the purposes of international search)	–	–
IX-7	TOTAL	65	

PCT REQUEST

(Original in Electronic Form)

	Accompanying Items	Paper document(s) attached	Electronic file(s) attached
IX-8	Fee calculation sheet	–	✓
IX-11	Copy of general power of attorney	–	✓
IX-19	Other	Pre-conversion archive Statement (Section 706): This is a complete and accurate copy of the international application prior to its conversion into the electronic document format in which it is filed.	✓
IX-20	Figure of the drawings which should accompany the abstract		
IX-21	Language of filing of the international application	English	
X-1	Signature of applicant, agent or common representative	(PKCS7 Digital Signature)	
X-1-1	Name	De Clercq & Partners	
X-1-2	Name of signatory	Annelies De Clercq 41099	
X-1-3	Capacity (if such capacity is not obvious from reading the request)	(Representative)	

FOR RECEIVING OFFICE USE ONLY

10-1	Date of actual receipt of the purported international application	
10-2	Drawings:	
10-2-1	Received	
10-2-2	Not received	
10-3	Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application	
10-4	Date of timely receipt of the required corrections under PCT Article 11(2)	
10-5	International Searching Authority	ISA/EP
10-6	Transmittal of search copy delayed until search fee is paid	

FOR INTERNATIONAL BUREAU USE ONLY

11-1	Date of receipt of the record copy by the International Bureau	
------	--	--

Acknowledgement of receipt

We hereby acknowledge receipt of your request for the processing of an international application according to the Patent Cooperation Treaty as follows:

Submission number	11246294	
PCT application number	PCT/EP2022/073638	
Date of receipt	25 August 2022	
Receiving Office	European Patent Office, The Hague	
Your reference	YARA-241-PCT	
Applicant	Yara International ASA	
Number of applicants	1	
Country	NO	
Title	Dual pressure system for producing nitric acid and method of operating thereof	
Documents submitted	eolf-pkda.xml eolf-appb.xml eolf-cgpa-000001.xml eolf-othd-000001.pdf (56 p.) eolf-othd-000002.zip	eolf-requ.xml eolf-fees.xml eolf-vlog.xml eolf-appb-P000001.pdf (5 p.) eolf-cgpa-I000001.pdf (1 p.)
Submitted by	CN=Annelies De Clercq 41099	
Method of submission	Online	
Date and time receipt generated	25 August 2022, 08:56 (CEST)	
Message Digest	96:75:AE:95:90:6F:2A:AF:AE:F6:D3:DC:64:6F:1A:FE:07:88:EE:1D	

/European Patent Office/

DAS access code

The access code generated for this application and used to retrieve the priority documents from WIPO's Digital Access Service (DAS) is indicated in the document appended to this acknowledgement of receipt. Please note that the appended document is non-public and will not be published.

/European Patent Office/

DAS access code

To access and retrieve the priority document from WIPO's Digital Access Service (DAS) in respect of

Application number

PCT/EP2022/073638

Applicant

Yara International ASA

the European Patent Office has generated the following code:

DAS access code

BD41

For further information, see OJ EPO 03/2019.

Date and time
receipt generated

25 August 2022, 08:56 (CEST)

This unique access code allows the applicant to authorise participating intellectual property offices to retrieve a certified copy of the present application (as priority document) via WIPO DAS.
The code will only be valid if the requirements for according a date of filing are met (see OJ EPO 03/2019).

PATENT COOPERATION TREATY

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:
De Clercq & Partners Edgard Gevaertdreef 10a 9830 Sint-Martens-Latem BELGIQUE

PCT

NOTIFICATION OF TRANSMITTAL OF THE INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY (PCT Rule 71.1)

Date of mailing
(day/month/year)

07.07.2023

Applicant's or agent's file reference YARA-241-PCT		IMPORTANT NOTIFICATION	
International application No. PCT/EP2022/073638	International filing date (day/month/year) 25.08.2022	Priority date (day/month/year) 25.08.2021	
Applicant Yara International ASA			

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary report on patentability and its annexes, if any, established on the international application.
2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.
3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

4. REMINDER

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary report on patentability. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

The applicant's attention is drawn to Article 33(5), which provides that the criteria of novelty, inventive step and industrial applicability described in Article 33(2) to (4) merely serve the purposes of international preliminary examination and that "any Contracting State may apply additional or different criteria for the purposes of deciding whether, in that State, the claimed inventions is patentable or not" (see also Article 27(5)). Such additional criteria may relate, for example, to exemptions from patentability, requirements for enabling disclosure, clarity and support for the claims.

Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Fax: +49 89 2399 - 4465	Authorized Officer Marchetto, Lisa Tel. +49 89 2399-2796 
--	---

PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

(Chapter II of the Patent Cooperation Treaty)

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference YARA-241-PCT	FOR FURTHER ACTION		See Form PCT/IPEA/416
International application No. PCT/EP2022/073638	International filing date (day/month/year) 25.08.2022	Priority date (day/month/year) 25.08.2021	
International Patent Classification (IPC) or national classification and IPC INV. C01B21/26			
Applicant Yara International ASA			
1. This report is the international preliminary examination report, established by this International Preliminary Examining Authority under Article 35 and transmitted to the applicant according to Article 36. 2. This REPORT consists of a total of <u>6</u> sheets, including this cover sheet. 3. This report is also accompanied by ANNEXES, comprising: a. ☐ a total of sheets, as follows: ☐ sheets of the description, claims and/or drawings which have been amended and/or sheets containing rectifications authorized by this Authority, unless those sheets were superseded or cancelled, and any accompanying letters (see Rules 46.5, 66.8, 70.16, 91.2, and Section 607 of the Administrative Instructions). ☐ sheets containing rectifications, where the decision was made by this Authority not to take them into account because they were not authorized by or notified to this Authority at the time when this Authority began to draw up this report, and any accompanying letters (Rules 66.4bis, 70.2(e), 70.16 and 91.2). ☐ superseded sheets and any accompanying letters, where this Authority either considers that the superseding sheets contain an amendment that goes beyond the disclosure in the international application as filed, or the superseding sheets were not accompanied by a letter indicating the basis for the amendments in the application as filed, as indicated in item 4 of Box No. I and the Supplemental Box (see Rule 70.16(b)). b. ☐ a separate electronic file containing a sequence listing (<i>sent to the International Bureau only</i>)			
4. This report contains indications relating to the following items: ☒ Box No. I Basis of the report ☐ Box No. II Priority ☐ Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability ☐ Box No. IV Lack of unity of invention ☒ Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement ☐ Box No. VI Certain documents cited ☐ Box No. VII Certain defects in the international application ☐ Box No. VIII Certain observations on the international application			
Date of submission of the demand 16.06.2023		Date of completion of this report 07.07.2023	
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Fax: +49 89 2399 - 4465		Authorized officer Gerwann, Jochen Telephone No. +31 70 340-8456 	

Box No. I Basis of the report

1. With regard to the **language**, this report is based on
- ☒ the international application in the language in which it was filed
 - ☐ a translation of the international application into , which is the language of a translation furnished for the purposes of:
 - ☐ international search (under Rules 12.3(a) and 23.1(b))
 - ☐ publication of the international application (under Rule 12.4(a))
 - ☐ international preliminary examination (under Rules 55.2(a) and/or 55.3(a) and (b))
2. With regard to the **elements*** of the international application, this report is based on (*replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report*):

Description, Pages

1-44 as originally filed

Claims, Numbers

1-18 as originally filed

Drawings, Sheets

1/5-5/5 as originally filed

- ☐ a sequence listing - see Supplemental Box Relating to Sequence Listing.
3. ☐ The amendments have resulted in the cancellation of:
- ☐ the description, pages
 - ☐ the claims, Nos.
 - ☐ the drawings, sheets/figs
 - ☐ the sequence listing (*specify*):
4. ☐ This report has been established as if (some of) the amendments annexed to this report and listed below had not been made, since either they are considered to go beyond the disclosure as filed, or they were not accompanied by a letter indicating the basis for the amendments in the application as filed, as indicated in the Supplemental Box (Rules 70.2(c) and (c-bis)):
- ☐ the description, pages
 - ☐ the claims, Nos.
 - ☐ the drawings, sheets/figs
 - ☐ the sequence listing (*specify*):
5. ☐ This report has been established:
- ☐ taking into account the **rectification of an obvious mistake** authorized by or notified to this Authority under Rule 91 (Rules 66.1(d-bis) and 70.2(e)).
 - ☐ without taking into account the **rectification of an obvious mistake** authorized by or notified to this Authority under Rule 91(Rules 66.4bis and 70.2(e)).

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

International application No.
PCT/EP2022/073638

6. ☒ With regard to top-up searches (Rules 66.1 *ter* and 70.2(f)):
- ☒ A top-up search was carried out by this Authority on 26.06.2023 (all discovered documents are listed in the Supplemental Box Relating to Top-up Search).
 - ☐ Additional relevant documents have been discovered during the top-up search.
 - ☐ No top-up search was carried out by this Authority because it would serve no useful purpose.
7. ☐ Supplementary international search report(s) from Authority(ies) has/have been received and taken into account in establishing this report (Rule 45bis.8(b) and (c)).

* If item 4 applies, some or all of those sheets may be marked "superseded".

Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes: Claims	<u>1-18</u>
	No: Claims	
Inventive step (IS)	Yes: Claims	<u>1-18</u>
	No: Claims	
Industrial applicability (IA)	Yes: Claims	<u>1-18</u>
	No: Claims	

2. Citations and explanations (Rule 70.7):

see separate sheet

Re Item V

Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

Reference is made to the following documents:

- D1 DE 10 2013 004341 A1 (THYSSENKRUPP UHDE GMBH [DE]) 18 September 2014 (2014-09-18)
- D2 US 6 264 910 B1 (MAURER RAINER [DE] ET AL) 24 July 2001 (2001-07-24)
- D3 "Latest nitric acid process design",
NITROGEN,,
no. 165, 1 January 1987 (1987-01-01), pages 32-40, XP001266113,

1 Articles 33(2), (3) PCT

Document D1 is regarded as being the prior art closest to the subject-matter of claim 1, and discloses a dual-pressure plant for producing HNO₃ (fig. 2). Air (100) is compressed (1) and directed via line (120) together with vaporized NH₃ (2) and O₂ depleted gas mixture (220) into oxidation reactor (3). The gas mixture, entering (3) has a molar ratio of O₂/NH₃ from 1.25 to 1.75. NO_x/H₂O, leaving (3) is first cooled in the heat-exchanger (4) and afterwards directed to the condenser (5), from which non-condensed NO_x leaves via line (140). Diluted HNO₃, leaving (5) is directed to the absorption tower (8) via line (150). NO_x, leaving (5) via (140) is compressed in (7) and directed to (8). HNO₃ is obtained from (8) and leaves via line (160). Tail gas leaves (8) via line (180) and is heated in the heat exchanger (4) and purified in (9). Purified tail gas leaves (9) via line (190) and is split in two streams, wherein one part is directed to the turbine (10) for recovering energy, while the remaining purified tail gas is expanded in (11), before redirected with the compressed air from compressor (1) via line (120) into the reactor (3) (D1: claims 1-27; paragraphs [0082]-[0104], [0107]-[0111]; fig. 1, 2).

The subject-matter of claim 1 therefore differs from this known document D1 in that the oxygen rich gas and recirculated tail gas (first tail gas) are mixed and in that the mixed gases are directed to a mixing apparatus for mixing the gas stream with an ammonia gas stream.

The subject-matter of claim 1 is therefor novel (Art. 33(2) PCT).

The technical effect linked with the differentiating feature is that the dual pressure nitric acid plant is operated without an air compressor, thereby reducing the energy consumption of the plant.

The problem to be solved by the present invention may therefore be regarded as to provide a dual pressure nitric acid plant with reduced energy consumption.

The solution to this problem proposed in claim 1 of the present application is considered as involving an inventive step (Article 33(3) PCT) for the following reasons:

Document D2 discloses a dual pressure nitric acid plant comprising the provision of a multi shaft geared a centrifugal compressor separately with process air and nitrous gas (D2: abstract).

Starting from D1, the skilled person would not arrive at a solution falling within the scope of the claims, because there is no teaching, suggestion or hint in D1, alone or in combination with any of the other cited documents, that would serve as motivation for carrying out the necessary modifications, i.e. providing a separate supply of oxygen-rich gas in order to allow the removal of the air compressor.

Therefore, the subject-matter of claim 1 and dependent claims 2-8 fulfils the requirements of the PCT with regard to novelty and inventive step (Art. 33(2), (3) PCT).

Claim 9 discloses a method for producing nitric acid at reduced power consumption and reduced emissions in a production plant according to any of claims 1-8, comprising the step of mixing the first tail with the oxygen-rich gas. With regard to novelty and inventive step, the same arguments apply mutatis mutandis to the subject-matter of claim 9 and dependent claims 10-16.

Claim 17 discloses the use of the production plant according to any of claims 1-8 for performing the method according to any of claims 9-16.

With regard to novelty and inventive step, the same arguments apply mutatis mutandis to the subject-matter of claim 17.

Claim 18 discloses a method for revamping an existing production plant for producing nitric acid comprising an air compressor, wherein in the revamping process the air compressor is replaced by e.g. means for splitting the tail gas into a first and second tail gas stream, wherein the first tail gas stream is in fluid communication with the oxygen rich gas.

With regard to novelty and inventive step, the same arguments apply mutatis mutandis to the subject-matter of claim 18, which is therefore considered to be novel and inventive (Art. 33(2), (3) PCT).

PATENT COOPERATION TREATY

From the RECEIVING OFFICE

PCT

To:

De Clercq & Partners
Edgard Gevaertdreef 10a
9830 Sint-Martens-Latem
BELGIQUE

NOTIFICATION OF THE INTERNATIONAL APPLICATION NUMBER AND OF THE INTERNATIONAL FILING DATE

(PCT Rule 20.2(c))

Date of mailing
(day/month/year)

22.09.2022

Applicant's or agent's file reference
YARA-241-PCT

IMPORTANT NOTIFICATION

International application No.

PCT/EP2022/073638

International filing date (day/month/year)

25 August 2022 (25-08-2022)

Priority date (day/month/year)

25 August 2021 (25-08-2021)

Applicant

YARA INTERNATIONAL ASA

Title of the invention

1. The applicant is hereby notified that the international application has been accorded the international application number and the international filing date indicated above.

2. The applicant is further notified that the record copy of the international application:



was transmitted to the International Bureau on see above date of mailing



has not yet been transmitted to the International Bureau for the reason indicated below and a copy of this notification has been sent to the International Bureau*:



because the necessary national security clearance has not yet been obtained



because (reason to be specified)

* The International Bureau monitors the transmittal of the record copy by the receiving Office and will notify the applicant (with Form PCT/IB/301) of its receipt. Should the record copy not have been received by the expiration of 14 months from the priority date, the International Bureau will notify the applicant (Rule 22.1(c)).

Name and mailing address of Receiving Office



European Patent Office, P.B. 5818 Patentlaan 2
NL-2280 HV Rijswijk
Tel. (+31-70) 340-2040
Fax: (+31-70) 340-3016

Authorized officer

Peschier-Van den Berg, Y.

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION CONCERNING SUBMISSION,
OBTENTION OR TRANSMITTAL
OF PRIORITY DOCUMENT
(PCT Administrative Instructions, Section 411)

To:

DE CLERCQ & PARTNERS
Edgard Gevaertdreef 10a
9830 Sint-Martens-Latem
BELGIQUE

Date of mailing (<i>day/month/year</i>) 29 September 2022 (29.09.2022)	IMPORTANT NOTIFICATION
Applicant's or agent's file reference YARA-241-PCT	
International application No. PCT/EP2022/073638	International filing date (<i>day/month/year</i>) 25 August 2022 (25.08.2022)
International publication date (<i>day/month/year</i>) Not yet published	Priority date (<i>day/month/year</i>) 25 August 2021 (25.08.2021)
Applicant YARA INTERNATIONAL ASA	

The applicant is hereby notified of the date of receipt (or of obtaining by the International Bureau) of the priority document(s) relating to all earlier application(s) whose priority is claimed. Unless otherwise indicated by the letters "NR", in the right-hand column or by an asterisk appearing next to the date of receipt, **the priority document concerned was submitted or transmitted to or obtained by the International Bureau in compliance with Rule 17.1(a), (b) or (b-bis)**. This Form replaces any previously issued notification concerning submission, transmittal or obtaining of priority documents.

<u>Priority date</u>	<u>Priority application No.</u>	<u>Country or regional Office or PCT receiving Office</u>	<u>Date of receipt of priority document</u>
25 August 2021 (25.08.2021)	21193029.2	EP	21 September 2022 (21.09.2022)
11 January 2022 (11.01.2022)	22150904.5	EP	21 September 2022 (21.09.2022)

The letters "NR" denote a priority document which, on the date of mailing of this Form, had not yet been received or obtained by the International Bureau in compliance with Rule 17.1(a), (b) or (b-bis). Where the applicant has failed to either submit, request to prepare and transmit, or to request the International Bureau to obtain the priority document within the applicable time limit under that Rule, the attention of the applicant is directed to Rule 17.1(c) which provides that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity, upon entry into the national phase, to furnish the priority document within a time limit which is reasonable under the circumstances.

An asterisk "*" next to a date of receipt, denotes a priority document submitted or transmitted to or obtained by the International Bureau but not in compliance with Rule 17.1(a), (b) or (b-bis) (the priority document was received after the time limit prescribed in Rule 17.1(a); the request to prepare and transmit the priority document was submitted to the receiving Office after the applicable time limit under Rule 17.1(b) or the request to the International Bureau to obtain the priority document was made after the applicable time limit under Rule 17.1(b-bis)). Even though the priority document was not furnished in compliance with Rule 17.1(a), (b) or (b-bis), the International Bureau will nevertheless transmit a copy of the document to the designated Offices, for their consideration. In case such a copy is not accepted by the designated Office as the priority document, Rule 17.1(c) provides that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity, upon entry into the national phase, to furnish the priority document within a time limit which is reasonable under the circumstances.

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland	Authorized officer Nora Lindner e-mail pct.team5@wipo.int Telephone No. +41 22 338 74 05
---	--

**PCT DEMAND FOR INTERNATIONAL
PRELIMINARY EXAMINATION (CHAPTER II)**

0	For International Preliminary Examining Authority use only	
0-1	Identification of IPEA	
0-2	Date of receipt of DEMAND	
0-3	Form - PCT/IPEA/401 PCT Demand	
0-3-1	Prepared Using	eOLF Version: FMMNGR5183, IBR4015182, FM_FOP0205
0-4	Demand under Article 31 of the Patent Cooperation Treaty: The undersigned requests that the international application specified below be the subject of international preliminary examination according to the Patent Cooperation Treaty and hereby elects all eligible States (except where otherwise indicated).	
0-5	International Preliminary Examining Authority (specified by the applicant)	IPEA/EP
I	Identification of the International application	
I-1	International Application No.	PCT/EP2022/073638
I-2	International Filing Date	25 August 2022 (25.08.2022)
I-3	(Earliest) Priority Date	25 August 2021 (25.08.2021)
I-4	Applicant's or agent's file reference	YARA-241-PCT
I-5	Title of Invention	Dual pressure system for producing nitric acid and method of operating thereof

**PCT DEMAND FOR INTERNATIONAL
PRELIMINARY EXAMINATION (CHAPTER II)**

II-1	Applicant	
II-1-1	Name	Yara International ASA
II-1-2	Address	Drammensveien 131 0277 Oslo Norway
II-1-3	State of nationality	NO
II-1-4	State of residence	NO
II-1-5	Telephone No.	
II-1-6	e-mail	
II-1-7	Applicant's registration No. with the Office	
III-1	Agent or common representative; or address for correspondence	
	The person identified below is hereby/ has been appointed to act on behalf of the applicant(s) before the competent International Authorities as:	Attorney (appointed earlier)
III-1-1	Name	De Clercq & Partners
III-1-2	Address	Edgard Gevaertdreef 10a 9830 Sint-Martens-Latem Belgium
III-1-3	Telephone No.	+3292802340
III-1-4	e-mail	info@dcp-ip.com
III-1-4a	The International Preliminary Examining Authority is authorised to use this e-mail address, if the Authority so wishes, to send notifications issued in respect of this international preliminary examination:	exclusively in electronic form (no paper notifications will be sent)
III-1-5	Agent's registration No.	458

**PCT DEMAND FOR INTERNATIONAL
PRELIMINARY EXAMINATION (CHAPTER II)**

IV	Basis for International Preliminary Examination			
IV-1-1	Statement concerning amendments: The applicant wishes the International Preliminary Examination to start on the basis of: International preliminary examination will start on the basis of the international application as originally filed or, where a copy of amendments to the claims under Article 19 and/or amendments of the international application under Article 34 are received by the International Preliminary Examining Authority before it has begun to draw up a written opinion or the international preliminary examination report, as so amended.	-the international application as originally filed		
IV-2	Language for the purposes of international preliminary examination:	English -(which is the language in which the international application was filed)		
V	Election of States	The filing of this demand constitutes the election of all Contracting States which are designated and are bound by Chapter II of the PCT.		
VI	Check list The demand is accompanied by the following elements, in the language referred to under item IV-2 for the purposes of international preliminary examination:	Number of sheets	Electronic file(s) attached	Received Y/N (For IPEA use only)
VI-6	Letter accompanying the amendments under Article 34 (Rule 66.8)	4	LETT.pdf	
	Accompanying Items The demand is also accompanied by the following item(s):	Details	Electronic file(s) attached	Received Y/N (For IPEA use only)
VI-8	Fee calculation sheet	1	fees.pdf	

**PCT DEMAND FOR INTERNATIONAL
PRELIMINARY EXAMINATION (CHAPTER II)**

VII-1	Signature of applicant, agent or common representative	PKCS7 Digital Signature: Annelies De Clercq 41099
VII-1-1	Name	De Clercq & Partners
VII-1-2	Capacity	Representative
VIII	Note(s) to IPEA/EP	

FOR INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY USE ONLY

8-1	Date of actual receipt of DEMAND	
8-2	Adjusted date of receipt of demand due to CORRECTIONS under Rule 60.1(b)	
8-3	The date of receipt of the demand is AFTER the expiration of 19 months from the priority date and items 8-4 and 8-5 below do not apply.	
8-3-1	The applicant has been informed accordingly	
8-4	The date of receipt of the demand is WITHIN the period of 19 months from the priority date as extended by virtue of Rule 80.5.	
8-5	Although the date of receipt of the demand is after the expiration of the 19 months from the priority date, the delay in arrival is EXCUSED pursuant to Rule 82.	
8-6	The date of receipt of the demand is AFTER the expiration of the time limit under Rule 54bis, 1(a) and item 7 or 8, below, does not apply.	
8-7	The date of receipt of the demand is WITHIN the time limit under Rule 54bis.1(a) as extended by virtue of Rule 80.5.	
8-8	Although the date of receipt of the demand is after the expiration of the time limit under Rule 54bis.1(a), the delay in arrival is EXCUSED pursuant to Rule 82.	

PCT DEMAND FOR INTERNATIONAL
PRELIMINARY EXAMINATION (CHAPTER II)

FOR INTERNATIONAL BUREAU USE ONLY

9-1	Demand received from IPEA on	
-----	------------------------------	--

European Patent Office
80298 MUNICH
GERMANY

Online Filing

Sint-Martens-Latem, June 16, 2023

Our Ref.: YARA-241-PCT
Re: International patent application PCT/EP2022/073638, filed on August 25, 2022
entitled "Dual pressure system for producing nitric acid and method of operating
thereof"

Dear Madam, Dear Sir,

In response to the International Search Report and Written Opinion in connection with the above-mentioned international application, issued by the International Searching Authority (ISA) on December 6, 2022, the applicant respectfully submits the following observations.

A request for Preliminary International Examination under Chapter II PCT is hereby filed.

The Written Opinion particularly cites DE102013004341 (D1), US6264910 (D2) and "Latest nitric acid process design (Nitrogen, 1987)" (D3), and the same numbering is used herein.

1. Observations

Novelty & Inventive Step

It is gratefully acknowledged that the Examiner finds the claimed subject-matter novel over the cited prior art.

The examiner is further of the opinion that the claimed subject-matter is not inventive over the cited prior art. Briefly, according to the examiner, D1 does not disclose that the plant comprises means for measuring and adjusting different gas concentrations. However, the examiner asserts that the skilled person would routinely apply these means for running the plant under optimized production conditions.

The applicant respectfully does not agree with this opinion.

First, the main aspects and advantages of the present invention can be summarized as follows.

MAIN OFFICE

Edgard Gevaertdreef 10a
B-9830 Sint-Martens-Latem
Belgium

HASSELT BRANCH

Corda Campus
Kempische Steenweg 309 bus 2.01
B-3500 Hasselt
Belgium

LEUVEN BRANCH

Groenveldstraat 13
B-3001 Leuven (Heverlee)
Belgium

As *inter alia* discussed in the background section, prior art plants and methods for producing nitric acid use compressed air as the primary air (i.e. used for oxidation of ammonia in the ammonia converter) and secondary air (e.g. used as stripping medium in a bleacher unit). However, operating the air compressor requires a high amount of energy. This also complicates upscaling the production plant, as it requires installing a new air compressor or revamping an existing one (see p.3, line 20 – p.4, line 10).

As explained on p. 7 and p. 17-18 of the present application, these drawbacks have been overcome and important gains compared to conventional dual pressure systems and methods have been obtained by essentially completely replacing the conventional primary air and/or secondary air consisting of pressurized air by the combination of (i) an oxygen-rich gas, in particular as a pressurized oxygen gas or oxygen-rich gas, such as produced by a high-pressure water electrolyser, and (ii) a recirculated tail gas stream with controlled oxygen content. In particular, the separate supply of pressurized oxygen-rich gas combined with the recirculation of the tail gas allows the complete removal of compressed air to be supplied. This goes hand in hand with the complete removal of the air compressor needed for operation of a conventional nitric acid plant (as explicitly stated in claim 18), while maintaining and ensuring an optimal oxygen concentration for the optimal conversion of ammonia to nitric oxide. This is clearly demonstrated in the examples, with example 1 showing that the combination of providing pressurized oxygen and recirculation of 99.3% of the tail gas during continuous operation of the plant allowed to produce nitric acid in the absence of further pressurized air (i.e. without an air compressor). This also allowed to export a higher amount of steam compared to a comparative example comprising an air compressor which is at least partially powered by a steam turbine.

It is respectfully submitted that these effects and advantages are not disclosed or acknowledged in the prior art and cannot be obtained in an obvious manner therefrom.

Considering D1 as the closest prior art, it is respectfully submitted that D1 at least does not disclose the feature of a supply of an oxygen-rich gas, such as e.g. a high pressure water electrolyser as specified in claims 7 and 15, and accordingly, the mixing of the oxygen-rich gas and a recirculated tail gas (i.e. the first tail gas stream). Considering claim 18, D1 also does not disclose the step of removing the air compressor.

As discussed above, this has at least the effect of operating the dual pressure nitric acid plant without an air compressor during continuous production, without compromising the conversion of ammonia to nitric oxide in the ammonia converter (see also e.g. p. 7 and p. 17-18 of the present application as filed), thereby significantly reducing the energy consumption of the plant.

The problem to be solved may thus be formulated as how to provide a dual pressure nitric acid plant (and related methods for the production of nitric acid) with reduced energy consumption, particularly with reduced energy consumption of the air compressor.

It is respectfully submitted that the solution is not disclosed nor suggested in the prior art.

First, it is respectfully submitted that D1 is silent on how to reduce the energy consumption of the production plant/process in general, and the air compressor in particular. Moreover, D1 is completely silent on the possibility of removing the air compressor all together, i.e. a feature which is explicitly stated in claim 18.

In addition, as already mentioned above, D1 does not disclose providing a separate oxygen-rich stream, such as generated by a high-pressure water electrolyser, and subsequently providing a mixture comprising the oxygen-rich stream and a tail gas stream to the ammonia converter. D1 aims to reduce the oxygen content (or the molar ratio of oxygen to ammonia) of the gas mixture before entry into the converter (catalyst bed) (see D1, [0036]). In this context, D1 discloses several options to dilute the compressed air stream, essentially by mixing the air with a low-oxygen gas, including a low-oxygen rail gas (residual gas) (see e.g. D1, [0082]-[0090], [0110]). Providing an oxygen-rich gas and mixing this gas with the recycled tail gas thus goes against the teachings of D1 which aims to limit the oxygen supply to the burner.

D2 provides a dual pressure nitric acid production plant and production process, comprising providing a multi shaft geared centrifugal compressor separately with process air and nitrous gas (D2, abstract). Providing an oxygen-rich gas and mixing this gas with the recycled tail gas to allow the complete removal of the compressor thus goes against the teachings of D2.

D3 is a publication discussing prior art nitric acid process design. It essentially discloses what is already mentioned in the background section of the present application. D3 thus does not teach, hint or motivate to provide an oxygen-rich gas and mixing this gas with recycled tail gas.

Accordingly, starting from D1, the skilled person would not arrive at a solution falling within the scope of the claims, because there is no teaching, suggestion or hint in D1, alone or in combination with any of the other cited documents, that would serve as motivation for carrying out the necessary modifications, i.e. providing a separate supply of oxygen-rich gas (e.g. a high pressure water electrolyser – see claims 5 and 12) in order to allow the removal of the air compressor.

In view of these observations, it is respectfully submitted that claims 1-18 involve an inventive step over the cited prior art.

2. Requests

In view of these amendments and observations, it is submitted that the claimed subject matter complies with the requirements of the PCT and a positive opinion is therefore requested. Should the examiner nevertheless still be of the opinion that the claims are not meeting the requirements of patentability, the applicant would appreciate a possibility to present further arguments, either orally or in writing.

Yours sincerely,

A handwritten signature in black ink, appearing to read 'K. Pappaert', with a large, sweeping flourish above the name.

ir Kris Pappaert, PhD
ir. Hans Goesaert, PhD
Professional Representatives before the EPO

Acknowledgement of receipt

We hereby acknowledge receipt of your Demand under Article 31 of the Patent Cooperation Treaty (PCT):

Submission number	12138826	
Application number	PCT/EP2022/073638	
Date of receipt	16 June 2023	
Filing Office / capacity	European Patent Office, The Hague	IPEA
Your reference	YARA-241-PCT	
Applicant	All applicants as on file	
Documents submitted	package-data.xml fee-sheet.xml pct-demand.pdf (5 p.) validation-log.xml LETT.pdf (4 p.)	demand.xml fees.pdf (1 p.) ValidLog.pdf (1 p.) olf-specific-data.xml
Submitted by	CN=Annelies De Clercq 41099	
Method of submission	Online	
Date and time receipt generated	16 June 2023, 09:27 (CEST)	
Message Digest	97:93:D1:1F:5E:D6:37:45:EE:17:B4:08:DF:B0:DE:9D:DB:07:83:07	

/European Patent Office/