Experimental investigation of black liquor pyrolysis using single droplet TGA

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ABSTRACT: Black liquor pyrolysis is studied in a single droplet gasification reactor. The reactor is equipped with online analytical instruments to measure mass, temperature, and concentration of released gases during the process. It is also possible to follow visually and to record droplet geometric changes through a glass window. The pyrolysis parameters measured in this study are: the droplet swelling profile, pyrolysis gas released, and temperature inside the droplet. The gas detected by the analytical instrument can be deconvoluted to obtain the gas released at the actual time of droplet pyrolysis, thus minimizing the effect of transportation time. These data are important for studying the kinetics of black liquor droplet pyrolysis.

Application: This investigation provides possibilities for better understanding of the physical and chemical phenomena that occur during the first stages of black liquor combustion or gasification. It will therefore be important for a fundamental modeling of pyrolysis of a single black liquor droplet.

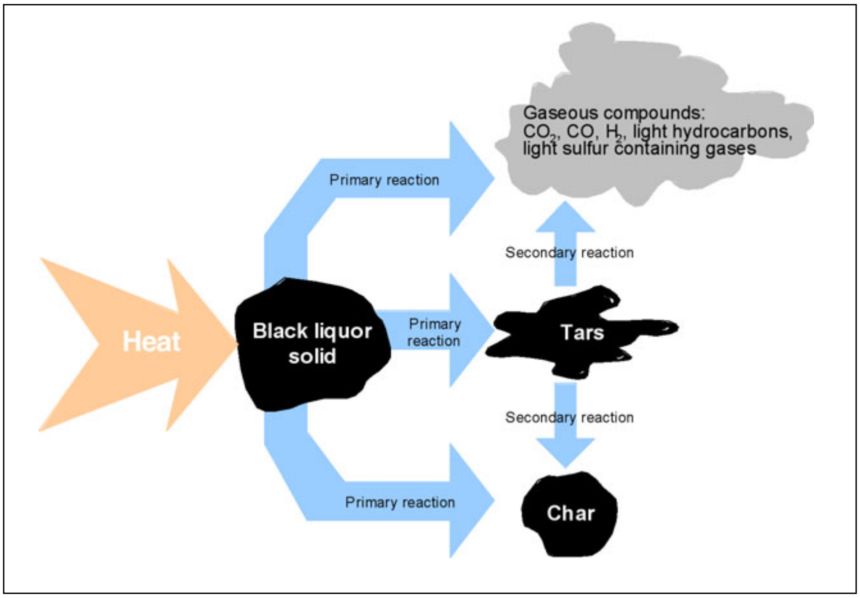
The kraft paper pulp process produces a large portion of a liquid side product, black liquor. Black liquor contains spent cooking liquor and organic compounds dissolved from the incoming wood. About half the organic material in wood, almost all lignin, dissolves into the liquor, which makes it rich in energy. For economic and environmental reasons, the spent pulping liquor must be recycled and the energy content utilized for generating heat and power.

Traditionally, chemical recovery and energy conversion from black liquor are performed in a kraft recovery boiler where the black liquor is combusted. The released heat is used for the production of high-pressure steam. This steam is then expanded in a steam turbine to generate electricity. Low and medium pressure steam from the turbine supplies the pulping process with the needed heat. Inorganic chemicals are separated at the bottom of the recovery boiler and exit the boiler as a smelt containing mostly Na_2S and Na_2CO_3. The pulping liquor, consisting of a water solution of NaOH and Na_2S, is then regenerated in the chemical recovery cycle. However, there are some drawbacks to this otherwise well established technology; including the risk of smelt explosion, a relatively low power-to-heat-ratio and rather high emissions of NO_x.

Gasification processes are currently being proposed as a substitute for the kraft recovery boiler in the chemical recovery and energy conversion processes. In a gasification system, the black liquor is gasified rather than combusted, which means that an energy-rich gas is produced. This gas can be combusted in a gas turbine to generate electricity and steam. This increases the power-to-heat ratio and makes it possible to export the surplus released energy as electricity. Another option is to use the produced gas as an intermediate process stream for the production of chemicals or liquid fuels. Inorganic chemicals are separated from the gas stream and can be processed to regenerate pulping chemicals. Another advantage of gasification is that sulfur and sodium may be recovered separately. Sulfur is, to some extent, released as H_2S in the gas phase and sodium is recovered as a dissolved solid or smelt. This provides the opportunity to control the OH and HS ratio in the pulping operation, which may improve the overall pulping process.

Today, black liquor is sprayed as droplets into a kraft recovery boiler [1]. This will also be the case in a gasifier. The droplets will, thus, pass through similar reaction pathways in both processes. First, the heat evaporates the water content in the droplets. The dried droplet is then pyrolyzed and a porous char matrix is formed. In the case of combustion, oxygen completely oxidizes the char, but in the gasification process, there is not sufficient oxygen to provide for complete combustion. Instead, the char is gasified into a mixture of combustible gases. Due to the temperature gradient inside the droplets, drying, pyrolysis, and gasification may occur simultaneously.

Pyrolysis refers to the decomposition of the organic material in the liquor caused by heat. Devolatilization, a release of volatile compounds without chemical reactions, occurs in combination with pyrolysis. Black liquor pyrolysis yields mainly light gaseous compounds, tars and char as presented in **Fig. 1**. During pyrolysis, the droplet may swell significantly [1-5]. This changes the internal structure of the droplet and increases porosity dramatically, both through the transformation



1. A simple diagram of the black liquor pyrolysis process.

of solid material into gaseous compounds and an increase in total volume. The internal structure of porous char affects the available surface area for gas-solid reactions and the transport properties inside the droplet. This is particularly important for the next stage of the process, the gasification reactions.

The main gaseous compounds released during black liquor pyrolysis are: CO_2, CO, H_2, light hydrocarbon and light sulfur-containing gases [6-16]. The types of gas species are also affected by the operating condition. Some oxygenated gas species (acetaldehyde, formaldehyde, acetone, and methanol) are rapidly produced in the beginning of the pyrolysis while hydrocarbon gases usually are produced at lower rates[11].

Tar consists of condensible organic substances that are released during pyrolysis. When these substances condense, a dark, viscous liquid is usually formed. Tar may be further converted by a secondary pyrolysis reaction into light gases and soot [15]. Reaction time and temperature are the two main factors that affect the secondary pyrolysis reaction for tar conversion [7, 15]. A high temperature and a long residence time reduce the presence of tar in the gas yield.

Purpose

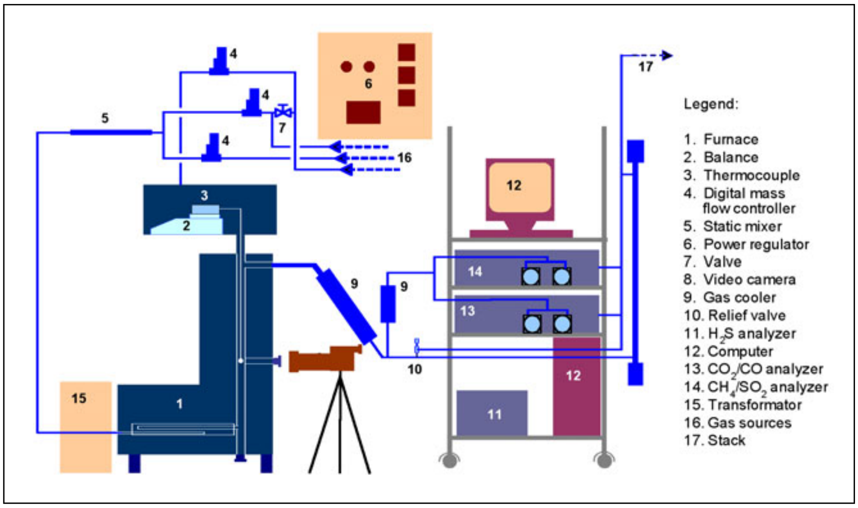
This work was performed to investigate the behavior of single black liquor droplets when they are dried and pyrolyzed at temperatures up to 900°C. Material balances were performed to determine the amount not analyzed (e.g., gaseous species of different tar compounds). There was also a need for establishing a swelling profile with respect to time, to understand the properties of the droplet/solid and corresponding gas production.

METHODOLOGY

Experimental set-up

A single droplet TGA, operating at atmospheric pressure, was used in this study. The equipment set-up is presented in **Fig. 2**. The furnace was built with a pipe made of a special alloy that can withstand a maximum temperature of 1150°C. The maximum temperature that can be achieved in the furnace is 1050°C. However, the experiment was always performed at temperatures below this level to avoid the risk of any metal burn out.

The black liquor droplet was placed at the tip of a special hook made from a thermocouple to measure the temperature inside the droplet. The gaseous products; i.e., CO_2, CO, CH_4, SO_2, and H_2S, were measured by online gas analyzers. Droplet changes were observed visually and recorded by a video camera. In addition, a scale was available on the top of the furnace. During the experiment, the thermocouple with the droplet was placed on the scale. Unfortunately, the scale was not stable when measuring the minor weight changes during the process. This may have been due to several reasons, one being that droplet weight was only about 40 mg and the thermocou-



2. Single droplet TGA set-up.

Components	Weight-% of dry solids (used black liquor)	Weight-% of dry solids (reference black liquor)
Carbon, C	36.3	34.9
Hydrogen, H	3.1	3.4
Nitrogen, N	0.07	0.1
Sulfur, S	2.8	5
Chlorine, Cl	0.32	0.11
Sodium, Na	19.7	19.4
Potassium, K	2.44	2.12
Oxygen, O (by difference)	35.27	34.97

I. Elemental composition of used black liquor and a typical reference black liquor from another Swedish kraft mill.

Sugar component	Concentration, mg/g dry content
Arabinose	4.29
Galactose	5.77
Glucose	1.28
Xylose	4.95

II. Sugar composition of black liquor used.

ple transmitter had a weight of approximately 200 g. Another cause could have been the changes in drag force resulting from changes in the geometry of the droplet during reaction.

In this study, black liquor pyrolysis experiments were conducted in a wide range of temperatures. The lowest temperature was 350°C and the highest was 900°C. The pyrolysis experiments were conducted in a nitrogen atmosphere. Both a technical grade nitrogen, with an oxygen content less than 200 ppm, and a purer nitrogen gas with an oxygen content less than 0.5 ppm were used in the experiments.

Black liquor characterization

Black liquor from an industrial kraft pulp mill was used in the experiments. Its elemental composition and sugar content are presented in **Tables I** and **II**.

DATA INTERPRETATION

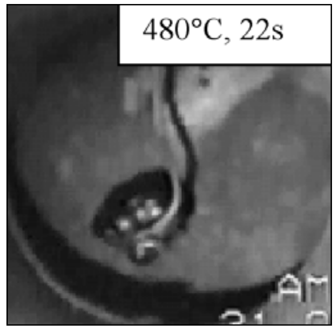
Droplet diameter

Geometrical changes, i.e., size and shape, in the droplet during pyrolysis was video recorded. In the following analysis, the 2-D picture was assumed to represent the overall geometry of the droplet. A metal wire, with a diameter of 1 mm, was used as a reference length to determine droplet size. An example of a droplet shape is presented in **Fig. 3**.

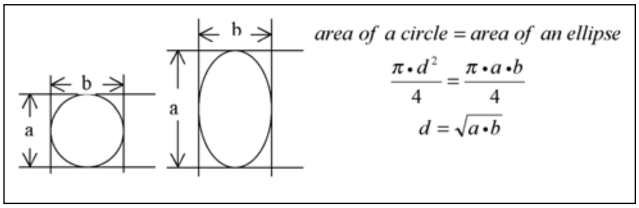
When the 2-D projection of the droplet was shaped like an ellipse, the average diameter was calculated as the diameter of a circle with the same projected area as the ellipse (**Fig. 4**).

Deconvolution

When gases are released during drying and pyrolysis they must first be transported out from the oven and cooled down before being analyzed. This will, together with the necessary analyzing time, create an offset in time between the analyzed result and the real process. In order to find the real-time behavior for the process, a mathematical procedure called deconvolution can be used [17] which is based on the signal from a pulse experiment with a known concentration. **Figure 5** presents an example of deconvoluted gas concentration data from a pyrolysis experiment at 900°C.



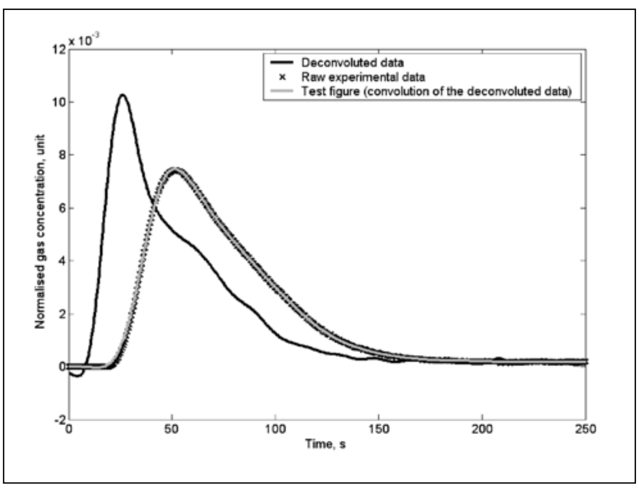
3. An example of black liquor droplet shape during pyrolysis.



4. Calculation of the average diameter of the droplet with an ellipse shape.

RESULTS AND DISCUSSION

Drying and pyrolysis experiments of kraft black liquor were performed to obtain important data: swelling behaviors, gas released, and temperature increase inside a black liquor droplet.



5. Comparison of raw data and deconvoluted data of CO_2 concentration detected in the gas analyzer for pyrolysis at 900°C.

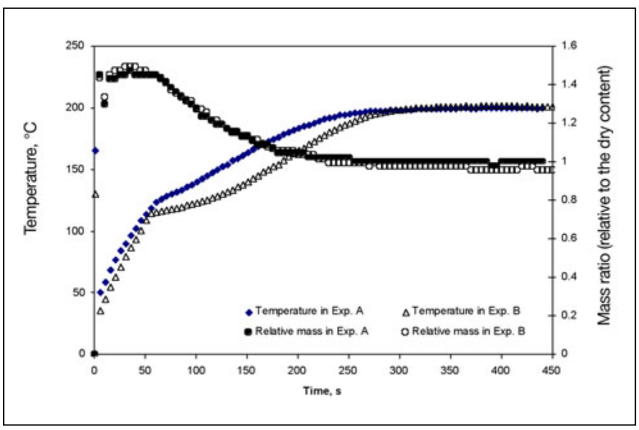
Droplet drying

Droplet drying can be studied in low-temperature experiments. The temperature of a droplet that enters the hot environment inside the reactor rises until it reaches the boiling point. The droplet is not isothermal, which means that the boiling point is reached on the surface first and the temperature then gradually increases inside the droplet. Once it reaches the boiling point, the water starts to evaporate quickly and the droplet's solid content increases accordingly. Temperature profiles of black liquor droplet drying from two experiments at 200°C are presented in **Fig. 6**. From the experiments, it was found that the rapid water evaporation starts at a temperature around 115°C. During evaporation, the droplet temperature continues to increase. This is because the increase in dissolved solid content raises the boiling point of the droplet.

Changes in droplet mass during drying are shown in Fig. 6. The two experiments yielded very similar profiles. Droplet mass levels off when all water content has been evaporated. None of the gas analyzing instruments detected any gas species in these two experiments. The change in droplet weight can be explained by loss of water, which means that devolatilization was negligible at these low temperatures. This is in agreement with earlier findings that devolatilization does not start until the temperature rises above 200°C [18]. Thus, up to 200°C, the predominant process in the droplet is water evaporation.

Fig. 6 shows also that the temperature profiles from the two experiments are different. This difference may be due to the different measurement positions of the thermocouple inside the droplet. Temperature measurement in experiment A may represent the temperature on the surface of the droplet and experiment B may show the temperature inside the droplet.

The droplet swelled to about 1.5 times its original diameter during drying. However, because of boiling, the shape of the droplet was not constant and, therefore, it was difficult to measure the diameter properly. This is consistent with previous findings, that estimates the swelling during drying at 1.54 times the original diameter [3].



6. Drying profile of black liquor droplet at temperature 200°C.

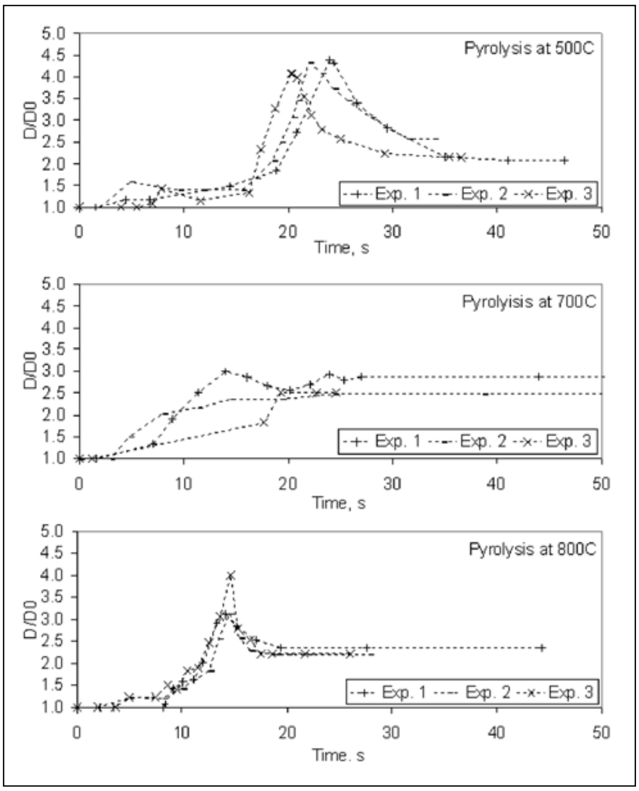
At higher temperatures, the drying and pyrolysis process occurs much more quickly and droplet swelling is more significant. The gas flow, inside and outward from the droplet, therefore, has a greater impact. These phenomena make it difficult to measure changes in mass at temperatures above 200°C.

Droplet pyrolysis

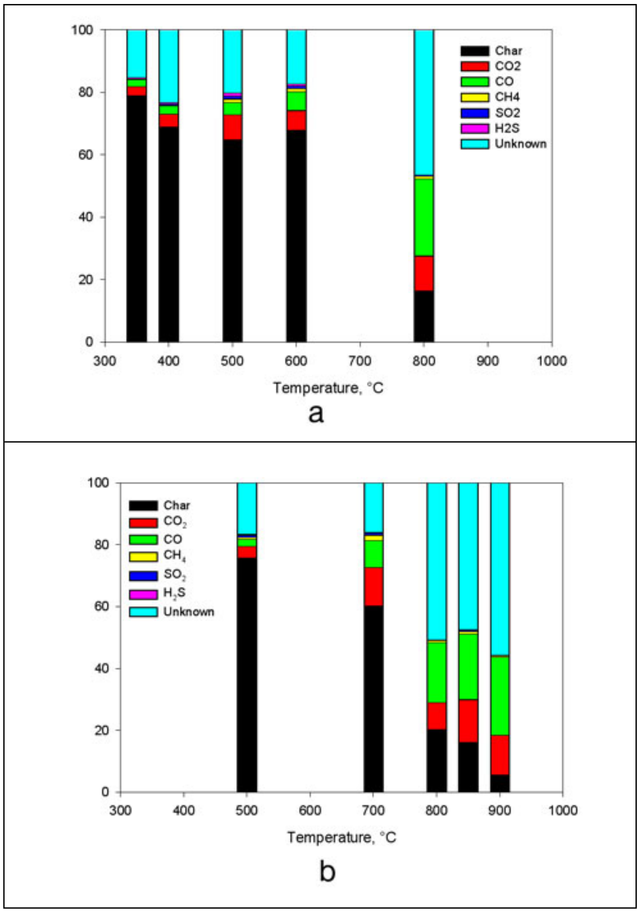
Pyrolysis reactions in the droplet start when the temperature is sufficiently high and the region is dried. (Pyrolysis from the surface of the droplet starts earlier than pyrolysis from the inside.) When the droplet reaches the pyrolysis onset temperature, the solid material is thermally degraded and gaseous components are released. When heated, the solid content of the droplet may also behave as a viscous plastic material and released gas may be trapped inside. The pressure increase is then the driving force for droplet swelling.

Swelling

Black liquor droplet swelling was recorded and analyzed to develop the swelling profile at different temperatures. **Figure 7** displays the swelling profile data obtained at 500°C, 700°C, and 800°C. We found that the droplets swell in the beginning of the pyrolysis, but shrink later. The swelling and shrinking behavior of the droplet during pyrolysis may be due to the different viscosity and elasticity of the solid matter in the sequence of the pyrolysis process. At the begin-



7. Swelling profile of black liquor droplet pyrolysis at 500°C, 700°C, and 800°C.



8. a). Overall mass balance of pyrolysis in nitrogen atmosphere (N_2 technical grade, O_2<200 ppm); b). Overall mass balance of pyrolysis in nitrogen atmosphere (N_2 detector grade, O_2<0.5 ppm).

ning of pyrolysis, most of the organic matter in the droplet is still in its original structure. When heated, it forms a plastic-like material [4, 5]. Trapped gas inside the plastic-like structure causes the material to swell as the gas expands with increasing temperature. At a certain degree of swelling, the plastic structure is stretched to its limit. Then, it may start to crack and the gas trapped inside is more easily released. The droplet loses the support of the inside gas pressure and may start to shrink. However, in some cases the material has been solidified at the outer position and will not shrink even though there is no longer any support from high gas pressure.

The three data series in Fig. 7 show that at 500°C, the droplet swells more than at 700°C and 800°C. This behavior of decreasing swelling with temperature has been recognized earlier [3, 4]. A possible explanation for this is that thermal degradation occurs more quickly at higher temperatures. After thermal degradation, the solid material becomes char, which has no viscous-plastic behavior. Therefore, the solid material in the droplet has less time to behave as viscous plastic-like material and, consequently, has less time to swell.

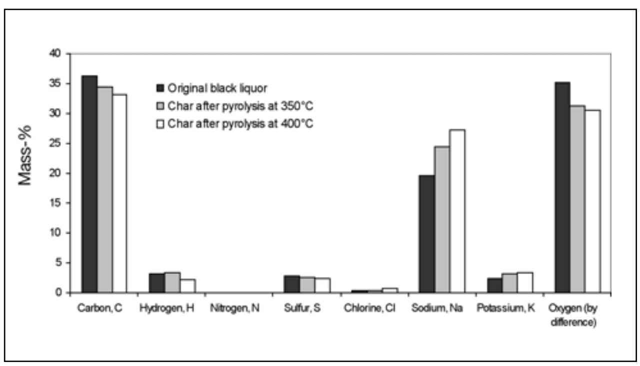
Mass balances

The char left after pyrolysis was recovered and weighed. This together with the analyzed gas species (CO_2, CO, CH_4, SO_2 and H_2S) summed up the known material after the process. Tars and other gases, e.g., hydrogen and water vapor, not measured during the process, are counted as unknown in the mass balance calculation. Results of overall mass balances during black liquor droplet pyrolysis are presented in **Figs. 8a** and **8b**. These experiments were performed in both technical grade nitrogen (concentration of O_2 less than 200 ppm) and in detector grade nitrogen (O_2 concentration less than 0.5 ppm). The mass balances at temperatures below 600°C were close to about 80% of the original solid material in the black liquor. The remaining 20% represented the other gaseous species released from the pyrolysis reaction and the tars. At higher temperatures, however, the unknown amount increased. This was probably due to more low-molecular weight carbohydrates and tars being formed and released at the higher temperatures in this investigation [19].

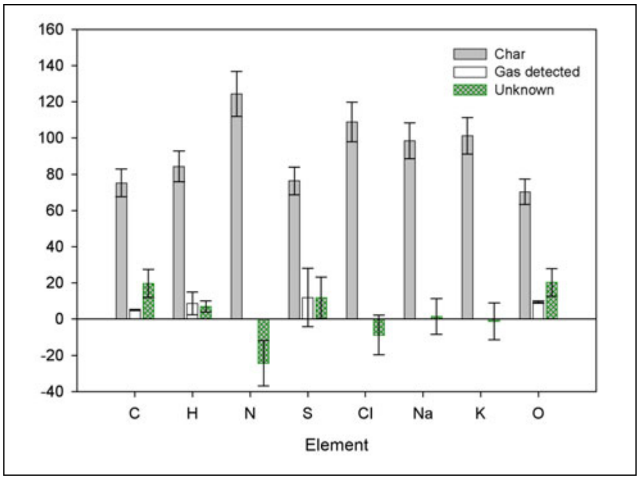
Although it was difficult to collect and measure chars, it was possible to obtain some general conclusions regarding reactivity from Fig. 8. Char left from the pyrolysis at temperatures lower than 700°C represented about 70% of the original dry solid matter in the original liquor. This figure dropped significantly at higher temperatures which indicates that pyrolysis in black liquor becomes more important at temperatures above 700°C. The recovered char in this study is low compared to other studies [9] where the amount of char at 800°C differed between 35%-70% depending on black liquor used.

Elemental mass balances

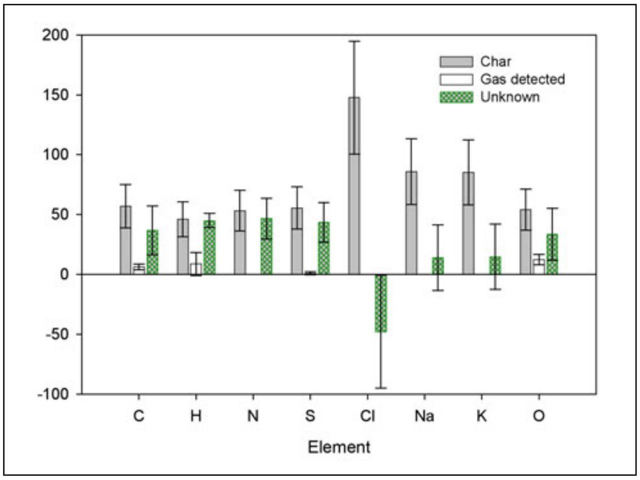
To determine the component balances during pyrolysis, chars were collected from experiments at 350°C and 400°C and analyzed for their elemental composition. **Figure 9** presents the elemental analysis. In order to have enough materials to perform the analyses, the values of chars from many



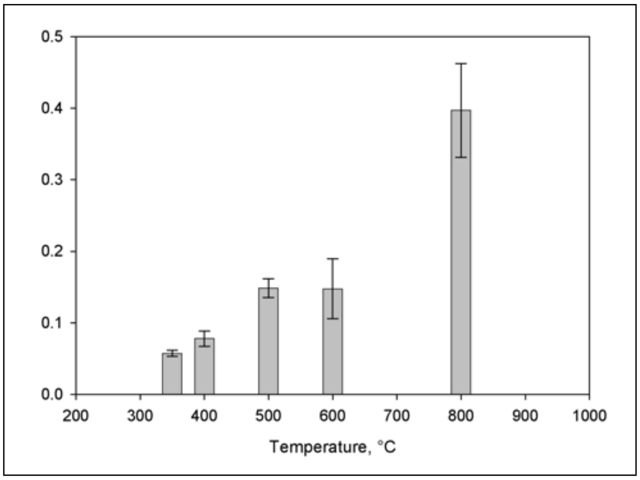
9. Elemental analysis of original black liquor and chars from pyrolysis at 350°C and 400°C.



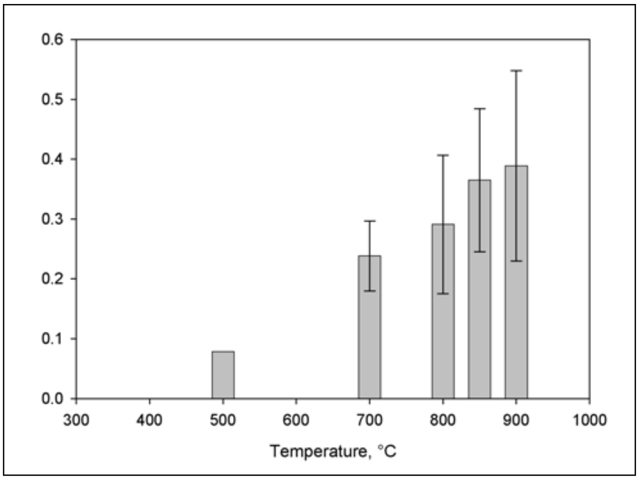
10. Elemental mass balances of black liquor pyrolysis at 350°C.



11. Elemental mass balances of black liquor pyrolysis at 400°C.



12. Pyrolysis gas yield at various temperatures in the atmosphere of technical grade nitrogen (O_2<200 ppm).



13. Pyrolysis gas yield at various temperatures in the atmosphere of detector grade nitrogen (O_2<0.5 ppm).

droplets were averaged.

Content of carbon, hydrogen, sulfur, and oxygen have a tendency to decrease from the original concentration in black liquor. These components were released as gases and tars during the process. In contrast, the concentration of sodium and potassium increased, since these elements were not significantly affected by the pyrolysis process at these temperatures.

Elemental mass balances for pyrolysis at 350°C and 400°C are presented in **Figs. 10** and **11**. Nitrogen and chlorine show negative values in the figure. This may be due to an error in the analyzing technique, since the amounts of them in char are very small (**Table I**).

Elemental mass balances at 400°C gave more unknown material compared to balances at 350°C for most of the investigated elements. This may be caused to some extent by the loss of char during recovery. The black liquor char was very fragile, which made it difficult to collect and weigh. Char collections and analyses were not performed at higher temperatures, because the higher the temperature rose, the more fragile the char became.

Gas yields

Figures 12 and **13** present gas yields from the pyrolysis. Both figures show that gas yields increase with increasing temperature. This is in accordance with the fact that pyrolysis is a thermal process: the higher the temperature the greater the reactivity. This behavior is consistent for both the technical grade nitrogen and the detector grade nitrogen.

CONCLUSION

Experiments in a single droplet TGA provided important data on drying and pyrolysis kinetics. The dynamic mass loss and the temperature profile during drying were obtained. The released gas, temperature, and swelling profile of a single black liquor droplet were measured simultaneously during pyrolysis. These sets of data are valuable for mathematical model validation in further study of the kinetics of black liquor droplet pyrolysis. The swelling profile is important to determine the inside transport properties with respect to mass and heat transfer. It also provides information about available surface area, which is important for reaction kinetics. **TJ**

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INSIGHTS FROM THE AUTHORS

This work is an important part in an effort to derive pyrolysis and gasification kinetics of black liquor in atmospheric and pressurized conditions.

The new part in this research is the usage of dynamic information from the thermo-gravity equipment combined with extensive mass balance and visual observations of the geometrical changes to investigate the whole scenario during pyrolysis.

One important issue when dealing with experimental work is repeatability and the accuracy of the experiments. We solved this issue by constantly searching for deviations and the origins of those and by performing a number of double and triple experiments at the same conditions.

This was the first research I made in pyrolysis of black liquor and one of the most amazing parts is the tremendous swelling that occurred and especially the rapid increase of the droplet as soon as the pyrolysis started.

This research in mainly focused on the gasification of black liquor and the benefits of the mills will be to have more options to choose between when it comes to chemical recovery and more specifically this research can be a part to get a better control of the process. It should also be mentioned that this part of the research is not limited to the gasification


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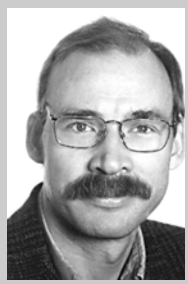
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but can be used as a part of the traditional recovery boiler as well in combination with existing combustion models.

The next step has already started and will be to utilize these findings to develop a mathematical model that describes the droplet behavior during pyrolysis and also to use that to derive kinetic expressions valid in both atmospheric and pressurized conditions.

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