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(54) Title: PROCESS AND PLANT FOR THE TREATMENT OF CARBONACEOUS SLURRY

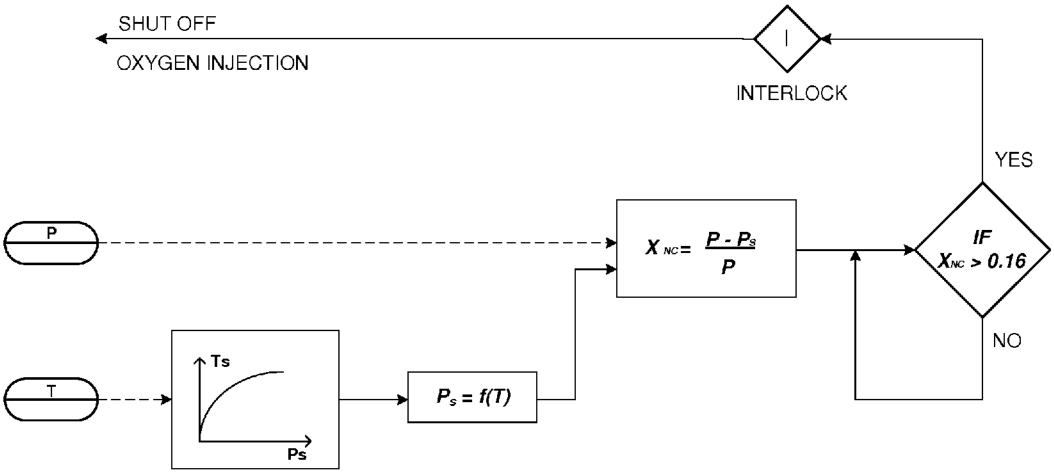

Fig. 1

(57) Abstract: The process for the treatment of carbonaceous slurry, comprises the steps of injecting a gas comprising oxygen into said slurry at temperatures of 150 °C to 350 °C and a pressure of above the associated boiling point pressures resulting in an gas-/vapor-mixture comprising at least water, oxygen and hydrogen, as well as determining the volume fraction of water in said vapor-/gas-mixture and stopping the injection of gas comprising oxygen in case the volume fraction of water is below 0.84 in said vapor-/gas-mixture. The volume fraction of water vapor in said vapor-/gas-mixture is determined by the IAPWS formulation for water and steam.

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Process and plant for the treatment of carbonaceous slurry

The present invention relates to a process and a plant for the treatment of carbonaceous slurry in general, produced by an upstream alumina production process in particular, comprising the steps of injecting a gas containing oxygen into said slurry at temperatures of 150 °C to 350 °C and pressures above the associated boiling points resulting in a vapor-/gas- mixture, mainly comprising water, oxygen. nitrogen and hydrogen, determining the volume fraction of water vapor in said vapor-/gas- mixture and stopping the injection of gas comprising oxygen, preferably oxygen enriched gas or pure oxygen, in case the volume fraction of water vapor is below 0.84 in said vapor-/gas- mixture.

In a process for the treatment of carbonaceous slurry, carbonaceous molecules are flamelessly combusted (i.e. oxidized) at elevated temperature and pressures by an oxidant, e.g. oxygen, contained in as air or as pure oxygen, which is commonly referred to as wet oxidation and is described in US 2,665,249. It is assumed that the oxygen is no longer in the gas phase when acting as an oxidant. It dissolves into the liquid first and the oxidized. Typically, the oxygen is supplied in substoichiometric and below solubility. The aim is to avoid excess O_2 in the off-gas to be oxidized matter. Compared to other processes for the limitation of the content of carbonaceous matter, wet oxidation is a rather energy and cost efficient process to produce a basically clean liquor phase. Modern understanding of the wet oxidation process chemistry is that the bi- radical oxygen starts a radical reaction by reaction with water and/or the carbonaceous molecules.

A common problem of wet oxidation is the increased generation of hydrogen as a by-product via recombination of a hydrogen atom and water molecules forming elemental hydrogen- and OH-radicals. Even in the produced small amounts of hydrogen may form an explosive mixture with any oxygen that may be present in the gas phase, wherein the mixture is easily ignited at the elevated temperatures and pressures required for the wet oxidation process.

To solve this problem, Arnswald ("Removal of organic carbon from Bayer liquor by wet oxidation in tube digesters", Light Metals 1991, pages 23 to 27) has suggested measurement of the oxygen content in the gases produced in the wet oxidation process. Since a mixture of hydrogen and oxygen is explosive when the oxygen content is between 3 and 97 vol.-% at the typical process temperatures of above 300 °C, Arnswald suggests to shut down the wet oxidation process in cases the oxygen content exceeds 3 vol.-%.

On the other hand a gas mixture containing the species water vapor, hydrogen and oxygen is not explosive, as long as the water vapor content in a mixture of water vapor, hydrogen and oxygen exceeds a volume fraction of 0.84.

Water content in a gas stream is difficult to determine under the high temperatures and pressures present in a wet oxidation process, which is why the oxygen content is used as reference by Arnswald.

Using the oxygen content as reference for an explosive mixture, a dead time between the extraction of the to be analyzed gas and the detection of an explosive hydrogen/ oxygen mixture of up to 90 seconds is to be expected, since the vapor-/gas- mixture is to be extracted and refined before the oxygen content is analyzed by analyzers downstream of the process.

Several efforts have been conducted to reduce the detection time of said formation, all using oxygen content as reference. One of the main advantages thereof is that oxygen detectors are readily available.

It is an object of the present invention to reduce the dead time in detection of an explosive oxygen / hydrogen mixture in a wet oxidation process as well as to reduce the investment costs and the maintenance requirements and to improve the reliability of the procedure employed.

This object is solved by the subject matter of independent process claim 1. Specifically, the present invention provides a process for the treatment of carbonaceous slurry, as for instance produced by an upstream alumina production process. By injecting a gas comprising oxygen, preferably an oxygen rich gas with an oxygen content of > 20 vol.-%, into said slurry at temperatures of 150 °C to 350 °C, preferably 150 to 300 °C and a pressure above the respective boiling points, a vapor-/gas- mixture at least comprising water, and hydrogen is obtained. This is due to the decomposition of the carbonaceous molecules resulting in the formation of water and hydrogen via a side reaction.

Oxygen potentially is omnipresent in the described process, since it is introduced in significant quantities. Whereas the prior art utilizes oxygen sensors for determination of the oxygen content in the vapor-/gas- mixture, the present invention proposes the determination of the volume fraction of water in said vapor-/gas- mixture. In case the volume fraction of water is below 0.84. preferably 0,9, the injection of gas comprising oxygen is immediately stopped, which prevents further formation of an explosive oxygen/ hydrogen mixture. According to the invention, the molar fraction of water in the vapor-/gas- mixture is determined as follows:

The pressure of the mixture of water vapor and non-condensables (NC) such as hydrogen and oxygen measured at any process point of the process represents the absolute pressure of that mixture, consisting of the sum of the partial pressures of water vapor and non-condensables.

Measuring the absolute pressure and the temperature at a given process point allows to determine the following:

- With temperature and pressure being linked (by the IAPWS formulation of water and steam) to one another for a pure water and saturated vapor phase, the temperature measured at a given process point is the temperature corresponding to the partial pressure of the saturated steam in the water vapor/non- condensable mixture at that process point. Via the IAPWS formulation the corresponding saturation pressure Ps can be calculated.

- The knowledge of the absolute pressure P of the water vapor/non- condensable mixture (NC) and the partial pressure Ps of the steam fraction in that mixture, allow for the calculation of the mole fraction X_{NC} of the non condensables (= volume share) in the mixture:

$$X_{NC} = \frac{P - P_S}{P}.$$

The volume fraction of a compound is defined as the amount of said compound in a given volume divided by the total amount of all constituents in the corresponding mixture.

Figure 1 shows the respective detection of an explosive vapor-/gas-mixture by temperature-/pressure-measurement.

Therefore, if the water content of the vapor-/gas- mixture is sufficient high to prevent a formation of an explosive mixture, the water content in the upstream process steps will be above the critical limit of 0.84, preferably 0.9, for the volume fraction of water in the vapor-/gas- mixture. In other words, the water content in the vapor-/gas- mixture deviates from the water content in the upstream process steps, in which wet oxidation occurs. Therefore, the continuous and instant determination of the volume fraction of water in the vapor-/gas- mixture allows a reduction of the dead time between formation and detection of an explosive oxygen/ hydrogen mixture.

However, it will still take just as long to purge out the Ngas - which may contain oxygen - as for an O_2 detected trip. To avoid dead time, it is necessary to have a trip on both, O_2 and partial pressure,

The temperature and pressure of the vapor-/gas- mixture are used to determine the volume fraction of water at the particular point of measurement. Said determination is based on the fact, that in each point of the wet oxidation process a water saturated gas phase is obtained. In other words a dynamic equilibrium between condensed (liquid) water and water vapor is observed. For a pure (100 vol.-% water) phase this equilibrium is described by the water vapor pressure saturation- curve. The water saturated gas phase in a wet oxidation process, however, also contains non-condensable gases such as hydrogen and oxygen. Due to the presence of these non-condensable gases, the equilibrium between condensed and vaporous water is "distorted", such that the temperature of a saturated water mixture is no longer correlated to the absolute pressure, but to the partial pressure of the water, which then allows to quantify volume fraction or molar fraction of water. In other words, the presence of the non-condensable gases results in a temperature measured, which is lower than if compared to the temperature to be expected for a pure water phase.

Therefore, temperature and pressure sensors are used in accordance with the invention. Since these sensors are required for the control of the wet oxidation process parameters, no additional sensors may be necessary. Further, temperature and pressure sensors are very robust and require little maintenance, the overall process costs are reduced.

Preferably, the molar fraction of water is 0.84 to 1.0, preferably 0.9 to 1.0 , the molar fraction of oxygen is 0 to 0.16 and the molar fraction of hydrogen is 0 to 0.16 and wherein the sum of the molar fractions of all constituents of the vapor-/gas- mixture is 1.

The molar fraction of water is determined by the procedure described above. Figure 2 shows temperature differences measured at a given system pressure with water vapor fraction of 0,84 in the water-vapor mixture.
It is preferred, that the temperature and the pressure of the vapor-/gas- mixture is measured after separation of a major part of water, e.g. via condensation in a condenser vapor-/gas- mixture. As an immediate safety mechanism, the condensation of water may be stopped same as the introduction of oxygen containing gas in cases the determined water vapor fraction is too low. The stopped condensation increases the water content downstream of the condenser and thus further prevents the formation of an explosive hydrogen / oxygen mixture downstream of the condenser.

In a further preferred embodiment, a chemically inert gas, e.g. nitrogen, is added to the vapor-/gas- mixture removed from the at least one flash tank. This may be done directly after the flash tank. However, it is particularly preferred to provide an inlet downstream of the separation of water, since a formation of an explosive mixture is promoted by water separation. The addition of a chemically inert gas further provides a procedure, which very rapidly, i.e. within less than 30 seconds, can adjust the hydrogen/ oxygen mixture to non-explosive conditions.

In this regard it is particularly preferred that the amount of inert gas such as nitrogen, is adjusted such that in case in the vapor-/gas- mixture in case a molar fraction of water of less than 0.84 is determined. This further prevents the existence of an explosive hydrogen/ oxygen mixture is prevented.

The object of the present invention is further solved by a plant for the treatment of carbonaceous slurry according to the features of plant claim 7.

Specifically, such a plant, in particular downstream of an alumina production process, comprises at least one flash tank with at least one inlet for introduction of –with respect to its content on carbonaceous matter- untreated and/or partially treated slurry provided via a supply tube. Further, a gas supply tube is provided for introduction of a gas comprising oxygen to said slurry upstream of the flash tank to allow for the necessary residence time for the dissolution of the oxygen into said slurry and its reaction with the carbonaceous matter. The gas supply tube comprises a valve for regulation of the oxygen amount introduced into the process. The flash tank has a gas-/vapor- outlet tube for discharging the vapor-/gas-mixture from at least one flash tank. The plant also comprises at least one temperature sensor for measuring the temperature of said vapor-/gas-mixture, and one pressure sensor for measuring the pressure of said vapor-/gas- mixture, and a control and computation unit for determining the volume fraction of water. The valve of the gas supply tube is closed in case the molar fraction of water vapor is below 0.84 in the vapor-/gas- mixture in order to avoid the formation of an explosive mixture.

In a preferred embodiment, the plant comprises at least one condenser vapor-/gas- mixture. One or more condenser(s) connected in series or parallel may be provided downstream of the last flash tank in order to remove water from the combined vapor-/gas- mixture streams of each flash tank. Such a plant layout reduces the overall construction costs, since only one or few condenser(s) are required. Alternatively, one condenser has to be provided for each flash tank. Thereby, the construction costs for the corresponding plant are higher, but the conditions (like temperature and pressure) of the wet oxidation process for each flash tank can be regulated independently.

In this regard it is further preferred, that the temperature sensor and the pressure sensor is (are) located downstream to the condenser.

In a further preferred embodiment, the gas supply tube emerges with the slurry supply tube such, that the gas comprising oxygen is introduced into the slurry upstream of the flash tank. Consequently, the reaction time between the oxygen and the carbonaceous is granted to be completed before entering the flash tank without an increase of the retention time of the slurry inside the flash tanks. In other words, a sort of pretreatment of the slurry before being introduced into the flash tank is achieved.

According to another preferred embodiment, the gas outlet tube, in particular directly, guides the vapor-/gas- mixture to a condenser in which water is separated from the vapor-/gas- mixture.

Further objectives, features, advantages and possible applications of the invention can be taken from the following description of the drawing. All features described and/or illustrated form the subject-matter of the invention per se or in any combination, also independent of their inclusion in individual claims or their back-reference.

Fig. 1 shows a detection scheme for explosive vapor-/gas-mixtures,

Fig. 2 shows a ratio between pressure and temperature in a system according to the invention and

Fig. 3 shows schematically a plant for the treatment of carbonaceous slurry according to the present invention

In fig. 3, carbonaceous slurry is introduced via supply tube 1 and conduit 2 into a flash tank 10. Inside the flash tank 10, the slurry is distributed via spraying unit 11 such that gas / liquid or slurry separation is enhanced. A gas containing oxygen or technically pure oxygen (> 95 vol.-%) is introduced into the plant and flash tank 10 via gas supply tube 3 and conduit 2. The amount of oxygen added is regulated by regulation valve 4. Said valve 4 is controlled by control unit 5. In the preferred embodiment shown in Fig. 3, the oxygen is directly introduced into the slurry and upstream of the flash tank 10, which increases the reaction time between oxygen and the carbonaceous materials without increasing of the retention time of the slurry in the flash tank 10.

Inside conduit 2 and flash tank 10 decomposition of the carbonaceous material occurs due to reaction between oxygen and the carbonaceous material. A vapor-/gas- mixture comprising water, oxygen and hydrogen is generated thereby. Said vapor-/gas- mixture is removed from flash tank 10 via conduit 20.

The remaining slurry is removed from flash tank 10 via conduit 21. As shown in Fig. 3, several flash tanks may be connected in series downstream of flash tank 10 with corresponding conduits for removal of the vapor-/gas- mixture produced in said subsequent flash tanks and conduits for removal of the remaining slurry. Downstream of each flash tank provided, the generated vapor-/gas-mixture is removed and either subsequently combined with the vapor-/gas-mixture from flash tank 10 in conduit 20, or, a separate vapor-/gas- mixture removal conduit for each flash tank is provided, which increases the flexibility of the process, since each flash tank may be controlled completely independently. Finally, the vapor-/gas- mixture from all flash tanks are guided into at least one condenser 30, preferably however into separate and designated condensers as shown in Fig. 3.

In a similar manner, the removal of the remaining slurry from each flash tank may be guided into the subsequent flash tank (as shown in Fig. 3) or each removal conduit for the remaining slurry may be combined into one discharge conduit for discharging the remaining slurry.

Regarding condenser 30 it is preferred to provide a condenser for each flash tank of the inventive plant. In said condenser 30 (or in each condenser assigned to each flash tank provided) water from the vapor-/gas- mixture is condensed and thus separated from non-condensable substances. The non-condensable substances are mainly hydrogen and oxygen, but may also include nitrogen, carbon dioxide, carbon monoxide, methane or other by-products exhibiting a very low boiling point, e.g. below - 50 °C.

From condenser 30, a condensate comprising water as main constituent is removed via conduit 33. The water removed from condenser 30 of the inventive plant is basically free of any contamination, in particular carbonaceous material, and may be used in an upstream process, as for instance as suspension medium in an upstream Bayer-process for producing aluminum. Consequently, the inventive plant may be included in a joint system thus reducing the amount of fresh water required. Alternatively, the water may be discharged into the environment as basically pure water, in particular after further after treatment, e.g. removal of inorganic substances.

Via conduits 20 to 20x the remaining vapor /gas mixture from the last flash tank (or from all flash tanks combined) is subjected to condensers 30 to 30x (or to the condenser assigned to each respective flash tank). In particular in the case the remaining slurry has passed each flash tank and is thus removed from the final flash tank, the remaining slurry is basically free of carbonaceous matter. In general, the carbonaceous matter is reduced by typically 50 to 90 % depending on process temperature, residence time and oxygen addition. In any case, the treated remaining slurry is removed via conduit 32 from the process.

Via valves 35 to 35x and control units 36 to 36x assigned to valves 35 to 35x, the amount of condensate removed from the process is regulated.

The non-condensable constituents of the vapor-/gas- mixture are removed from the condensers 30 to 30x via conduits 37 to 37x. In the preferred embodiment shown in Fig. 3, a temperature sensors 40 to 40x and a pressure sensors 41 to 41x determine the temperature and pressure of the non-condensable constituents left after removal of the major part of water in condensers 30 to 30x. Due to the removal of water inside condensers 30 to 30x, the most critical (i.e. least) volume fraction of water is present together with hydrogen and oxygen in conduits 37 to 37x. In the case the volume fraction of water less than 0.84, the oxygen supply via conduits 3 and 2 is stopped by closing valve 4 and the formation of an explosive mixture upstream of the condenser is prevented in the first place. Further, the condensation of water in the condensers 30 to 30x may be stopped in case of an explosive mixture of hydrogen and oxygen is about to be formed downstream of the condenser.

The removal of non-condensable constituents of the vapor-/gas- mixture via conduits 37 to 37x and 38 to 38x is controlled by valves 50 to 50x together with the assigned control units 51 to 51x.

The invention and the reduction of the dead time is further illustrated by means of a following example:

Example 1

For four different pressures (50, 30, 10, 5 bar abs) measured of a water vapor/non- condensable mixture, the temperatures to expected for a pure water vapor phase and the temperatures actually measured in case of non- condensable mole-/volume fractions of 0,05, 0,1 and 0,15 are indicated.

P [bar abs] measured	T [°C] measured	T [°C] without non-condensables	P_S[bar abs] calculated via IAPWS	X_{NC} [-] calculated
50	260,8	263,9	47,5	0,05
50	257,4	263,9	45	0,10
50	254,0	263,9	42,5	0,15
30	231,0	233,9	28,5	0,05
30	228,0	233,9	27	0,10
30	225,0	233,9	25,5	0,15
10	177,7	179,9	9,5	0,05
10	173,3	179,9	9,0	0,10
10	172,9	179,9	8,5	0,15
5	149,9	151,8	4,75	0,05
5	147,9	151,8	4,5	0,10
5	145,8	151,8	4,25	0,15

Reference numbers

1	supply tube
2	conduit
3	supply tube
4	regulation valve
5	control unit
10	flash tank
11	spraying unit
20-20x	conduit
21	conduit
30-30x	condenser
32 -34	conduit
35-35x	valve
36-36x	control unit
37-37x	conduit
37-38x	conduit
40-40x	valve
41-41x	control unit
50-50x	valve
51-51x	control unit
60x,61x	conduit

Claims

1. A process for the treatment of carbonaceous slurry, comprising the steps of injecting a gas comprising oxygen into said slurry at temperatures of 150 °C to 350 °C and a pressure of above the associated boiling point pressures resulting in an gas-/vapor-mixture comprising at least water, oxygen and hydrogen, determining the volume fraction of water in said vapor-/gas-mixture and stopping the injection of gas comprising oxygen in case the volume fraction of water is below 0.84 in said vapor-/gas-mixture, **characterized in that** the volume fraction of water vapor in said vapor-/gas-mixture is determined by the IAPWS formulation for water and steam.

2. A process according to claim 1, **wherein** the temperature and pressure of the vapor-/gas-mixture is measured.

3. A process according to claims 1 or 2, **wherein** volume fraction of water is 0,84 to 1,0 the molar fraction of oxygen is 0 to 0,16 and the molar fraction of hydrogen is 0 to 0,16.

4. A process according to any of claims 2 or 3, **wherein** the volume fraction of water is determined by the IAPWS formulation of water and steam.

5. A process according to any of the preceding claims, **wherein** the temperature and pressure of said vapor-/gas-mixture is measured after separating water via condensation.

6. A process according to any of the preceding claims, **wherein** a chemically inert gas is added to said vapor-/gas-mixture in case a given water vapor fraction is fallen below.

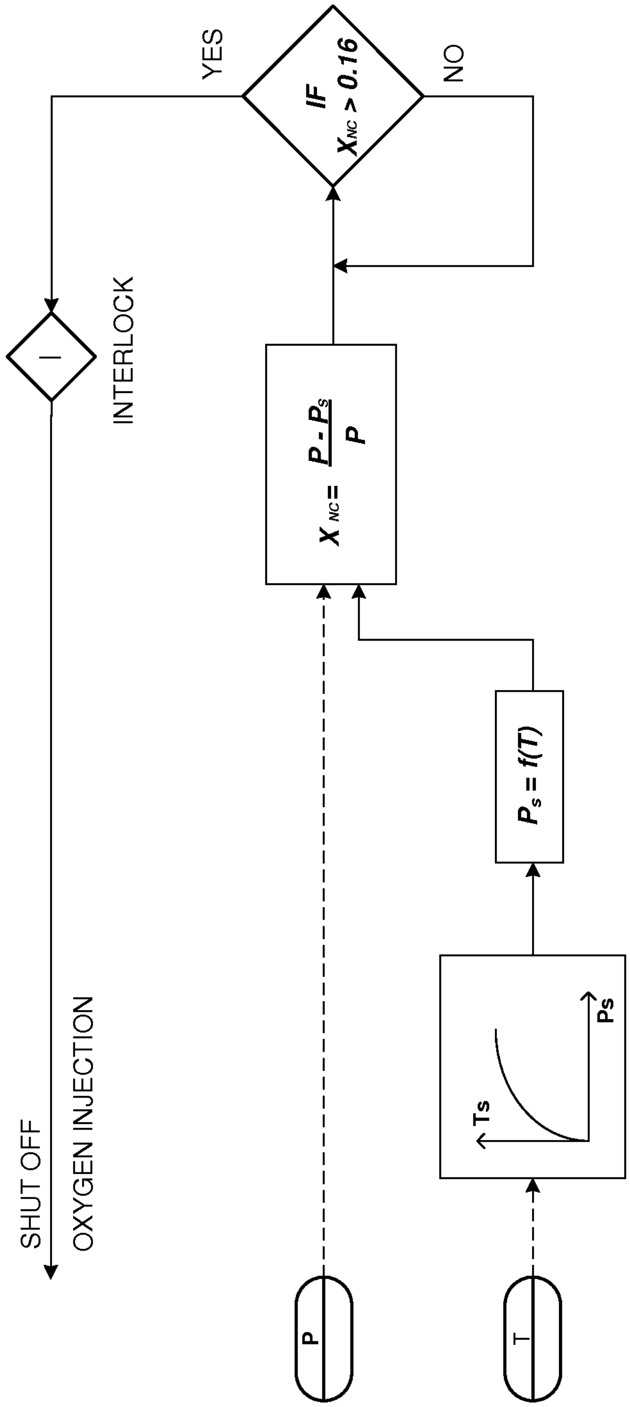
7. A plant for the treatment of carbonaceous slurry comprising at least one flash tank (10) with at least one inlet conduit (2) for introduction of untreated and/or partially treated slurry provided via a slurry supply tube (1), a gas supply tube (3) comprising a valve (4) for introduction of a gas comprising oxygen to said slurry, a gas outlet tube (20) for discharging vapor-/gas-mixture from at least one flash tank (10), at least one temperature sensor (40) for determining the temperature of said vapor-/gas-mixture and one pressure sensor (41) for determining the pressure of said vapor-/gas-mixture, a control (5) for closing said valve (4) in case the volume fraction of water is below 0.84 in said vapor-/gas-mixture.

8. A plant according to claim 7, further comprising at least one condenser (30) for separating water from the vapor-/gas-mixture.

9. A plant according to claim 7 or 8, **wherein** the gas supply tube (3) directly emerges with the slurry supply tube (1) such that the gas comprising oxygen is introduced into the slurry upstream of the flash tank (10).

10. A plant according to any of claims 7 to 9, **wherein** the gas outlet tube (20) guides the vapor-/gas-mixture to the at least one condenser (30) in which water is separated from the vapor-/gas-mixture.

11. A plant according to claim 10, **wherein** the temperature sensor (40) and the pressure sensor (41) are located downstream to the at least one condenser (30).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Ps = f(T)
X NC = (P - PS) / P
IF X_NC > 0.16
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OXYGEN INJECTION

Fig. 1

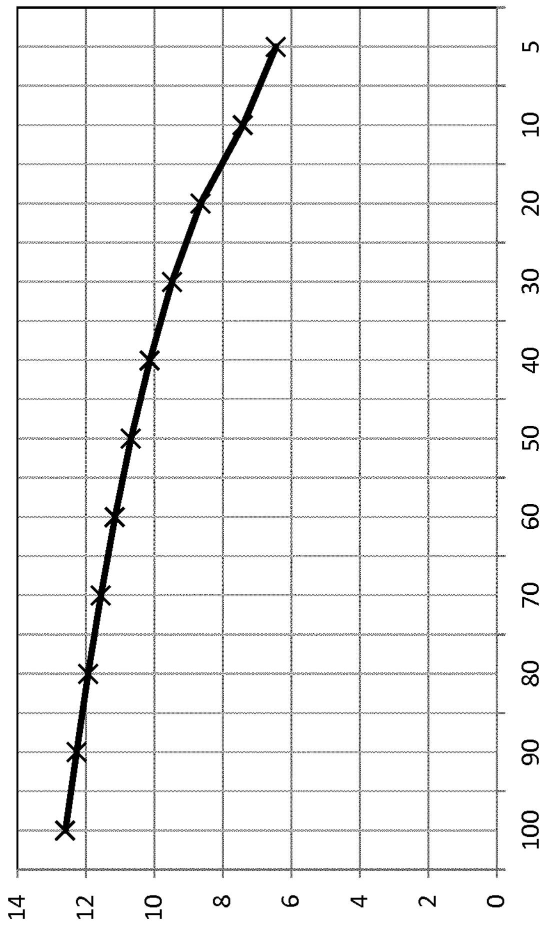

Fig. 2

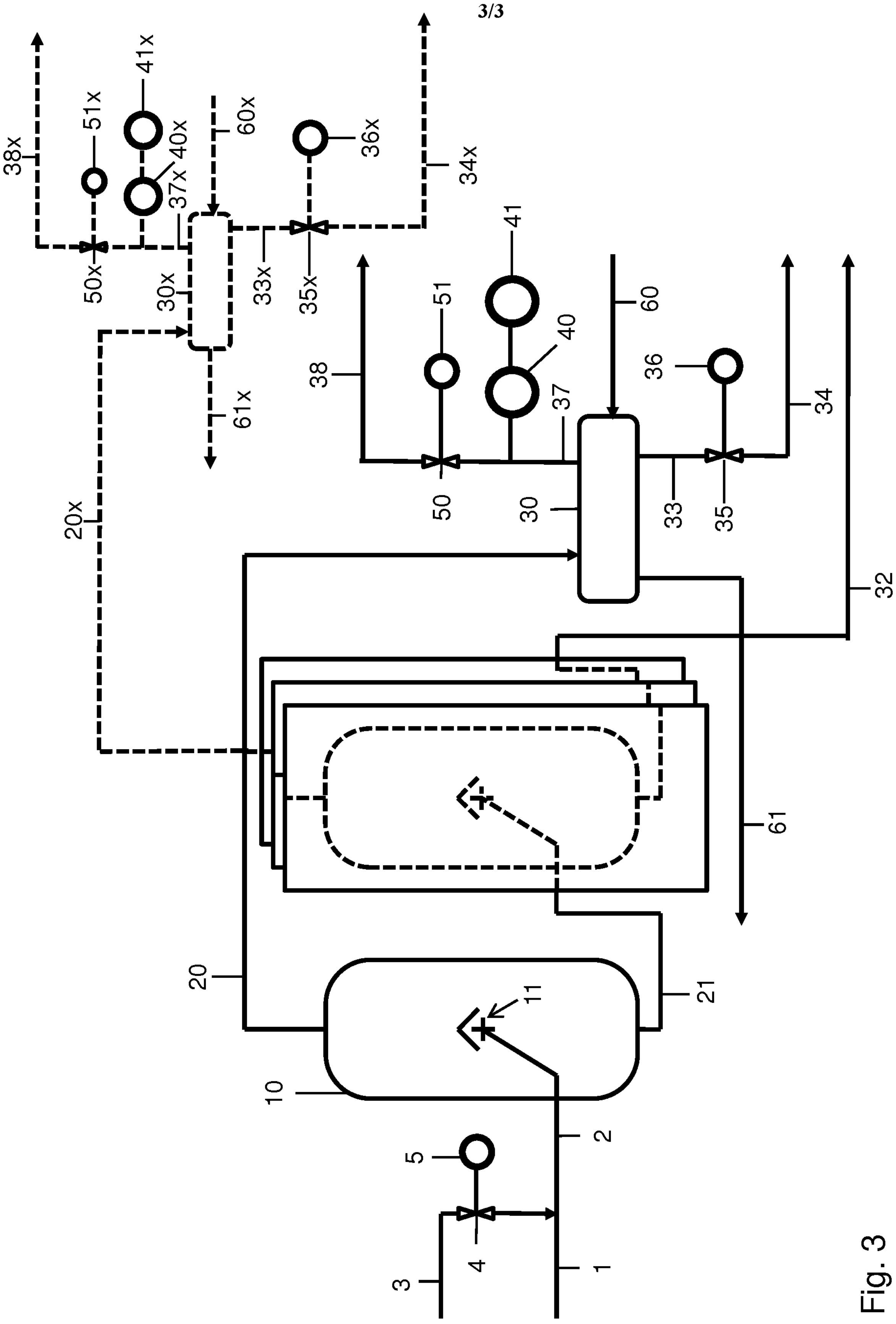
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Fig. 3

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/077687

A. CLASSIFICATION OF SUBJECT MATTER
INV. C02F11/08
ADD. C02F103/16

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)
C02F C22B C01F

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, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	US 4 744 908 A (PETERSCHECK HERMANN W [US] ET AL) 17 May 1988 (1988-05-17) figure 1 column 4, line 57 - column 8, line 58	7-11 1-6
X A	JP 2008 207136 A (UNIV SHIZUOKA NAT UNIV CORP) 11 September 2008 (2008-09-11) figure 1 paragraph [0002] paragraph [0018] - paragraph [0024] paragraph [0034]	7-11 1-6
X A	US 6 423 236 B1 (SHIOTA YUSUKE [JP] ET AL) 23 July 2002 (2002-07-23) figure 1 column 1, line 5 - line 10 column 3, line 55 - column 5, line 54 column 11, line 55 - line 67	7-11 1-6

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☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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Date of the actual completion of the international search

1 March 2017

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09/03/2017

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/077687

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	ARNSWALD: "Removal of organic carbon from Bayer liquor by wet oxidation in tube digesters", LIGHT METALS, 1991, pages 23-27, XP000366101, cited in the application	1-6
A	"Abstract"; page 23 "Risk potential of wet oxidation"; page 24 "Wet Oxidation in Tube digester units"; page 24 -----	7-11
A	GB 1 537 695 A (STERLING DRUG INC) 4 January 1979 (1979-01-04) page 2, line 44 - line 57 -----	1-11
A	EP 1 289 893 A1 (VOEST ALPINE IND ANLAGEN [AT]) 12 March 2003 (2003-03-12) claim 16 -----	1-11

2

Form PCT/ISA/210 (continuation of second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2016/077687

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