TKK Dissertations 53
Espoo 2006

SPRAY FORMATION OF HIGH DRY SOLIDS BLACK LIQUOR IN RECOVERY BOILER FURNACES

Doctoral Dissertation

Pasi Miikkulainen

Helsinki University of Technology
Department of Mechanical Engineering
Laboratory of Energy Engineering and Environmental Protection

TKK Dissertations 53
Espoo 2006

SPRAY FORMATION OF HIGH DRY SOLIDS BLACK LIQUOR IN RECOVERY BOILER FURNACES

Doctoral Dissertation

Pasi Miikkulainen

Dissertation for the degree of Doctor of Science in Technology to be presented with due permission of the Department of Mechanical Engineering for public examination and debate in Auditorium K216 at Helsinki University of Technology (Espoo, Finland) on the 14th of December, 2006, at 12 noon.

Helsinki University of Technology
Department of Mechanical Engineering
Laboratory of Energy Engineering and Environmental Protection

Teknillinen korkeakoulu
Konetekniikan osasto
Energiatekniikan ja ympäristönsuojelun laboratorio

Distribution:
Helsinki University of Technology
Department of Mechanical Engineering
Laboratory of Energy Engineering and Environmental Protection
P.O. Box 4400
FI - 02015 TKK
FINLAND
URL: http://eny.tkk.fi/
Tel. +358-9-451 3631
Fax. +358-9-451 3418
E-mail: pasi.miikkulainen@tkk.fi

ISBN-13 978-951-22-8507-5
ISBN-10 951-22-8507-X
ISBN-13 978-951-22-8508-2 (PDF)
ISBN-10 951-22-8508-8 (PDF)
ISSN 1795-2239
ISSN 1795-4584 (PDF)
URL: http://lib.tkk.fi/Diss/2006/isbn9512285088/

TKK-DISS-2220

Picaset Oy
Helsinki 2006

HELSINKI UNIVERSITY OF TECHNOLOGY
P. O. BOX 1000, FI-02015 TKK
http://www.tkk.fi

ABSTRACT OF DOCTORAL DISSERTATION

Author	Pasi Miikkulainen
Name of the dissertation	Spray Formation of High Dry Solids Black Liquor In Recovery Boiler Furnaces
Date of manuscript	June 12, 2006
Date of the dissertation	December 14, 2006
☐ Monograph	☒ Article dissertation (summary + original articles)
Department	Mechanical Engineering
Laboratory	Energy Engineering and Environmental Protection
Field of research	Energy Engineering and Environmental Protection
Opponent(s)	Professor Rikard Gebart and Professor Mikko Hupa
Supervisor	Professor Carl-Johan Fogelholm
(Instructors)	Mika Järvinen, D.Sc.(Tech.) and Esa Vakkilainen, D.Sc.(Tech.)

Abstract

This thesis focuses on the characteristics of high dry solids black liquor sprays under in-furnace conditions, more specifically, on how the atomization process starts and the nature of the initial properties such as velocity, opening angle, and trajectory of a high dry solids content black liquor spray, which is sprayed well above its atmospheric boiling point. The experiments were carried out in operating recovery boiler furnaces. The results were compared with full-scale spraying chamber tests. The information and measurement data of black liquor spraying achieved in the furnace environment give valuable information for furnace modeling, boiler design and control, and help to understand the in-furnace processes involved. Validated initial data for CFD calculations is essential.

The spray research under in-furnace conditions is introduced as a very useful method of studying black liquor spraying practice with real black liquor, in a real environment with industrial-scale nozzles. The furnace endoscope, developed during this work, made this possible. It was the first attempt to systematically obtain information about high dry solids black liquor spraying under in-furnace conditions.

Flashing inside the nozzle was found to be a factor key to the whole spraying process of high dry solids black liquor. It has a major role in spray disintegration and initial velocity, both of which correlate very well with the final drop size and shape. A dry solids content of approximately 75% was observed to be the limit that forced boiler operators to change their spraying practice from non-flashing to flashing mode. Dimensionless velocity can be used in categorizing the disintegration processes. Regardless of the disintegration mechanism, it is possible to find the dominating frequency in disintegrating spray with techniques based on image analysis.

Keywords Black liquor, Recovery boiler, Furnace, Spray

ISBN (printed)	951-22-8507-X	ISSN (printed)	1795-2239
ISBN (pdf)	951-22-8508-8	ISSN (pdf)	1795-4584
ISBN (others)		Number of pages	65 p. + app. 96 p.

Publisher TKK, Laboratory of Energy Engineering and Environmental Protection

Print distribution TKK, Laboratory of Energy Engineering and Environmental Protection

☒ The dissertation can be read at http://lib.tkk.fi/Diss/2006/isbn9512285088

TEKNILLINEN KORKEAKOULU
PL 1000, 02015 TKK
http://www.tkk.fi

VÄITÖSKIRJAN TIIVISTELMÄ

Tekijä Pasi Miikkulainen

Väitöskirjan nimi
Korkeakuiva-aineisen mustalipeän pisaroituminen soodakattilan tulipesässä

Käsikirjoituksen jättämispäivämäärä 12.6.2006
Väitöstilaisuuden ajankohta 14.12.2006

☐ Monografia ☒ Yhdistelmäväitöskirja (yhteenveto + erillisartikkelit)

Osasto	Konetekniikka
Laboratorio	Energiatekniikka ja ympäristönsuojelu
Tutkimusala	Energiatekniikka ja ympäristönsuojelu
Vastaväittäjä(t)	Professori Rikard Gebart ja Professori Mikko Hupa
Työn valvoja	Professori Carl-Johan Fogelholm
(Työn ohjaajat)	Mika Järvinen, TkT ja Esa Vakkilainen, TkT

Tiivistelmä

Tässä työssä tutkittiin korkeakuiva-aineisen mustalipeän pisaroitumista tulipesäolosuhteissa. Tutkittiin, miten pisaroituminen alkaa ja minkälainen lähtönopeus, avautumiskulma ja lentorata on mustalipeällä, jota ruiskutetaan huomattavasti kiehumispisteen yläpuolella. Ruiskutuskokeet tehtiin toiminnassa olevien soodakattiloiden tulipesissä ja tuloksia verrattiin täyden mittakaavan ruiskutuskammiokokeisiin. Tulipesässä mitatut mustalipeäsuihkun ominaisuudet ovat tärkeitä mallinnuksen lähtötietoina ja kokeelliset tulokset auttavat ymmärtämään paremmin soodakattilan tulipesän prosesseja. Luotettava mittaustieto on välttämätöntä CFD-mallinnukselle.

Suihkun ominaisuuksien mittaaminen tulipesäolosuhteissa on käyttökelpoinen menetelmä mustalipeän pisaroitumisen tutkimiseen – oikealla mustalipeällä, todellisessa ympäristössä ja täydessä mittakaavassa. Tämän työn aikana kehitettiin tulipesäendoskooppi, jonka avulla saatiin ensimmäistä kertaa systemaattisesti tietoa korkeakuiva-aineisen mustalipeän ruiskutuksesta soodakattilan sisällä.

Paisuntakiehuminen suutinputken sisällä havaittiin korkeakuiva-aineisen mustalipeän ruiskutuksen merkittävimmäksi tekijäksi. Se vaikuttaa eniten suihkun hajoamiseen ja lähtönopeuteen, jotka korreloivat hyvin syntyvien pisaroiden koon ja muodon kanssa. Havaittiin, että 75 % kuiva-ainepitoisuus on käytännössä raja, jonka yläpuolella soodakattilaan ruiskutettavan mustalipeän pisaroitumistapahtumaa hallitsee paisuntakiehuminen. Dimensiotonta nopeutta voidaan käyttää hajoamismekanismien luokitteluun ja ennakointiin. Kuva-analyysimenetelmien avulla voidaan suihkusta löytää hallitseva taajuus hajoamismekanismista riippumatta. Näin on mahdollista arvioida syntyvää pisarakokoa.

Asiasanat Mustalipeä, Soodakattila, Tulipesä, Pisara

ISBN (painettu) 951-22-8507-X	ISSN (painettu) 1795-2239
ISBN (pdf) 951-22-8508-8	ISSN (pdf) 1795-4584
ISBN (muut)	Sivumäärä 65 + 96 (liitteet)

Julkaisija TKK, Energiatekniikan ja ympäristönsuojelun laboratorio

Painetun väitöskirjan jakelu TKK, Energiatekniikan ja ympäristönsuojelun laboratorio

☒ Luettavissa verkossa osoitteessa http://lib.tkk.fi/Diss/2006/isbn9512285088

Preface

The work for this dissertation was carried out during the period 1998-2006 at the Laboratory of Energy Engineering and Environmental Protection at Helsinki University of Technology. The main part of the research work, the measurements at the six mills, was carried out as a part of the National Modeling Tools for the Combustion Process Development Technology Programme (CODE) 1999-2002 supported by Tekes, the Finnish Funding Agency for Technology and Innovation. Financial support for the projects and for this thesis was also provided by the Academy of Finland (project 53606), Andritz Corp., Kvaerner Power, the Walter Ahlström Foundation, Tekes (Chemcom 2005-2007) and the Department of Mechanical Engineering, Helsinki University of Technology. All these supporters are acknowledged for making this work possible.

I wish to express my sincere thanks to my colleague and co-author Ari Kankkunen Lic.Sc. for his time, valuable advice and overall help. His continuous enthusiasm for challenging experimental research work greatly encouraged me to finish this thesis. I would also like to thank my instructor, colleague, and co-author Mika Järvinen D.Sc. and my instructor Esa Vakkilainen D.Sc. for their helpful guidance and discussions. I would like to express my thanks to the supervisor of this work, Professor Carl-Johan Fogelholm, for his advice and for giving me the opportunity to carry out this interesting and enjoyable research work at the Laboratory of Energy Engineering and Environmental Protection.

The extensive spraying experiments at the mills required a great deal of preparation and building work, not forgetting participation in long periods of measurement. Without the technical staff and other personnel at the Laboratory of Energy Engineering and Environmental Protection, such experiments could never have succeeded. Helinä, Pertti, Seppo, Taisto, Timo, and Vadim, thank you for your great efforts.

Finally, sincerest thanks go to my dear wife Päivikki and to our sons Pessi and Sisu for their love and support.

Espoo, October 2006

Pasi Miikkulainen

Contents

List of publications

This dissertation consists of an overview and the following publications.

I. Miikkulainen, P., Kankkunen, A. & Järvinen, M.P. 2004, "Furnace endoscope - Measuring fuel spray properties in hot and corrosive environments", *Experiments in Fluids,* vol. 37, no. 6, pp. 910-916.

II. Miikkulainen, P., Järvinen, M. & Kankkunen, A. 2000, "Black Liquor Spray Properties in Operating Recovery Boiler Furnaces", *INFUB 5th European Conference on Industrial Furnaces and Boilers, Porto, Portugal, 11-14 April.*

III. Miikkulainen, P., Järvinen, M. & Kankkunen, A. 2002, "The effect of a furnace environment on black liquor spray properties", *Pulp and Paper Canada,* vol. 103, no. 9, pp. 34-38.

IV. Miikkulainen, P., Kankkunen, A. & Järvinen, M. 2002, "The Effect of Excess Temperature and Flashing on Black Liquor Spray Properties", *IFRF Finnish - Swedish Flame Days 2002, Vaasa, Finland, 24-25 September*

V. Kankkunen, A. & Miikkulainen, P. 2003, "Particle Size Distributions of Black Liquor Sprays with A High Solids Content in Recovery Boilers", *IFRF Online Combustion Journal,* [Online], Article Number 200308, December 2003. Available from: http://www.journal.ifrf.net/library/december2003/200308Kankkunen.pdf

VI. Miikkulainen, P., Kankkunen, A., Järvinen, M. & Fogelholm C.-J. 2005, ”Predicting droplet size from black liquor spray characteristics”, *TAPPI Journal*, vol. 4, no. 5, pp.11-17.

Author’s contribution

The author was the leading author and the writer of Publications I-IV and VI. The first four publications are based on the experimental work carried out with a furnace endoscope developed during this thesis. Publications IV to VI connect the spray research to the final drop size. Discussions and team work with co-authors Kankkunen and Järvinen played a very important role, both in carrying out the experiments and improving all the papers.

Publication I introduces a new instrument and a method for black liquor spray research under furnace conditions. An air-cooled optical measurement probe, called a furnace endoscope, was developed. The furnace endoscope was the first measurement instrument developed for spray research taking place in hot and very corrosive recovery boiler conditions. The furnace endoscope and its development work, as well as the accuracy of the method, are described in detail. The method and the new measurement tool were used and developed further, as reported in the following publications. The author was responsible for the development process, carrying out the experiments and analyzing the results. The author was the leading author of the paper.

Publication II presents black liquor spray characteristics measured in five recovery boilers with the furnace endoscope. This was the first attempt to systematically obtain information about black liquor spraying under furnace conditions. Within the operation range of the endoscope, no droplets were observed, but the spray velocity and shape could be compared to previously published spraying chamber data. Publication II confirms that spray properties in both environments depend on the same spraying parameters, but due to too many variables between the cases, a final conclusion could not be drawn. Järvinen was responsible for collecting the process data and pressure measurements. He also calculated the theoretical maximum of the relative velocity of the spray, which corresponds to the choking condition of the flow in the nozzle. The author carried out the spray measurements and was the leading author of the paper.

Publication III deals with the validity and relevancy of the spraying chamber measurements, which were more easily measured than those taken under real furnace conditions. Simultaneous spraying tests with high dry solids black liquor in a full-scale horizontal spraying chamber and in a recovery boiler furnace confirmed that spray formation was similar in both spraying environments. The spray velocity and disintegration mechanism depended mainly on the mass flux and spraying temperature. This was verified in the nearby area of the nozzle exit when flashing took place. It was concluded also that reliable essential furnace modeling data would be available through the more inexpensive furnace endoscope measurements. The author was responsible for designing and constructing the full-scale horizontal spraying chamber and carried out the spray measurements. He was the leading author of the paper.

Publication IV presents the sensitiveness of spray formation – spray disintegration and velocity – and resulting drop size to temperature and mass flux when spraying high dry solids black liquor within the normal range. When the firing temperature was lowered by 2°C outside the operational temperature range of a recovery boiler, an unexpectedly long, uniform liquor sheet appeared. This doubled the mass median drop size and formed more non-spherical drops. Until now, black liquor droplets have been considered spherical, 2-3 mm in size, in the boiler calculations and models. The fraction of spherical drops was small, even within the normal operation range. Ari Kankkunen carried out the drop-size measurements. The author carried out the spray measurements and was the leading author of the paper.

Publication V discusses the shape of the drop-size distribution measured in Publication IV. Four theoretical drop-size distributions were compared. In contrast to other experiments, the spray consisted of spherical and non-spherical particles. The volume median diameters were higher than those detected in measurements with lower dry solids content. The drop size correlated well with the spray velocity and thereby with excess temperature. The corresponding author of Publication V was Ari Kankkunen. The author carried out the velocity measurements and wrote that part of the paper, and contributed comments to the rest of Paper V.

Publication VI describes a new image-analysis-based method to predict droplet size from spray properties. Spraying chamber measurements are not necessary if the final drop size can be predicted from the spray properties that are measurable with the furnace endoscope. A dominating wave length was searched for on the assumption that it could be found if the disintegration process was complete. The dominating wave length was used for calculating the diameter of a forming ligament. In order to calculate the volume of the forming ligament, sheet breakup point was measured in all directions from the nozzle exit with an image-analysis-based algorithm developed and programmed by the author. The author also developed the method for determining the dominating wavelength, carried out the programming process, and was the leading author of the paper.

Nomenclature

A	the smallest cross-sectional area of the nozzle, m^2
d	distance from the endoscope lens to the object, m
d_{fr}	vertical size of the frame, pixels
d_{p}	inner diameter of the nozzle pipe, m
d_{px}	distance in the frame, pixels
$\dot{m}$	mass flow rate, kg/s
$\dot{m}''$	mass flux, g/mm^2s ($6 kg/cm^2 min$)
p	pressure, Pa
s	the distance the spray moved during the exposure time and delay time, m
T	temperature, °C
t	time, s
u^*	dimensionless velocity, -
u_{c}^*	critical dimensionless velocity, -
u_{p}	velocity of the non-flashing case at the smallest cross-sectional area, m/s
u_{s}	sheet velocity, m/s
$\dot{V}$	volume flow rate, m^3/s

Greek letters

α	angle of view of the furnace lens, °
α	angle, at which the fluid exiting the nozzle orifice strikes the splashplate, °
ΔT_{e}	excess temperature, °C
$\Delta T_{e,c}$	critical excess temperatrure, °C
ε	absolute error, m/s
ε^*	relative maximum error, %
ϕ	outer diameter of the endoscope pipe, m
λ_{c}	minimum or critical wavelength of instability, m
λ_{opt}	the wave length of the disturbance of maximum growth, m
ρ_{gas}	density of the gas, kg/m^3
σ	surface tension, N/m

Abbreviations

AOI	Area Of Interest
BPR	Boiling point rise
CCD	Charge-Coupled Device
CFD	Computational Fluid Dynamics
FFT	Fast Fourier Transformation

List of Figures

1 Introduction

Kraft pulping is the most common method of producing pulp. Global chemical kraft pulp production is about 120 million tons per year. In Finland, the production was 7.8 million tons in 2004 (Metsäteollisuus ry., 2005). In the kraft pulping process, lignin, aliphatic acids and other organics are dissolved from wood chips during the strongly alkaline cooking process, where Na_2S and NaOH are used as cooking chemicals. The fibers are washed and the pulp is used for a large variety of paper products. The excess water of the spent kraft pulping liquor (inorganic and the dissolved organic materials) is removed in an evaporation station and the strong black liquor is burned in a recovery boiler. A recovery boiler has two main functions: to recover the valuable inorganic cooking chemicals and to utilize combustion energy from the organic portion of the black liquor. In modern pulp mills, the heat and power generation covers more than the internal consumption.

The production of a kilogram of air dry pulp produces about 1.5 kg of black liquor solids. US production of chemical wood pulp by the kraft process was about 45 million tons in 2004 (FAOSTAT data, 2006). This means that 100 million tons of black liquor of 67% dry solids content is burned in recovery boilers per year. There are more than 400 kraft pulp mills in the world, eighteen of them in Finland. Black liquor as a fuel plays an important role in Finnish energy production. It corresponds to 11% of the total heat and power generation and 46% of the energy generated from biofuels (Helynen et al., 2002). Even a modest improvement in avoiding malfunctions or reducing emissions by greater efficiency in recovery-boiler combustion is significant.

1.1 Spraying black liquor into a recovery boiler

The transformation of liquids into sprays is of importance in several industrial processes and has many applications in agriculture, meteorology, and medicine. The process of spray disintegration is one in which a liquid jet or sheet is disintegrated by the kinetic energy of the liquid itself, or by exposure to high-velocity gas, or as a result of mechanical energy applied externally through a rotating or vibrating device. The random nature of the atomization process makes the resultant spray become characterized by a wide drop size distribution. The combustion of liquid fuels is dependent on effective atomization to increase the specific surface area of the fuel, and thereby achieve a high mixing rate. In some applications however, small droplets must be avoided in order to achieve the desired rates of heat and mass transfer (Lefebvre, 1989).

The desired drop size of black liquor differs from those of other fuels. An ideal black liquor drop is not too small to get entrained among the flue gases and form carry-over in the upper parts of the boiler furnace, nor is it too large to fall into the char bed located at the bottom of the boiler without drying and causing cooling of the char bed. Figure 1.1 presents the lower part of a recovery boiler, including liquor guns, air ports, and the char bed with smelt spouts.

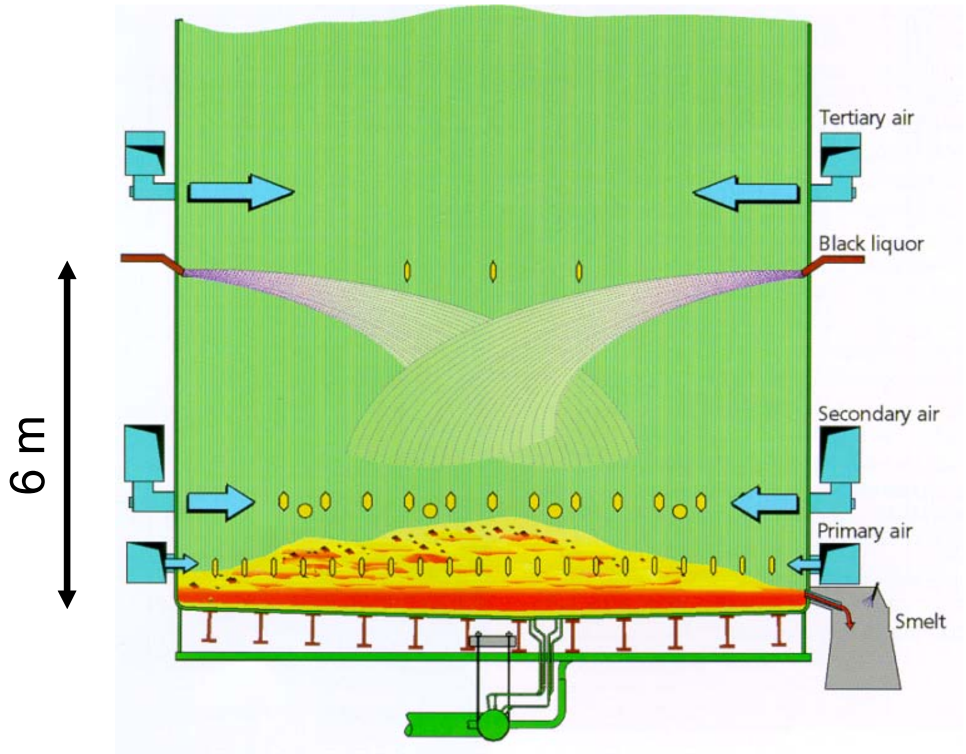


Figure 1.1 Recovery boiler lower furnace (Vakkilainen, 2000)

The dimensions of a modern (4000 tons dry solids/day) recovery boiler are ~15 m x 14 m x 70 m. The size and capacity of this kind of boiler are increasing all the time. Black liquor is commonly sprayed into a recovery boiler furnace by a set of splashplate nozzles. The swirl-cone and V-jet types are also used at a small number of boilers. Splashplate nozzles produce a thin liquid sheet, which breaks up, forming a wide distribution of large (mass median diameter of 2 – 10 mm) irregular drops (Kankkunen et al., 2001; Kankkunen and Miikkulainen, 2003).

Black liquor has one of the lowest heating values of industrial fuels because of its high fraction of oxidized inorganic matter. High ash and water content make combustion of black liquor difficult. Sprayed droplets go through the sequential or partly overlapping process of drying, pyrolysis and combustion of the pyrolysis gases, char burning and reactions of the inorganic residue (Hupa et al., 1987; Järvinen, 2002).

The disintegration mechanism of a spray results from spraying parameters, liquid-specific parameters and the spraying environment. Fraser (1956) suggested that three different disintegration mechanisms exist, namely rim disintegration, wavy-sheet disintegration, and perforation. Spielbauer and Aidun (1992a) found that the main disintegration mechanisms of black liquor sprays are wavy-sheet disintegration and perforation. In both cases, ligaments are formed first and drops later. Helpiö and Kankkunen (1996) discovered that flashing accelerated spray velocity and that higher temperatures decreased drop size. If the temperature difference between the spraying temperature and the atmospheric boiling point is more than approximately 8°C, flashing may take place inside the nozzle and accelerate the liquor flow and increase the rate of sheet breakup (Empie et al., 1992a). This brings a third disintegration mechanism, flash-breakup, to black liquor spraying.

The flashing phenomenon is a very important characteristic of black liquor spraying and drop formation. Spraying above the atmospheric boiling point of black liquor is common, especially in modern recovery boilers with high dry solids content. The spraying temperature must be high enough to enable the pumping of the black liquor as well as the drop formation process. The dry solids content of 75% can be considered as a limit for high solids content. The average dry solids content has increased during the past years, especially for the latest very large recovery boilers. (Vakkilainen, 2005).

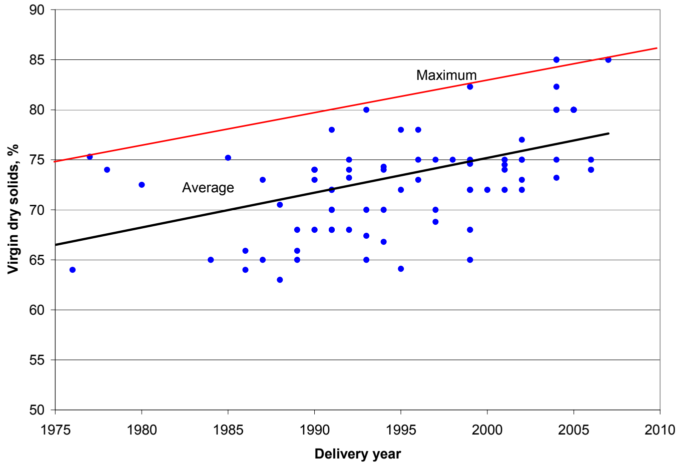


Figure 1.2. Black liquor dry solids as a function of purchase year of recovery boiler (Vakkilainen, 2004).

Research work on black liquor spraying has been carried out for more than 20 years, mostly in Finland and the USA. At an early stage, substitute liquids and laboratory scale equipment were used. After that, low solids black liquors were used in small-scale and full-scale spraying chambers. It was difficult to scale the tests to correspond to the real spraying situation, especially in the flashing case. In the USA, researchers considered the black liquor viscosity as the most important connecting factor for different studies and spraying cases, and little attention was paid to the spraying temperature and especially to its difference from the boiling point. In Finland, the spray research went more towards high dry solids black liquors and spraying under flashing conditions, corresponding to the research into the development process of recovery boilers. The next step for black liquor spray research was to conduct it in a real recovery boiler furnace and to compare the results to those derived from spraying chamber tests.

1.2 Outline of the thesis

This thesis discusses the method devised to carry out non-intrusive spray research inside a recovery boiler using a furnace endoscope developed at Helsinki University of Technology (TKK). The objective of the present thesis was to obtain information on the spraying of black liquor under in-furnace conditions, both to gain a better understanding of black liquor drop formation and to gather initial data for the modeling of recovery boilers. The three main objectives were 1) to find and develop suitable methods to obtain this information, 2) to find out how the spraying processes in a cold spraying chamber environment correspond to hot recovery boiler furnace conditions, 3) to determine the key factors affecting black liquor spraying and to discover how to predict spray properties from spraying parameters.

Chapter 2 summarizes the research work related to black liquor spray research carried out prior to this study. There is a brief history of black liquor spray research and an account of the work of the main research groups in this area. The chapter focuses on different spray disintegration mechanisms and on the reasons for them. The objective and the scientific significance of this dissertation are presented in more detail in Chapter 3. The work in Publications I to VI is aggregated in Chapters 4 to 7, and the conclusions are summarized with recommendations for future work in Chapter 8. Appendix I lists the significant quantities and dimensionless parameters involved in the test cases.

2 Literature review

This chapter gives an overall picture of the spraying process of black liquor and the research work carried out in the field of black liquor drop formation prior to this thesis. The main focus is on the experimental work of spraying and drop formation of black liquor or very viscous substitute liquids and on the spray formation of black liquor nozzles and especially on splashplate nozzles. Drop-size measurements and studies of drop size distributions and combustion of black liquor are mainly excluded.

Bennington and Kerekes (1985) summarized the parameters affecting black liquor sprays as black liquor physical properties, furnace operation, and nozzle geometry. Nozzle geometry is determined by nozzle type and diameter. The parameters of furnace operation that can be somewhat controlled are firing rate, number of nozzles used, i.e., the flow through a nozzle, dry solids content and spraying temperature. The most important controllable parameter is the spraying temperature. The physical properties (viscosity, surface tension, density and boiling point rise) are determined by the composition, temperature and pressure of the fluid. This literature review describes first generally the picture of the previous research work on black liquor spraying during the last two decades. There is a separate paragraph for the black liquor spraying related research work carried out in the TKK.

Most of the published studies on black liquor spraying during the last two decades have been carried out at the Institute of Paper Technology (IPST) (Adams et al., 1990; Spielbauer and Aidun, 1992a, 1992b, 1992c; Empie et al., 1995a, 1995b; Loebker and Empie, 1998, 2001, 2002) and the TKK. Some research work, especially during the early stages, was also carried out at Tampere University of Technology (Mäntyniemi, 1987), University of British Columbia (Bennigton and Kerekes 1985), and University of Maine (Bousfield, 1990; Stockel, 1985) The research work at different institutes differed according to whether real black liquor, dilute black liquor or substitute liquids were used, as well as according to nozzle types. The spraying conditions also separate these studies to spraying chamber and in-furnace tests. The main difference, however, is whether the spraying temperature is below or above the boiling point, i.e., whether the flashing phenomenon exists or not. Research work has been carried out both with small-scale and mill-scale nozzles and the normal dry solids content of the black liquor used in the research has increased significantly, from around 60% to 80%, during the last two decades.

Black liquor spray research in TKK started in 1990. At first, the experiments were carried out with small-scale splashplate nozzles with water, water-glycerol and black liquor. The focus was on the dimensional analysis and on the effect of flashing. Due to findings of large and often non-spherical droplets, image analysis was adapted for drop-size measurements (Paloposki and Kankkunen, 1991; Mikkanen, 1991; Rantanen et al., 1993; Kankkunen et al., 1994). The pressurized gasification related spraying was studied by Helpiö et al. (1994). In 1994, TKK started full-scale experiments with splashplate nozzles in a vertical spraying chamber that was built next to a recovery boiler. The focus was on the effect of mass flow rate and temperature on drop size, and on the pressure loss inside the nozzle pipe. The breakup process and the velocity of the black liquor sheet and the performance of different nozzle types were also studied and the results compared to small-scale experiments (Helpiö and Kankkunen, 1995; Kankkunen, 1995; Nieminen, 1996a). In 1997, TKK introduced the black liquor spray research under in-furnace conditions with a furnace endoscope. The parameters affecting spraying were studied in several operating recovery boilers (Miikkulainen, 1997). In 2000, a full-scale, horizontal, spraying chamber was built next to a recovery boiler at the liquor gun level and extensive spraying experiments were carried out with two commercial black liquor nozzles, both in the spraying chamber and under in-furnace conditions (Kankkunen et al., 2001; Miikkulainen et al., 2002). Prior to these extensive spraying tests under furnace conditions, Adams et al. (1990b) and Spielbauer et al. (1991) videotaped black liquor sprays inside an operating recovery furnace through a liquor gun port. They sprayed downwards as parallel to with the boiler wall as possible. Helpiö and Kankkunen (1995) obtained a reference for the phenomena observed in the spraying chamber similarly, except they sprayed horizontally.

2.1 Spraying-related physical properties of black liquor

The spray disintegration process is affected by the properties of the fluid being atomized; black liquor properties are highly dependent upon wood species, cooking conditions, evaporation process and additional chemical streams. The main spraying related physical properties of black liquor are dry solids content, viscosity, boiling point rise, surface tension, and density.

Additional streams, such as makeup chemicals, biosludge, acid from chlorine dioxide generation, and particulate from the boiler and economizer hoppers as well as the electrostatic precipitator are usually added in a mix tank or at the evaporation plant. In the evaporation process black liquor will further decompose as cooking is continued resulting in non-condensable gases (NCG) generation and lowered viscosity. Depending on the evaporation process, the dry solids content before spraying is usually 60-80%, of which approximately 60% is combustible organic matter and the rest is inorganic salts (Hupa and Hyöty, 1995). An example of elemental mass and organic compound distribution in the black liquor solids before the mix tank is shown in Table 2.1. The density of black liquor depends on the dry solids content and liquor type, and is in the range of 1400 to 1500 kg/m^3 when the dry solids content is between 60-80% (Frederick, 1997).

Table 2.1 Elemental mass distribution in the black liquor solids (Torniainen, 2003)

	%
C	34 - 39
H	3 - 5
O	33 - 38
N	0.04-0.2
S	3 - 7
Na	17 - 25
K	0.1 - 2
Cl	0.2 - 2
Others	0.1 – 0.3

The chemical composition of black liquor has an effect on the spraying-related physical properties of black liquor. The organic solids in kraft black liquors are mainly composed of degraded lignin and polysaccharide degradation products (aliphatic carboxylic acids). There is a minor fraction of extractives and other organics (mainly hemicellulose residues). The organic material also contains small amounts of sodium and sulfur (Alén, 2004).

Table 2.2 Typical composition (%) of the organic dry solids of pine and birch kraft black liquors (Alén, 2004)

Component	Pine	Birch
Lignin	46	37
Aliphatic acids	43	50
Other organics	11	13
Extractives	6	4
Carbohydrates	3	7
Miscellaneous	2	2

Inorganic material consists of residual active cooking chemicals (NaOH and NaSH), and other compounds, such as Na_2CO_3, Na_2SO_4, $Na_2S_2O_3$, Na_2S_x, and Na_2SO_3 (Alén, 2004).

High-molecular-weight lignin and polysaccharide fractions and lignin-carbohydrate complexes affect the viscosity of black liquor (Torniainen, 2003). It is possible to decrease the black liquor viscosity by holding liquor at a high temperature for a period of time. The lowered viscosity makes pumping and storing liquor at 75-80% dry solids in an atmospheric tank possible (Holmlund and Parviainen, 2000). Black liquor viscosity can also be decreased by increasing the temperature, adding auxiliary substances and oxidizing the black liquor with a gas containing oxygen (Niemelä and Alén, 1999).

The viscosity of black liquor is known to change greatly with temperature and dry solids. In the case of non-Newtonian behavior viscosity is also a function of shear rate. Figure 2.1 shows the typical softwood black liquor viscosity as a function of dry solids content in different temperatures. The liquor sample is from the experiments reported in Papers III-V of the present thesis. The range of the dry solids content where the mill operated was 75-79% at the spraying temperature of 129-135°C. The black liquor viscosity was 90-260 mPas.

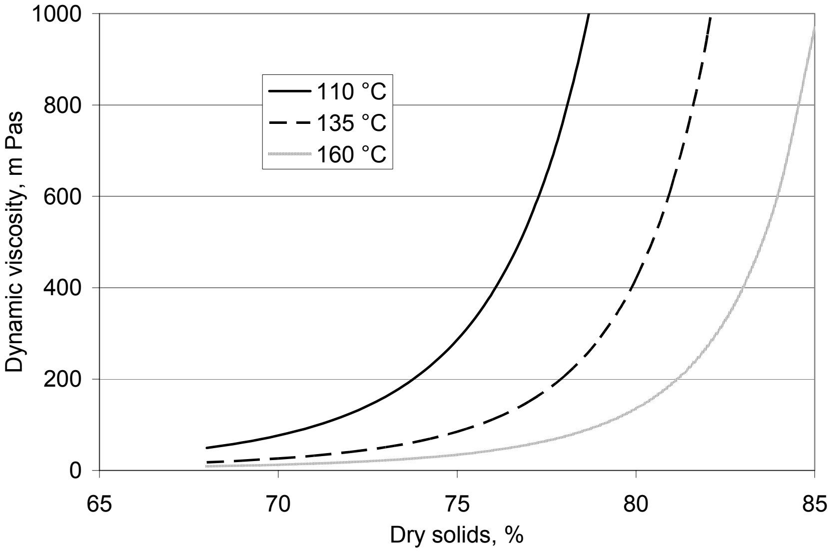


Figure 2.1 The effect of dry solids content and the spraying temperature on black liquor viscosity, (Shear rate = 288 s^{-1})

Empie et al. (1995a) studied the effect of black liquor type on droplet formation with liquors from five mills and found that the type of black liquors studied was not a significant variable. The two most important variables were the jet velocity and viscosity of the liquor. An increase of velocity produces sprays with decreasing diameters, while an increase in viscosity produces sprays with increasing diameters. The initial dry solids of the liquors were rather low (40-67.5%), while the main difference between the liquors was the viscosity.

Boiling point rise (BPR) is the difference in boiling temperature between the solution and the pure solvent when measured at the same pressure. Figure 2.2 shows the dependency of BPR on the dry solids content. Above the 50% dry solids content, the BPR increases rapidly. The liquor of the example is the same as in Figure 2.1.

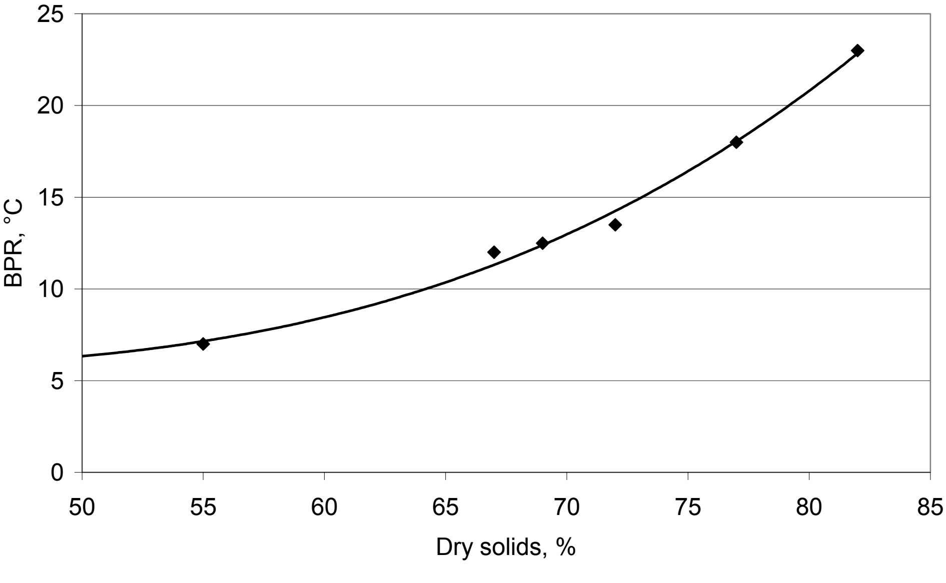


Figure 2.2 Black liquor boiling point rise (BPR)

The addition of soluble material to black liquor changes its boiling properties. The inorganic composition (concentration of aqueous salts) has the largest impact on the boiling point (Torniainen, 2003).

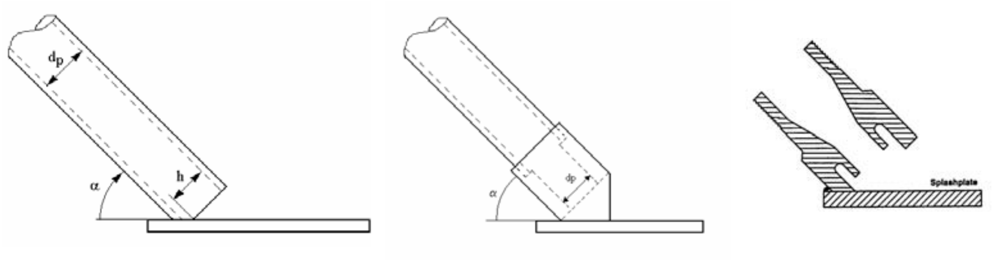
In order to have viscosity low enough for pumping and ensuring the atomization process takes place, the spraying temperature is usually in the same range as the boiling point of black liquor. This makes the spraying temperature a very important factor in black liquor spraying. Empie et al. (1992a) sprayed black liquor at several different temperatures. They noticed a dramatic change in the behavior of the spray discharge (much smaller droplets) from the nozzle above certain temperatures. Operation above the boiling point results in flash evaporation of water from the liquor within the nozzle. The transition temperature was estimated to be several degrees above the atmospheric boiling point of the liquor and is dependent upon the dissolved solids content of the liquor. In their work, the transition temperatures were observed to be about 5°C above the atmospheric boiling point at 60% solids and about 9°C at 70%.

The surface tension of a fluid is associated with the free energy of its surface. This property is responsible for the minimization of the surface area per unit volume of the fluid and causes the break-up of fluid filaments during spray formation and results in the formation of spherical droplets (Frederick, 1997). There is practically no information available on high dry solids content black liquor surface tension. High viscosity prevents the surface tension measurements.

2.2 Internal flow in splashplate nozzles

The recovery boiler nozzles have three main objectives: (1) to deliver production rates of liquor in a drop-size range that gives acceptable combustion and reduction efficiencies, (2) to deliver the liquor reliably with minimal nozzle or boiler pluggage, and (3) to be able to operate stably with large variation in black liquor spraying conditions . The most common nozzle type is the splashplate nozzle, which this thesis focuses on. Other types of nozzles are the swirl-cone nozzle and the V- and U -type nozzles.

Splashplate nozzles differ from each other mainly by size and the connection point of the nozzle pipe and the splashplate. This study limits to the most typical splashplates as seen in figure 2.3. The inner diameter of the nozzle pipe (d_p) can vary from 10 mm to 45 mm. The splashplate can be connected directly to the nozzle pipe or it can cut a part of the exit area and throttle the flow (Case A in Figure 2.3). In some commercial nozzles, the splashplate is attached to a larger pipe that surrounds the actual nozzle pipe and the exit of the nozzle pipe is a few centimeters from the splashplate (Case B in Figure 2.3). The shape of the splashplate and the angle (α), at which the fluid exiting the nozzle orifice strikes the splashplate, also have an effect on the spray. The fluid can be accelerated through a tube with a short entrance length (Case C in Figure 2.3); in this case, the free jet travels a short distance before striking the splashplate. The cup region at the rear of the nozzle redirects the backward-flowing portion of the fluid toward the front of the splashplate (Spielbauer and Aidun, 1992b).



a) Splashplate reduces the exit of the nozzle pipe.

b) The exit of the nozzle pipe does not touch the splashplate.

c) The cup region at the rear of the nozzle redirects the flow (Spielbauer and Aidun, 1992b).

Figure 2.3 Schematic pictures of three types of splashplate nozzles

The proper selection of nozzle size and number requires knowledge on the flow and pressure drop characteristics of these nozzles. Spielbauer and Adams (1990) investigated experimentally the flow and pressure drop characteristics of black liquor nozzles, including splashplate nozzles (c-type in Figure 2.3), below the boiling point of the fluid. They measured the pressure, temperature, and the flow of the fluid (two kraft black liquors (66-69% dry solids) and corn syrup (73% dry solids)) immediately ahead of the nozzle. Viscosity was measured continuously in a by-pass line located ahead of the spray nozzle. Viscosity was found to be an unimportant parameter in the flow characteristics of the nozzles studied. The flow characteristics would be nearly independent of black liquor viscosity, temperature and solids at the normal operation conditions. Operating pressure seemed to be a good indicator of black liquor flow.

Kankkunen (1998) studied the flow regimes inside a splashplate nozzle and used the two-phase flow regime map of Taitel and Dukler (1976) to indicate the type of flow. The studied cases were on the single phase or on the dispersed flow regime. He measured the mass flow rate and the pressure inside the pipe of a nozzle and studied the analogous sheet breakup process and its connection to dimensionless numbers defining the type of pipe flow.

2.3 Black liquor sprays

Black liquor spraying differs from conventional fuel atomization in many ways. The desired drop size is very large. Mass flow rate through a nozzle is large and the nozzles are large. The common agreement is that black liquor droplets should reach the char bed completely dried and substantially combusted. When a droplet hits the char bed, there must be sufficient amount char left for maximizing the reduction degree. The control of black liquor spraying is difficult due to a broad drop size distribution. Undersized droplets may form carry-over. Burning in wrong locations in the boiler causes a decrease in bed temperature, poor reduction, poor heat transfer, plugging and corrosion of heat exchanger tubes, excessive use of steam for soot blowing and the danger of black-outs from over-sized drops and a cold bed (Bousfield, 1990).

Black liquor is commonly sprayed into a recovery boiler furnace by a set of splashplate nozzles. Splashplate nozzles produce a thin liquid sheet, which breaks up forming a wide distribution of large (mass median diameter of 2-10 mm) odd-shaped drops (Kankkunen et al., 2001; Kankkunen and Miikkulainen, 2003).

2.4 Disintegration mechanisms and drop formation

The disintegration mechanism of a spray results from spraying parameters, liquid-specific parameters and the spraying environment. Knowing the disintegration mechanism of a spray enables an estimation of the final drop size (Spielbauer and Aidun, 1992b, 1992c; Kankkunen and Nieminen, 1997). Fraser (1956) suggested that three different disintegration mechanisms exist, namely rim disintegration, wavy-sheet disintegration, and perforation.

Spielbauer and Aidun (1992b, 1992c) found that the two main disintegration mechanisms of black liquor sprays are wavy-sheet disintegration and perforation. In both cases, ligaments are formed at first and drops later. Due to high solids content, black liquor is often sprayed above or well above the atmospheric boiling point. If the difference is more than approximately 8°C, flashing may take place inside the nozzle and accelerate the liquor flow and increase the rate of sheet breakup (Empie et al., 1992a). This brings a third disintegration mechanism, flash-breakup, to black liquor spraying.

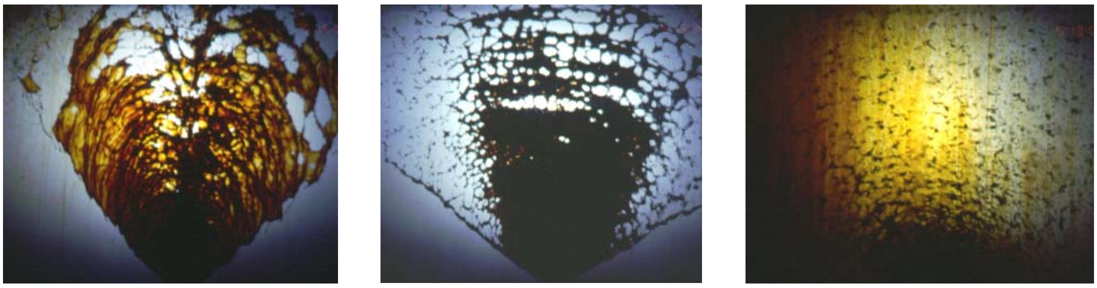
2.4.1 Observations on breakup processes

Spielbauer and Aidun (1992b) carried out a study of black liquor sheet breakup mechanisms. They found that the initial step in the disintegration process results from the growth of waves in the sheet. Thin holes occur and rupture in the sheet due to gas bubbles or solid particles in the black liquor. These perforations in the sheet then grow and the result is a network of ligaments. Ligaments become unstable and break up into droplets under surface tension and aerodynamic forces.

Nieminen (1996b) studied the sheet break-up mechanism both with industrial-scale and small-scale nozzles. He found that the sheet broke up both by wave and by perforated sheet disintegration simultaneously, but he did not observe a dominant disintegration mechanism.

Kankkunen and Nieminen (1997) measured the drop size of mill-scale nozzles and studied the sheet breakup mechanisms with a system based on video and image-analysis. The measurements were carried out both below and above the boiling point of black liquor. Wavy sheet was observed at lower temperatures, while perforation took place at temperatures above the boiling point. They observed that, when the disintegration mechanism changed from wave formation to perforation, the drop size increased, as Fraser (1956) had suggested. The reason for increase in drop size was probably the beginning of flashing inside the nozzle. Gas bubbles perforated the sheet, which broke up into ligaments earlier (when the sheet was thicker) than in the case when the temperature was below boiling point. The velocity of the spray increased when the temperature was increased above boiling point; when the mass flow rate was low and the temperature high, the sheet obviously disintegrated by flashing.

Kankkunen (1998) studied breakup processes and their connection to dimensionless numbers defining the type of the nozzle pipe flow. The Reynolds number was in laminar, turbulent and transition regimes and wave formation was the main breakup mechanism below boiling point. When the Reynolds number increased, the sheet length decreased, but the Reynolds number did not seem to have a clear connection to the breakup process. The breakup process changed from wave formation to perforation when a value of the Euler number was changed from positive to negative, Figure 2.4.



ΔT_e = -4.1 °C

ΔT_e = 4.7 °C

ΔT_e = 14.8 °C

Figure 2.4 Effect of the spraying temperature on the sheet disintegration process. ΔTe is the excess temperature. From the left: wave formation, perforation and flash breakup. Modified from Kankkunen (1998).

Appendix I presents the dimensionless numbers involved in the test cases of this thesis. The Reynolds number of the nozzle pipe flow in the experiments was between 680 and 4900. Jakob number was used instead of Euler number for characterizing the potential of flash evaporation inside the nozzle.

2.4.2 Wave formation

The position of gas-liquid interfaces will fluctuate as a result of random disturbances present in all real systems. When the position of the interface is perturbed locally, the balance of the aerodynamic, inertial, viscous, and surface tension forces determine the stability of the boundary. In a wave disintegration mechanism, sheet breakup results from the temporal or spatial growth of the unstable modes.

Dombrowski and Fraser's (1954) model of the breakup process of the spray sheet assumes that the sheet breaks at the crests and troughs of waves. Each half-wave-length contracts under surface tension to form a cylindrical thread. The thread then breaks down to produce droplets. This physical model oversimplifies the real process, but provides general indications of the characteristics of sprays generated by a number of types of atomizers (Chigier, 1991a).

According to Rayleigh's (1878) classic theory, the liquid sheet breaks up at the half wavelength of the most rapidly growing wave, forming unstable liquid threads. Surface tension forces rapidly contract this fluid into cylindrical strands that ultimately break up into drops when their length surpasses their circumference, see Figure 2.5 (Dombrowski and Johns, 1963).

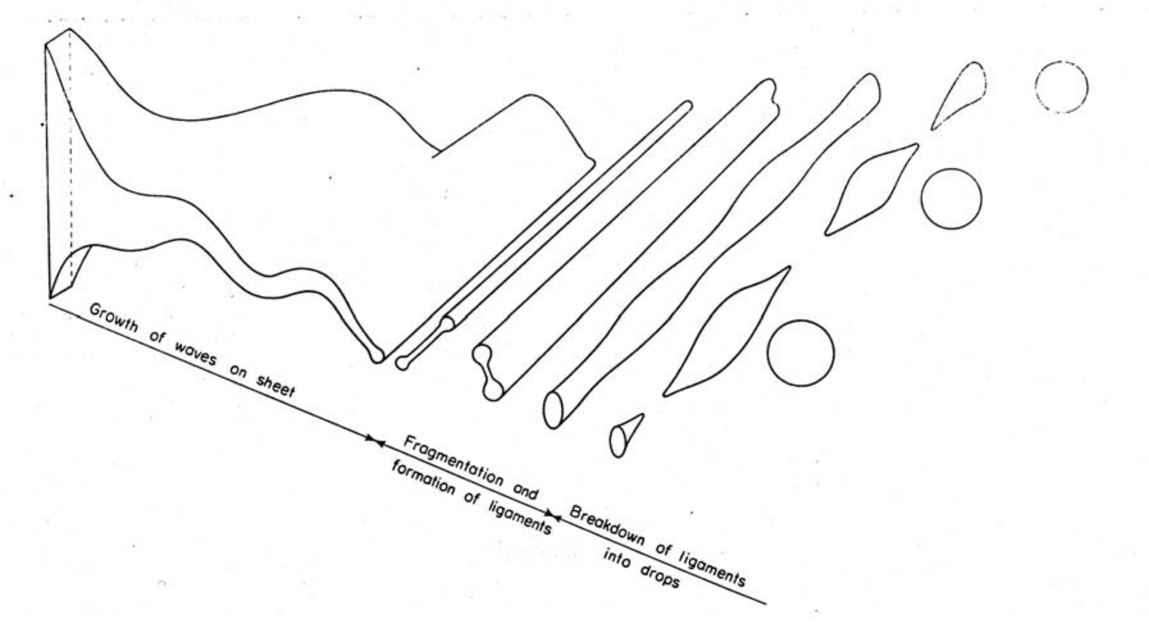


Figure 2.5 Disintegration of sheet by wave formation (Dombrowski and Johns, 1963)

The growth of disturbances in fluid sheets has been studied in several analytical studies (Hagerty and Shea, 1955; Squire, 1953; Fraser et al., 1962) that assumed an ideal flow. An ideal flow is incompressible, inviscid, and irrotational. Hagerty and Shea (1955) found that only two wave forms, sinuous and dilational or varicose, could exist in the sheet, but the calculated and experimentally observed growth rate of the antisymmetric wave was greater than the corresponding symmetric wave in all conditions under which these disturbances were temporally unstable (Squire, 1953).

Equation 2.1 gives the minimum or critical wavelength of instability (Hagerty and Shea, 1955; Fraser et al., 1962).

$$\lambda_c = \frac{2\pi\sigma}{\rho_{gas} u_s^2} \qquad (2.1)$$

where σ is the surface tension, ρ_{gas} the density of the gas and u_{s} the sheet velocity. The wave length of the disturbance of maximum growth, Eq. 2.2, was predicted by Squire (1953) and Fraser et al. (1962).

$$\lambda_{opt} = \frac{4\pi\sigma}{\rho_{gas} u_s^2} \qquad (2.2)$$

These expressions are valid only when the magnitude of the disturbance is small compared to the sheet thickness. However, it is generally assumed that the optimally growing wave will also dominate at breakup when the amplitude is large (York et al., 1953).

Dombrowski and Johns (1963) included the effects of a finite liquid-phase viscosity and decreasing sheet thickness in the results obtained for inviscid planar sheets. They made an assumption that the sheet could be treated as planar at any given position (the rate of change in sheet thickness is small). They found that the wave of maximum growth was not affected by sheet thickness and could be calculated with Eq. 2.2. The growth rate of a disturbance in viscous sheets was predicted to be a function of both wave length and sheet thickness. Because the sheet is thinner farther from the nozzle, the wave of maximum growth rate cannot be the optimally growing wave. However, the results of this analysis were used to demonstrate the existence of a wave of maximum amplitude at all positions downstream. Therefore, the breakup of the sheet is expected to be dominated by a disturbance of a particular wavelength. Because the viscous forces retard the growth of perturbations, the growth rate of a disturbance in a viscous sheet is less than the growth rate for the corresponding disturbance in an inviscid sheet (Dombrowski and Johns, 1963).

2.4.3 Features of wave-breakup theories

- While the cause of the wave disturbances is unknown and all result from random fluctuations in the sheet and surrounding air, all wavelengths are equally likely to occur, and all initial amplitudes will be of the same order of magnitude (Dombrowski and Johns, 1963).
- A disturbance of a particular wavelength will dominate in a region of a breakup.
- At the critical value of the amplitude of this particular wave, the sheet will break into ribbons, which will collapse into cylindrical strands and ultimately form drops.

Following these features of wave-breakup theories leads to the prediction of a discrete number of drop sizes; because the single wave is predicted to cause the formation of strands from the sheet, all strands so produced will have the same diameter (Spielbauer and Aidun, 1992b).

2.4.4 Perforation

A hole occurs in a fluid sheet and expands rapidly by surface tension forces, and the fluid is drawn up into a thick rim around the hole (Dombrowski and Fraser, 1954). The expansion of the hole is halted when the rim reaches another rim or the edge of the sheet. Taylor and Michael (1973) carried out experiments where holes were made in sheets of water and in mercury under water. They suggested that holes in a thin sheet of fluid in which surface tension forces predominate will open out if the holes are large in relation to the thickness of the sheet. Perforations of diameter smaller than the thickness of the sheet will close back into the sheet.

Fraser et al. (1962) estimated the growth rate of a perforation in a thinning sheet. They predicted a uniformly expanding perforation. A number of parameters affects the radius of a strand formed via the perforation mechanism, including the location downstream at which the strand was formed, the time for growth, and interactions with other strands. Therefore, unlike the wave mechanism, strands are expected to form over a range of sizes. This seems to be necessary for the formation of the wide drop size distribution observed in spray experiments (Spielbauer and Aidun, 1992b).

Spielbauer and Aidun (1992c) studied the disintegration process with three different nozzle types, including the splashplate nozzle. Liquid sheets were formed by the perpendicular impingement of a circular jet on a polished disc. They suggested that the main mechanism of black liquor sheet disintegration is perforation. However, they did not consider real black liquors above the boiling point. The formation of perforations in a liquid sheet can be caused by particle impingement, solid particles in the sheet, and local thinning or bubble growth. Spielbauer and Aidun (1994) found no evidence of the first two mechanisms and therefore investigated the local thinning of the sheet formed on a splashplate. They used glycerol/water solution as the test liquid. They counted the radial distribution of perforations as a function of nozzle diameter and the jet velocity and found a critical distance downstream at which rapid perforation occurred.

2.4.5 Flash breakup

Flashing results from a sudden lowering of the pressure of a liquid, or solution of gas in liquid, below the bubble point. The generation of vapor is not restricted to the surface of the liquid phase but can originate at any suitable nucleus in the liquid phase. Rapidly growing bubbles cause displacement of adjacent liquid. Brown and York (1962) studied sprays formed by flashing cylindrical liquid jets. They found that a substantial increase of temperature above saturation must be provided in order to achieve significant flashing.

Increasing the black liquor solids content requires higher spraying temperatures. Increasing the temperature beyond the boiling point produces a sudden phase change in spraying, i.e. flashing at the unknown location in the nozzle or immediately after the exit. Two flashing modes have been reported: the complete flashing mode and two-phase effluent flashing mode or external flashing mode and internal flashing mode, respectively (Park and Lee, 1994). For black liquor, in the normal range of spraying, the flashing takes place inside the nozzle tube.

Järvinen et al. (2006) modeled bubble growth in flashing black liquor and found that surface tension and viscous forces control the initial bubble growth, and heat transfer to the bubble surface is the limiting mechanism during later stages. Referring to measured spray velocities and coarse static pressure distribution measurements in the nozzle (Miikkulainen et al., 2002; Kankkunen, 1998) flashing may start less than 5 cm before exiting the nozzle and residence time for flashing would be in the order of milliseconds. Reliable information about the residence time would be needed in order to be able to validate the model.

The mechanism of drop formation involved in flashing sprays is discussed by, for example, Empie et al. (1992a, 1992b) and Helpiö and Kankkunen (1995). Empie et al. (1992a) estimated the flashing transition temperature for typical liquor firing solids levels to be about 8°C above the atmospheric liquor boiling point. The transition temperature is several degrees above the atmospheric boiling point of the liquor, since the vapor pressure must exceed the pressure in the nozzle. With the splashplate nozzle, the central plane of the spray moved away from the plane of the nozzle plate. The angle of this deviation was estimated to be 20-40°, and was concluded to be a result of the flashing steam imparting a momentum component normal to the plate, and therefore normal to the original plane of the spray.

Bennington and Kerekes (1985) studied the effect of temperature on the drop size of black liquor sprays using small-scale nozzles. The change in spraying temperature produced a change in the drop size, mostly by changing liquor viscosity. They found that increasing the temperature of black liquor through its boiling point reduced the mean drop size of the spray by the magnitude expected from the decreased viscosity.

Helpiö and Kankkunen (1995) focused on the effect of temperature on atomization performance, especially above the boiling point of liquor. It was determined that, even though temperature increase near the boiling point results in an increase of drop diameters, the phenomenon of flashing, which occurs several degrees above the boiling point, leads to significantly smaller drop sizes.

Loebker (1998) and Loebker and Empie (1998, 2001, 2002) presented a two-phase flow nozzle, an effervescent nozzle, for black liquor spraying. In the experiments, air was mixed with corn syrup inside the nozzle to produce a bubbly two-phase flow; drop size distributions were measured for a wide range of viscosities and air-liquid ratios. The resulting median drop diameter depended on the gas-liquid ratio, as well as on the standard operating parameters of nozzle size, liquor solids, flow rate and viscosity. The idea was to have better control over the drop size without exceeding the boiling point. The method requires higher pumping pressures.

2.5 Mass flow rate distribution

An uneven mass distribution of the liquor across the furnace cross-section could lead to uneven combustion and localized hot spots, which can accelerate the corrosion rates of the furnace walls and result in premature shutdowns. Mass flow rate distribution has a significant effect on the sheet thickness and length and therefore on the drop size distribution.

Nieminen (1996a) compared the results from full- and small-scale experiments with black liquor and water-glycerol solution, respectively, to find out whether small-scale experiments can be used in predicting the spraying characteristics in the full-scale. The nozzle type was throttled (a-type in Figure 2.3). He observed a mass flow rate concentration on the spray centerline and average difference of 20% in mass flow rate distribution between small- and full-scale measurements. This was probably partly due to the different spraying orientation – water-glycerol spray was horizontal and black liquor spray was vertical. The throttling of the nozzle and the plate angle has a great effect on the shape of the mass flow rate distribution. The results from both the small- and full-scale experiments suggest that there is a linear dependence on the plate angle.

Empie et al. 1997 studied and modeled the mass flow rate distributions in black liquor sprays. They carried out the research work with splashplate and V-jet nozzles using a spray chamber. There was a central core with a fairly uniform flow rate in the area within about 15° of the sheet centerline. Outside this region, the flow dropped off steadily to the outer edge of the sheet. They observed a thick, slow-moving rim at the very outer edge of the sheet. The conclusion was that mass flux exhibited a parabolic dependence on angular position, decreasing in magnitude out to the edge of the sheet. Model predictions agreed to within 20% of the experimental values for the splashplate nozzle.

2.6 Drop size distributions

Bennigton and Kerekes (1985) reported first the size and size distribution of droplets from black liquor nozzles. They used small-scale grooved-core (swirl-cone) nozzles with the orifice size of 0.7 mm and 65% glycerol-water solution (room temperature) and 55% solids content black liquor at 120°C. The results showed that the size distribution and mass median diameter of black liquor was much broader than with water/glycerol.

The dry solids content of black liquor has increased during recent years. This has enabled capacity increase of recovery boilers and reduction in their emissions. The change in the black liquor properties has led to changes in the spraying practices. There are only a few experimental studies into high solids content black liquor spraying and drop size distributions available. It is important to be able to describe the drop size distribution of a fuel spray. Inaccurate droplet size distribution leads to poor chances of optimizing combustion. Optimal spraying parameters can be chosen only if the drop size is known with sufficient accuracy. Probability density functions enable the drop size distribution to be estimated so that the spraying parameters can be varied in a controlled way (Kankkunen and Miikkulainen, 2003).

Empie et al. (1992b) applied several drop size distribution models to the experimental data of three solids levels (50, 60 and 70%), including log-normal, square root-normal, upper limit-normal, and Rosin-Rammler. They found the best choice to be Square Root-Normal distribution. Kankkunen and Miikkulainen (2003) had similar observations with high solids black liquor.

2.7 Velocity

Velocity and density are the most important operating parameters that influence the mass-median drop diameter. They are related to the kinetic energy of the liquor leaving the nozzle, suggesting that the more energy dissipated, the smaller the median drop size. At high solids levels, liquor viscosity becomes important (Empie et al., 1992b). Operating at temperatures above the boiling point results in a two-phase flow inside the nozzle pipe; this increases the nozzle exit velocity (Empie et al., 1992a). It is common to calculate the spray velocity from the pipe flow. With splashplate nozzles and especially in the case of two-phase flow the velocity of a black liquor spray is not the same as the velocity of the liquor flow inside the nozzle pipe. It depends on the nozzle geometry (the splashplate can decrease the area of the exit) and the spraying temperature.

Ligament velocities were shown to increase two-fold when compared to the velocities measured below the transition temperature at constant mass flow rate by Helpiö and Kankkunen (1996). This was concluded to be a clear indication of two-phase flow taking place in the nozzle flow tube. The estimation of the sheet velocity if sprayed above the boiling point is difficult. The exact location where the flashing takes place and its intensity inside the nozzle tube are unknown.

The velocity of the sheet can be measured with, for example, image analysis systems capable of multiple exposures (Merzkirch, 1987). The camera triggers several images in the same frame. When the exposure time and delay between the exposures are known, the velocity can be calculated on the basis of the distance the object has moved. An automatic image analysis system is aimed at supplementing or replacing human involvement in extracting size and velocity data from stored spray images. Thousands of video frames can be stored during the tests, and digitized and processed afterwards. Spray statistics are computed and data is accumulated for all images after analysis (Chigier, 1991b).

2.8 In-furnace conditions

2.8.1 The effect of hot environment

Clark and Dombrowski (1974) examined the flow and disintegration of sheets of water in combustion gas environment at temperatures ranging up to 950°C. The experiments were performed with flat and conical sheets. They found that above 300°C high frequency symmetric waves and localized disturbances are superimposed on the sheet and disintegration occurs by the combined action of aerodynamic waves and perforations, the latter predominating with increasing temperature. The drop size was found to be critically dependent upon the nature of the disintegration process.

Black liquor spraying experiments reported by other research groups prior to this thesis were carried out mainly in spraying chambers, which means in a relatively cold environment compared to the recovery boiler furnace. Kankkunen (1995) estimated theoretically the effect of heat transfer on atomization process of black liquor sprays. Differences between the spraying chamber environment and a recovery boiler environment are density, viscosity, and flow field of the surrounding gas. The warming-up of black liquor during the spraying in the boiler whereas cooling down inside the spraying chamber may have an effect on the drop formation process. Kankkunen assumed an area of 1 m^2 of liquid sheet (the length of 1 m, opening angle 120°) and velocity of 10 m/s, which breaks up into ligaments of 2 mm diameter, and length of 20 mm. He concluded that the radiation heat transfer vaporizes water from the surface of black liquor sheet and ligaments. This increases the viscosity on the surface, which may stop the droplet formation in the case of spraying below the boiling point. Flashing increases the velocity of the spray and the atomization process is more rapid.

Bousfield (1990) reported experiments involving the droplet formation of low solids content black liquor (46-47%) inside and outside a tubular furnace system. A coherent jet was needed for the experiments and higher solids content black liquor would form a “spray” and coat the outside of the furnace. The diameter of the piston-controlled nozzle exit was 1.54 mm and the furnace temperatures 950°C and 1110°C. Room temperature and hot (108°C) black liquors were tested. Breakup length of a room temperature spray passing through the furnace was smaller than without the furnace. The decrease in the breakup length was not as significant for the higher temperature furnace. With high-temperature black liquor, the result was the opposite. The breakup length increased when the jet went through the furnace. The effect of the high-temperature environment on hot black liquor jets was therefore to increase the breakup length. The effect of the hot environment on drop quality was not clear. Bousfield (1990) concluded that an increase in liquid temperature would decrease the viscosity of the jet. The reduction of viscosity would act to shorten the breakup length. If the energy absorbed by the jet went into the evaporation of water, the solids content would increase, but not enough to noticeably change the physical properties of the liquid jet. The case would be different if the increase of solids content took place only at the outer layer of the jet and caused a large increase in the viscosity of this layer.

Kankkunen et al. (1996) analyzed the drop formation mechanisms of two splashplate nozzles and the factors affecting it, and discussed and calculated the usability of spraying chamber test results in the furnace environment. The velocity and the direction of the gas flow facing the black liquor sheet in the furnace fluctuate. That has an effect on the direction of the spray. The different viscosity and density of the gas may have an effect on drop formation. The air flow through the liquor gun ports diminishes this effect. The major difference between these two environments is the heat transfer and especially radiation heat transfer. It may cause a major difference to the drop formation mechanism in the furnace.

Helpiö and Kankkunen (1996) obtained a qualitative reference for the phenomena observed in the spray chamber by video-imaging the spray from a liquor gun port at a mill. High-speed video imaged the sheet breakup. They observed a decreasing sheet length and an increase in sheet velocity when flashing occurred at a higher spraying temperature.

2.8.2 Furnace cameras

Measurements in furnaces are usually carried out with water-cooled probes that are inserted through furnace openings. It is difficult to maintain clean windows in particle laden streams, and also difficult to prevent damage to, and deposits on, the lenses. The measuring instrument must be designed to cause the minimum of interference to the flow (Chigier, 1991c).

Commercial furnace control cameras are available and have been installed as part of some original boiler-equipment packages for almost half a century. Optical probes are used to monitor flames, and especially flame failures, in fossil-fuel-fired furnaces. For example, Lu et al. (2000) reported determining geometrical and luminous parameters of the entire flame in the furnace from the images obtained. Furnace cameras can also be used to control, for instance, NO_x-emissions by monitoring combustion-equipment changes in the boilers (McCarty and Lang, 2002). The cameras have been developed to obtain a view from a hole or window in the boiler wall; they are usually water cooled. None of these cameras are applicable to spray studies inside a recovery boiler.

When Kankkunen et al. (1996) compared the hot and cold measuring environments, they concluded that it was obvious that measurements in the furnace are needed to obtain quantitative and qualitative information about the black liquor drop size and drop formation mechanisms in the furnace. They suggested that an endoscope was needed. Helsinki University of Technology developed a furnace endoscope for black liquor spray studies and the first results from spray studies under furnace conditions were published by Miikkulainen (1997).

3 Focus of the present thesis

Experimental research into the spray of black liquor has a history of two decades. During that time, the size and effectiveness of kraft recovery boilers have increased due to the demand for higher capacity and higher dry solids content. High dry solids content (more than 75%) and a requirement for a higher spraying temperature in order to keep the liquor viscosity at an acceptable level have changed the atomization process from wave formation and perforation to a flash-dominated process. Prior to this thesis, no measurements existed on high dry solids black liquor under in-furnace conditions.

This thesis focuses on the characteristics of high dry solids black liquor sprays under in-furnace conditions, more specifically, on how the atomization process starts and the nature of the initial properties such as velocity, opening angle, and trajectory of a high dry solids content black liquor spray, which is sprayed well above its atmospheric boiling point. The experiments were carried out in the operating recovery boiler furnaces and the results were compared with full-scale spraying chamber tests. As the literature review showed, the results published prior this thesis come mainly from the spraying chamber tests with low solids content black liquor sprayed below the boiling point or in the transition temperature. The main focus of research prior this study was more on the effect of viscosity rather than on the temperature increasing above the boiling point.

3.1 Developing a technique for in-furnace spray measurements

The development of a measurement method to take black liquor spray research into the furnace environment was one of the main objectives of this thesis. When it is possible to obtain information on the spraying of black liquor under in-furnace conditions, the initial data needed for realistic modeling work is available. The major part of the experimental work was accomplished through the extensive spraying experiments, which were carried out almost simultaneously under in-furnace conditions and in the full-scale, horizontal, spraying chamber built next to the recovery boiler on the liquor gun level. In the spraying chamber, the results could be checked with additional cameras to be sure the method was adequate for the purpose of research into the spray of black liquor. The hypothesis was that, if the droplet formation processes in a furnace and a test chamber were sufficiently similar, then the conclusions drawn from the drop formation process in the test-chamber could be applied to the furnace.

An air-cooled optical measurement probe, called a *furnace endoscope*, was developed to carry out in-furnace measurements of black liquor sprays. This was the first attempt to systematically obtain information about black liquor spraying under furnace conditions. The main focus was on the determination of initial velocity, on the opening angle and trajectory of a flat spray leaving a splashplate nozzle, and on developing the ability to compare the results with similar sprays in the spraying chamber. Information on the trajectory resulted from the determination of the scale of the images. Visualization of spray breakup into the droplets was also of interest.

The accuracy of the velocity measurement method was tested in a laboratory test and an error analysis suggested that the method – based on multi exposure technique and image-analysis – was suitable for black liquor spray research. Error analysis showed the importance of determining the image scale and the optimum measurement distance. The endoscope was first tested in five recovery boilers in order to study different spraying practices in different boilers. The boilers differed in size, nozzle types, liquor specific properties and mass fluxes. Within the operation range of the furnace endoscope, the disintegration process from black liquor sheet into ligaments and droplets was observed to be incomplete, but the range was large enough for studies of disintegration mechanisms.

3.2 Comparison of in-furnace and spraying chamber measurements

The applicability and comparability of the furnace tests to spraying chamber tests were confirmed by building a full-scale, horizontal spraying chamber next to a recovery boiler. Two commercial nozzles were studied with the furnace endoscope in both environments in as similar a spraying situation as possible (Table A1 in appendix I). The comparison between results from the test chamber and furnace showed that the spray properties in both environments depend mainly on the mass flux and spraying temperature. The latter is especially important when spraying above the atmospheric boiling point of black liquor, which was the focus of this research.

In addition to the comparison of different spraying environments, horizontal mass flow rate distribution and velocity distribution were measured at a distance of 0.6 m from the nozzle exit in the spraying chamber. The spray velocity was found to be equal in all directions, while most of the mass flow went to the middle section. Both measured nozzle types produced insignificant edges on both sides of the spray. This was probably the reason why the opening angle was approximately 15° smaller in the furnace environment. Mass flow rate distribution was needed in the calculations of ligament volumes.

3.3 Determining the key factors affecting black liquor spraying

The effect of excess temperature on the spray disintegration mechanism and drop formation, velocity, and their connection to final drop size was determined in a horizontal spraying chamber almost simultaneously with furnace tests. The tests were carried out within the normal operational range of the recovery boiler for two nozzles in three temperatures and three mass flow rates. Flashing accelerated the flow inside the nozzle and affected the spray velocity and disintegration. An increase in flashing decreased the length of a black liquor sheet and, in the case of heavy flashing, no uniform sheet existed and therefore drop formation was sudden.

An image-analysis-based method was used to measure the drop size of black liquor spray from two industrial-scale nozzles in three temperatures and mass flow rates. Spray consisted of spherical and non-spherical droplets, but in the size calculations it was assumed that non-spherical particles would form spherical droplets. A square-root-normal distribution fitted the measurement data best. The volume median diameters were higher than those detected in measurements with lower dry solids content. The drop size correlated well with the spray velocity and thereby with excess temperature.

The flash-dominated disintegration mechanism was studied systematically. An image-analysis-based method was developed to measure the shape and size of the uniform black liquor sheet. The objective was to find the correlation between the spray disintegration and drop size. In order to be able to predict the forming drop size from black liquor spray characteristics, the length of a sheet and break-up frequencies were measured with a specially developed algorithm. A dominating wave length could be found even if the spray flashed heavily. In cases when it was difficult to find the dominating frequency, the disintegration was noticed to be incomplete. The wave length was used for calculating the size of the forming ligament. The assumption was that a flat spray breaks up at the distance of measured sheet length to ligaments, the volume of which can be calculated with their dominating wave length and measured volume flow rate. For comparison with results from drop-size measurements, Rayleigh’s model of ligaments breaking up to equal-sized droplets was used.

4 Experiments

In this chapter, a furnace endoscope is introduced as an in-furnace measurement tool for spray research. The furnace endoscope was tested in the experiments carried out in six recovery boilers and a full-scale, horizontal spraying chamber. Following spray properties were measured: Velocity, trajectory, and opening angle. Spray disintegration was studied visually and drop size was measured only in the spraying chamber. In addition the furnace endoscope, the horizontal spraying chamber and its instrumentation is presented, and a short overview of a previous vertical spraying chamber is given.

4.1 Furnace endoscope and spraying environments

A furnace endoscope was developed to carry out in-furnace measurements in order to discover the initial velocity, opening angle and trajectory of the spray. The hypothesis is that, if the droplet formation processes in a test chamber and a furnace are sufficiently similar, then the test-chamber measurement results, including the drop size, can be applied to the furnace. Measuring spray properties in a furnace environment – in this case, in a chemical recovery boiler furnace – is a challenging task. Not only is the temperature in the furnace 900-1200°C, but corrosive, sticky particles hit the measurement probe. Such particles can also be falling deposits from the upper parts of a recovery boiler furnace and the size of them can be huge.

Suitable material for an outer protection tube was found and tested. The requirement that the material should be as stiff as possible without being subject to corrosion damage in temperatures as high as 1000°C was difficult to meet. The most suitable material for the stiff structure of the furnace endoscope was found to be a titanium-stabilized stainless steel tube. It has been used in a number of experiments, in which it has showed good durability.

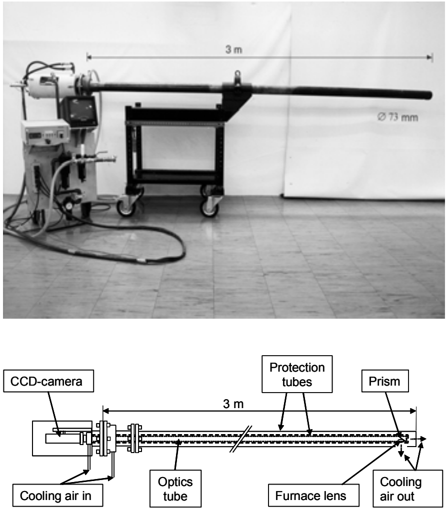


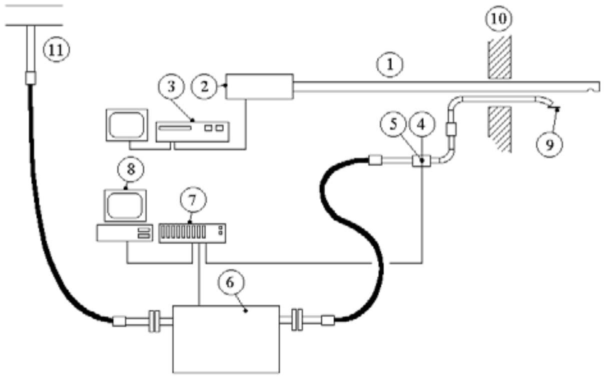
Figure 4.1 Furnace endoscope

Figure 4.2 Furnace endoscope entering the recovery boiler furnace through a liquor gun opening

An air-cooled endoscope tube is 3 m long; there is a high-shutter-speed CCD-camera at one end of the tube and a furnace lens at the other, Figure 4.1. The diameter of the replaceable outer protection tube is 73-76 mm with 4 mm thick walls. The outer diameters of the second protection tube and the optics tube are 38 mm and 35.5 mm, respectively.

The optical setup was designed to take images of black liquor sprays whose velocity is between 5 to 20 m/s. An air-cooled quartz lens faces the furnace. The hostile environment in the recovery boiler furnace, and air used as a coolant, forces the furnace lens diameter to be rather small, 10 mm. In addition to the small furnace lens, the long tube limits the light available for the camera. The long distance from the furnace lens to the camera causes the optical system to be sensitive to bending in a hot furnace.

The measurement method is based on a procedure whereby the spray appearance is videotaped or captured directly onto the hard disk of a computer. Images are processed with image analysis software to measure the required characteristics of a spray. The nozzle and the endoscope both enter the furnace from the same liquor gun hole, whose dimensions limit the outer diameter of the endoscope tube, Figure 4.2. The idea is to get a right angle view from above the black liquor spray at different distances from the nozzle. Figure 4.3 shows the schematic picture of the experimental setup when measuring under in-furnace conditions.



1	Furnace endoscope
2	CCD – Video camera
3	Video recorder or hard disk
4	Pressure sensor
5	Temperature measurement
6	Mass flow meter
7	Data Acquisition / Control Unit
8	Computer
9	Splashplate nozzle
10	Furnace wall
11	Black liquor from ring header

Figure 4.3 Experimental configuration in an operating recovery boiler (Miikkulainen et al., 2000)

4.1.1 Defining the scale

To be able to measure distances from an image with image-analysis, one has to know the scale of the image. To determine the scale, the distance from the endoscope lens to the object (*d* in Figure 4.4) must be known. A simple method was developed to measure this distance. A steel weight, controlled by means of a wire rope, is lowered until it reaches the spray; the length of the wire used is then measured. This can be observed from the monitor of the endoscope. The method measuring the distance gives surprisingly accurate results, which have been confirmed by comparing the weighted wire rope method to manual measurement in a laboratory environment. The maximum absolute error of the distance measured is estimated with total differential analysis to be approximately 7 mm, depending on the spray behavior and the existence of a flat spray (Miikkulainen et al., 2004).

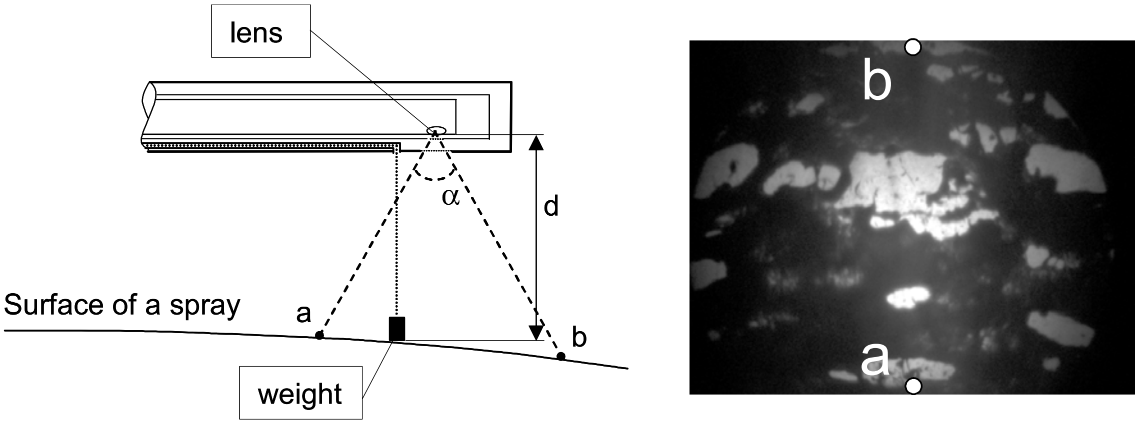


Figure 4.4 Defining the spray trajectory with a wire rope and steel weight (Miikkulainen et al., 2004)

4.2 Horizontal spraying chamber

The setup in the horizontal spraying chamber tests differed from in-furnace measurements only by environment. (Except in Publication II, where the earlier results from the vertical spraying chamber were used for comparison.) A 13-m black liquor hose came from the ring header of the boiler. The hose was well insulated. The spraying chamber enabled horizontal spraying of black liquor. The endoscope was located 0.3 to 0.5 m above the splashplate nozzle. The liquor spray was illuminated with eight studio lamps operating beneath a plexiglass window. In the furnace, the required backlight came from the char bed. To get an over-all image of the spray, another camera was located in the roof structure of the spraying chamber. These images were compared to images taken with the endoscope so as to verify the results. The main dimensions of the spraying chamber were 5.5 m x 3 m x 2 m. The facility for the liquor gun and endoscope insertion extended the length to 10 m, Figure 4.5.

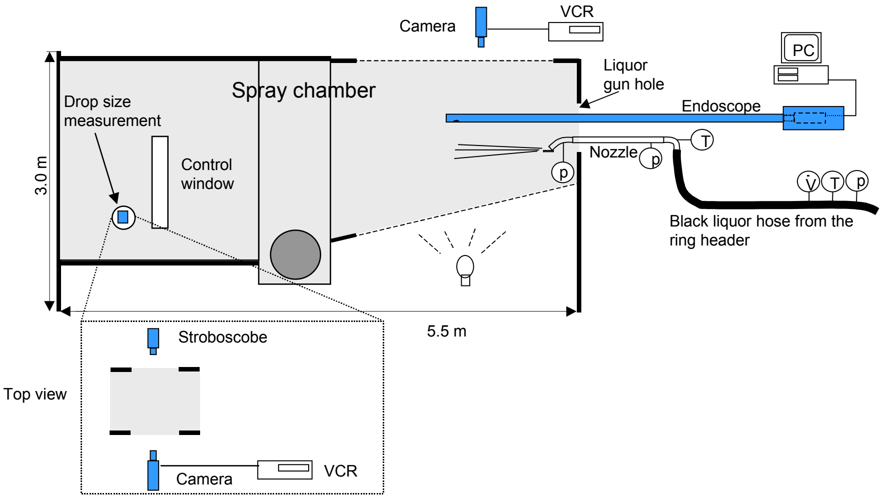


Figure 4.5 Experimental configuration in the test chamber

The width of the first section of the chamber, where the nozzle was located, was 1.2 m. The last section, where the drop size measurements took place, was 0.6 m wide. The chamber was equipped with control windows through which the spray height was measured. Another window was used to ensure the right spray location for the drop size measurement. The spray width was restricted by spray separation baffles, so that only a narrow, undisturbed, part of the spray was allowed to reach the drop size measurement chamber. The nozzle was located horizontally to ensure close similarity to spraying in a furnace. Odorous gases were drawn away through the end wall and the top of the chamber. Substituting air entered the chamber through the liquor gun hole. The temperature in the chamber was 60-80°C. The black liquor was returned after dilution to the recovery cycle.

4.3 Vertical spraying chamber

The commensurable spraying chamber test results presented in Paper II (Miikkulainen et al., 2000) are from the earlier test series described by Helpiö and Kankkunen (1996). A 6 m high, vertical spray chamber with a 1 x 3 m cross-sectional area was constructed next to an operating recovery boiler. The nozzle was at the top of the chamber and the direction of the flow was downwards, so that the splashplate was in the vertical position. The spray chamber results in Paper II are used for comparison with the results measured in five recovery boilers with the furnace endoscope. Similar spraying cases and nozzle geometries, mass flux and the excess temperatures were used; these made this comparison reasonable.

4.4 Spraying parameters at the mills

The tests were carried out in six Finnish recovery boilers of various sizes and capacities. They all used softwood liquor, while their dry solids content was from 72 to 80%. Paper II of this thesis deals with the results from the mills A to E; the results for the rest of the papers are from Mill F. At Mill F, the spraying experiments were very extensive and were carried out both inside an operating recovery boiler and inside the horizontal spraying chamber built next to the boiler at liquor-gun level for comparison and drop-size measurements. Table 4.1 presents the main spraying parameters within the limits of the tests carried out. The significant quantities involved in the tests are listed more detailed in Appendix I.

Table 4.1 Spraying-related parameters at the test mills

Mill		**A**	**B**	**C**	**D**	**E**	**F**
Paper in this thesis		II	II	II	II	II	I,III,IV,V
Dry solids content	%	72-76	76	73-76	75-80	73-77	75-79
Viscosity	Pa s	0.04-0.10	0.12	0.07-0.12	0.11-0.17	0.07-0.08	0.09-0.26
Mass flow rate	kg/s	3.1-4.8	2.5–5.7	5.0-6.4	5.7–7.3	3.7–4.7	4.3-6.1
Mass flux	g/mm^{2}s	8-12	4 - 9	9 - 13	6 - 9	5 - 8	4 - 13
Excess temperature, ΔT_e	°C	4 - 8	8 - 9	4 - 7	11 - 13	2 - 3	13 - 19
Type of the nozzle		A	B	A	A	A	A, B
Nozzle tube, d_p	mm	27	26, 30	27	34.5, 40	27	27, 28
Splashplate angle	°	25	35	25	25	20	23, 36

5 Methods for analysis

5.1 Velocity measurements

The method of measuring velocity with the furnace endoscope is described in detail in Publication I. This method was used in all the velocity measurements discussed in this thesis and it is noteworthy that the velocity measurement method described here gives an average velocity from a small area of the sheet, i.e., from the area of interest (AOI). The AOI is at the centerline of the spray unless the measurement deals with the velocity distribution.

The velocity of a spray can be measured by the multi-exposure method (Merzkirch, 1987). The camera triggers several images in a single frame. When the exposure time and delay between the exposures are known, the velocity can be calculated on the basis of the distance the object has moved. The distance can be measured manually in each image using image analysis software. To achieve an accurate result, the number of images must be high; since manual measurement is very time consuming, the use of fully or partly automated analysis is warranted. The velocity of a spray (u) can be calculated from the expression shown in Eq. (5.1).

$$u = \frac{s}{t} = \frac{2\ d\ d_{px} \tan\alpha}{d_{fr}} \frac{1}{t} \tag{5.1}$$

where s is the distance the spray moved during the exposure time and delay time, t, between images. The measured distance from the endoscope lens to the spray surface is d (Figure 4.4), and the distance in the frame measured in pixels is d_{px}. α is the angle of view. The vertical size of the frame d_{fr} depends on the sensitivity and size of the CCD-cell used. The resolution of a frame in the studies presented in this thesis is 1280 x 1024 pixels or 640 x 512 pixels, depending light available.

The measurement procedure can be carried out semi-automatically by image-analysis software. The Fast Fourier Transformation method (FFT) is used to edit a grayscale image in its spectral form (Image Pro Plus Reference Guide, 1998). In order to find out the displacement field in the image, which is formed from the three known exposures of the motion in the same frame, the FFT needs to be carried out twice. The first FFT yields a fringe pattern in which the fringe orientation is perpendicular to the direction of the displacement and the fringe spacing is inversely proportional to the magnitude of the displacement (Westerweel, 1997). The second two-dimensional FFT produces the displacement field.

After the second FFT, some threshold and filtration of noise for the image is usually needed before the object count. The filtration or threshold can be carried out as long as the coordinate of the center point of the dot of interest does not change. This is usually the case, because the area of a single disturbance is much smaller than the area of dots of interest. In the object count, the x-coordinate and y-coordinate of the result points are stored. The distance the spray has moved during the delay and the exposure time can be calculated from the coordinates (Miikkulainen et al., 2004).

5.1.1 Accuracy of the measurement

The velocity measurement is made up of a chain of components, each of which is subject to individual inaccuracy. The components of possible inaccuracy are the measured distance from the endoscope lens to the spray surface (*d*), i.e., the scale of the image, the measured distance in a frame (d_{px}) in pixels, and time (*t*) the camera used for the exposure and the delay. The absolute error ε of the measured velocity can be approximated using a total differential analysis (Doebelin, 1990).

$$\varepsilon = \left|\frac{\partial u}{\partial d}\right| \Delta d + \left|\frac{\partial u}{\partial d_{px}}\right| \Delta d_{px} + \left|\frac{\partial u}{\partial t}\right| \Delta t \qquad (5.2)$$

The effect of different components on the absolute error is shown in Figure 5.1. The velocity of the spray is 15 m/s. As can be seen, the time used for exposure and delay has a negligible effect on the absolute error. The effect of any error in a distance measurement (*d*) decreases as distance increases. The error of distance measured (in pixels), $d_{px,}$ is the main source of the absolute error when considering relevant measurement distances that are 0.3 m and over. The vertical size of a frame (d_{fr}), i.e., the number of usable pixels, intensifies the effect of error in d_{px}. The minimum of absolute error (0.63 m/s) in measuring the velocity of 15 m/s can be found at the distance of 0.35 m, when the vertical size of the frame is 512 pixels (Miikkulainen et al., 2004).

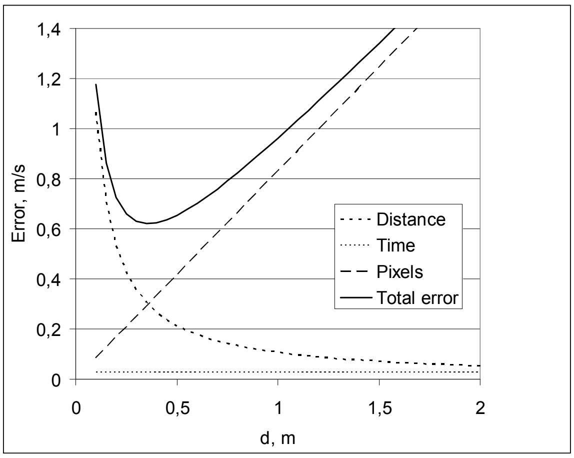


Figure 5.1 The effect of different components on the absolute error. Δd =7mm , Δd_{px}= 1 pixel, Δt=2µs, d_{fr}=512 pixels (Miikkulainen et al. 2004).

Relative maximum error can be expressed as $\varepsilon^* = \varepsilon / u$.

$$\varepsilon^* = \frac{\Delta d}{d} + \frac{\Delta d_{px}}{d_{px}} + \frac{\Delta t}{t} \qquad (5.3)$$

With the individual error assumptions presented in Figure 5.1, the measurement distance can be optimized to minimize the relative error.

$$\frac{\partial \varepsilon^*}{\partial d} = -\frac{\Delta d}{d^2} + \frac{\Delta d_{px}\, 2\tan\alpha}{u\, d_{px}\, t} = 0 \qquad (5.4)$$

Figure 5.2 presents the relative error as a function of distance d at different velocities and the minimum of the relative error when the vertical size of the frame is 1024 pixels. For example, in the case of a spray velocity of 10 m/s, the minimum of the relative error can be achieved at the distance of 0.35 m. The depth of focus of the optics is, in practice, from 300 mm to infinity (white area in Figure 5.2) and the distance from the lens to the object is from 0.3 to 0.6 m, due to the geometrical limitations of a liquor gun hole in a boiler wall.

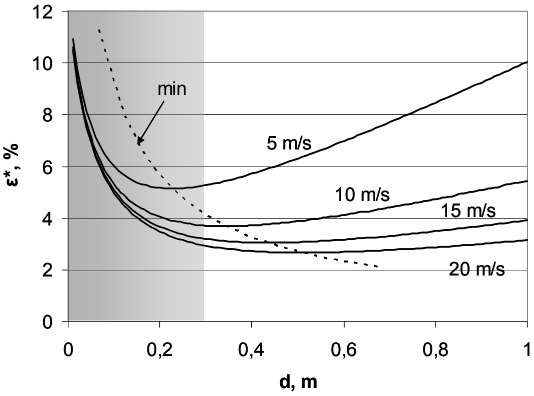


Figure 5.2 Relative error for different velocities as a function of distance from the lens to the object (d), and its minimum (dotted line). d_{fr} = 1024 pixels (Miikkulainen et al., 2004).

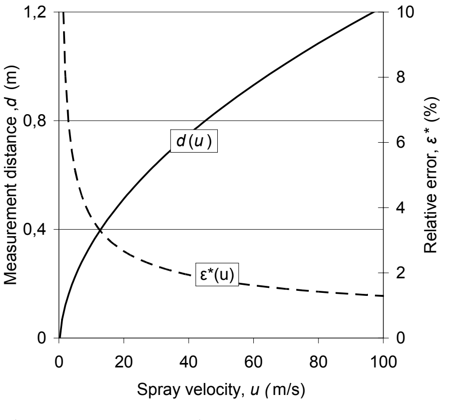


Figure 5.3 Optimum measurement distance (solid line) for different velocities for obtaining minimum relative error (dashed line). dfr = 1024 pixels (Miikkulainen et al., 2004).

It can be seen that the measurements have been carried out within the range of minimum error. The relative error of the measurements was from 3 to 7% in the experiments, when assuming that the individual errors are as presented in Figure 5.1, depending on the vertical frame size. Figure 5.3 presents the distance *d* in which the minimum error can be achieved and the corresponding relative error as a function of spray velocity. For example, a minimum error of measuring a spray velocity of 15 m/s can be achieved at the distance of 0.4 m with ~ 3% of relative error.

5.2 Length of a black liquor sheet and wavelength determination

Information about the uniform sheet length is needed when carrying out predicting calculations of the volume of forming ligaments. An image-analysis-based algorithm was developed for determining the length of the sheet of black liquor spray systematically from large amount of images. From the frame sequence of 100 pictures, the intensity analysis functions of an image-analysis program were used to collect data from the images based upon the intensity values they contain. Intensity values (8-bit, grey scale) along a line from the nozzle exit to a specific angle from the spray centerline were plotted and the profile analyzed. Intensity values greater than 90 corresponded to holes in the sheet. Several limits for the first hole in a particular angle were tested; the result did not greatly change when the limit of the size was decreased. 15 mm was chosen as the limit of the diameter of the first hole. 15 mm also seemed to be a reasonable value for the limit when ascertained by visual examination of video material. The intensity profiles were processed independently. When covering the range of 180 degrees with the interval of one degree, 18000 data points were received. Figure 5.4 shows the graph of average lengths of black liquor sheet sprayed in three temperatures. When spraying temperature was increased 4°C, the length of the sheet was cut to half.

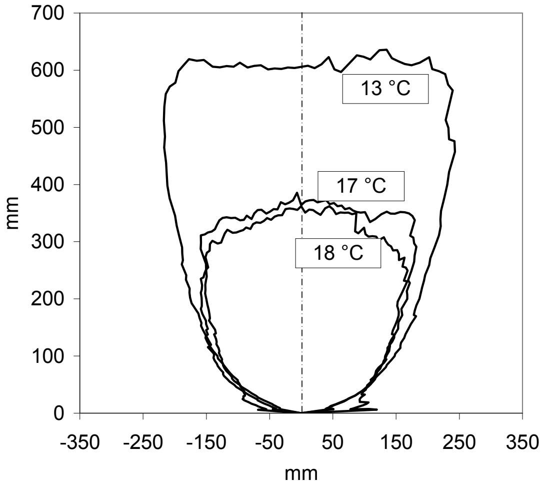


Figure 5.4 Effect of the spraying temperature (ΔTe) on the average length of the sheet, $\dot{m} = 4.3$ kg/s (Miikkulainen et al. 2005)

Dominating wavelength was searched in order to calculate the diameter of a forming ligament. The distances between all the forming holes at the spray centerline were measured and the number fraction of each distance was counted. The distances were measured roughly by determining the edges of the ligaments and holes and calculating the center of a hole. Intensity values along a given line were plotted and the profile analyzed to search for the frequency at which a possible wave formation took place, see Figure 5.5.

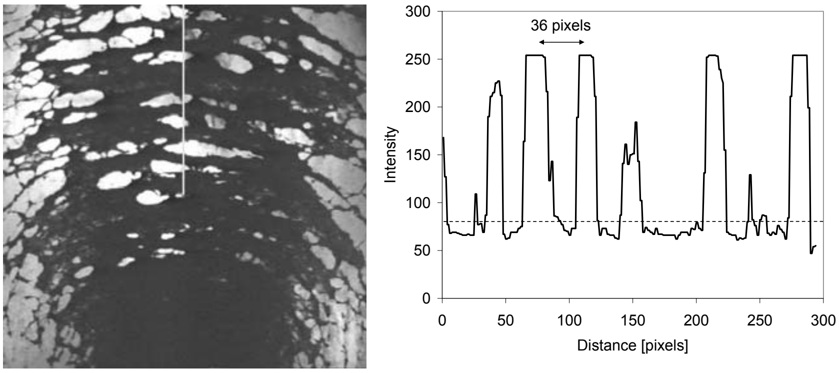


Figure 5.5 Example of a location of a given line and its intensity values

An autocorrelation function was used to detect non-randomness in the data. The result of the autocorrelation is a series of peaks; if one dominant wavelength exists, the peaks after the first one were mainly considered as multiples of the first peak. This means that the shortest dominating wavelength of each case was used in the drop size calculations. The intensity of the first lag was not measured, only the existence of it. The idea was to analyze systematically 100 pictures from each spraying case to receive enough information about the suitability of the method. Autocorrelation was used over the intensity data and the dominating wavelength was found regardless of the disintegration mechanism of the sheet.

6 Velocity of the spray

6.1 Dimensionless velocity and excess temperature

The most important parameters that affect the velocity of the black liquor spray are the mass flow rate and flashing of the liquor inside the nozzle tube. Flashing occurs inside the nozzle tube if the spraying temperature is high enough, and the pressure is low enough. It is common in modern recovery boilers with high dry solids content that the excess temperature, the temperature difference between the spraying temperature and the atmospheric boiling point, is in the range of 15-25°C. In this work, the excess temperature is defined to positive above, and negative below, the boiling point. The location in the nozzle tube where the flashing takes place depends on the geometry of the nozzle, i.e., on the location of the pressure drop.

Flashing produces water vapor that has a large specific volume and therefore accelerates the flow. This phenomenon can be described by the dimensionless velocity:

$$u^* = \frac{u_s}{\frac{\dot{m}}{A\rho_{BL}}} = \frac{u_s}{u_p} \tag{6.1}$$

where u_s is the measured velocity at the centerline of the black liquor sheet and u_p is the velocity of the non-flashing case at the smallest cross-sectional area, A, of the nozzle with the same mass flow rate, $\dot{m}$. The use of dimensionless velocity and mass flux (g/mm^2 s) instead of mass flow rate makes it possible to compare different sizes of nozzles with the same geometry.

6.2 The effect of different environments on the velocity of a spray

A horizontal spraying chamber was built in the boiler room at the nozzle level of the recovery boiler (Mill F). Velocity, shape of the spray and spray break-up mechanisms were determined in an operating recovery boiler and in a spraying chamber. The same liquor, nozzles and operational parameters were used in both environments to make the comparison relevant. The rationale behind this was that, if the droplet formation processes described above in the test chamber and the furnace were sufficiently similar, then the test chamber measurement results could be applied to a furnace.

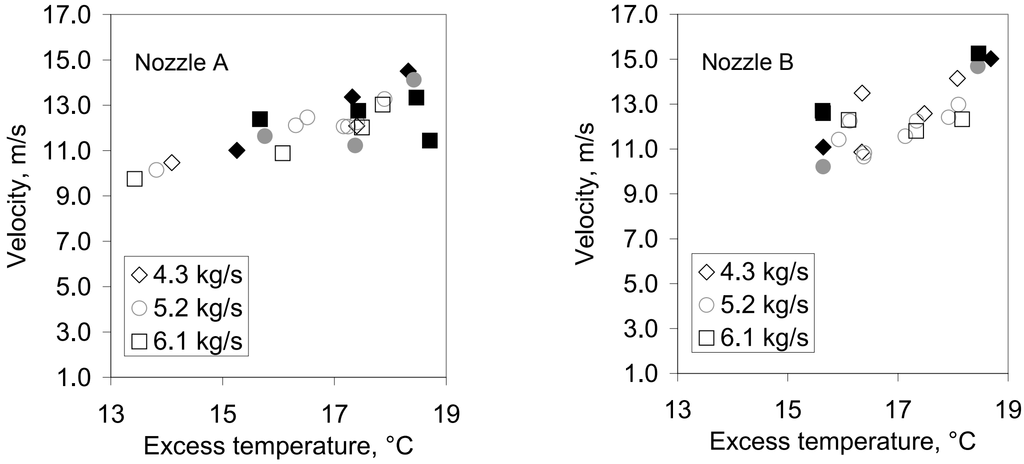


Figure 6.1 Spray velocity as a function of the excess temperature in two environments and three mass flow rates. The open and closed symbols represent the test chamber and furnace, respectively.

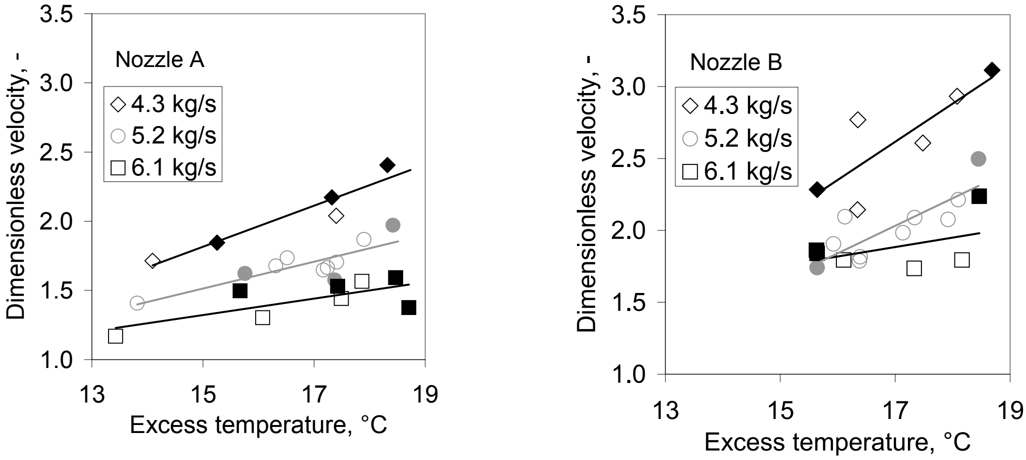


Figure 6.2 Dimensionless velocity as a function of the excess temperature in two environments and three mass flow rates. The open and closed symbols represent the test chamber and furnace, respectively.

Figure. 6.1 shows the spray velocity as a function of the excess temperature at three different mass flow rates for nozzles A and B. Mass flow rate does not seem to have as much effect on the spray velocity as the increasing temperature does. Figure 6.2 shows the dimensionless velocity as a function of the excess temperature at three different mass flow rates. The increasing mass flow rate decreases the effect of flashing inside the nozzle tube. The smaller the mass flow rate and the higher the ΔT_e, the higher the dimensionless velocity. Some variation can be observed, especially in the furnace measurements. The cases studied here show that the furnace environment has a negligible effect on the spray velocity. This suggests that the furnace radiation heat transfer to the liquor gun tube generates little additional water vapor and that flash evaporation dominates in both environments. Therefore, the spraying chamber results can be applied to a furnace. Different liquor flow conditions in the nozzle might give a different result. For example, a case without flashing inside the nozzle tube would probably produce a longer liquor sheet, thus increasing the effect of furnace heat radiation on the spray, as explained by Kankkunen et al. (1996).

6.3 Effect of spraying temperature and pressure on the velocity

As was shown in the literature review, Empie et al. (1992a) found that, when the excess temperature was high enough, dramatic changes in the behavior of the spray occurred. The transition temperature was estimated to be several degrees above the atmospheric boiling point of the liquor. In their work, the transition temperatures were observed to be about 5°C above the atmospheric boiling point at 60% solids and about 9°C at 70%.

In this work, spray velocities were measured in six recovery boilers. The dry solids content varied between the mills from 72 to 80%. Figure 6.3 presents the dimensionless velocities measured under in-furnace conditions with nozzle type A. All the measured dimensionless velocities are above 1, because the splashplate throttles the flow. Flashing inside the nozzle tube accelerates the flow, when the excess temperature is high enough. According to measured points in Figure 6.3 the excess temperature range of 5-7°C only slightly shifts the dimensionless velocity from the temperature range of 2-5°C. At the excess temperature of 7°C, the decrease of mass flux does not result in a remarkable increase of dimensionless velocity within the measured mass flux area, but, in the case of 10°C, acceleration takes place. It seems that dimensionless velocity of 1.5 is quite clearly a value for separating the flashing and non-flashing regions for the nozzle type A and the measured mass flux and temperature ranges, and can be used as a measurable quantity. Mass fluxes more than 12 g/mm^2 s would probably give a non-flashing spray even if the excess temperature was above 19°C. These observations are similar to those of Empie et al. (1992a), even though the nozzle type and the spraying conditions are different.

The trend lines in Figure 6.3 are to make the observation of different excess temperature ranges easy. The mills and the range of excess temperature and dry solids content are presented in Table 6.1. It can be seen that different boilers prefer different firing philosophies. In some experiment cases, the normal mass flow rate through the measured nozzle was limited by the mass flow meter. Approximately dry solids content of 75% seems to be the threshold at which the spraying practice shifts from the non-flashing to flashing condition. Liquor type and viscosity are the limiting factors.

Table 6.1 Ranges of excess temperatures in Figure 6.3 and the corresponding mills and the range of black liquor dry solids content

Excess temperature range	Mills	Dry solids content
2 – 5 °C	A, C, E	72 – 77 %
5 – 7 °C	A, C	72 – 76 %
10 – 13 °C	D	75 – 80 %
13 – 16 °C	F	75 – 79 %
17 – 19 °C	F	75 – 79 %

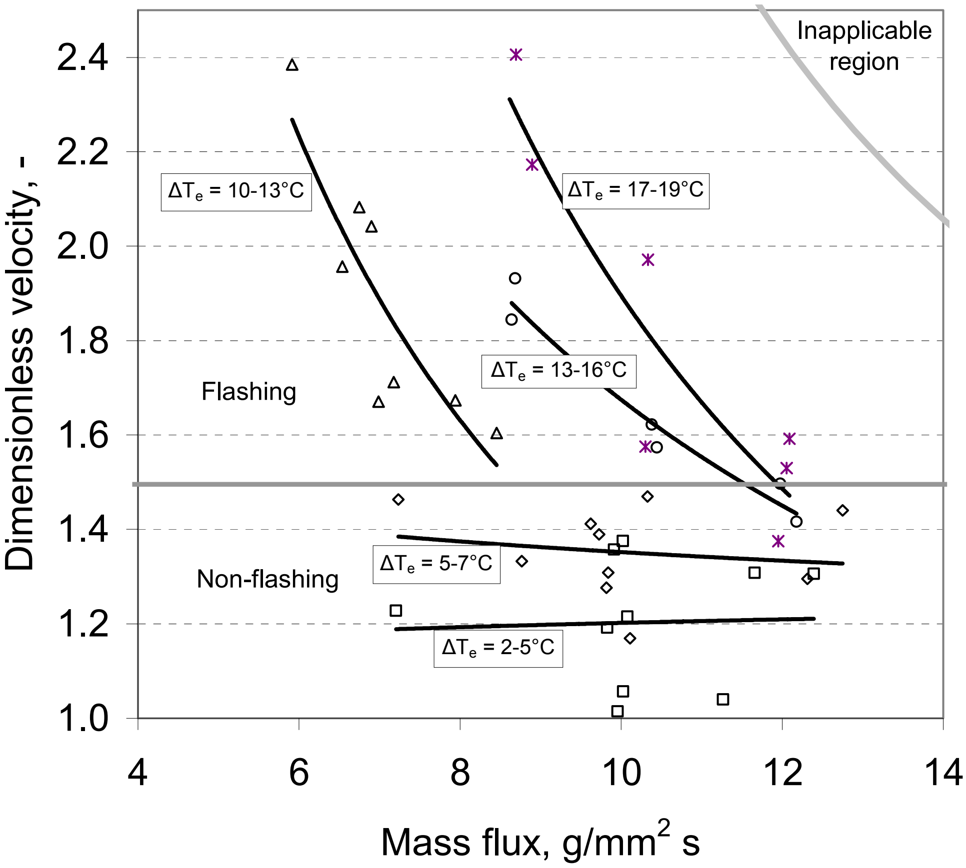


Figure 6.3 Effect of the temperature and mass flux on the spray velocity. Dimensionless velocities measured in five recovery boiler furnaces with nozzle type A. Nozzle pipe diameter: 27-40 mm.

6.4 Correlation model for spray velocity in flashing cases

The dimensionless velocity equation presented below consists of three elements: critical velocity, u_c*, excess temperature, $\Delta T_{e,}$ and mass flux, $\dot{m}''$. These elements were found to be reasonable characters for spray velocity and could be fitted to experimental data by two constants, *a* and *b*. These constants differ for different liquor types and nozzle types, and have to be experimentally determined.

$$u^* = u_c^* + \left(\Delta T_e - \Delta T_{e,c}\right)\frac{a}{\dot{m}''^b} \qquad (6.2)$$

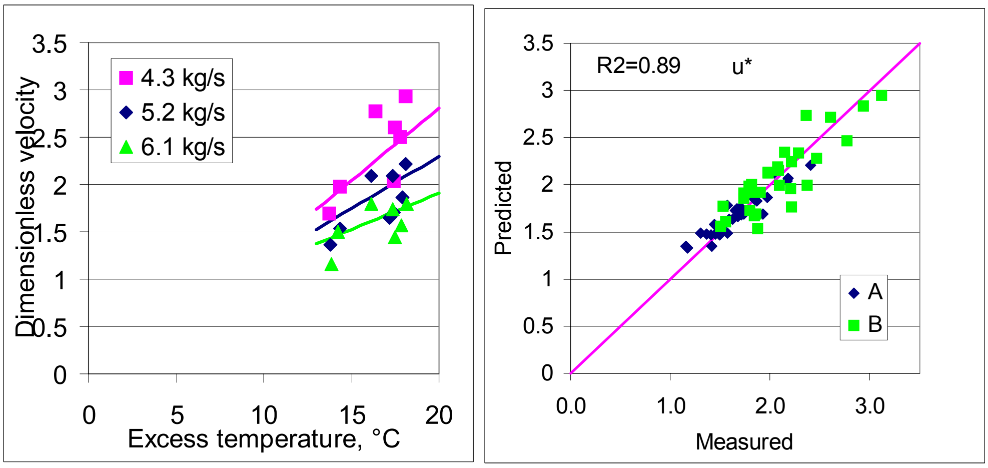


Figure 6.4 The dimensionless velocity measured compared to the correlation model (left side) and all the measured points (Nozzles A and B) from Mill F plotted against the predicted ones (right side).

The critical velocity is the velocity for the non-flashing case and the temperature difference (ΔT_e - $\Delta T_{e,c}$) between excess temperature and critical excess temperature has to be equal to, or larger than, zero. Critical excess temperature is typically 7-8°C (Empie et al., 1992a) This correlation is based on the experimental data gained from Mill F. The spraying took place mainly in the flashing range (see Figure 6.4). In the range of the transition temperature, the effect of temperature on spray velocity diminishes. This correlation model should be used only in the flashing cases.

7 The effect of spraying environment and flashing on sheet disintegration and drop formation

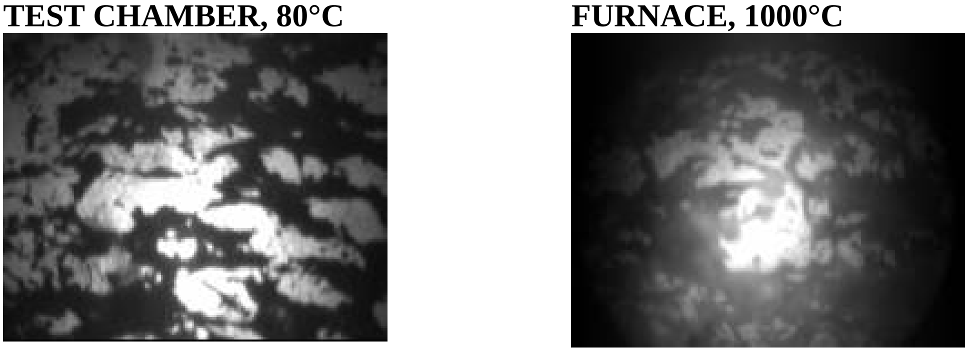
This chapter describes the measured spray properties, in addition to velocity, which can be used both in the comparison work in determining the applicability of spraying chamber results in a furnace environment and in producing initial data for spraying and furnace models. Understanding the parameters affecting these properties is the key to better control of the atomization process. The connection between the sheet properties and the final drop size was studied by visual observation in the Publication IV and the connection was found to be obvious.

7.1 Breakup process

The objective was to study the effect of the furnace environment and spraying parameters on black liquor spray disintegration, the spray opening angle and liquor sheet length. The spraying parameters studied were temperature and pressure. In this thesis, the disintegration mechanisms were studied by visually comparing images from different test cases taken with the furnace endoscope or the camera in the spraying chamber. The disintegration mechanisms described in the literature review section were used as a guide to qualitatively analyzing the observations. No numerical analysis of disintegration mechanisms was carried out at this stage. Only opening angles were measured.

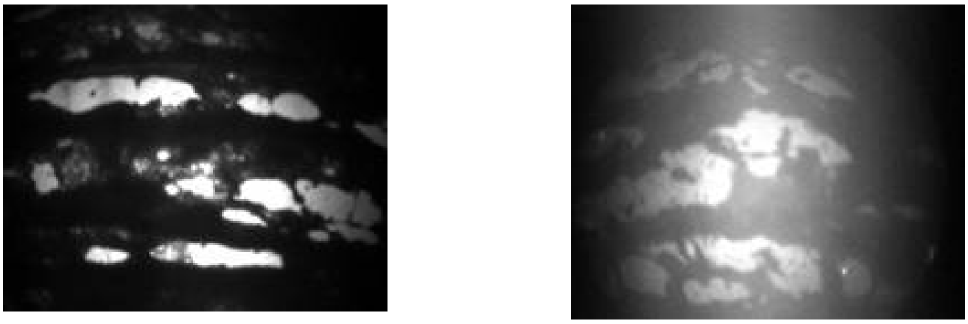
The same spraying situations were filmed in both hot and cold environments. Figure 7.1 shows the pictures taken in the spraying chamber and furnace on the left and right, respectively. Pictures 1 and 2 represent the flashing case and pictures 3 and 4 the non-flashing, or, at least, non-flash-dominated, case. The pictures show that the disintegration mechanism is similar in both environments. The breakup processes are in the same stages and the size of the ligaments is about the same. Flashing changes the atomization process. There the orientation of the ligaments is more random and the disintegration of the sheet is completed. At the lower temperature, the alignment of the ligaments is more horizontal than at the higher temperature.

If the excess temperature is constant and the mass flow rate is increased, the increasing pressure decreases the flashing inside the nozzle tube until the disintegration mechanism changes from flash dominated back to perforation and wave formation, resulting in a longer uniform liquid sheet. The decrease in temperature has a similar effect. Figure 7.2 presents a series of pictures of sprays from a spraying chamber with nozzle B as a function of temperature and mass flow rate. Only a minor change, from 14 to 16°C, in excess temperature caused a dramatic change in the sheet breakup mechanism. At a 2°C higher excess temperature, flashing broke up the liquid sheet rapidly after the splashplate and no uniform liquid sheet was formed.



TEST CHAMBER, 80°C **FURNACE, 1000°C**

1. ΔT_e = 18°C, 211mm x 169mm **2.** ΔT_e = 18°C, 211mm x 169mm



3. ΔT_e = 14°C, 224mm x 179mm **4.** ΔT_e = 14°C, 224mm x 179mm

Figure 7.1 Black liquor sprays in two environments and two excess temperatures at the distance of 0.5 m from the nozzle exit. Parameters: Nozzle A, Dry solids content 76%, mass flow rate 5.2 kg/s (Miikkulainen et al., 2004)

A uniform and long liquor sheet was unexpected for nozzle B. The splashplate is attached to a nozzle tube with a jacket whose inner diameter is larger than the nozzle tube exit. One could assume that, at an excess temperature as high as 14°C, flashing would take place in the liquor flow immediately after the nozzle tube exit before the flow hits the splashplate and no sheet would form. It is also noteworthy that the mill operated normally at the excess temperature of 16°C. For nozzle type A, the change in disintegration mechanism was not so sharp, but still recognizable.

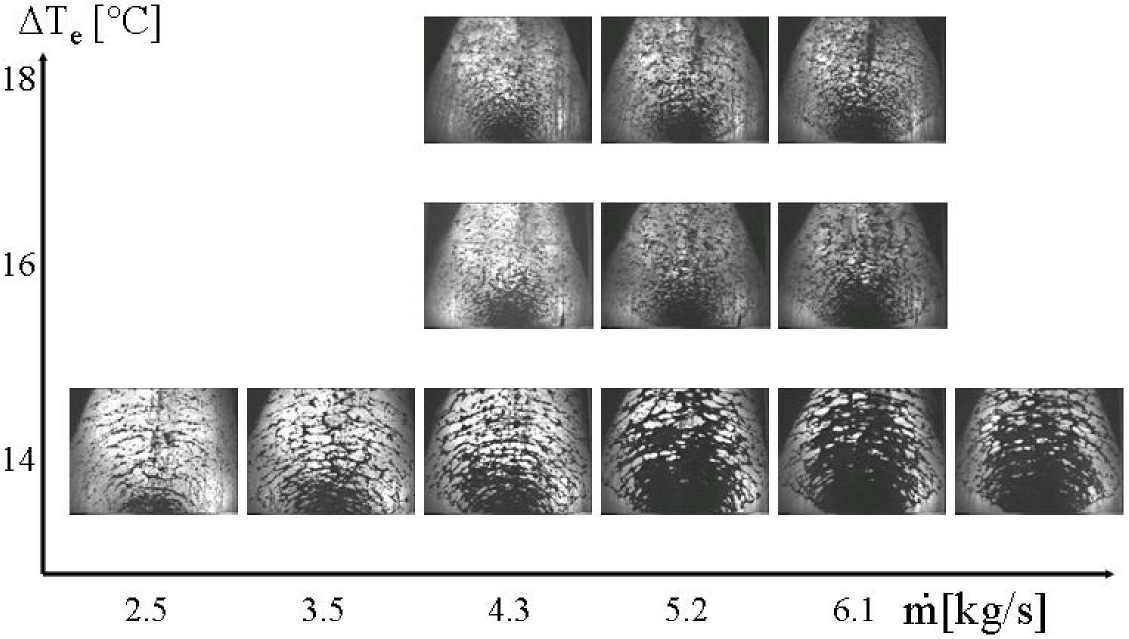


Figure 7.2 The effect of excess temperature and mass flow rate on black liquor sheet breakup, Nozzle B, Mill F.

7.2 Relations between spray disintegration and drop formation

The flashing phenomenon has a great effect on spray formation and the sheet disintegration process and therefore affects the formation of drop size and shape. It was observed that in the case of decreased spraying temperature a half-meter-long uniform liquid sheet was formed, which then broke up into a spray with a high fraction of large non-spherical droplets. At higher temperatures, the sheet was either shorter or non-existent, see Figure 7.2.

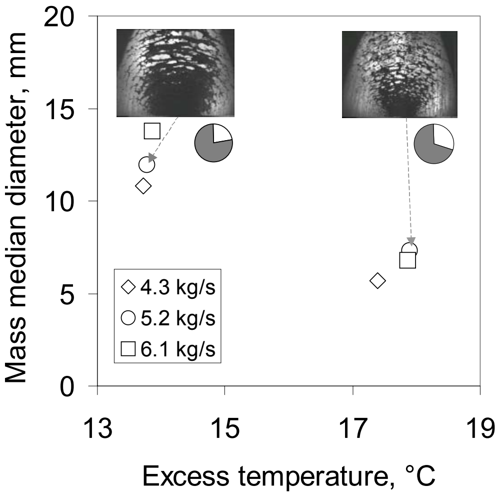


Figure 7.3 Drop size as a function of excess temperature. The white area in the pie charts presents the fraction of spherical drops. Nozzle A.

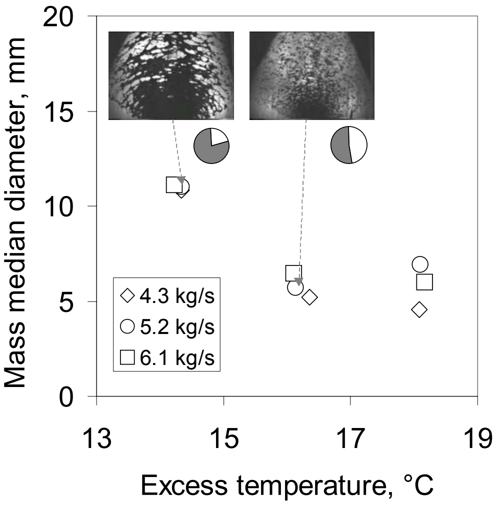


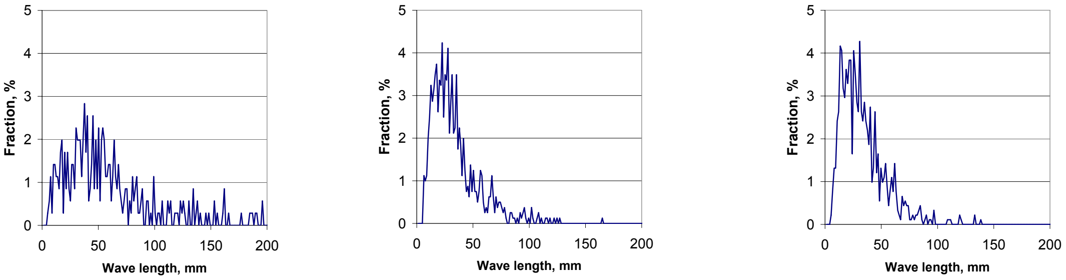
Figure 7.4 Drop size as a function of excess temperature. The white area in the pie charts presents the fraction of spherical drops. Nozzle B.

All particles, droplets and non-spherical particles were assumed to form spherical particles. The resulting mass median diameter is larger than the mass median diameter of spherical droplets alone, or the equivalent smaller mean diameter of non-spherical particles of the corresponding case. This is a natural consequence of the transformation of the volume of non-spherical particles to equivalent spherical particles. Rosin-Rammler, normal distribution, square-root normal distribution and log-normal distribution were fitted to experimental data. All four distribution functions fitted the experimental data quite well, especially for the mean part of the distribution. The least square method produced best results most often for the square-root normal distribution function.

Figures 7.3 and 7.4 present the dependence of the mass median diameter of droplets on the excess temperature. Either decreasing the temperature or increasing the mass flow rate increased the mass median diameter. The median drop size was affected mostly by excess temperature. An increase of excess temperature of only 2°C (from 14 to 16°C) in the case of nozzle B decreased the median drop size to approximately 50%, see Figure 7.4. Note also the huge change in the spray appearance. In Figures 7.3 and 7.4, there are pie charts under each of the spray pictures. The white area in the chart presents the fraction of spherical particles detected. In the case of nozzle B, the fraction of spherical particles increased noticeably when sheet disintegration changed to the flash dominated mode. In the case of nozzle A, the change in the sheet disintegration mechanism is not as sharp, but the mass median diameter of drops decreases as excess temperature increases. It was observed that flashing started to dominate the sheet disintegration mechanism when the excess temperature was high enough to result in approximately 50% smaller drops for both the nozzles.

7.3 Predicting drop size

An image-analysis-based technique was developed for finding different wavelengths from the black liquor sheet. The algorithm counted all the distances between forming holes in the sheet at the spray centerline. The lowest spraying temperature in Figure 7.5 gives a wide distribution of wavelengths. This indicates the incompleteness of the disintegration process. Larger ligaments disintegrate into smaller ligaments before forming droplets. Autocorrelation was used over the intensity data and the dominating wavelength was found regardless of the disintegration mechanism of the sheet. This wavelength was used to calculate the size of the forming ligament. The ligament was assumed to break up to equal-sized droplets.



$\Delta T_e = 14°C$ $\Delta T_e = 17°C$ $\Delta T_e = 18°C$

Figure 7.5 Effect of excess temperature on wave distribution (mass flow rate 5.2 kg/s)

Autocorrelation was used over the intensity data and the dominating wavelength was found regardless of the disintegration mechanism of the sheet. This wavelength was used to calculate the size of the forming ligament. The diameter of the ligament was assumed to break up to equal-sized droplets. According to Rayleigh's (1878) model, the diameter of the forming droplet is 1.89 times the diameter of the corresponding ligament. The measured drop size from three spraying cases in three excess temperatures and three mass flow rates were compared to predicted drop size.

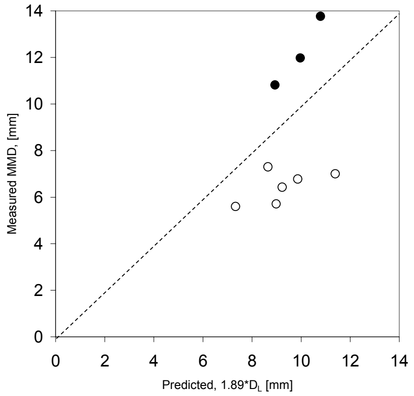


Figure 7.6 Predicted drop size and measured mass median diameter. Open symbols for clearly flash-dominated cases.

Calculated drop size is compared with the measured mass median diameter in Figure 7.6. In clearly flash-dominated cases the predicted drop size is larger than the corresponding measured mass median drop size. When the disintegration mechanism was not flash dominated, the calculated drop size was smaller than the measured drop size.

8 Conclusions

This thesis presents results from the first published experiments on black liquor sprays of high dry solids content. It focuses on the characteristics of high dry solids black liquor sprays under in-furnace conditions. The experiments were carried out in the operating recovery boiler furnaces and the results compared with those of full-scale spraying chamber tests.

The equipment and a method for studying black liquor spraying inside an operating recovery boiler furnace were developed. Flat sprays were studied with the furnace endoscope, which entered the boiler furnace through a liquor gun port just above the liquor gun. It was possible to measure accurately the average velocity and opening angle. The sheet disintegration process could be observed closely with this setup.

The furnace endoscope was used in six recovery boilers with different dry solids contents and nozzle types. Different boilers preferred different firing philosophies. Dimensionless velocity was found to describe the quality of a spray accurately. Dimensionless velocity of 1.5 is a clear limit for the flashing and non-flashing region, and can be used as a measurable quantity. The highest measured dimensionless velocity was 2.4 for the nozzle type A. Increasing the mass flow rate decreases the effect of flashing inside the nozzle tube. The smaller the mass flow rate and the higher the ΔT_e, the higher the dimensionless velocity. A dry solids content of approximately 75% was observed to be the limit that forced boiler operators to change their spraying practice from non-flashing to flashing mode. It corresponded with the dimensionless velocity shift to above 1.5.

The velocity measurements and the observations of the sheet disintegration mechanisms in the two environments of the spraying chamber and recovery boiler furnace showed that the furnace has an insignificant effect on the spray when the spray disintegration is flash-dominated. In both environments, flashing was visually confirmed as a dominating disintegration mechanism and the shape of the sprays were similar. This suggested that the furnace radiation heat transfer to the liquor gun tube generated no additional water vapor. The comparison of the spraying in these two environments was carried out with the furnace endoscope. A large, full-scale, spraying chamber was built at the liquor gun level, next to a recovery boiler, to ensure a similar spraying practice in both environments. Two commercial liquor guns were used at three spraying temperatures and three mass flow rates, which were selected inside the normal operation range of the recovery boiler.

Spraying several degrees above the boiling point of black liquor is common in modern recovery boilers with high solids content black liquors. An unexpected result was the narrow operational range in spraying temperature. Only a minor change, from 14 to 16°C, in excess temperature caused a dramatic change in the sheet breakup mechanism and doubled the drop size. The drop size was measured in the spraying chamber at a distance of 4 m from the nozzle exit. The flashing phenomenon has a great effect on spray formation and the sheet disintegration process. Therefore it affects the formation of drop size and shape. It was observed that, in the case of decreased spraying temperature, a 0.5 m-long uniform liquid sheet was formed, which then broke up into a spray with a large fraction of large non-spherical droplets.

The flash-dominated disintegration mechanism was studied systematically. A correlation between the spray disintegration and drop size was obvious. In order to be able to predict the forming drop size from black liquor spray characteristics, the length of a sheet and break-up frequencies were measured with a specially developed algorithm. A dominating wave length could be found even if the spray flashed heavily. In the cases when it was difficult to find the dominating frequency, the disintegration was noticed to be incomplete. The wave length was used for calculating the size of the forming ligament. For comparison with results from drop-size measurements, Rayleigh's model of ligaments breaking up to equal-sized droplets was used. Rayleigh (1878) analyzed the instability of inviscid liquid jets that were disintegrated by surface tension forces. For highly viscous and flashing black liquor sprays, in cases when flashing is not clear, it underestimates the final drop size, while, in other flashing cases, the final drop size is overestimated.

8.1 Contribution of this work

In order to have accurate validation data for the modeling and design of recovery boilers, it is important to study the sheet properties in harsh furnace conditions. The spray research under in-furnace conditions, where the temperature and flow direction of surrounding gas differs from test chamber conditions, is introduced as a very useful method of studying black liquor spraying practice with real black liquor, in a real environment and with industrial-scale nozzles. The furnace endoscope, developed during this work, made this possible and was the first attempt to systematically obtain information about high dry solids black liquor spraying under furnace conditions. The spray properties, such as velocity, opening angle and the trajectory of the spray can be measured and information can be obtained about disintegration mechanisms.

Flashing inside the nozzle was found to be the factor that is key to the whole spraying process of high dry solids black liquor. It has a major role in spray disintegration and initial velocity, which both correlate very well with the final drop size and shape. Dimensionless velocity can be used in categorizing the disintegration processes and, regardless of the disintegration mechanism, it is possible to find the dominating frequency in disintegrating spray with image-analysis-based techniques.

The information and measurement data of black liquor spraying achieved in the furnace environment give better information for furnace modeling, boiler design and control, and help to understand the in-furnace processes. Validated initial data for CFD calculations is essential; without them, models are useless. The initial velocity of the spray is much higher (approximately 1.5 - 2 times) than used commonly in calculations where flashing and its accelerating effect has been ignored. The shape of the spray – opening angle and trajectory – are now available for modeling. Mass flow rate distribution and velocity distribution can be included into calculations of flashing cases. Drop size was measured to be much larger than used in the recovery boiler models; a large fraction of the droplets was found to be non-spherical. Järvinen et al. (2004) suggested that the particle shape has a significant effect on the combustion and flight behavior of single black liquor particles. Up to the present, recovery boilers have been modeled with low dry solids black liquor data. Therefore, combustion and spraying models of black liquor particles should be updated and the non-spherical shape should be considered in furnace simulations using accurate initial velocity, mass flow distribution, and opening angles.

8.2 Future work

The correlations and correlation models presented in this dissertation should be processed to spraying models to improve boiler-control and furnace modeling. A suggestive correlation spraying model could be created for a narrow range of use with data already available. It is recommendable that each spraying case should be validated and adjusted with experimental data. The furnace endoscope could also be used for adjusting and improving the spraying practice at the recovery boiler.

The applicability of the furnace endoscope data to drop-size predictions inside a recovery boiler will be analyzed. The work towards actually being able to measure drop size inside a recovery boiler goes on.

Flash-boiling will be studied by experimentally determining pressure change inside a nozzle tube. Bubble growth will be modeled.

References

Adams, T.N. 1997, "Characteristics of Kraft Black Liquor Recovery Boilers" in *Kraft Recovery Boilers*, ed. T.N. Adams, American Forest & Paper Association, TAPPI Press Atlanta, GA, USA.

Adams, T.N., Empie, H.L., Obuskovic, N. & Spielbauer, T.M. 1990, *Kraft Black Liquor Delivery Systems*, Institute of Paper Science and Technology, Atlanta, Georgia, USA.

Adams, T.N., Empie, S.J., Lien, N. & Spielbauer, T.M. 1990b, *Kraft Black Liquor Delivery Systems*, Report No.2, Institute of Paper Science and Technology, Atlanta, Georgia, USA.

Alén, R. 2004, "Combustion Behavior of Black Liquors from Different Delignification Conditions", *40 Years Recovery Boiler Co-operation in Finland,* Finnish Recovery Boiler Committee, Helsinki, Finland, p. 31.

Bennington, C.P.J. & Kerekes, R.J. 1985, "Effect of Temperature on drop size of black liquor sprays", *1985 International Chemical Recovery Conference, TAPPI* Press, Atlanta, GA, USA, New Orleans, LA, USA, p. 345.

Bousfield, D.W. 1990, *Research on Droplet Formation for Application to Kraft Black Liquors*, The University of Maine, Orono, Maine.

Chigier, N.A. 1991a, "Physics of atomization", *Proceedings of the 5th International Conference on Liquid Atomization and Spray Systems - ICLASS-91, Jul 15-18 1991* Publ by Natl Inst of Standards & Technology, Gaithersburg, MD, USA, Gaithersburg, MD, USA, p. 1.

Chigier, N. 1991b, "Optical imaging of sprays", *Progress in Energy and Combustion Science,* vol. 17, no. 3, pp. 211-262.

Chigier, N. (ed) 1991c, *Combustion Measurements*, Hemisphere Publishing Corp., USA.

Clark, C.J. & Dombrowski, N. 1974, "An experimental study of the flow of thin liquid sheets in hot atmospheres", *J. Fluid Mech.,* vol. 64, no. Part 1, pp. 167-175.

Doebelin, E.O. 1990, *Measurement Systems Application and Design,* Fourth edn, McGraw – Hill, pp. 58-59, Singapore.

Dombrowski, N. & Fraser, R.P. 1954, "A Photographic Investigation into the Disintegration of Liquid Sheets", *Philos. Trans. R. Soc. London Ser A,* vol. 247, pp. 101-130.

Dombrowski, N. & Johns, W.R. 1963, "The aerodynamic instability and disintegration of viscous liquid sheets", *Chemical Engineering Science,* vol. 18, pp. 203-214.

Empie, H.J., Lien, S.J. & Yang, W. 1992a, "Effect of Temperature on Black Liquor Droplet Formation from Commercial Spray Nozzles", *1992 AIChE Annual Meeting, Forest Products Division* AIChE, p. 57.

Empie, H.J., Lien, S.J., Yang, W.R. & Adams, T.N. 1992b, "Spraying characteristics of commercial black liquor nozzles", *Proceedings of the 1992 International Chemical Recovery Conference. Part 2 (of 2), Jun 7-11* Publ by TAPPI Press, Atlanta, GA, USA, Seattle, WA, USA, p. 429.

Empie, H.J., Lien, S.J., Yang, W. & Samuels, D.B. 1995a, "Effect of black liquor type on droplet formation from commercial spray nozzles", *Journal of Pulp and Paper Science,* vol. 21, no. 2, pp. 63-67.

Empie, H.J., Lien, S.J., Yang, W. & Adams, T.N. 1995b, "Spraying characteristics of commercial black liquor nozzles", *Tappi Journal,* vol. 78, no. 1, pp. 121-128.

Empie, H.J., Lien, S. & Samuels, D.B. 1997, "Distribution of Mass Flows in Black Liquor Sprays", *AIChE Symposium Series No. 315,* vol. 93, pp. 58-66.

FAOSTAT data, 2006, last updated 7 February 2006, URL: http://faostat.fao.org/

Fraser, R.P. 1956, "Liquid Fuel Atomization", *6th Symposium (International) on Combustion*, p. 687.

Fraser, R.P., Eisenklam, P., Dombrowski, N. & Hasson, D. 1962, "Drop Formation from Rapidly Moving Liquid Sheets", *AIChE Journal,* vol. 8, no. 5, pp. 672-680.

Frederick, W.J. 1997, "Black Liquor Properties" in *Kraft Recovery Boilers*, ed. T.N. Adams, American Forest & Paper Association, TAPPI Press Atlanta, GA, USA.

Hagerty, W.W. & Shea, J.F. 1955, "A Study of the Stability of Plane Fluid Sheets ", *Journal of Applied Mechanics*, no. Dec, pp. 509-514.

Helpiö, T. & Kankkunen, A. 1995, "The Effect of Black Liquor Firing Temperature on Atomization Performance", *TAPPI Engineering Conference* TAPPI, p. 717.

Helpiö, T., Paloposki, T. & Saviharju, K. 1994, *Atomization of black liquor in pressurized ambient conditions*, Helsinki University of Technology, Laboratory of Energy Engineering and Environmental Protection, Espoo, Finland.

Helpiö, T.E.J. & Kankkunen, A.E.P. 1996, "Effect of black liquor firing temperature on atomization performance", *Tappi Journal,* vol. 79, no. 9, pp. 158-163.

Helynen, S., Sipilä, K., Peltola, E. & Holttinen, H. 2002, *Eduskunnan kanslian julkaisu 6/2002, Renewable Energy Sources in Finland by 2030,Tulevaisuusvaliokunta, teknologian arviointeja 12*, Eduskunnan kanslia, Helsinki.

Holmlund, K. & Parviainen, K. 2000, "Evaporation of black liquor" in *Papermaking Science and Technology, Book 6B*, *Chemical Pulping* eds. J. Gullichsen & C.J. Fogelholm, Finnish Paper Engineers' Association and TAPPI, Helsinki, Finland.

Hupa, M. & Hyöty, P. 1995, "Mustalipeän poltto ja soodakattila" in *Poltto ja palaminen*, eds. R. Raiko, I. Kurki-Suonio, J. Saastamoinen & M. Hupa, IFRF International Flame Research Foundation, Gummerus Kirjapaino Oy Jyväskylä.

Hupa, M., Solin, P. & Hyöty, P. 1987, "Combustion Behaviour of Black Liquor Droplets", *Journal of Pulp and Paper Science,* vol. 13, no. 2, pp. 67-72.

Image Pro Plus Reference Guide for Windows, 1998, Media Cybernetics, pp. 209-219.

Järvinen, M.P., Kankkunen, A.P., Miikkulainen, P.H. & Zevenhoven, R. 2004, "Combustion and flight characteristics of non-spherical black liquor droplets", *2004 International Chemical Recovery Conference, Jun 6-10* Technical Assoc. of the Pulp and Paper Industry Press, Norcross, GA 30092, United States, Charleston, SC, United States, p. 81.

Järvinen, M.P. 2002, "Numerical modeling of the drying, devolatilization and char conversion processes of black liquor droplets", *Acta Polytechnica Scandinavica, Mechanical Engineering Series*, no. 163, p. 77.

Kankkunen, A. 1998, "Flow Regimes inside a Black Liquor Splashplate Nozzle", *Proceedings of ILASS-Europe '98*ILASS-Europe, p. 412.

Kankkunen, A. 1995, *Black liquor droplet formation on a splashplate nozzle*, Helsinki University of Technology, Faculty of Mechanical Engineering, Energy Technology and Environmental Protection.

Kankkunen, A. & Miikkulainen, P. 2003, "Particle Size Distributions of Black Liquor Sprays with A High Solids Content in Recovery Boilers", *IFRF Online Combustion Journal,* [Online], no. Article Number 200308, December 2003. Available from: http://www.journal.ifrf.net/library/december2003/200308Kankkunen.pdf.

Kankkunen, A. & Nieminen, K. 1997, "Black Liquor Sheet Breakup Mechanisms and the Effect on Drop Size", *Proceedings of The 7th International Conference on Liquid Atomization and Spray Systems*ILASS - Korea, p. 62.

Kankkunen, A., Nieminen, K. & Helpiö, T. 1996, "Black Liquor Droplet Formation on Splashplate Nozzles", *Finnish-Swedish Flame Days* IFRF.

Kankkunen, A., Rantanen, P. & Helpiö, T. 1994, "Small scale measurement of black liquor spraying with splashplate nozzles", *TAPPI Engineering Conference* TAPPI, p. 207.

Kankkunen, A., Miikkulainen, P. & Järvinen, M. 2001, "The ratio of ligaments and droplets of black liquor sprays", *International Chemical Recovery Conference, Jun 11-14*Technical Assoc. of the Pulp and Paper Industry Press, Whistler, BC, p. 51.

Lefebvre, A.H. 1989, *Atomization and sprays,* Hemisphere Publishing Corporation, New York, USA.

Loebker, D.W. 1998, *Effervescent Spraying of High Viscosity Fluids*, Institute of Paper Science and Technology.

Loebker, D.W. & Empie, H.J. 2002, "Independently controlled drop size in black liquor sprays using effervescent atomization. Part II: Splashplate nozzles", *Journal of Pulp and Paper Science,* vol. 28, no. 8, pp. 251-258.

Loebker, D.W. & Empie, H.J. 2001, "Independently controlled drop size in black liquor sprays into the kraft recovery boiler using effervescent atomization", *Journal of Pulp and Paper Science,* vol. 27, no. 1, pp. 18-25.

Loebker, D. & Empie, H.J. 1998, "Effervescent spraying: A new approach to spraying high solids black liquor", *Proceedings of the 1998 TAPPI International Engineering Conference. Part 1 (of 3), Sep 13-17* TAPPI Press, Norcross, GA, USA, Miami, FL, USA, p. 157.

Lu, G., Yan, Y. & Ward, D.D. 2000, "Advanced monitoring, characterization and evaluation of gas-fired flames in a utility boiler", *Journal of the Institute of Energy,* vol. 73, no. 494, p. 43-49.

McCarty, B.C. & Lang, B. 2002, "Furnace cameras assist in No_x reduction", *Power Engineering (Barrington, Illinois),* vol. 106, no. 11, p. 138-140.

Merzkirch, W. 1987, *Flow Visualization,* Second edn, Academic Press Inc., London.

Metsäteollisuus ry. 2005*, Metsäteollisuuden tuotanto tuoteryhmittäin Suomessa* [Homepage of Metsäteollisuus ry.], [Online]. Available: http://www.metsateollisuus.fi/tilastot/#tuotanto_ja_vienti [2005, 08/16] .

Miikkulainen, P. 1997, *Furnace Endoscope in the Research of Drop Formation of Black Liquor*, Helsinki University of Technology, Department of Mechanical Engineering.

Miikkulainen, P., Järvinen, M. & Kankkunen, A. 2000, "Black Liquor Spray Properties in Operating Recovery Boiler Furnaces", *INFUB 5th European Conference on Industrial Furnaces and Boilers,* INFUB, Porto, Portugal .

Miikkulainen, P., Järvinen, M. & Kankkunen, A. 2002, "The effect of a furnace environment on black liquor spray properties", *Pulp and Paper Canada,* vol. 103, no. 9, pp. 34-38.

Miikkulainen, P., Kankkunen, A. & Järvinen, M.P. 2004, "Furnace endoscope - Measuring fuel spray properties in hot and corrosive environments", *Experiments in Fluids,* vol. 37, no. 6, pp. 910-916.

Mikkanen, P. 1991, *Atomization of a black liquor sheet*, Helsinki University of Technology.

Mäntyniemi, J. 1987, *Atomization of liquor in swirl and splashplate nozzles*, Tampere University of Technology, Department of Mechanical Engineering.

Niemelä, K. & Alén, R. 1999, *Puun delignifioinnin eri vaiheissa muodostuvat liukoiset ja haihtuvat yhdisteet, Kirjallisuuskatsaus Suomen Soodakattilayhdistykselle, KCL seloste 2397*, KCL, Espoo, Finland.

Nieminen, K. 1996a, *Experiments on black liquor splashplate nozzle performance*, Helsinki University of Technology, Faculty of Mechanical Engineering, Institute of Energy Engineering, Espoo, Finland.

Nieminen, K. 1996b, "Experiments on Black Liquor Splashplate Nozzle Performance", *12th Annual Conference of ILASS-Europe*ILASS-Europe, p. 185.

Paloposki, T. & Kankkunen, A. 1991, "Dimensional analysis and spray modeling", *Sprays and Aerosols '91*, p. 144.

Park, B. & Lee, S. 1994 ″Experiments An Experimental Investigation of the Flash Atomization Mechanism", *Atomization and Sprays*, vol.4, pp.159-179.

Rantanen, P., Paloposki, T. & Kankkunen, A. 1993, *Image analysis in the measurement of droplet size*, Helsinki University of Technology, Faculty of Mechanical Engineering, Department of Energy Engineering, Espoo, Finland.

Rayleigh, F. R. S. 1878, "On the Instability of Jets", *Proc. Lon. Math. Soc.*, p. 4.

Spielbauer, T.M. & Adams, T.N. 1990, "Flow and pressure drop characteristics of black liquor nozzles", *TAPPI Journal,* no. September 1990, pp. 169-174.

Spielbauer, T.M., Verrill, C., Damon, B. & Adams, T. 1991, "Imaging black liquor sprays in an operating recovery furnace", *IPST Technical paper series*, number 396.

Spielbauer, T.M. & Aidun, C.K. 1992a, "The Distribution of Perforations in a Radially thinning Liquid Sheets", *TAPPI Engineering Conference* TAPPI, p. 823.

Spielbauer, T.M. & Aidun, C.K. 1992b, "Mechanisms of liquid sheet breakup and the resulting drop size distributions Part1: types of spray nozzles and mechanisms of sheet disintegration", *Tappi Journal,* , no. February 1992, pp. 136-142.

Spielbauer, T.M. & Aidun, C.K. 1992c, "Mechanisms of liquid sheet breakup and the resulting drop size distributions Part 2: strand breakup and experimental observations", *Tappi Journal,* no. March 1992, pp. 195-200.

Spielbauer, T.M. & Aidun, C.K. 1994, "Wave-thinning and breakup of liquid sheets", *Journal of Fluids Engineering, Transactions of the ASME,* vol. 116, no. 4, pp. 728-734.

Squire, H.B. 1953, "Investigation of the instability of a moving liquid film", *British Journal of Applied Physics,* vol. 4, pp. 167-169.

Stockel, I.H. 1985, *Research on Droplet Formation for Application to Kraft Black Liquors*, Office of Scientific and Technical Information, United States Department of Energy, University of Maine, Orono, Maine.

Streeter, V.L. & Wylie E.B. 1983, "Fluid Mechanics, First SI Metric Edition" Mc Graw Hill Book Co, Singapore, p.239.

Taitel, Y. & Dukler, A.E. 1976, "Model For Predicting Flow Regime Transitions in Horizontal And Near Horizontal Gas-Liquid Flow", *AIChE Journal,* vol. 22, no. 1, pp. 47-55.

Tate, R.W. & Marshall, W.R. 1953, "Atomization by Centrifugal Pressure Nozzles", *Chemical Engineering Progress,* vol. 49, no. 4, pp. 169-174.

Taylor, G.I. & Michael, D.H. 1973, "On making holes in a sheet of fluid", *Journal of Fluid Mechanics,* vol. 58, no. 4, pp. 625-639.

Torniainen, J. 2003, "Spraying related physical properties of black liquor", *Nordic Universities Kraft Chemical Recovery Course, Black Liquor Spraying and Combustion in Kraft Recovery Boilers* Helsinki University of Technology.

Vakkilainen, E. 2000, "Recovery Boiler" in *Papermaking Science and Technology, Book 6B, Chemical Pulping*, eds. J. Gullichsen & C.J Fogelholm, Finnish Paper Engineers' Association and TAPPI, Helsinki, Finland.

Vakkilainen, E.K., Kankkonen, S. & Suutela, J. 2004, "Advanced efficiency options - Increasing electricity generating potential from pulp mills", *2004 International Chemical Recovery Conference, Jun 6-10 2004* Technical Assoc. of the Pulp and Paper Industry Press, Norcross, GA, United States, Charleston, SC, United States, pp. 1-12.

Vakkilainen, E. 2005, "Kraft recovery boilers – Principles and practice", Suomen Soodakattilayhdistys r.y., Helsinki, Finland

Westerweel, J. 1997, "Fundamentals of digital particle image velocimetry", *Measurement Science & Technology,* vol. 8, no. 12, pp. 1379-1392.

York, J.L., Stubbs, H.E. & Tek, M.R. 1953, "The Mechanism of Disintegration of Liquid Sheets", *Transactions of the ASME,* , no. October 1953, pp. 1279-1285.

APPENDIX I: Significant quantities and dimensionless numbers

The experiments presented in this thesis were carried out with real black liquor; only mill-scale splashplate nozzles were used. Nozzle size and liquor-specific properties varied in some ranges. The experiments were carried out mainly under in-furnace conditions, but relatively cold spraying chamber conditions were also used. In order to establish the experiments and results in the research field of spraying, dimensionless parameters are often useful. This appendix lists the significant quantities and dimensionless parameters involved in the test cases. The ranges at each mill are presented in Table A1.

The quantities involved in the spraying process and the ranges of the experiments are:

Density of black liquor, ρ_{BL}	1407 – 1458 kg/m^3
Viscosity of black liquor, μ_{BL}	40 - 256 mPa s
Surface tension, σ (used in calculating the We)	0.05 N/m
Heat capacity of black liquor (130°C, 75%), c_{pBL}	2841 J/kg/°C
Dry solids content	73 – 79 %
Mass flow rate	2.5 – 7.4 kg/s
Excess temperature	2 – 19 °C
Pressure in the nozzle (not available)	
Dimensions of nozzle (pipe diam./splashplate angle)	26 – 40 mm / 23 – 36°
Density of surrounding gas (air 20°C /nitrogen 1000°C)	1.293 / 0.275 kg/m^3
Viscosity of surrounding gas (air 20°C /nitrogen 1000°C)	0.018 / 0.0483 mPa s

The *Reynolds number (Re)* is the ratio of the inertia and viscous forces.

$$\mathrm{Re} = \frac{\rho_{BL} u_p d_p}{\mu_{BL}} \qquad \text{(A.1)}$$

where u_p is the calculated velocity of pipe flow, d_p is the nozzle pipe diameter and μ_{BL} is the dynamic viscosity of black liquor. The Reynolds number of the nozzle pipe flow in the experiments was between 680 and 4900 when the transition zone, where the flow may be either laminar or turbulent, is about 2000 to 4000 (Streeter and Wylie, 1983).

The *Weber number (We)* is the ratio of inertia to surface tension forces.

$$We = \frac{\rho_{BL} u_p^2 d_p}{\sigma} \qquad \text{(A.2)}$$

There is practically no reliable information available on high dry solids content black liquor surface tension. In Table A1, $\sigma = 0.05$ N/m was used for all the cases (Frederick, 1997). The Weber number of the nozzle pipe flow in the experiments was between 6000 and 60000. In clearly non-flashing cases, the Weber number could be used for calculating the breakup point of the thin liquid sheet (Squire, 1953).

The *density and viscosity ratios* were calculated in a furnace environment and a spraying chamber environment with assumptions of surrounding gases being nitrogen (1000°C) and air (20°C), respectively. The density ratio in the furnace environment was 0.0002, but in the spraying chamber it was 0.0009. The viscosity ratio was from 0.0002 to 0.00121 in the furnace environment and from 0.0001 to 0.0002 in the spraying chamber. The main difference between the two environments was probably the flow of the surrounding gas, which was not defined.

The *Jakob number (Ja)* is the ratio of available sensible energy to latent energy. It characterizes the potential of flash evaporation inside the nozzle. *Ja* is equal to the adiabatic equilibrium steam quality.

$$Ja = \frac{c_{p_{BL}}(t_f - t_b)}{h_w} \qquad \text{(A.3)}$$

where c_{pBL} is the heat capacity of black liquor (Frederick, 1997), t_f and t_b are black liquor firing temperature and boiling temperature, respectively, and h_w is the heat of the evaporation of water. In the experiments, the Jakob number was between 0.003 and 0.023.

Dimensionless velocity (Eq. 6.1) describes the acceleration of the flow inside the nozzle tube and requires measurements for its definition. Acceleration is a consequence of the flash evaporation inside the nozzle tube and is proportional to Jakob number and inversely proportional to the pressure.

Table A1. Spraying-related quantities and dimensionless numbers at test mills A to F and the spraying chamber (SC). The number of measurement cases is presented in brackets after the mill letter.

	Mill	**A (13)**		**B (3)**		**C (6)**		**D (8)**		**E (1)**		**F (35)**		**F_{SC} (59)**	
Black liquor	unit	min	max	min	max	min	max	min	max	min	max	min	max	min	max
Dry solids content	%	73	75	76	76	74	76	75	77	76	76	75	78	75	79
Viscosity, μ_{BL}	mPa s	40	100	120	120	70	120	108	165	65	65	93	256	93	200
Density, ρ_{BL}	kg/m^3	1407	1430	1421	1423	1424	1431	1435	1435	1436	1436	1437	1458	1436	1453
Boiling temperature, t_b	°C	116	118	117	117	117	119	117	119	119	119	116	119	116	118
Adjustable parameters															
Mass flow rate	kg/s	3.1	4.8	2.5	4.6	5.0	6.4	5.7	7.3	3.9	3.9	4.3	6.2	2.5	7.4
Mass flux	g/mm^{2}s	7.2	11.3	3.9	8.7	9.9	12.8	5.9	8.5	7.2	7.2	6.9	12.2	4.1	13.4
Excess temperature, ΔT_e	°C	4.1	6.5	7.7	9.3	4.0	7.0	10.6	12.5	2.4	2.4	13.7	18.7	13.4	18.2
Nozzle geometry															
Type of the nozzle		A		B		A		A		A		A, B		A, B	
Nozzle tube, d_p	mm	27		26, 30		27		34.5, 40		27		27, 28		27, 28	
Splashplate angle	°	25		35		25		25		20		23, 36		23, 36	
Dimensionless numbers															
Reynolds number, *Re*		1404	4905	980	1877	1947	4293	1266	2423	2816	2816	773	2946	686	2917
Weber number, *We*		8281	20358	6484	27431	26116	43411	12294	26197	16577	16577	18756	42543	6395	56033
Density ratio, ρ_{gas}/ρ_{BL}		0.0002		0.0002		0.0002		0.0002		0.0002		0.0002		0.0009	
Viscosity ratio, μ_{gas}/μ_{BL}		0.0005	0.0012	0.0004	0.0004	0.0004	0.0007	0.0003	0.0004	0.0007	0.0007	0.0002	0.0005	9E-05	0.0002
Jakob number, *Ja*		0.0052	0.0082	0.0097	0.0117	0.0050	0.0088	0.0133	0.0157	0.0030	0.0030	0.0173	0.0236	0.0169	0.0228
Dimensionless velocity, u^*		1.0	1.5	1.7	3.4	1.3	1.5	1.6	2.4	1.2	1.2	1.3	3.1	1.2	3.5

ISBN-13 978-951-22-8507-5
ISBN-10 951-22-8507-X
ISBN-13 978-951-22-8508-2 (PDF)
ISBN-10 951-22-8508-8 (PDF)
ISSN 1795-2239
ISSN 1795-4584 (PDF)