Aalto University
School of Engineering

Combustion technology
EEN E2002

Black liquor combustion in Kraft Recovery boilers

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Day 1: Introduction

Pre-assignment 1: Read Material PA1 before the lecture

- Why do we need recovery boilers?
- What is the their main difference to power boilers?

Lecture 1: Introduction to Kraft pulping and chemical recovery

- Principles of pulp and papermaking.
- Recovery furnace processes.
- Recovery cycle and boiler material and energy balances.

Exercise 1: Recovery boiler mass and species balance calculation part 1: Black liquor organics and smelt composition.

Intended learning outcomes

- To understand what is black liquor and how it relates to papermaking.
- To understand the main functions of a recovery boiler - to recover chemicals and heat.
- To know the main boiler components.
- To learn to estimate material balance of a recovery boiler, need of air, amount of flue gases and amount of inorganics flowing out from the boiler.

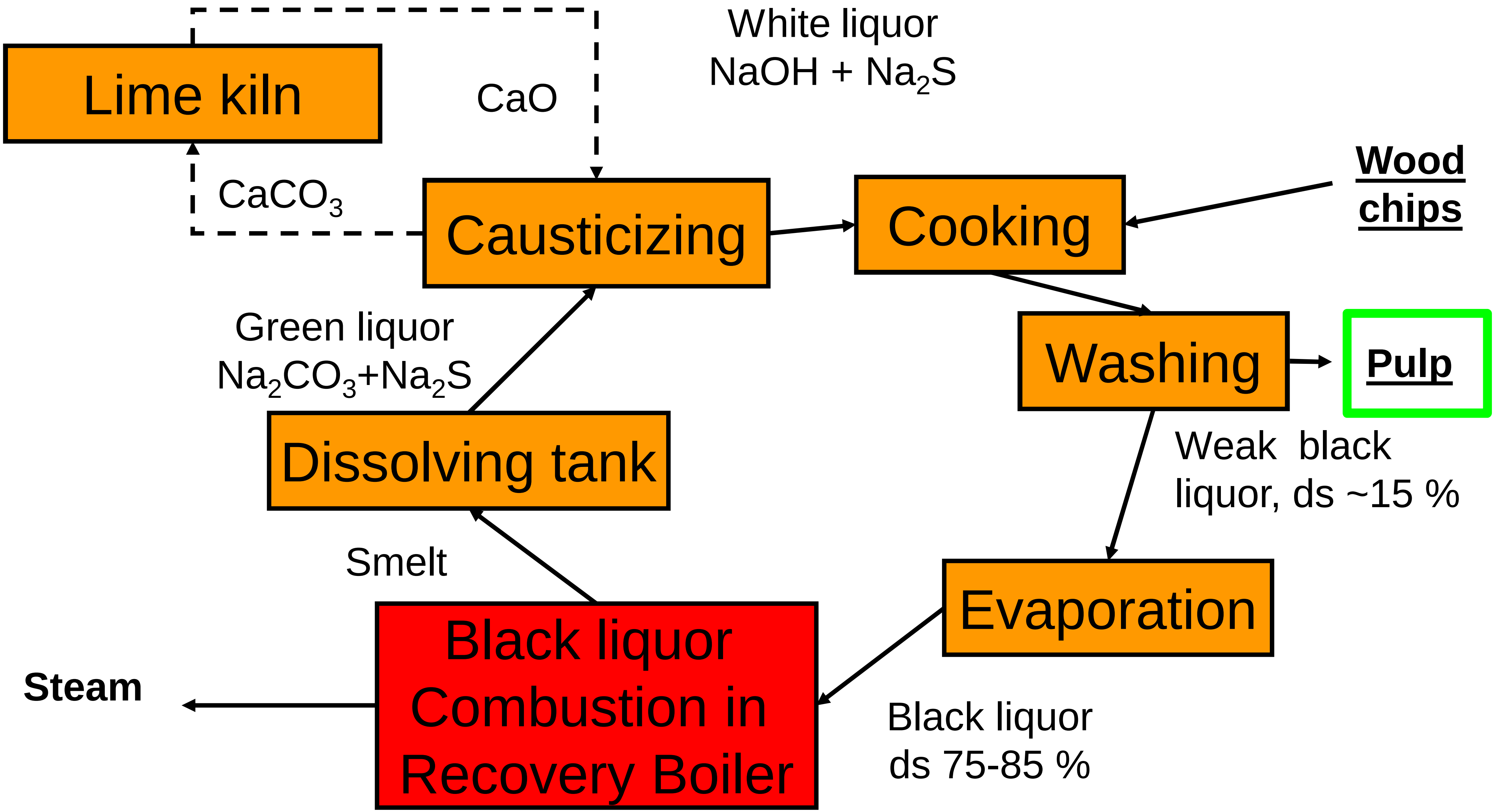
Contents

1. What is black liquor?
2. Modern paper mill.
3. Significance of black liquor to Finland.
4. Main recovery boiler processes and material balance.
5. Summary, what should you remember from this lesson?

What is black liquor?

- Black liquor is the pulp and papermaking process liquid after chemical cooking and evaporation
- Only the fibers of the wood are used in paper

Modern **paper** mill



Lime kiln

CaO

White liquor
NaOH + Na_2S

$CaCO_3$

Causticizing

Cooking

Wood chips

Green liquor
$Na_2CO_3 + Na_2S$

Washing

Pulp

Dissolving tank

Weak black liquor, ds ~15 %

Smelt

Evaporation

Steam

Black liquor Combustion in Recovery Boiler

Black liquor
ds 75-85 %

Black liquor composition

	Wood	Black liquor
water	20-40	20-25
C	50	39.8
H	6	4.2
O	43	36.0
N	1	0.1
S	**-**	**4.0**
Na	**-**	**15.5**
K	-	0.1
Cl	-	0.3

Numbers given as weight-%

Main organic species lignin, aliphatic acids and extractives

Inorganic species Na_2S, $NaOH$, Na_2SO_4, Na_2CO_3, $NaCl$ and same with K-basis etc….

Heating value

Effective heating value of black liquor is low 12-13 MJ/kg.

For comparison, coal 28 MJ/kg, peat 22 MJ/kg and wood 17 MJ/kg.

This means that less heat can be produced in black liquor combustion, resulting in lower combustion temperature

Volatile matter

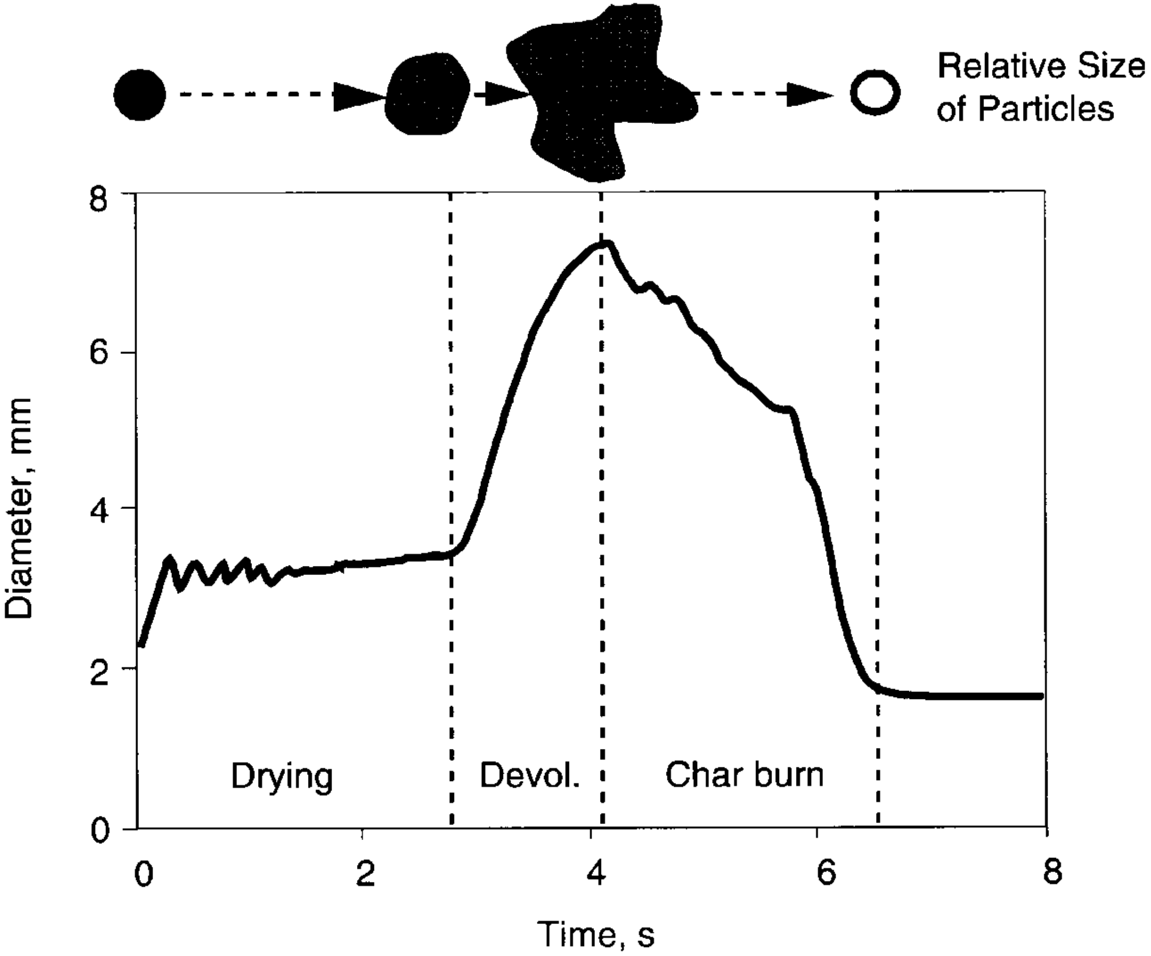
Organic matter in black liquor is very easily volatilizable, more than 80 % of organic matter can release as gases in pyrolysis → Most of organic combustion takes place in gas phase.

Other fuels:

Coal 30 % volatile, Brown coal 60 % and Peat 70 %.

Swelling and reactivity

- significant swelling during pyrolysis
- char reactivity very high due to swollen structure and catalysing inorganics



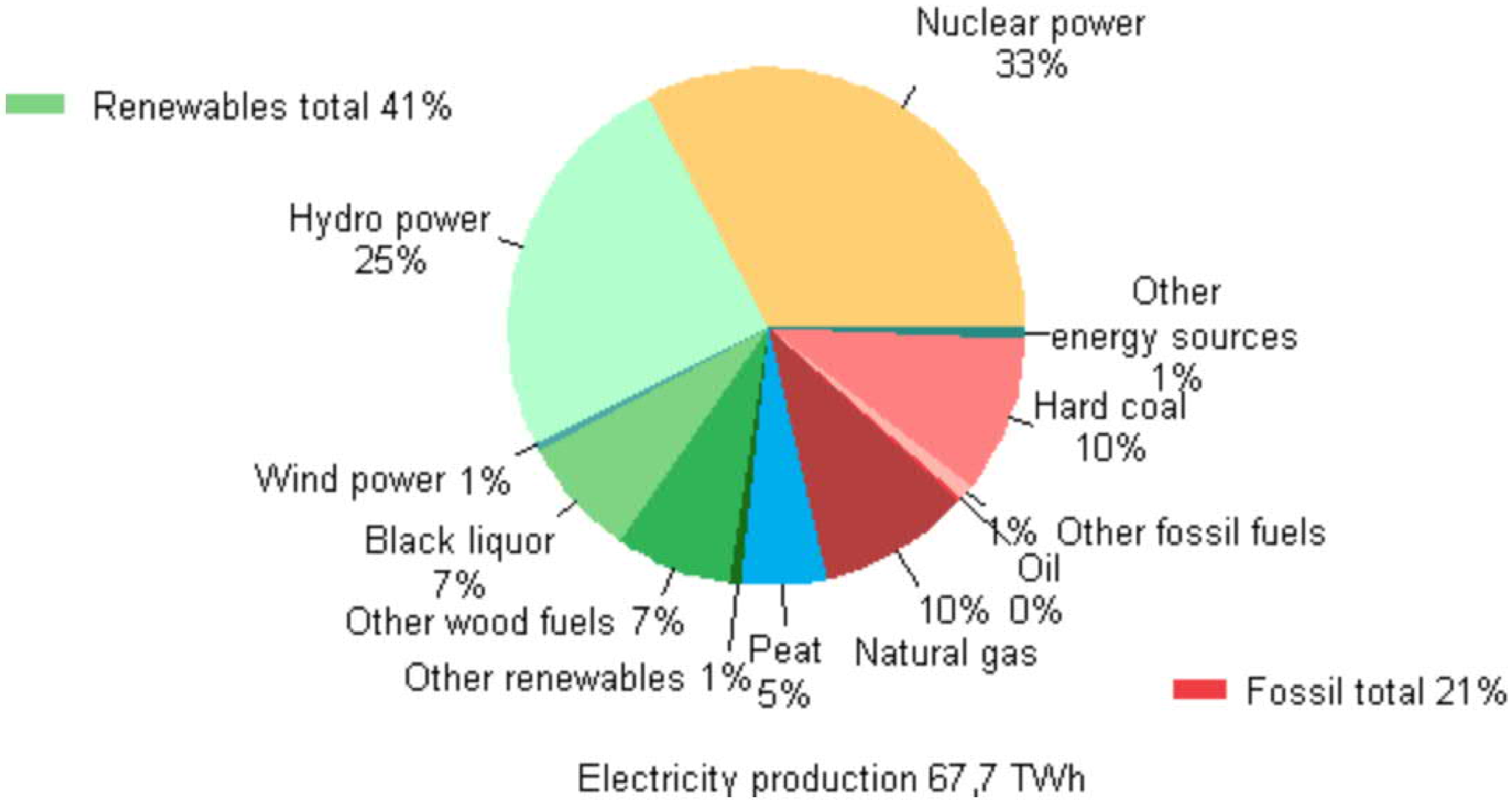
Fouling behavior of salts

”Ash” content of black liquor is very high 35 %. Due to chemical composition ash will melt at very low temperature ~ 750 °C → boiler gets easily fouled or even plugged. Difficult fuel!

Other fuels:

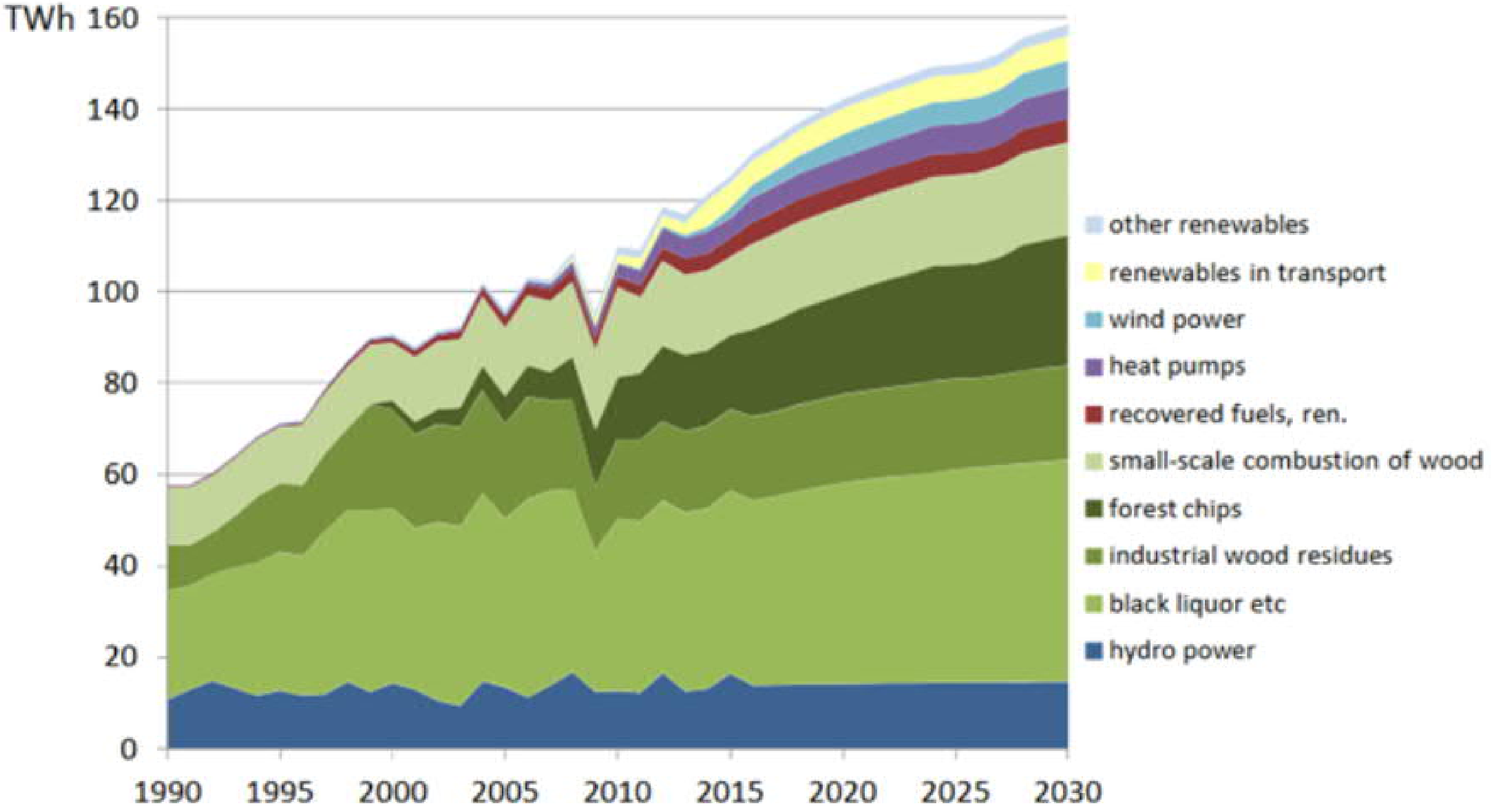
Coal 12 % ash, melts at 1200 °C, Brown coal 22 %, 1100 °C and wood 2 %, 1300 °C.

Significance to Finland



Electricity production 2012

Significance to Finland



Consumption of renewable energy

Total energy consumption 2016, 378 TWh, renewables 34 %!!!!

Main recovery boiler processes

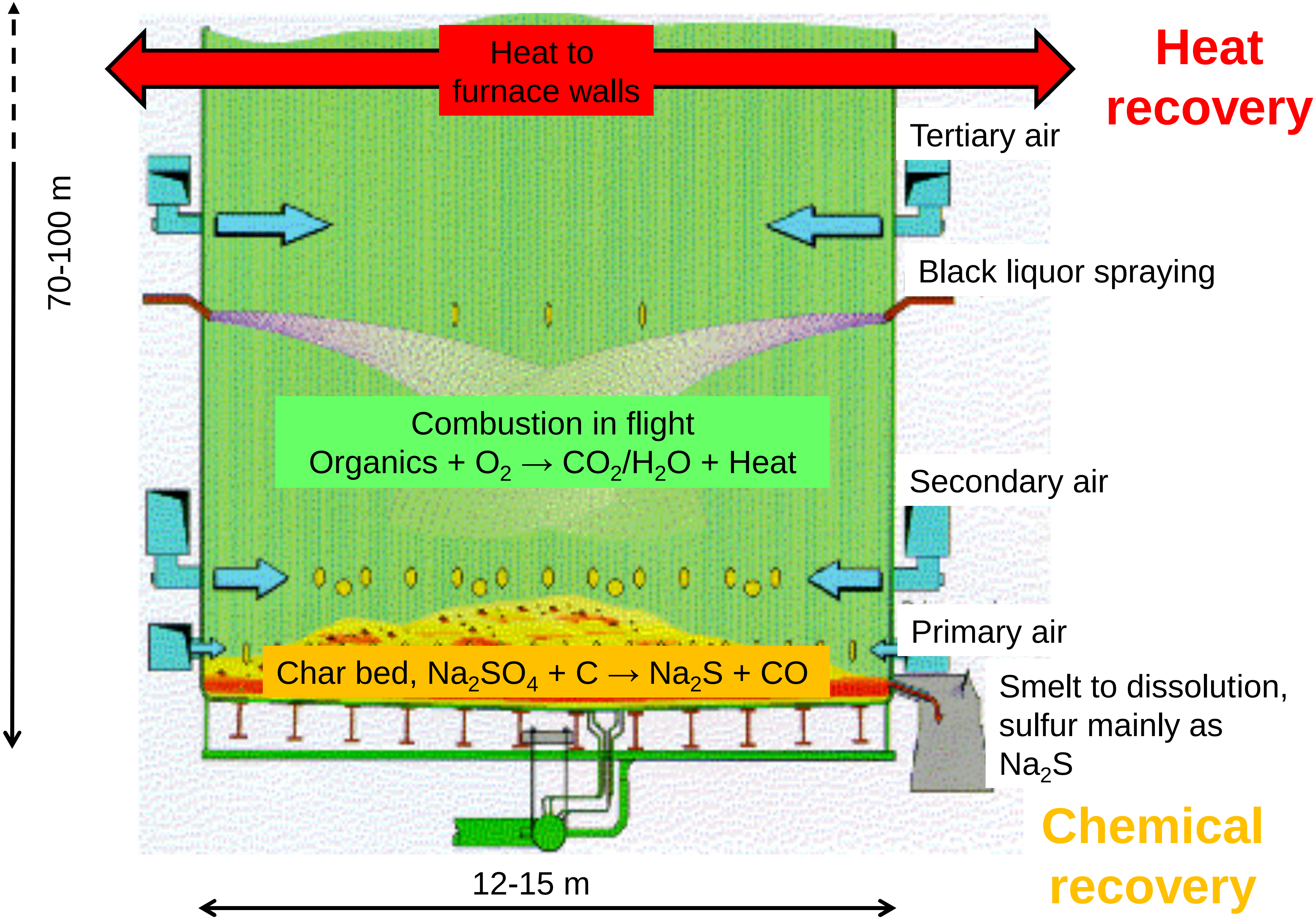
Objectives of Recovery Boiler

1. To burn the organic matter in black liquor for heat and steam production: Organics + O_2 = H_2O/CO_2

2. To convert chemicals back into valuable form:

   $Na_2SO_4 + 4C = Na_2S + 4CO$

3. Minimize emissions of SO_2, NO and CO_2



Heat recovery

Heat to furnace walls

Tertiary air

Black liquor spraying

Combustion in flight
Organics + $O_2 \rightarrow CO_2/H_2O$ + Heat

Secondary air

Primary air

Char bed, $Na_2SO_4 + C \rightarrow Na_2S + CO$

Smelt to dissolution, sulfur mainly as Na_2S

70-100 m

12-15 m

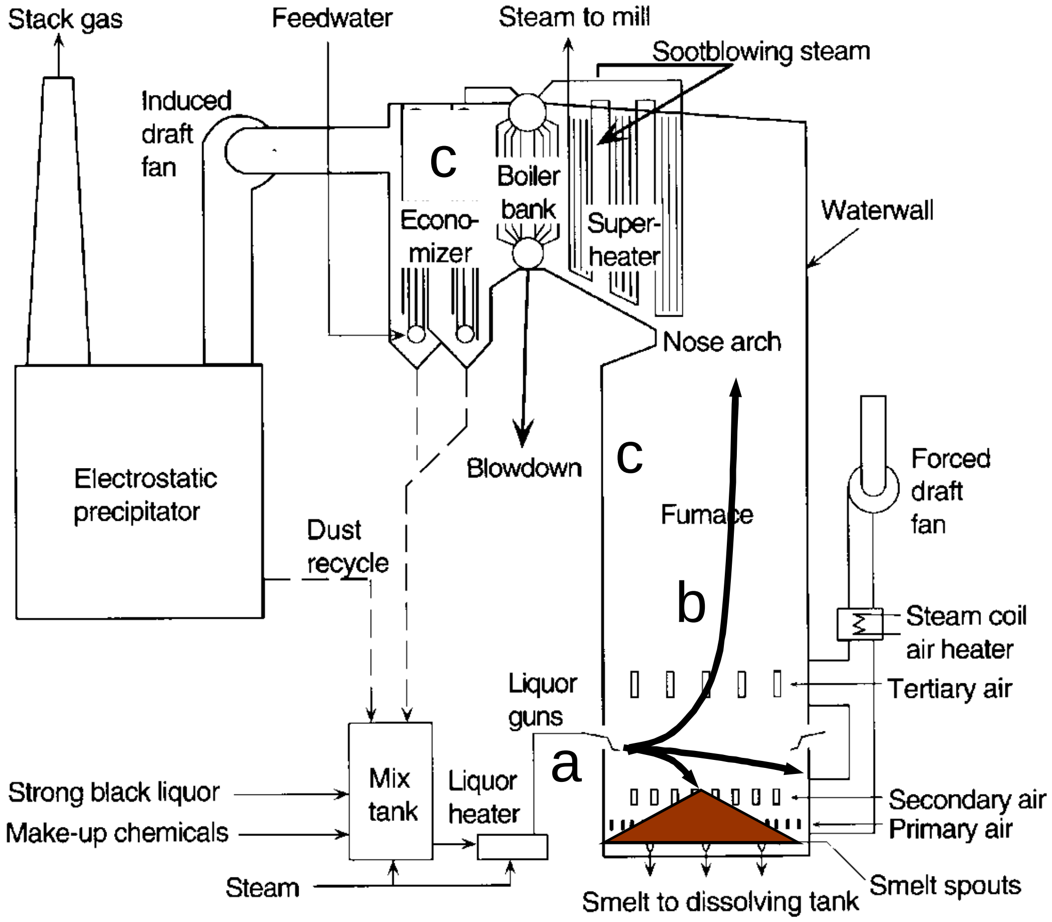
Chemical recovery

Recovery boiler schematic

a) Liquor is sprayed to the furnace

b) particles burn in furnace

c) combustion heat is recovered by heat exchangers

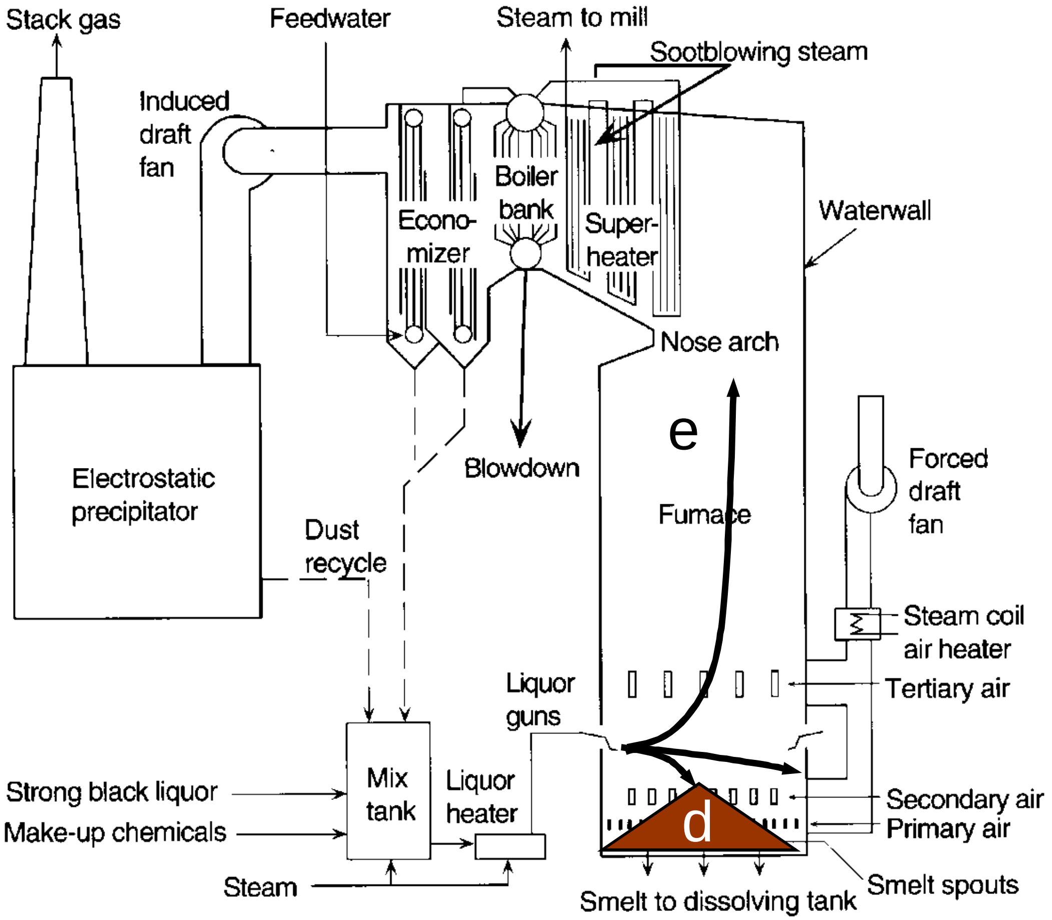


https://www.youtube.com/watch?v=ynC7xyOpaGc

Recovery boiler schematic

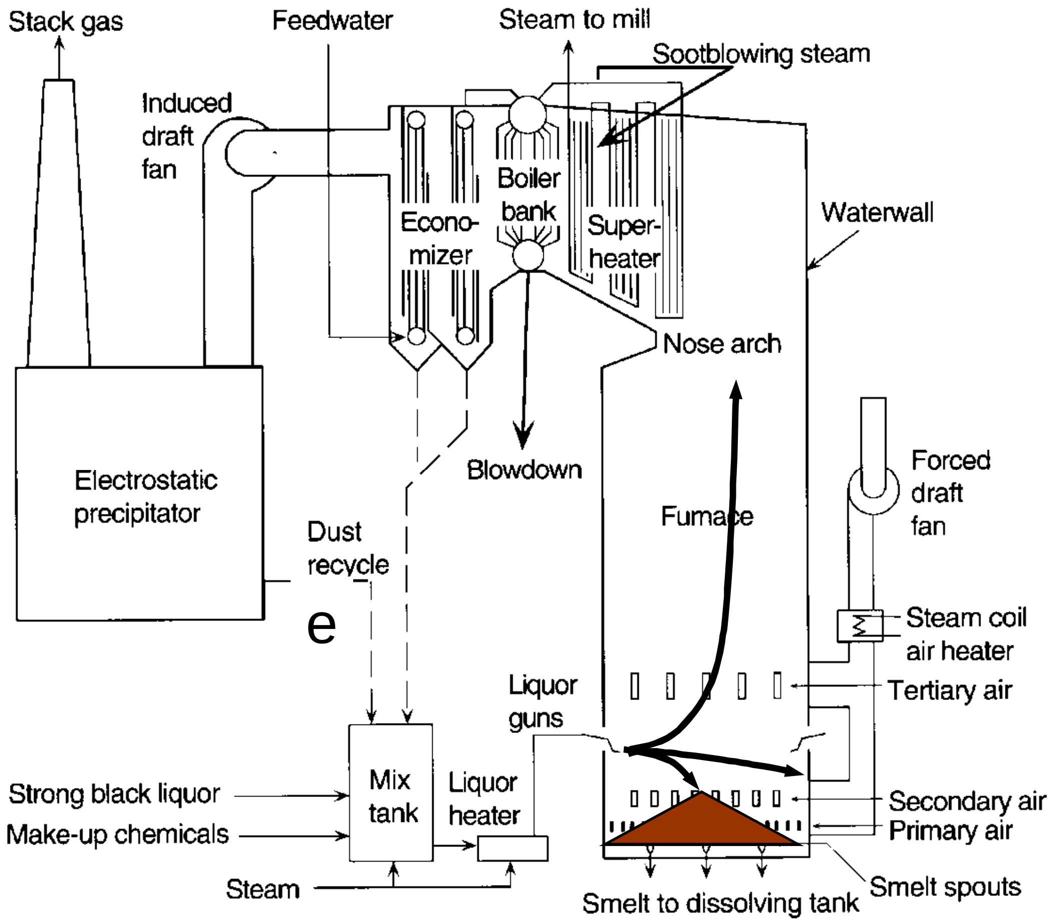
d) Large particles fall into char bed, Na_2SO_4 is reduced into Na_2S, smelt flows to dissolving tank

e) Small particles are entrained by flue gases



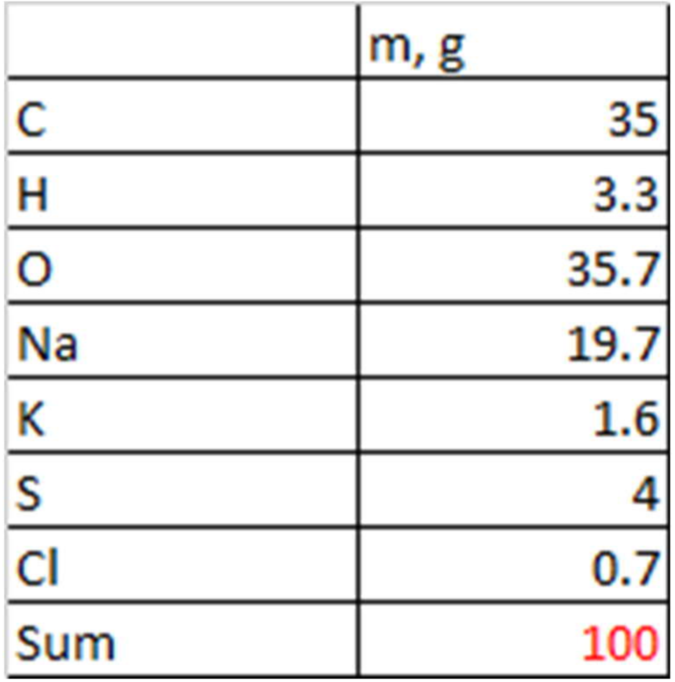
Recovery boiler schematic

d) Flue gas salts are captured at ESP and returned to mixing tank

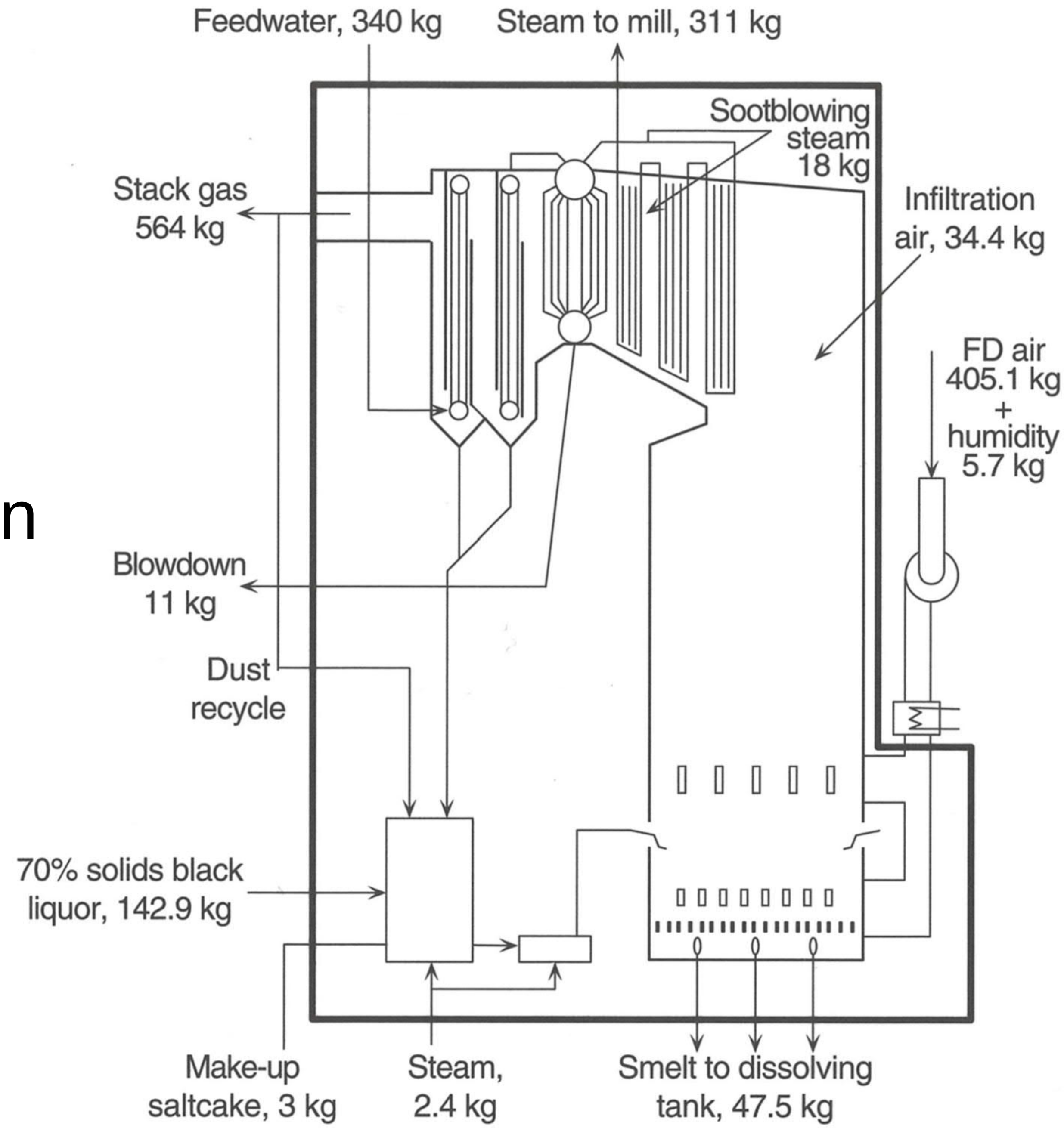


Material balance

This will be studied in the exercise 1 and 2 in detail



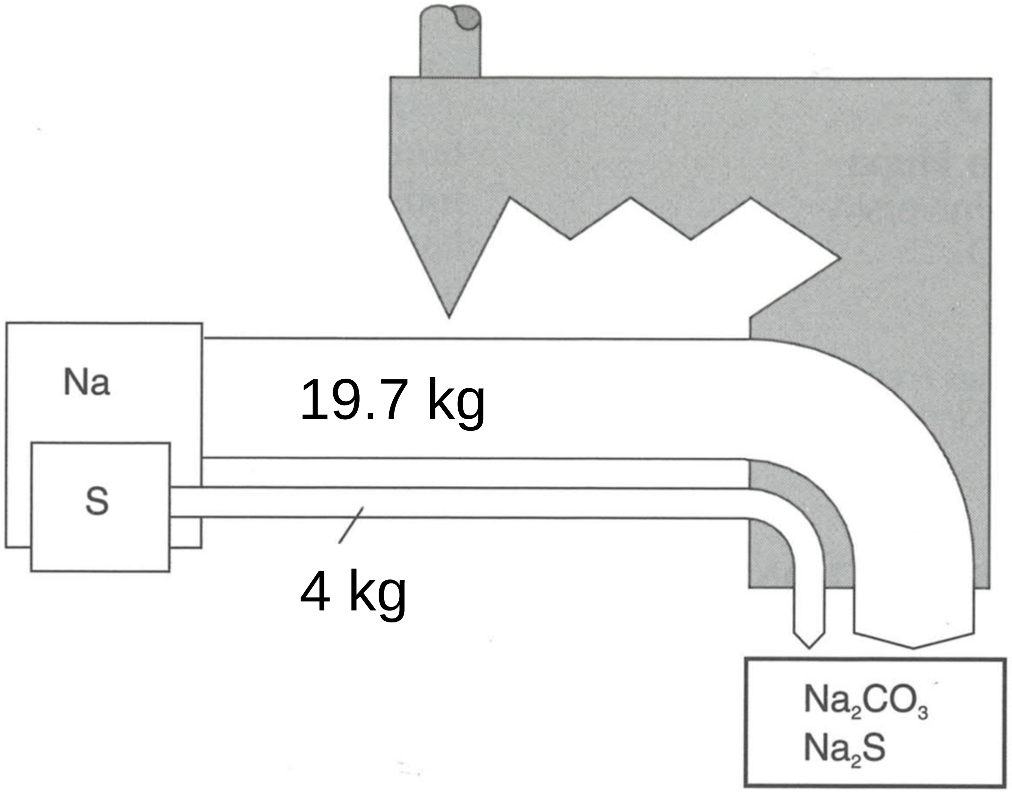
	m, g
C	35
H	3.3
O	35.7
Na	19.7
K	1.6
S	4
Cl	0.7
Sum	100



per 100 kg of dry solids

Ideal inorganic chemistry

- 100 kg dry solids
- In the ideal case, all sulfur is reduced to Na_2S and rest of the sodium forms Na_2CO_3
- Reduction degree is then $\eta = 100\%$.



$\eta = Na_2S / (Na_2S + Na_2SO_4)$

Na_2S and Na_2CO_3 are mixed with water to make green liquor

Summary

- Black liquor is the pulp and papermaking process liquid after chemical cooking and evaporation.
- Main functions of a recovery boiler are to recover chemicals and heat.
- 7 % of electricity need of Finland is obtained from black liquor, 1/3 of renewables.
- After the exercises 1 and 2, you know how to estimate material balance of a recovery boiler, the need of combustion air, the amount of flue gases and the amount of inorganics flowing out from the boiler.

Exercise 1

Day 2: Combustion

Pre-assignment 2: Read Material PA2 before the lecture

- Is the combustion of black liquor more similar to liquid or solid fuel combustion?
- What are main differences to traditional fuels?

Lecture 2: New Principles of black liquor combustion

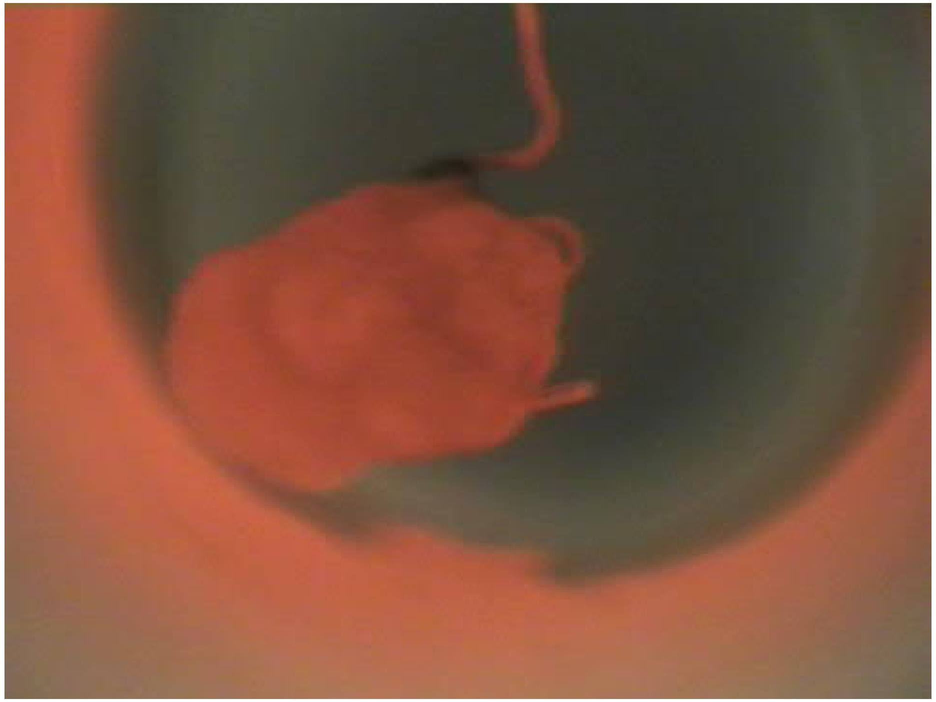
- Observations from combustion experiments and modeling.
- Importance of droplet size and swelling on flight and combustion behavior.

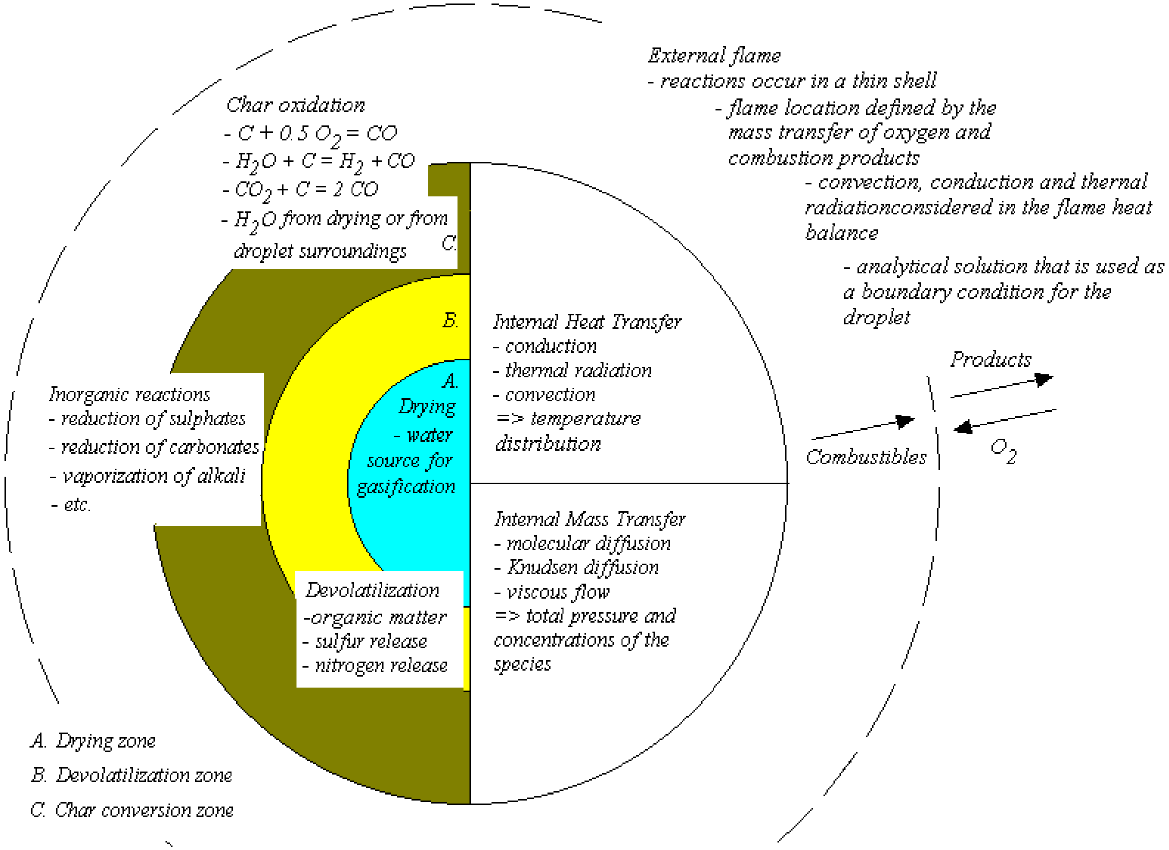
Exercise 2: Recovery boiler mass and species balance calculation part 2: Flue gas calculations based on day 1 results.

Intended learning outcomes

- To know the black liquor droplet combustion stages: drying, devolatilization, char conversion, smelt reduction and smelt re-oxidation
- To understand effect of particle size and swelling on the combustion and particle trajectories.
- In the Exercise 2, we continue from the last time, to learn to calculate the composition of flue gases from burning black liquor, and closing the boiler the mass balance.

Principles of droplet combustion + input from modeling work





External flame
- reactions occur in a thin shell
  - flame location defined by the mass transfer of oxygen and combustion products
    - convection, conduction and thermal radiationconsidered in the flame heat balance
      - analytical solution that is used as a boundary condition for the droplet

Char oxidation
- $C + 0.5\ O_2 = CO$
- $H_2O + C = H_2 + CO$
- $CO_2 + C = 2\ CO$
- H_2O from drying or from droplet surroundings

Inorganic reactions
- reduction of sulphates
- reduction of carbonates
- vaporization of alkali
- etc.

Internal Heat Transfer
- conduction
- thermal radiation
- convection

=> temperature distribution

Internal Mass Transfer
- molecular diffusion
- Knudsen diffusion
- viscous flow

=> total pressure and concentrations of the species

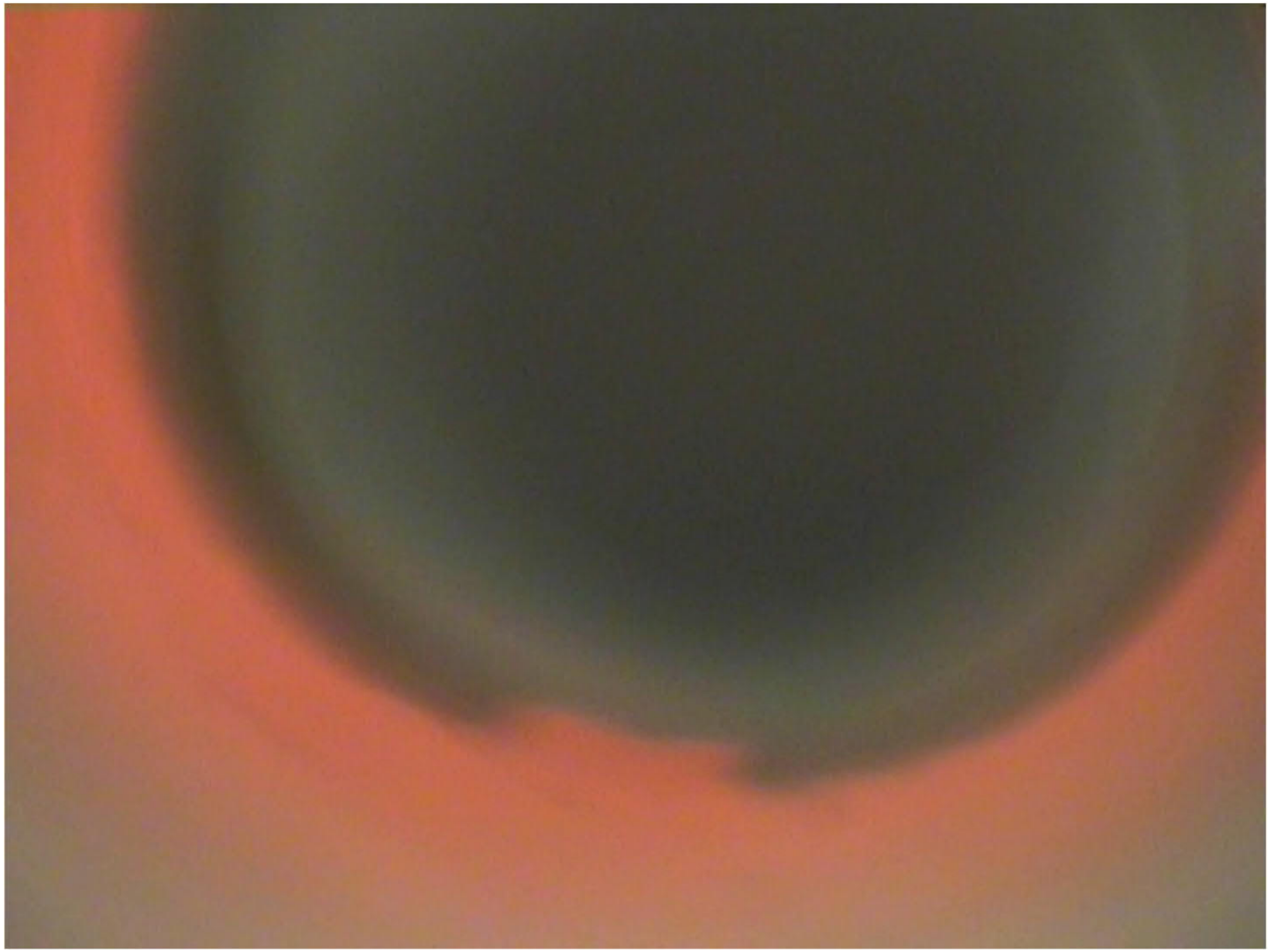
Devolatilization
-organic matter
- sulfur release
- nitrogen release

A. Drying
- water source for gasification

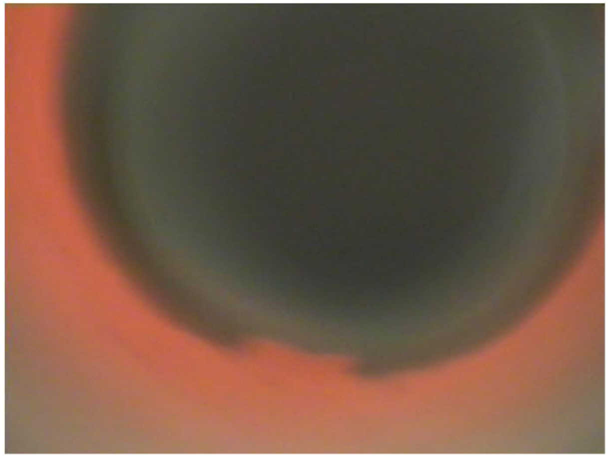
A. Drying zone
B. Devolatilization zone
C. Char conversion zone

Combustion experiment

- Combustion of a single 10 mg droplet in 800°C, 3% O_2
- Courtesy of ÅA University, Hupa’s group, co-operation in modeling and experiments



Heat-up and drying



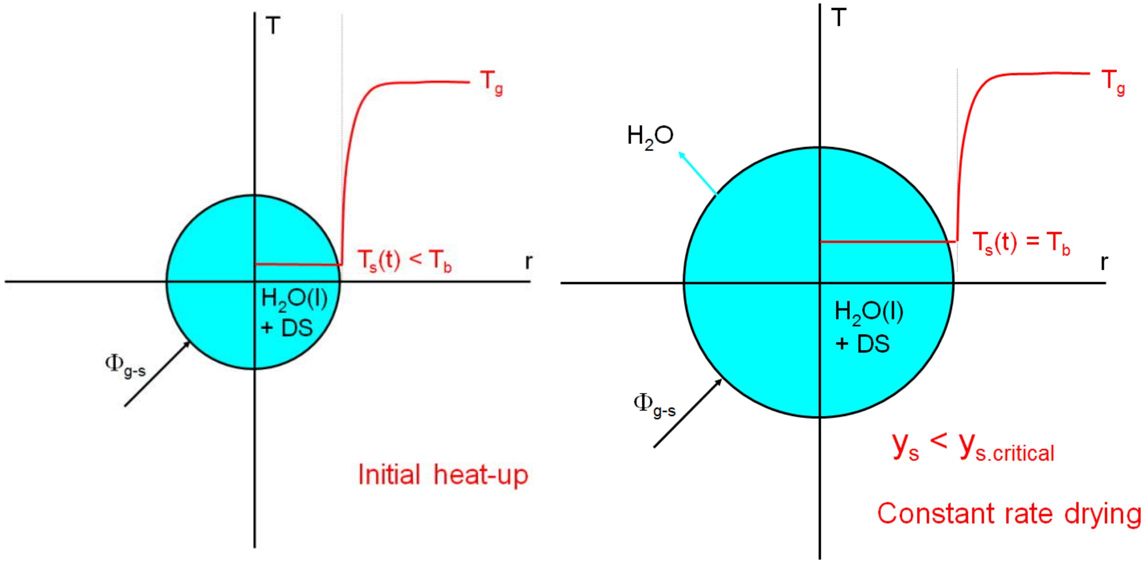
water
20 %

Dry solids
content
80%

Dries in
0.5 s

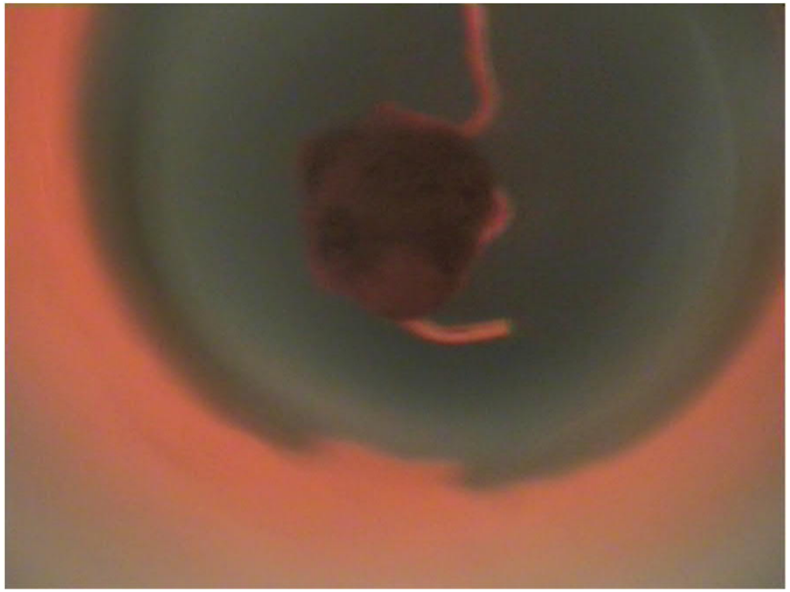
Organic
matter
60 %

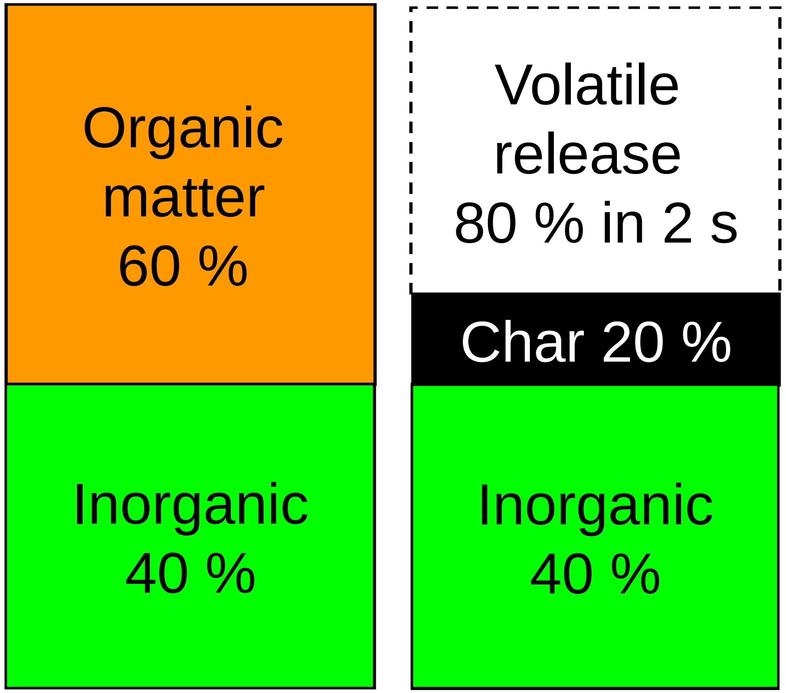
Inorganic
40 %

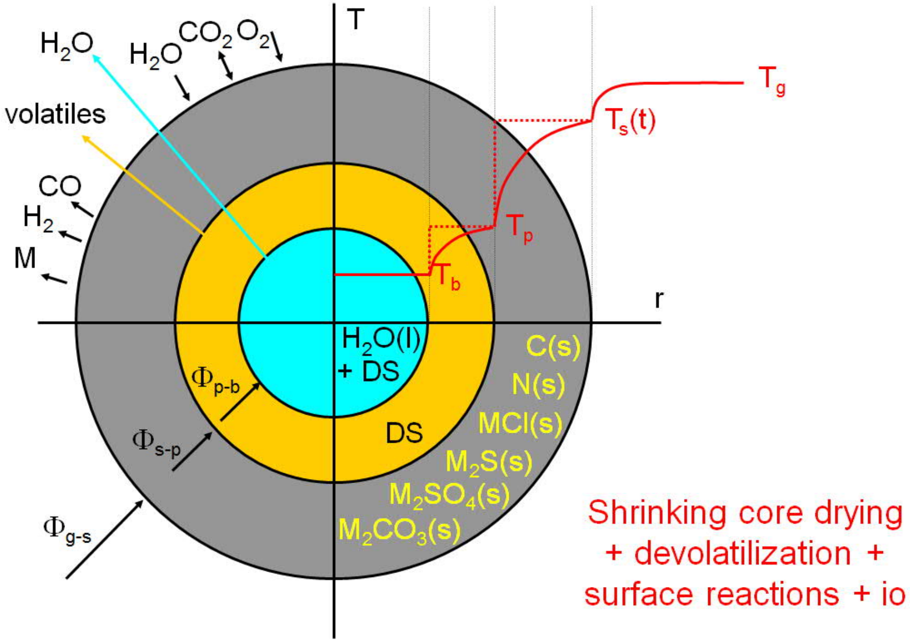


- Droplet heats up to 150°C
- Boiling and swelling to 1.5 times initial size
- Heat transfer controlled process

Pyrolysis

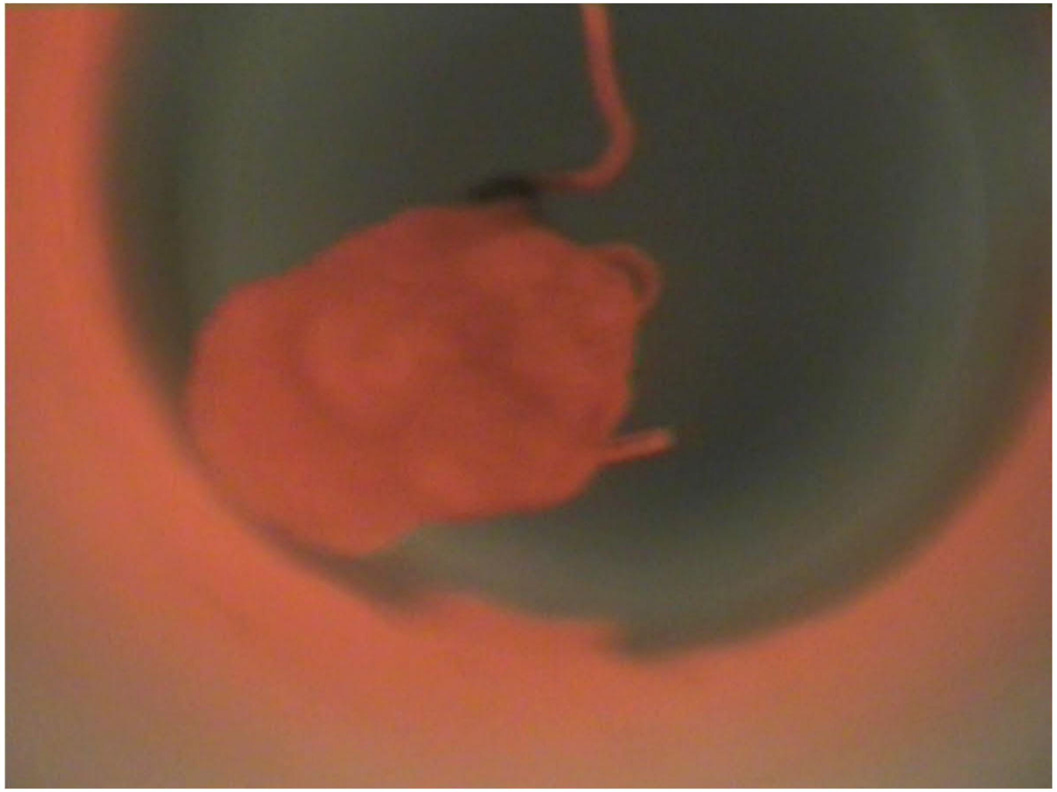


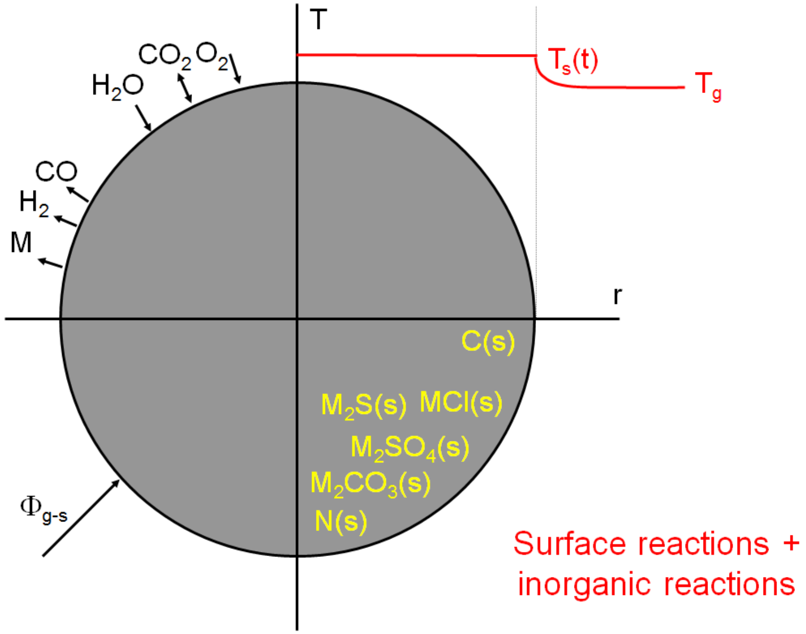




- Temperature increases and organics decompose
- Swelling 3 times initial size
- Overlapping stages
- Heat transfer controlled

Char burning





Surface reactions + inorganic reactions

Char reactions 18 s

Char 20 %

Inorganic 40 %

Char 20 %

Na_2S

Na_2CO_3

- Oxidation by H_2O, CO_2 and O_2 mass transfer controlled
- Reduction $Na_2SO_4 + 4C \rightarrow Na_2S + 4CO$ chemically controlled

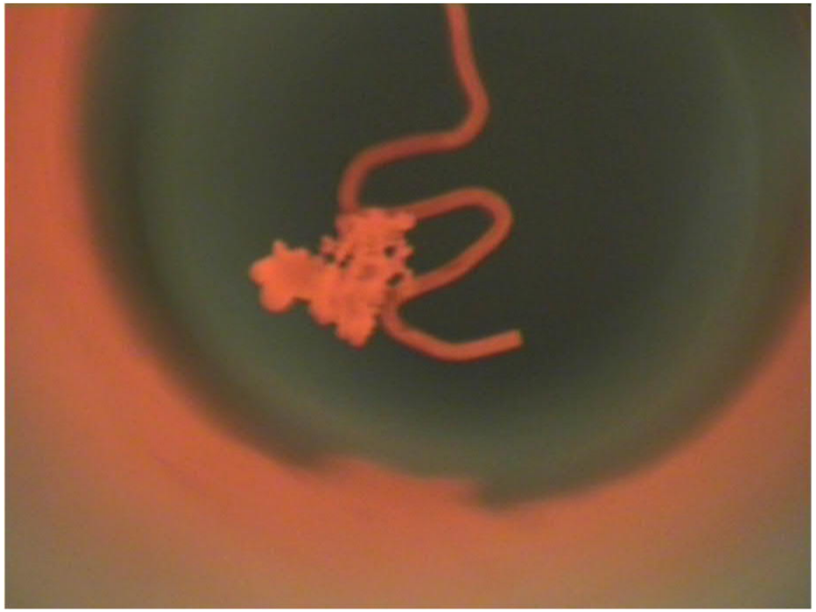
Char reactions

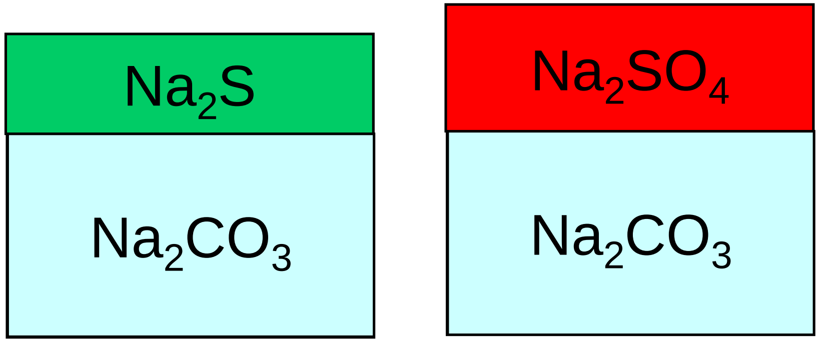
$\text{Char} + 0.5O_2 \rightarrow CO$
$\text{Char} + H_2O \rightarrow CO + H_2$
$\text{Char} + CO_2 \rightarrow 2\,CO$

When O_2 reaches particle surface, it will react to CO. Very fast and exothermic reaction.

Endothermic gasification reactions are slower than O_2 oxidation (H_2O reactions faster than CO_2). However, as O_2 concentration in furnace is low < 5 %-vol, these reactions play a major role.

Smelt reactions





Na_2S

Na_2CO_3

Na_2SO_4

Na_2CO_3

While char is present, sulfate is reduced

$\text{Char} + Na_2SO_4 \rightarrow Na_2S + CO_2$

Without char we have un-wanted re-oxidation

$Na_2S + O_2 \rightarrow Na_2SO_4$

Reduction of sulfate

$Na_2SO_4 + 2\ C \rightarrow Na_2S + 2\ CO_2$

Sulfate Na_2SO_4 in black liquor will consume char effectively. One of the main objectives of recovery boiler is to recovery inorganic cooking chemicals. This reaction produces desired Na_2S. Trhe effectiveness of the reduction is determined by the “Reduction ratio” R.

R ~ [sulfur in Na_2S] / [sulfur in Na_2S+ sulfur in Na_2SO_4]

Reduction of sulfate

In modern boilers R > 0.95. Another important reaction here is the oxidation of sulfide Na_2S

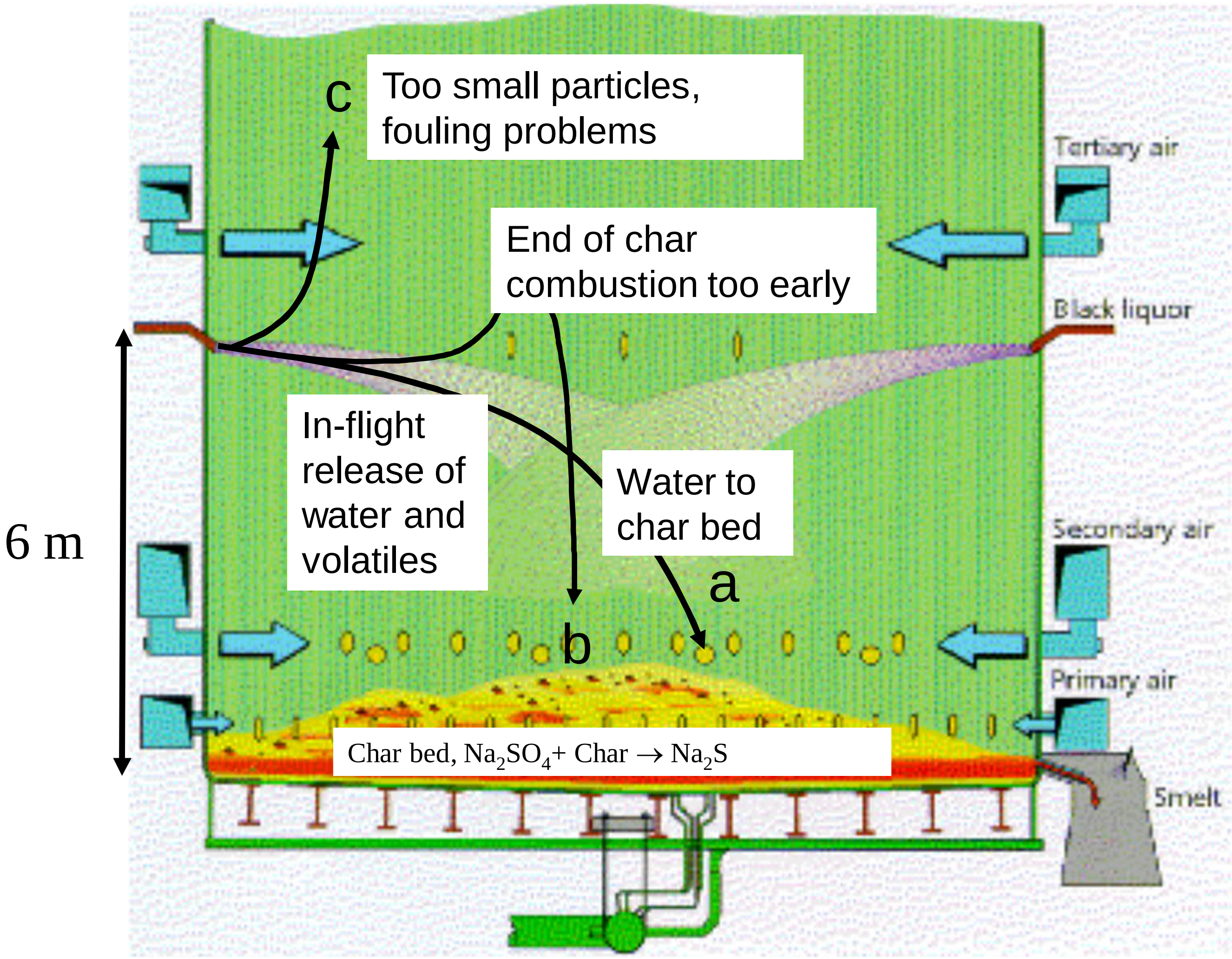
$$Na_2S + 2\ O_2 \rightarrow Na_2SO_4$$

This is not desired *during in-flight* combustion as is consumes valuable sulfide Na_2S. However, combination of these two reactions may form an important char conversion route in *char bed* referred as “sulfide-sulfate cycle”.

In-flight combustion

Droplet size and swelling affects to trajectory

https://www.youtube.com/watch?v=ynC7xyOpaGc



Too small particles, fouling problems

End of char combustion too early

In-flight release of water and volatiles

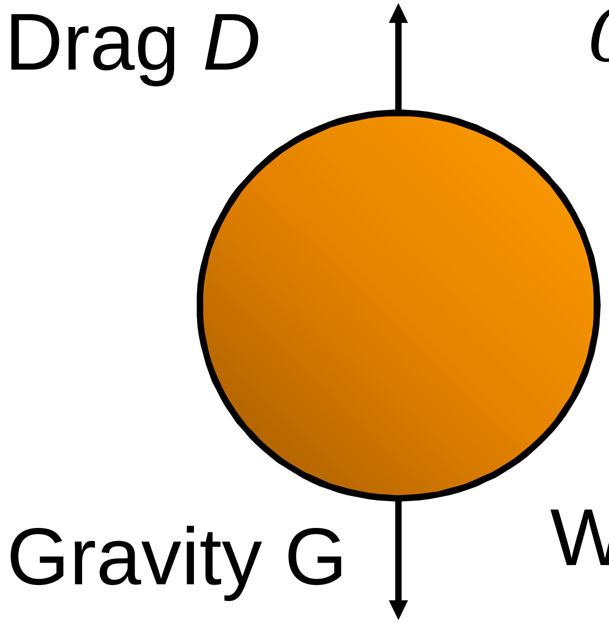
Water to char bed

Char bed, Na_2SO_4+ Char → Na_2S

a. Too large, ends up to char bed while still wet
b. Char burnout in flight, poor reduction
c. Too small, carry over formation

I need a volunteer ☺

Terminal velocity



Drag *D*

Gravity G

$$D = C_D A \rho \frac{\left(u_g - u_p\right)^2}{2} = C_D \frac{\pi}{4} d_p^2 \rho_g \frac{\left(u_g - u_p\right)^2}{2}$$

$$G = m_p g = \frac{\pi}{6} d_p^3 \rho_p g$$

$$C_D = 27 Re^{-0.84}, Re < 80$$

$$C_D = 0.271 Re^{0.217}, Re > 80$$

When droplet is levitating $u_p = 0$ and $G = D$

$$C_D(d_p, u_g)\, \rho_g {u_g}^2 = \frac{4}{3} d_p \rho_p g \longrightarrow u_g$$

Terminal velocity

Levitation of a Styrox ball

$\rho_p = 14$ kg/m^3

$d_P = 40$ mm

measured 4.9 m/s,
calculated 5.1 m/s

$d_P = 56$ mm

measured 7.3 m/s,
calculated 5.8 m/s

Effect of droplet size on reaction time

$$\dot{N}_{O_2} = h_m \pi d^2 c_{O_2} = \frac{2D_{O_2}}{d}\pi d^2 c_{O_2}$$

$$= -\frac{\pi}{2} d^2 \frac{\rho_C}{M_C}\frac{dd}{dt}$$

$$-\frac{dN_C}{dt}$$

BL: $\rho_C = 0.02$ g/cm^2

Coal: $\rho_C = 1\text{-}2$ g/cm^2

Char combustion time

$$t = Kd^2 = \frac{\rho_C}{8M_C D_{O_2} c_{O_2}} d^2$$

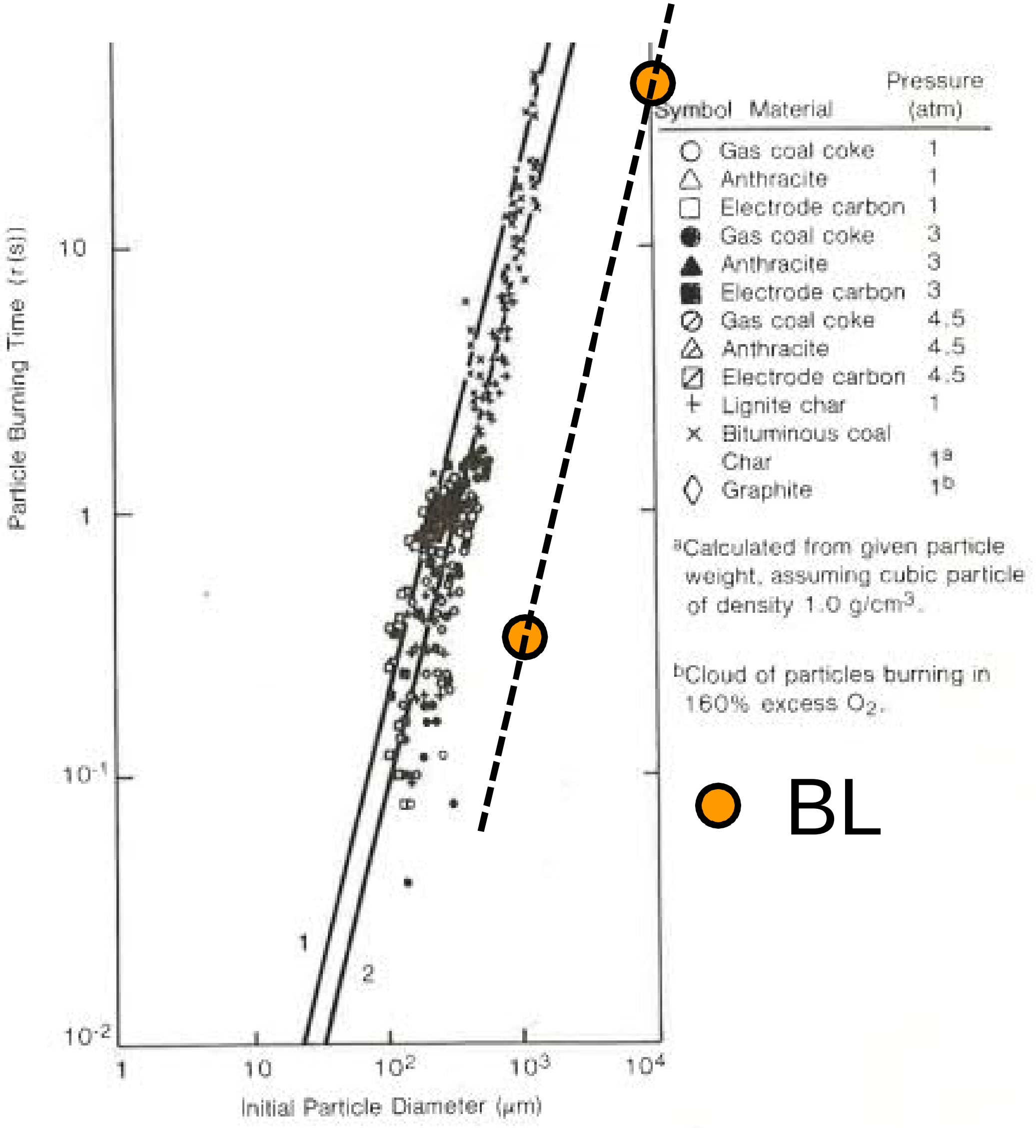
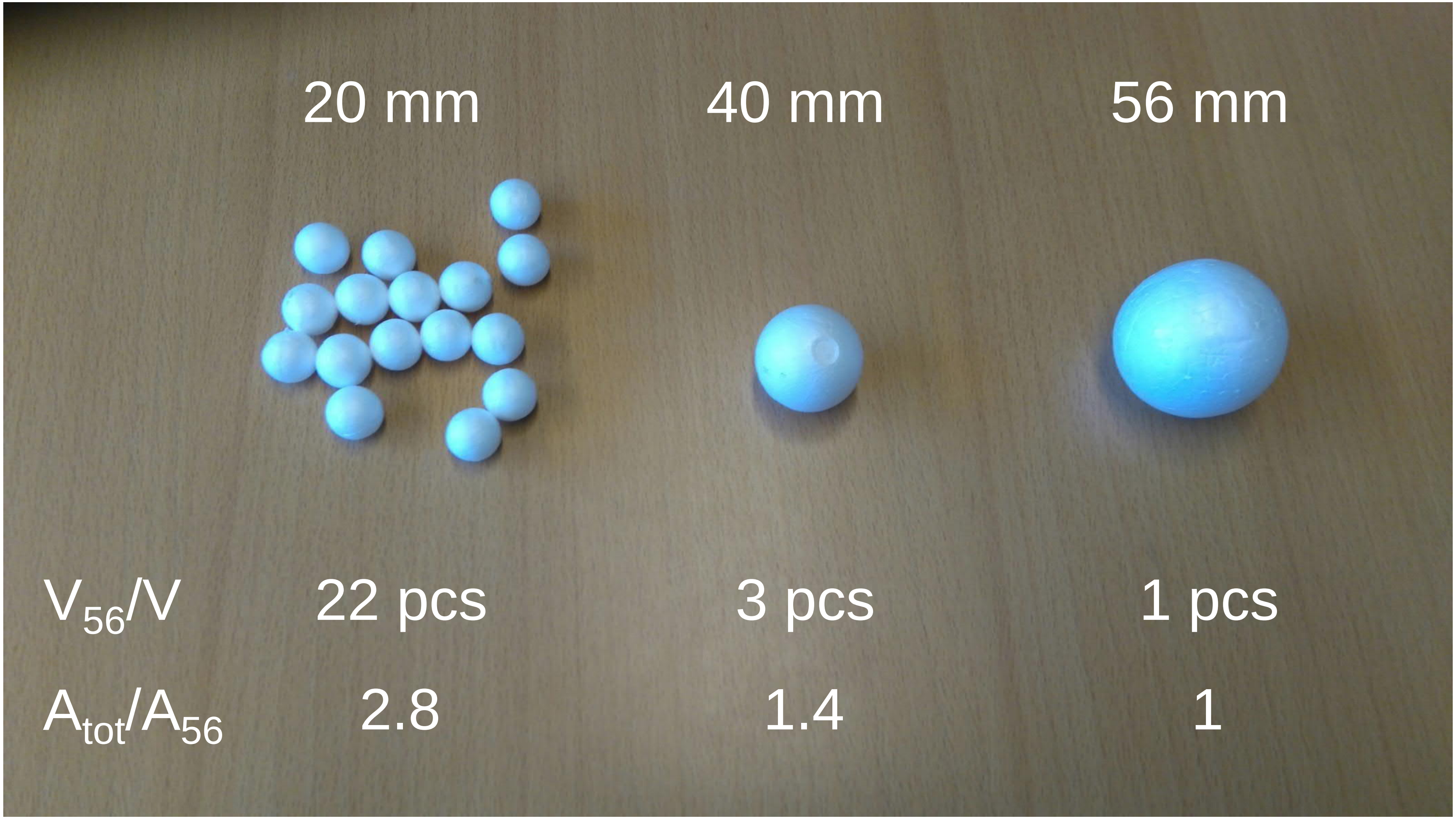


Figure 5.4. Comparison of experimental and theoretical particle burning times. 21% v/v O_2, calculated from Eqn. 5.3 for 1500 K. Curve 1: $\rho_{ap} = 2.0$ g/cm^3. Curve 2: $\rho_{ap} = 1.0$ g/cm^3. (Figure used with permission from Essenhigh, 1981.)

Smaller droplets, more area for same volume, higher rate of reaction



	20 mm	40 mm	56 mm
V_{56}/V	22 pcs	3 pcs	1 pcs
A_{tot}/A_{56}	2.8	1.4	1

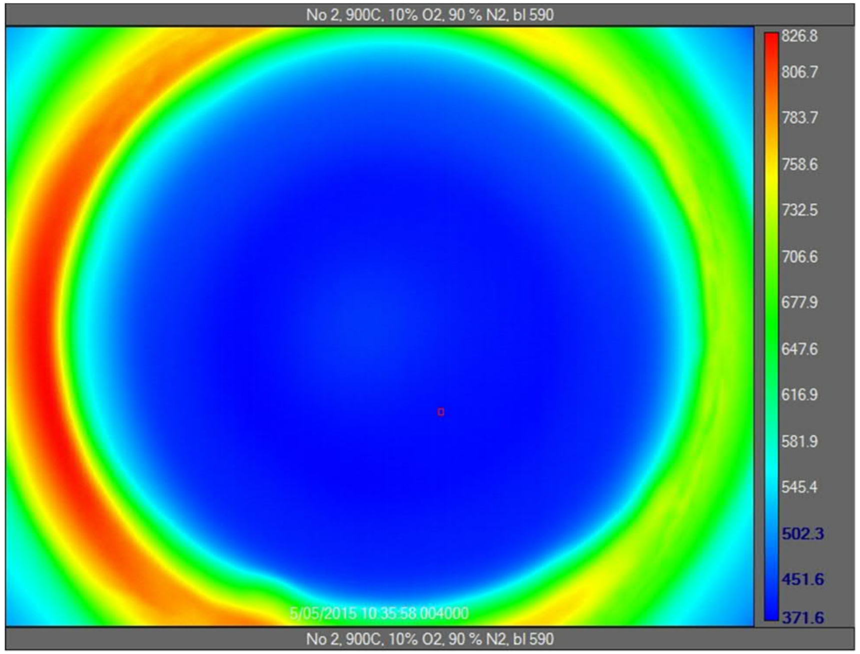
Was this all there is?

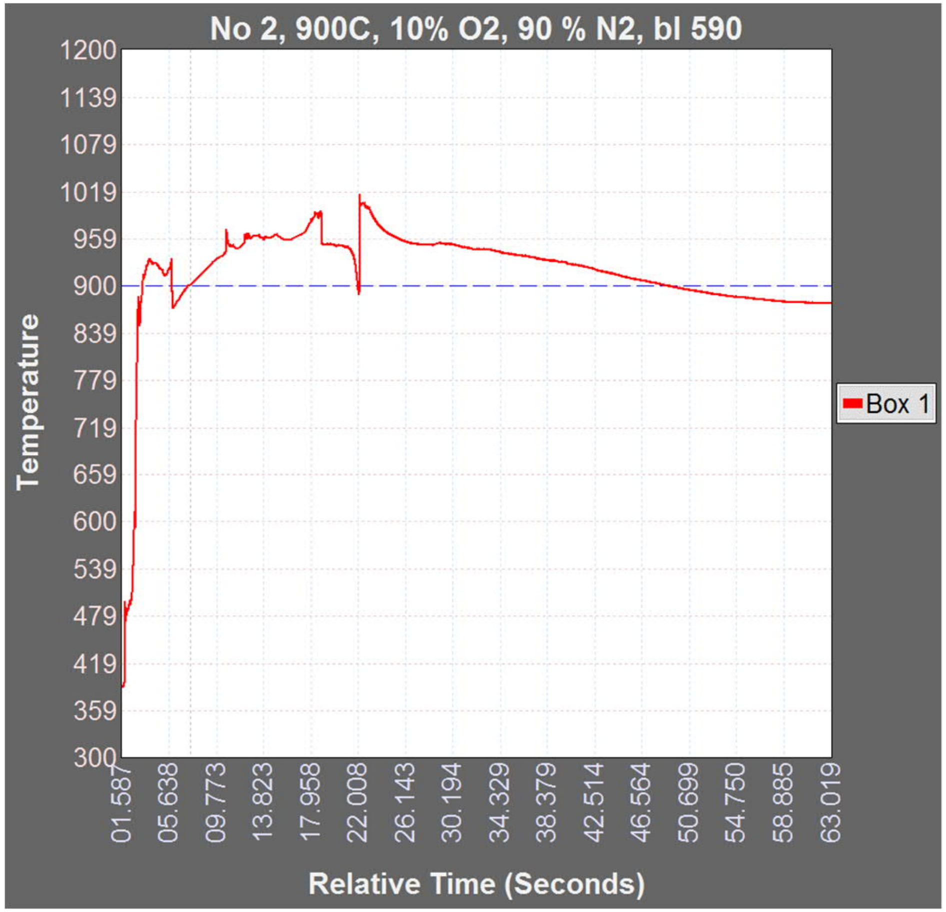
- The previous videos showed us very useful information on the combustion characteristics; swelling and duration of the combustion stages can be measured.
- Using thermal IR camera technology, we can obtain much more detailed information on the single droplet combustion characteristics, such as temperature distribution of the particle surface, and we can also measure releasing gas species.

Modern experimental methods

- Our FLIR SC6700 MWIR Medium Wave Infrared camera has been successively used for droplet studies in collaboration with ÅA/Turku but also in furnace spray studies.

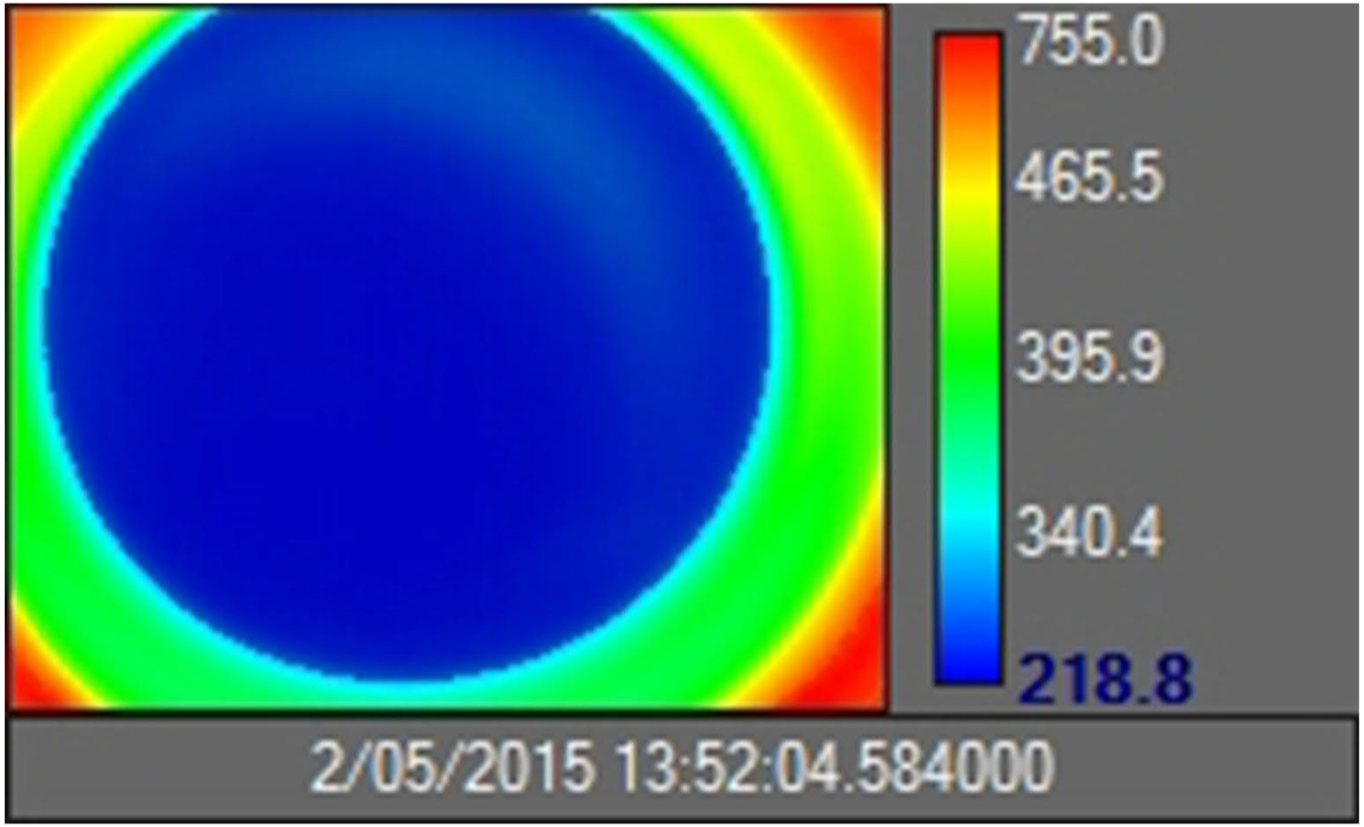
Temperature measurement





Droplet combusted in $10\%\ O_2$, 900 °C environment

New phenomena during smelt reactions



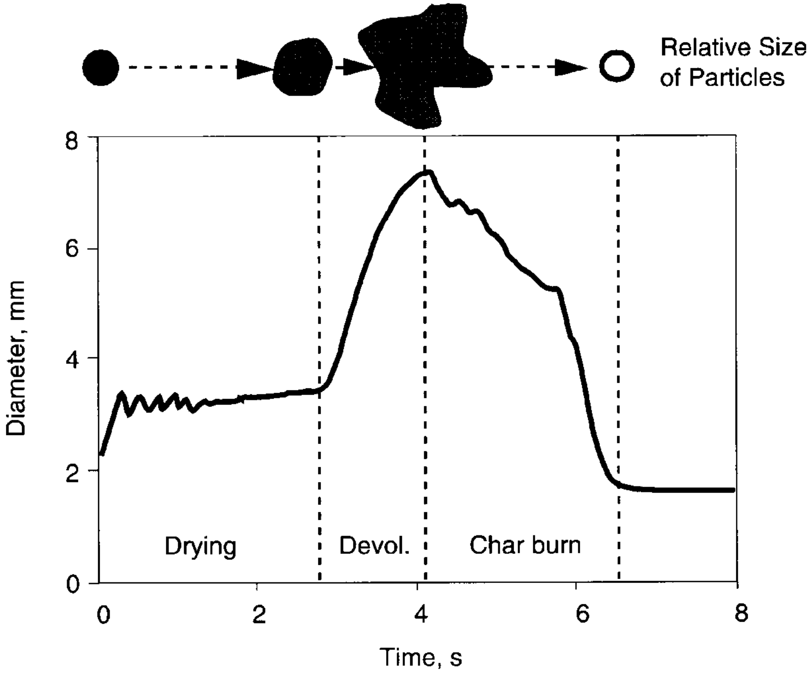
Something is vigorously released after the char combustion is complete.

Droplet combustion summary

- significant swelling during pyrolysis, this affects greatly both on trajectory and reaction rates

- char reactivity is very high mainly due to highly swollen structure

- Inorganic reactions are also important



- Modeling can be effectively used to better understand experimental observations
- Terminal velocity is important parameter defining the carry over formation, you will learn to calculate this is in LE5.
- The world is not ready yet, plenty to discover still, welcome to do your PhD studies ☺

Exercise 2

Day 3: Spraying, individual work

Pre-assignment 3: Read Material PA3 before the lecture

- What are the main targets in black liquor spraying?

Lecture 3: Black liquor spraying

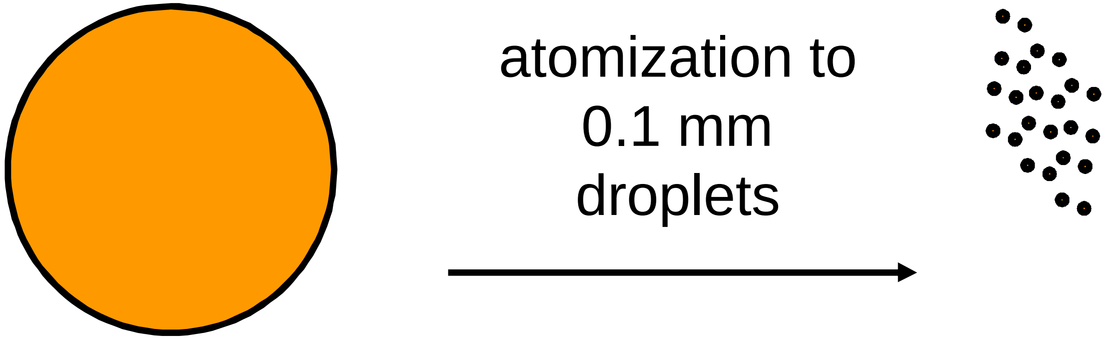
- Objectives of spraying.
- Spraying related physical properties of black liquor,
- Basic processes in black liquor atomization, breakup regimes.
- Spray characterization.
- Controlling of spray properties.

Intended learning outcomes

- To understand main objectives in black liquor spraying.
- To know the typical spraying practice and liquor gun type, splashplate, of a modern boiler.
- To know the principles of spraying under flashing conditions.
- To learn to calculate mass median diameter from droplet size distribution.

General

- In spraying, a large amount of liquid in broken into smaller volumes = atomization
- At the same time the surface area through which the transfer processes take place increases significantly
- Reaction time decreases as size decreases



one 10 cm sphere

0.031 m^2 surface area

atomization to 0.1 mm droplets

10^9 x 0.1 mm drops

A = 31 m^3

Spraying in different applications

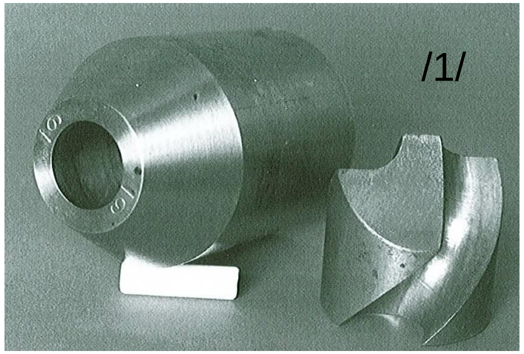
- Atomization is used in many applications
  - Food processing (instant coffee, coating)
  - Medical industry (pulverization, coating)
  - Energy application (combustion, flue gas cleaning, spray cooling)
  - Internal combustion engines
  - Painting and printing applications
  - Fire sprinklers
- Depending on application, the requirements for the droplets and sprays can be very different

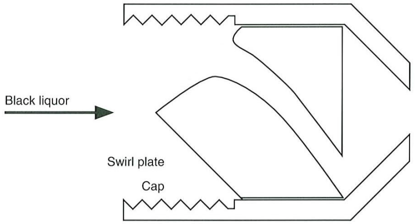
Droplet size in different applications

- Painting applications 5-100 μm
- Combustion
  - Oil combustion 10-500 μm
  - Black liquor combustion 1 – 10 mm
  - Black liquor gasification 100-300 μm
  - Diesel engines 1-10 μm
- Fire sprinklers 100-1000 μm

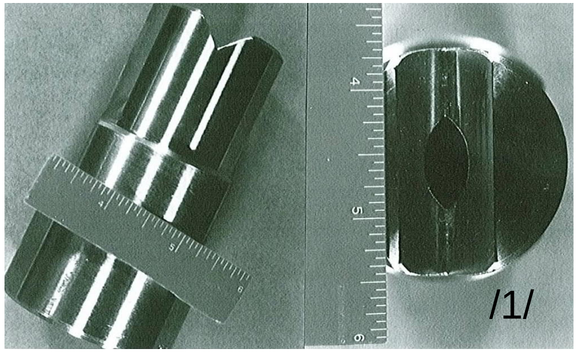
Spray nozzles used for black liquor

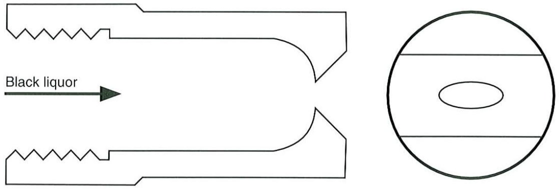
Swirl-cone



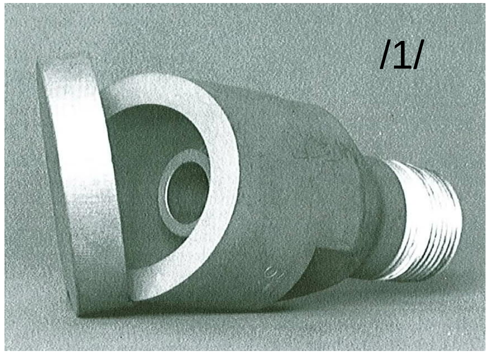


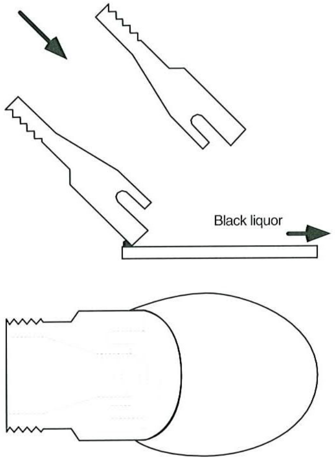
V-jet



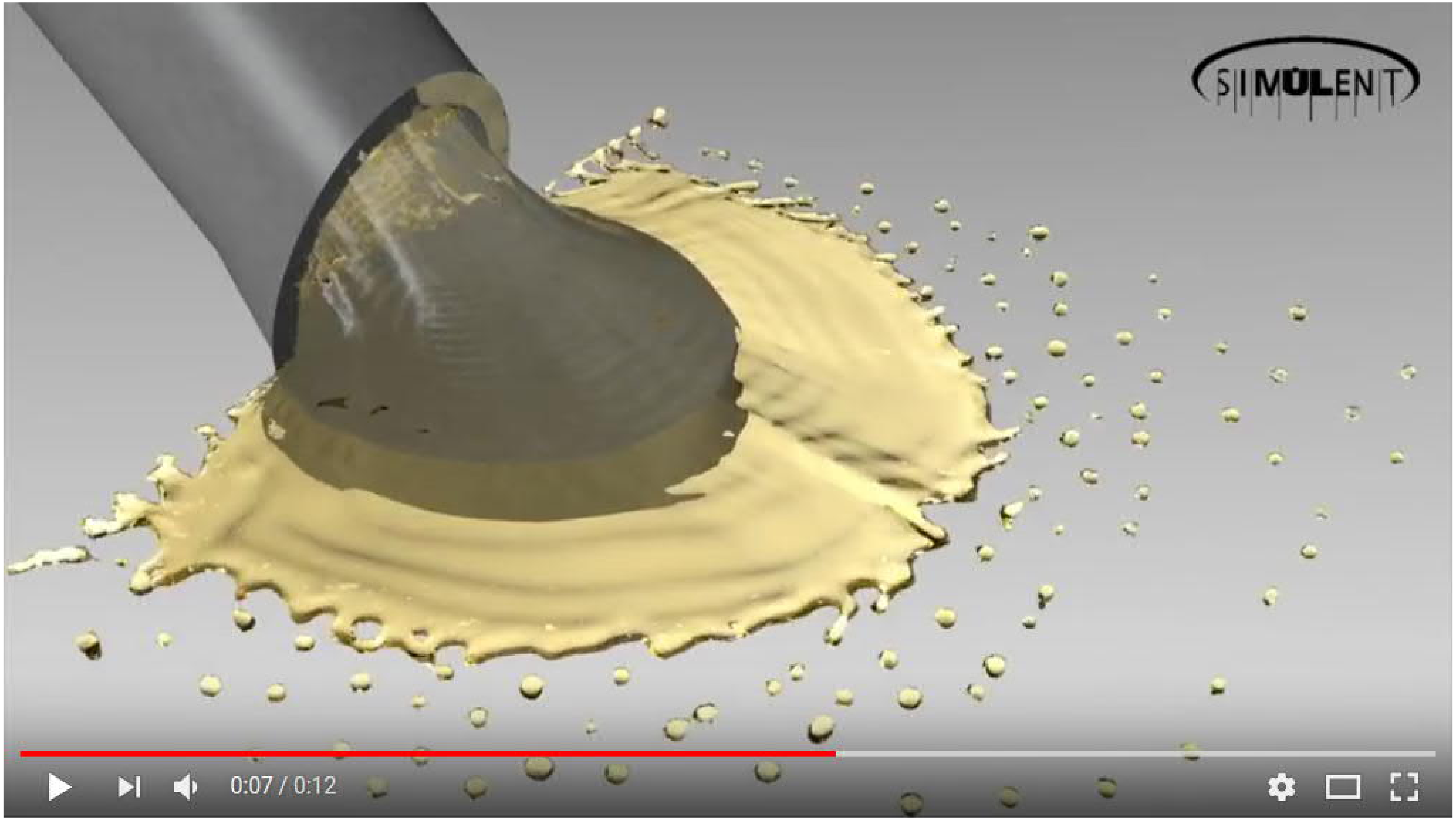


Splashplate





Splashplate nozzle

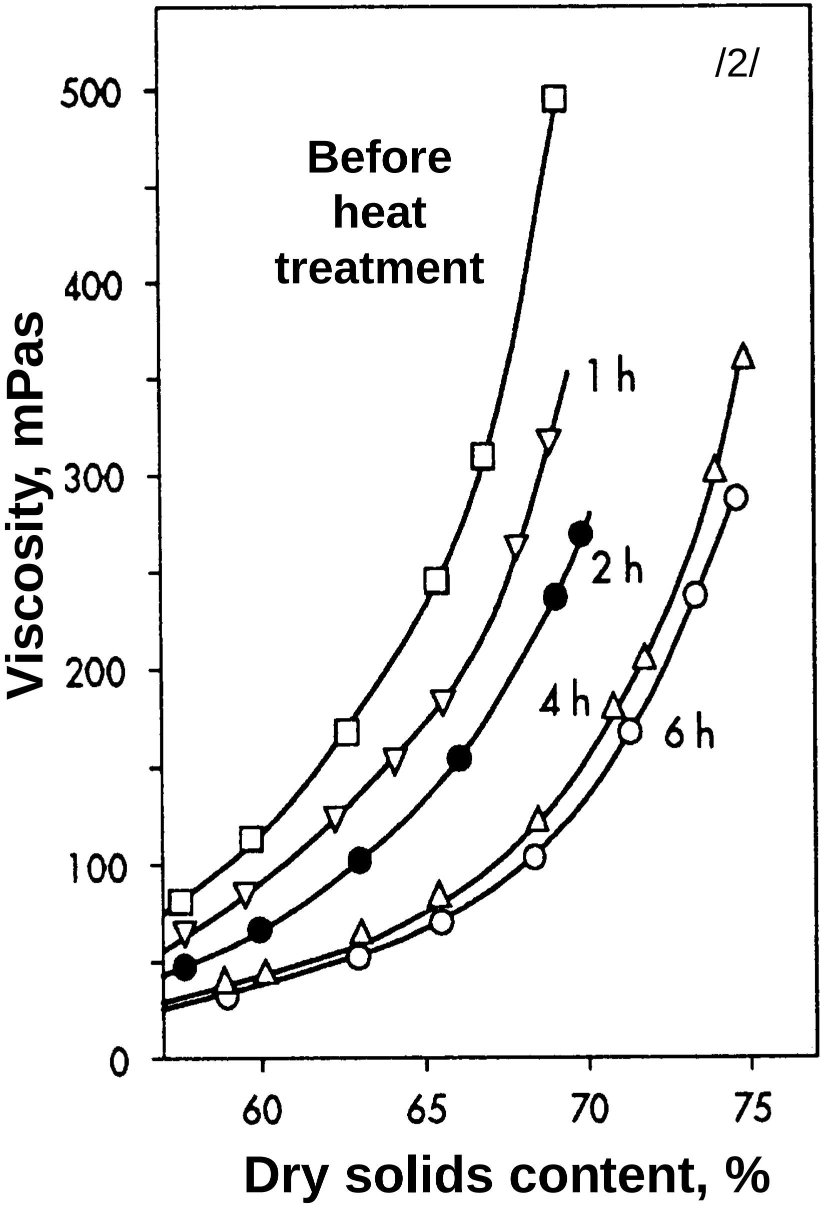


https://www.youtube.com/watch?v=c68wHih1Dk8

Spraying related physical properties of black liquor

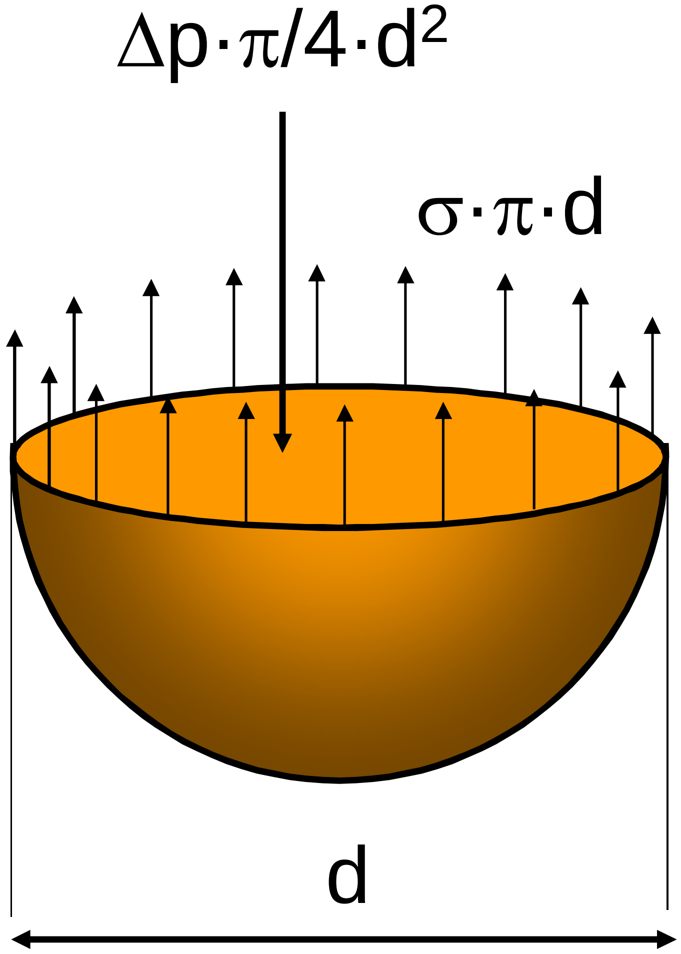
Viscosity

- At room temperature, black liquor is in solid form
- In order to pump and spray liquor, it has to be heated up to 120-150 °C.
- By heat treatment, viscosity can be reduced effectively.



Surface tension

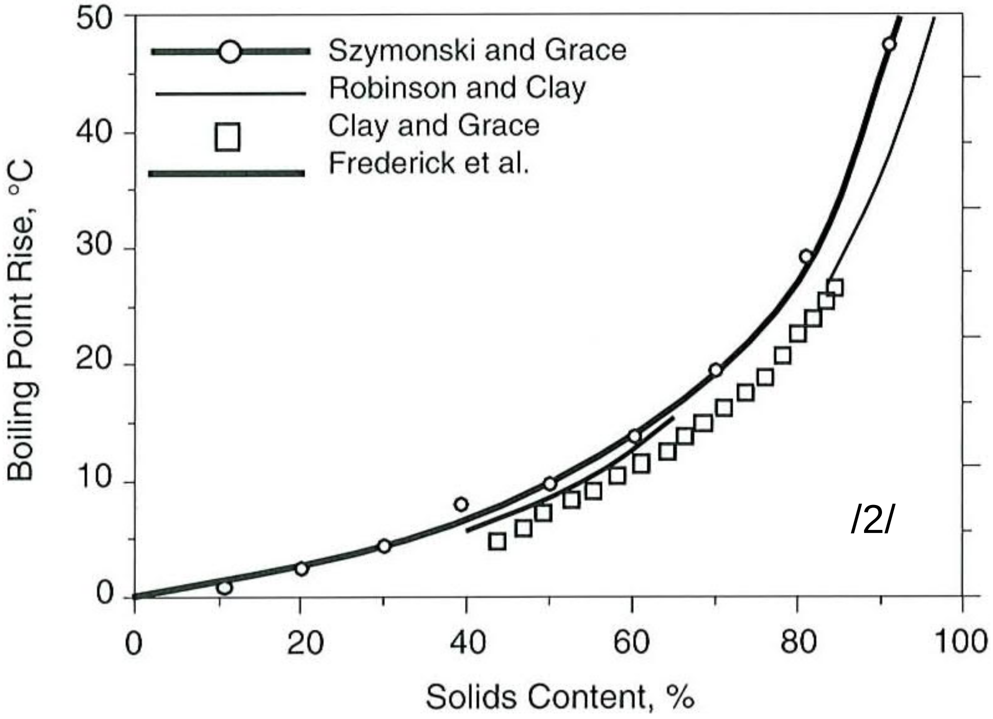
- Surface tension is the length unit force that holds to droplet in a spherical shape against internal pressure Δp
- Black liquor $\sigma \sim 0.05$ N/m, water $\sigma = 0.07$ N/m, liquid iron $\sigma \sim 1$ N/m
- $d = 0.01$ mm, $\Delta p = 20000$ Pa
- $d = 0.1$ mm, $\Delta p = 2000$ Pa
- $d = 1$ mm, $\Delta p = 200$ Pa



$$\Delta p = 4\sigma/d$$

Boiling point rise BPR

- BPR = atmospheric boiling point of black liquor – 100 °C
- Black liquor is heated up to 120-150 °C.



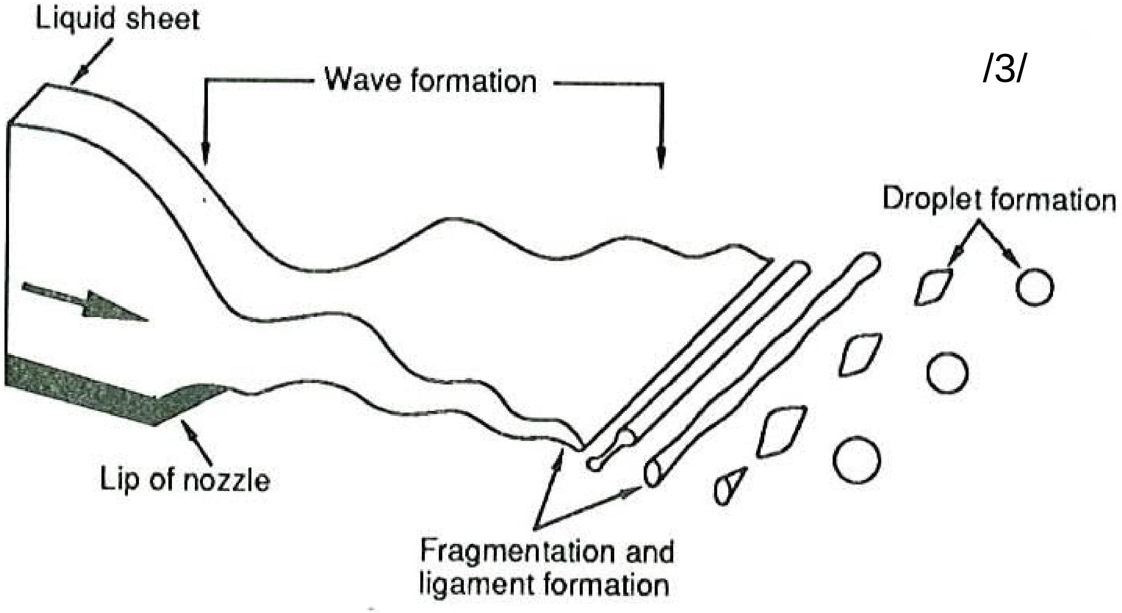
/2/

- Temperature is above atmospheric boiling point by 5…20 °C → liquor will boil during spraying process when pressure decreases in the nozzle

Basic processes in black liquor atomization

Breakup of liquid sheets, wavy breakup

- In non-flashing case the sheet is affected by inertial and aerodynamic forces
- These make the sheet to oscillate and finally to breakup into ligaments



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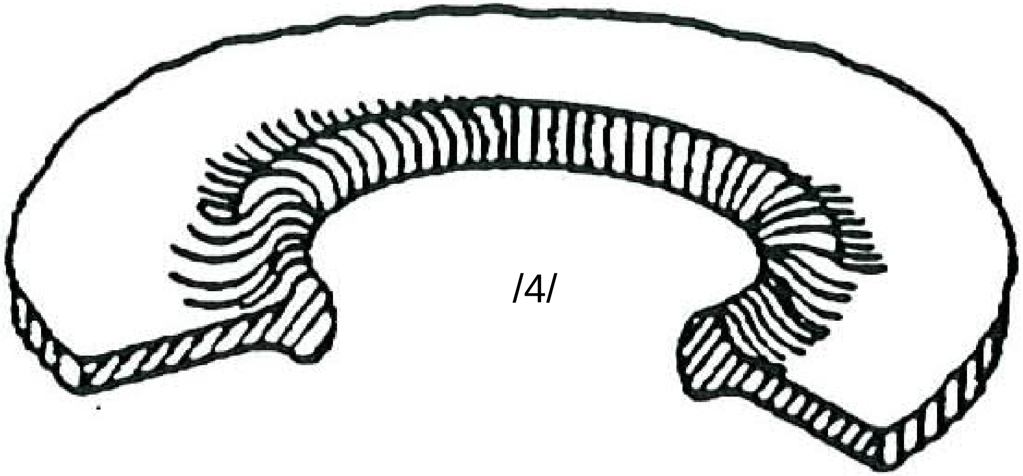
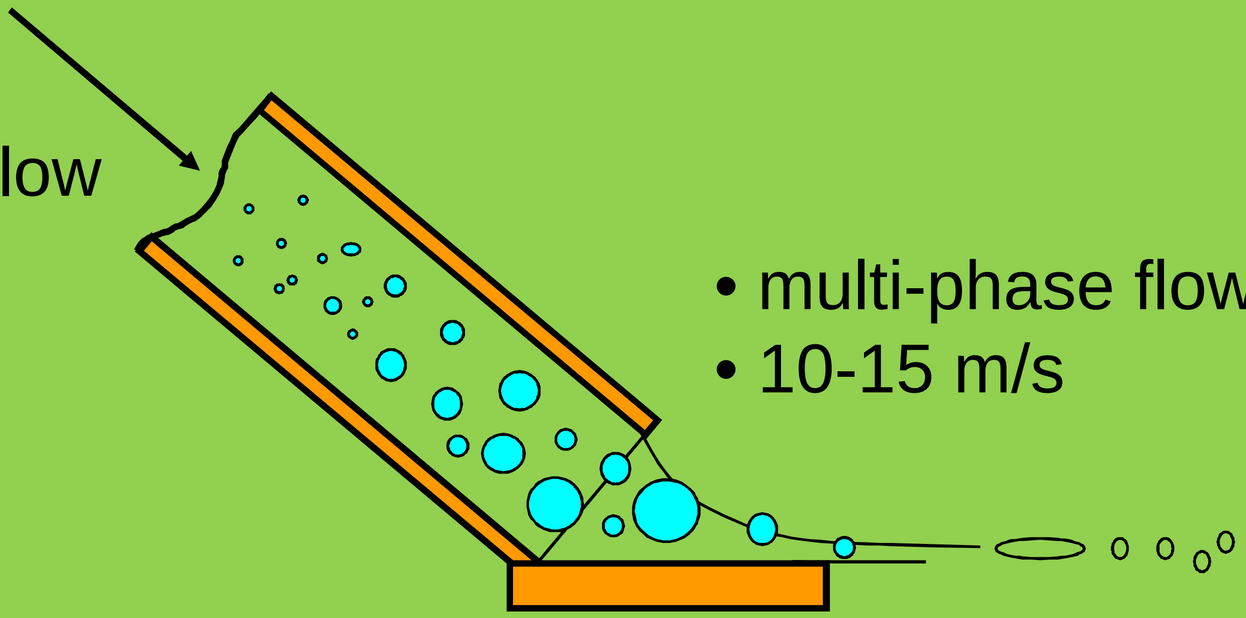
Breakup of liquid sheets, perforation

- The sheet may be perforated by by solid particles in the sheet or gas bubbles bursting from the sheet
- Surface tension is the driving force after hole growth



Breakup of liquid sheets, flash-breakup

- In the flashing case steam is generated already inside the nozzle when superheated liquid is de-pressurized
- The flow is formed of gas and liquid and when it hits the plate, no sheet can be formed



- 1-phase flow
- 5-7 m/s

- multi-phase flow
- 10-15 m/s

- ligaments and droplets

Breakup of liquid jets and rims

- Sheet is first broken into rims and ligaments
- They are affected by intertial and aerodynamical forces and finally break up into smaller parts that will form droplets

/1/

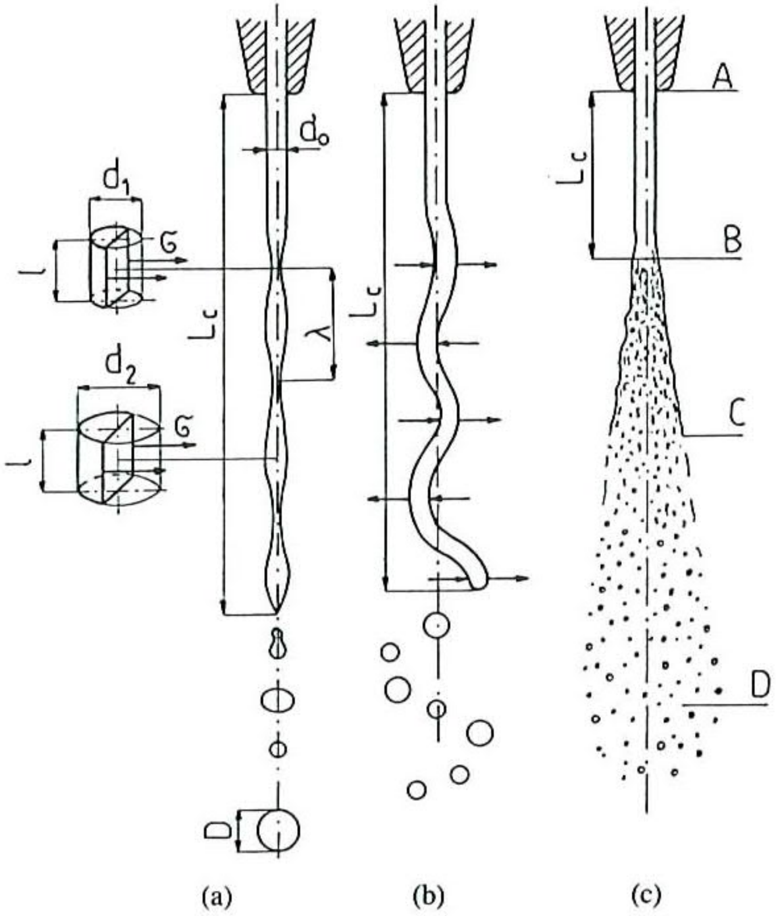


Figure 2-1 Disintegration of a cylindrical jet of liquid caused by (a) axialsymmetric waves; (b) asymmetric waves; (c) aerodynamic forces.

/6/

BL sprays from splashplate nozzles

Wave breakup

$\Delta T_e = -4.1$ °C

/modified from 7/

Wave/perforation breakup

$\Delta T_e = 4.7$ °C

/7/

Flash breakup

$\Delta T_e = 14.8$ °C

/7/

(ds = 69%, BPR = 15°C)

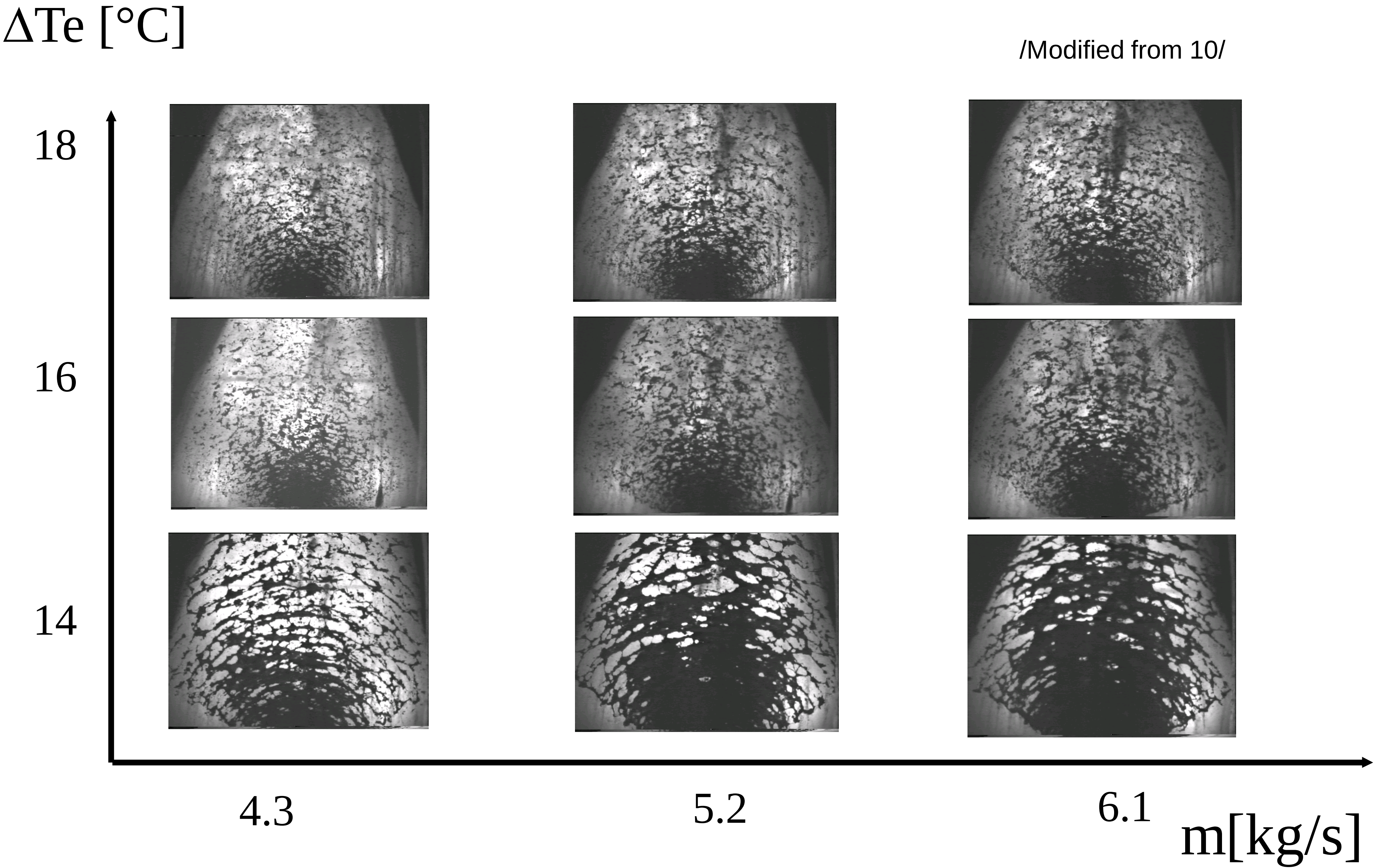
Increasing spraying temperature

Excess temperature

- The temperature difference between the spraying temperature and the atmospheric boiling point
- The bigger is the value, the larger is the potential for flashing.
- VERY IMPORTANT PARAMETER IN SPRAYING

$$\Delta T_e = T_{spraying} - T_{boiling}(p = 1 \text{ atm})$$

Effect of mass flow rate and temperature on sheet break-up mechanism



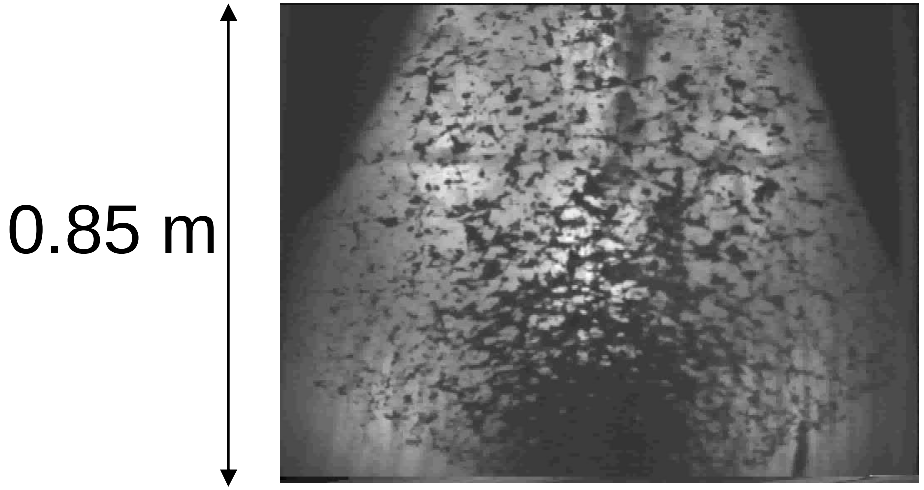
/Modified from 10/

Nozzle B

Nozzle B, 5.2 kg/s

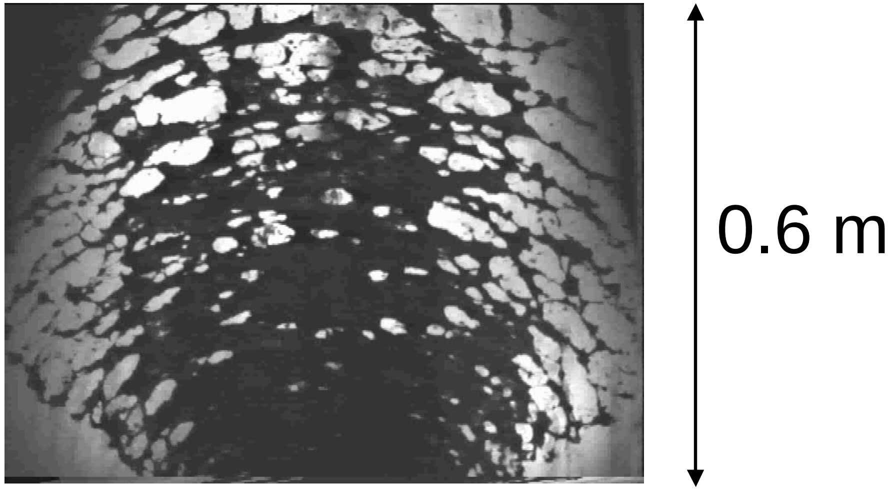
u = 12.2 m/s

dTb = 16.1 °C



u = 8.9 m/s

dTb = 14.3 °C



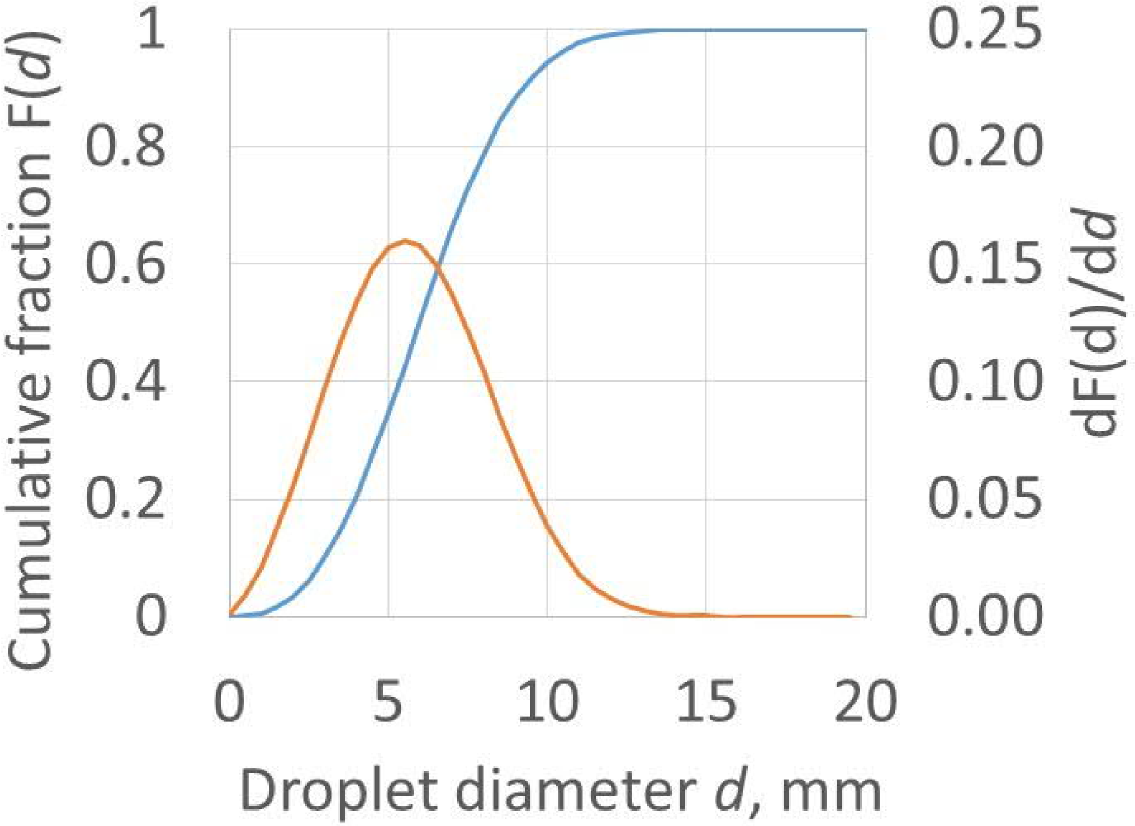
/10/

Minor change in excess temperature can cause remarkable change in sheet disintegration

Droplet characterization

Droplet size distribution

- Spray contains always a distribution of different sizes of droplets
- It is very important to consider this in studying the combustion behavior, rate ~$1/d^n$



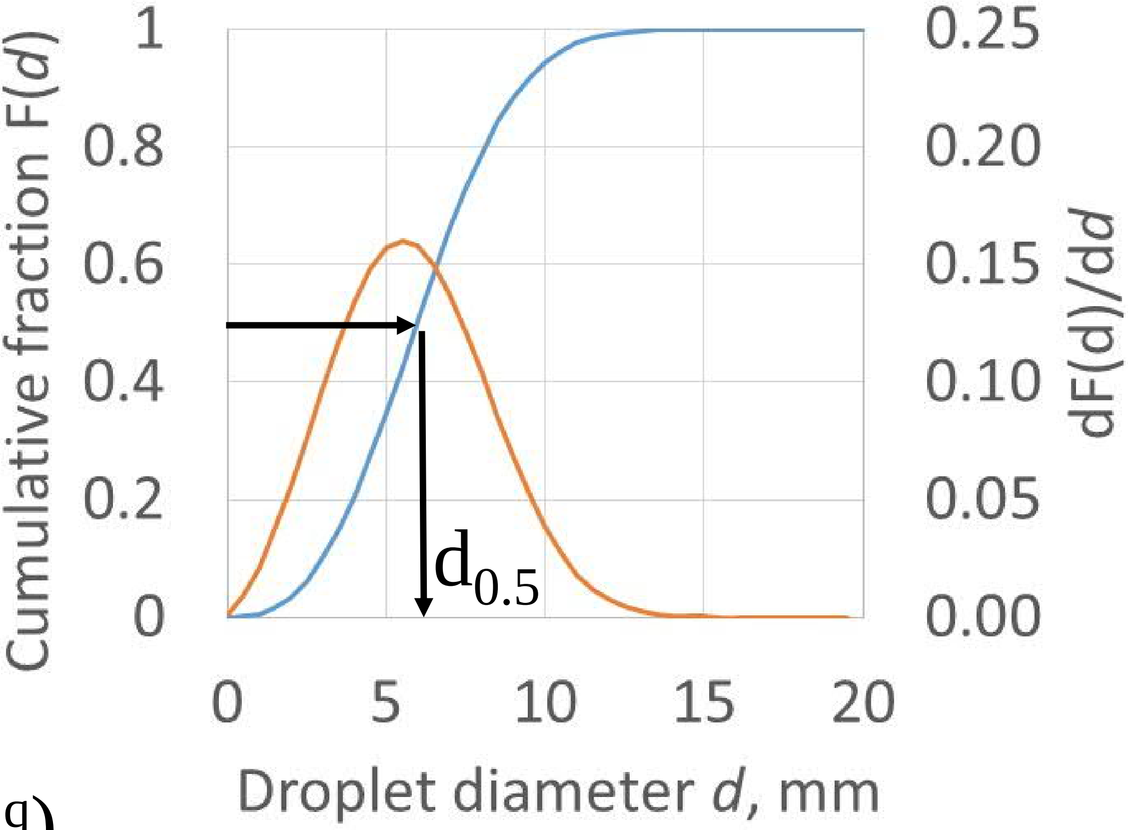
Rosin-Rammler (LE5)

$$F(d) = 1 - \exp(-(d/X_m)^q)$$

X_m = 6.81 mm, q = 2.75

Mass median diameter

- 50% of the liquid volume is formed by droplets smaller than mass median diameter, $d_{0.5}$ from RR distribution gives.



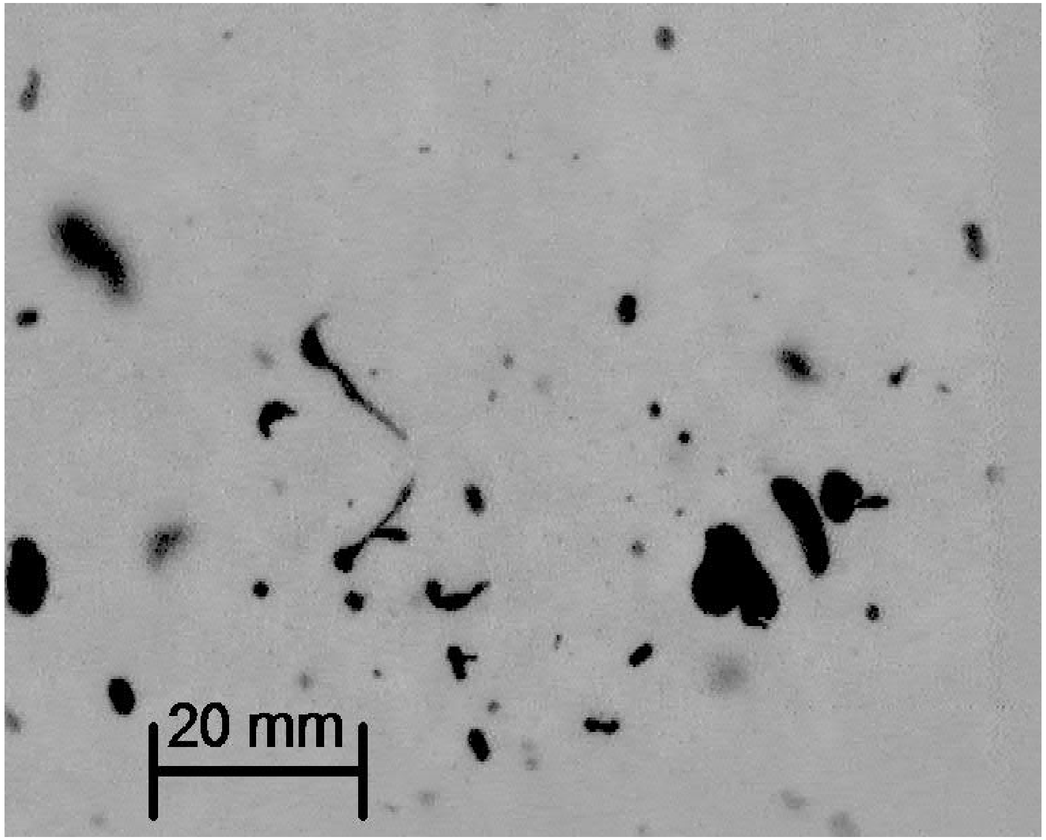
$$0.5 = 1 - \exp(-(d_{0.5}/X_m)^q)$$

Solve $d_{0.5}$ = ?

$X_m = 6.81$ mm, $q = 2.75$

Droplet shape

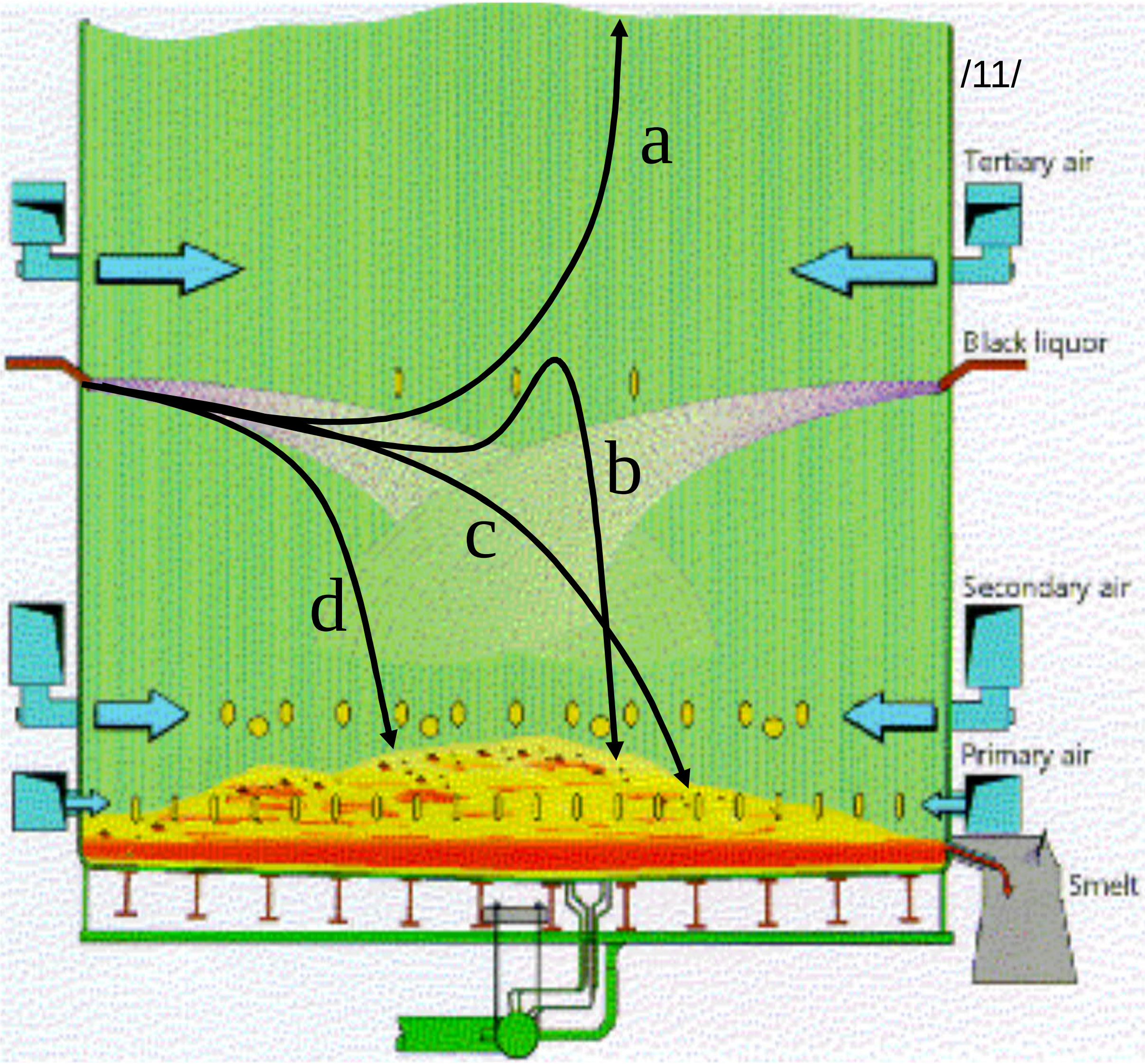
- When droplet size is very large and viscosity is high, the surface tension is not able to draw the droplet into spherical shape
- Shape affects the flight and combustion behavior



How to control spray properties

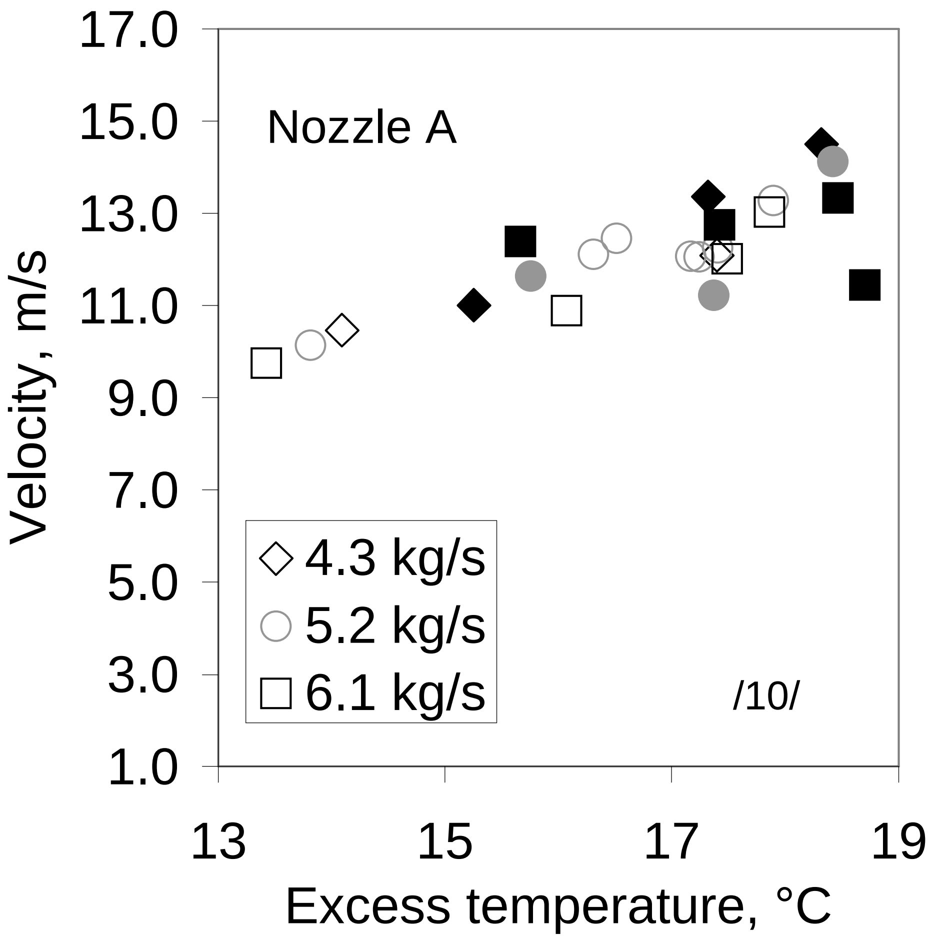
Objectives of spraying

- minimize droplet entrainment to heat transfer section (a)
- evaporate water before landing on char bed (d)
- deliver carbon to char bed, case (b) not good



/Modified from 11/

Controlling initial velocity

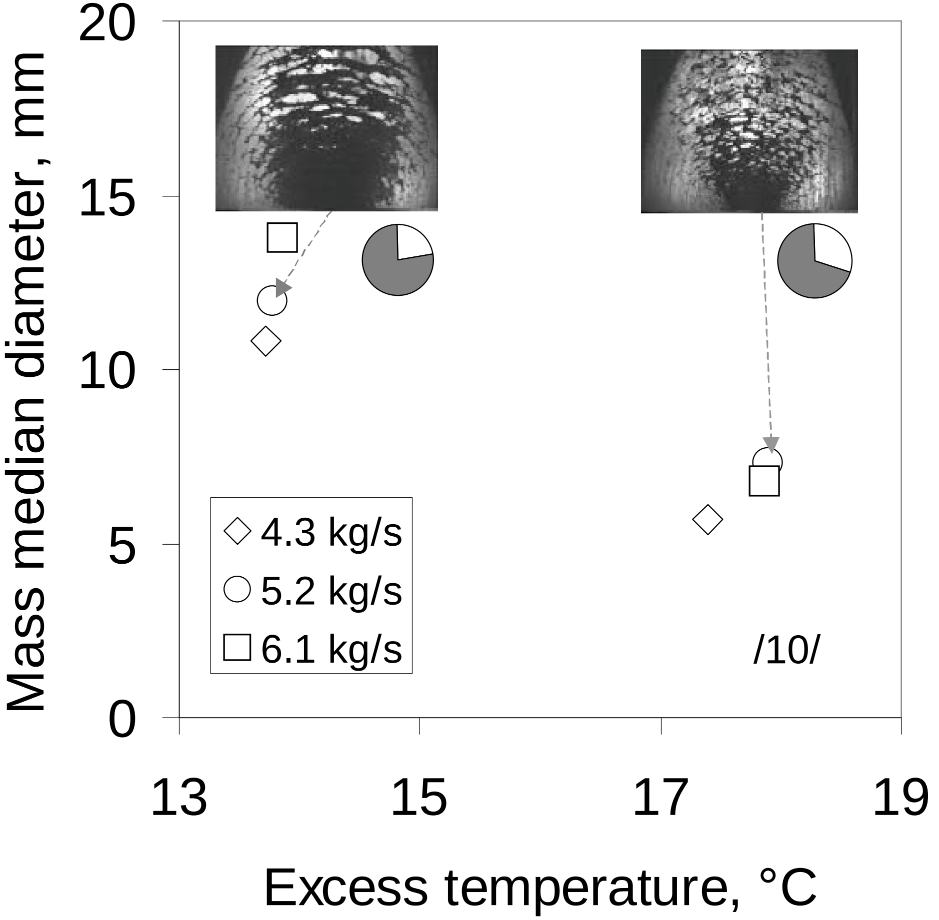


- Increasing temperature accelerates the flow, boiling flow

- increasing mass flow rate decreases the velocity when flashing takes place

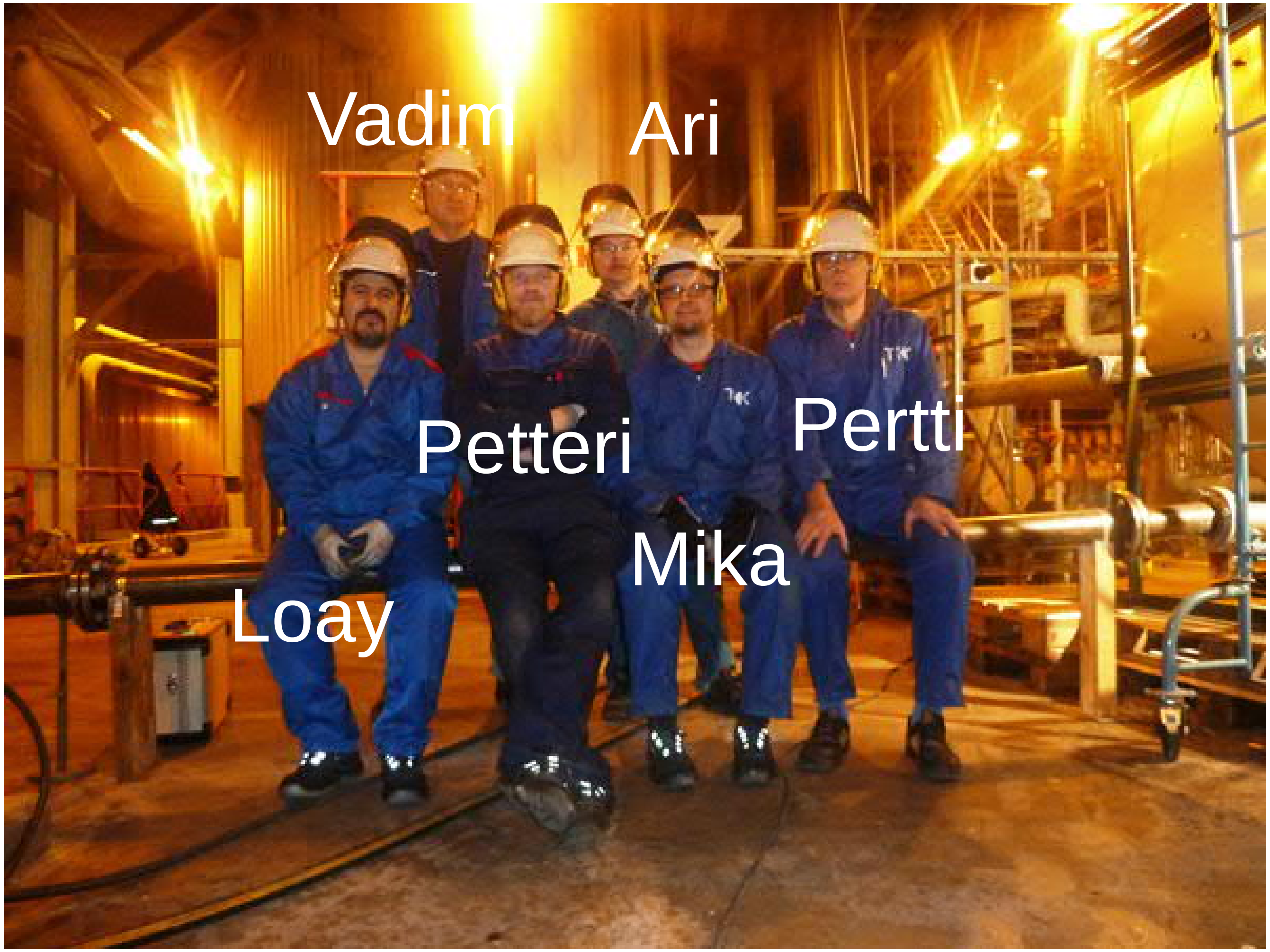
- opposite trend for non-flashing case, because increasing temperature decreases viscous pressure loss!!!

Controlling droplet size (and shape)



- Increasing temperature decreases droplet size and amount of non-spherical droplets
- increasing mass flow rate decreases flashing → increases droplet size, trend not clear at higher temperatures

Thank you!



Greetings from Rauma recovery boiler, our ”home” for 5 weeks during spring 2012 ☺, many weeks during fall 2013 too…