# Black liquor recovery: how does it work?

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Black liquor (BL), a by-product of the papermaking process, is an important liquid fuel in the pulp and paper industry. It consists of the remaining substances after the digestive process where the cellulose fibres have been cooked out from the wood. In figure 1 a simple schematic description of the pulping process is shown.

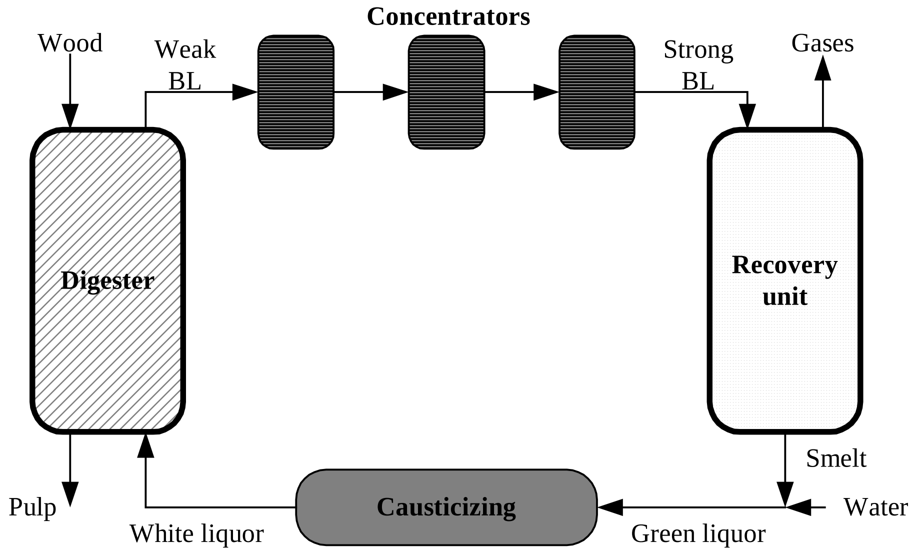


*Figure 1: Schematic description of the pulping process.*

Wood chips are fed into a digester. An aqueous solution, white liquor, flows through the digester and neutralises the organic acids in the chemical matrix of the wood. The lignin and other organic material, which contributes to about half of the mass of the wood, dissolves into the white liquor and exits the digester as weak black liquor. The remaining material, pulp, consists of wood fibres and is used in the papermaking process.

The weak black liquor has a solid content of approximately 15% by weight, which is far too low for combustion. To raise the solid content in the liquor it is being evaporated by a sequence of concentrators. When the resulting strong black liquor reaches the recovery unit (boiler or gasifier) it has a solid content of around 75%. In this unit the black liquor converts some of its chemical energy either by full (recovery boiler) or partial (gasifier) combustion of the liquor which yields an inorganic smelt and gases. The composition of the smelt and gases differ depending on which type of recovery technology that has been used. Most of the chemicals in the smelt that leaves the recovery unit is then led back into the pulping process as white liquor after a couple of recovery processes (e.g. causticizing).

Chemically, black liquor is a mixture of several basic elements where the largest fractions are carbon, oxygen, sodium and sulphur. Results from an elemental analysis done by SP, Sveriges Provnings- och forskningsinsitut, on a dryblack liquor sample is given in table 1. The sample was taken from AssiDomän Kraftliner in Piteå in January 2000.

*Table 1: Elemental analysis of a black liquor (dry solids) sample.*

| **Element** | **w/w (%)** |
|---|---|
| C | 36.40 |
| Na | 18.60 |
| S | 4.80 |
| H | 3.50 |
| K | 2.02 |
| Cl | 0.24 |
| N | 0.14 |
| O (by diff.) | 34.30 |
| **TOTAL** | **100.00** |

This report is aimed to provide a comparison of the recovery boiler with a pressurised gasifier for black liquor. Fundamentals concerning the conversion of black liquor, some details about the two recovery technologies and differences between these two will be presented.

## Conversion of black liquor

In order to convert the chemicals and energy in the black liquor in an efficient way, the black liquor has to be atomised to droplets and sprayed into the recovery unit in some way. Independent of choice of either a recovery boiler or a gasifier the conversion stages of the black liquor droplets are mainly the same.

As the black liquor droplets enters the recovery unit they are being exposed for hot gases and will undergo drying, pyrolysis and char conversion. During these stages the droplets undergo morphological changes which lead to changes in both the heat transfer and aerodynamic properties of the droplets. In figure 2 these three main stages are shown graphically.

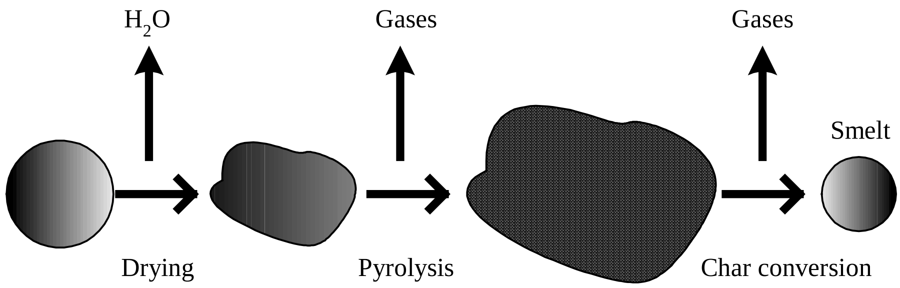


*Figure 2: Conversion stages of a black liquor droplet.*

First the black liquor droplet dries and loses its contained moisture. The rate at which the material dry is controlled by the heat transfer, thus the droplets will dry faster at higher temperature. Then the droplet goes through a pyrolysis stage where the organic matter in the liquor degrades, forming various gaseous compounds from volatile substances. The rate at which the gases are formed is controlled by the heat transfer rate to a droplet where a low oxygen content will increase the the time for pyrolysis [Frederick 1990]. The resulting gases from pyrolysis are mainly $H_2$, CO, $CH_4$, TRS-gases (Total Reduced Sulphur), $CO_2$, $H_2O$ and some heavier carbonates [Grace 1992]. The result is a swollen porous char particle, which contains about 25% non-volatile organic coal material and about 75% inorganic salts ($Na_2CO_3$, $Na_2S$, $Na_2SO_4$ and corresponding potassium salts). The charcoal is the main frame and the salts are in liquid form [Hupa et al. 1994]. At this stage the droplet volume might have increased by as much as 30 times the original volume [Grace 1992]. This is the case for liquors coming from a sulfate mill. For liquors coming from a sulfite mill the swelling is much less [Forssén et al. 2000]. The final stage is char conversion, during which mostly gas phase species react with organic constituents in the char particle, converting them into gaseous species. The main reactions that convert the carbon in the char particle are [Grace 1994]

$$C + \frac{1}{2}O_2 \rightarrow CO\,, \qquad (1)$$
$$C + O_2 \rightarrow CO_2\,, \qquad (2)$$
$$C + CO_2 \rightarrow 2CO\,, \qquad (3)$$
$$C + H_2O(g) \rightarrow CO\,, \qquad (4)$$
$$C + \frac{1}{2}Na_2SO_4 \rightarrow CO_2 + \frac{1}{2}Na_2S\,, \qquad (5)$$

and

$$C + \frac{1}{4}Na_2SO_4 \rightarrow CO + \frac{1}{4}Na_2S \qquad (6)$$

where reaction 3 and 4 are dominating. If the $O_2$-concentration is low compared to $CO_2$ and $H_2O(g)$ then most of the oxygen will be consumed by combustion of gases surrounding the particle and the char combustion will be dependent on the gasification reactions, (3) and (4).

At the end of the char conversion stage the droplet (particle) is impoverished of coal and collapse to a small droplet of smelt that consists, in the ideal case, only of inorganic material. The diameter of the droplet is now about half the original diameter [Hupa et al. 1994] and consists mainly of $Na_2S$ and $Na_2CO_3$ (plus $Na_2SO_4$ and NaCl) in ionized form.

## Recovery boiler

Recovery boliers used today are mostly of the Tomlison type (figure 3) and acts both as a high-pressure steam boiler and as a chemical reactor with reductive and oxidative zones.

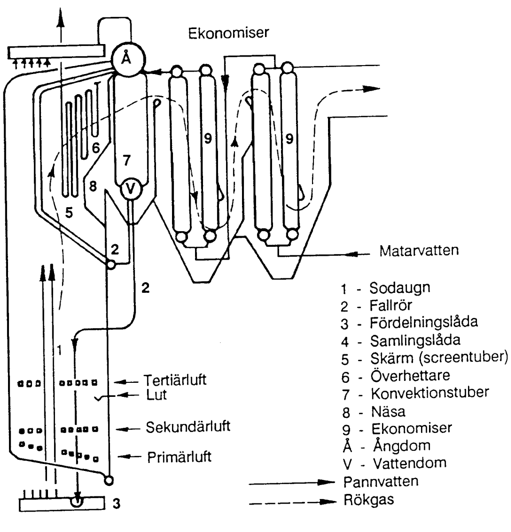


*Figure 3: A schematic drawing of a conventional recovery boiler (descriptions in Swedish).*

Black liquor (~120°C) are sprayed into the boiler (~900°C) by, so called, liquor guns right below the tertiary air register. The droplets then go through the first two conversion stages (drying and pyrolysis) very quickly before they, mostly before the end of total conversion, fall onto a bed of char at the bottom of the boiler. Here, the conversion is completed before the smelt exits by a channel through the boiler wall. The resulting combustible gases are burned completely by the different air registers along the wall of the boiler. This produces steam in the surrounding water pipes of the boiler, over heaters and economiser. The steam is then used in other mill processes and to run a steam turbine in order to produce electrical energy.

The different conversion zones and layers in the char/smelt bed in a recovery boiler can be seen in figure 4 (left picture) as well as some of the corresponding chemistry (Right picture).

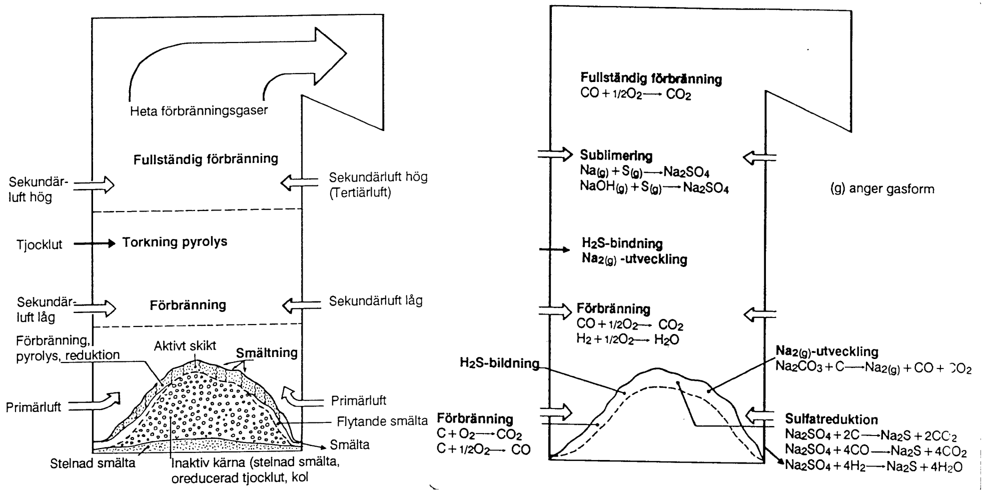


*Figure 4: Conversion zones (left picture) and corresponding chemistry (right picture) in a recovery boiler.*

## Black liquor gasification

During the last decade, extensive efforts have been made in order to develop alternative recovery technologies based on black liquor gasification to supplement and/or replace the conventional recovery boiler. One of the major driving forces for the interest in black liquor gasification is the possibility of using the product gas for combined-cycle power generation. Studies have indicated that this has the potential for a significant increase in the amount of electrical power that can be produced from the black liquor.

Black liquor gasification processes convert the organic substances in the liquor into combustible fuel gases (e.g. $H_2$, $CH_4$, CO, etc) and the inorganics into compounds suitable for regeneration of pulping chemicals. The heat necessary to drive the gasification process is derived from partial combustion of the fuel gas or some other fossil fuel. The proportion of the black liquor fuel value consumed in meeting this heat requirement is an important process variable.

The black liquor gasifier processes that has been under development can mainly be broken down into three general types as follows [Grace et al. 1995]:

1. Partial combustion in short-residence-time entrained-flow reactors,
2. Partial combustion in long-residence-time fluidized beds,
3. Steam gasification in indirect heated fluidized beds.

The most successful process in each of these types have been the Chemrec process, the ABB process and the TRI (MTCI) process, respectively. For the moment are only the Chemrec process and the TRI process ready to introduce commercialised units. Chemrec AB has their atmospheric booster as a supplement to a recovery boiler for an increased capacity and TRI (ThermoChem Recovery International) has their PulseEnhanced Steam Reforming unit for mid-sized black liquor recovery applications.

Maybe the most promising technology is Chemrec's pressurised black liquor gasification process (PBLG) with an integrated combined cycle for power generation. This technology is not ready to be commercialised however a lot of R&D effort is made for that purpose. At the laboratory of Energy Technology Centre (ETC) in Piteå, Sweden, a pressurised black liquor gasification unit, is under construction. This new, world unique unit (owned by Chemrec) will form the basis for a development program of a full-scale commercial unit and bring Sweden to the front of the research in black liquor gasification. Brief descriptions of this gasification plant and the gasification process are presented below.

The PBLG unit consists mainly of two parts (figure 5), a gasifier and a counter-current condensor.

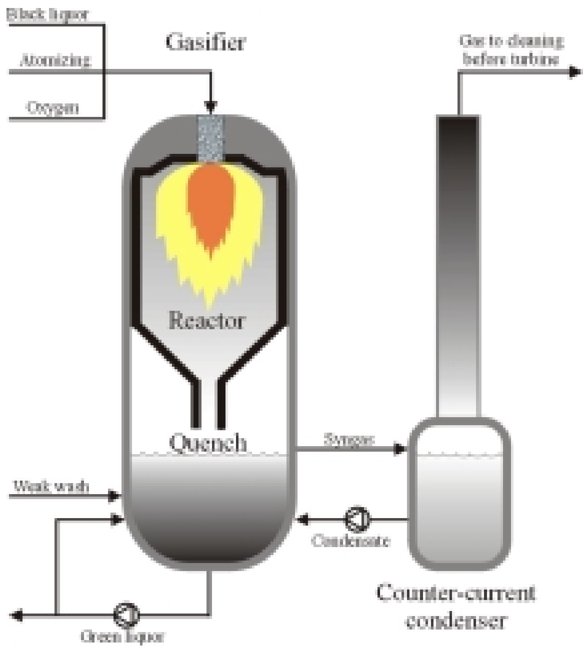


*Figure 5: Schematic drawing of a black liquor gasification plant.*

The gasifier can be split into two parts. Apart from the reactor in the upper part, a quench-cooler is placed in the lower part. At the top of the reactor black liquor is sprayed into the hot environment (~1000°C) through nozzles together with oxygen. The droplets first dries and devolatilize due to the heat and some of the resulting fuel gas mix and burn with the under-stoichiometric amount of oxygen. The amount of oxygen supplied is an important process variable and should be as small as possible since it is favourable with a high heating value on the resulting gas for use in a combined cycle.

Finally the resulting char is gasified mainly through reactions (3) and (4) before it leaves the reactor as inorganic (ideally) smelt. Since gasification of char is a relatively slow process it is important with high enough residence times for the droplets in order to prevent organic material in the resulting smelt.

To prevent the reactor from being overheated and severely corroded a cooling screen, consisting of water pipes placed around it, can be used. Other wise is the reactor mostly constructed by some ceramic material.

The quench-cooler is needed for separation of the products exiting the reactor (gases and smelt). The exiting gases from the reactor first passes through the counter-current condenser where some volatile substances are condensed and then further on to a cleaning process before the gas can be used in a gas turbine.

## Comparison

The investment cost for a full-scaled PBLG unit is estimated to be slightly higher than for a new conventional recovery boiler [Warnqvist et al. 2000]. However, pressurised black liquor gasification with an integrated combined cycle (BLGCC) has the potential to double the amount of net electrical energy for a kraft pulp mill compared to a modern recovery boiler with a steam turbine [Axegård 1999]. For more closed systems with less need of steam, this increase in electrical energy will be even higher.

Another advantage with the PBLG process is the increased control of the fate of sulphur and sodium in the process that can be used to improve the pulp yield and the quality for the mill. This control is very important for the green liquor quality and is quite limited with a conventional recovery boiler. A disadvantage with gasification is that it will increase the causticizing load. However, BLG has a lower requirement for make-up saltcake compared to the recovery boiler.

Even though the PBLG process might have a lot of advantages compared to the recovery boiler there is still a number of uncertainties for this technology. These are not only chemical questions but also some mechanical and material (refractory) questions need to be answered before it can be taken into full use.

## References

Axegård, P. (ed.), “Kretsloppsanpassad massafabrik-Slutrapport,” KAM 1 1996-1999, KAM-rapport A31, Stiftelsen för Miljöstrategisk forskning, 1999

Forssén, M., Backman, R., Wallén, J., Hupa, M., “Flygaskans sammansättning och nedsmutsande tendens i sodapannan”. Stockholm: Värmeforsk service AB, 2000

Frederick, W.J., Combustion Processes in Black Liquor Recovery: Analysis and Interpretation of Combustion Rate Data and an Engineering Design Model. UsDOE, 1990. DOE/CE/40637-T8

Grace,T.M., “Chemical Recovery Process Chemistry,” Chemical Recovery in the Alkaline Pulping Processes 3ed, pp. 57-78, Atlanta: TAPPI press, 1992

Grace, T.M., Timmer, W.M., “A comparison of alternative black liquor technologies,” International Chemical Recovery Conference, 1995

Hupa, M., Backman, R., Frederick, W.J., “Black liquor combustion properties,” International Conference Baltic Sea, Finnish Recovery Boiler Committee, 1994

Warnqvist, B., Delin, L., Theliander, H., Nohlgren, I., “Teknisk ekonomisk utvärdering av svartlutförgasningsprocesser”. Stockholm: Värmeforsk service AB, 2000