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RESUMO:

ECONOMIC AND PROCESS CONSIDERATIONS IN THE USE OF OXYGEN FOR BLACK LIQUOR OXIDATION

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Introduction

The black liquor oxidation process has developed significantly since it was introduced in Sweden in 1939 and 1941. Air was used as the oxidant for all the early work, and today, air oxidation units are very common. The possibility of using pure oxygen was first considered in the late 1950's and the first commercial unit in North America was installed at Orange, Texas in 1968 (ref 1). Since then there have been numerous tests and development projects and there are now approximately ten commercial, pure oxygen, BLO systems, operating in North America.

The objective of this work is to describe the technical and economic feasibility of the use of oxygen versus air for black liquor oxidation and the results of two operating installations.

The primary objective of every existing air and oxygen BLO system is to lower TRS (total reduced sulfide) emissions from the mill's direct contact evaporator (DCE). CO_2 and SO_2 in the hot flue gases react with residual Na_2S in the black liquor to produce H_2S; a process referred to as "stripping". If the Na_2S is oxidized to $Na_2S_2O_3$, it becomes stable and will not be stripped in the DCE. Normally, mills target Na_2S levels below 0.1 gm/l entering the DCE.

The theoretical oxygen requirement to oxidize 100% of the Na_2S to $Na_2S_2O_3$ is called the "stoichiometric oxygen requirement". It can be calculated using the formulae:

$$Q_{O_2} = 0.o246 \text{ x } Na_2S \text{ Level x B.L.Flow}$$

Where: Q_{O_2} = the oxygen requirement in kg/hr
Na_2S level = The concentration of sodium sulfide in the black liquor in gm/l
B.L.Flow = The black liquor flow rate in l/min.

Oxygen vs. Air

A significant difference between black liquor oxidation with air and with oxygen is the speed of the reaction. Most air BLO systems are sized to provide an hour or more of contact between the liquor and the air in order to obtain complete conversion of the Na_2S to $Na_2S_2O_3$, which means that large oxidation tanks are necessary. Pure oxygen reacts with the Na_2S in black liquor in seconds because of the higher partial pressure of oxygen, so a pipeline reactor with a residence

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time ranging from 30 seconds to 5 minutes is sufficient. This difference in size has a significant effect on the capital cost. Oxygen BLO systems can usually be installed for less than $200.000 (US), while an air system will be in order of magnitude more expensive. In addition, an oxygen system is very compact and requires very little space.

Another major difference between an air and an oxygen system is the absence of nitrogen in the oxygen system. Air contains four parts of inert nitrogen per one part of oxygen, which means that a significant amount of gas must be vented from an air oxidation unit. This can be a source of TRS and often leads to foaming problems with liquors that have a high foaming tendency. Oxygen BLO units do not need to be vented because all of the gas added will be consumed.

A combined effect of the fast reaction rate and the fact that no venting is required is that heat recovery is much more efficient with an oxygen unit. The black liquor oxidation reaction is strongly exothermic, producing about 78 kcal per kg of liquor solids (ref.2). This heat is largely wasted in an air oxidation unit. It is dissipated in the vapour and excess gases vented from the unit or lost through radiation. The net effect is that there is littler or no temperature rise in an air BLO system. In a well-insulated oxygen system the process is essentially adiabatic and a significant increase in the liquor temperature will result. This can be ifficiently recovered and can have a positive effect on the economics of an air versus an oxygen system.

Oxygen Reactor

The oxygen reactor is designed to provide good mixing between the oxygen and black liquor, and, it is essential that a well-designed reactor with good mass-transfer characteristics be used. The reaction of Na_2S with oxygen is quite rapid. If there is good mixing, essentially all the oxygen will be consumed by this reaction, while the slower unwanted side-reaction- such as the oxidation of lignins, or the oxidation of thiosulfate to sulfate - will not have a chance to occur. If there is poor mixing, the reaction will slow down, resulting in incomplete conversion of the Na_2S, unwanted side reactions and excess consumption of oxygen. Figure 1 shows the effect of improved reactor design on oxygen consumption. The graph is based on full-scale trials at a U.S. pulp mill. Both reactors were sized for turbulent flow and provided the same retention time. The differences in design were slight and inexpensive, yet had a significant effect on turbulence, mixing efficiency and oxygen consumption.

Oxidation systems have been commissioned that use as little as 104% of the stoichiometric oxygen requirement. However, due to the presence of undetected polysulfides in most liquors, which also must be oxidized to prevent TRS formation, oxygen requirements are typically 125 - 130% of stoichiometric.

The specific design of an oxygen/liquor reactor will vary with the location of the unit in the recovery cycle and the supplier. However, in-line reactors with no moving parts are generally used. High shear mixers are not required. A pump to boost the liquor pressure and a back pressure control valve may be required. The installed cost of the reactor (excluding oxygen supply and controls), will be else less than

$100,000 (US) in most situations.

Weak Black Liquor Oxidaton

The location of the black liquor oxidation reactor can be varied to suit the particular requirements of the situation. Weak liquor oxidation, oxidation between effects in a multiple-effect evaporator and strong liquor oxidation before and after storage have all been successfully practiced. Oxidation of the weak liquor is by far the simplest method to use, and has several advantages:

I) The relatively dilute concentration of Na_2S means that there will be a relatively low volume of oxygen to liquor. This makes it more simple to design a reactor which provides good distribution of the oxygen in the liquor and a fast reaction rate.

II) The low Na_2S concentration means that temperature rise in the reactor will be moderate, reducing the pressure needed to prevent flashing.

III) The sulphur compounds will be stablized before the multiple-effect evaporator reducing sulphur losses in the foul condensate.

IV) There are reports of up to 10% better tall-oil recovery from oxidized liquor (ref.1).

V) The mild process conditions have been found to minimize side reactions and therefore improve oxygen efficiency (actual O_2 consumption/stoichiometric oxygen consumption).

Due to the effect of "reversion", in which partially-oxidized polysulfides can revert back to sulfide (ref.3) most weak liquor BLO systems must be followed by a "polishing" BLO reactor in which strong liquor is oxidized to convert any remaining Na_2S to a stable form just prior to the DCE. This two-stage oxidation process, in which approximately 90% of the oxidation occurs in the weak liquor and 10% in the strong liquor, is very effective and reliable.

Strong Black Liquor Oxidation

One major drawback of the use of weak black liquor oxidation is that only about 20% of the heat generated can be effectivelly recovered. The liquor entering the multiple-effect evaporators will be hotter following BLO, reducing the steam requirement to the ME, but due to the steam economy of an evaporator train, the benefit will be quite small. By performing the BLO stage between effects in the ME evaporator, or in the strong liquor after the evaporator most of the heat can be recovered (ref.4). This can result in a credit of 200 kg of steam per admt of pulp versus air oxidation or weak liquor oxidation with oxygen.

A drawback of strong BLO is that side reactions are more likely to occur at the higher temperatures, reducing the oxygen efficiency. Also, a more complex reactor is required to handle the high gas to liquor ratios and the abrupt 30º to 60ºC temperature rise. A careful control strategy must be installed to prevent over-oxidation which has been reported to cause polymerization and plugging of strong liquor systems.

Black Liquor Polishing

Many mills with DCE's have existing air oxidation units. Often these units are not sufficient to meet new and stricter emission regulations, or become overloaded as mill production is increased. BLO Polishing with pure oxygen is a method to further lower Na_2S levels as required. Readings from a Na_2S meter or TRS levels can be used to automatically control oxygen addition, allowing the mill to handle peaks in Na_2S levels due to upsets or high production rates. Since it is difficult to eliminate small residuals of Na_2S polishing systems normally require 150% of the stoichiometric oxygen requirement to effectively lower the Na_2S to an acceptable level.

Economic Comparison

The economics of air versus oxygen for BLO will depend to a large degree on the cost of oxygen. Oxygen can be supplied in several ways. One common method is as a bulk cryogenic liquid, trucked from merchant production plants and stored on-site in insulated storage tanks. This supply method is economical for requirements ranging from less than one tonne per day to 20 tonne per day or more depending on proximity to oxygen supply. The cost of oxygen supplied in this manner will vary depending on the transportation distance, but will usually be about $150/tonne. For mills requiring 20 tonne/day or more, dedicated on-site plants may be economical and will lower the oxygen cost to less than $100/tonne. In both cases the capital cost to the mill will be low because the O_2 supplier will own and operate the necessary equipment. The mill would be responsible for foundation work, an oxygen pipeline and oxygen flow controls. This would typically cost less than $100,000 (US).

For example, a mill requiring a BLO system capable of fully oxidizing 4000 l/min of 15% solids liquor with 9 gm/l of Na_2S. An oxygen BLO system would consume roughly 27 tonnes per day of oxygen at a cost of $2700 to $4000 per day. The capital cost would be roughly $200,000 (US), ($300,000 (US) if a polishing reactor were required). The system may have a further credit of $1000 per day to energy savings (based on $8/tonne of steam), versus an air system. This compares with an air system which will cost between $2 million and $5 million. The operating cost will be low consisting only of maintenance and power to run air blowers. Payback on installing an air system versus an oxygen system will range from 1 to 8 years.

Another example would be a mill requiring a polishing system to remove 1 or 2 mg/l of Na_2S from a strong liquor stream after an air system. The oxygen requirement would be only 1 to 5 tonne/day. The cost of an oxygen system would compare very favourably with the cost of a new or upgraded air oxidation system.

Mill Experience

The first example of an operating BLO system is a polishing reactor installed at Northwood Pulp and Timber Limited in Prince George, B.C., Canada. The mill underwent a significant expansion in the early 1980's that included a new low-odour recovery boiler. The environmental permit was changed from B to the more stringent A level. The old recovery boiler, equipped with direct-contact cascade evaporator, has a single stage of strong black liquor oxidation with air. Following start-up, and extensive optimization, including the installation of a Pulp and Paper Research Institute of Canada sodium sulfide probe, it was found that the mill could not reliably meet TRS emission level restrictions. The source of the TRS was the direct contact evaporator. The liquor firing rate to the recovery boiler was periodically restricted by the ability of the air BLO system to oxidize the liquor. A Linde black liquor oxidation polishing reactor was selected as a low-cost method to increase production while still allowing the mill to meet 'A' permit levels. The oxygen polishing reactor has allowed the mill to meet TRS restrictions on a continuing basic while increasing liquor firing rates to the furnace. Only in cases when the primary air oxidation stage is out of service or performing very poorly does the reactor have trouble maintaining specified sodium sulfide levels. Oxygen consumption averages about 150% of stoichiometric - normal for a polishing stage - which corresponds to between 0.25 and 1.5 tonne per day of oxygen depending on the sulfide level. The system cost approximately $150,000 (Cdn) to install and since it allowed the mill to increase production, the payback has been very quick. Figures 2 and 3 show the effect on mill operation.

Control of the system has been a problem. Originally the system was designed to be based on the use of a PPRIC sodium sulphide probe on the outlet of the reactor to control oxygen flow. Those probes have worked very well in other installations, and Northwood uses one to control their air oxidation system. Unfortunately, the probe has not worked at the polisher outlet. This has been investigated by PPRIC but no reasons have been determined for the faulty operation. currently, the TRS monitor on the old recovery boiler stack is used to automatically control the oxygen flow. If the TRS level at the stack reaches a predetermined level, the control system automatically steps up oxygen addition to the reactor. To prevent overoxidation of the liquor, which might cause lignin polymerization and excessive loss of liquor heating value, a minimum TRS residual of 3-4 ppm is targeted for the stack. There is no formal recovery of the heat of reaction, although the reactor and transfer pipes are insulated to maintain liquor temperature to the cascade.

In summary the system has proven to be a reliable and cost-effective method of oxidizing the mill's black liquor.

The second installation is a BLO system operating at St. Joe Paper in Port St. Joe, Florida. The system uses pure oxygen for 100% of the oxidation requirements.

In order to reduce TRS emissions, the company installed a BLO system in 1981. A Linde oxygen system was selected because of the low capital cost and rapid installation. The system was originally started with a single stage of strong black liquor oxidation. This performed reasonably well and lowered TRS emissions to an acceptable level. However, oxygen consumption was high - roughly 160% of stoichiometric - and insufficient liquor pressure was available to prevent steam flashing in the reactor on occasion due to the sharp temperature rise. This made control of the system difficult. A second stage was added in the weak black liquor in 1984 and the system currently operates with 90% of the oxidation performed on the weak liquor and 10% on the strong. The system operates very reliably in this configuration. Oxygen consumption has remained higher than normal at approximately 150% of stoichiometric. This is attributed to the presence of unusually high levels of easily oxidized compounds in the liquor other than Na_2S. An unexpected drawback of the BLO system is the adverse effect of the reduction in heating value of the liquor, reported to be more than 5%. The recovery boiler at St. Joe Paper does not benefit from a lower heating value and extra fuel oil has been required.

In summary, in spite of higher than expected operating costs, the BLO system at St. Joe Paper has performed well as a low-cost solution to TRS emissions. It will continue to be operated, but only until capital is available for a low-odour conversion or a TRS scrubber.

Heating value Reduction

It should be noted that St. Joe Paper is not a typical situation. Many overloaded recovery furnaces, particularly those with steam-side or air limitations, will benefit from a liquor with a lower heating value. For most mills, up to a 5% lowering of heating value will produce a corresponding increase in recovery capacity due to the lower heat load. BLO is calculated to lower heating value by 2 to 3 percent (ref.2) although actual installations have reported larger reductions. For some recovery-limited mills, BLO may be justified on the basis of increased production alone.

Conclusions

1. Black liquor oxidation with oxygen, either as a complete system or as polishing stage will effectively lower TRS emissions from the DCE.

2. A well-designed system can be operated reliably and with good oxygen use efficiency.

3. The capital costs are very modest compared with air systems although the operating costs will normally be higher in spite of energy savings. Economics will favour air BLO systems for a complete oxidation system except for cases in which inexpensive oxygen is available. For temporary, or polishing systems, oxygen will be more economical.

4. BLO (with air or oxygen), will reduce liquor heating value by 2 to 5 percent, a potential drawback or advantage depending on the recovery furnace situation.

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<u>List of Figures:</u>

TÍTULO	PROJETO	Nº		
	DATA	EXEC.	VERIF.	REV.
	FOLHA			

FIGURE 1 – O_2 -BLO SYSTEM PERFORMANCE CURVES

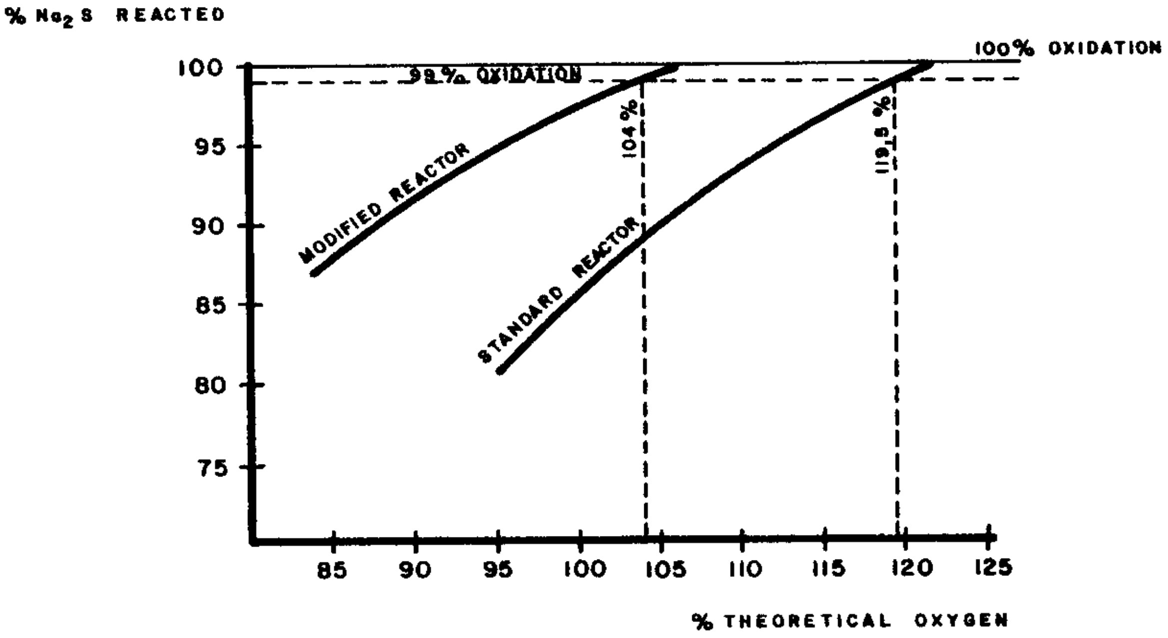

FIGURE 2

GOVERNMENT AIR PERMIT EXCURSIONS (BUBBLE CONCEPT) VS TIME

(SIMPLIFIED)

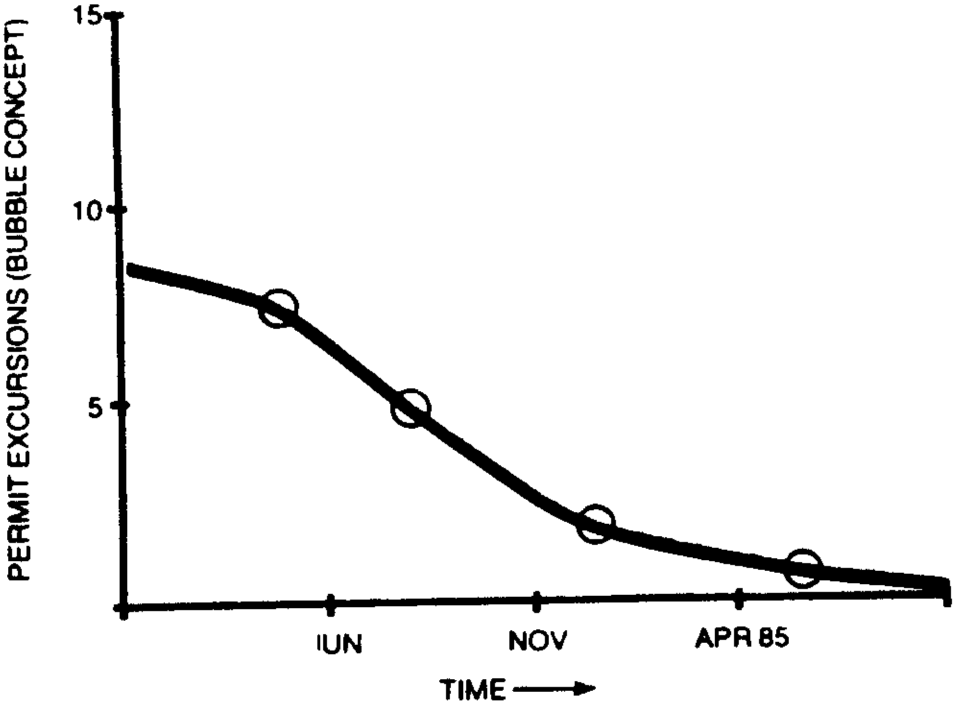

FIGURE 3

MONTHLY DAILY AVERAGES FOR FEBRUARY AND JUNE 1985