Introduction

Kittiwake Procal has a long and established association with paper and pulp mills supplying continuous emission monitoring systems (CEMS) to mills in Canada, South Africa, the Far East and Australia. Kittiwake Procal supply integrated CEM systems, enabling plant-wide monitoring and reporting of gaseous emissions. Kittiwake Procal provide reliable and low maintenance CEMs for various paper and pulp processes such as power boilers, Kraft recovery furnaces, lime kilns, bleach plants and thermal oxidisers. Emissions from each type of process unit can be affected by changes in fuel type, wood species, control devices and process operating conditions. Procal's experience and process knowledge can help determine the right monitoring solution for each customer.

For example, NO_X emission levels from a lime kiln depend on the type of fuel burned whether it be natural gas, fuel oil or petroleum. Additional gases, containing ammonia and reduced sulphur compounds removed and carried by steam from other processes can be routed to the lime kiln for oxidation changing the emissions picture. The Procal 2000 and Procal 5000 are able to measure multiple gas species and monitor rapid emission changes providing useful data for process control and for maintaining energy efficiency.

Kraft recovery furnaces, which are used to burn black liquor, can produce malodorous air emissions due to hydrogen sulphide, methyl mercaptan, dimethyl sulphide and dimethyl disulphide gases. The Procal 5000 is designed to measure these individual gases, known collectively as total reduced sulphide (TRS) gases, and provide a continuous emission monitoring solution to meet the strict emission limit requirements set down by regulatory authorities.

Power boilers, recovery boilers and lime kilns generate SO_2 and NO_X emissions due to combustion of fossil fuels. Other emissions such as CO_2 from the lime kiln and methane (CH_4) from wastewater treatment are sources of significant emissions. The Procal 2000 can measure these emissions in-situ with an accuracy of ±2% of the full scale range. Kittiwake Procal CEM systems are fully integrated with analyser control software that can provide reports on average daily pollution emissions as required by regulatory bodies.

The Procal 2000 analyser is compliant with international standards, meeting the stringent requirements of Environment Agencies. Certified under the MCERTS monitor certification scheme and therefore suitable for use in Europe, the Procal 2000 and 5000 are also compliant with US EPA 40 CFR part 60 and 75.

Pulp Mill Process

The function of the pulp mill is to convert wood chips to thick fibre board. In the pulp process the bulk structure of the fibre source (wood chips, stems or other plant parts) is broken down into constituent fibres using mechanical, semi-chemical or fully chemical methods (Kraft and sulphite processes).

Kraft Process Advantages

Pulp produced by the *Kraft* process is stronger than that made by other pulping processes. The tensile strength of the paper (the resistance to tearing) produced from the pulp is provided by hydrogen bonds formed between cellulose (and hemicellulose) in the fibres. The presence of lignin (the intercellular material that binds the fibres together in the wood), interferes with the formation of the hydrogen bonds and weakens the paper. In the Kraft process the lignin is removed leading to stronger paper and for this reason the Kraft process has become the dominant production method. The *sulphite* process also removes the lignin but is acidic and degrades the cellulose fibres making them weaker. The Kraft process has been further advanced by the invention of the recovery boiler that enables the recovery and reuse of the expensive inorganic chemicals used in the pulping process.

Kraft pulp is darker than other wood pulps, but it can be bleached to make very white pulp. Fully bleached kraft pulp is used to make high quality paper where strength, whiteness and resistance to yellowing are important.

The weaker sulphite pulps can be bleached more easily. However, the efficiency and effectiveness of the sulphite process is dependent on the type of wood used and the absence of bark. For these reasons, the sulphite pulping process has been in decline. The level of Sulphur dioxide (SO_2) emissions from mills using the sulphite process also tend to be higher than emissions from Kraft mills.

Mechanical pulping

Mechanical processes are also used to produce pulp in which cellulose fibres are physically separated from one another with the lignin remaining attached to the fibres. Mechanical pulp mills use either refiner mechanical pulping (RMP) where chips are ground with ridged metal discs called refiner plates or thermo-mechanical pulping (TMP) where the chips are steamed whilst being refined. The steam treatment significantly reduces the total energy required to make the pulp and decreases the damage (cutting) to fibres. Mechanical pulping processes have the advantage of generating significantly lower emissions as less chemicals are used.

Chemi-mechanical pulping

In this pulping technique the wood chips are pre-treated with chemicals prior to refining with equipment similar to a mechanical mill. The conditions of the chemical treatment are much less vigorous (lower temperature, shorter time, less extreme pH) than in a chemical pulping process. The method does not remove the lignin but makes the fibres easier to refine. Hybrid processes using combinations of chemical, thermal and mechanical methods have also been developed to improve energy efficiency.

Sources of fibre

Pulpwood is the most common fibre source for pulp mills. Other common sources are sugar cane fibre and other fibre crops.

The Kraft process

Figure 1 shows Procal analysers installed on a typical Kraft paper and pulp mill

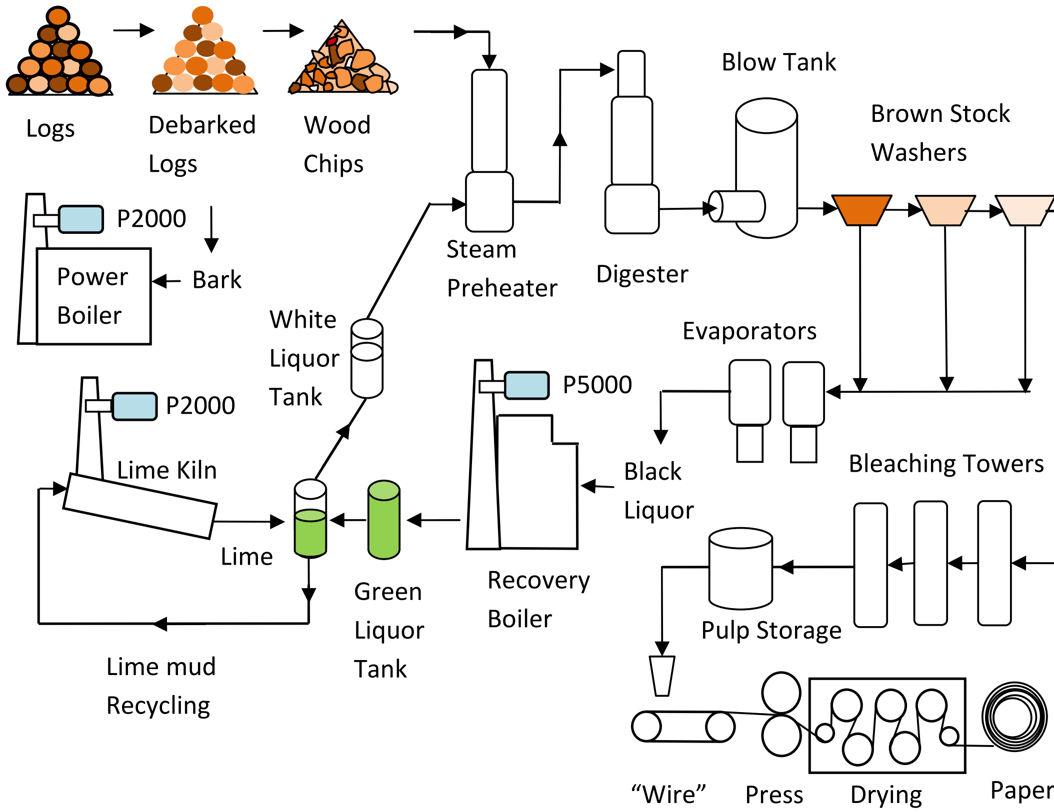

Figure 1 The Kraft process with Continuous Emission Measurement provided by Procal analysers

Bark from the wood is first removed in a barker (or debarker) as it contains few usable fibres and darkens the pulp. The bark is recycled providing fuel for the power boiler which generates steam and electricity for the mill. If the bark used in the power boiler is substituted for coal or fuel oil then high levels of sulphur dioxide and nitrogen oxides together with fly ash can be emitted. The Procal 2000 emissions analyser is ideally suited to the harsh environment of the power boiler. In-situ sampling and an integrated auto-calibration facility remove the need for intervention by maintenance staff under normal conditions. Typical power boiler emissions are as follows

Gas	***Ranges***
NOx	0 – 400ppm
CO	0 – 600ppm
SO_2	0 – 200ppm
H_2O	0 – 10%

After debarking the wood is chipped into uniform sized pieces suitable for use in the digester. The chips are usually wetted and preheated with steam to expel air trapped inside the chips.

After chipping the wood pieces are impregnated with pulping chemicals. The wood chips are cooked in an alkaline solution of sodium hydroxide (NaOH) and sodium sulphide (Na_2S), known as “white liquor”. The chips and the white liquor are mixed in a pressurised vessel known as the digester where the lignin, binding the wood fibre, degrades and dissolves into the liquor. Typically delignification requires several hours at temperatures of 130 to 180 °C (266 to 356 °F). After cooking the contents of the digester are discharged under pressure into a blow tank in a process known as blowing. As the mass of softened, cooked chips impact on the entry of the blow tank, the chips disintegrate into fibres or “pulp.” As the pressure is decreased large amounts of steam and volatiles are released. The steam released is used to heat the pulp mill and for power generation.

The solid pulp and used cooking liquor (known as black liquor) are subsequently separated in a series of brown stock washers. The remaining fibres are held in suspension in a brown liquid known as *brown stock*.

Recovery Boiler

A recovery boiler is used to recover the pulping chemicals from the black liquor that contains wood lignin, organic materials and inorganic compounds. The liquor undergoes a series of evaporation processes to increase the concentration of solids from approximately 15 to 50 wt%. The black liquor can then be either oxidised in the black liquor oxidation (BLO) system and concentrated further in a direct contact evaporator (DCE) or passed to a non-direct contact evaporator (concentrator).

Oxidation of the black liquor prior to evaporation in a DCE reduces emissions of odorous total reduced sulphur (TRS) compounds, which are stripped from the black liquor in the DCE when it contacts hot flue gases from the recovery furnace.

After the final evaporator/concentrator stage the concentration of solids in the black liquor is between 65 and 70%. At this stage the black liquor is then combusted in the recovery furnace to produce molten inorganic material, known as molten smelt. The molten smelt contains sodium sulphite, sodium carbonate, and sodium sulphate and forms in a bed on the furnace floor. The smelt flows from the furnace through smelt spouts and is dissolved in a weak wash forming green liquor.

The combustion of the black liquor must be carefully controlled as the high concentration of sulphur requires optimum process conditions to limit the production of sulphur dioxide and reduced sulphide gases. The Procal 2000 is also well suited to the demanding environment of recovery boilers with the availability of chemically resistant materials such as Hastelloy C276 to provide longer life under aggressive sample conditions. The Procal 2000 is easy to install and has no expensive extractive sample handling system. The Procal 2000 is therefore a low maintenance analyser with low operating costs. The Procal 2000 analyser, with associated Procal 1000 controller is capable of receiving inputs from other devices such as Oxygen, Dust and Flow analysers to provide complete emission measurement requirements in one system. Outputs from the system can be analogue or serial (MODBUS) depending on the site standard. Several Procal 2000 analysers can be controlled by one Procal 1000 which also includes a data logging and reporting capability. Additional features include remote access for both reporting and verification of the analyser's status. Typical emissions measured by the Procal 2000 on recovery boilers are as follows

Recovery boiler application

Gas	***Ranges***
H_2O	0 – 5%
NO	0 – 500ppm
NO_2	0 – 250ppm
SO_2	0 – 200ppm
CH_3OH	0 – 200ppm

Alternative Main Stack Application

Gas	***Ranges***
NOx	0 – 400ppm
HCl	0 – 300ppm
SO_2	0 – 200ppm

Chemical reactions and burning of organic materials releases a considerable amount of heat energy which is recovered by transferring it through water-filled tubes in the walls of the recovery boiler. The water vaporizes into steam that drives a turbine and generates electricity. In addition, some of the steam can be used in different stages of the process (e.g. heating the cooking process and soot-blowing in the recovery boiler itself).

Lime Kiln

The green liquor is fed into the causticizing plant. With the addition of water and lime (calcium oxide) the green liquor is processed through the lime kiln and converted to white liquor that can be used again in the digester. The lime kiln is an important processing unit on the mill site and large quantities of Carbon Dioxide (CO_2) are emitted in the production of lime. The Procal 2000 has a proven record of emission measurements on lime kilns. The Procal 2000 is designed for unattended operation, diagnostic routines with appropriate alarms ensure the analyser operates within specification. The Procal 2000 in-situ probe is heated to prevent condensate forming when process temperatures are low. The heated probe option is especially suited to application in the lime kiln as it efficiently deals with variations in process temperature. The probe is kepts hot, ensuring immediate availability when the plant is restarted after an outage. Typical gas emissions measured by the Procal 2000 in the lime kiln are as follows:-

Lime Kiln application

Gas	*Ranges*
CO_2	0 – 20%
CO	0 – 200ppm
H_2O	0 – 50%

Bleaching plant

Kraft pulp contains residual lignin which discolours the pulp. The bleaching process removes the residual lignin from the pulp by the addition of chemicals that depend on the end use of the product. The most common bleaching chemicals are chlorine, chlorine dioxide, hydrogen peroxide, oxygen, caustic, and sodium hypochlorite. Concerns over chlorinated compounds such as dioxins, furans, and chloroform have resulted in a shift away from the use of chlorinated compounds in the bleaching process. In modern mills, oxygen is normally used in the first stage of bleaching. Bleaching chemicals are added to the pulp in stages in the bleaching towers.

Mechanical pulp is either used without bleaching to make news print or can be bleached with peroxides and hydrosulphites.

Paper mill operation

After bleaching the pulp is processed in the paper mill. Modern paper manufacturing machines are based on the continuous Fourdrinier paper machine. The modern machine uses a specially woven plastic fabric mesh (known as a wire) in the form of a conveyor belt.
Pulp stock is sprayed onto the moving “wire” and water drains through the porous screen. The water content is further reduced by pressing the pulp sheet and collecting the surface water. Further water is removed by drying, on a series of hollow-heated cylinders (calender rollers). Finally, the paper surface is smoothed and chemical additives are added to impart specific properties to paper, and pigments may be added for colour.