CHAPTER 2
LITERATURE REVIEW

2.1 Introduction
This chapter discusses about the sources of pulp, pulp manufacturing process, characteristics of black liquor, handling & processing of black liquor, recovery boiler operations and the various models used in the study of black liquor droplet dynamics in a recovery boiler.

2.2 Sources of pulp
Pulp, which is required for paper manufacturing, can be obtained from three resources (Rao, 1996)
 a) Wood: It is mostly procured from slow growing forests.
 b) Non-wood plants: It consists mainly of agriculture residues i.e. rice straw, wheat straw, bagasse, bamboo.
 c) Recycled fibre paper: Waste paper is the source of recycled paper.

2.3 Pulping process
The pulping process (Rao, 1981) is the separation of cellulose fibers from wood and non-wood feed stock. The pulping process is divided into three categories namely 1) Mechanical pulping 2) Semi-chemical pulping 3) Chemical pulping.

2.3.1 Mechanical pulping
Wood and agro-residues are exposed to grinding or shredding to free the cellulose fibers. This process produces high pulp yield i.e. of the order of 90-95%. Lignin is retained with pulp in this process. Pulp produced in this process is normally used for newsprint production.

There are different types of mechanical pulping processes as briefly listed below.
 a) Stone ground wood pulping: Wood logs of 1-1.5 m length are fed into the grinder and forced mechanically against the grinding stone to extract the pulp.
 b) Refiner mechanical pulping: The fibre separation is done in disc refiner.
c) **Thermo mechanical pulping:** Wood chips are softened in a pre-heater and then refined in a disc refiner to extract pulp.

### 2.3.2 Semi-chemical pulping

Semi chemical pulping is a mechanical pulping process which involves pretreatment with chemical solution to reduce the energy requirements during processing.

### 2.3.3 Chemical pulping

Chemical pulping is a process of extraction of cellulose fibers present in wood-based or non wood-based stock by freeing the lignin content in the media of chemical solution preferably at elevated temperature and pressure and it is called cooking process. Lignin acts as a bonding agent to the cellulose fibers. In this process, the pulp yield is around 50% and most of the (~ 95%) lignin present in the wood is dissolved by the chemical solution. Chemical pulping can be produced by three methods (Rao, 1981) i.e., Soda pulping, Kraft or Sulfate pulping and Sulfite pulping. Kraft pulping is the most adopted process in modern times. In chemical pulping, the fibers are less likely to be damaged than in other pulping processes. Chemical pulping is more expensive than mechanical pulping but it has better strength and brightness properties.

In Chemical pulping process, extracted fibres are washed, filtered and sent to the paper making process. The filtrate, separated out in the cooking process, is called black liquor which is further processed in a recovery boiler for recovering inorganic chemicals and organics in the form of heat energy. The focus of the study is to understand the behavior of black liquor droplets in the chemical recovery boiler.

A brief comparison of all the three pulping process are given in Table 2.1.

<table>
<thead>
<tr>
<th>Pulping process</th>
<th>Pulp yield (%)</th>
<th>Pulp strength</th>
<th>Energy requirement</th>
<th>Life/Stability</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mechanical pulping</td>
<td>90-95</td>
<td>Poor</td>
<td>High</td>
<td>Moderate</td>
</tr>
<tr>
<td>Semi-chemical pulping</td>
<td>55-90</td>
<td>Medium</td>
<td>Moderate</td>
<td>Moderate</td>
</tr>
<tr>
<td>Chemical pulping</td>
<td>45-55</td>
<td>Excellent</td>
<td>Low</td>
<td>High</td>
</tr>
</tbody>
</table>
2.4 Black liquor characteristics

As already indicated, black liquor is a byproduct of chemical pulping process essentially aqueous solution containing the inorganic chemicals used during cooking along with dissolved organics (essentially lignin) from fibrous raw material. The quantity of black liquor generated per unit of unbleached pulp depends on the chemicals charged, bath ratio and dilution during filtration. Typically, the black liquor solids generated are around 1.5 ton (with almost 1:2 inorganic to organic ratio) and 8-18% concentration. This liquor is processed to recover the inorganic chemicals and energy content (from organics) in chemical recovery system.

Black liquor thermal and transport properties directly affect the performance of recovery boiler and any change in these properties shall have a shift in the steady state operation of the boiler. These properties can primarily be categorized as follows for better understanding of the operation of the recovery boiler.

2.4.1 Chemical composition

Black liquor is a complex solution containing lignin as well as its degradation products, polysaccharides, extractives and several inorganic compounds (Rao, 2002; Gullichsen and Fogelholm, (1999)). The chemical composition of the black liquor depends on the nature of raw material i.e. woody, non woody etc. cooking chemicals used, process conditions set in pulping. Generally Indian black liquors are analyzed for Na₂SO₄, NaOH, Na₂CO₃, Na₂S, pH, ratio of organic and inorganic contents which are key parameters for processing and handling. Silica content in black liquor can adversely affect the recovery of solids.

2.4.2 Rheological properties

Viscosity, density and surface tension are some of the important properties which have large impact on the processing of black liquor coupled with heat and mass transfer phenomena.

a) Viscosity

Viscosity is strongly dependent on the wood species that are used during the pulping process, operating conditions during pulping, concentration, pH of the liquor and
temperature of the black liquor. With the increase in solids concentrations, viscosity goes up and beyond some limit, pumping of liquor becomes a constraint. Hence, viscosity is one of the critical parameters which decide the operating capacity of the evaporation (concentration) system and recovery boiler. If the black liquor is exposed to high temperature for longer periods (Liquor heat treatment) (Nikkanen, 1993), large molecular polymer content i.e. lignin & hemicelluloses start breaking down to small molecules and this process result in reduction in viscosity. With the decrease in viscosity, evaporation plant capacity and black liquor solids concentration can be increased resulting in increased black liquor concentration suitable for firing. A typical heat treated liquor viscosity is comparable with the viscosity of the normal liquor having 10% or even lower dry solids. Hence viscosity is strongly affected by the temperature of the liquid.

Llamas et al. (2007) developed a novel additive (Dimethyl formamide) for reducing the viscosity of black liquors with high dry solids content that are produced in the Kraft pulp industry. The addition of Dimethyl formamide resulted in larger reductions in the viscosities of liquors cooked with white liquors of higher sulphidity for liquors coming from the same species of eucalyptus. The authors expressed the opinion that the mechanism for the reduction in viscosity provided by the additive is probably the breaking of polysaccharide-S-lignin linkages. In liquors with solids contents of less than 55%, the reduction in viscosity produced by the additive is negligible. The additive is effective when the concentration in dry solids is higher than 55-60%. For a higher shear rate, the reduction in viscosity is larger. Under high shear rate conditions, linkages between molecules are broken and the molecules are forced to reorient and align with the shear.

Cardoso et al (2009a) analyzed the effects of black liquor properties on its recovery unit operation. An experimental methodology for characterizing the principal chemical and physical properties of eucalyptus Kraft and bamboo soda black liquors has been developed, including sample collections from six Brazilian mills. On comparing the results obtained for both liquors, bamboo and eucalyptus, the former has the lowest sulfur level, highest silicon and lignin concentration and consequently the highest apparent viscosity.

Nikkanen (1993) discussed the liquor-heat-treatment process (LHT) developed by A. Ahlstrom corporation, and also the evaporation and combustion of LHT liquor in the light
of the results gained from mill-scale tests and long-term operational experience. The black liquor viscosity can be decreased by holding the liquor at a high temperature long enough. A lower viscosity facilitates pumping and storing of black liquor significantly. Thus the liquor-dry-solids concentration can be increased to 75-80% in a conventional evaporation plant, whereas the normal dry-solids concentration was previously 65-70%.

The liquor-heat-treatment system (LHT) is based on de-polymerization of large lignin and hemi-cellulose molecules of the black liquor. As per the mill scale studies and tests, LHT reduces viscosity to such a level that the liquor is pumpable at 75-80% dry solids, the normal limit for pumping being 68-70% dry solids. The steam-generation capacity and the over-all energy balance for the boiler, evaporation plant, and lime kiln are 7% higher than without the LHT system and high-dry-solids evaporation. In the overloaded boiler, increased high dry solids result in improved boiler capacity.

Typical BL viscosity values (Clay, 2008) are given in Table 2.2.

Table 2.2: Viscosity of a typical black liquor at different solids concentration and temperatures

<table>
<thead>
<tr>
<th>BL dry solids, %</th>
<th>Temperature, °C</th>
<th>Viscosity, cP</th>
</tr>
</thead>
<tbody>
<tr>
<td>18</td>
<td>66</td>
<td>1</td>
</tr>
<tr>
<td>34</td>
<td>110</td>
<td>1.3</td>
</tr>
<tr>
<td>42</td>
<td>116</td>
<td>2.3</td>
</tr>
<tr>
<td>51</td>
<td>121</td>
<td>4.9</td>
</tr>
<tr>
<td>70</td>
<td>127</td>
<td>88</td>
</tr>
</tbody>
</table>

b) Density

The density of black liquor is important in calculation of flow characteristics and static heads. The density of the black liquor depends on the composition i.e. organic and inorganic components. Presence of inorganic components contributes for higher density of the black liquor. Typical density values (Clay, 2008) are presented in Table 2.3

Table 2.3: Density of a typical black liquor at two different solids concentration and temperatures

<table>
<thead>
<tr>
<th>BL dry solids, %</th>
<th>Temperature, °C</th>
<th>Density, kg/m³</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>82</td>
<td>1.06</td>
</tr>
<tr>
<td>49</td>
<td>93</td>
<td>1.26</td>
</tr>
</tbody>
</table>
c) Surface tension

Droplet formation depends on the surface tension and any change in surface tension finally affects the operation of the boiler. Surface tension decreases with the increasing temperature and with decrease of concentration of the solution. The presence of soaps and organic components also decreases the surface tension. Experiments were conducted by Ferreira et al. (2005) on black liquor produced from eucalyptus wood and determined the surface tension at various BL solids concentrations and temperatures. The experimental results are presented in Table 2.4.

Table 2.4: Surface tension (mN/m) of a typical black liquor at different solids concentration and temperatures (from Ferreira et al. (2005)).

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>BL solids concentration (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3.7</td>
</tr>
<tr>
<td>35</td>
<td>38.12</td>
</tr>
<tr>
<td>40</td>
<td>37.1</td>
</tr>
<tr>
<td>45</td>
<td>37.25</td>
</tr>
<tr>
<td>50</td>
<td>35.44</td>
</tr>
<tr>
<td>55</td>
<td>34.98</td>
</tr>
</tbody>
</table>

2.4.3 Thermal properties

Specific heat, thermal conductivity and boiling point rise (BPR) are some of the critical properties which need to be well understood for processing of the black liquor.

a) Specific heat

Specific heat($C_p$) of black liquor decreases with increase in solids content and increase in temperature. Typical black liquor specific heat (Clay, 2008) is in the range of 2700-3900 J/kg/°C.

b) Thermal conductivity (K)

Thermal conductivity decreases almost linearly with increase in temperature and increase in concentration. Empirical correlation for determining the thermal conductivity (Rao, 2002) is given as below.
\[ \begin{align*}
K &= 0.504 - 0.262C + 1.35 \times 10^{-3}T
\end{align*} \tag{2.1} \]

Where the units of the respective terms are:

- K: Kcal/hr.m.K
- C: Black liquor solids concentration, (%W/W)
- T: Temperature (°C)

c) **Boiling point rise**

The boiling temperature of the black liquor is higher than that of water at the same pressure and varies with the composition of organic, inorganic solids. This difference in temperature is called boiling point rise (BPR). Its range for 0-80% solids concentration is 0-50°C approximately (Adams et al., 1988).

**2.4.4. Combustion properties**

Heating value is very important and required to be known for better operational performance of black liquor recovery boiler.

Black liquor releases heat when it burns in the furnace. The higher heating value (HHV) is a measure of the amount of heat that can be released and typical HHV values for Kraft black liquor are in the range of 13,400-15,500 kJ/kg of black liquor solids (Adams et al., 1988). NHV indicates the actual energy released. Heating value depends on the composition of the liquor which is decided by the operating conditions of the digester.

**2.4.5 Polymeric properties**

Swelling and volatile content of black liquor needs to be understood for better operation of the boiler.

a) **Swelling**

Alen (1994) conducted experimental studies and attempted to understand the swelling behavior of pine and birch Kraft black liquors and their main organic components (lignin and hydroxy carboxylic acids) during heating treatment under a stagnant inert atmosphere. The black liquors began to swell considerably in the temperature range of 180-270°C. No marked differences in the swelling properties of the two liquors were found. The author, on the basis of a comparison of the swelling behavior of the organic
components of the black liquors to that of the whole liquors, concluded that the aliphatic acid fraction is the main source of the volatile degradation products necessary for swelling, while the lignin fraction has an essential role in hindering the escape of the volatile compounds from within the particle.

Whitty et al. (2008a) conducted experiments in a laboratory scale pressurized reactor (reconfigured thermo-gravimetric analyzer) to determine swelling of black liquor during pyrolysis in the pressure range of 1 to 20 bar and 650 to 1100°C. Two industrial Kraft liquors were tested for determining the degree of swelling during pyrolysis and swelling was found to decrease over the range 1 to 20 bar, with the most dramatic decrease observed at lower pressures between 1 and 5 bar. The specific swollen volume measured at 20 bar was roughly one-quarter of that measured at 1 bar. The decrease was roughly logarithmic with pressure, and an expression has been developed to predict swelling at higher pressures if the specific swollen volume at atmospheric pressure is known. Char bulk density increase with pressure by a factor of roughly 4 over the range 1 to 20 bar.

Puertolas et al. (2001) studied the pyrolysis of dried black liquor solids collected from a pulp mill (which produces black liquor by alkaline pulping of straw), influence of an oxidation stage at low temperature prior to pyrolysis, on specific surface area of the char and on the black liquor swelling, is studied. The authors’ analyzed two main variables i.e. time of pre-oxidation and final temperature of pyrolysis. The resulting chars obtained showed a clear decrease in swelling level of the black liquors, as well as an increase on their specific surface area, with the increase of pyrolysis temperature and pre-oxidation time.

b) Volatile content

Volatile content of the black liquor is the key parameter for the steady operation of the boiler. Variations in volatile content change the temperature profile of the boiler. Volatile release depends on the temperature of the droplet and type of the raw material used in the digester.

From Hupa, (2008) typically 65% solids concentration of black liquor will contain around 30% of organic content (equivalent to around 60% of black liquor solids; remaining is inorganic content) in-turn the organic content is further composed of around 20% fixed
carbon and 80% volatile matter which translates into the volatile matter constituting around 32% of the black liquor.

2.5 Handling & processing of black liquor

The economic viability of chemical pulping process depends strongly on efficient recovery systems for chemicals and energy as is evident from the literature. From Figure 2.1, it is noted that about 1 ton of pulp produces 1.5 ton black liquor solids.

![Diagram of black liquor production](image)

**Figure 2.1:** Mass balance of black liquor production.

Hence it is absolutely necessary to develop efficient methods for handling of black liquor and ensure that chemical pulp mills meet strict environmental norms. Some of the major steps in modern recovery processes are (Rao, 1996) given below.

a) Concentration of the spent liquor by evaporation.

b) Combustion of the concentrated spent liquor in a recovery boiler producing steam and recovering inorganic chemicals as either ashes or smelt. In some processes, gas components are also recovered.

c) Conversion of the gas /ash/smelt inorganic chemicals into active cooking chemicals. It may be noted that the above steps are typical of a modern recovery system. Interest is also focused on black liquor gasification to produce steam and electric power.
Evaporation of wood-based black liquor is generally accomplished by multiple-effect evaporators followed by concentrators so as to obtain black liquors of 55-75% solids concentration. Non-wood black liquors are concentrated using short tube vertical evaporators because of their high viscosity and high silica content.

Reductive combustion of black liquors is generally carried out in a tomlinson type recovery boiler followed by causticizing with lime to produce white liquors. Other technologies which are being tried are gasification, fluidized combustion and molten salt gasification (Rao, 1996; UNEP-IE, 1992).

2.5.1 Black liquor evaporation

Gidner et al. (1996) studied the optimal energy conservation strategies where an absorption heat transformer unit (AHT) is integrated with both the existing black liquor evaporation plant and the proposed bleach effluent evaporation process.

Johnsson et al. (2009) conducted experimental studies on heat transfer during black liquor evaporation. The authors observed that the Nusselt number (Nu) increases in the turbulent region. However, at a specific Reynolds number (Re) for each Prandtl number (Pr) level, Nu ceases to increase with increasing Re. The authors presented a new correlation, taking this observation into account, on the basis of experimental data in the region of $4.7 < Pr < 170$ and $47 < Re < 6740$. A dry solid content dependence is included in the new correlation for improving its predictions.

Cardoso et al. (2009b) carried out computer simulations in a Brazilian pulp mill for minimizing energy consumption in pulp mills. Chemical process simulation has proven to be an effective tool for performing a systematic and global analysis of energy systems to identify routes for maximizing the process efficiency concerning to the heat recovery.

Karlsson et al. (2013) developed a new method to overcome the problems with fouling under crystallizing conditions which enabled reliable measurements of heat transfer for black liquor evaporation at dry solids mass fractions up to 0.75. Viscosity was found to be the most dominant parameter for the heat transfer for the investigated conditions in the region of high-to-very high Prandtl numbers. For the measured conditions the heat transfer increased at higher specific mass flow rates, but the dependence was weak and not statistically significant.
2.5.2 Black liquor gasification, conversion and extraction process

Preto et al (2008) studied steam gasification of carbon residue in bed solids of a low temperature black liquor gasifier using a thermo gravimetric system at the pressure of 3 bar.

Naqvi et al. (2009) studied two potential technologies of producing Di-methyl ether (DME) and methane (CH₄) as alternative fuels from black liquor gasification integrated with the pulp mill.

Laaksometsa et al. (2009) studied the potential for energy savings and possibilities by lignin extraction in a real pulp mill in Portugal. The authors determined that the steam-saving potential was 4.2 GJ/ADt or 33%.

Naqvi et al. (2010) discussed advantages of gasification technologies over conventional recovery boiler and its associate process.

2.6 Recovery Boiler

2.6.1 General features

Recovery boiler is sectionalized as lower furnace and upper furnace, where bull-nose separates both the sections. Upper furnace consists of super heater, boiler bank and economizer whereas lower furnace consists of water walls, black liquor injection nozzles, combustion airports and char bed. Some of the features which are very important in design and operation of the recovery boiler are discussed as under.

a) Hearth loading

Conventional recovery boilers are generally designed to have hearth loading (Adams et al., 1988) of 2.5 MW/m² which decides the cross sectional area of the furnace based on the processing capacity of black liquor solids and its heating value.

b) Combustion air system

Air is supplied to the furnace through a series of ducts attached to the boiler at different elevations for completing the combustion of the hydrocarbon volatiles and char efficiently. It is normally supplied in three tier air distribution systems.
Primary air supply is used to control the shape & position of the char bed. The primary air ports are located approximately 1 m above the furnace floor and approximately 35 ports are provided on each of the four walls with the size of the each port is 5 by 25 cm (approximately).

Secondary air is supplied to control the tip of the char bed and burn the hydrocarbon volatiles, CO emitted from the char bed. The air ports are located approximately 2 m above the furnace floor these are generally large compared to primary ports and size would be around 5 by 25 cm to 12.5 by 67.5 cm.

Tertiary air is supplied to complete the combustion of the un-burn gases and the air ports are provided above the liquor guns, approximately 8 m above the floor of the furnace. These ports are generally largest and arranged on two opposite walls, normally the front and rear wall. Typically these would be around 3 to 8 ports with the size of 10 by 45 cm to 15 by 75 cm.

c) Char bed

Char bed sits on the bottom of the furnace consisting of molten smelt covered with burning char particles, a mixture of devolatilized carbon residue and inorganic chemicals that were added during the pulping process. Burning char particles cover the molten smelt protect the molten smelt to devoid any contact of water and the molten smelt is drained through spouts into dissolving tank. Char bed reactions are oxidative and reductive. Hence the heat released in oxidation reaction supplements the heat requirement of reduction reaction and any imbalance in heat supply-demand disturbs the temperature profile of the char bed and recovery boiler.

2.6.2 Black liquor droplet formation

Empie et al. (1993) studied the effect of temperature on black liquor droplet formation from commercial spray nozzles. Droplet size distributions from commercial nozzles have been measured for several mill liquors sprayed at typical operating conditions. The effect of temperature on drop size has been quantified, showing a weak dependence on temperatures up to the boiling point. At a temperature a few degrees above the boiling point, there is a step change in the mean droplet size which is related to flashing. The mechanism for this demands that several degrees of superheat are required for flashing to
occur, resulting in smaller than expected droplet diameters and the average change in droplet size as a consequence of operation above the transition temperature was a decrease of about 20%. This would result in almost doubling the number of drops being fired into the boiler. The smaller drop size would increase droplet surface area and hence in-flight rate processes; however, liquor carryover rates would also increase. This needs to be understood.

Empie et al. (1995) developed method for drop size modification in black liquor sprays from commercial nozzles using vibratory assist from commercial nozzles using vibratory assist. Image analysis techniques were developed from high-speed video images which gave good two-dimensional representations of black liquor sprays. Vibratory assist in the axial direction, as applied to black liquor spraying, was accomplished with a novel nozzle design. Achieving a pulsed flow by inducing periodic flow interruptions showed some promise in changing the mean drop size without changing the normal process operating parameters. A harmonic frequency existed where a minimum of small size drops was made.

Miikkulainen et al. (2000) studied the spray properties in an operating furnace with the furnace endoscope developed at the HUT. Velocity, shape and length of the black liquor sheet were measured with the furnace endoscope in five operating recovery boiler furnaces by using a multiple exposure CCD camera and an image analysis system. The comparison between results from the test chamber and furnace showed that the spray properties in both environments depend on same main parameters (operating temperature, pressure, liquor viscosity and density). Final conclusions could not be expressed by the authors due to different dry solids content, viscosity and orifice sizes. When the temperature difference is below 7°C, the relative velocity is fairly constant in both test chamber and in furnace. When the difference to boiling point is larger than 7°C, the flashing phenomena seems to take place and accelerates the flow. The relative velocity could be as high as 3.4 m/s when mass flux was low enough (4 g/mm²s) and the temperature difference to boiling point 8°C. The smaller the mass flux is, the greater the relative velocity. The dominating sheet break-up mechanism are found in most cases if firing temperature is not more than 7-8°C above the atmospheric boiling point.

Miikkulainen et al. (2002a) studied the effect of a furnace environment on black liquor spray properties. Black liquor spray properties such as velocity, opening angle and
disintegration mechanisms were determined in an operating recovery boiler and in a horizontal spraying chamber by using a furnace endoscope. The black liquor dry solids content, temperature, feed rate and the nozzle geometry are the main operating parameters that determine spray properties. The authors found that the sheet break-up mechanism and other spray properties are similar in both environments in the tests, which were carried out within the normal operating range of a modern Kraft recovery furnace. The smaller the mass flow rate and higher the difference in boiling point, the higher is the dimensionless velocity.

Miikkulainen et al. (2002b) carried out series of spraying experiments at a modern Finnish recovery boiler within its normal operational range. The droplet size and size distribution were measured simultaneously in a full scale test chamber which was built next to the operating recovery boiler furnace. It was observed that the range of spraying temperature in which the modern recovery boilers operate is very narrow due to the dramatic changes in the spray properties, caused by the changing flashing phenomenon. Increasing mass flow rate decreases the effect of flashing inside the nozzle tube. The smaller the mass flow rate and higher the excess temperature, the higher the dimensionless velocity. Dimensionless velocity characterizes the acceleration of liquor flow inside the nozzle tube caused by flashing.

Kankkunen et al. (2003) studied the particle size distribution of black liquor sprays with high solids content in recovery boilers. The drop size and drop size distribution of black liquor sprays were measured by an image analysis based method. High solids content black liquor spraying was studied in a test series with two splash plate nozzles. Three mass flow rates 4.3, 5.2, and 6.1 kg/s were examined. The excess temperature varied between 14-18°C. The spraying temperature varied from 130 to 135°C. An important observation was the large median drop size. The large drop size occurred in connection with the high fraction of non-spherical particles that were found in high solids content black liquor sprays. Large, non-spherical particles occur when flashing inside the nozzle tube decreases (lower dimensionless velocity of a spray) and a long uniform black liquor sheet is formed at the splash plate. It was found that less than 3.7% of black liquor could form carry-over particles smaller than 2 mm. This roughly corresponds to a maximum concentration of 2.6 g/Nm$^3$ inorganic dust in flue gases. On the other hand, 2-76% of
particles are larger than 6 mm and hit the char bed or furnace wall without adequate drying which is important for optimizing furnace operation.

Miikkulainen et al. (2004) developed a furnace endoscope to carry out in furnace measurements of black liquor sprays in order to discover the initial velocity, opening angle and trajectory of the spray and compare spray disintegration mechanisms and spray appearance with the ones measured in a spray chamber. An error analysis of the velocity measurement method was carried out, and the meaning of the optimum measurement distance from the optics to the observed object is discussed.

Miikkulainen et al. (2005) carried out experiments at three spraying temperatures and three mass flow rates with high solids content black liquor for studying spray disintegration mechanism, length of the sheet and estimation of drop size from the wavelength of a black liquor sheet. An image-analysis-based algorithm to measure the sheet length was developed and tested. Investigation was carried out to predict the droplet size from spray characteristics near the splash plate.

Miikkulainen et al. (2008) studied the differences in splash plate performance and fouling behavior of six different splash plate nozzles in similar spraying conditions inside two recovery boiler furnaces. Velocity, opening angle, trajectory of the sprays in addition to pressure inside the nozzle and nozzle surface temperature were measured. Interesting findings of the study are surface temperature of the nozzles inside the furnace is very sensitive to nozzle setup and nozzle fouling does not have a significant effect on spray formation.

Miikkulainen et al. (2009) performed tests in six finnish recovery boilers of various sizes and capacities with two mill scale commercial nozzles. Images of the spray appearance were videotaped and processed using image analysis software to measure the required characteristics of the spray. Black liquor spray velocity and drop size are very sensitive to the spraying temperature as found from the experiments.

CFD-based modeling was carried out by Engblom et al. (2012b) to investigate furnace load and liquor spraying as causes for asymmetric furnace temperatures in a 4450 TDS/day Kraft recovery boiler. Simulation results were compared against validation measurements and the following conclusions are made.
a) Some extent of asymmetric in-furnace gas flows and temperatures are expected in most cases as a result of asymmetries in inflows of combustion air and/or black liquor, caused by, e.g., air port positions, fouling of air ports, damper positions, liquor gun positions, number of liquor guns, gun tilts, and wear or fouling of liquor gun nozzles.

b) A decrease in furnace load is expected to increase the temperature asymmetry.

Aho et al. (2013) conducted studies on the influence of organically bound metals on pyrolysis of pine and gasification of pine chars. Selective leaching of the major ash-forming elements in pine wood was performed with different acids, namely, nitric, sulfuric, hydrochloric and oxalic acids. No other major changes in the chemical composition of the biomass were observed except the removal of the metals. Removal of the metals (sodium, potassium, magnesium and calcium) had a positive effect on the pyrolysis, resulting in higher bio-oil, lower char and gas yields.

### 2.6.3 Studies on black liquor devolatilization

Devolatilization (pyrolysis) is a phenomenon of releasing of volatiles from the droplet due to thermal degradation of black liquor solids and simultaneously volatiles burn in the boiler hot environment. The char left out from the devolatilization process consist of residual organic carbon and inorganic chemicals that were consumed during the digestion/cooking process.

Sricharoenchaikul et al. (2002a) conducted the experimental studies on gasification of black liquor solids at high heating rates in the temperature range of temperatures from 700 to 1100°C and the following conclusions were made:

a) Less than 15% of the carbon input as black liquor solids was converted to light gases during devolatilization.

b) Upon continued heating in N₂, especially at higher temperatures (900-1100°C), additional carbonaceous material from primary tar species was converted to light gases through secondary reactions.

c) At lower temperatures, additional carbon-containing matter was volatilized more slowly. Part of this continuing conversion at the higher temperatures was due to the formation of CO via reduction of Na₂SO₄ and Na₂CO₃ by carbon in the char residue.
d) The effect of black liquor composition and gas atmosphere (nitrogen versus water vapor/nitrogen) on the transformation to light gases during devolatilization was minimal. These parameters also had little impact on the evolution of light gases during secondary reactions at low temperatures (700-800°C). However, at higher temperatures (900-1100°C), the impact of these variables became more significant. The water gas shift reaction played a major role in the distribution of carbon between CO and CO$_2$ in gasification environments at longer residence times and higher reactor temperatures.

Sricharoenchaikul et al. (2002b) performed laminar entrained flow reactor (LEFR) experiments to investigate the tar formation during devolatilization of black liquor at high heating rates and following observations were made from the experimental results.

a) The tar compounds detected were grouped into two categories, semi volatiles and non-volatiles, based on their molecular weights and boiling points.

b) Over the range of experimental conditions employed, semi volatile tar yields ranged from 0.1-5% of the carbon in black liquor, while the non-volatile tar accounted for 0.02-1% of the carbon in black liquor.

c) Tar characterization revealed a strong similarity between the lignin substructure and some of the tar compounds produced.

d) Tar yields were controlled by a number of competitive formation and decomposition reactions, which are influenced by the residence time, temperature, and gas composition.

e) In general, low temperatures favor the formation of more aromatic tar species with diversified substituted groups such as toluene and xylene. These compounds formed relatively slowly, at a rate measurable within the time frame of the experiments, and their concentrations increased with the residence time.

f) Tars formed more rapidly and decomposed more rapidly at higher temperatures.

g) Non substituted aromatics such as benzene were more stable at higher temperatures and were formed by decomposition of substituted aromatics.

h) Oxidizing gases enhanced both the formation and destruction of tars, depending on the temperature and residence time.

Jarvinen et al. (2003a) presented results from a detailed physical model for single black liquor droplet pyrolysis & swelling and validated them against experimental data from a
non oxidizing environment using two different reactor configurations. In the mathematical model heat transfer and gas phase mass transfer in the droplet was solved and thereby intra particle gas-char and gas-gas interactions during drying and devolatilisation were studied. In the experimental part, the mass change, the swelling behavior and volume fraction of larger voids was studied. The characteristics of cenospherical swollen black liquor particles were determined for modelling purposes. In addition, detailed modelling was used to study how the changes in internal structure caused by swelling affect the role of simultaneous devolatilization and char gasification. The model predicted the rate of pyrolysis mass loss for 700°C & 900°C temperatures. Particle swelling during these experiments was also recorded and satisfactory predictions from the model were obtained. Detailed simulations showed that the auto gasification mechanism described is greatly affected by the swelling and formation of larger voids. The greater the swelling and smaller the cenospheric volume fraction, the larger the conversion of char at the end of devolatilization.

Whitty et al. (2008b) carried out the experiments in two laboratory scale furnaces to study the influence of pressure on pyrolysis of black liquor, char yields and components release in the pressure range of 1 to 20 bar and temperature range of 650 to 1100°C. Char yields were calculated and based on analysis of some of the chars, the fate of carbon, sodium, potassium and sulfur was determined as a function of pyrolysis pressure. A shift in pyrolysis behavior was observed at roughly 800°C. Above this temperature, char yields were very dependent on furnace temperature. Additionally, increasing pyrolysis pressure resulted in higher char yields above 800°C while pressure had little influence in the low temperature experiments. The shift in behavior is due to lesser decomposition of inorganic species in the char, particularly sodium carbonate, at higher temperatures.

Savo et al. (2011) conducted laboratory scale study as a first step in evaluating the concept by comparing the combustion behavior of different levels of biomass addition. Observations of the study are a) The average maximum swollen volume of the black liquor at 900°C, 10% O_2 was more than twice as much as that at 1100°C, 3.3% O_2. b) At 900°C, there was a steady decrease in swelling with increased biomass addition.
2.6.4 Pyrolysis and kinetic parameters estimation

Bhattacharya et al. (1986) conducted studies on pyrolysis of black liquor solids. Black liquor solids of -30+60, -60+80, and -80+150 mesh size were pyrolyzed in a fixed-bed reactor in an inert atmosphere of nitrogen at 863-1013 K and atmospheric pressure. The effect of reaction time, temperature, feed particle size on the product yields and the composition of product gases were investigated. The main components of the product gases identified were hydrogen, methane, carbon monoxide, carbon dioxide, and hydrogen sulfide. A reaction model, in which the black liquor solids decomposed into gas, tar, and char by three parallel first-order reactions, was proposed, the frequency factors and activation energies of the rate constants were determined.

Backman et al. (1993) carried basic studies on black liquor pyrolysis and char gasification. Pressurized gasification of black liquor is a promising alternative for increasing the electrical-energy production in chemical pulp mills. The authors’ observations are listed below.

a) Complete gasification of the organic fraction of black liquor is thermodynamically possible with air ratios exceeding 0.3.

b) The theoretical temperature limit for complete gasification decreases with increasing air ratio and decreasing pressure.

c) Conversion of the organic fraction to gases during pyrolysis is kinetically controlled and increases with increasing pyrolysis temperature.

d) Significant sodium aerosol formation, in the order of 20% of the sodium in black liquor, is expected during pyrolysis at high heating rates.

Frederick et al. (1994) studied the volatiles and char carbon yields for spent pulping liquors by pyrolyzing single liquor droplets in N₂/CO atmospheres at 600-1200°C, weighed the droplet residue, and analyzed the residue for carbon content. Observations of the study are as follows.

a) The volatiles yield in these experiments increased from 33 to 75% over the temperature range investigated.

b) The carbon content of the char residue decreased from 65 to 12% of the carbon initially in the droplets over the same temperature range.

c) Droplet mass had no effect on volatiles or char carbon yield over the range studied.
d) In experiments with six Kraft liquors at 800°C, the volatiles yield ranges from 35 - 47% of the dry liquor solids while the carbon in the char ranged from 26-48% of the carbon originally in the black liquor solids.

Alen et al. (1995) studied the slow thermal degradation of various black liquors and their organic components (lignin, aliphatic carboxylic acids, extractives and poly-saccharides) in the temperature range of 25-700°C under an inert nitrogen atmosphere and at a heating rate of 20°C/min. Oven-dried samples of pine and birch black liquors from Kraft and soda-anthra quinone pulping were tested. Similar tests with black liquor components were carried out both in the absence and in the presence of alkali. In all cases, the mass loss occurred primarily in the temperature range 250-500°C. The thermo-grams of the various black liquors were very similar even though there were significant differences in the thermo-grams of the individual black liquor components. The possible roles of the individual components in the thermal degradation of black liquor are discussed.

Sricharoenchaikul et al. (2001) measured the yields of char residue, fixed carbon, and inorganic carbonate in a laboratory laminar entrained flow reactor (LEFR) for oxidized black liquor char residues produced. The char residue yields at the end of devolatilization decreased linearly with temperature, from 75% at 700°C to 58% at 1100°C. From the experimental results, Char residue yields seemed to depend mainly on the temperature to which the particles or droplets were exposed and were not very sensitive to heating rate. Fixed carbon yields behaved similarly to those of the char residue. The fixed carbon remaining at the end of devolatilization decreased from 67% at 700°C to about 45% at 1100°C. The carbonate content in black liquor changed very little before and after devolatilization.

Demirbas (2002) conducted experimental studies on pyrolysis and steam gasification processes of black liquor and presented the following observations. The black liquor composition was assumed to be C_{10}H_{12.5}O_{7}Na_{2.4}S_{0.36}, which corresponds to Kraft liquor with a molar ratio of S/Na_{2} of 0.3.

a) The yields of liquid products from the black liquor pyrolysis increase from 17.2 to 26.5% with increasing temperature from 600 to 800 K.

b) The yields of liquid and gaseous products from pyrolysis of the black liquor samples increase with increasing temperature.
c) The yield of (H₂ plus paraffin) in the gaseous products from the black liquor steam gasification run (Water/Black liquor = 1.9) increase from 38.0 to 50.3% with increasing temperature from 975 to 1325 K.

d) The highest hydrogen rich gas yield was obtained from the catalytic steam gasification run (Water/Black liquor = 1.9) at 1325 K.

Babu and Chaurasia (2003a) carried the work for estimating the optimum parameters in the pyrolysis of biomass for both non isothermal and isothermal conditions. The modelling equations were solved numerically using the fourth order Runge-Kutta method over a wide range of heating rates (25-360 K/s) and temperatures (773-1773K). The range of operating conditions used for simulating the model equations is small in the case of the earlier investigators work, but the results obtained using a wide range of operating conditions in the present study show that the final pyrolysis time initially decreases and then increases as the net heating rate or temperature is increased, giving an optimum final pyrolysis time corresponding to the optimum net heat rate or temperature. Whereas the earlier investigations indicate a decrease in final pyrolysis time as the net heating rate or temperature is increased.

Babu and Chaurasia (2003b) developed a mathematical model to describe the pyrolysis of a single solid particle of biomass by incorporating improvements to their earlier developed model. In the present model, authors coupled the heat transfer equation with the chemical kinetics equations. The pyrolysis rate is simulated by a kinetic scheme involving three reactions (primary and secondary): two parallel reactions and a third for the secondary interactions between the volatile and gaseous products and the char. The dependence of convective heat transfer coefficient on Reynolds number and Prandtl number is incorporated in the model. Simulated results were compared with the available experimental results and literature reported simulated results and the obtained results are better matching.

Sanchez et al. (2004) studied the kinetics of pyrolysis reaction of black liquor solids at low temperatures (i.e. <500°C). Very little literature is available on pyrolysis of dry black liquor solids available and authors have attempted to find out the kinetic parameters at low temperature decomposition for gasifying the black liquor.
Demirbas and Balat (2007) discussed about the various pyrolysis process such as conventional, fast and flash which can produce solid (char coal), liquid (tar and other organics) and gaseous products (H$_2$, CO$_2$, CO). Pyrolysis has been used for commercial production of a wide range of fuels, solvents, chemicals and other products from biomass feed stocks. The yield of products resulting from biomass can be maximized with the following processes

a) Char coal: low temperature and low heating rate
b) Liquid products: Low temperature, high heating rate and short gas residence time
c) Fuel gas: High temperature, low heating rate and long gas residence time.

Olivella and De Las Heras (2008) carried out a comparative study of six different linear methods: three methods based on several curves and three based on a single curve for deriving kinetic parameters from Thermo-gravimetry/Differential thermogravimetry (TG/DTG) curves in the interval related to oil and hydrocarbon generation. Respective equations were simulated by the use of a simulation program to find out the most accurate methods based on a single TG/DTG curve.

Cai and Liu (2008) developed a new distributed activation energy model considering the reaction order and the dependence of frequency factor on temperature. Two numerical examples to illustrate the proposed method were presented. The traditional DAEM and new DAEM have been used to simulate the pyrolytic process of some types of biomass. The new DAEM fitted the experimental data much better than the traditional DAEM as the dependence of the frequency factor on temperature was taken into account. The pyrolysis kinetic behavior of some types of biomass has been described by the new DAEM, whose kinetic parameters were determined using the pattern search method, a class of direct search methods.

Sonobe and Worasuwanrak (2008) investigated the pyrolysis behaviors of several agricultural residues by using thermo-gravimetric analysis and measured the evolving rates of the gaseous products during the pyrolysis such as H$_2$, CH$_4$, H$_2$O, CO and CO$_2$.

a) The feature common to all the samples was that the evolving behaviors of CH$_4$, H$_2$O, CO, and CO$_2$ were well accompanied by the sharp decomposition seen in the DTG curves.
b) Each biomass showed quite different devolatilization behaviors while they showed the similar elemental composition.

c) The catalytic effects of alkali and alkaline earth metals during the pyrolysis play a major role in the variation of distribution of activation energy ($f(E)$) curve among the different biomass species.

Fletcher et al. (2012) applied the chemical percolation model (CPD) to describe the pyrolysis behavior of black liquor, lignin, and cellulose using limited data from the literature. The CPD model and kinetic parameters were originally developed for coal pyrolysis, using 13C NMR spectroscopy analyses to determine the chemical parameters for different coals. In this work, the chemical structure parameters were determined using a combination of 13C NMR analysis and theoretical analysis based on known structures. The model was then fit to the pyrolysis data with as few deviations in the kinetic parameters from the coal base case as possible. Only one activation energy parameter was changed to match the black liquor data. Additional parameters were changed to match the lignin, cellulose, and hemi-cellulose data.

Lycksam et al. (2012) used the holographic interferometry to measure the velocity of the gases released during heating of a black liquor drop as well as the swelling of the drop. The velocities were found to be several meters per second close to the drop but interaction with the surrounding air quickly reduced the speed of the ejecting gas. The directions of the ejected gas just after the start of the laser heating tend to be close to the direction of the incoming laser light. After a while however the gas bursts were emitted more uniformly. It is also possible to roughly estimate the temperature profile of the ejected gas bursts but because of the relatively low gas temperatures involved and the fact that the gas composition is not known with sufficient accuracy at all points there will be uncertainties in the calculated temperatures.

2.6.5 Char combustion

Jarvinen et al. (2002a) studied the combustion of single 0.5-4 mm black liquor particles and the formation of a localized flame around the particle by means of numerical simulations using a detailed physical model. A critical Damkohler number (The ratio of residence time and reaction time, Da) for a localized CO flame was determined from pyrolysis experiments. These results were extrapolated to furnace conditions i.e. higher temperatures, higher slip
velocities and lower $O_2$ concentrations. The general trend found was that particles will act mainly as a source of combustible gases. If no gases are oxidized around the particle, and no flame sheet is formed, $O_2$ may reach the particle surface during pyrolysis. For smaller particles, $O_2$ will penetrate more effectively into the particle and react with char. During char combustion internal particle temperature is more uniform. The larger the particle the higher the internal mass transfer resistance and the thinner the relative thickness of the char conversion region.

Engblom et al. (2012a) presented a mathematical model of char-bed burning in the presence of a chemically reactive boundary layer. Simulations of the Institute of paper science and technology (IPST) char-burning experiments were carried out and the following conclusions were drawn.

a) Boundary-layer reactions consume oxygen, which has a net exothermic impact on overall combustion, increasing both gas-phase and char-bed temperatures.

b) Oxygen in the bulk gas contributes to carbon conversion, although carbon conversion involving gas-phase reactants can occur entirely through gasification reactions.

c) Overall carbon conversion can be decreased either because of the direct effect of boundary-layer gas-phase chemistry or because combustion inside the boundary layer affects mass transfer through this layer.

2.6.6 Smelt and smelt treatment

Char bed is a distinctive feature of the recovery boiler and it adds criticality in design and operation in comparison to any other type of boilers. A char bed, consist mostly of dried de-volatilized black liquor particles in the upper layers, is at the bottom of the furnace. Because of explosion hazards, the absence of water in the char bed is one of the most important safety requirements in the operation of the recovery boiler.

Clement et al. (1995) presented the improvement in boiler operations with fundamental approach to black liquor combustion. Combustion of black liquor in a recovery boiler has been optimized to change the ash characteristics and rate of deposition to substantially improve the super heater steam temperature performance over time. Modifications to the approach of spraying black liquor into the furnace and distributing air demonstrate the importance of depositing the liquor char on the bed and at the perimeter of the furnace.
Optimum lower furnace operating conditions result in a stable bed and higher quality smelt.

2.7 Various models used in the study of BL droplets dynamics

Blasiak et al. (1997) presented three-dimensional, steady-state computer simulation of the flow and combustion process in a recovery boiler. The numerical algorithm of the original code was modified and extended to cater for certain special aspects of recovery boilers, such as the in-flight combustion of black liquor droplets and char bed burning. In this work, a highly flexible, unstructured and mixed cell topology grid with local mesh refinement was employed. A number of computations were carried out using various firing arrangements including the ROTAFIRE system. The results show considerable potential and reliability in the use of computer simulations for the improvements and optimization of recovery boilers. CFD indirectly provides information on the thermal and chemical performance of recovery furnace including tendencies for corrosion, entertainment and carry-over. However, careful design of the whole system is necessary in order to avoid negative effects.

Costa et al. (2004) proposed a new (hybrid) approach for the mathematical description of the black liquor burning process in an industrial recovery boiler furnace. The system is divided into four different regions and the concentration of each chemical substance in each region is calculated through direct minimization of the corresponding Gibbs free energy. The particulate formation is described separately through a neural network trained with industrial data. The resulting hybrid model reproduces satisfactorily black liquor burning data obtained from industrial sources, and also data reported in the open technical literature.

2.8 Environmental issues

2.9 Proposed work

From the literature survey presented in this chapter, it is clear that black liquor contains valuable organic and inorganic content which need to be recovered for better economics of the pulp and paper industry. Recovery of these chemicals & organic content (in the form of heat energy) in a chemical recovery boiler is one of the most efficient and traditional method widely used in the pulp and paper industry. Though the recovery boiler has proved successful, the operation of the boiler is very critical in nature and therefore requires better understanding of the boiler operation and dynamics for efficient, safe and trouble-free operation. The identified major concerns in recovery boiler operation are:

a) Fouling of convective heat transfer surfaces due to carry over and deposition of droplets due to fines carryover.

b) Smelt-water explosion due to contact of water with smelt due to wet particles entering the combustion zone

Hence, considering the above reasons, it is proposed to develop a simple mathematical model for understanding the black liquor droplet dynamics inside the chemical recovery boiler. From the results of simulation, it is hoped to achieve the following objectives:

1) Operating maps consisting of droplet diameters and understanding the influence of various parameters such as black liquor density, initial black liquor solids concentration, initial droplet velocity, swelling factor etc.

2) Determination of design height of black liquor injection nozzles from the furnace floor for various influencing parameters.