

A Novel Oxidation Process for Elimination of Organic Compounds in Aqueous Waste Liquors

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Abstract

A novel process designed to eliminate, by thermal oxidation, organic compounds creating chemical oxygen demand (COD) in aqueous waste liquors with low calorific value is presented. The process complies with stringent environmental regulations. In the process the liquor is oxidised by pure oxygen in a reactor pressurised to 10-bars. The liquor is atomised into small droplets and combusted at a temperature higher than 1200 °C. An in-built direct-contact evaporator makes it possible to oxidise aqueous solutions with a total dissolved solids (TDS) content of 30–40%. Inorganic components of the liquor are extracted as concentrated brine. Heavy metals contained in the brine are separated as insoluble carbonates embedded in a larger amount of calcium carbonate. The off-gas contains about 75–90% carbon dioxide. The equipment can handle chloride-containing liquids, and the risk for synthesis of chlorinated organic compounds is largely eliminated.

Introduction

Many types of waste liquor have, in addition to a high amount of inorganic components, also a considerable content of organic contaminants. Such liquors are, e.g., concentrates obtained when contaminated process waters are purified by evaporation or membrane processes. The concentrates contain the harmful substances that must be eliminated in an environmentally acceptable way.

In the 90s influential paper buyers in central Europe joined forces with the Green movement, demanding environmentally acceptable production methods in the forest industry. This triggered a large activity to change production processes. The situation also initiated development work aiming at the reduction of process water used and its internal purification in order to close the process water loops. This development work has been successfully completed [1], and the results are now commercially available to the forest industry as well as other branches of the process industry.

The Oxidiser

The oxidiser [2] has the following features:

- The waste liquor is atomised into small droplets and the organic components are completely oxidised by using pure technical oxygen into carbon dioxide and water vapour.
- The oxidation takes place in a reactor chamber pressurised to 10-bars.
- The gas temperature in the reaction chamber exceeds 1200 °C and the gas is rapidly quenched to a temperature of about 200 °C at the reactor chamber outlet.
- The inorganic substances in the liquor form a slag that is dissolved in a concentrated water solution; insoluble components of the slag are separated from the brine.
- The calorific value of the organic components in the liquor is utilized for steam generation with high thermal efficiency.
- The exhaust gas is efficiently scrubbed.

The operating principle of the new device named CONOX (CONcentrate OXidiser) is described with reference to Figure 1. The oxidiser comprises the following main components:

- Reactor designed for suspension firing of concentrate.
- Slag dissolver.
- Direct-contact evaporator, also working as a rapid gas quench.
- Reactor cooling system generating 10-bar steam.
- 3-bar steam generator, also working as a wet scrubber of the gas.
- 1-bar steam generator, working as a second gas scrubber.

Oxidation

The oxidation of the liquor takes place in the reactor chamber at a pressure of 10-bars. The chamber is totally submerged into a water-filled pressure vessel. The pressure in this vessel is kept equal to the pressure in the reactor chamber. Therefore there is no substantial pressure difference across the reactor wall. A water trap guarantees that the allowable pressure difference of 0,5 bar is not exceeded.

Because the reactor is pressurized and there is no nitrogen from air in the combustion gas, the gas volume is small, only about 2% of the corresponding volume if the liquor would be burnt by combustion air in an atmospheric furnace. Because the gas volume determines the size of the equipment, a very compact design is obtained. This makes it possible to install the oxidiser in a skid and to deliver it to the site in a standard container.

After final evaporation and preheating to the boiling point (about 180 °C), the concentrate is pumped to the burner located at the top of the reaction chamber. Here the liquor is atomised with pressurized and preheated oxygen into small droplets that ignite and burn. To reach complete combustion, secondary oxygen is injected around the flame. Experience has shown that about 5% surplus oxygen has to be used in order to reach complete oxidation. A small amount of fuel oil (about 5 kg/h) is injected in the centre of the liquor burner to secure a stable flame. This small oil flame is also used for start-up of the process.

At the high combustion temperature, the inorganic components of the concentrate form droplets of molten slag. When these droplets hit the water-cooled reactor wall, they adhere to the wall and solidify. The solid slag layer grows until the inner slag surface reaches the slag melting point. Then molten slag starts running down the slag layer into the slag dissolver located below the reactor chamber. This solidified slag layer reduces the heat transfer to the surrounding water jacket and prevents the gas from cooling. The hot inner surface of the slag layer, typically more than 700 °C, supports the reaction in the chamber. Because the kinetics of chemical reactions in solid phase are very slow, the solidified slag layer prevents corrosion of the reactor wall.

Slag Handling

The molten slag runs by gravity into the slag dissolver that is in direct contact with the reactor chamber and thus also at 10-bar pressure. Hot water is pumped into the dissolver and kept in continuous movement by an efficient agitator. The slag droplets are partly dissolved and partly kept in suspension. The concentration of the resulting brine is automatically controlled and extracted from the dissolver through a control valve into an atmospheric vessel, from which expansion steam is collected. If the slag contains calcium and heavy metals and the brine is alkaline, insoluble carbonates of the heavy metals will be co-precipitated with calcium carbonate. This precipitate can be separated from the brine, and the heavy metals extracted as a small amount of solid matter.

The concentration of the brine can even be kept so high that the slag droplets do not dissolve. By doing so the slag can be extracted in solid phase from the device. Then special attention has to be paid to the corrosive nature of the concentrated brine.

Gas Handling

The combustion gas flows through the slag dissolver into a pressure vessel acting both as a direct-contact evaporator and a rapid gas quench. Incoming concentrate is dispersed as small droplets into the gas, and because of the large contact area between the gas and droplets, the gas is rapidly cooled to a temperature close to the water boiling temperature. Simultaneously water is evaporated from the liquid being heated to the boiling point. From the bottom of this direct-contact evaporator the liquor is pumped to the burner.

The quenched gas, now saturated with water vapour at 10-bar pressure, flows to a heat exchanger where water vapour is condensed from the gas. The latent heat released is transferred to pure water on the tube-side of the heat exchanger, generating process steam at typically 3-bar pressure. At the outlet of this heat exchanger there is still condensable water vapour in the gas. Therefore a second heat exchanger is applied with atmospheric pressure in the tubes. In this heat exchanger almost all remaining water vapour in the gas is condensed, and the exhaust gas, still at 10-bar pressure, is released at about 110 °C into the atmosphere. Alternatively, carbon dioxide can be recovered from the exhaust gas.

In these vertically installed heat exchangers, water condensed from the gas is running along the outside surface of the tubes. The gas is led in cross-flow through the tube bundle at high velocity. Liquid droplets and solid particles in the gas are efficiently collected into the condensate covering the tubes and running down along them. By injection of sodium hydroxide into the gas, the condensate can be made alkaline and thus also extract acidic gas components such as HCl and SO₂ from the gas. These heat exchangers act as efficient gas scrubbers, too, and no external gas cleaning equipment is needed.

Energy Efficiency

The energy efficiency of the oxidiser is very high. The heat content of the concentrate, given by the calorific value of the organic matter, is used to create the high-temperature gas needed for complete oxidation of the organic matter. The energy content of the hot gas is then utilised twice, first to evaporate water from the incoming concentrate and then for steam generation. Because the off-gas does not contain the nitrogen ballast present in the gas when combustion takes place with air, there is a very low “flue gas loss” from this device. A typical mass and energy balance for the device when combusting 4184 kg/h of a liquid with a tds content of 26% and a net gross calorific value of the feed of 12.5 MJ/kg is shown in Table 1.

Environmental Performance

Because of the very high oxidative environment at high pressure and temperature in the reactor, practically all organic matter in the concentrate fed into the reactor is degraded into CO₂ and H₂O. The COD reduction achieved is thus practically 100%.

Heavy metals in the concentrate can be separated into a small amount of solid matter from the liquid brine, containing only water-soluble harmless salts. If there are restrictions for discharging the brine, the inorganic residue can be extracted in solid form from the device.

Because the gas is very rapidly quenched from a temperature exceeding 1000 °C to below 250 °C, the *de novo* formation of chlorinated organic components is efficiently avoided. This has been experimentally verified when highly chlorinated concentrate from a pulp mill bleach plant has been oxidised in the device. Results from these trials are given in Table 2. Traces of chlorinated organic compounds are detected, but the content of polychlorinated dioxins and furans was below the detection limit that is indicated in the table.

Conclusions

The CONOX oxidiser was originally developed to eliminate organic components causing COD and AOX in bleach plant effluent concentrated by evaporation. Later on, several other applications have been studied, including substitution of expensive recovery boilers for black liquor from small and medium scale non-wood pulping processes [3, 4], elimination of concentrates from landfill leachate treatment, different waste liquors from the chemical industry, the car industry, etc.

Table 1: oxidizer mass and energy balance

Incoming	kg/h	°C	MJ/h
Strong concentrate	4 184	80	14 498
Fuel oil	10	60	450
Oxygen	1 104	30	30
Feed-water	5 086	95	2 023
Incoming, total	10 384		17 001
Outgoing			
Off-gas	1 407	110	411
Salt solution	2 368	103	849
10-bar steam	1 804	180	4 992
3-bar steam	2 771	134	7 546
1-bar steam	1 041	100	2 787
Sec. condensate	993	100	416
Outgoing, total	10 384		17 001

Table 2: measured emissions

Component	mg/m ³ n
PAH	0.005
PCB	0.000 01
Chlorinated benzenes	0.000 02
Chlorinated phenoles	0.0000 06
Dioxin/furan	<0.000 000 008

**Figure 1:** Operating principle of CONOX(CONcentrate OXidator) process:

1. reactor
2. slag dissolver
3. direct-contact evaporator
4. 3-bar steam generator
5. 1-bar steam generator

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