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(54) PROCESS FOR INCREASING THE AMOUNT OF OXIDIZED WHITE LIQUOR PRODUCED IN AN AIR-BASED OXIDATION REACTOR AND AN OXYGEN INJECTION SYSTEM FOR AN AIR-BASED OXIDATION REACTOR

(57) The present application relates to an oxygen injection system for an air-based oxidation reactor (1), wherein the oxygen injection system comprises a recirculation loop (2). The application also relates to a process for increasing the amount per unit of time of oxidized of white liquor produced by adding oxygen to white liquor via the oxygen injection system. An air-based oxidation reactor (1) comprising at least one oxygen injection system is also disclosed herein.

The present invention allows to produce between 40 and 100% more oxidated white liquor with the same air-based reactor.

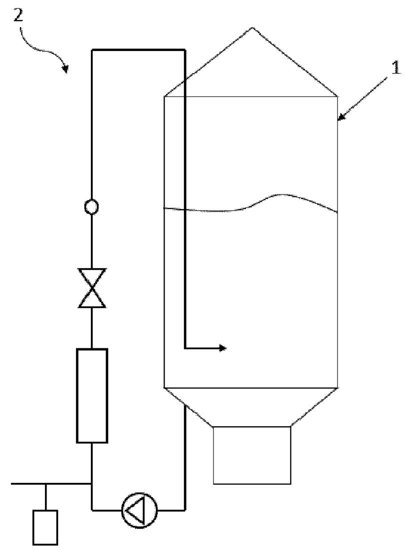

Figure 1

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Description

Technical field

[0001] This application relates to a process for increasing the amount per unit of time of oxidized of white liquor produced in an air-based oxidation reactor, to an oxygen injection system for an air-based oxidation reactor, and to an air-based oxidation reactor comprising at least one oxygen injection system.

Background art

[0002] The kraft process is a process for the conversion of wood into wood pulp consisting of almost pure cellulose fibers. It entails treatment of wood chips with a mixture of sodium hydroxide (NaOH) and sodium sulfide, known as white liquor, which breaks the bonds that link lignin to the cellulose.
[0003] The price of pure NaOH in the European Market has been increasing over time. The price of pure NaOH rose - in Europe - four fold in the last five years. The main goal for pulp mill companies is thus to reuse process streams present in their site to produce a solution containing NaOH which can be used as a substitute for the NaOH that is currently purchased. In order to substitute the purchased NaOH used in the alkaline steps of the fiberline, methods to produce NaOH by the oxidation of white liquor are a solution to the increasing prices of NaOH.
[0004] These companies aim to reduce the high cost related to the purchased NaOH and this can be done by the reuse of process streams currently present in the kraft process, which is by far the most common pulping process, to produce NaOH.
[0005] In the same technical field, document EP1345680B1 discloses a method for oxidation, using an oxidation gas, of a liquid contained in a reactor in which during the mixing step of the gas and of the liquid, the means of stirring the liquid creates a liquid flux in the space in the immediate neighbourhood of the end of the pipe discharging into the liquid and generates a gas/liquid dispersion in a zone in the neighbourhood of said space, called the pre-reaction zone, in which the liquid reacts with the gas, then conveys said gas/liquid dispersion and ejects it at its periphery in a substantially horizontal direction, so that the gas is dissolved in the liquid in a zone extending from the stirring means to the liquid surface, called the mixing zone.

Summary

[0006] The present application relates to an oxygen injection system for an air-based oxidation reactor (1) having a recirculation loop (2) for the addition and mixing of O_2 with white liquor comprising:

- a first pipe (2.1.1) having a first end to fluidly connect with the air-based oxidation reactor (1) and a second end fluidly connected with at least one mixing means (2.4), the first pipe (2.1.1) being suitable to circulate white liquor from inside the air-based oxidation reactor (1) to the at least one mixing means (2.4); and
- a second pipe (2.1.2) having a first end fluidly connected with at least one mixing means (2.4) and a second end terminating inside the air-based oxidation reactor (1), the second pipe (2.1.2) being suitable to circulate the resulting mixture back into the air-based oxidation reactor (1);

- the first pipe (2.1.1) comprises at least one pump (2.2);
- the second pipe (2.1.2) comprises at least one temperature probe (2.6);
- at least one O_2 injection line (2.3) arranged in pipe (2.1.1);
- at least one valve (2.5) arranged in the second pipe (2.1.2); and an oxygen dosing cabinet (2.7) arranged in the O_2 injection line.

[0007] In one embodiment the second end of the second pipe (2.1.2) is immersed at a depth of the white liquor between 5 cm to 5 meters.
[0008] In one embodiment the at least one mixing means (2.4) is selected from a static mixer or a venturi mixer.
[0009] In one embodiment an additional valve is arranged in the first pipe (2.1.1) close to the O_2 injection line.
[0010] In one embodiment the oxygen dosing cabinet (2.7) comprises an authorization on/off valve for O_2 injection, a proportional control valve for O_2 injection modulation and an oxygen mass flow meter outlet
[0011] In one embodiment the recirculation loop (2) further comprises a water cooling heat exchanger (2.8).
[0012] The present application also relates to a process for increasing the amount per unit of time (m^3/h) of oxidized white liquor produced in an air-based oxidation reactor (1) comprising the following steps:

- Circulating white liquor from inside an air-based oxidation reactor (1) to at least one oxygen injection system as described in any of the claims 1 to 6;

- Adding and mixing O_2 with the white liquor circulating in the oxygen injection system;
- Circulating the resulting mixture back into the air-based oxidation reactor (1).

[0013] In one embodiment O_2 is added in a quantity between 10 to 400 kg of O_2/m^3 of white liquor.

[0014] In one embodiment the white liquor circulates at a temperature below 100°C and a pressure below 1.02 bar abs.

[0015] In one embodiment the addition of O_2 starts between 5 to 1800 seconds after the operational start of the recirculation loop (2) of the one oxygen injection system.

[0016] In one embodiment pure O_2 is added with a purity degree between 90 and 100% v/v.

[0017] In one embodiment impure O_2 is added with a purity degree between 70 and 89% v/v.

[0018] In one embodiment O_2 is added as a gas phase or liquid phase.

[0019] The present application also relates to an air-based oxidation reactor comprising at least one oxygen injection system.

General description

[0020] Companies in this technical field already have air-based oxidation reactors for the oxidation of white liquor operating in the kraft pulp process to improve the sodium/sulfur balance, and these reactors can benefit from an oxygen booster in the oxidized white liquor (OWL) production process to produce at least 40% more OWL. In air-based white liquor systems such as these, air is fed to the oxidation reactor containing white liquor and oxidized white liquor is obtained. This is clearly an interesting market, first to boost an air-based oxidation reactor with oxygen and afterwards, if needed, install a full oxidized white liquor system and process. Either way, for the company, the payback for investing in an O_2 boosting system will take less than one year at present NaOH market prices.

[0021] The present application relates to a process for increasing the amount per unit of time (m^3/h) of oxidized white liquor produced.

[0022] The present application also relates to an oxygen injection system that increases the amount per unit of time (m^3/h) of oxidized white liquor produced from a given maximum amount, for example 9 m^3/hour, solely with air, between 40 and 1000 with air + oxygen. The oxygen injection system is suitable for an air-based oxidation reactor of an air-based white liquor system.

[0023] The main reactions occurring during the oxidation process of white liquor are:

$$2\ Na_2S + 2\ O_2 + H_2O \text{ -> } Na_2S_2O3 + 2\ NaOH$$

$$Na_2S_2O3 + 2\ O_2 + 2\ NaOH \rightarrow 2\ Na_2SO_4 + H_2O$$

[0024] Both reactions are exothermic. The air-based white liquor oxidation system only needs a small amount of saturated steam (water) since due to air injection a fraction of the water from the reactional mixture (i.e., white liquor) evaporates and cools the system.

[0025] The oxygen injection system will only need to operate above a certain white liquor amount per unit of time (m^3/h). Production of oxidized white liquor is limited by the capacity of air to oxidize the white liquor. Therefore, the presently disclosed invention operates when said limitation of oxidation with air occurs, and particularly when an increase of sulfide concentration is detected in the white liquor oxidized with air.

[0026] In order to use the oxygen efficiently, the addition of O_2 in the compressed air stream of an air-based white liquor system is not advisable. Depending on the system used to compress the air, the air could contain droplets of oil which could create safety concerns with the oxygen injection (e.g., fire or even explosion risk). The efficiency of the coarse bubble system through which the air is blown is poor and thus the efficiency of the oxygen would be similar. Instead, the presently described oxygen injection system should be provided in an air-based oxidation reactor to overcome problems related to direct addition of O_2.

[0027] The oxygen injection system of the present invention comprises a recirculation loop, which itself comprises at least one pump, at least one valve, pipes, at least one mixing means and at least one O_2 injection line.

[0028] The heat produced by the exothermic reactions for an extra amount of white liquor produced will be relevant (0.5 to 1.5 Mw depending on the flow of white liquor) . In this case the recirculation rate of white liquor to the oxygen injection system must be chosen in such a way that flash does not occur inside the pipes. By the same reason, one pipe, a second pipe, must be immersed in the reactional mixture (i.e., white liquor) inside the air-based oxidation reactor.

[0029] The mixing means must be chosen considering a sufficient recirculation rate in order to avoid flash of steam in the piping.

[0030] The rate of the reactional mixture in the recirculation loop must be adequate, for example between 10 to 50 times the amount per unit of time (m^3/h) of oxidized white liquor produced so that flash does not occur due to exothermic reaction of sulfide and oxygen at a pressure of 2.0 barg.

[0031] The material of the oxygen injection system elements in contact with the white liquor should be at least AISI 316L stainless steel.

Brief description of drawings

[0032] For easier understanding of this application, figures are attached in the annex that represent the preferred forms of implementation which nevertheless are not intended to limit the technique disclosed herein.

Figure 1 illustrates one embodiment of the oxygen injection system of the present invention.
Figure 2 illustrates one embodiment of the oxygen injection system arranged in an air-based oxidation reactor.
Figure 3 illustrates one embodiment of the oxygen injection system of the present invention.

Detailed description of embodiments

[0033] Now, preferred embodiments of the present application will be described in detail with reference to the annexed drawings. However, they are not intended to limit the scope of this application.

[0034] The present application relates to an oxygen injection system for an air-based oxidation reactor, a process for increasing the amount per unit of time (m^3/h) of oxidized of white liquor produced, and an air-based oxidation reactor comprising at least one oxygen injection system.

[0035] The oxygen injection system of the present invention comprises a recirculation loop (2) for the addition and mixing of O_2 with white liquor and is suitable to be mounted on an air-based oxidation reactor (1).

[0036] Figure 1 shows the oxygen injection system of the present invention comprising the recirculation loop (2) arranged in an air-based oxidation reactor (1) containing white liquor.

[0037] Figure 2 shows the oxygen injection system arranged in an air-based oxidation reactor (1). In one embodiment, a standard air-based oxidation reactor (1) comprises a raw white liquor inlet (4), an air inlet (6) and a steam inlet (5).

[0038] As shown in Figure 2, the recirculation loop (2) itself comprises at least one pump (2.2), at least one valve (2.5), pipes (2.1.1, 2.1.2), at least one mixing means (2.4), at least one O_2 injection line (2.3), at least one temperature probe (2.6) and an oxygen dosing cabinet (2.7).

[0039] In one embodiment, the recirculation loop (2) comprises pipes, more specifically:

- a first pipe (2.1.1) having a first end to fluidly connect with an air-based oxidation reactor (1) and a second end fluidly connected with at least one mixing means (2.4), the first pipe (2.1.1) being suitable to circulate white liquor from inside the air-based oxidation reactor (1) to the at least one mixing means (2.4) to mix O_2 with the white liquor; and
- a second pipe (2.1.2) having a first end fluidly connected with at least one mixing means (2.4) and a second end terminating inside the air-based oxidation reactor (1), the second pipe (2.1.2) being suitable to circulate the resulting mixture back into the air-based oxidation reactor (1).

[0040] In a preferred embodiment, the second end of the second pipe (2.1.2) becomes immersed in the white liquor inside the air-based oxidation reactor (1), as shown in Figures 1 and 2.

[0041] In one embodiment the second end of the second pipe (2.1.2) is immersed at a depth of the white liquor between 5 cm to 5 meters, in order to maintain a minimum pressure of 1.1 Bar abs inside the second pipe (2.1.2) and thus avoid flash of steam inside said pipe.

[0042] The first pipe (2.1.1) comprises at least one pump (2.2) suitable to circulate white liquor from inside the air-based oxidation reactor (1) to the at least one mixing means (2.4) where it is mixed with O_2.

[0043] The second pipe (2.1.2) comprises at least one temperature probe (2.6).

[0044] In one embodiment, O_2 is added to the white liquor circulating in the recirculation loop (2) via at least one O_2 injection line (2.3) arranged in pipe (2.1.1).

[0045] The at least one mixing means (2.4) are suitable to emulsify the O_2 and mix the white liquor with O_2. In one embodiment, the at least one mixing means (2.4) are selected from, but not limited to, a static mixer, a venturi mixer, or any other mixing means suitable for the purpose.

[0046] Optionally, a self-suction venturi device can also be used. This is a venturi device where the liquid passing through the venturi device creates a vacuum that entrains the O_2 to be mixed in said venturi. It means that the off-gas from the reactor can be aspirated through this self-suction venturi. Said venturi device is, for instance, inserted in a recirculation loop that is arranged parallel to the recirculation loop where the at least one mixing means (2.4) is installed. Excess gas will be purged to the atmosphere through a pressure control valve operating at low pressure, for instance 1.02 Bar abs.

[0047] The recirculation loop (2) further comprises at least one valve (2.5) arranged in the second pipe (2.1.2). An additional valve can be arranged in the first pipe (2.1.1) close to the O_2 injection line.

[0048] In one embodiment, as shown in Figure 3, the recirculation loop (2) can optionally comprise a water cooling heat exchanger (2.8) suitable to control the temperature of white liquor in circulation below 100°C and reduce the risk of flash.

[0049] The oxygen injection system further comprises an oxygen dosing cabinet (2.7) arranged in the O_2 injection line and at least comprising the following features that will interact with a distributed control system:

- Authorization on/off valve for O_2 injection (preferably of 24 V AC);
- Proportional control valve for O_2 injection modulation;
- Oxygen Mass Flow Meter outlet (preferably of 4-20 mA).

[0050] All the variables linked to the addition of O_2 can be followed in trend graphics.

[0051] The process for increasing the amount per unit of time (m^3/h) of oxidized white liquor produced in an air-based oxidation reactor (1) comprises the following steps:

- Circulating white liquor from inside an air-based oxidation reactor (1) to at least one oxygen injection system as described above;
- Adding and mixing O_2 with the white liquor circulating in the oxygen injection system;
- Circulating the resulting mixture back into the air-based oxidation reactor (1).

[0052] In one embodiment, the process is suitable to be performed in an air-based oxidation reactor of an air-based white liquor system.

[0053] In one embodiment, the white liquor circulates at a temperature below 100°C and a pressure below 1.02 bar abs.

[0054] In one embodiment, O_2 is added in a quantity between 10 to 400 kg of O_2/m^3 of white liquor.

[0055] In one embodiment, the addition of O_2 starts when the recirculation pump of the oxygen injection system is in operation after 20 seconds. The addition of O_2 occurs above the maximum amount per unit of time (m^3/h) of white liquor that was able to be oxidized with air inside the reactor.

[0056] In one embodiment, the addition of O_2 starts between 5 to 1800 seconds after the operational start of the recirculation loop (2) .

[0057] In one embodiment, pure O_2 is added with a purity degree between 90 and 100% v/v. In another embodiment, impure O_2 is added with a purity degree between 70 and 89% v/v.

[0058] In one embodiment, O_2 is added as a gas phase or liquid phase.

[0059] The present invention is also related to an air-based oxidation reactor comprising at least one oxygen injection system.

[0060] With the present invention, it is possible to produce at least 40% more oxidized white liquor in an air-based oxidation reactor, regardless of the size of the reactor. Common air-based oxidation reactors can produce a range of white liquor anywhere from 4 m^3/hour to 30 m^3/hour, and the present invention can be adapted to any of these reactors.

[0061] This description is of course not in any way restricted to the forms of implementation presented herein and any person with an average knowledge of the area can provide many possibilities for modification thereof without departing from the general idea as defined by the claims. The preferred forms of implementation described above can obviously be combined with each other. The following claims further define the preferred forms of implementation.

Claims

1. An oxygen injection system for an air-based oxidation reactor (1) **characterized by** having a recirculation loop (2) for the addition and mixing of O_2 with white liquor comprising:

   - a first pipe (2.1.1) having a first end to fluidly connect with the air-based oxidation reactor (1) and a second end fluidly connected with at least one mixing means (2.4), the first pipe (2.1.1) being suitable to circulate white liquor from inside the air-based oxidation reactor (1) to the at least one mixing means (2.4); and
   - a second pipe (2.1.2) having a first end fluidly connected with at least one mixing means (2.4) and a second end terminating inside the air-based oxidation reactor (1), the second pipe (2.1.2) being suitable to circulate the resulting mixture back into the air-based oxidation reactor (1);
   - the first pipe (2.1.1) comprises at least one pump (2.2);
   - the second pipe (2.1.2) comprises at least one temperature probe (2.6);
   - at least one O_2 injection line (2.3) arranged in pipe (2.1.1);
   - at least one valve (2.5) arranged in the second pipe (2.1.2); and an oxygen dosing cabinet (2.7) arranged in

the O_2 injection line.

2. The oxygen injection system according to the previous claim, wherein the second end of the second pipe (2.1.2) is immersed at a depth of the white liquor between 5 cm to 5 meters.

3. The oxygen injection system according to any of the previous claims, wherein the at least one mixing means (2.4) is selected from a static mixer or a venturi mixer.

4. The oxygen injection system according to any of the previous claims, wherein an additional valve is arranged in the first pipe (2.1.1) close to the O_2 injection line.

5. The oxygen injection system according to any of the previous claims, wherein the oxygen dosing cabinet (2.7) comprises an authorization on/off valve for O_2 injection, a proportional control valve for O_2 injection modulation and an oxygen mass flow meter outlet

6. The oxygen injection system according to any of the previous claims, wherein the recirculation loop (2) further comprises a water cooling heat exchanger (2.8).

7. A process for increasing the amount per unit of time (m^3/h) of oxidized white liquor produced in an air-based oxidation reactor (1) comprising the following steps:

- Circulating white liquor from inside an air-based oxidation reactor (1) to at least one oxygen injection system as described in any of the claims 1 to 6;
- Adding and mixing O_2 with the white liquor circulating in the oxygen injection system;
- Circulating the resulting mixture back into the air-based oxidation reactor (1).

8. The process according to the previous claim, wherein O_2 is added in a quantity between 10 to 400 kg of O_2/m^3 of white liquor.

9. The process according to the previous claim, wherein the white liquor circulates at a temperature below 100°C and a pressure below 1.02 bar abs.

10. The process according to any of the claims 7 to 9, wherein the addition of O_2 starts between 5 to 1800 seconds after the operational start of the recirculation loop (2) of the one oxygen injection system.

11. The process according to any of the claims 7 to 10, wherein pure O_2 is added with a purity degree between 90 and 100% v/v.

12. The process according to any of the claims 7 to 10, wherein impure O_2 is added with a purity degree between 70 and 89% v/v.

13. The process according to any of the claims 7 to 12, wherein O_2 is added as a gas phase or liquid phase.

14. An air-based oxidation reactor comprising at least one oxygen injection system described in any of the claims 1 to 6.

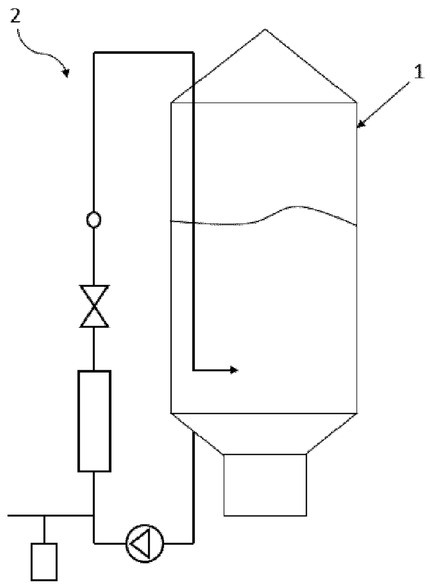

Figure 1

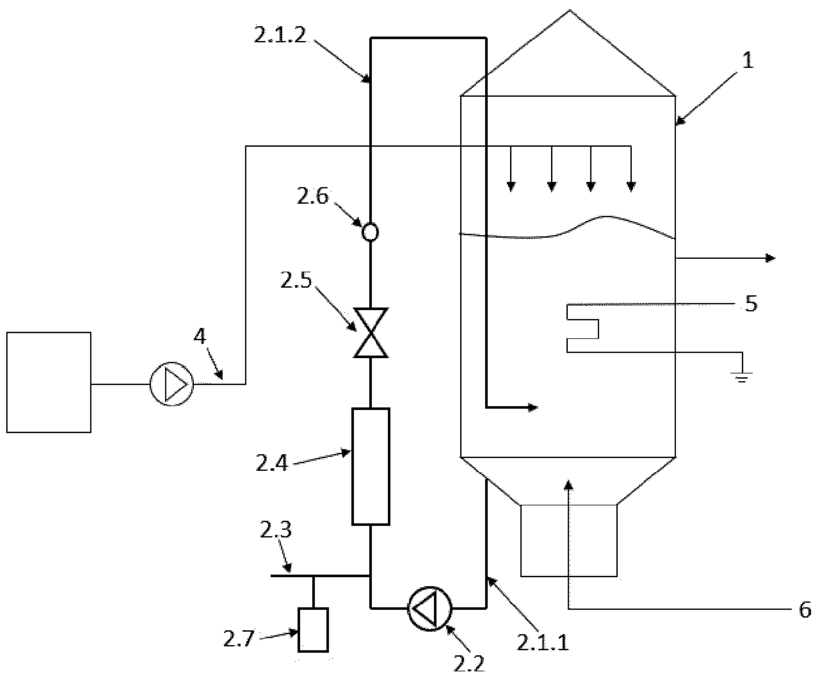

Figure 2

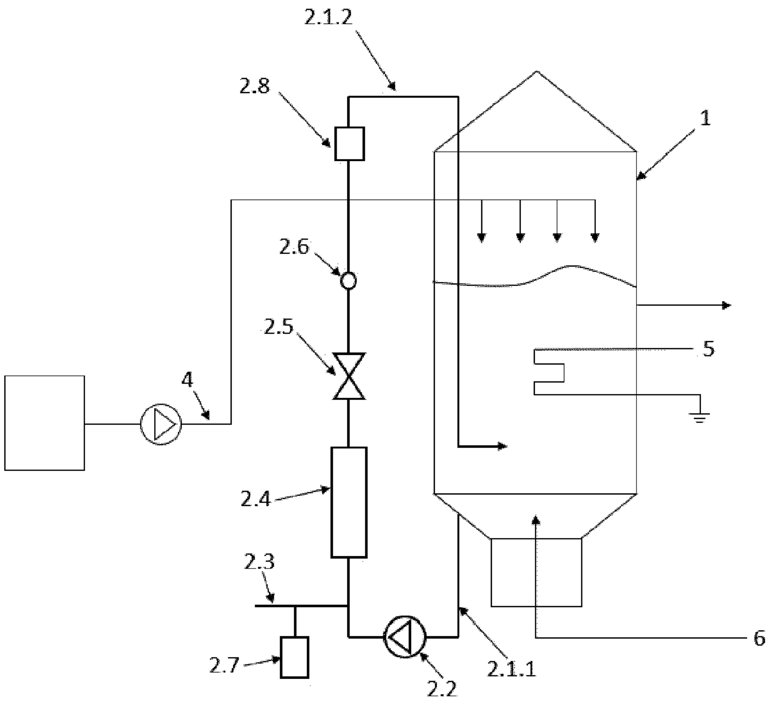

Figure 3

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The present search report has been drawn up for all claims

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Place of search	Date of completion of the search	Examiner
Munich	18 August 2023	Karlsson, Lennart

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