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Combustion Chemistry
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Pyrolysis and Gasification Behavior of Black Liquor under Pressurized Conditions

Kevin Whitty



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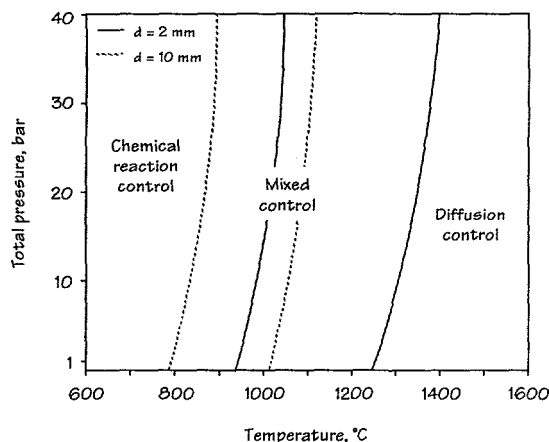
p. iv, 2nd full paragraph: "207 kJ/mol" should be "236 kJ/mol"

p. 1, line 3: Should read "Considering *the* sheer size..."

p. 15, 3rd paragraph, first sentence: Should end with "...sulfide and elemental *sulfur*."

p. 49, middle of page: Should read "It is worth noting that Equation 6-14 is..."

p. 51: The lower figure is incorrect. The correct figure is given below:



p. 53, 2nd full paragraph, line 8: Should read "...reaction of Na_2S and CO_2 . This is..."

p. 53, 2nd full paragraph, line 9: Should read "...according to reaction 1-6."

p. 55, 3rd paragraph, line 6: Should read "...in sections 5.1.1 and 5.1.2..."

p. 61, 2nd line from bottom: Should read "...and over the *pressure* range 1-100 bar..."

p. 62, bottom paragraph, lines 4-5: Should read "...approximately 236 kJ/mol for H_2O gasification and 207 kJ/mol for CO_2 gasification [90]."

p. 64, first paragraph, last sentence: Should read "Data regarding changes in the gasification rate at any pressure are useful, however, and are discussed in section 6.3.6."

p. 69, below Equation 6-19: Should read "Equations 6-12 and 6-18 were..."

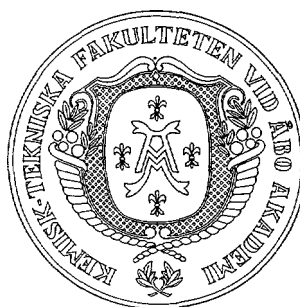
p. 70, 3rd paragraph, last line: Should read "...Equations 6-19 and 6-20."

p. 72, top line: "207 kJ/mol" should be "236 kJ/mol"

Åbo Akademi

Pyrolysis and Gasification Behavior of Black Liquor under Pressurized Conditions

Kevin Whitty



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**PYROLYSIS AND GASIFICATION BEHAVIOR OF BLACK
LIQUOR UNDER PRESSURIZED CONDITIONS**

Kevin Whitty

Academic dissertation for the degree of Doctor of Technology

MASTER

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PREFACE

The work in this thesis has been performed within the Combustion Chemistry Research Group at Åbo Akademi University during the years 1991-1997. The projects were conducted within the Finnish national combustion and gasification research programs JALO, LIEKKI and LIEKKI 2.

I wish to give my most sincere thanks to the leader of the Combustion Chemistry Research Group, Professor Mikko Hupa, for giving me the opportunity to work in the group and to write my thesis under his direction. I have appreciated his calm demeanor and utmost professionalism in all regards. He has made me feel like a colleague more than a student during the years I have worked with him. I have also enjoyed the many discussions we have had on topics ranging from ice skating to jazz music.

I would like to thank all my co-authors. Rainer Backman has assisted me countless times on issues relating to thermodynamics and has always found time to help me when I have come to him for advice. Mikael Forssén was very helpful with the liquor-to-liquor studies and with the analysis of experimental data. Mika Kullberg and Janne Rainio are acknowledged for their excellent experimental work with the pressurized grid heater. Vesa Sorvari gave valuable suggestions regarding interpretation of the grid heater data and Chris Verrill, now with Babcock and Wilcox, did a fine job with the preparation of the synthetic black liquors. I am also indebted to Jim Frederick, now with The Institute of Paper Science and Technology, for having invited me to Finland and for introducing me to the field of black liquor.

Peter Backman deserves a medal for his dedication and meticulousness in operating the pressurized thermogravimetric reactor, and this work simply would never have come to be without him. We have had numerous valuable discussions and I admire not only his comprehension of the work he performs, but his appreciation for such things as the finer aspects of dump trucks.

The other members of the Combustion Chemistry Research Group have all been very supportive and most enjoyable to work with. I would feel lucky to find another working environment that is as friendly and comfortable as it has been here. Clifford Ekholm has also been a great pleasure to work with, both in the office and on the battlefield.

I would like to thank Christian Mueller for his assistance during my exchange to Ruhr-Universität Bochum, Germany, during the fall of 1996. The time I spent there was valuable and I was able to complete much of this thesis during those months.

This work would not have been possible without the financial support of TEKES (Technology Development Center of Finland), Ahlstrom Machinery, Tampella Power and later also Kvaerner Pulping, to whom I am indebted. The Graduate School in

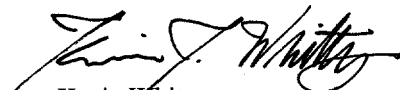
Chemical Engineering (GSCE) program and the Academy of Finland are also gratefully acknowledged for providing financial support both in Finland and during my exchanges abroad.

The Nordic Energy Research Program also acknowledged for providing the opportunity to meet Nordic colleagues at many useful seminars regarding thermochemical biomass conversion. I also thank the International Flame Research Foundation for arranging many valuable courses on combustion-related issues.

My special thanks go to Dr. Thomas Grace for his many extremely useful suggestions for improvement of this thesis. I have greatly appreciated his punctuality and professionalism.

I would like to thank my family, particularly my parents John and Teri, for their support and encouragement throughout my education. Many thanks to Beepa for his ceaseless faith and prayers over the years, as well. Finally, I would like to thank Tesse for her patience, concern and understanding.

Åbo/Turku, May 1997



Kevin Whitty

ABSTRACT

Black liquor is the spent solution which results from digestion of wood chips during pulp production. When concentrated to more than 60-65% solids, black liquor is combustible and is conventionally burned in large units called recovery boilers for the dual purposes of energy production and recovery of the pulping chemicals. Pressurized gasification of black liquor offers an alternative to the recovery boiler, and has the potential to increase the electrical output from the liquor by a factor of two or more. Such a system also has safety advantages and may require less capital due to the smaller equipment size.

Despite these advantages, little data regarding pressurized gasification of black liquor are available. The purpose of this study has been to enhance the understanding of the processes involved in pressurized black liquor gasification. Gasification is known to occur in three stages: drying, pyrolysis and char gasification. The work presented here focuses on the pyrolysis and gasification stages.

Experiments were carried out primarily in two laboratory-scale reactors. A pressurized grid heater was used to study black liquor pyrolysis under pressurized conditions. Char yields and the fate of elements in the liquor, as well as the degree of liquor swelling, were measured in this device. A pressurized thermogravimetric reactor was used to measure the rate of the char gasification process under different temperatures and pressures and in various gas atmospheres. Pyrolysis experiments were also carried out in this device, and data on swelling behavior, char yields and component release were obtained.

The degree of black liquor swelling was found to decrease as a function of pressure. The decrease in the specific swollen volume was found to be roughly logarithmic with pressure, and the volume of char formed at 20 bar was roughly one-quarter that of a char formed at atmospheric pressure. An expression is presented which estimates the specific swollen volume of a char formed under pressure if the swollen volume at atmospheric pressure is known.

The microstructure of char formed under pressure was observed to be more compact and less porous than that of char formed at atmospheric pressure. Measurement of the internal surface area of such chars by BET analysis was not entirely accurate, but a large difference between char formed at atmospheric pressure and char formed at 20 bar could be detected. While the difference could not be accurately quantified, the results indicate that the internal surface area of char formed at atmospheric pressure is at least twice that of char formed at 20 bar, and may be many times more.

Pressure was found to have little influence on volatiles yields during pyrolysis at temperatures less than 850°C. Above this temperature, inorganic decomposition reactions, particularly decomposition of sodium carbonate, contributed to the observed mass loss during pyrolysis. Sodium carbonate decomposition is retarded at higher pressures, so the mass loss during pyrolysis at higher temperatures was observed to

decrease with pressure. Correspondingly, sodium release in these experiments was lower at higher pressures.

Sulfur release during pyrolysis ranged from 35% to 70% and increased with pressure. An additional 15% of the sulfur originally in the liquor was released at 10 bar compared to that at atmospheric pressure. The mechanism behind the increase with pressure is not fully understood, but may be related to the residence time of the liquor in the temperature range critical for sulfur release.

The rate of char gasification was found to be controlled by the chemical reaction rate under conditions relevant for "low temperature" schemes which operate under the melting point of the inorganic material in the liquor. The activation energy measured for pressurized gasification with steam was 207 kJ/mol, which corresponds to an increase rate increase by a factor of roughly 20 over the temperature range 600-700°C.

The conditions under which black liquor char was formed were found to have a great effect on its reactivity during gasification. High char formation pressures resulted in lower reactivities, presumably as a result of the lower internal surface area available for reaction. Prolonged exposure to high temperatures also lessened the char reactivity. The presence of carbon monoxide during char pretreatment could result in carbon deposition on the char. This elemental carbon partially masked the alkali catalysis responsible for the high reactivity of black liquor char, thus reducing the observed gasification rates. The carbon deposition rate increased with pretreatment pressure, so the reduction in the gasification rate was greater for chars which underwent pretreatment at higher pressures.

Black liquor char gasification is highly catalyzed by alkali species. The gasification rate was found to increase with alkali content up to roughly 0.1 mol alkali/mol carbon, after which additional alkali had no significant influence on the rate. The alkali content in industrial liquors is above this "saturation level." Gasification rates of different industrial liquors varied by as much as a factor of seven, with soda and sulfite liquors being much less reactive than kraft liquors. Amongst the kraft liquors studied the rates varied by a factor of 2.2. No correlation could be found between the composition of these liquors and the char gasification rate. The comparatively low reactivities of the soda and sulfite liquors could be explained by their much lower degree of swelling.

The composition of the reacting gas was found to influence the char gasification rate. Higher partial pressures of H_2O or CO_2 resulted in higher gasification rates while H_2 and CO were found to inhibit the reaction. CO was a particularly strong inhibitor, and the presence of 2% CO in the reacting gas slowed the rate more than 4% H_2 under otherwise identical conditions.

Preliminary results indicate that the influence of total pressure on the rate of char gasification is much less than previously reported when the liquor is introduced directly into the gasification atmosphere. No significant difference in the gasification rate was observed for such experiments over the pressure range 1-30 bar. Further work is necessary in order to fully understand the influence of pressure on the rate of black liquor gasification.

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APPENDICES:

Paper I: Liquor-to-liquor differences in combustion and gasification processes: Pyrolysis behavior and char reactivity.

Paper II: Influence of pressure on pyrolysis of black liquor: 1. Swelling.

Paper III: Influence of pressure on pyrolysis of black liquor: 2. Char yields and component release.

Paper IV: Influence of char formation conditions on pressurized black liquor gasification rates.

Paper V: Morphological studies of black liquor char during formation and conversion.

Paper VI: Gasification of black liquor char with steam at elevated pressures.

Paper VII: An empirical rate model for black liquor char gasification as a function of gas composition and pressure.

Paper VIII: Pressurized gasification of black liquor — Effect of char sodium content.

1. INTRODUCTION

In a modern pulp mill the largest, most expensive piece of equipment is the black liquor recovery boiler. In this unit, black liquor is burned both to obtain energy and to recover chemicals. Considering its sheer size of the unit and the number of processes that take place simultaneously within it, the recovery boiler accomplishes these tasks amazingly well. Nonetheless, there is plenty of room for improvement in the black liquor recovery process.

One alternative to the conventional recovery boiler is a pressurized black liquor gasification process. Such a process offers the potential to increase the electrical output from black liquor by a factor of two or even more. A pressurized gasification system may also require less capital due to smaller equipment size and the risk of the smelt-water explosion that exists for recovery boilers is nonexistent. Despite these advantages, little is known regarding the behavior of a pressurized gasification system. The work presented here aims to enhance the understanding of this system.

In the next sections, the terms "black liquor" and "gasification" are clarified and processes during black liquor gasification are introduced. In the chapters that follow, the current state of knowledge regarding black liquor pyrolysis and gasification is reviewed. The approach used in this work is then presented and finally results and conclusions are discussed.

1.1 Black liquor

Black liquor is a substance unique to the pulping process, and many people may not be familiar with what it is. In this section, black liquor is introduced and its origins and properties are discussed.

1.1.1 Description of black liquor

Black liquor is an essential part of the papermaking process. The chief chemical cycle for a typical pulping process is depicted in Figure 1-1. In this process, wood chips are fed into a digester. White liquor, an aqueous solution of sodium hydroxide and sodium sulfide, flows through the digester and neutralizes the organic acids in the chemical matrix of the wood. Approximately half the mass of the wood, containing lignin and other organic material, dissolves into the white liquor. The remaining part, containing the wood fibers, is separated and exits the digester as pulp which goes on to become paper.

The solution exiting the digester, the black liquor, contains both the dissolved organic material from the wood and the residual pulping chemicals. At this point the black liquor is approximately 15% solids by weight, much too low to support combustion. Therefore the solution is sent through a series of evaporators which concentrate the liquor and raise its solids content to at least that at which combustion can take place. Previously the solids content of the liquor was increased to roughly 65%, but modern evaporators can increase the concentration to as much as 85% solids.

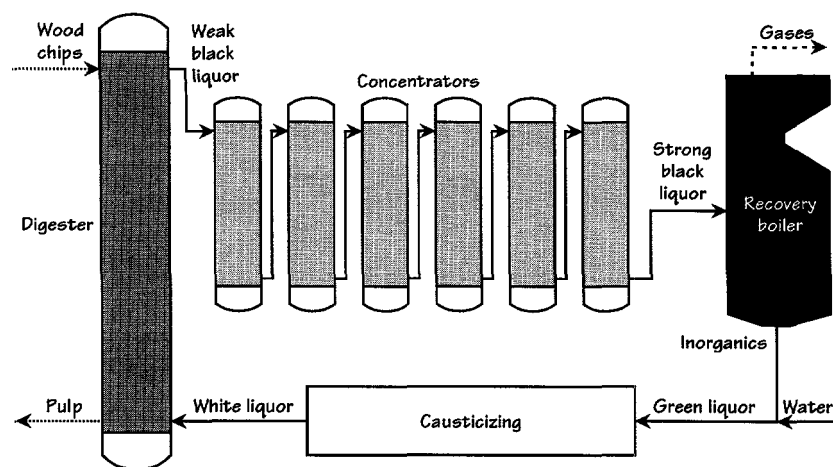


Figure 1-1. The primary chemical cycle in a typical pulping process.

The concentrated black liquor is fed into the recovery boiler. The purpose of the recovery boiler is twofold. The liquor releases heat as it burns and this energy is used to generate steam for mill processes and for power production. The amount of energy is by no means trivial. In Finland, for instance, 9% of the nonnuclear energy production results from black liquor combustion. The other function of a recovery boiler is to recover the pulping chemicals contained in the liquor. The inorganic material forms a smelt bed at the bottom of the boiler. The hot smelt flows into a dissolving tank, and the resulting solution, green liquor, is sent through a causticizing process to make white liquor, thus completing the chemical cycle.

1.1.2 Black liquor properties

Black liquor is a dark viscous liquid with a high concentration of inorganic material. The approximate composition of black liquor is given in Table 1-1, as is the composition of the char that remains after pyrolysis. The concentration of sodium is much higher than in other fuels and results from the chemicals used in the pulping process.

Despite being a liquid, the combustion behavior of black liquor is more like that of solid fuels, such as coal, than to oil or other liquid fuels. Rather than evaporating and burning in the gas phase like a typical liquid fuel droplet, the liquor undergoes the same stages of combustion as a solid fuel. The heating value of black liquor is relatively low compared to other fuels. The higher heating value is on the order of 15,000 kJ/kg dry solids [1].

1.2 Gasification

Chemically speaking, gasification is the term applied to a process in which a solid material reacts with a gas to form gaseous products. Industrially speaking, however, gasification refers to a processing method for a fuel. Gasification of coal is a common process for energy production. In this process the coal is fed into a *gasifier* and allowed to react with oxygen, air, water vapor or carbon dioxide with a mixture of combustible

TABLE 1-1. TYPICAL ELEMENTAL COMPOSITION OF
BLACK LIQUOR SOLIDS AND CHAR, WT. %

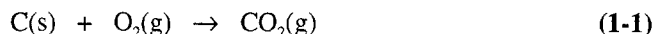
Element	Solids	Char
C	33.8	34.0
H	2.9	1.6
O	34.8	36.0
S	3.8	4.0
Na	21.8	22.6
K	1.2	1.3
N	0.1	0.1
Cl	0.2	0.2
Other	1.4	0.2

gases (H_2 , CO, CH_4) as a result. The term "gasification" is used in yet another sense when one speaks of the stages of combustion or the stages of gasification. (See section 1.2.2.) The final stage of gasification is char gasification.

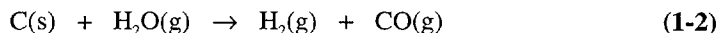
Obviously, these different applications of the same word can become confusing. Therefore in this work the following distinctions will be made. When referring to reaction during final stage of the black liquor conversion process, as described in section 1.2.2, the term *char gasification* will be used, and the chemical reaction that occurs is the *gasification reaction*. Otherwise the term *gasification* refers to the whole conversion process, and can be compared to the alternative, *combustion*.

1.2.1 Gasification versus combustion

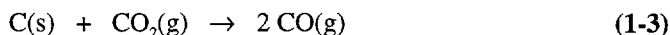
The most common reaction for conversion of carbon is combustion with oxygen:



Combustion is an exothermic reaction which takes place under oxidative conditions. Because the reaction gives off heat, it is self-perpetuating provided that enough oxygen or air is available. But char combustion is not the focus of this work. Rather, the studies presented here focus on gasification with steam:



and gasification with carbon dioxide:



These reactions are endothermic, so heat must be provided in order for them to occur. Providing this heat and generating steam and carbon dioxide for the reactions may seem unnecessarily complicated. But the ultimate goal of these processes is energy production and through clever engineering it is possible to obtain more electrical output per unit of fuel by gasification than by combustion. The products of reactions 1-2 and 1-3, hydrogen and carbon monoxide, are themselves fuels. By subsequent combustion of these gases energy is released and can be used for power production. An example of such a system is given in section 1.2.3.

1.2.2 Processes during black liquor gasification

A droplet of black liquor goes through three stages of conversion in a gasification reactor: *drying*, *pyrolysis* (also known as devolatilization) and *char gasification*. The progression of these stages is shown schematically in Figure 1-2.

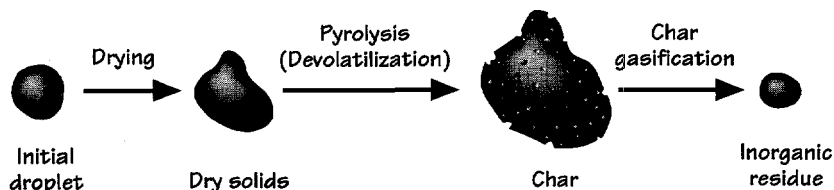


Figure 1-2. Stages of black liquor gasification.

Drying. Drying is the first process that occurs when the droplet is introduced into a hot environment, and simply involves evaporation of water from the droplet. The process is heat-transfer controlled, so the rate of drying depends on how quickly heat can be supplied to the droplet. Typically, black liquor droplets dry in less than one second. The drying time decreases with increasing temperature and decreasing droplet size. During drying black liquor droplets swell somewhat, so that the diameter of the dry solids that result is roughly 1.5 times that of the original droplet.

Pyrolysis. In this thesis, the terms *pyrolysis* and *devolatilization* are synonymous and are used interchangeably. During pyrolysis, the organic matter in the liquor degrades, forming various gaseous compounds such as carbon dioxide, carbon monoxide, hydrogen, methane, other light hydrocarbons, hydrogen sulfide, other gaseous sulfur compounds and heavier hydrocarbons known as tars, which themselves decompose to form lighter species. The reactions responsible for this degradation of organic matter are called *pyrolysis reactions*. The result of this process is a char which contains the non-volatile organic material as well as most of the inorganics.

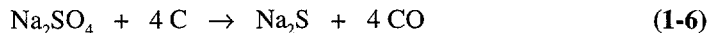
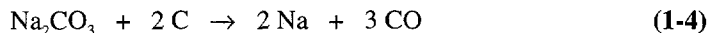
As with drying, the rate of pyrolysis is determined by the rate of heat transfer to the droplet. Substantial swelling also occurs during this phase, and the volume of the char that remains after pyrolysis can be 30 or more times that of the original droplet. The pyrolysis stage generally lasts less than a second, with smaller particles and higher temperatures leading to faster devolatilization times.

Char gasification. The final stage is char gasification, during which gas phase species (gasifying agents) react with organic constituents in the liquor, converting them into gaseous species. These reactions, such as reactions 1-2 and 1-3 above, are called *gasification reactions*.

Char gasification is an endothermic process and is generally the slowest stage of conversion. At low temperatures, less than roughly 900°C, the rate is determined by the reaction rates of the gasification reactions. The gasification reaction is very temperature sensitive, and as the temperature rises the reaction rate increases dramatically. At temperatures above roughly 1100°C, transport of gases to and within the particle dictate the overall rate of char gasification. The particle has been observed to shrink during gasification and when this stage is complete only inorganic material, or smelt, remains.

For small droplets or at low temperature the stages take place more or less consecutively, so pyrolysis doesn't begin until the droplet is dry, for instance. For larger droplets or at higher temperatures, however, there can be substantial overlap of the stages. It is possible for the surface of a large drop to begin devolatilization or even char gasification while the interior of the droplet is still drying.

Inorganic decomposition reactions. This view of the conversion process is complicated somewhat by inorganic decomposition reactions. Inorganic decomposition reactions are defined as those in which inorganic species in the liquor, most notably sodium carbonate, decompose, commonly by reaction with carbon. In this thesis, *inorganic decomposition reactions are classified as neither pyrolysis nor gasification reactions*. The primary inorganic decomposition reactions are decomposition of sodium carbonate and decomposition of sodium sulfate:



In most practical situations, these reactions occur during the char gasification stage. However, they may occur any time the liquor is exposed to high temperatures for prolonged periods of time, for instance in pyrolysis experiments with long holding times.

The contribution of each of these categories of reactions to conversion of black liquor solids during gasification is presented schematically in Figure 1-3. Pyrolysis reactions occur first, after which gasification and inorganic decomposition reactions proceed. The individual curves indicate the fraction of total conversion attributable to each type of reaction. At the end of the gasification stage, both gasification and inorganic decomposition reactions cease because no more organic carbon is available for reaction.

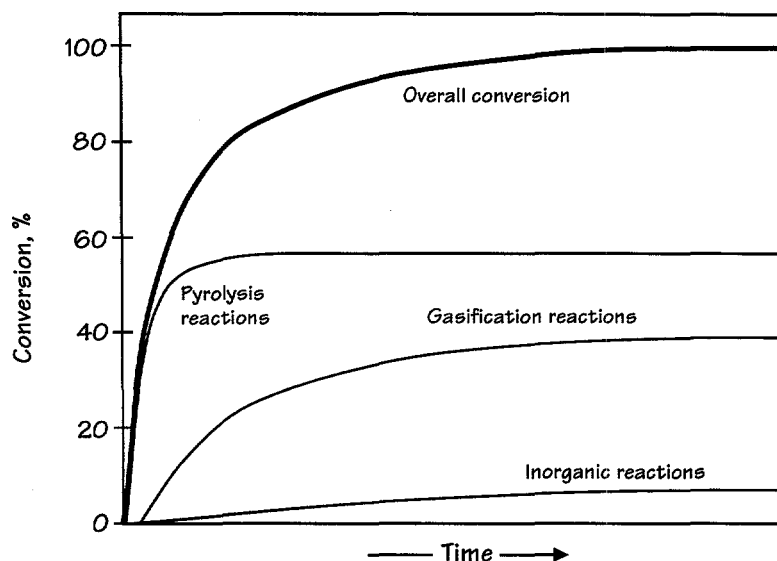


Figure 1-3. Schematic diagram indicating the contribution of the various types of conversion reactions to overall conversion.

1.2.3 Industrial gasification

In this section it is explained how the reactions described above are applied on an industrial scale. Figure 1-4 depicts a hypothetical scheme for gasification of black liquor. This process, the so-called integrated gasification combined-cycle (IGCC) process, is founded on that for coal gasification. This particular diagram is for a pressurized system. By operating the process under pressurized conditions a higher electrical/thermal energy ratio can be achieved.

First consider the gasifier. For reactions 1-2 and 1-3 to proceed there needs to be input of steam and/or carbon dioxide. It is possible to have an external system for production of these reactants. A much simpler approach, however, is to take advantage of reaction 1-1 by supplying air or oxygen to generate the necessary carbon dioxide. Air is cheap and readily available. The liquor contains water when it is fed into the reactor so evaporation of the water also produces steam. By feeding less oxygen than is necessary for complete conversion it is possible to generate enough carbon dioxide and steam to convert the rest of the carbon in the liquor by reactions 1-2 and 1-3. Stoichiometric ratios of roughly 0.4 are typical for such gasification units.

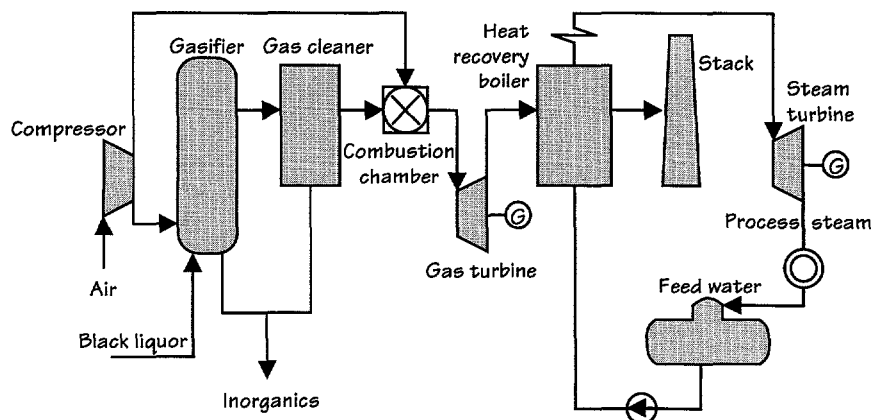


Figure 1-4. Schematic diagram of an IGCC process for black liquor gasification.

The gas exiting the gasifier is rich in hydrogen and carbon monoxide. It is cleaned to remove particulates and then combusted. The hot, pressurized products pass through a gas turbine to generate electricity. The temperature of the gases after this stage is still high, so the gases are passed through a heat exchanger, or heat recovery boiler, to produce steam. This steam is used to drive a steam turbine and produce additional electricity. Through a pressurized IGCC process such as this, it is possible to more than double the electrical/thermal energy ratio compared to a traditional recovery boiler [2,3]. Details of proposed gasifiers are presented in section 2.1.

1.3 Outline of this thesis

The chapters that follow start with a review of the literature relevant to the present study. Chapter 3 then discusses the aims of this work and introduces the specific studies performed to achieve these goals. In Chapter 4 the experimental equipment and methods are presented. The results from the present study are broken down into two chapters. Chapter 5 concerns pressurized pyrolysis of black liquor and Chapter 6 addresses char gasification under pressurized conditions. Conclusions from this study are given in Chapter 7, and in Chapter 8 a short summary of each of the appended papers is presented.

2. LITERATURE REVIEW

Before discussing the results from the current work, it is instructive to review previous research on black liquor pyrolysis and gasification. In this chapter the relevant literature is reviewed. Proposed black liquor gasification concepts are discussed below, and research on black liquor pyrolysis and char gasification are considered in the following sections.

2.1 Proposed black liquor gasification concepts

A number of preliminary studies have been carried out to determine the feasibility of a gasification system for black liquor [2,4-6]. These studies indicate that an integrated gasification system has the potential to increase the electrical power-to-steam ratio obtained from black liquor, and that such a system may double the power output of a conventional recovery system. A gasification system would also eliminate the possibility of water contacting the molten smelt due to a tube break. Other benefits include greater flexibility and a potential for reduced cost.

Several designs have been proposed for black liquor gasification. These can be divided into those that operate below the melting range of the inorganic material in the black liquor, ("solid phase" gasification) and those that operate above the melting point ("molten phase" gasification). The studies presented in this work are most relevant to low-temperature gasification schemes. An comparison of proposals for black liquor gasification has been reported by Grace and Timmer [7].

Stonechem process (formerly MTCI). The Stonechem process [8,9] is a low-temperature process involving steam gasification in a bubbling fluidized bed. Sodium carbonate, a product of the gasification, is used as a bed material. Steam is both the primary fluidizing agent and the reacting gas. The unique feature of the Stonechem process is indirect heating of the fluidized bed by pulse combustion heaters. The gasifier operates at roughly 600°C and atmospheric pressure. A large scale pilot reactor has been built parallel to the existing recovery boiler at a mill in New Bern, North Carolina. Preliminary tests indicate that the unit operates as planned, but the system is still far from optimized.

ABB Process. The ABB process [10] is a low-temperature design involving direct air-blown gasification in a circulating fluidized bed. Black liquor is sprayed into the gasifier and coats the bed material, sodium carbonate. Air is used both as a fluidizing medium and to control the temperature, and the gasifier operates at about 700°C. A large scale atmospheric pressure unit was built at ABB's research center in Västerås, Sweden in 1991. Currently, however, ABB is not pursuing development of their system.

Chemrec Process. The Kamyr (Kvaerner) Chemrec process [11,12] is arguably the most advanced, and is the only process to be in commercial operation. In this high-temperature process air or oxygen is fed co-currently into a refractory-lined entrained flow reactor with an integrated quench cooler for separation of the products. Operating temperatures are in the range 900-1000°C. The process is able to achieve very high carbon conversions and sulfate reduction efficiencies are reportedly high. A commercial unit is operating at the New Bern mill in the US, and another unit is in operation in

Sweden. Both air-blown and oxygen-blown versions are being considered for operation at elevated pressures.

Tampella Process. The Tampella process [13,14] is similar to the Chemrec process in that both involve direct air (oxygen) gasification in a co-current entrained flow system. The Tampella process, however, uses a smelt cyclone for separating the entrained smelt from the product gas. The gasifier operates at 900-1000°C. In atmospheric pilot-scale tests carried out in Kotka, Finland, the gasifier has been successfully demonstrated. Future plans include development of a pressurized system.

2.2 Black liquor pyrolysis

The process of black liquor pyrolysis is extremely complex, involving changes in both the structure and chemistry of the liquor. A considerable amount of research has been carried out in an effort to understand the process and to identify factors that affect its behavior. The most significant physical phenomenon which takes place during devolatilization is swelling of the liquor. The literature regarding swelling is reviewed here, and literature regarding the process of volatiles release is discussed in the following section.

2.2.1 Swelling

The importance of swelling during combustion of black liquor was first recognized by Baklien in 1960 [15]. In his work, Baklien measured the swelling tendency of small samples of black liquor in a crucible under standardized laboratory conditions. From these tests, he identified a relationship between the "burning quality" of a liquor and its tendency to swell when heated. In 1968 Björkman [16] published a series of photographs taken with a movie camera depicting the "life" of a calcium sulfite liquor droplet undergoing pyrolysis in a reducing atmosphere at 1000°C. The swelling behavior of the liquor is clear in the photographs and Björkman was able to identify stages of expansion, bursting, surface boiling and solidification. In the 1970's Oye *et al.* [17,18] observed swelling of black liquors at low temperatures. Despite these works, the 20 years following Baklien's original observations of liquor swelling produced little to further the understanding of black liquor swelling during pyrolysis.

In 1982, Hupa *et al.* introduced the so-called single droplet burning technique as an aid to measure and characterize swelling of black liquors during combustion [19]. Their brilliantly simple laboratory procedure, somewhat similar to that used earlier by Monaghan for study of calcium sulfite liquor combustion [20], involved suspending a small droplet of black liquor from a wire hook and filming it as it underwent combustion in a muffle furnace. The characteristic swelling behavior could then be examined closely when the films were replayed, and in these first studies it was observed that liquors from sodium sulfate pulping processes swell much more than liquors from sodium sulfite processes. Five years later, Hupa *et al.* published what is arguably the pioneering article on black liquor combustion [21] and demonstrated the value of the single droplet method as a tool for black liquor combustion research. In that paper they defined that black liquor burns in stages (drying, devolatilization and char burning). Also, they were not only able to measure the maximum swelling during burning, as Baklien had done previously, but were able to generate swelling and droplet temperature profiles as a function of the liquor

combustion time. Hupa *et al.* found that liquors swell primarily during the pyrolysis stage, and that the extent of swelling varies widely between liquors. Essentially all investigations of black liquor swelling that have been carried out since that time have employed the single-droplet technique.

Factors influencing swelling. Studies on black liquor swelling can be broken down into those that focus on liquor-specific variables and those that focus on furnace conditions. Most literature on the subject seems to take into consideration the influence of more than just one variable, and in many cases a particular variable has been investigated by several researchers. For this reason, and for the sake of readability, the rest of this section is presented in terms of the variables which have been investigated, rather than as a chronology of the research that has been performed.

Liquor solids content. In their early investigations of black liquor swelling, Miller and Clay [22] and Miller *et al.* [23] studied the influence of solids content on swelling of laboratory-produced liquors in a nitrogen environment. In their experiments a single liquor particle was placed on a wire and pyrolyzed by flowing a hot nitrogen stream past the particle. They found that at temperatures between 400 and 600°C, increasing solids (from 65% to 100%) decreased the degree of swelling by nearly a factor of two. Outside this temperature range, however, the effect of solids content was negligible. Subsequent analysis revealed that the composition of the chars formed from liquors with different solids contents varied somewhat. In particular, chars formed from liquors with higher solids contents had higher carboxyl contents and higher associated degrees of swelling. The carboxyl content was attributed to the sugar acid fraction of the liquor. But no mechanism was proposed to explain exactly how solids content influences swelling during pyrolysis, other than a suggestion that "the differences in swelling behavior due to the original solids content of black liquor cause a more subtle difference in the pyrolysis of the material." [23].

Frederick *et al.* [24] performed a study specifically to investigate how liquor solids content affects swelling during combustion at temperatures closer to those found in a recovery boiler. They found little effect of solids content for a hardwood kraft and a sulfite liquor. But the softwood kraft liquor used displayed an increase in swelling with solids content over the range 55% to 85%. However, no explanation was given for this behavior.

Liquor type. A number of investigations have considered differences in swelling between liquor types, namely softwood kraft, hardwood kraft, and sulfite liquors. Hupa *et al.* [19] were the first to note that sulfite liquors swell much less than sulfate liquors. This was confirmed in a later study by Hupa *et al.* [21], as well as by Frederick *et al.* [24-26]. Noopila *et al.* [27] measured swelling for a soda-anthraquinone liquor and found that it swelled less than kraft liquors. Softwood and hardwood kraft liquors generally seem to have similar swelling behavior, although some studies conclude that one or the other swells more. The research of Frederick *et al.* [24] may provide some insight into this issue. They found that the degree of swelling for the softwood liquor used in their study was dependent on the liquor solids content while no such behavior was observed for their hardwood kraft liquor.

Kraft lignin to sugar acids ratio. Miller *et al.* [23] studied the influence of liquor composition on swelling of laboratory-prepared black liquors in nitrogen at 500°C. They found that the ratio of kraft lignin to sugar acids (polysaccharides) in a liquor dramatically affects its swelling behavior during pyrolysis, and that a ratio of roughly 1:1 of these components yields maximum swelling. They suggest that the decomposition of the sugar acids, which occurs around 240°C, provides the bubbles necessary to cause expansion of the droplet while the lignin fraction impacts the viscosity of the material, and that the balance of these two forces is found at a ratio near 1:1. Alén *et al.* [28] found the same trend for hardwood lignin at temperatures more closely reflecting those found in a recovery boiler. One result by Noopila *et al.* [27] shows a similar maximum for swelling versus the ratio of hardwood lignin to the sum of aliphatic acids and other organics. But when the ratio of lignin to aliphatic acids (without other organics) was considered, swelling only increased over the range studied, revealing no particular ratio which yielded maximum swelling. However this study considered a much narrower range of ratios. Miller *et al.* [23] reported that the swelling decreases with increasing molecular weight of the lignin. Söderhjelm *et al.* [29] later observed just the opposite for industrial kraft liquors and suggested that the difference in the results could be due to differences in liquor origins.

Liquor viscosity. Söderhjelm *et al.* [29] investigated a number of industrial liquors with varying viscosities in an attempt to identify a relationship between swelling and liquor viscosity. No general trend resulted, although there did appear to be a correlation for data taken at 700°C suggesting that higher viscosities result in lower degrees of swelling. Miller *et al.* [23] also alluded to the importance of viscosity in determining the degree of liquor swelling, but their analysis was largely speculative.

Sodium sulfate concentration. Both Hupa *et al.* [21] and Miller *et al.* [23] found that increasing sodium sulfate concentration decreases the degree of liquor swelling. The data from both studies are quite comparable, but the analysis of Miller *et al.* indicates that the decrease in swelling up to 20 wt% addition is simply due to the diluting effect of additional sodium sulfate.

Extractives. Miller *et al.* [23] found a very strong correlation indicating that higher concentrations of extractives in the liquor result in decreased swelling at 500°C. Noopila *et al.* [27] confirmed this behavior for pyrolysis at 420°C. However, at higher temperatures, when proper ignition and burning of the droplet took place, this was not necessarily found to be the case. While the hardwood liquors did display a slight decrease in swelling when extractives were present, the extractive-containing softwood liquors swelled more than those without. Additionally, Hupa *et al.* [21] found that addition of tall oil decreased the extent of swelling.

Temperature. Miller and Clay [22] investigated the influence of furnace temperature on swelling in nitrogen, when the droplet did not undergo ignition. They found that maximum swelling occurred at 500°C, and that at temperatures between 400° and 600°C the swelling was decidedly greater than outside this range. Many studies since then have used conditions which more closely resemble those of a recovery boiler and most have found that swelling decreases with temperature under these conditions (Frederick *et al.* [24-26,30], Alén *et al.* [28], Söderhjelm *et al.* [29]). In some cases swelling was found to be insensitive to furnace temperature (Frederick *et al.* [25,31]). Contrary to

these findings, Lee *et al.* [32] report that swelling *increases* with temperature. Their experiments were carried out in a reactor very similar to those used by Frederick *et al.* but pyrolysis took place in a reducing gas mixture of 5% CO in nitrogen, rather than in an oxidizing environment. As noted below, gas composition also influences swelling and it may be that for some reason swelling behavior differs between oxidizing and reducing atmospheres. More study is necessary to resolve this issue.

Gas atmosphere. Frederick *et al.* [26,31] studied how the presence of oxygen, carbon dioxide or steam in the pyrolysis gas influences swelling. Under otherwise identical conditions, droplets swelled least in air or high concentrations of CO₂ or H₂O. Swelling was greater in pure nitrogen, but the greatest swelling was found in reduced concentrations (4-12%) of oxygen. In a later paper [30], Frederick and Hupa analyzed the data more closely and took into consideration the temperature increase around a droplet when it is pyrolyzed in an oxygen-containing environment, thus forming a flame. In this paper they developed an expression for estimating swelling based on the furnace temperature and oxygen concentration.

The influence of the local temperature around the droplet cannot explain all effects of gas composition, however. When no oxygen is present, the surrounding gas temperature would be lower due to the absence of a flame, and according to the analysis of Frederick and Hupa one would expect higher degrees of swelling. But swelling in atmospheres containing H₂O or CO₂ and no oxygen is significantly less than in atmospheres containing equivalent concentrations of oxygen [26,30]. The reason for this difference in behavior in the presence or absence of oxygen is not fully understood, but deserves further attention.

Pressure. There is essentially no published data on the influence of pressure on black liquor swelling during pyrolysis. McKeough *et al.* [33] made a qualitative observation that swelling during pyrolysis in a grid heater decreases when the pressure is raised from 2 to 21 bar, but no quantitative data has been published.

Modeling of swelling. Despite considerable effort to characterize and understand swelling, there is still no model available to adequately estimate swelling based on known properties of the liquor. Modeling of the influence of furnace variables has been more successful. As previously mentioned, Frederick and Hupa [30] developed an expression for predicting swelling at a particular furnace temperature and gas concentration when the swelling factor at one set of conditions is known. Clay *et al.* [34-36] measured swelling for a wide range of gas flow rates and temperatures and developed an empirical expression relating the observed degree of swelling to these variables as well as other measurable properties of the char.

Recently, Saastamoinen [37] presented a detailed model for the local swelling inside a black liquor droplet in the devolatilization region. The model accounts for the fact that the stages of combustion may overlap in a droplet, and that any particular point in a droplet undergoes the stages of water evaporation, softening of the dry material, release of volatiles through this soft layer, forming bubbles, and solidification of the droplet. The model can also explain why char particles are often observed as being hollow. It cannot predict the degree of swelling based on liquor properties, but is nonetheless a valuable aid to the understanding of how swelling within a droplet occurs.

Frederick [31] succeeded in simplifying the swelling process somewhat by considering the change in the *dimensionless* droplet diameter (the extent between the minimum and maximum diameters) as a function of the *dimensionless* devolatilization time (the fraction of the total pyrolysis time). An empirical expression was developed such that the dimensionless droplet diameter was roughly equal to the dimensionless time (or the dimensionless heat input) to the power of 0.8.

The impact of black liquor swelling on the trajectory of particles in a recovery furnace has been modeled by Walsh and Grace [38] as well as by Frederick *et al.* [26]. In the model of Walsh and Grace, the droplet diameter is assumed to increase linearly throughout the devolatilization stage. Frederick *et al.* used this model as a foundation but included correlations for the droplet diameter versus the degree of combustion which were obtained from experimental data.

2.2.2 Devolatilization

Much less research has been performed regarding the actual loss of volatile material from black liquor during pyrolysis than has been done on other aspects of pyrolysis, such as swelling. Much of the work regarding the devolatilization process has been performed either to investigate the feasibility of black liquor as a source for fuels production or in order to characterize the composition of black liquor. The conditions used in these experimental investigations are hardly representative of those found in a recovery boiler, but nonetheless the results do provide some insight into the devolatilization process, particularly with regard to the temperature range in which thermal decomposition occurs.

Volatiles and char yields. Backman *et al.* [39] provide a good overview of the carbon conversion processes that occur during black liquor pyrolysis. Frederick and Hupa [40] studied the influence of liquor type, droplet size, dry solids content, furnace temperature and pyrolysis time on the volatiles yield of single liquor droplets undergoing pyrolysis. The volatiles yields for the different kraft liquors ranged from 35% to 47% of the initial dry mass of the liquor, and volatiles yields were found to be independent of droplet size and solids content. The volatiles yield after pyrolysis for 10 seconds was found to increase with temperature by roughly 10 wt-% units per 100°C over the range 700-1200°C, and although the majority of devolatilization took place within the first five seconds, volatiles continued to be released for at least another minute (the maximum time studied). McKeough *et al.* [33] studied fast pyrolysis of black liquor in a grid heater, and their data support these findings. The continued weight loss was found to result from inorganic decomposition reactions, primarily reduction of sodium carbonate. As explained in section 1.2.2, these reactions are not truly "devolatilization" in the sense that they don't involve thermal degradation and release of volatile material in the liquor, but they do contribute to the observed mass loss.

Kymäläinen [41] studied the influence of heating rate on the char yield of an industrial softwood liquor. She found that heating rate had little influence except under low pressure, high temperature (1000°C) conditions. McKeough *et al.* [33] performed pyrolysis experiments at elevated pressure at both 675° and 900°C. Their data indicate that pressure has negligible effect on char yields at the lower temperature, but at 900°C char yields increased somewhat with pressure. Similar experiments performed by Harju [42] at 600°C and Kymäläinen [41] at 1000°C support these observations. The

increase in char yield with pressure was attributed to suppression of the sodium carbonate decomposition reaction, and McKeough *et al.* showed that for pyrolysis at 900°C, char formed at 21 bar contained more carbonate than that formed at 2 bar. Pyrolysis of black liquor under pressurized conditions has been studied by other researchers, as well [43-45].

Product gas composition. In 1967, Feuerstein *et al.* [46] and Brink *et al.* [47] made a very thorough analysis of products from black liquor pyrolysis at very low heating rates. Carbon monoxide and carbon dioxide were the major products, and their concentration increased with increasing temperature. Other major products were methane, ethane, hydrogen sulfide, hydrogen, methyl mercaptan and dimethyl sulfide.

Bhattacharya *et al.* [48] studied pyrolysis of black liquor solids at temperatures between 590° and 750°C in order to investigate the use of black liquor as a source for fuels production. In their experiments, samples of dry black liquor were immersed into a hot reaction chamber filled with nitrogen and allowed to pyrolyze for up to 15 minutes. The char, tars and gases were collected and analyzed and measured as a function of pyrolysis time. Their results indicate that as the pyrolysis temperature is increased the total amount of gases released after 15 minutes increases while the fraction of tars and solid char decreases. At 750°C the fractions of char, tars and gases were 0.47, 0.35 and 0.18, respectively. However, these values do not translate well to a recovery boiler, which operates at higher temperature and has a liquor residence time of only a few seconds. One useful result from this work is the composition of the pyrolysis gases that were produced. As with Feuerstein's work the major products were CO₂, CO, H₂, CH₄ and H₂S. As the pyrolysis temperature was increased, the concentrations of CO₂, CH₄ and H₂S decreased while the CO and H₂ concentrations increased. The same behavior was found in an equilibrium analysis of black liquor gasification with an air ratio of 0.0 performed by Backman and Hupa [49].

McKeough *et al.* [33,50] measured the concentrations of gases produced during pyrolysis of black liquor in a grid heater at different temperatures and pressures. They found that the release of H₂ and CO and light hydrocarbons increases with temperature while release of CO₂ and sulfur-containing species decreases. Higher pressures resulted in decreased production of H₂ and CO but increased the quantity of CO₂ and light hydrocarbons released.

Recently, Sricharoenchaikul *et al.* [51] probed the mechanism of tar and gas evolution during pyrolysis. Their laminar entrained-flow pyrolysis reactor allowed analysis at very short residence times (< 0.5 s.). They concluded that for extremely high heating rates (>10,000 K/s in their experiments) the initial pyrolysis product (after ~0.3 seconds) consists of between 30% and 60% tars, depending on the temperature, and that these undergo secondary reactions to produce lighter gases. As the pyrolysis temperature increases the rate of tar conversion to lighter compounds increases, so that at longer residence times less tar is observed at higher temperatures. The gases resulting after secondary reactions included CO₂, CO, methanol, aldehydes and light hydrocarbons.

Fate of elements. Recently there has been great interest in the release of elements, particularly carbon, sulfur and sodium, from black liquor during pyrolysis.

Carbon. Most of the studies just mentioned (Frederick and Hupa [40], Bhattacharya *et al.* [48], Backman and Hupa [49], McKeough *et al.* [33,50] and Sricharoenchaikul *et al.* [51]) investigated the release of carbon during pyrolysis and the form in which it is released. The research indicates that carbon is first released primarily as tars, which then decompose to form CO, CO₂, methane and other light hydrocarbons. McKeough *et al.* [33] found that carbon release decreases with pressure at 900°C but found no relation between carbon release and pressure at 675°C.

Sulfur. A considerable amount of literature exists regarding the release of sulfur species during pyrolysis of black liquors. As early as 1967, Feuerstein *et al.* [46] and Brink *et al.* [47] published a pair of papers regarding "malodorous products" from a recovery boiler. They found that the major gaseous sulfur species resulting from slow pyrolysis of black liquor were hydrogen sulfide, methyl mercaptan, dimethyl sulfide and dimethyl disulfide. Li and van Heiningen [52] also observed this. Feuerstein *et al.* [46] found that as the pyrolysis temperature was increased the concentrations of hydrogen sulfide and dimethyl disulfide increased while that of methyl mercaptan decreased. At temperatures in the range of those found in a recovery boiler about half the sulfur released was in the form of hydrogen sulfide. Dimethyl sulfide displayed no systematic variation with temperature. Subsequently, Thomas *et al.* [53] and Brink *et al.* [54] studied the mechanism of sulfur compound production during pyrolysis and suggested that release of malodorous compounds could be limited by a multistage pyrolysis-combustion system which would minimize exothermic recombination reactions which are responsible for the production of malodorous compounds.

In order to obtain a better understanding of which species in black liquor contribute to hydrogen sulfide formation, Douglass and Price [55] studied volatilization of five different inorganic sulfur compounds: sulfate, sulfite, thiosulfate, sulfide and elemental sodium. Each compound was mixed with either soda lignin or glucose, and pyrolyzed in nitrogen at 600°C until evolution of gaseous products ceased. In their study, elemental sulfur, thiosulfate and sulfide were the major contributors to H₂S formation, and very little H₂S was formed from sulfate and sulfite. Intrigued by the similarity of H₂S production by thiosulfate and sulfide, Strohbeen and Grace [56] later repeated this approach, but performed more thorough gas and residue analysis and used sodium gluconate and vanillic acid as organic compounds. They did not include organic sulfur. Like Douglass and Price, they found that sulfate and sulfite were quite unreactive, while thiosulfate and sulfide produced large quantities of H₂S. However, in their study sulfide released nearly all its sulfur in the form of H₂S while thiosulfate released less than half. The difference in results was thought to perhaps stem from the different choices for organic compounds.

Harper [57] also investigated the influence of the form of sulfur on sulfur release. In his experiments, a soda liquor was doped with either sodium sulfate, sulfite, thiosulfate or sulfide in order to simulate a kraft liquor. By this procedure the form of sulfur could be controlled. The liquors were then pyrolyzed through rapid heating in a grid heater over the range 250° to 750°C with pyrolysis times of up to 15 seconds. As expected based on the aforementioned studies, the liquors containing sulfate and sulfite displayed little sulfur release (<2%). For thiosulfate and sulfide, maximum release was observed at approximately 500°C, and 40-50% of the sulfur was released at this temperature. Most of the release was observed to occur during the first few seconds of pyrolysis. Clay *et*

al. [35] also observed maximum sulfur release in this temperature range, and postulated that release was responsible for the increase up to the maximum, and the decrease at higher temperatures was due to a sulfur recapture mechanism.

Thoen *et al.* [58] studied how changing conditions in a recovery boiler affect the release of odorous sulfur compounds. In their study they sampled the exhaust gas from a recovery boiler both before and after the direct-contact evaporator and measured the concentration of odorous gases in the samples. They concluded that black liquor oxidation prior to firing has little influence on the amount of odorous compounds exiting the boiler prior to the direct-contact evaporator, but that oxidation does make a great deal of difference with respect to the emission from the direct-contact evaporators. Operation within the design capacity, sufficient oxygen and good gas mixing in the upper regions of the furnace were suggested to help eliminate such odorous compounds. Borg *et al.* [59] studied emissions from a recovery boiler with no direct contact evaporator. Based on their field data and theoretical calculations they came to the same conclusion as Thoen *et al.* that sufficient oxygen availability and mixing in the upper furnace is key. Additionally, it was concluded that all gaseous sulfur originates as H_2S and that most of it originates either from the char bed or from the liquor gun level. Larger droplets and higher solids contents were also found to decrease sulfur emissions. Cantrell *et al.* [60] studied the effects of droplet size, solids content, added sulfur and pyrolysis gas oxygen content on sulfur release from single droplets of black liquor pyrolyzed at $1090^\circ C$. They also found that sulfur release decreases with increasing drop size, from 86% for a 1.3 mm droplet to 10% for a 3.9 mm droplet at 72% solids. Increasing dry solids content reduced sulfur release, as well. Additional sulfur and gas oxygen content had negligible influence. Bruley *et al.* [61], focusing on the black liquor properties, found that sulfur release can be reduced by removing the lignin fraction from the black liquor by precipitation.

Recently, several investigations have been carried out on black liquors at conditions which are representative of those encountered in a recovery furnace. McKeough *et al.* [50] studied sulfur release during rapid pyrolysis of black liquor in a grid heater. Their results confirmed those observed previously, namely that sulfur release decreases with increasing temperature and solids content. Based on their results and other work, they proposed a mechanism for sulfur release during pyrolysis in which the majority of sulfur release is due to lignin demethylation by sodium sulfide to form methyl mercaptan and dimethyl sulfide. These reactions only occur at temperatures below $500^\circ C$, so the effective reaction time at or below $500^\circ C$ during heating governs the extent of sulfur release. Indeed, it was demonstrated that the amount of sulfur released in their experiments corresponded well with the residence time of the liquor in the interval 400 - $500^\circ C$. According to their mechanism, the formation of H_2S results primarily from sodium sulfide decomposition.

Kymäläinen [41] also studied sulfur release during pyrolysis in a grid heater device, with focus on the form of sulfur remaining in the char. It was found that at high temperatures (900 - $1000^\circ C$) the majority of sulfate originally in the liquor was either released or perhaps was transformed to sulfide. Possible oxidation of the sulfide in the chars during handling makes it impossible to conclude which is the case. At $700^\circ C$ most of the sulfate remained in the char. The sum of measurable sulfur anions in the char increased slightly with pyrolysis pressure.

Forssén *et al.* [62,63] and Frederick *et al.* [64] pyrolyzed single droplets of black liquor in conditions similar to those found in recovery furnace. They found that sulfur release began with the onset of devolatilization — none occurs during drying. By measuring the time for 50% completion of the sulfur release process they were able to determine that the rate of release increases with furnace temperature. At lower temperatures this is due to the chemical reaction rate of sulfur release but at higher temperatures increased heat flux contributes to the increased rate. Heat transfer was found to dominate the rate of sulfur release at temperatures above 700°C. The extent of release was found to go through a maximum with temperature at roughly 600°C. At higher temperatures it is suspected that recapture of the sulfur contributes to the lower release. The relative degrees of sulfur and carbon release were found to be liquor dependent. In some liquors the degree of release versus conversion is the same for both components while for others sulfur release was found to exceed that of carbon. A recent report by Frederick *et al.* [65] summarizes much of what has been learned regarding sulfur release from black liquor and proposes an empirical model for predicting the rate and total amount of sulfur released during devolatilization of black liquor. The rate of sulfur release is assumed to be proportional to the rate of carbon release, while the total amount of sulfur released is a fraction of the total sulfur in black liquor. That fraction depends only on furnace temperature.

Sodium. As early as 1968, Björkman [16] observed that sodium is released from sulfite liquor during pyrolysis. He was not specifically investigating sodium release. Instead, he was measuring carbon release during flash pyrolysis and would hoping he could simplify carbon analysis in the char by comparing it to sodium, which he assumed would be inert. However, he observed that some of the sodium disappears from the particles. In order to solve his problem with the carbon analysis, he made the ambiguous assumption that the sodium loss was always 25% of the total sodium. The best explanation Björkman could provide about the sodium loss was that perhaps pyrolysis released some "fines" of inorganics which are not retained on the filter he used.

In a study carried out in 1973, Borg *et al.* [59] were able to identify sodium release in a recovery boiler. They observed that release increased with increasing temperature and noted that the majority of sulfur release occurred in the gas phase near the gun level, rather than from the char bed. The sodium was assumed to vaporize primarily as Na(g) and NaOH(g) which later react with gaseous sulfur species to form sodium sulfate fume.

Li and van Heiningen [66] studied sodium emission during slow pyrolysis of black liquor and observed that sodium loss occurs at temperatures above 675°C and increases with temperature and holding time. They found that, at longer holding times, sodium carbonate was reacting with carbon in the char to form sodium vapor. The presence of carbon monoxide or carbon dioxide in the gas suppressed carbonate decomposition at temperatures up to 800°C. Frederick and Hupa [67] found that during pyrolysis of single liquor droplets at 700-800°C, 15 to 20% of the sodium in the liquor was released, much of it in the form of submicron fume. In subsequent experiments Frederick *et al.* [64] found that the amount of release increased dramatically with furnace temperature, and that at 900-1000°C sodium release continued with time. Gairns *et al.* [68] noted the same, and observed the suppressing effect of carbon monoxide and carbon dioxide in the gas phase up to 900°C. McKeough *et al.* found the same effect of time and temperature for fast pyrolysis of black liquor in a grid heater [50,69]. They also found that sodium release at higher temperatures decreases with pressure and ascribed this observation to

slower carbonate decomposition under pressure. Kymäläinen [41] found this to be the case at 1000°C as well, and was able to establish that the carbonate concentration in chars formed at higher pressures is higher than that of chars formed at low pressure. Sorvari *et al.* [70] observed roughly the same amount of sodium release at 850°C during pyrolysis in a grid heater under pressurized (10 bar) conditions. For pyrolysis at 10 bar, 1100°C, they observed that roughly 70% of the sodium was released and concluded that at such high temperatures, sodium carbonate decomposition is responsible for nearly all of the sodium release. Dayton and Frederick [71] recently analyzed gas-phase alkali metal salts resulting from combustion at 1100°C using a molecular beam mass spectrometer and found that NaCl was the dominant sodium gas-phase species.

Verrill and Nichols [72] studied sodium release during single droplet combustion and postulated that sodium release is largely due to physical transport of sodium-containing material from the particle by eruptions during pyrolysis. A later study by Verrill and Nichols [73] identified two size fractions of sodium aerosol formation during black liquor combustion. Larger particles, 5 to 20 microns in diameter were observed and thought to result from physical ejection of sodium-containing material, or "ejecta." A smaller, submicron fraction was also observed which was thought to originate from sodium vaporization during char burning and smelt oxidation. Kauppinen *et al.* [74] was able to measure the amount of this submicron fraction using an electrical low-pressure impactor and concluded that less than 3% of the sodium in black liquor is released as such aerosol, and that the remainder of sodium released likely is in the form of ejecta. Kymäläinen *et al.* [75] performed similar experiments and found that between 3% and 6% of the sodium in the liquor ended up as fume.

Critical analysis of sodium release has only been studied within this decade. Frederick *et al.* [65] provide a good overview of much of the experimental work in this field and Verrill and Wessel [76] give an excellent overview of the primary sodium release mechanisms.

2.3 Char gasification

As mentioned in the previous chapter, gasification of black liquor is a promising alternative recovery process. Accordingly, a fair amount of research has been conducted on the topic, mostly with regard to the most time consuming step in the process, heterogeneous reaction of the char with either steam or carbon dioxide. But since black liquor gasification research is still relatively young there are many open questions. These will undoubtedly be solved in time, but for the present it is instructive to look at work that has been done in similar fields, primarily that of coal gasification. Many fundamental aspects of black liquor gasification, such as alkali catalysis, have also been studied previously. In this section research in the field of black liquor gasification is reviewed, followed by a review of work that has relevance to black liquor gasification, namely coal gasification and the mechanism of alkali-catalyzed carbon gasification.

2.3.1 Black liquor char gasification research

Black liquor gasification research is a relatively new area, with the majority of studies having taken place over the last 10 years. Earlier studies focused on gasification at atmospheric conditions, and more recent work considers pressurized gasification. Most

of the research has aimed at identifying the influence of process variables on the rate of gasification with carbon dioxide and steam and modeling the gasification mechanism.

Atmospheric gasification. Li and van Heiningen [77] published the pioneering article on black liquor char gasification kinetics in 1986. In their study they used a thermobalance to study the rate of gasification of black liquor char by CO_2 . A cup-shaped sample holder was filled with dry black liquor powder and placed into a furnace containing nitrogen and, in some experiments, CO, which suppressed sodium carbonate decomposition. The temperature was raised from 20° to 750°C over a period of roughly half an hour, during which time the black liquor pyrolyzed to form a char. When the temperature had stabilized, CO_2 was added to the gas mixture and the char was gasified. Most of the work was focused on determining to what extent mass transfer influences the observed rate. The measured rates were found to be free from external and inter-particle diffusion effects, but it was concluded that for particle sizes larger than a few millimeters inter-particle diffusion would become significant. Although it was observed that the gasification rate decreased with particle size it was concluded that this was a result of differences resulting from pyrolysis rather than intra-particle diffusion.

Subsequently, Li and van Heiningen used the same system to study the influence of temperature and gasifying atmosphere on the rate of CO_2 gasification of black liquor char [78,79]. They found that the rate was first order in carbon over most of the conversion range. The rate increased with CO_2 concentration and was retarded by increased CO and could be described by a Langmuir-Hinshelwood mechanism. Some of the char was prepared by "fast pyrolysis" and was found to be 2-5 times more reactive than the char formed as described above. Activation energies of 187 and 250 kJ/mol were measured for the slow- and fast-pyrolysis chars, respectively. A comparison of black liquor char, alkali-impregnated coal char and electrode carbon revealed that black liquor char is more than 10 times more reactive than alkali-impregnated coal char and over 3 orders of magnitude more reactive than electrode carbon. The explanation for this was that the distribution of the alkali catalyst in black liquor char is much more uniform than in the alkali-impregnated coal char. Sulfur release during CO_2 gasification was also studied by Li and van Heiningen [80]. They concluded that sulfur was primarily released as COS through the reaction of Na_2S and CO_2 .

Goerg and Cameron [81] also measured the CO_2 gasification rate of black liquor char, but in a bath of molten sodium carbonate at 927-1010°C. Their measured rates were less than that of Li and van Heiningen, despite that the temperature was 200°C higher. The evidence suggests (as do Li and van Heiningen [78]) that the low rates are a result of transport limitations of CO_2 external to and inside the char particles.

Li and van Heiningen also investigated gasification of black liquor char by steam [82]. The experiments largely paralleled their CO_2 gasification work, but they also analyzed the product gases and had to take into consideration the water-gas shift reaction. They found that increasing the H_2O concentration increased the gasification rate while increasing H_2 caused a decrease. The activation energy was found to be 210 kJ/mol and the rate could again be described a Langmuir-Hinshelwood mechanism. The concentration of CO_2 in the product gas was higher than would be expected by equilibrium, but this could be explained by the mechanism they proposed for the gasification reaction. The production of hydrogen sulfide was monitored and in a separate paper [83] Li and van Heiningen

explain that its emission results from reaction of sodium sulfide with steam and carbon dioxide to produce sodium carbonate and H_2S . The carbon dioxide results from a combination of the steam gasification reaction forming CO and the water-gas shift reaction in which CO and H_2O form CO_2 and H_2 . By this mechanism CO_2 production results from the steam gasification reaction and thus the rate of steam gasification largely controls the H_2S emission rate.

In a later paper, van Heiningen *et al.* [84] considered the influence of other variables on the rate of steam gasification. Specifically, the influence of the heating rate during char formation and the type of black liquor were investigated. Black liquor chars were prepared by heating black liquor at rates ranging from 0.3 to 750 °C/s. As observed in their earlier work, chars formed at higher heating rates were more reactive than those formed by slow pyrolysis by a factor of roughly 2. The rate of the fast pyrolysis chars was roughly of zero order in carbon and was found to correlate with the ratio of sodium to carbon in the char. The rate of the slow pyrolysis chars was closer to first order in carbon and seemed to correlate with the BET surface area of the chars. Amongst the liquors tested, the kraft liquors produced a more reactive char than the soda-AQ liquors.

To better understand processes that occur in the char bed of a recovery boiler, Cameron and Grace [85] and Grace *et al.* [86] investigated reduction of sodium sulfate by carbon. Char carbon reacts with the sulfate to form sodium sulfide, and the carbon is gasified to carbon monoxide and carbon dioxide. The rate of the reaction was found to be first order in carbon and independent of the sulfate concentration up to reduction efficiencies of 95%. The reaction was observed to be quite temperature-sensitive, with the rate doubling over a temperature rise of 60°C.

In addition to information on gasification rates, some studies have been carried out to identify physical changes that occur during gasification of black liquor droplets. Frederick and Hupa [87] used the single-droplet videotaping technique to monitor the diameter of black liquor droplets during atmospheric gasification with both steam and CO_2 . After an initial period of constant particle size the diameter of the droplets were observed to decrease quite linearly with time as the char was gasified. Lee *et al.* [32,88] studied changes in the swollen volume and bulk density of black liquor char during gasification. The bulk density was found to go through a minimum at roughly 10% conversion and then to increase throughout the remainder of gasification. The density of the char at 90% conversion was roughly 5 times that at 10% conversion.

Pressurized gasification. Many of the proposed alternative black liquor recovery processes involve gasification of black liquor under pressure. In response to this, Wåg [89] and Frederick and Hupa [90] used a pressurized thermobalance to investigate the rate of pressurized black liquor char gasification with carbon dioxide in the range 1-30 bar, 600-800°C. A sample holder was loaded with pre-formed char and lowered into CO/N_2 mixture, either at 200°C or at the desired gasification temperature. For experiments with an initial temperature of 200°C, the temperature was raised at 20 °C/min to the reaction temperature. When the sample weight was stable, the gas was changed to the desired mixture of CO_2 , CO and N_2 and the weight loss was recorded. Analysis indicated that the experiments were not affected by film mass transfer or pore diffusion. The rate was found to be roughly of order 0.85 in CO_2 , and CO dramatically decreased the rate. As the total pressure was increased at constant gas composition the

gasification rate decreased, by a factor of roughly 5 over the range 1-30 bar. This somewhat surprising result was attributed to a more severe increase in the inhibiting effect of CO compared to the gasifying effect of CO₂. Experiments at different temperatures indicated an activation energy of 205 kJ/mol.

In a later paper, Frederick *et al.* [91] made further analysis of the CO₂ gasification rate data. They found that the rate, defined as the instantaneous mass loss per time divided by the initial mass of carbon, increased with conversion up to roughly 35%, after which it decreased. This was explained by the increase in the catalyst/carbon ratio as the carbon was consumed. Several mechanistic models were tested to see which most adequately describes the observed rate behavior as a function of gas composition. The chosen model was one that had been developed for potassium-catalyzed CO₂ gasification of activated carbon and involves (1) adsorption of CO₂, (2) oxidation of the catalyst, (3) transfer of oxygen from the catalyst to a free carbon site, (4) decomposition of the oxidized carbon to yield CO.

Very little data exists regarding black liquor char gasification with steam under pressurized conditions. Harju [42] studied the influence of total pressure on the gasification rate over the range 1-20 bar and concluded that the time for 50% conversion is 3.4 times longer at 10 bar than at atmospheric pressure. The pyrolysis pressure during char formation was also observed to decrease the char reactivity.

More recently, Saviharju *et al.* [92] measured gasification rates of char prepared by fast pyrolysis of a laboratory-prepared black liquor in a grid heater, and scrutinized the experimental methods that had been used in previous studies of black liquor char gasification. The point in question was the addition of carbon monoxide to the nitrogen used in the pre-gasification stage. The carbon monoxide was present to prevent sodium carbonate decomposition (*cf.* Li and van Heiningen [77]). Saviharju *et al.* were able to demonstrate that the presence of CO, particularly at high pressure, resulted in condensation of elemental carbon "soot" on the sample. This deposited carbon could diminish the observed reactivity of the char during subsequent gasification, particularly at low conversions, but they indicated that the mechanism for CO₂ gasification suggested by Frederick *et al.* [91] was still valid. The activation energy for CO₂ gasification of their laboratory-prepared liquor, 368 kJ/mol, was also found to be much higher than that reported by Frederick *et al.* [90] for gasification of industrial kraft liquor chars.

2.3.2 Gasification of other fuels

The amount of literature available on gasification of fuels other than black liquor, particularly coal, is quite overwhelming, and a review of all these studies is far beyond the scope of this thesis. Much of the information is also not relevant to black liquor gasification, since it involves non-catalyzed gasification. As noted by Li and van Heiningen [78,79,82] and Moilanen *et al.* [93], black liquor gasification is so strongly catalyzed that its reactivity is several orders of magnitude higher than those of other fuels. Therefore this review focuses on studies which could be of use in our understanding of pressurized black liquor gasification, i.e. studies involving alkali-catalyzed gasification and studies of gasification at elevated pressures. Studies on the influence of char pretreatment (pyrolysis conditions) are also of interest and are included here.

Influence of fuel-specific variables on gasification rate. The factors which influence the gasification behavior of a fuel can be broken down into those that are fuel-specific (e.g. composition, morphology) and those that are process-specific (e.g. temperature, pressure, gas composition). Here we review those variables which are fuel-specific. The influence of process-specific variables is then considered.

Catalytic species. Gasification of coal is an important process for the production of synthesis fuels, and a number of studies have attempted to determine the most important variables influencing the behavior of the process. At least four studies have investigated a large number of chars in hopes of finding the most important fuel-specific parameters affecting the gasification rate [94-97]. In all of these studies it was concluded that the concentration of catalytic material, primarily calcium and sodium species, has the most impact on char reactivity. The benefits of catalysis have long been recognized and addition of catalysts to coal char in order to improve the rate of the gasification process is common practice. Studies of which materials make the most efficient catalysts inevitably return to the same conclusion that alkali metal salts, particularly those of potassium and sodium, result in the highest gasification rates [98-101]. Potassium carbonate is particularly effective. Several studies have also shown that the rate of gasification increases linearly with catalyst loading up to a "saturation point," roughly 0.10 mol alkali/mol carbon, and that further catalyst addition has little effect on the rate [102-104]. Sams and Shadman [104] concluded that at high catalyst loadings blockage of pores in the char by accumulation of the catalyst. Cerfontain *et al.* [105] studied alkali carbonate catalysts and found that sodium in particular has a tendency to form bulk carbonate that does not assist in the catalytic mechanism. The mechanism of alkali-catalyzed gasification is reviewed in section 2.3.3.

Fuel morphology. One of the significant factors in determining how quickly a fuel particle is converted is its surface area, which is closely related to its porosity. At high temperature, when mass transfer controls the overall rate, the external surface area is important. But for lower temperature schemes (such as black liquor gasification treated in this work) the *internal* surface area of a fuel particle is key. The overall rate of gas-solid reactions increases if more surface area is available for reaction. Thus it is vital to take the internal surface area into account when considering fuel reactivity. Not only does this area vary between fuels, but it changes during conversion of a particular particle.

Ghetti *et al.* [106] found that the surface area of coal chars, as measured by CO₂ adsorption, corresponded to the observed reactivity of the chars. Khan [107] measured the *active* surface area (by O₂ adsorption), and found it to be a better parameter for char reactivity than either BET surface area (as measured by N₂ adsorption) or surface area as measured by CO₂ adsorption. He also found that the surface area is a function of the char-formation temperature. Chars formed at lower temperatures (500°C) were found to much higher active surface areas and reactivities than those formed at higher temperatures (950°C).

A number of studies have been performed in an attempt to explain and model the development of a char's porosity and internal surface area as it is converted [108-111]. The "classic" model is the Random Pore Model, developed by Bhatia and Perlmutter [108]. By assuming a random geometry of cylindrical pores, and considering overlapping of pores (which thus results in a lower pore volume and surface area) they

created a mathematical model for the development of internal surface area during char conversion. The model has since been applied to observed reactivity profiles of coal chars and describes the observed behavior well. Li and Do [112] recently tested several models for their applicability to high-ash chars and found that a modified version of the Random Pore Model suitably described pore evolution for such chars. Hurt *et al.* [113] also examined pore structure evolution during gasification, and in their analysis they took into consideration particle shrinking and associated char densification during conversion.

Influence of process variables on gasification rate. Fuel-specific properties paint only half the picture of how a fuel behaves during conversion. Process conditions, such as temperature, pressure and gas composition, also impact the rate. These are reviewed briefly here.

Temperature. As one would expect, increasing temperature increases the rate of gasification in the chemical reaction controlled regime. Reported activation energies vary widely between fuels, from 131 kJ/mol for pure carbon [114] to 268 kJ/mol for peat [93]. Activation energies for alkali-catalyzed gasification of coal tend to be in the range 180-230 kJ/mol.

Gasifying atmosphere. The gas composition during gasification greatly influences the rate of the process. Laurendeau [115] reviewed the results of earlier studies on coal char gasification. Several more recent studies have been conducted to identify how the composition affects the rate during CO₂ and H₂O gasification of coals [95,116-123] and biomasses [124,125]. Under otherwise identical conditions, gasification with steam has been found to proceed 3-4 times faster than gasification with carbon dioxide. The CO₂ gasification rate of coal char has been found to be roughly first order in CO₂ at low pressures, but to decrease as the pressure is increased, becoming effectively zero order at pressures of 10 atmospheres and higher [117]. Carbon monoxide and hydrogen inhibit gasification by both CO₂ and H₂O.

Less literature is available regarding the influence of gas composition on the gasification rate specifically of *alkali-catalyzed* gasification of char [103,122,126]. But the indication is that the gas composition effects are the same in this case.

Pressure. The influence of pressure on alkali-catalyzed gasification of coal has been reported by Schumaker *et al.* [103] and Mühlen *et al.* [126]. At constant gas composition, the rate of steam gasification was found to increase with pressure, with a more severe increase noted at lower pressures (1-5 bar). At pressures higher than 20 bar the rate increase with pressure was much less. Increasing partial pressures of hydrogen and carbon monoxide inhibited the rate, again with more influence observed at lower pressures.

Pretreatment (pyrolysis) conditions. One final variable which can have dramatic impact on the gasification rate is the pretreatment procedure for the fuel, which in this work is defined as anything that has occurred prior to char gasification, including pyrolysis. Two samples of the same coal can be gasified under identical conditions and behave entirely differently if they have been subjected to different pretreatment procedures. Radovic *et al.* [127] found that the pyrolysis rate and residence time influence subsequent char

reactivity. Coal samples were pyrolyzed at 1000°C in nitrogen with heating rates ranging between 0.17 and 10⁴ K/s and for pyrolysis times ranging from 0.3 second to 1 hour. The chars which were pyrolyzed for the longest times (and at the slowest rates) were only about 4% as reactive as those pyrolyzed for the shortest times. Their conclusion was that the calcium oxide in the char sintered at over the long pyrolysis times, thus reducing its dispersion and catalytic efficiency.

Other research has also come to the conclusion that increasing heating rate increases the reactivity of the char [128-130]. The belief is that higher heating rates increase the porosity of the char, and indeed Gale [131] showed that this is true for some coals. Surprisingly, in a subsequent study Gale [132], reported a reactivity decrease with heating rate. However, these experiments were performed in entrained flow reactors and the higher heating rates were associated with higher pyrolysis temperatures, and increasing pyrolysis temperature is known to decrease reactivity.

Kasaoka *et al.* [133] studied the influence of temperature, heating rate (5-420 °C/min), gas atmosphere (N₂, H₂, H₂O and CO₂) and degree of carbonization on the steam gasification reactivities of chars made from 12 coals. No influence was observed for any of the variables at temperatures below 1000°C. At 1100°C and above, increasing temperature led to decreased reactivity, which was attributed to a decrease in the micropore volume of the char. Similar behavior has been found in many other studies [128-132], leading to the generalization in the field of coal gasification research that char reactivity decreases with the *severity* (temperature and time) of pyrolysis. The same has been found to be true for biomass [134,135].

Literature regarding the influence of pyrolysis pressure on char reactivity is limited. Güell *et al.* [129] and Cai *et al.* [130], working jointly, found that increasing the pressure during pyrolysis of coal chars in the presence of hydrogen decreases the subsequent reactivity for pyrolysis pressures in the range 1-30 bar. At higher pressures, however, a slight increase in char reactivity was observed.

2.3.3 Mechanism of alkali-catalyzed carbon gasification

The amount of research that has been put into determining the mechanism of catalyzed carbon gasification is quite staggering. Reviews of the research have been prepared by McKee [114,136] for catalyzed gasification of carbon and by Wood and Sancier [137] for catalytic gasification of coal char. In order to narrow the scope of this review, only literature regarding *alkali*-catalyzed gasification, either of elemental carbon or of coal chars, is considered.

CO₂ gasification. A number of studies have focused on identifying the reaction steps of alkali-catalyzed gasification of carbon [138-143] and coal char [102-104] with CO₂. Moulijn *et al.* [139] provide an excellent review of earlier published mechanisms. They then propose a scheme for gasification which is able to account for observations made in previous investigations. According to their analysis gasification starts with adsorption of a CO₂ molecule onto an active catalyst site (*) and subsequent release of a CO molecule:





The result is an oxidized catalyst site, O--*. An oxygen exchange reaction then occurs with a free carbon atom on the surface of the char to form a surface complex:



The surface complex decomposes to yield CO, thus freeing the catalyst site:



In a later paper [140] Cerfontain *et al.* expand on this mechanism and suggest that the O-* species in the above scheme is more likely CO₃-* due to the strong chemisorption of CO₂ onto the alkali catalyst. They then propose a mechanistic expression for alkali-catalyzed CO₂ gasification, and conclude that desorption of the carbon monoxide (Eq. 2-4) is the rate-limiting step in the process. Their mechanism is consistent with earlier proposals and fits experimental data well.

H₂O gasification. The mechanism of H₂O gasification is somewhat more complex than that of CO₂ gasification due to the presence of hydrogen. Steam gasification inevitably involves not only carbon and H₂O, but H₂, CO₂ and CO as well [144]. Largely due to this, development of a mechanism for H₂O gasification has lagged behind that of CO₂ gasification. A number of studies have been carried out in an effort to clarify the mechanism of alkali-catalyzed steam gasification [144-150].

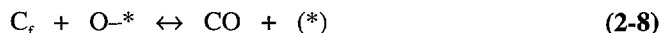
The most advanced model for this reaction is arguably that proposed by Meijer *et al.* [144]. Unlike many previously proposed models, the influence of the reaction between CO and H₂O to form H₂ and CO₂, the so-called water-gas shift reaction, was taken into account. The reaction scheme paralleled that suggested by Moulijn *et al.* [139] for CO₂ gasification. A water molecule first adsorbs onto an active catalyst site and releases hydrogen:



Oxygen-exchange reactions can occur through the oxidized carbon species:



and carbon monoxide is produced by reaction of a free carbon site, C_f, with an oxidated catalyst site:



According to this mechanism, with Equation 2-8 as the rate-limiting step, an expression was derived to describe the rate of alkali-catalyzed steam gasification of carbon [144]. The expression is necessarily more involved than that given by Cerfontain *et al.* [140] for CO₂ gasification, and includes not only the partial pressures of H₂O and H₂, but unlike other proposed mechanisms [145] also includes the partial pressure of CO.

2.4 Concluding remarks

Indeed, a great deal of research has been performed on issues related to pressurized pyrolysis and gasification of black liquor. In most instances the results reported by different researchers are consistent with one another. But in a surprisingly large number of cases, particularly those regarding black liquor, the results are contradictory. While some of these inconsistencies are undoubtedly due to differences in experimental methods, many result from the complex nature of black liquor and highlight the difficulty of studying such an inconstant material.

One of the phenomena that did give consistent results was the influence of the lignin to sugar acids ratio on swelling. A maximum was observed to exist at a ratio of roughly 1:1. Swelling generally decreased with increasing temperature in oxygen-containing environments, as well, but the influence of gas composition on swelling deserves further study. Research on the influence of liquor solids content, liquor type, liquor viscosity and extractives concentration has not provided consistent results and as such the impact of these variables is still not fully understood. Several factors may account for this. The experimental setups vary widely between studies, as do the form and composition of the liquor used. In some investigations synthetic liquors were prepared while in others industrial liquors were used.

Research on the devolatilization process has produced more uniform results. Measured char yields and product gas compositions were similar between different studies. Data regarding sulfur release during devolatilization has been quite consistent, as well. The major sulfurous gas species observed were hydrogen sulfide, methyl mercaptan, dimethyl sulfide and dimethyl disulfide. Sulfate and sulfite consistently released little sulfur while thiosulfate and sulfide were largely responsible for H₂S production. Sodium release invariably increased with pyrolysis temperature, and several researchers observed that two size fractions of sodium compounds resulted from devolatilization.

Data relating to gasification of black liquor is sparse, so it is difficult to compare results from different studies. Amongst those that have been performed, the observed activation energy has been relatively consistent at about 220 kJ/mol. Increasing the H₂O and CO₂ concentrations has consistently increased the rate of reaction while H₂ and CO have been observed to inhibit the reaction in all studies.

Studies on alkali-catalyzed coal gasification invariably conclude that the catalytic influence of the alkali species is the primary property affecting the gasification rate. Comparison between the behavior pressurized black liquor char gasification and pressurized alkali-catalyzed coal gasification reveals some major inconsistencies, however. At constant gas composition, increasing the total pressure results in a rate increase for coal gasification, and analysis of the mechanism of alkali-catalyzed carbon gasification suggests that this

should be the case. The gasification rate of black liquor char, however, was observed to decrease with pressure at constant gas composition.

Despite the large amount of literature available issues relevant to pyrolysis and gasification of black liquor, a number of questions are still left unanswered. For instance, the influence of pressure on swelling of black liquor has never been studied, nor has the morphology of chars formed under pressure. Devolatilization behavior under pressure is still poorly understood, as well. While the rate of pressurized CO_2 gasification of black liquor has been studied, the rate of pressurized gasification with H_2O or mixtures of CO_2 and H_2O has not. The influence of pyrolysis conditions, particularly pressure, on the reactivity of the resulting char is also not clear.

3. PURPOSE OF THE PRESENT STUDY

The goal of the work presented here was to enhance the understanding of black liquor behavior during gasification under pressurized conditions, and to generate data that is valuable for the design of practical gasifiers. The work focuses on *low temperature* gasification processes that operate below the melting range of the inorganic material in the black liquor (approximately 750°C).

Several factors can be identified which are important for the design of practical gasifiers:

1. *Yields.* What fraction of the liquor ends up in the gas phase? What is the fate of the components in the liquor? Do they remain in the solid phase or are they released to the gas phase? How do temperature and pressure affect yields?
2. *Rates.* How quickly does the process occur? What is the rate-limiting step? Is the process controlled by the chemical reaction, or do diffusional effects control the rate? How does the rate vary with temperature? How does pressure influence the rate?
3. *Particle behavior.* What happens to black liquor particles during gasification? How much do they swell under pressurized conditions? How do the structure and internal surface area develop during conversion?
4. *Differences between liquors.* What differences, if any, can be expected between liquors? How large are these differences? Is there any correlation between the properties of a liquor and its behavior during gasification?

The aim of the studies presented here was to clarify these issues. Specifically, the work focused on the processes of pyrolysis and char gasification as described in section 1.2.2.

Pressurized pyrolysis. The studies regarding pyrolysis under pressurized conditions emphasized physical and chemical changes that occur during this process. The behavior of the liquor was considered with regard to pressure as well as temperature and liquor type. The influence of pressure on the structure and composition of the resulting char was also taken into account. The experiments were designed to represent the conditions that black liquor would experience in an industrial gasification unit. Pyrolysis experiments at low heating rates (<10 K/s) were not performed because the data obtained in such experiments is not very representative of the case in an industrial gasifier. Similarly, low temperature pyrolysis, such as that used in fuels production, was not considered.

Char gasification. The studies on black liquor char gasification focused on physical and chemical changes that occur during this process as well as the rates of the gasification reactions. Changes in the size and microstructure of the char during conversion were also considered. The question of how process variables, particularly pressure, influence the gasification rate was addressed, as well. The work concerned only low temperature gasification and the experimental work was restricted to the chemical reaction controlled regime.

The eight papers that make up the appendices to this thesis each concern a particular aspect of the black liquor gasification process as presented in section 1.2.2 of the introduction. The three stages that a particle goes through during gasification were shown in Figure 1-2 of that section. To illustrate the contribution of each of the appended papers to the overall conversion process, that figure is shown again here (Figure 3-1), with the number of each paper labeling where it fits into "the big picture."

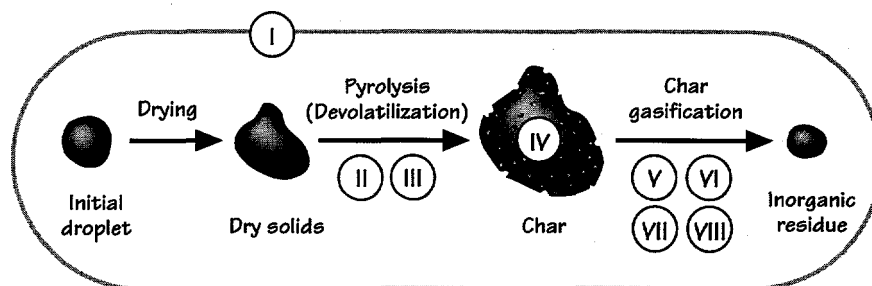


Figure 3-1. Illustration of the contribution of each paper in this thesis to the overall gasification process.

Paper I takes into consideration the whole conversion process, focusing on how differences between black liquors affect the behavior of each stage.

Paper II concerns swelling during pyrolysis under pressurized conditions.

Paper III deals with char yields and component release during pyrolysis under pressure.

Paper IV doesn't specifically deal with the char, as suggested in the figure. Rather, it concerns the influence of pyrolysis conditions on the reactivity of the resulting char during gasification.

Paper V focuses on changes in the morphology and composition of the char during gasification.

Paper VI investigates gasification of black liquor char with steam under pressurized conditions.

Paper VII introduces an empirical model to predict the rate of gasification with both steam and carbon dioxide under pressurized conditions.

Paper VIII examines the influence of sodium content on the rate of char gasification under pressurized conditions.

4. MATERIALS AND METHODS

This chapter explains the approach that was taken for researching black liquor pyrolysis and gasification and introduces the experimental equipment used.

4.1 Experimental approach

Due to the complexity of the black liquor gasification process, most of the experiments in this work focused on either the pyrolysis or char gasification stage of conversion. The methodology behind these two types of experiments is presented here.

4.1.1 Pyrolysis experiments

In order to focus specifically on the pyrolysis stage of gasification, it is necessary to minimize the possibility of either drying or char gasification taking place. The drying stage can be avoided by starting with a pre-dried liquor. The char gasification stage can be avoided by performing the experiments in an inert environment. The pyrolysis experiments presented in this work were conducted in this manner.

As noted in section 1.2.2, conversion of black liquor can occur via three types of reactions: pyrolysis, gasification and inorganic decomposition reactions. Generally, pyrolysis experiments effectively single out the pyrolysis reactions. However, at longer holding times and at higher temperatures, inorganic decomposition reactions will also

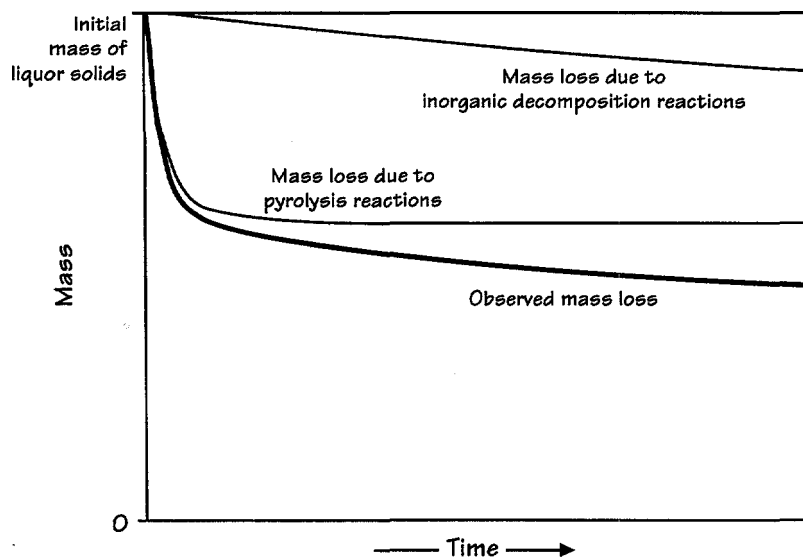


Figure 4-1. Schematic diagram indicating the contribution of pyrolysis and inorganic decomposition reactions during a pyrolysis experiment.

become apparent during these experiments. This is shown schematically in Figure 4-1. The pyrolysis reactions take place relatively quickly, then cease. The inorganic decomposition reactions continue, so the observed weight loss at longer holding times is partially a result of inorganic decomposition reactions. If the yield from the pyrolysis reactions alone is of interest, it is important to avoid excessively long holding times.

4.1.2 Char gasification experiments

In order to focus on the char gasification stage, it is necessary to minimize the possibility of drying and devolatilization occurring. The most efficient way to do this is to start with a pre-pyrolyzed char. This is what was done in the majority of the experiments presented here. The sample was allowed to remain in an inert environment until no further weight loss could be detected, indicating that pyrolysis was complete. The gas was then changed to the gasification mixture and the char was allowed to react.

In experiments performed in this manner, char conversion occurs due to both gasification reactions and inorganic decomposition reactions, as defined in section 1.2.2. This is shown schematically in Figure 4-2. Both reactions cease when no more organic carbon is available in the char. The inorganic decomposition reactions are quite temperature sensitive, and their contribution to the rate at low temperatures, such as those used in the studies presented here, is quite low. At higher temperatures, the inorganic decomposition reactions may occur very rapidly and contribute significantly to the observed rate.

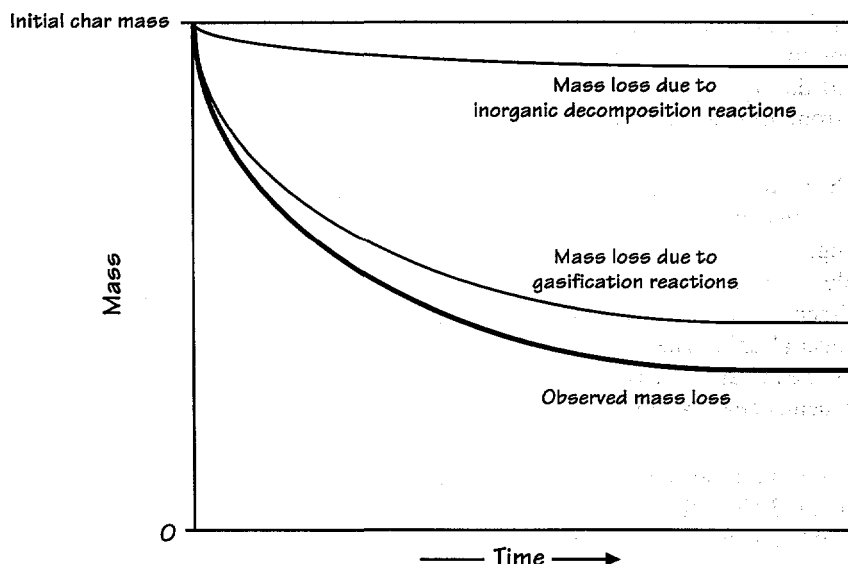


Figure 4-2. Schematic diagram indicating the contribution of gasification and inorganic decomposition reactions during a gasification experiment.

4.2 Experimental equipment

The data for the studies in the present work were obtained by performing experiments in laboratory-scale devices. Ultimately, the goal was to simulate as closely as possible the conditions that black liquor would be subjected to in an industrial unit. But the processes that take place during each of the stages of gasification are different enough that it was technically infeasible to perform all experiments in a single device. Rather, the experiments were performed in three devices, a pressurized grid heater, a pressurized thermogravimetric reactor and a single-particle tube reactor. These devices and the experimental procedures are introduced here.

4.2.1 Pressurized grid heater

A pressurized grid heater (PGH, Figure 4-3) was used to study the behavior of black liquor during pyrolysis under pressurized conditions. The heart of the device was a fine wire net measuring approximately 2 cm x 2 cm. The net was secured between two copper electrodes and by passing a current through the net heating rates up to 3000 °C/s could be achieved. A Pt/Pt-Rh thermocouple was welded to the center of the net and acted both as a sample temperature indicator and as feedback to the heating controller. The whole electrode/net assembly was housed inside a pressure chamber which could be pressurized up to 40 bar. Two viewing ports in the top and side of the pressure chamber allowed for illumination and observation of the grid.

The reactor was pressurized with nitrogen, so pyrolysis took place under inert conditions. Prior to heating the grid, a number of purging cycles were carried out in order to remove oxygen from the reactor chamber. For a typical experiment at 10 bar pressure the oxygen concentration was less than 0.02%. No gas flow was used in the experiments, so any gas evolved during the experiments remained in the reactor vessel instead of being swept away from the char sample surface.

The ability to achieve relatively high heating rates as well as the ability to control the heating rate make the PGH a good device for study of black liquor pyrolysis. Traditional thermogravimetry is often used to study pyrolysis of other fuels, and this approach is suitable if the end use will be fuels production. But the low heating rate in such an experiment is hardly representative of those that a droplet of black liquor experiences in an industrial unit. The conditions in a grid heater are much more representative. Also, the grid heater allows easy determination of the char yield, a known problem for other experimental devices which can achieve high heating rates, such as entrained flow reactors.

The samples for the experiments were prepared by diluting the black liquor, if necessary, to roughly 30% solids. The black liquor was "painted" onto the net which was then placed into an oven at 80°C in order to dry the liquor. By this procedure a very thin layer of liquor solids, 5-10 microns thick, resulted on the grid. The mass of dry solids was roughly 10 mg.

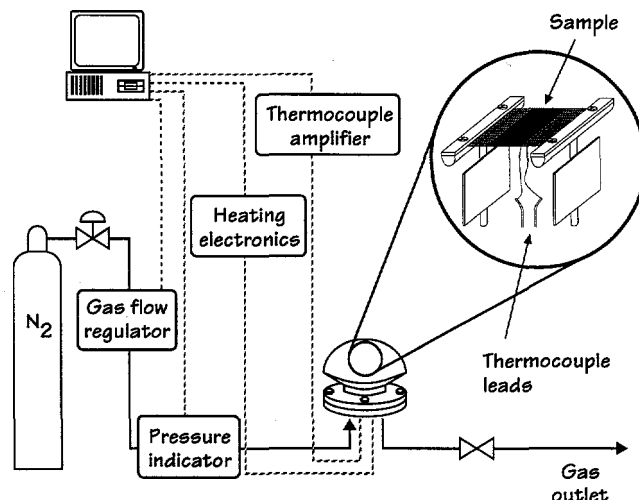


Figure 4-3. Pressurized grid heater device. Max. 1200°C, 40 bar, 3000 °C/s heating rate.

The net was secured between the electrodes and the reactor was sealed shut. The conditions for the experiment (pressure, final temperature, heating rate, holding time) were programmed into the controlling computer, which then automatically purged and pressurized the reactor. The grid was then heated at the set rate to the desired temperature, which was held for the chosen amount of time. The current was then switched off and the grid was allowed to cool naturally. The reactor was slowly depressurized and the grid containing the char was carefully removed.

Char yields in the grid heater were measured by weighing the net before and after the experiment was performed and calculating the mass percentage that remained after pyrolysis. Reproducibility was good, with measured char yields in replicate runs all falling within 5% of the average. The composition of the char was analyzed in some cases, as well. From these data component release (defined as that amount which did not remain in the char) could also be calculated.

The swollen volume of the char that remained after pyrolysis was determined for some experiments. After the experiment the net was removed and photographed from the side under a microscope. From the photographs the thickness of the char could be measured. The length and width of the char on the grid were also measured and the volume of the char was calculated.

4.2.2 Pressurized thermogravimetric reactor

A pressurized thermogravimetric reactor (PTGR, Figure 4-4) was used to measure the rate of the char gasification reaction. In addition, the device was used as a pressurized single droplet reactor for some pressurized pyrolysis studies. The main part of the PTGR consisted of a vertical reactor tube which could be heated to 1150°C. The whole device could be pressurized to 100 bar, though experiments were carried out within the range

1-30 bar. Up to four gases could be mixed and fed to the reactor. The gases used in the studies presented here were CO_2 , CO , H_2 and N_2 . Additionally, a steam generator allowed water vapor to be used as a reacting gas. Both the gas line and the steam line had 3-way valves so that the flow could be directed either to the reactor or to a bypass line around the reactor. Above the reactor a helium-purged, water cooled sample lock allowed insertion and removal of the sample holder.

The sample holder hung within the reactor from a chain suspended to a microbalance. In experiments to measure gasification rates a cylindrical sample holder was used. The sample holder had a solid core surrounded concentrically by fine netting. This design provided a thin sample layer, which is important in minimizing mass-transfer and diffusion-related effects. In experiments in which chars were formed under pressure, either a small platinum bowl-shaped sample holder or a platinum wire hook was used.

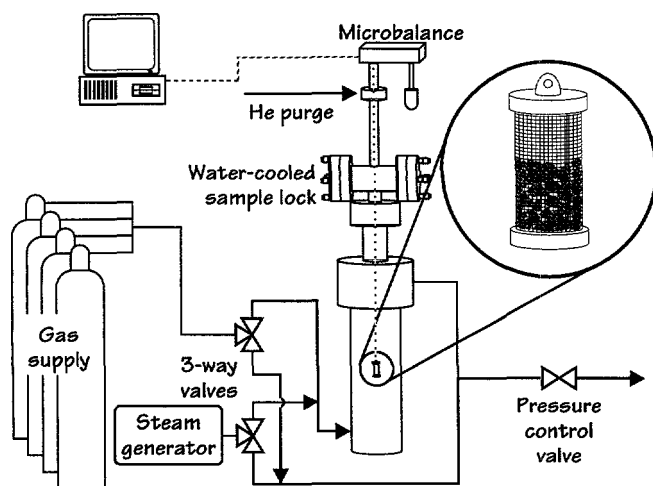


Figure 4-4. Pressurized thermogravimetric reactor.

Char gasification studies. In experiments to study the rates of the char gasification reactions the cylindrical sample holder was loaded with approximately 100 mg of black liquor char and hung on the chain attached to the microbalance. The sample lock was closed and the reactor was heated to the desired temperature.

The gasification experiments were generally carried out in two phases. In *Phase I* the sample was lowered into either pure nitrogen or a mixture of CO in nitrogen and held there for a specified period of time, usually 400 seconds. During this period additional devolatilization took place and the sample weight stabilized so that the starting material at the beginning of *Phase II* was well defined.

In *Phase II* the reacting gas was changed to that for char gasification. The gases used in this phase were H_2O , CO_2 , H_2 and CO . The concentrations of the species were different

in different studies. The carbon in the sample was gasified during this phase, as were sulfur and other species. The gasification reaction was allowed to proceed until no further weight loss could be detected, generally from 15 minutes to three hours. During this period the sample mass was recorded as a function of time. Reproducibility studies were performed in Paper VI and by Frederick and Hupa [90]. The measured gasification rates all fell within 6% of the average in these studies, and the coefficient of variation, which can be used to assess the uncertainty in measured rates, was determined to be 5%.

While most experiments consisted of *Phase I* followed by *Phase II*, some involved just *Phase II* alone. For these experiments the sample was lowered directly into the gasification gas. For experiments with both phases the sample holder was not raised back into the sample lock between phases, but the gas composition was just changed from that for *Phase I* to that for *Phase II*.

Pressurized pyrolysis studies. For some studies the PTGR was modified to function as a pressurized single particle reactor, or PSPR. No weight signal was obtained in these experiments. Rather, droplets of black liquor were lowered into the hot pressurized environment so that the properties of chars formed under pressure could be studied. In most of these experiments roughly 35 mg of liquor was placed into a platinum bowl-shaped sample holder. But recently the well-known technique of pyrolyzing small (~2.5 mm) droplets on a wire hook was successfully carried out under pressurized conditions. The sample of concentrated liquor was rapidly lowered from the cool, inert sample lock into the hot reactor and allowed to pyrolyze for the desired amount of time (usually 15 seconds) after which it was lifted back into the sample lock. The char yield and specific swollen volume could be determined by weighing the sample before and after the experiment and measuring the size of the char particle formed. These experiments are a good compliment to those carried out in the grid heater since they provide information about droplets, the usual form for black liquor in industrial units.

4.2.3 Single-particle tube furnace

Some pyrolysis and gasification experiments were also carried out in a single-particle tube furnace (Figure 4-5). The apparatus consisted of a quartz tube situated inside a cylindrical furnace. The top of the quartz tube had a special fitting that allowed a quartz rod to slide into and out of the furnace. A droplet of black liquor was placed either on a wire hook or on a sintered quartz disc attached to the end of the quartz rod. Two gas ports in the fitting allowed feeding of nitrogen to keep the droplet and the top of the reactor in a cool, inert environment prior to and after the experiment.

For pyrolysis experiments, nitrogen was fed into the reactor. The droplet was quickly lowered into the furnace and allowed to stay there for 15 seconds, after which it was lifted back into the upper part of the quartz tube. Measurement of the droplet mass before and after the experiment allowed determination of the char yield, and by measuring the size of the char particle formed the specific swollen volume could be determined.

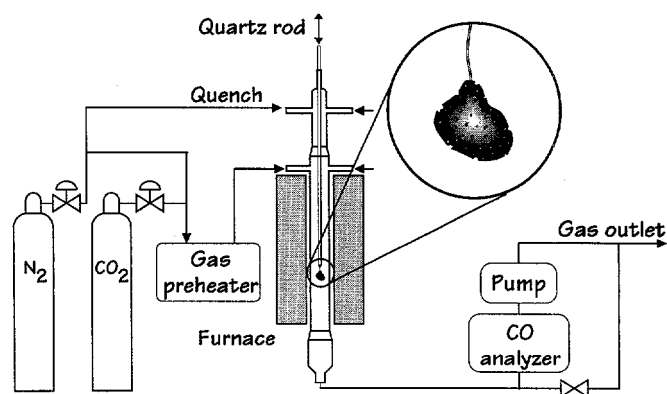


Figure 4-5. Single-particle tube furnace.

For gasification experiments the droplet was kept in the hot nitrogen atmosphere for 200 seconds, after which carbon dioxide was introduced and the particle was gasified. The progression of gasification was monitored with a CO meter and the experiment was allowed to proceed until no further reaction could be detected. The gasification rate could be determined as a function of the CO evolution profile. These gasification experiments provided a good compliment to those carried out in the PTGR.

5. RESULTS: PRESSURIZED PYROLYSIS OF BLACK LIQUOR

As described in section 1.2.2, the second stage of the black liquor gasification process is pyrolysis, or devolatilization. During this stage volatile material in the liquor is released to the gas phase. The reactions responsible for thermal degradation of the organic fraction of black liquor and generally occur in the temperature range 200-600°C. The rates of these reactions are very fast and as such, pyrolysis of black liquor is typically a heat-transfer controlled process. Heat transfer efficiency is lower for larger droplets, and thus they require more time for devolatilization.

During pyrolysis the black liquor also undergoes significant physical transformations. In some of the proposed gasification systems these processes occur under pressure. But to date there has been very little data obtained on how pressure affects pyrolysis processes. In this section the behavior of black liquor during pyrolysis under pressure is presented. The impact of pressure on black liquor swelling is first covered, followed by discussion of the actual devolatilization process and its behavior under pressure.

5.1 Swelling under pressure

A unique characteristic of black liquor is its tendency to swell dramatically during pyrolysis. As mentioned previously, volumetric increases by a factor of 30 or more are not uncommon in black liquor combustion. In many regards swelling is the most important characteristic of black liquor combustion since it governs the trajectory of a droplet and ultimately determines whether it will be entrained in the gas flow or fall onto the char bed. Since many of the proposed alternative recovery processes operate under pressurized conditions it is important to know how swelling during pyrolysis is affected by pressure. Prior to this work, no known research into this topic has been carried out.

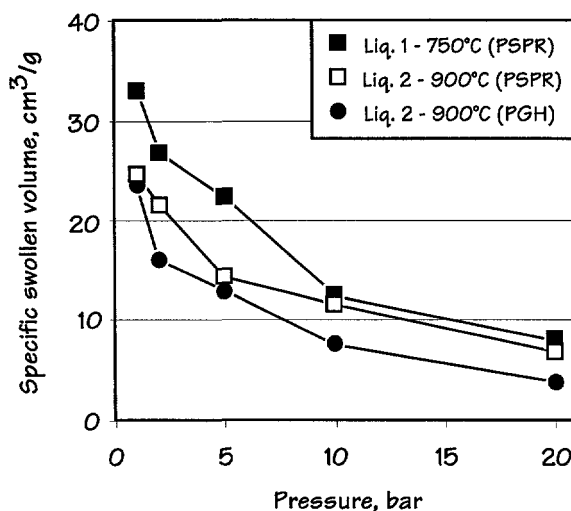


Figure 5-1. Influence of pressure during pyrolysis on char specific swollen volume.

5.1.1 Influence of pressure on swelling

Swelling during black liquor pyrolysis under pressurized conditions was the focus of **Paper II**. Chars were formed from two different liquors by pyrolysis in two reactors, the pressurized grid heater and the pressurized single particle reactor. Pressures between 1 and 20 bar, and temperatures between 650°C and 1100°C were used. The specific swollen volumes of the chars were then determined and analyzed as a function of pyrolysis pressure.

It was found that increasing the pressure during pyrolysis resulted in a less-swollen char particle. The relationship between the specific swollen volume was not linear, nor was it proportional to the inverse of the pressure as would be the case if the relation could be described by the ideal gas law ($P \times V = \text{constant}$). Rather the decrease in the specific swollen volume was approximately logarithmic, as can be seen in Figure 5-1.

It is valuable to be able to estimate how much a liquor will swell under pressurized conditions. As seen in Figure 5-1, the shape of the curves is similar despite the temperature or liquor used. With this in mind, a normalized degree of swelling can be defined by dividing the specific swollen volume at a particular pressure with the specific swollen volume at 1 bar pressure. It was found that this normalized degree of swelling could be described well by a logarithmic expression in which the coefficients were determined by fitting the equation to all conditions:

$$\frac{SSV_p}{SSV_{1\text{ bar}}} = 1 - 0.254 \ln \left(\frac{P}{P_{1\text{ bar}}} \right) \quad (5-1)$$

where P is the pressure of interest. According to the equation, a plot of $1 - SSV_p/SSV_{1\text{ bar}}$ versus $\ln(P/P_{1\text{ bar}})$ should yield a straight line. Such a plot is presented in Figure 5-2, and the relationship is clearly linear. The correlation coefficient (R^2) for the line in the figure is 0.977.

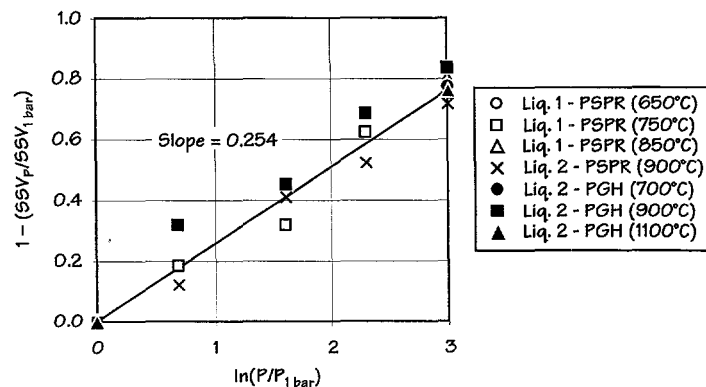


Figure 5-2. $1 - SSV_p/SSV_{1\text{ bar}}$ versus $\ln(P/P_{1\text{ bar}})$. The line was fit by regression ($R^2 = 0.977$).

Equation 5-1 gives a simple method of estimating the specific swollen volume at a particular pressure if the specific swollen volume at atmospheric pressure conditions is known. The agreement between Equation 5-1 and the experimental data is presented in Figure 5-3. According to the equation, one would expect that liquors with high swelling tendencies at atmospheric pressure would also swell more than other liquors under pressure. This was found to be the case in a study of 15 different industrial liquors described in Paper I. The ordering of the liquors according to their degree of swelling in nitrogen at atmospheric pressure was nearly identical to their ordering based on the degree of swelling at 10 bar pressure.

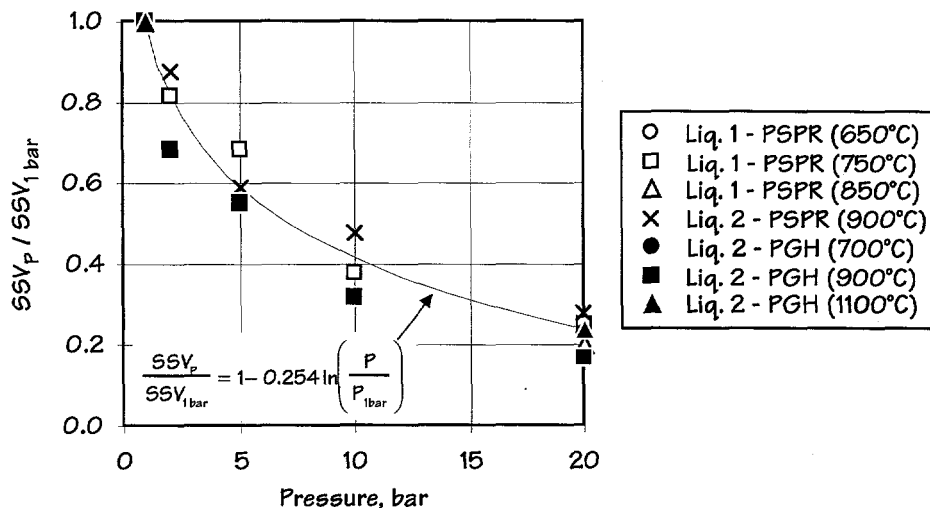


Figure 5-3. Normalized degree of swelling as a function of pressure, with the trend predicted by Equation 5-1 indicated.

5.1.2 Effect of pressure on char morphology

By nature of the manner in which black liquor char is formed, its tendency to swell is related to its morphology, or microstructure. Therefore it is worthwhile to consider how pressure during pyrolysis affects the morphology of the char. Perhaps an even more important reason for studying this is the fact that it provides insight into the subsequent reactivity of the char during gasification. Chars with a high internal surface area, for example, may be expected to react more rapidly than chars with less area available for reaction.

The influence of pyrolysis conditions on the morphology of the resulting char was the focus of **Paper V**. Chars were formed by pyrolysis at various temperatures and pressures, and the chars were subsequently analyzed by scanning electron microscopy (SEM). SEM photos of two chars are shown in Figure 5-4. The upper photo is of a char formed at 1 bar. The lower photo is of a char formed at 20 bar, but at otherwise identical conditions. The char formed at 20 bar appears much less porous than

that formed at 1 bar, and it has a more compact structure. This compactness is consistent with observations of the degree of swelling for these liquors.

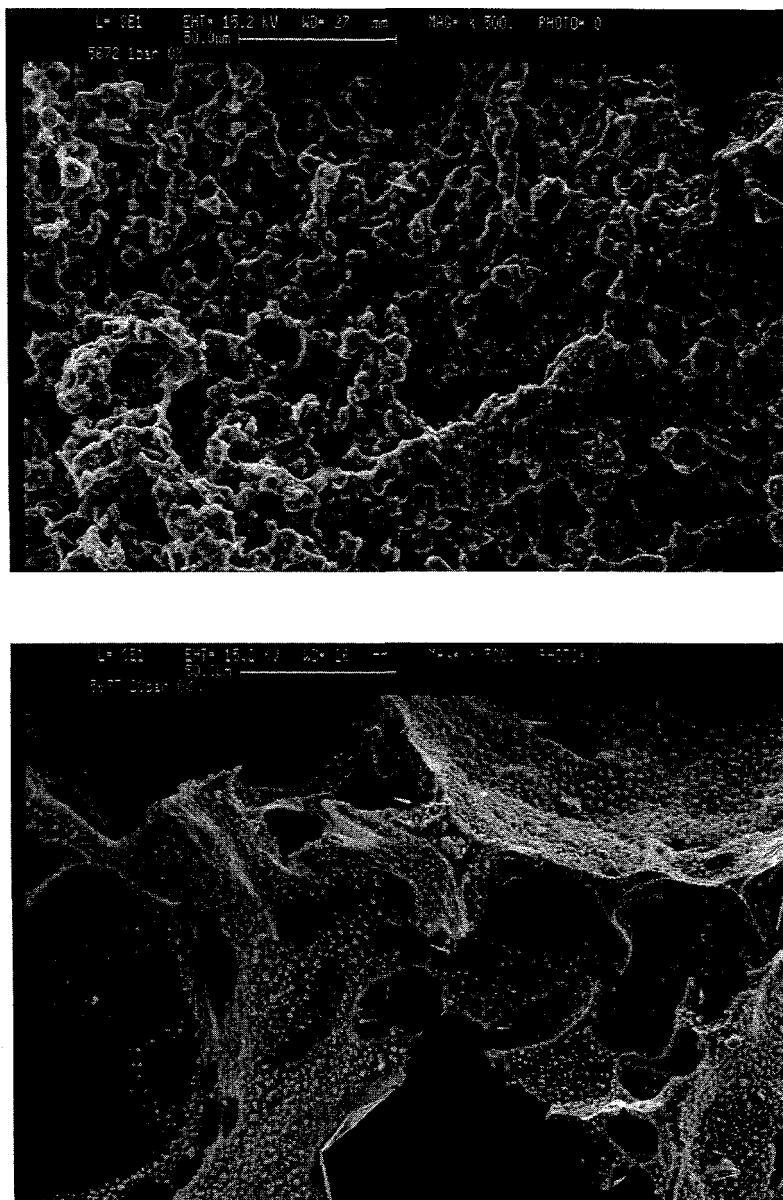


Figure 5-4. SEM photos of chars formed at 1 and 20 bar pressure.

It would be valuable to be able to measure the internal surface area of chars formed under different pressures. Unfortunately, the available devices for production of chars at

pressurized conditions are not able to generate enough material for reliable BET (nitrogen absorption) analysis. Attempts have been made to measure the surface area of chars produced in the PSPR. It was concluded that the sample size was much too small for precise quantitative analysis, but it could be determined that the surface area of a char formed at 1 bar was much greater (at least double) that of a char formed at 20 bar but otherwise identical conditions.

Three approaches can be employed to improve the accuracy of internal surface area analysis for chars formed under pressure: (1) A more sensitive analysis technique can be sought, (2) equipment capable of generating larger quantities of char under pressure can be used and (3) multiple experiments can be performed with the available equipment in order to generate sufficient char for analysis. Efforts to quantify the internal surface area of chars formed under pressure continue.

Until such quantitative data is available for chars under pressure, it is instructive to look at other data regarding black liquor char internal surface areas. Van Heiningen *et al.* [84] found that the BET surface areas of chars formed at atmospheric pressure correlate well with specific volume of the char. Thus it seems reasonable that high swelling chars formed at lower pressures would have larger surface areas than low swelling chars formed under pressure.

5.2 Devolatilization under pressure

From a chemical point of view, the most important process that occurs during pyrolysis is thermal degradation of the liquor and release of volatile components to the gas phase. The behavior of this process determines the volatiles yield as well as the composition and amount of char which remains. Release of individual components into the gas phase is also an important consideration. Little has been published regarding the influence of pressure on the devolatilization process, so the issue is considered here. The influence of pyrolysis conditions, particularly pressure, on char yields and component release is treated in **Paper III**, while more general information about char yields is discussed in **Paper I**.

5.2.1 Influence of pressure on char yield

Pyrolysis experiments were carried out in the pressurized single particle reactor over the range 650-900°C and in the pressurized grid heater at temperatures between 700° and 1100°C. Pressures between 1 and 20 bar were used in both reactors. Char yield measured in the PSPR was found to increase with pressure for pyrolysis carried out at temperatures higher than roughly 800°C. Below this temperature no correlation was observed between char yields and pyrolysis pressure. The dependence of char yields on pressure at higher temperatures can be explained in terms of the sodium carbonate decomposition reaction. McKeough *et al.* [33,69] indicate that this reaction occurs more slowly at higher pressures. Analysis of chars formed by pyrolysis for 10 seconds at 900°C reveals that those formed at 21 bar contain significantly more sodium carbonate than those formed at 2 bar, and that the observed difference in char yields between these chars is almost entirely due to the differing sodium carbonate contents [69]. McKeough *et al.* suggest that this is due to increased local partial pressures of CO and CO₂ near the char surface at higher pressures, and as demonstrated by Li and van

Heiningen [66], sodium carbonate decomposition is suppressed by the presence of carbon monoxide in the gas. The rate of the sodium carbonate decomposition reaction is slow enough below 800°C that variations with pressure are not observable.

The char yields from the grid heater decreased with pressure for all temperatures, but this trend was found to be a peculiarity of that particular setup. Under high swelling conditions, heat conduction to and within the char was less, particularly for the outer edges of the char that were in contact with the cooler gas and further from the grid. This resulted in a lower effective heating rate for the sample and presumably lower volatiles release. As seen previously, chars formed at higher pressures swell less. The result is more efficient heat transfer in these chars, higher volatiles release and lower char yields. A correlation resulted between char yield and swelling in the PGH. No such correlation was found in the PSPR, however. The influence of swelling on char yields in the PGH can be minimized by improving heat transfer by, for example, using a folded net.

5.2.2 Influence of pressure on char composition

Chars from two series of experiments were analyzed for carbon, sulfur, sodium and potassium. The two series were performed with different liquors at different temperatures in different reactors, but both involved pressures in the range 1-20 bar. The percentages of carbon, sodium and potassium in the chars did not vary significantly between chars formed at different pressures but at otherwise identical conditions.

The amount of sulfur in the chars decreased with increasing char formation pressure. The char formed at 20 bar pressure contained roughly 60% as much sulfur as the char formed at 1 bar, but at otherwise identical conditions. The reason for this is related to the amount of sulfur released during pyrolysis, which is treated in the next section.

5.2.3 Influence of pressure on component release

If the char yield and compositions of both the char and the original liquor are known, it is possible to calculate what percentage of a particular element is released to the gas phase during devolatilization. This was done for the chars mentioned in the previous section, and the results for carbon, sodium and sulfur are presented here.

Carbon. The carbon analysis technique used in these studies was not particularly accurate, so small differences in carbon release were not able to be detected. One might expect that carbon release would decrease with pressure because the reaction of sodium carbonate with carbon is slower at higher pressures. Carbon analysis was too inaccurate to make such determination in the present study. But McKeough *et al.* [33] found that for pyrolysis at 900°C, roughly 8% more of the carbon in the liquor was released at 2 bar as compared to 21 bar. No influence of pressure on carbon release was observed for pyrolysis at 675°C. In their work the holding time at maximum temperature was 10 seconds, which allowed for significant carbonate decomposition at the higher temperature. On the other hand, similar experiments performed by Kymäläinen [41] at 1000°C displayed no variation with pressure. But in those experiments the holding time was just 3 seconds.

Sodium. The fraction of sodium released during the experiments increased as the temperature increased, from roughly 10% at 700° to over 50% at 1100°C. At higher temperatures most of the sodium release resulted from decomposition of sodium carbonate. Measured sodium and sulfur release are plotted as a function of pyrolysis pressure in Figure 5-5. Sodium release decreased with pressure for all conditions, but the sensitivity to pressure was higher at higher temperatures. At 900°C the amount of sodium released at 20 bar was roughly half that released at 1 bar. At temperatures in this range similar dependencies on pressure were observed by both McKeough *et al.* [69] and Kymäläinen [41]. Again the behavior can be explained by decreased carbonate decomposition. The influence of pressure was more pronounced for the experiments at 900°C in the PGH than for those at 750°C in the PSPR due to the faster rate of decomposition at the higher temperature.

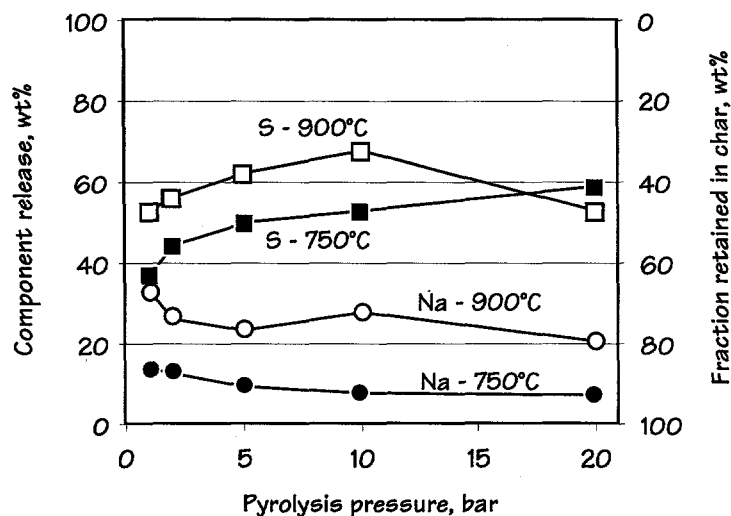


Figure 5-5. Sodium and sulfur release as a function of pyrolysis pressure. Closed symbols - measured in PSPR. Open symbols - measured in PGH.

Sulfur. Sulfur release was in the range 35-70%. As seen in Figure 5-5, sulfur release *increased* with pressure in these experiments. The data at 20 bar, 900°C are suspect due to the minute sample size analyzed. The data of McKeough *et al.* [50] also indicate that sulfur release increases with pressure. In their experiments at 675° and 900°C, the amount of sulfur retained in the char was less for pyrolysis at 15 bar than for pyrolysis at 1 bar. Kymäläinen [41] measured the amount of sulfur anions present in chars formed at various pressures and compared the total to the total number of sulfur anions measured in the original liquor. In contrast to the results presented here, it was found that the amount of sulfur anions in chars formed at 20 bar was slightly more than those formed at 1.5 bar. It is difficult to compare these results, however, since total sulfur was not measured in the work of Kymäläinen.

Several explanations can be proposed to explain the higher sulfur release values at higher pressures. McKeough, *et al.* [50] indicate that the extent of sulfur release is governed by the effective reaction time at temperatures at and below 500°C as the liquor is heated. Indeed, they have demonstrated that the amount of sulfur release correlates with the residence time of the liquor in the temperature interval 400-500°C. Thus, one would expect to see more sulfur release with lower heating rates. As we have seen, liquors swell less at higher pressures. For liquors pyrolyzed in the pressurized single particle reactor this means that the external surface area is less, so the heat flux due to radiation and convection is also less. The result is a lower heating rate.

The experiments in the pressurized grid heater are more difficult to explain. It was indicated in section 5.2.1 that the effective heating rate in this device is higher at higher pressure. This surely contradicts the thinking described above. Another mechanism that has been proposed regarding sulfur release is that at temperatures above roughly 500°C, a fraction of the volatilized sulfur is recaptured by alkali compounds and remains in the char. The exit path for volatilized sulfur would be longer for more swollen chars, so there would presumably be more opportunity for recapture. This would result in lower sulfur release for high swelling chars, such as those formed at lower pressures. For the moment, no conclusive explanation can be provided for the variation in sulfur capture with pressure, and the mechanism behind sulfur release under pressure deserves further study.

6. RESULTS: PRESSURIZED BLACK LIQUOR CHAR GASIFICATION

As discussed in section 1.2.2, the final stage of the black liquor gasification process is char gasification. The primary reactions which occur during this stage are the heterogeneous reactions of char carbon with H_2O and CO_2 (reactions 1-2 and 1-3). Inorganic decomposition reactions (reactions 1-4 through 1-6) may take place as well.

Under most conditions the char gasification stage requires the most time for completion and therefore is the "bottleneck" in the conversion process. As noted in section 2.3.1, data regarding black liquor char gasification is sparse, particularly for gasification under pressurized conditions. In this section the black liquor char gasification reaction is considered, starting with an analysis of the controlling mechanism for the reaction. Changes in the properties of the char during conversion are then discussed. Finally, the reactivity of black liquor is considered and the influences of key variables on the reaction rate are identified.

6.1 Mass transfer in char gasification

In gas-solid reactions such as gasification of black liquor char, three processes may determine the overall rate: mass transfer of the reacting gas species from the bulk gas to the particle and transfer of the product gas from the particle (film mass transfer), diffusion of the species into and within the pores of the particle (pore diffusion) and the chemical reaction of the gas with the solid. Each of these processes requires a certain amount of time to occur. If any one process requires significantly more time than the other two, then it controls the overall rate.

At low temperatures the rate of black liquor char gasification is quite slow, so the time required for the chemical reaction to proceed is longer than the time required for diffusion of the gas species. Hence the overall rate is *chemical reaction controlled*. As the temperature is increased, the rate of the chemical reaction proceeds more rapidly and eventually a point is reached where the time required for the chemical reaction is negligible compared to the time required for gas diffusion. In this case the rate is *diffusion controlled*.

It is of interest to know where the boundaries are for the different controlling mechanisms. For experimental work, it is important to stay within the chemical reaction controlled regime if the focus of the study is the rate of the chemical reaction. In an industrial-scale unit it may be easy to increase the rate of conversion simply by increasing the temperature. But when the chemical reaction no longer controls the rate, further increases in temperature have little influence since gas mass-transfer and diffusion are much less temperature-sensitive.

The influence of the chemical reaction rate and diffusional effects on the overall rate of steam gasification of a single spherical particle of black liquor char was modeled in order to determine the boundaries of the different controlling mechanisms. The approach used is based on a procedure outlined by Levenspiel [151] for determining the controlling mechanism in a gas-solid reaction with the following stoichiometry:



In this simplified analysis the reactant A corresponds to either H₂O or CO₂ and B is char carbon. Thus, *b* equals 1. The theoretical time for complete conversion of a spherical particle can be calculated for each of the resistances:

τ_{film} = time for complete conversion if film mass transfer were the sole resistance

τ_{pore} = time for complete conversion if pore diffusion were the sole resistance

τ_{rxn} = time for complete conversion if the chemical reaction were the sole resistance

The time required to reach a particular conversion *X* (0.0 - 1.0) can be determined for each of these cases, as well. The relation between the time to conversion *X* and the total time is a function of the geometry of the particle. For a spherical char particle the relations are as follows:

$$\frac{t_{\text{film}}}{\tau_{\text{film}}} = X \quad (6-2)$$

$$\frac{t_{\text{pore}}}{\tau_{\text{pore}}} = 1 - 3(1 - X)^{2/3} + 2(1 - X) \quad (6-3)$$

$$\frac{t_{\text{rxn}}}{\tau_{\text{rxn}}} = 1 - (1 - X)^{1/3} \quad (6-4)$$

where

t_{film} = time to reach conversion *X* if film mass transfer controls

t_{pore} = time to reach conversion *X* if pore diffusion controls

t_{rxn} = time to reach conversion *X* if chemical reaction controls

The true time required to reach conversion *X* is the sum of the times for the three resistances:

$$t_{\text{actual}} = t_{\text{film}} + t_{\text{pore}} + t_{\text{rxn}} \quad (6-5)$$

Similarly,

$$\tau_{\text{total}} = \tau_{\text{film}} + \tau_{\text{pore}} + \tau_{\text{rxn}} \quad (6-6)$$

The time for complete conversion can be determined for each of the resistances according to established laws for mass transfer and diffusion. For the case of film mass transfer this time depends on the gas film diffusion coefficient and the concentration of the reacting species in the gas phase:

$$\tau_{\text{film}} = \frac{\rho_B d}{6bk_g c_{Ag}} \quad (6-7)$$

where

- ρ_B = molar density of reactant B in the solid, mol/m³
- d = particle diameter, m
- b = stoichiometric coefficient for reactant B as per Equation 6-1. For carbon gasification with H₂O or CO₂, equals 1.
- k_g = gas film coefficient, m/s
- c_{Ag} = concentration of reactant A in the gas phase, mol/m³

Each of these parameters can be either calculated or estimated based on known values. The gas film coefficient was estimated from the following relation:

$$k_g = \frac{D}{d} (2 + 0.6(\text{Re})^{0.5} (\text{Sc})^{0.33}) \quad (6-8)$$

where

- D = diffusion coefficient of the gas, m²/s
- Re = Reynolds number for gas flowing past the particle, dimensionless
- Sc = Schmidt number for the gas mixture, dimensionless

The Reynolds number is a dimensionless quantity for relating inertial and viscous effects for a flowing fluid. The Schmidt number relates viscous and diffusion effects for a gas. These quantities are defined as:

$$\text{Re} = \frac{vd}{\nu} \quad (6-9)$$

$$Sc = \frac{v}{D} \quad (6-10)$$

where

v = gas velocity, m/s

ν = gas viscosity, m²/s

The time required for complete conversion if pore diffusion is the controlling resistance is related to the diffusivity and concentration of the gas as well as the size of the particle:

$$\tau_{\text{pore}} = \frac{\rho_B d^2}{24 b D c_{Ag}} \quad (6-11)$$

In order to determine τ_{rxn} , the time required for complete conversion if the chemical reaction rate controls the overall rate, we need information about the rate of the char gasification reaction. In this analysis the rate of char gasification is determined by an expression developed in Paper VI for gasification with steam:

$$r = 10^{-4} \cdot \exp \left[28000 \left(\frac{1}{923} - \frac{1}{T} \right) \right] \cdot \frac{9.01}{1 + \frac{P_{H_2}}{0.449 P_{H_2O}} + 7.09 P_{CO}} \quad (6-12)$$

where

r = gasification rate, (mg/s)/mg total gasifiable material

T = temperature, K

p_i = partial pressure of species i , bar

The observed activation energy of the reaction was incorporated into the above rate expression, so variations with temperature are taken into account. While the gasification rate is known to vary with conversion, the simplification was made that the instantaneous rate at any conversion can be calculated by Equation 6-12. Therefore the time for complete conversion if chemical reaction rate controls the overall rate is simply

$$\tau_{\text{rxn}} = \frac{1}{r} \quad (6-13)$$

and the time required to reach any fractional conversion X is

$$t_{\text{rxn}} = X\tau_{\text{rxn}} \quad (6-14)$$

In this analysis, and throughout the remainder of this chapter, the conversion at any time t is defined as the fraction of the total mass loss during char gasification:

$$X = \frac{m_{\text{char},i} - m_{\text{char},t}}{m_{\text{char},i} - m_{\text{residue}}} \quad (6-15)$$

where

$m_{\text{char},i}$ = initial mass of char, mg

$m_{\text{char},t}$ = mass of char at time t , mg

m_{residue} = mass of residue that remains when no further reaction can be detected, mg

The majority of experiments, including those from which Equation 6-14 were developed, were conducted in a pressurized thermogravimetric reactor which measures the mass of the sample. The one exception to this concerns the experiments described in section 6.3.3. By necessity, conversion was defined differently in those experiments as described in that section.

It is worth noting that Equation 6-12 is different than Equation 6-4. Equation 6-4 is for the case of a solid particle undergoing reaction by a shrinking core mechanism. However, this is not the situation for black liquor char in the chemical reaction controlled regime. Because of its high porosity, gas diffusion into the particle is not restricted, so the particle is converted uniformly. Therefore the geometric term in Equation 6-4 is not necessary. For high reaction rates, however, the gaseous reactant is consumed immediately on coming in contact with the char particle. In such a case the reacting gas is not able to diffuse inside the char particle and it does indeed react by a shrinking core mechanism. In this scenario Equations 6-2 and 6-3 are appropriate.

With the above expressions it is possible to estimate the amount of time each mechanism contributes to the overall rate of reaction. Another way of viewing this is that it is possible to determine the *resistance* of each mechanism. The mechanism in question in this analysis is that of the chemical reaction between the char carbon and the steam. It is not particularly interesting to know the individual contributions of film mass transfer and pore diffusion, but rather we are interested in how their combined resistances compete with that of the chemical reaction.

For this analysis the boundaries for the controlling mechanism were defined as follows. If the chemical reaction rate contributed to 90% of the overall resistance or more, the reaction was considered to be in the *chemical reaction controlled* regime. If the

combined resistances of film diffusion and pore diffusion contributed to 90% of the overall resistance or more, the reaction was considered to be in the *diffusion controlled* regime. For conditions between these boundaries, where the chemical reaction and diffusion both contributed significantly to the overall resistance the reaction was considered to be in the *mixed control* regime.

The conditions of the scenario presented here are given in Table 6-1. Values for the gas diffusivity and viscosity were calculated from relations which take into account changes in these properties with temperature and pressure.

TABLE 6-1. CONDITIONS FOR CONTROL REGIME ANALYSIS

Temperature	600-1600 °C
Pressure	1-40 bar
Particle diameter	1-20 mm
H ₂ O concentration	20%
H ₂ concentration	2%
CO concentration	2%
Gas velocity	0 m/s
Molar density C in char	500 mol/m ³

The results of the analysis are presented in Figure 6-1 and Figure 6-2. As the gasification temperature increases the controlling mechanism shifts from the chemical reaction to gas diffusion. At a particular temperature, an increase in the particle size shifts the controlling mechanism towards diffusion control.

According to Figure 6-2, increasing the gasification pressure will shift the controlling mechanism towards chemical reaction control. This is largely due to the rate equation used in this analysis (Equation 6-12), which predicts that the gasification rate decreases as the total pressure is increased at constant gas composition. The influence of pressure on gas diffusivity and viscosity are quite negligible in the range of conditions considered here. While the diffusion coefficient D in Equation 6-11 decreases proportionally with pressure the concentration of the reacting species in the gas phase, c_{Ag} , is proportional to the total pressure at constant gas composition, so the pressure influence cancels out.

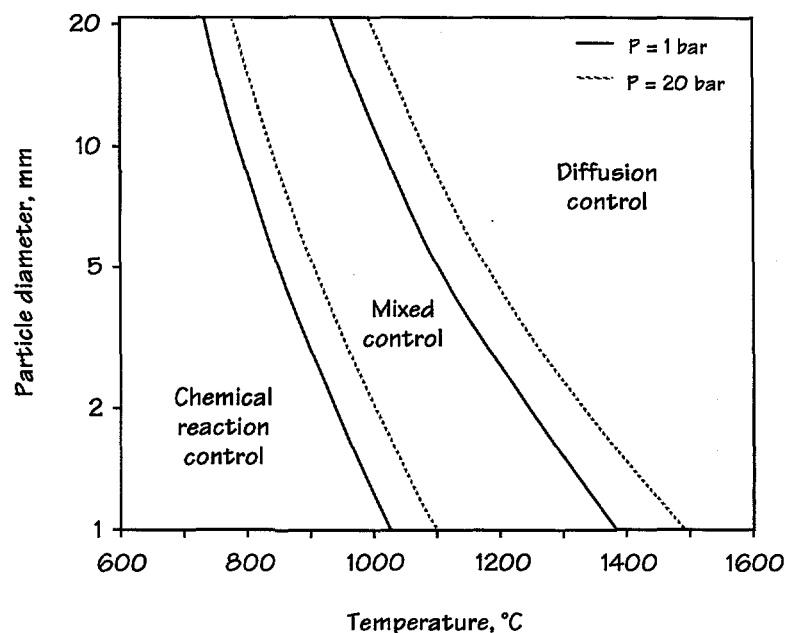


Figure 6-1. Reaction control regimes for black liquor char gasification as a function of temperature and particle size.

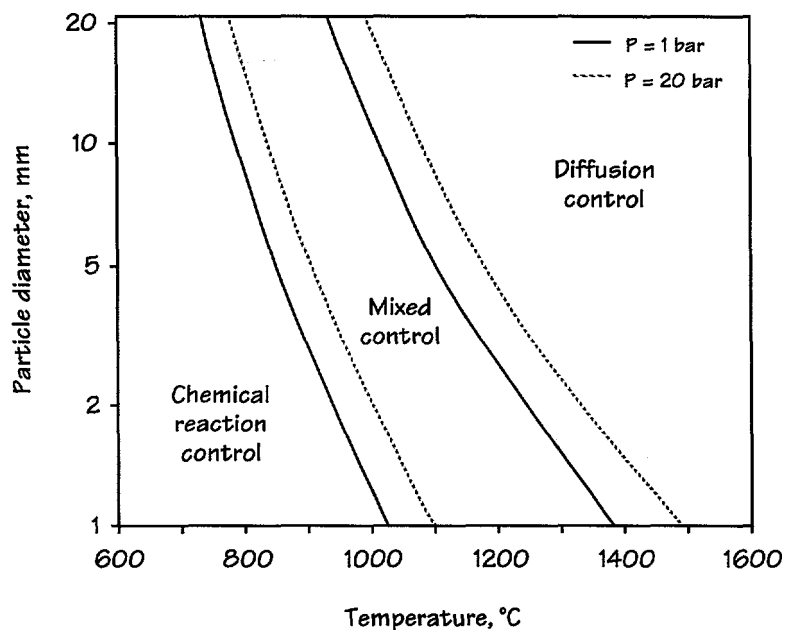


Figure 6-2. Reaction control regimes for black liquor char gasification as a function of temperature and pressure.

6.2 Char transformations during conversion

It is of interest to know how the properties of black liquor char change as it is converted. Studying how a char's morphology varies with conversion helps to understand associated rate processes. Changes in the composition of the char not only affect its chemical properties but give insight into how components are released during gasification.

6.2.1 Morphological changes during char gasification

It is valuable to understand changes in the structure and size of black liquor char during gasification. As the particle size changes its entrainability and trajectory are affected. Changes in the porosity and microstructure of the char will influence its observed reactivity. Changes in the char structure are discussed in **Paper V**. Information regarding the particle size progression during gasification is unavailable for pressurized conditions because the reactor used in these studies does not allow for observation of the gasifying sample. However, information regarding changes in particle diameter during gasification at atmospheric pressure is available. We can use this data as an approximation of how the diameter changes under pressurized conditions.

Frederick and Hupa [87] videotaped droplets of black liquor as they were gasified with CO_2 and H_2O at atmospheric pressure in a laboratory muffle furnace. During the char gasification stage the particle diameter remained constant for a short period, after which it decreased almost linearly with time. The progression of conversion was not monitored in these experiments so we do not know how the size of the droplet changed with conversion.

In the study reported in **Paper V**, samples of black liquor char were gasified by CO_2 at 700°C to various conversions, after which the sample was removed from the reactor and quenched with helium. The partially-converted chars were then analyzed via scanning electron microscopy to study changes in the microstructure with conversion. Two pressures, 1 and 20 bar, were investigated. At both pressures, the initial char was highly porous and the structure resembled that of a sponge. For the char formed at 1 bar, three classes of pores could be identified: tiny ($<2\ \mu\text{m}$) pores within the skeletal material itself, somewhat larger ($\sim 10\ \mu\text{m}$) voids between crests in the material and even larger ($>50\ \mu\text{m}$) open voids between regions of skeletal material. There are undoubtedly even smaller, submicron pores that cannot be detected via SEM.

As the char was converted, little variation was observed in the microstructure up to roughly 80% conversion. Between 80% and 100% conversion, however, the porosity decreased significantly and the material appears to have fused together. At these high conversions the char is composed primarily of sodium salts and partial melting of these salts is likely responsible for the observed effect. The inorganic residue that remained after full conversion was quite smooth and only the larger gaps in the material remained.

It would be of interest to study changes in the internal surface area of char as it is converted under pressurized conditions. Unfortunately, as discussed in section 5.1.2, experimental limitations have made such investigation infeasible. In order to generate enough sample for accurate BET analysis, several experiments would have to be made at each set of conditions and to each conversion. Not only would this be a massive

experimental undertaking, but it would be nearly impossible to stop each of the experiments at the exact same conversion. The best we can do at this point is to refer to similar studies that have been carried out for other fuels, such as coal. The internal surface area of coal is known to increase up to roughly 30% conversion as pores are opened by gasification. The surface area then decreases throughout the rest of the conversion. The initial area increase may not occur for black liquor since it is extremely porous to begin with. But the decrease in surface area would probably be similar to that of other fuels, at least up to the point where melting and fusing of the char cause a significant decrease in internal surface area.

6.2.2 Compositional changes during char gasification

In the study mentioned above, the chars that were gasified to various degrees of conversion were analyzed by x-ray scanning in the SEM in order to estimate the chemical composition of the material. Due to the nature of the analysis absolute values for the mass fraction of the elements were not available. Instead, the results are given as a ratio between species. It is assumed here that the decrease in the total amount of sodium during conversion was negligible because of the low temperature used (700°C), so the amounts of other elements are given in terms of their mass ratio to sodium.

As expected, the C/Na ratio decreased throughout conversion for both pressures, and at full conversion very little carbon remained. The carbon that did remain was in the form of carbonate. The results for potassium, sulfur and chlorine at 1 and 20 bar are presented as a function of conversion in Figure 6-3. Sulfur decreased rather linearly throughout conversion, and no sulfur could be detected in the residue that remained after gasification. This was observed by Kymäläinen, as well [41]. Li and van Heiningen [80] concluded that the major reaction leading to sulfur release during CO₂ gasification is the formation of COS by reaction of Na₂S and CO₂ (reaction 6-5). This is presumably the case in this study, as well. Any sulfate in the char is reduced to sulfide according to reaction 6-3. This sulfide is then gasified by CO₂.

At 1 bar pressure, chlorine disappeared throughout conversion while potassium decreased only slightly. At 20 bar, however, the chlorine stayed in the char as did all the potassium. The apparent increase in chlorine and potassium at 100% conversion is obviously wrong, and is likely a result of some sodium loss at this high conversion. For this particular experiment the residue remained in the hot reactor for an extended period of time. SEM scans of the residue from gasification at 20 bar revealed concentrations of potassium chloride along "seams" of the inorganic melt. This was not observed for the residue from gasification at 1 bar. This behavior can be explained by suppression of NaCl and KCl vaporization at higher pressures.

6.3 Black liquor char gasification rates

Of the three stages of gasification the last, char gasification, is the slowest in most conditions of practical interest for low temperature gasification. At lower temperatures this stage can require an hour or more for completion while drying and pyrolysis require only a few seconds. Thus it is certainly worthwhile to study this final stage, to try to understand how black liquor behaves during gasification and to understand what affects the rate of gasification. As noted in section 2.3.1, the rate of black liquor char gasification

at atmospheric pressure has been studied previously. But since some of the most interesting proposed alternative recovery processes operate at elevated pressures it is important to investigate gasification under pressure, as well. Little data on pressurized black liquor char gasification are available [87-92]. In this section new and relevant information on this subject is presented.

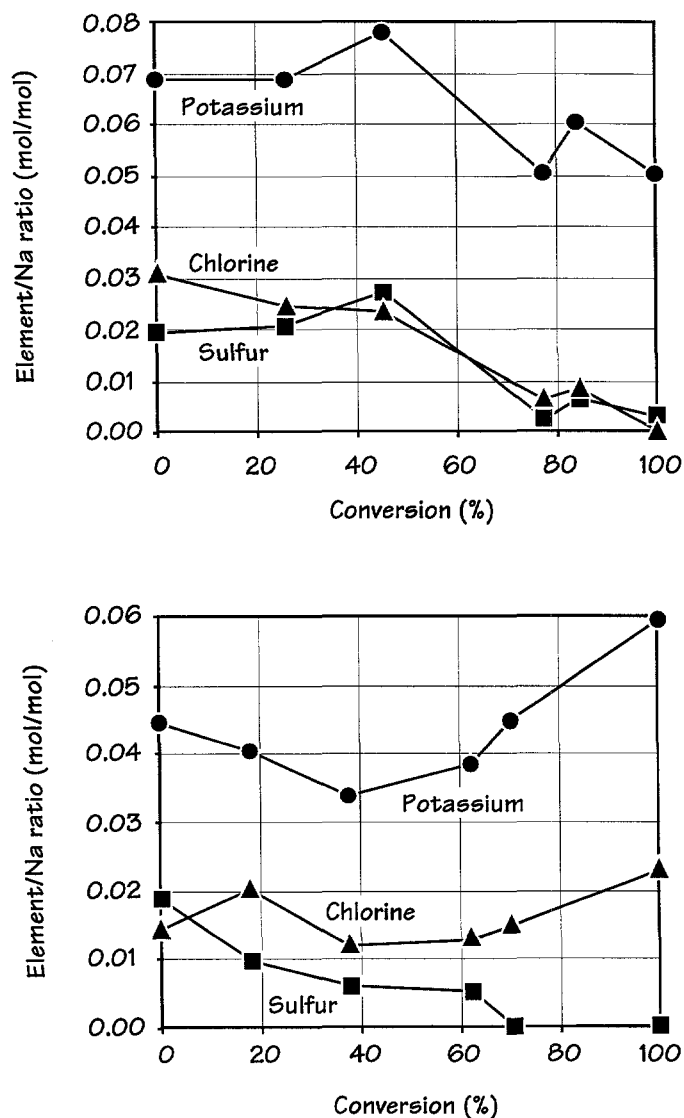


Figure 6-3. Fate of potassium, sulfur and chlorine during gasification of char at 1 bar (upper) and 20 bar (lower).

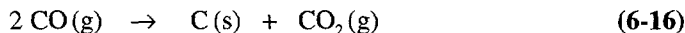
Before looking at the rate of char gasification, it is valuable to consider the substance of interest itself, the black liquor char. The char results from the devolatilization process, and the manner in which this process is carried out affects the properties of the char. The char properties, in turn, affect the manner in which the char behaves during gasification. This point was overlooked in many of the earlier investigations presented here. In those studies the starting material was black liquor char, and the focus was on measuring its reactivity during gasification. In order to eliminate any effects associated with further devolatilization of the sample upon introduction to the furnace, the char was first placed in the heated reactor containing an inert gas, nitrogen, until the weight signal stabilized. In order to prevent sodium carbonate decomposition 10% CO was added to this gas, a procedure which had been successfully employed by others researching black liquor gasification [78,79,82,90]. The sample weight stabilized within a few minutes of introducing the char sample to the reactor. In order to "cover all the bases" a standard pretreatment time of 400 seconds was established.

That experimental procedure was used in many of the sections below, which discuss the rate of black liquor gasification under pressure. However, a side effect of this pretreatment procedure was that the char properties were altered, thereby affecting the subsequent reactivity during gasification. **Paper IV** discusses the influence of char formation and pretreatment conditions on subsequent reactivity.

6.3.1 Influence of char formation and pretreatment conditions

There are three parameters during pyrolysis and char pretreatment which can have a profound effect on the observed reactivity of the char during gasification: temperature, pressure and gas composition, specifically the presence of carbon monoxide. Prolonged exposure to high temperature leads to a decrease in reactivity due, among other things, thermal annealing. This has been observed for other fuels as well [128-133,146]. As noted in sections 0 and 5.1.2, pressure during pyrolysis influences the swollen volume and microstructure of the resulting char. If the internal surface area is higher, there will be more opportunity for solid-gas contact and the observed rate will be higher.

The influence of gas composition is not as obvious. If the char undergoes a pretreatment period prior to gasification, and if there is carbon monoxide in the pretreatment gas, it is possible for elemental to form on the char as a result of the Boudouard reaction:



This was demonstrated for black liquor chars by Saviharju *et al.* [92]. As the partial pressure of CO increases, this reaction takes place more rapidly. For a certain CO concentration (e.g. 10%) the CO partial pressure rises proportionally with pressure, with the result that carbon buildup is more extensive at higher pretreatment pressures.

It was mentioned in section 2.3.1 that black liquor char gasification is highly catalytic. The alkali metals in the char are extremely efficient catalysts, which is why black liquor gasifies much more rapidly than most other carbonaceous materials. Elemental carbon is several orders of magnitude less reactive than black liquor char [91]. Therefore if there is

a layer of carbon on the surface of the char the gasification rate will be much slower, at least until it has been removed and the catalytic gasification can proceed.

In order to investigate this, three chars were formed by pyrolysis at 20 bar. One char was formed in pure nitrogen while the other two were formed in nitrogen plus 2% or 10% CO, corresponding to CO partial pressures of 0.4 and 2.0 bar, respectively. The samples were allowed to remain in this gas for 400 seconds, during which time carbon formed on the char surface. Based on the rate of carbon deposition measured by Saviharju *et al.* [92] it is estimated that the mass of deposited carbon accounted for less than 1% of the total mass gasified. The resulting gasification rates of these chars are shown in Figure 6-4. While the difference in rates between the cases of 0% and 2% CO is not outside the range of experimental reproducibility at conversions greater than 25%, addition of 10% CO to the pretreatment gas clearly retarded the rate. For the chars formed in gases with higher CO partial pressures, more carbon was deposited on the surface so these samples gasified more slowly. The two chars formed in CO-containing gas display an initially low rate, due to gasification of the elemental carbon. At higher conversions the gasification rates of all the chars are similar. It is interesting to note that while the mass of carbon deposited is only a small fraction of the total mass gasified, it has a large impact on reactivity.

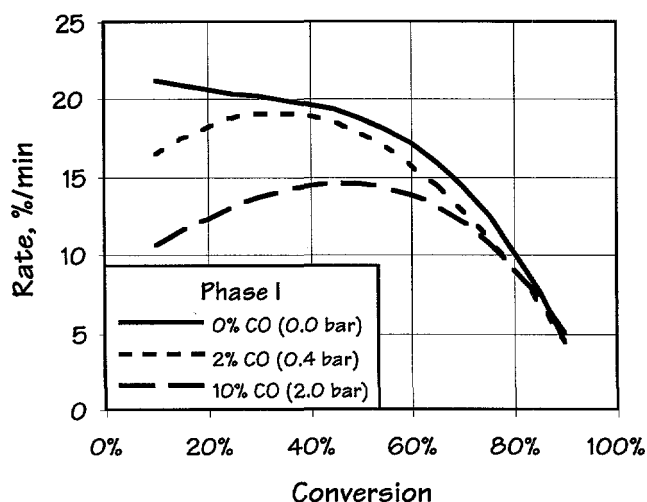


Figure 6-4. Influence of carbon buildup during char pretreatment on the resulting gasification rate. Conditions: 750°C, 20 bar. Pretreatment: 400 s in 10% CO, 90% N₂. Gasification: 20% CO₂, 4% CO, 76% N₂. Uncertainty in the rates is ±5%.

It is important to establish how significant carbon deposition is in experiments which involve pretreatment in a CO-containing atmosphere. The influence of carbon deposition can be summarized as follows:

- For a particular concentration of CO during pretreatment, the rate of carbon deposition increases with total pressure. Therefore it is not appropriate to compare experiments which have involved pretreatment at different pressures.
- For experiments with identical pretreatment conditions, the degree of carbon deposition is the same and affects all samples equally. Data from such experiments are valid. Measured rates may be lower than if no pretreatment existed, but trends with respect to other variables (e.g. gas composition) are presumably not affected.

Pyrolysis pressure alone also influences the reactivity. In another series of experiments chars were formed at different pressures but at otherwise similar conditions. The chars were then gasified under identical conditions and it was observed that those formed at higher pressures were less reactive. This can be explained by the lower internal surface area for these chars, as explained in section 5.1.2. Thus, for pyrolysis in a CO-containing atmosphere there are two effects which lessen the reactivity at higher pyrolysis pressures: carbon deposition and changes in char morphology. The results indicate that of the two, carbon deposition has the largest influence on reactivity.

6.3.2 Influence of char composition on gasification rate

Black liquor gasification is a catalytic reaction in which alkali species, primarily sodium, are the catalysts. It has been shown that for other fuels the rate of gasification is strongly dependent on the concentration and form of catalyst. In order to get some impression of how black liquor char reactivity is affected by the catalyst concentration a study was carried out in which synthetic black liquors were prepared with varying sodium concentrations. The details and results of this study are given in **Paper VIII**. In preparing the synthetic liquors the sodium content was varied by using different ratios of sodium hydroxide and ammonium hydroxide. When the liquors were dried any ammonia present evaporated. By this technique it was possible to form liquors with sodium contents ranging from essentially zero to levels on the order of those found in industrial kraft liquors.

Chars were formed from these liquors and subsequently gasified under identical conditions. As expected, it was found that the chars containing higher concentrations of sodium were more reactive. This can be seen in Figure 6-5. An increase in char sodium content of the liquor from 1% to 6% resulted in a rate increase by roughly a factor of 50. The data in Figure 6-5 was obtained from experiments involving pretreatment in a CO-containing atmosphere. But, since the pretreatment conditions were the same for all experiments, any carbon deposition affected the samples equally. Consequently, the results are still valid.

As discussed in 2.3.2, the presence of alkali species greatly enhances the rate of coal gasification. As the amount of alkali in the coal increases, the rate increases up to a loading of roughly 0.1 mol alkali per mol of carbon. Beyond this "saturation level," little influence of additional alkali addition is observed [102-104]. As seen in Figure 6-5, the same saturation effect appears to exist for black liquor as well, and the saturation level, 0.1 mol alkali/mol carbon, is the same as that which has been reported for alkali-catalyzed gasification of coal.

In this study it was assumed that observed differences in reactivity were a result of the different catalyst concentrations. However, the gasification rate is also related to the internal surface area of the char. Due to the small samples used in this study and the difficulty in producing enough char for reliable BET analysis alluded to in section 6.2.1, measurement of the internal surface area was not possible. Thus there is some uncertainty in the results.

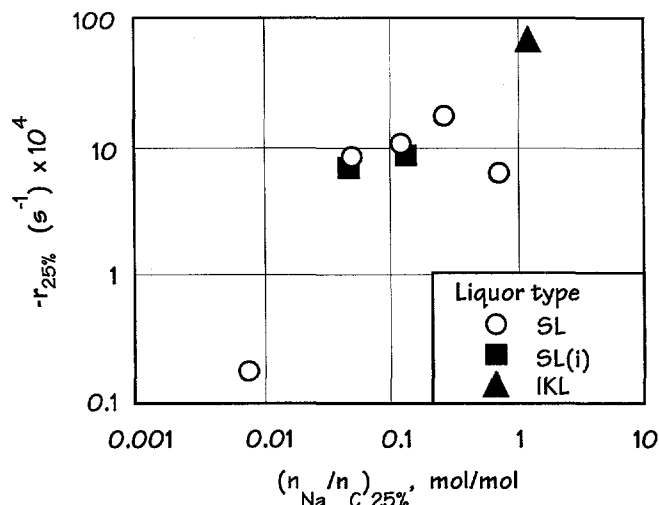


Figure 6-5. Influence of black liquor char sodium content on gasification rate. Liquor types: SL = synthetic liquor prepared from liquid precursors, SL(i) = synthetic liquor prepared by Na_2CO_3 impregnation of synthetic liquor solids containing no sodium., IKL = industrial kraft liquor.

The form of the catalyst also influences the reactivity of the char. Studies on alkali-catalyzed coal gasification indicate that alkali carbonates are the most efficient catalysts. Roughly 20-25% of the sodium in black liquor is in the form of carbonate, with another 5-10% in the form of sulfate and the remainder chemically linked to lignin and hydroxy acids [79]. In the study reported in **Paper I**, efforts were made to correlate gasification reactivity with liquor composition, including carbonate content, but no relationships were found.

6.3.3 Liquor-to-liquor differences in gasification reactivity

As discussed in Chapter 2, it has long been recognized that there are large differences in the combustion behavior of different liquors. It is of interest to determine how differently black liquors behave during gasification, as well. In particular, it is important to know the range of reactivities during char gasification. In **Paper I**, 15 different black liquors were subjected to a number of tests in order to identify liquor-to-liquor differences. Much of the information presented there is relevant to pressurized black liquor gasification. In that paper it was reported that pressurized gasification rates differed by as much as a factor

of 3.5 between liquors. Though these experiments were carried out with a pretreatment procedure as discussed in section 6.3.1, the pretreatment was the same for all liquors and affected them equally, so the information is still valid.

More recently, another study was conducted to determine liquor-to-liquor differences in gasification reactivities at atmospheric pressure. Gasification experiments were carried out on 17 industrial liquors in a single-particle tube reactor (Figure 4-5). Droplets of black liquor were pyrolyzed in pure nitrogen and then the char was gasified by CO_2 at 750°C . The progression of the gasification reaction was monitored with a carbon monoxide meter. The CO evolution profile for a typical experiment is displayed in Figure 6-6. Four experiments were performed for each liquor and reproducibility was excellent. Analysis of the system indicates that the experiments all took place within the chemical reaction controlled regime [152]. The fastest experiment, however, was just on the border of entering the mixed control regime as defined in section 6.1.

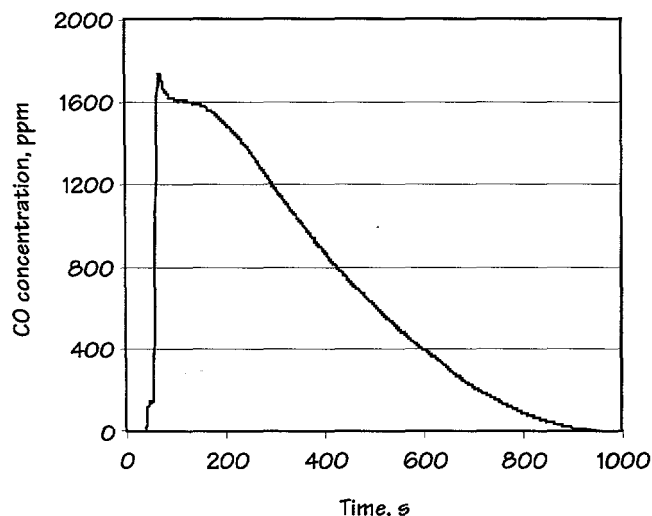


Figure 6-6. CO evolution profile for a typical gasification experiment conducted in the single-particle tube reactor.

The concentration of CO in the product gas is proportional to the carbon gasification rate. Based on the total gas flow rate the instantaneous carbon consumption rate could be calculated. The rate of gasification was then determined as a function of *carbon conversion*. Note that, by necessity, this definition of conversion is not based on mass loss as is otherwise the case in this chapter. The gasification rate is defined based on the initial amount of gasifiable carbon in the sample:

$$\text{rate} = \frac{dm_c}{dt} \frac{1}{m_{c,i}} \quad (6-17)$$

where m_c is the mass of carbon remaining at time t and $m_{c,i}$ is the initial mass of gasifiable carbon in the sample as determined by integration of the CO evolution curve.

Plots of the instantaneous gasification rate versus conversion are shown for four of the liquors in Figure 6-7. The samples in the figure represent the extremes of the 17 liquors. The shapes of the curves are quite different. The two kraft liquors were much more reactive than either the soda or sulfite liquor, and after an initial plateau the rates decreased with conversion. The gasification rates of the soda and sulfite liquors first increased and went through a maximum at roughly 30% conversion, then decreased throughout the remainder of the experiment. These liquors were also observed to swell much less than the kraft liquors, and the shape of the conversion curves may be related to this. Similar shapes have been observed for gasification of coal chars and coke particles [107-112]. For coal chars and coke, the initial rate increase is due to an increase in the internal surface area as pores open up [108,111]. The rate decrease then results from a combination of lower surface area as pores overlap and less carbon available for reaction. It may be that a similar phenomenon occurs during gasification of soda and sulfite liquors. The absence of such behavior for the kraft liquors could be due to the fact that their initial porosity is so large that changes in surface area at low conversions are not reflected in the gasification rate. Differences in pore size distribution could also account for this behavior.

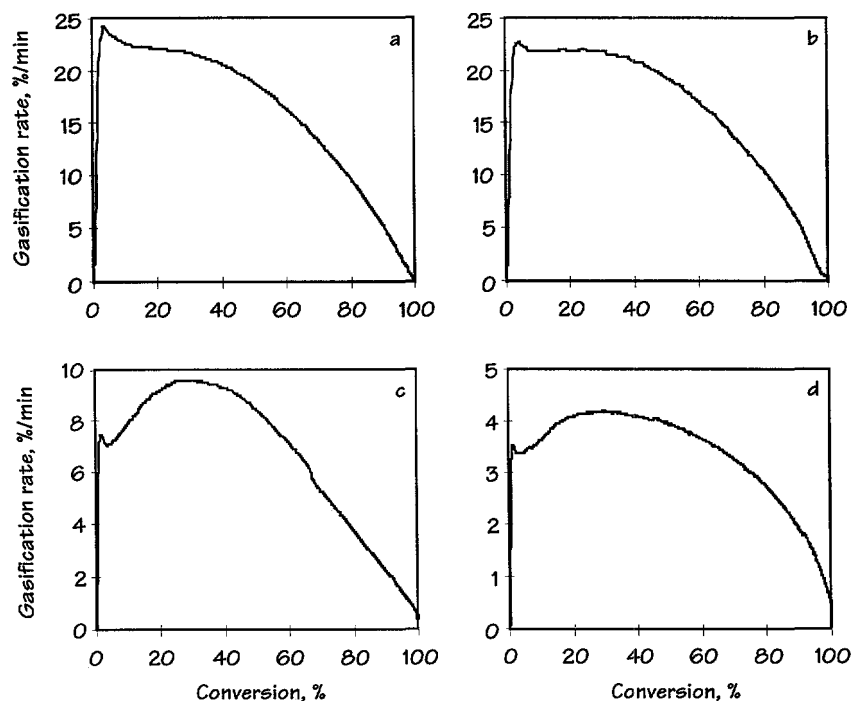


Figure 6-7. Rate versus char carbon conversion during gasification for four liquors: (a) kraft hardwood, (b) kraft softwood, (c) soda bagasse, (d) NSSC hardwood.

The average gasification rate at 25% carbon conversion for was chosen as a reactivity index for comparison between liquors. The distribution of the measured rates is shown in Figure 6-8. The kraft liquors were much more reactive than either the soda or sulfite liquors, and the lowest and highest reactivities differed by a factor of 7. Among the kraft liquors, reactivity varied by as much as a factor of 2.2.

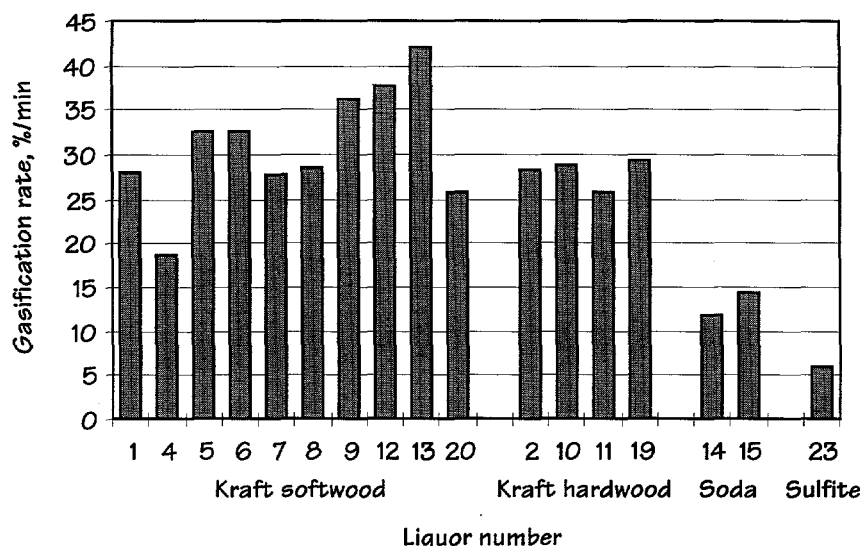


Figure 6-8. Distribution of measured gasification rates at 25% carbon conversion.

Role of sodium sulfate during gasification. The higher rates observed for the kraft liquors is intriguing, suggesting that perhaps something in the composition of these liquors causes them to be more reactive. Kraft liquors contain much higher concentrations of sodium sulfate than other liquors, which may account for the difference. Decomposition of sodium sulfate (Equation 1-6) occurs during gasification and contributes to the consumption of carbon. The fraction of total conversion which can be accounted for by this reaction can be estimated. Grace *et al.* [86] suggest that, prior to burning, the char contains 16.4% sodium sulfate and 24.9% carbon. If it is assumed that all sulfate reacts according to Equation 1-6, it can be calculated that 16% of the carbon is converted by this reaction. This alone cannot explain the much higher gasification rates of the kraft chars.

Black liquor char burning is known to occur largely via a sulfate-sulfide cycle, in which sodium sulfide is oxidized to form sulfate, which then reacts with carbon according to Equation 1-6 [85,86]. However, it seems very unlikely that sulfide would oxidize to form sulfate under gasification conditions. Backman and Hupa [49] performed thermodynamic analysis on pressurized gasification of black liquor char over the temperature range 400-1500°C and over the temperature range 1-100 bar using three air ratios: 0.0, 0.3 and 0.9. Except at an air ratio of 0.9 (which can hardly be considered

gasification), no sodium sulfate existed at equilibrium. Moreover, if such a sulfate-sulfide cycle were to account for the high reactivities of kraft chars, one would expect the sulfite liquors to display higher rates.

A more likely explanation for the high gasification rates of the kraft chars is that they have more internal surface area available for reaction due to their higher degree of swelling. As noted in the literature review (section 2.2.1) and reported in Paper I, soda and sulfite liquors are observed to swell much less than kraft liquors. Van Heiningen *et al.* [84] found that the internal surface area of black liquor char increases with increasing specific swollen volume. The limited results presented in section 5.1.2 are consistent with this. Data on the specific swollen volumes of the chars shown in Figure 6-8 at conditions near those used for gasification are available. The gasification rates of these chars are plotted against their swollen volumes in Figure 6-9. Clearly the two properties correlate. Over the range of swollen volumes in the figure, the internal surface areas measured by van Heiningen increased by a factor of roughly 5. It therefore seems reasonable that the higher reactivities of the kraft chars result from their larger internal surface areas.

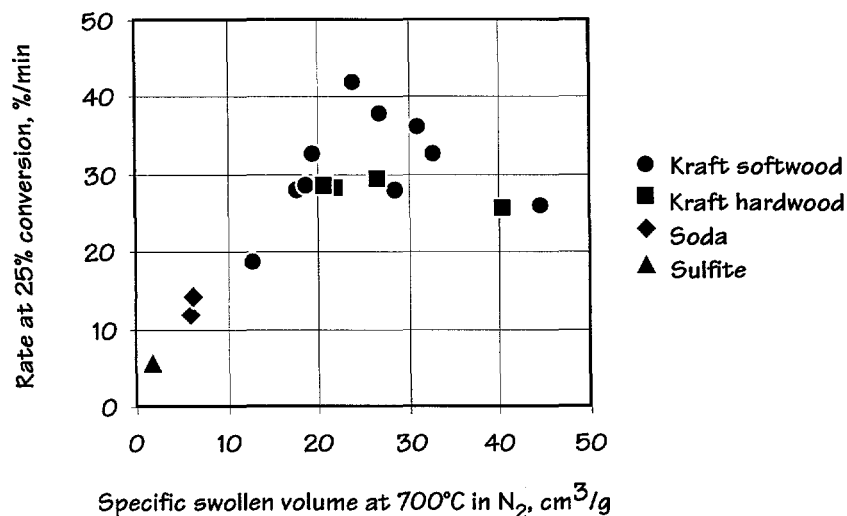


Figure 6-9. Rate versus specific swollen volume. Swelling measured at 700°C in N₂. Gasification rates measured at 750°C.

6.3.4 Influence of temperature on gasification rate

The black liquor char gasification reaction is extremely temperature sensitive. Activation energies have been measured previously for pressurized gasification with CO₂ [90] and the activation energy of pressurized gasification with H₂O was determined in Paper VI. The observed activation energies are approximately 207 kJ/mol for H₂O gasification and 236 kJ/mol for CO₂ gasification [90]. These values are of the same magnitude of those reported by Li and van Heiningen for atmospheric gasification of black liquor char with CO₂ (250 kJ/mol [79]) and H₂O (210 kJ/mol [82]). An activation energy of 230 kJ/mol

corresponds to a rate increase by a factor of 14 over the temperature range 700-800°C. The influence of temperature on the observed gasification rate is shown in Figure 6-10. The conditions represented in the figure are all within the chemical reaction controlled regime. But it must be remembered that at higher temperatures the rate of char conversion will no longer be dependent on the rate of the chemical reaction, but that mass transfer will control the rate (see section 6.1).

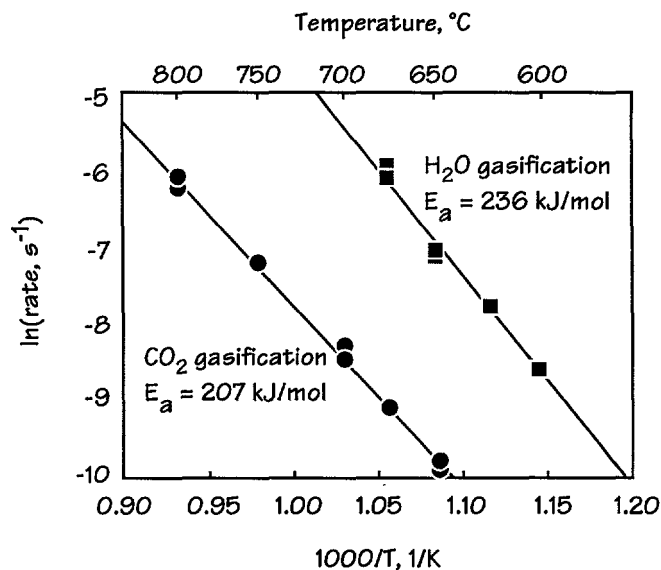


Figure 6-10. Influence of gasification temperature on the rate of reaction.

6.3.5 Influence of total pressure on char gasification rate

In many regards, the most critical aspect of pressurized black liquor gasification is the influence of pressure on the rate of char gasification. Earlier investigation at Åbo Akademi considered this issue for gasification with carbon dioxide [89-91]. In the current work, **Paper VI** and **Paper VII** discuss the influence of pressure during gasification with H_2O and mixtures of H_2O and CO_2 , respectively. In all of these studies it has been found that at constant gas composition the rate of char gasification decreases with pressure. Figure 6-11 shows an example of this for gasification with H_2O . The data points have been removed in this figure but are given in Paper VI. The gasification rate decreases by a factor of roughly 5 over the range 1-30 bar for a gas composition of 20% H_2O and 2% H_2 in nitrogen. Decreases of similar magnitude were found for gasification with CO_2 and in mixtures of H_2O and CO_2 .

The observed decrease with pressure in these studies and shown in Figure 6-11 is not entirely a result of changes in the gasifying atmosphere. In these earlier studies the explanation for the slower rates at higher pressures was that the inhibiting influence of CO and H_2 increases more rapidly with pressure than the positive effect associated with

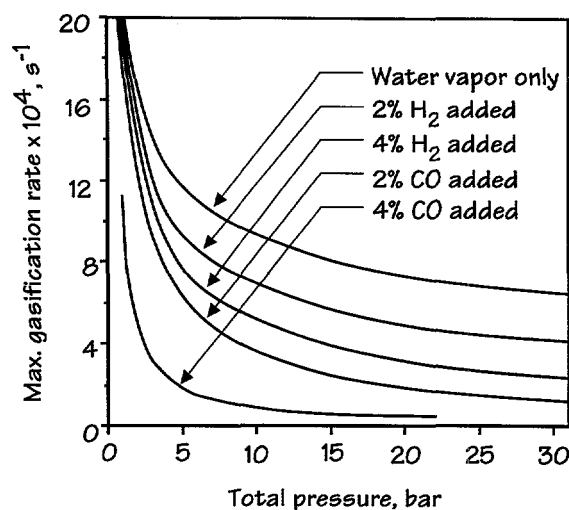


Figure 6-11. Influence of pressure on the rate of steam gasification. Pretreatment: 400 s in 10% CO, 90% N₂ at pressure indicated. Gasification: 20% H₂O, nitrogen carrier. 650°C. Note that the effect of total pressure shown in the figure is not valid, but that H₂ and CO do decrease the rate.

higher CO₂ and H₂O partial pressures. The gasification rates surely do change with pressure. But as discussed in section 6.3.1 and in **Paper IV**, much of the decrease with pressure is associated with changes in the char, particularly carbon buildup, which resulted from the char pretreatment procedure used. In other words, the influence of pressure during the period *prior to* gasification was responsible for much of the observed rate decrease with pressure *during* gasification. Higher pretreatment pressures resulted in more carbon deposition, which translated to lower gasification rates. *The influence of total pressure indicated in Figure 6-11 is therefore not valid.* Data regarding changes in the gasification at any particular pressure are useful, however, and are discussed in section 0.

It has been shown that the true influence of pressure on the rate of black liquor gasification cannot be determined from these earlier studies. In order to identify the real influence of pressure, two new approaches were taken. The first attempts to ascertain how much of the observed rate decrease is associated with carbon deposition and how much, if any, results from changes in the gas environment. The second approach looks at the whole issue of gasification from the point of view of a droplet entering an industrial gasification reactor, where no char pretreatment occurs.

Reconsideration of experimental data. In Paper IV a series of experiments was carried out to identify the influence of char pretreatment conditions on the observed gasification rate. The idea was to take a black liquor char (the same one used in Paper VI) and perform a series of experiments in which it is pretreated at different pressures but gasified at a standard set of conditions. The opposite approach was also taken. That is, chars were pretreated at a standard set of conditions and then gasified at different pressures.

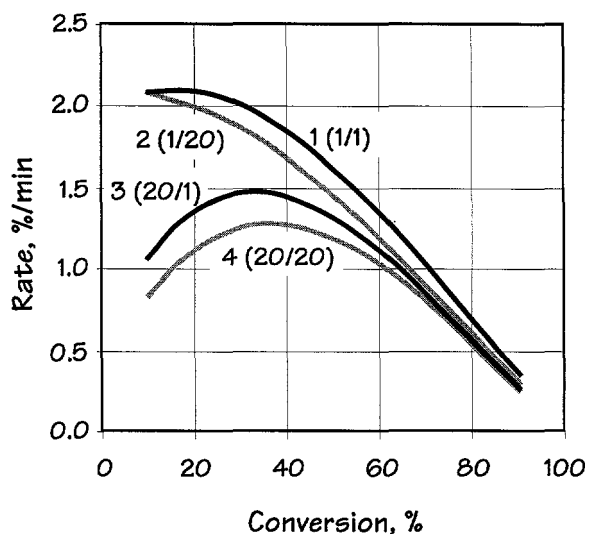


Figure 6-12. Influence of char pretreatment and gasification pressure on the gasification rate. The labels indicate experiment number (pretreatment pressure/gasification pressure). Uncertainty in the rates is $\pm 5\%$.

The results of this study are summarized in Figure 6-12. Four chars were pretreated exactly as in previous experiments, two at 1 bar, two at 20 bar. The chars pretreated at 1 bar were then gasified at 1 bar and 20 bar, as were the two chars pretreated at 20 bar. Details of the experimental procedure are given in Paper IV.

Results that have been reported previously compare experiments performed similar to cases 1 and 4 in the figure. Clearly, the rate of reaction for the experiment at 20 bar (case 4) was much less than that of the experiment at 1 bar (case 1). But to see how much influence the pretreatment pressure has one must compare experiments 1 and 3 (or 2 and 4). Even though gasification was carried out at the same pressure, the samples still reacted at very different rates. This can only be a result of the pretreatment pressure. The excessive carbon deposition on chars pretreated at 20 bar is visible as a much slower rate at low conversions for these chars.

On the other hand, to look exclusively at the influence of gasification pressure one must compare those experiments with identical pretreatment conditions. Experiments 1 and 2 are the best for this, since the chars were pretreated at a lower pressure and carbon deposition was minimized. The data does in fact indicate that the rate of gasification may be somewhat less at higher pressure, but the difference between these curves is just within the range of experimental uncertainty. In any case the impact of this finding is critical — the rate decrease with pressure, if it does exist at all, is much less than has been reported previously.

Simultaneous pyrolysis and gasification of black liquor. Up to this point, all the gasification experiments that have been discussed have been carried out in two phases, a phase in which the sample is in an "inert" environment (*Phase I*) and a phase where the actual char gasification takes place (*Phase II*). In some instances the initial sample has been a pre-formed char, so that during *Phase I* the material undergoes additional heat treatment prior to gasification. In other instances the initial material has been black liquor, in which case a char is formed during *Phase I*. The experiments have been carried out in this manner so that reactions during the char gasification phase could be clearly focused upon. But as we have seen, conditions during *Phase I* may affect the observed rates.

Optimally, we would like to study the gasification reaction in conditions representative of those that would be found in an industrial-scale gasifier. Such a reactor would not involve 400 seconds of thermal treatment prior to char gasification. Rather, the black liquor would likely be introduced directly into the gasifying environment where it would undergo all three stages of gasification: drying, pyrolysis and char gasification. Studying such a system with laboratory-scale equipment presents a serious challenge. But recently an experimental technique was developed which allows such study.

The pressurized thermogravimetric reactor was used, and a sample of concentrated black liquor was introduced directly into the gasifying mixture at the desired temperature and pressure. Upon entering the hot environment the sample dries and devolatilizes and a char is formed. Due to the dynamics of these processes and the time required for the microbalance to stabilize no weight signal was received during drying and most of pyrolysis. But careful examination of the first few data points obtained revealed that the beginning of the char gasification stage could be identified. The weight-loss curve for this portion of a typical experiment is shown in the inset in Figure 6-13. Note that the first few data points have a much steeper slope than the rest of the curve. These points correspond to weight loss due to devolatilization of the sample. The shift in slope corresponds to the beginning of the char gasification stage. In these experiments the initial mass of char was defined as the mass at the point where straight lines fit to the two slopes intersect, as shown in the figure. Reproducibility for these experiments carried out in this manner was very good.

The gas in the reactor flowed upwards past the sample, so dynamic buoyancy effects made it appear lighter than it really was. As long as the sample geometry in the horizontal is constant, the dynamic buoyancy will remain the same throughout the experiment. But a droplet being gasified shrinks during conversion. If the droplet were perfectly spherical it might be possible to model the dynamic buoyancy changes with conversion and to make a correction in the received weight signal. But swollen droplets can assume quite exotic shapes, frequently far from spherical, and such modeling is basically impossible. The way this problem was solved was to use a sample holder which contained the char as it swelled and ensured that the geometry in the horizontal plane (that is, the projection of the sample as seen by the upwards flowing gas) remained unchanged throughout the experiment. The sample holder is shown in Figure 4-4. Black liquor was painted onto the solid stem of the holder and the net was placed concentrically around this stem. When the sample swelled the net contained it and kept the sample inside the holder. This was verified by a number of preliminary experiments. The major drawback to this method is that the sample holder must be heated along with the sample,

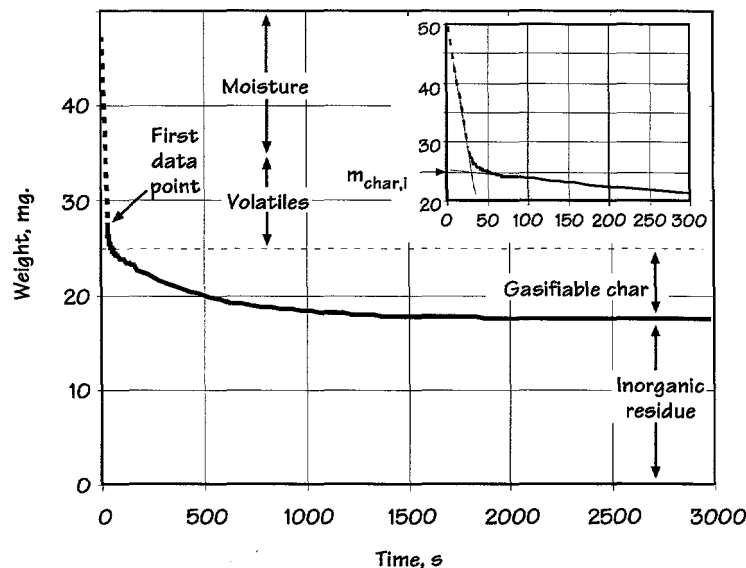


Figure 6-13. Experimental weight-loss curve for simultaneous pyrolysis and gasification.

resulting in a heating rate much lower than would be experienced by a droplet entering an industrial-scale unit.

Using this technique the influence of pressure on gasification of black liquor was studied. These new results are considered to be much more representative of the case in an industrial gasifier. The gasification rate as a function of char conversion is shown for experiments carried out over the pressure range 1-30 bar in Figure 6-14. Contrary to earlier findings, the observed gasification rate appears to be unaffected by pressure under these conditions. At low conversions gasification at 1 bar displayed a slightly higher rate. Otherwise, the rates were essentially the same.

The results in Figure 6-14 provide additional support for the results reported above and shown in Figure 6-12 that, at constant gas composition, there is little influence of pressure on the observed rate during gasification. Analysis and modeling of the system indicates that the experiments were well within the chemical reaction controlled regime. The experiments required roughly 15 minutes to achieve 90% char conversion. The time required if film mass transfer and diffusion controlled the rate was estimated to be less than 40 seconds, so the experiments were within the chemical reaction controlled regime.

It is possible that the observed lack of dependency on pressure is a result of competing factors. As the total pressure rises the partial pressure of CO_2 increases, which should increase the gasification rate. However, the partial pressure of CO also rises, which should decrease the rate. Additionally, the structure of the char formed at higher pressures will be different and will probably influence reactivity. As the results presented in section 6.3.1 indicate, chars formed at higher pressures are less reactive. It is possible

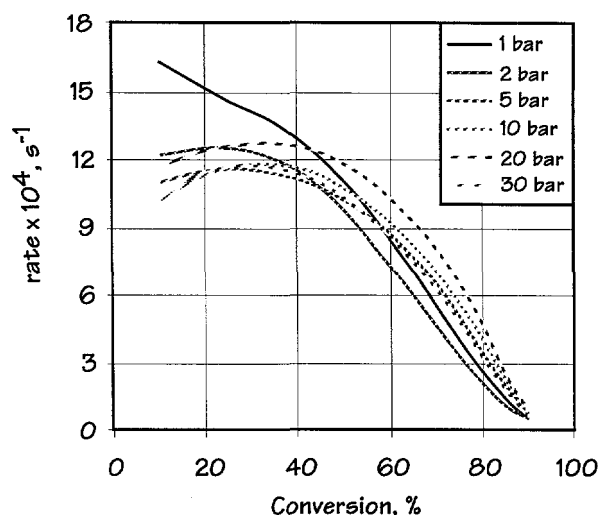


Figure 6-14. Influence of pressure on gasification rate during simultaneous pyrolysis and gasification. Conditions: 725°C, 20% CO₂, 4% CO, 76% N₂. Uncertainty in the rates is ±5%.

that the combination of these effects cancelled out each other in the experiments shown in Figure 6-14. More study into the influence of pressure on the rate of conversion during simultaneous pyrolysis and gasification of black liquor is warranted, and efforts continue at Åbo Akademi.

6.3.6 Influence of gas composition on char gasification rate

The driving forces for the char gasification reactions are the partial pressures of the gasification agents, H₂O and CO₂. The product gases, H₂ and CO, inhibit the gasification reactions. Two mechanism-based rate expressions have been developed for pressurized black liquor char gasification, one for gasification with steam and one for gasification with carbon dioxide. In Paper VI, the following expression was presented for pressurized gasification with steam, based on a mechanism proposed for alkali-catalyzed gasification of carbon:

$$r = 10^{-4} \cdot \exp \left[28000 \left(\frac{1}{923} - \frac{1}{T} \right) \right] \cdot \frac{9.01}{1 + \frac{p_{H_2}}{0.449 p_{H_2O}} + 7.09 p_{CO}} \quad (6-12)$$

where

- r = gasification rate, (mg/s)/mg total gasifiable material
- T = temperature, K
- p_i = partial pressure of species i , bar

Frederick *et al.* [91] suggest the following expression, based on one developed for potassium-catalyzed gasification of carbon, for gasification of black liquor char with carbon dioxide under pressurized conditions:

$$r = \frac{p_{\text{CO}_2} - p_{\text{CO}}^2 / K_{eq}}{\frac{k' p_{\text{CO}_2}}{Y_{\text{C},0}} + \frac{k'' p_{\text{CO}}}{Y_{\text{C},0} N_{\text{Na+K}}}} \quad (6-18)$$

where

K_{eq} = equilibrium constant for the reaction $\text{C} + \text{CO}_2 \leftrightarrow 2 \text{CO}$

k', k'' = constants determined by fitting experimental data
 k' has units of (g carbon)(s)/(g char)
 k'' has units of (g carbon)(moles Na+K)(bar CO_2)(s)/(g char)²(bar CO)

$Y_{\text{C},0}$ = initial mass fraction of carbon in the char

$N_{\text{Na+K}}$ = total moles alkali metal per gram of char

Based on their experiments at 700°C, Frederick *et al.* obtained values for k' and k'' of 623 and 42.1, respectively. The initial mass fraction of carbon in their chars, $Y_{\text{C},0}$, was 0.312 and the value of $N_{\text{Na+K}}$ was 0.00811 mol alkali per gram of char. At 700°C, the equilibrium constant K_{eq} is 0.990. Inserting these values into Equation 6-1 and simplifying yields the following:

$$r = 10^{-4} \cdot \frac{p_{\text{CO}_2} - 1.01 p_{\text{CO}}^2}{0.200 p_{\text{CO}_2} + 1.66 p_{\text{CO}}} \quad (6-19)$$

Equations 6-12 and 6-1 were both developed based on experiments which involved pretreatment in a CO-containing atmosphere. It is difficult to assess the validity of these expressions since the range of conditions of experiments upon which they are based varies considerably. It is suspected that the predicted gasification rate at higher pressures is lower than would be the true case since the experiments they are based on displayed such behavior. Nonetheless, they can be used as an aid to gain insight into the influence of particular gas species on the gasification rate.

No mechanism-based expression exists for gasification in the presence of both steam and carbon dioxide, but in Paper VII an empirical expression was developed which predicts the rate of black liquor char gasification as a function of the partial pressures of H_2O , CO_2 , H_2 and CO:

$$r(10^4) = 3.31 + 1.16 p_{\text{H}_2\text{O}} + 0.0712 p_{\text{CO}_2}^2 - 2.94 p_{\text{H}_2} - 3.87 p_{\text{CO}} + 0.660 \left(\frac{1}{p_{\text{CO}}} \right) \quad (6-20)$$

The validity of this expression is doubtful due to differences in the degree of carbon deposition during pretreatment between experiments carried out at different total pressures, as discussed in section 6.3.1. A more direct method of determining the influence of H_2O , CO_2 , H_2 and CO is to compare experiments in which the concentration of only one of these gases is varied. It is important to ensure that the comparison is between experiments which have undergone identical pretreatment, as well.

H_2O . Increasing the concentration of H_2O while keeping all other variables the same results in an increase in the gasification rate. In Paper VI, a series of experiments was carried out at constant pressure, temperature, and H_2 concentration, and with identical pretreatment conditions. Only the concentration of H_2O during gasification was varied. The data indicate that the steam gasification reaction is of order 0.56 in H_2O . Equation 6-12 also indicates that a rate increase occurs as the partial pressure of H_2O is increased. The denominator becomes less as $p_{\text{H}_2\text{O}}$ increases, resulting in a higher rate. The positive influence of H_2O partial pressure can be seen in Equation 6-20, as well.

CO_2 . Increasing the concentration of CO_2 while keeping all other variables the same results in an increase in the gasification rate. This was demonstrated in a study by Frederick and Hupa [90]. In experiments similar to those described above for H_2O , they varied the concentration of CO_2 in the reacting gas while keeping all other variables, temperature, total pressure, CO concentration and pretreatment conditions, constant. They reported that the rate of pressurized CO_2 gasification was of order roughly 0.85 in CO_2 for the conditions studied. The influence of CO_2 can also be discerned from Equations 6- and 6-20. At constant p_{CO} , increasing p_{CO_2} causes the rate to increase.

H_2 and CO . Increasing the concentrations of H_2 and CO while keeping all other variables the same causes a decrease in the gasification rate. In Paper VI, experiments were carried out in which only the concentration of H_2 or CO was varied. All other variables, including the pretreatment conditions, were kept the same. A number of different total pressures were investigated. The data are summarized in Figure 6-11. The data points are not shown in this figure, but can be seen in Figures 9 and 11 of Paper VI. For any particular total pressure, it can be seen that increasing the concentration of either H_2 or CO decreases the gasification rate. Carbon monoxide is a much stronger inhibitor than hydrogen, and addition of 2% CO results in a larger rate decrease than 4% H_2 . The influence of H_2 and CO can also be seen in Equation 6-12. As their partial pressures increase, the denominator becomes less, resulting in a lower rate. The coefficient for CO , 7.09, is larger than that for H_2 , 2.28 ($= 1/0.449$), indicating that its impact on the observed rate is significantly more. The decrease in the rate with at higher partial pressures of H_2 and CO is also visible in Equation 6-20.

Gas mixtures. It is not clear how the gasification rate is affected by gas composition when the concentrations of several species are changed. Due to gaseous interactions and the complexity of the chemical reaction mechanism it is unlikely that the individual contributions of each gas are additive. Equation 6-20 is the only known expression which takes into consideration all four of the gaseous species discussed above. But as stated previously, its validity is questionable. Also, as noted in Paper VII, the expression is only applicable within the range of conditions used in its development. Additional work is necessary before the influence of composition in gas mixtures is fully understood.

7. CONCLUSIONS

This thesis concerns pyrolysis and gasification of black liquor under pressurized conditions. Conclusions from this work are presented below, followed by suggestions for future work.

7.1 Conclusions from this work

Black liquor swells considerably during pyrolysis under pressurized conditions. The degree of swelling decreases roughly logarithmically with pressure, and the specific swollen volume at higher pressures can be predicted from Equation 5-1 if the specific swollen volume at 1 bar is known. The specific swollen volume of char formed at 20 bar is roughly one-quarter of that formed at atmospheric pressure, but at otherwise identical conditions. Scanning electron microscopy reveals that chars formed at higher pressures have a more compact, less porous microstructure than those formed at lower pressures, and BET analysis indicates that such chars have a lower internal surface area.

Mass loss during pyrolysis experiments results from a combination of pyrolysis reactions and inorganic decomposition reactions. In experiments at higher temperatures ($>850^{\circ}\text{C}$), particularly with longer holding times, the inorganic decomposition reactions can contribute significantly to the observed mass loss. The measured mass loss during pyrolysis increased with reactor temperature under all conditions studied, with a 100°C increase in reactor temperature corresponding to an additional 5% of the initial mass entering the gas phase.

Increasing pressure resulted in increased char yields at temperatures greater than 850°C , where decomposition of sodium carbonate contributes to the observed mass loss. This dependence on pressure is due to retardation of the sodium carbonate decomposition reaction at higher pressures.

Under the conditions studied, roughly 40-60% of the carbon in black liquor was released to the gas phase during pyrolysis. Sodium release during pyrolysis was roughly 10% at 750°C and 30% at 900°C . The increase with temperature is due primarily to the higher rate of sodium carbonate decomposition. Sodium release decreased with pressure. At 900°C the amount released at 20 bar was roughly half of that released at 1 bar, which can be explained by suppression of sodium carbonate decomposition at higher pressures.

Sulfur release during pyrolysis was in the range 35-70%, and increased with pressure. Under the conditions studied, an additional 15% of the sulfur originally in the liquor was released at 10 bar compared to that at atmospheric conditions. The reason for the observed increase is not clear, but may be related to the residence time of the liquor in the temperature range critical for sulfur release, or perhaps due to less efficient recapture in the less-swollen chars at higher pressures. More study is needed before this issue can be resolved.

Under conditions relevant for low temperature black liquor gasification, the rate of char gasification is controlled by the chemical reaction rate. The rate of this process is very temperature sensitive. The activation energy for pressurized steam gasification measured

in this work was 207 kJ/mol. Based on this activation energy the rate of gasification can be expected to double for a temperature increase of 20-30°C.

The reactivity of black liquor char during gasification depends largely on the conditions under which it was formed. In particular the temperature-time history, pressure and presence of carbon monoxide during char formation are critical. Prolonged exposure to high temperature reduces the reactivity of the char, most likely as a result of thermal annealing. Chars formed at higher pressures are less porous and have lower internal surface areas than those formed at low pressure. They therefore have less area available for reaction and display a lower gasification rate. If carbon monoxide is present in the pyrolysis gas, elemental carbon may build up on the surface of the char as a result of the Boudouard reaction. The rate of carbon buildup increases with increasing CO partial pressure, and the amount deposited increases with time. Gasification of carbon is much slower than gasification of black liquor, so char reactivity is reduced considerably.

The composition of the reacting gas influences the rate of black liquor char gasification. Increasing the partial pressure of steam or carbon dioxide increases the gasification rate. The rate of steam gasification was determined to be of order 0.56 in H_2O partial pressure. Hydrogen and carbon monoxide inhibit gasification, with carbon monoxide being the stronger inhibitor of the two. Addition of 2% CO causes a larger rate decrease during steam gasification than addition of 4% H_2 . A mechanism-based rate equation has been developed for pressurized steam gasification. In addition, an empirical expression for determining the gasification rate in the presence of H_2O , CO_2 , H_2 and CO has been developed. The usefulness of these rate expressions, as well as one developed by Frederick and Hupa for pressurized CO_2 gasification, is doubtful. All three rate expressions were developed based on experiments in which the rate was influenced by factors other than reacting gas composition, namely carbon buildup during char pretreatment.

Previously reported results indicating that the rate of char gasification decreases with pressure at constant gas composition have been found to be erroneous. The rates at higher pressures were lower due in part to more carbon deposition on the char surface during pretreatment.

Preliminary results indicate that the influence of total pressure on the rate of char gasification is much less than previously reported when the black liquor is introduced directly into the gasification atmosphere. Experiments carried out in this manner showed little variation in gasification rate with pressure over the range 1-30 bar. It is possible that competing factors essentially cancelled each other out in these experiments. Higher partial pressures of the gasifying species would tend to increase the rate at higher pressures, while lower char surface areas and higher partial pressures of CO and H_2 would tend to decrease the rate. The influence of total pressure on the rate of black liquor gasification is still not fully understood and deserves further study.

The structure of the char becomes less porous and more compact during char gasification. Under the conditions investigated, the char microstructure, as observed with a scanning electron microscope, remained essentially the same up to roughly 80% conversion (defined based on the mass of gasifiable char). Beyond that conversion the porosity decreased significantly and the material fused together.

The sulfur content of the char decreases roughly linearly with char conversion, defined based on the mass of gasifiable char. This was found to be the case at both 1 and 20 bar, and at full conversion no sulfur could be detected in the solid residue. Chlorine displayed similar behavior at 1 bar, but at 20 bar the chlorine remained in the char. The difference with pressure can be explained by suppression of volatilization of potassium and sodium chloride salts at higher pressures. Indeed, concentrations of potassium chloride were observed in the residue that remained after gasification at 20 bar.

7.2 Recommendations for future work

The pressurized grid heater and pressurized thermogravimetric reactor used in this study are suitable for investigation of black liquor pyrolysis and gasification, provided that they are used properly. If char yields are measured in the pressurized grid heater, it is important to ensure that heat transfer between the grid and the sample is not affected by swelling of the liquor. Using a folded net would help avoid this problem. The pressurized thermogravimetric reactor can be an excellent tool for measuring gasification rates. However, it is essential that the starting material is consistent between experiments and that any pretreatment which may alter sample properties is avoided.

Sulfur release during pressurized pyrolysis of black liquor deserves further study. Specifically, the increase in sulfur release with pressure needs to be explained. If a pressurized grid heater is used, it should not be assumed that the heating rate of the sample is the same as that of the grid. The system should be modelled in order to determine what the local heating rate is in the char, taking into account differences in swelling at different pressures. Based on the local heating rates, the residence time of the liquor in the temperature interval 300-500°C should be calculated and compared to the measured sulfur release. Similar modelling should be conducted for experiments involving droplets of black liquor in pressurized single particle reactors.

A method for determining the internal surface area of chars formed under pressurized conditions needs to be developed. Currently, it is only known that chars formed under pressure have lower internal surface areas than atmospheric pressure chars. The differences in surface areas and the relation to char formation pressure need to be quantified. This is particularly important for comparison of reactivities of chars that have been produced at different pressures.

The influence of total pressure on the rate of black liquor char gasification needs to be resolved. Two experimental approaches are suggested. First, experiments should be carried out on chars which have not been altered by pretreatment. Ensuring that the char properties prior to gasification are identical at different pressures promises to be a challenge. Experience from this work shows that even pre-formed chars undergo some additional devolatilization upon introduction to the hot reactor. If this additional devolatilization occurs at different pressures it is likely that the char properties will not be identical. One approach to minimizing this effect would be to use chars that have been formed at temperatures higher than those that will be used in the experiments. This should reduce the extent of additional devolatilization.

The other suggestion for investigating the influence of total pressure on gasification is to continue the experiments developed in this work which involve immersion of the liquor sample directly into the gasification atmosphere. While the individual stages of gasification are more difficult to identify, such experiments more closely represent the case in an industrial unit. One drawback to the system used in this study was the low heating rate achieved as a result of heating the large sample holder. Future experimentation should attempt to achieve heating rates more representative of those in industrial applications. Further experimentation under a variety of different gas compositions and total pressures is suggested.

8. SUMMARIES OF THE PAPERS IN THIS THESIS

There are eight papers which make up the appendices to this thesis. In this section the purpose, approach and primary results of each paper are summarized.

Paper I: Liquor-to-liquor differences in combustion and gasification processes: Pyrolysis behavior and char reactivity.

The purpose of this paper was to gain an understanding of how different industrial liquors behave during pyrolysis, combustion and gasification and to identify relationships between liquor properties and observed behavior. Fifteen black liquors from different mills around the world were subjected to eight different experiments in order to gain insight into their burning properties. The experiments were carried out in four different laboratory-scale devices. A single-droplet muffle furnace was used to study burning stage durations and the degree of liquor swelling during combustion at furnace temperatures of 700° and 800°C. A single-particle tube furnace was used to measure volatiles yields and liquor swelling during devolatilization in nitrogen at 700° and 900°C. A pressurized grid heater was used to investigate volatiles yields during pyrolysis at 10 bar pressure. Additionally, the specific swollen volumes of the chars produced in this device were determined. Finally, a pressurized thermogravimetric reactor was employed to study volatiles yields and char reactivity during gasification at 20 bar.

Specific swollen volumes varied by as much as a factor of 3.3 between liquors, with the sulfite liquor swelling significantly less than the kraft liquors. The ordering of the liquors with respect to swelling was consistent between different types of experiments. Volatiles yields of the kraft liquors at 900°C varied between 23% and 34%, but no correlation could be identified between either swelling or volatiles yield and the composition of the liquor.

The total combustion time, defined as the sum of the devolatilization and char burning times, correlated well with the degree of liquor swelling. Heat transfer modeling suggests that the pyrolysis and char burning times should be proportional to the specific swollen volume to the power of $2/3$. This was indeed found to be the case. Gasification reactivities varied by as much as a factor of 3.5, but did not seem to correlate with the other burning properties. The gasification experiments did involve pretreatment in a CO-containing atmosphere. But the extent of any carbon deposition would have been the same for all samples, so the measured rate distributions are valid.

Paper II: Influence of pressure on pyrolysis of black liquor: 1. Swelling.

This paper reports the findings of the first study ever performed specifically to identify how pressure influences swelling of black liquor during pyrolysis. Experiments were carried out in an inert environment using two reactors, a pressurized single-particle reactor and a pressurized grid heater. Chars were formed from two industrial black liquors by pyrolysis in nitrogen under a variety of pressures and temperatures and the swollen volumes of these chars were measured.

Swelling was found to decrease over the pressure range 1-20 bar with a more dramatic decrease observed at lower pressures. The specific swollen volume measured at 20 bar was roughly one-quarter of that measured at 1 bar. The decrease was roughly logarithmic

with pressure, and expression was developed to predict swelling at higher pressures if the specific swollen volume at 1 bar is known.

Paper III: Influence of pressure on pyrolysis of black liquor: 2. Char yields and component release.

The aim of the study reported in this paper was to obtain fundamental data regarding char yields from black liquor during pyrolysis under pressurized conditions. Additionally, the distribution of carbon, sodium, potassium and sulfur between the char and pyrolysis gases was investigated. Experiments were carried out in nitrogen in both a pressurized single-particle reactor and a pressurized grid heater over the temperature range 650-1100°C and between pressures of 1 and 20 bar. Char yields were measured by weighing the sample before and after pyrolysis and component release was determined based on analysis of the chars and original liquor.

Char yields decreased with temperature, particularly above 800°C. At lower temperatures, little influence of pressure on char yields was observed. But at higher temperatures, (>800°C) char yields increased with pressure. At such temperatures sodium carbonate decomposition contributes significantly to mass loss and the decomposition reaction is retarded at higher pressure. Char yields measured in the pressurized grid heater were found to be skewed by heat transfer inefficiencies associated with higher swelling. Consequently char yields were observed to decrease with pressure in this device.

Sodium release was observed to decrease with pressure and was a result of slower sodium carbonate decomposition at higher pressures. Sulfur release increased with pressure at both 750° and 900°C. Several factors may have contributed to this. At lower pressures, where chars swelled more, there was more opportunity for sulfur to be recaptured as it exited the particle. Lower sodium release may have also contributed to less capture. The boiling point of water in the liquor increased with pressure, so overlap of drying and pyrolysis was more excessive and the effective sample heating rate was lower within the critical temperature range for sulfur release. The longer duration within this temperature range resulted in more sulfur release.

Paper IV: Influence of char formation conditions on pressurized black liquor gasification rates.

The focus of this paper was to gain insight into how the conditions in which a char is formed, particularly pressure, affect its subsequent reactivity during gasification. The paper also considered the influence of char pretreatment conditions on the gasification rate. Chars were formed by pyrolysis in a pressurized single particle reactor at various pressures, temperatures, in different gas atmospheres and for different saturation times. The chars were collected and subsequently gasified at identical conditions. In other experiments pyrolysis was followed immediately by gasification without removal of the sample. In still other experiments the sample was simply immersed directly into the gasification atmosphere, in which it underwent simultaneous pyrolysis and gasification in a manner similar to that of an industrial unit.

One of the key findings in this study was that the gasification rate was severely reduced when the char was exposed to a CO-containing atmosphere for extended periods of time. Elemental carbon coats the chars under these conditions as a result of the Boudouard reaction and the degree of carbon buildup is higher at higher CO partial pressures. Gasification of black liquor is highly catalyzed by alkali species, and the reaction of black liquor is consequently much faster than that of carbon. The result of the carbon buildup was to reduce the observed gasification rate, particularly at lower conversions. The impact of this finding is particularly significant in light of previous gasification research in which experiments involved a lengthy char pretreatment period.

Higher char formation pressures and longer thermal treatment periods in the absence of CO were also found to decrease the reactivity of the char. Such conditions affect the morphology of the char, presumably reducing the porosity and internal surface area available for reaction. The results indicate that the impacts of pressure and thermal treatment are much less than that of carbon buildup.

Paper V: Morphological studies of black liquor char during formation and conversion.

Black liquors were introduced into a pressurized thermogravimetric reactor at 700°C, where they underwent drying, pyrolysis and char gasification. Two pressures, 1 and 20 bar, were investigated. By careful analysis of the weight-loss curve, the transition from pyrolysis to gasification, and thus the initial weight of the char, could be identified. At each pressure, a series of runs was performed in which the char was gasified to various conversions. Conversion was defined on the basis of the mass of char gasified, with 100% conversion corresponding to the mass at which no further reaction could be identified. After the experiments the chars were removed and analyzed with a scanning electron microscope (SEM) in order to follow changes in the char morphology with conversion. The char formed at 1 bar was initially very porous and the structure resembled that of a sponge. As the char was gasified the porosity decreased, particularly during the final 20% of conversion when the inorganic material fused together. One peculiarity was that at intermediate conversions crystals of sodium carbonate were visible on the surface of the char. The char formed at 20 bar was much more compact and less porous than that formed at 1 bar. The change in morphology at higher pressure was similar to that at 1 bar, including the presence of sodium carbonate crystals at intermediate conversions.

X-ray analysis was performed while viewing the chars with the SEM. From the x-ray data the concentrations of sulfur, potassium and chlorine could be estimated as a function of conversion. Sulfur was observed to decrease roughly linearly with conversion so that no traces were visible in the final residue. The concentration of potassium appeared to decrease slightly at 1 bar, but remained constant at 20 bar. Chlorine decreased during conversion at 1 bar and little was visible in the residue. At 20 bar, however, much of the chlorine remained in the char in the form of potassium chloride which was visible in high concentrations along "seams" in the inorganic residue.

Paper VI: Gasification of black liquor char with steam at elevated pressures.

The purpose of this work was to obtain fundamental data on the rate of black liquor char gasification with steam under pressurized conditions. A pressurized thermogravimetric reactor was used to measure the rate of black liquor char conversion at temperatures between 600° and 675°C and over the pressure range 1-30 bar. Experiments were carried out in two phases, a heating phase in which the char was in an unreactive environment and a gasification phase.

The gasification rate was observed to decrease as the total pressure was increased at constant gas composition. Under the conditions studied the rate at 30 bar was only 29% of that at 2 bar. These results were influenced by the pretreatment procedure as discussed in section 6.3.5, however, and are considered to be of little value.

The products of the gasification reaction, hydrogen and carbon monoxide, were found to decrease the rate. Carbon monoxide was particularly inhibitive. The reaction was found to be of order 0.56 in steam partial pressure, and the rate of steam gasification was 3.8 times that of gasification with CO₂ under otherwise similar conditions. The activation energy of the reaction was measured as roughly 230 kJ/mol. Though these results are based on experiments involving pretreatment in a CO-containing atmosphere, the pretreatment was the same for any particular series of runs so any carbon deposition would have affected the samples equally. Therefore these results are still considered to be valuable.

A model is presented which estimates the rate of black liquor char gasification as a function of temperature, pressure and gas composition. The value of the model is doubtful, however, since the parameters were fit based on data from experiments in which carbon deposition during pretreatment affected the rate.

Paper VII: An empirical rate model for black liquor char gasification as a function of gas composition and pressure.

Earlier work had considered pressurized black liquor char gasification with either carbon dioxide or steam. The study reported in this paper considered the case when gasification was carried out under pressure in an atmosphere containing both carbon dioxide and steam. Due to the large number of variables in such a system (temperature, pressure and H₂O, CO₂, H₂ and CO concentrations) an empirical modeling approach was chosen. A matrix of conditions for 30 experiments with different gas compositions and pressures was generated based on statistical experimental design. The experiments were performed in a pressurized thermogravimetric reactor and an empirical model was fit to the resulting data by linear regression. The model predicts the rate of gasification as a function of the partial pressures of H₂O, CO₂, H₂ and CO.

The model was used to predict the behavior of gasification with regard to different process variables. At constant gas composition the predicted rate went through a minimum with pressure. The pressure corresponding to this minimum increased as the ratio of reductive species (H₂ and CO) to oxidative species (H₂O and CO₂) increased. The model was applied to a theoretical gasifier, and the gasification time decreased as the

air ratio increased. As the pressure of the reactor increased, additional air was necessary to maintain the same gasification rate.

The experiments in this study included pretreatment in a CO-containing atmosphere. Due to the large range of pressures and corresponding degrees of carbon deposition, the experimental data, particularly that at higher pressures, are of little value. The equation is appropriate for the data in this study, but is not considered to be representative of properly prepared chars.

Paper VIII: Pressurized gasification of black liquor — Effect of char sodium content.

This paper reports the results of an investigation to quantify how sodium in black liquor char influences its rate of gasification. Black liquor char gasification reactions are strongly catalyzed by alkali species, resulting in gasification rates several orders of magnitude higher than those of non-catalyzed carbon gasification. In order to more closely study the role of sodium, a series of synthetic black liquor chars was produced with varying sodium content. The chars were gasified in a pressurized thermogravimetric reactor at 800°C and 10 bar by either steam or carbon dioxide. These experiments involved identical char pretreatment procedures in a CO-containing environment, so the degree carbon deposition was the same for all samples. The data are therefore still valuable.

The rate of gasification increased with increasing sodium content up to a ratio of 0.20 moles sodium per mole of organic char carbon, beyond which it decreased slightly. An increase in char sodium content from 1% to 6% was associated with a rate increase by a factor of 50. The gasification rate of the highest sodium content char, formed from a liquor containing 16.1% sodium on a dry basis, was an order of magnitude less than that for an industrial kraft liquor. Chars formed from dry mixtures of organic solids and sodium carbonate gasified at a lower rate than chars made from homogeneous liquid mixtures.

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Paper I

Liquor-to-liquor differences in combustion and gasification processes: Pyrolysis behavior and char reactivity

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Liquor-to-Liquor Differences in Combustion and Gasification Processes: Pyrolysis Behaviour and Char Reactivity

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Fifteen black liquors were chosen from a special bank, which has been established specifically to make comparisons between liquors. Each liquor was subjected to eight different experiments carried out in four different reactors over a wide range of temperatures and pressures to measure specific burning properties (swelling during devolatilization, volatiles yield, burning stage durations and char reactivity). The ranges of measured values are presented and generalizations are given regarding the behaviour of black liquors with respect to particular burning properties. Additionally, correlations between burning properties are identified and explanations for the observed behaviour are presented.

INTRODUCTION

The recovery boiler has long been the heart of the chemical recovery process in the pulp and paper industry. But, as technology advances and tighter regulations are placed on the industry, it becomes necessary to reconsider conventional processes, and to attempt to improve upon these. This holds true for recovery boiler, and an important key to such development is a thorough understanding of the burning behaviour of the black liquor itself. Combustion behaviour varies widely from liquor to liquor, and understanding the differences quantitatively, as

well as qualitatively, is vital to the development and improvement of recovery systems. The aim of this study is to identify and characterize such liquor-to-liquor differences during combustion. This work focuses on liquor behaviour during pyrolysis and the reactivity of the char that remains.

Conventional black liquor characterization includes measurement of the dry solids content, composition, inorganic/organic ratio, viscosity, and heating value of the liquor. Traditionally, design and dimensioning of recovery units has been based largely on these data. However, these properties do not provide a very clear indication of the combustion behaviour of the liquor, and their relation to furnace performance is not well understood. For example, different liquors with the same solids content can behave very differently in the same recovery boiler and require different furnace volumes to burn optimally. Such behaviour is not explained easily by conventional characteristics.

A preferable approach is to quantify burning behaviour, and identify and measure processes that occur during kraft liquor combustion. As early as 1963, Monaghan filmed the combustion of calcium sulphite liquor droplets and identified that this liquor burns in stages [1]. Later, Hupa et al. studied kraft (sulphate) liquor with a similar technique and labeled the burning stages as drying, devolatilization (pyrolysis) and char burning [2,3]. Drying involves evaporation of water from the droplet. During devolatilization, heat causes volatile components in the liquor to be released to the gas phase, and some inorganic material may be released. The solid char that remains is combusted or gasified during the final stage, char burning.

The burning stages overlap to varying degrees, meaning that devolatilization begins before the particle is totally dry, and char burning commences before the completion of the devolatilization stage.

Other researchers have investigated the burning properties of black liquor as well. In 1960, Baklien performed laboratory tests on small samples of spent pulping liquor and reported that the "burning quality" of a liquor is related to its tendency to swell when heated [4]. In his work, swelling was measured in a crucible under standardized laboratory conditions. Others have since used the same system to classify black liquors according to their "combustibility" [5-7]. Filming such as that done by Hupa has proven to be a valuable research technique and has been applied in a variety of conditions to study burning phenomena such as swelling and duration of burning stages [3,8-16]. Recently, researchers have studied pyrolysis of black liquor by using grid heaters [17-19], and char reactivities have been measured by means of thermogravimetric devices [20-26]. However, none of these studies has specifically made industrial black liquor the variable of focus, and none has investigated a wide range of combustion properties for the same set of liquors. The current work attempts to bridge this gap in our understanding, and does so by studying several different combustion properties for a large number of industrial black liquors.

The work presented here is a compilation of results for black liquors taken from 15 different paper mills specifically for the purpose of liquor-to-liquor comparison. The investigation focuses on four burning characteristics that help define combustion

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TABLE I
BLACK LIQUORS USED IN THIS STUDY

Liquor number	Liquor description	Kappa number	C (%)	H (%)	N (%)	Na (%)	K (%)	S (%)	Cl (%)
1	Kraft, softwood, Scandinavian	27	35.8	3.6	0.06	19.6	1.8	4.6	0.5
2	Kraft, hardwood, Scandinavian	n/a	33.1	3.4	0.07	20.8	1.8	5.0	0.6
4	Kraft, softwood, Scandinavian	50	34.4	3.3	0.06	22.8	1.6	3.7	0.5
5	Kraft, softwood, Scandinavian	24	33.9	3.3	0.07	19.6	3.2	5.7	0.3
6	Kraft, softwood, Scandinavian	25	34.6	3.4	0.07	17.2	3.2	5.4	0.3
7	Kraft, softwood, Scandinavian	n/a	34.1	3.4	0.07	19.9	1.2	5.5	0.2
8	Kraft, softwood, Scandinavian	n/a	34.2	3.4	0.07	19.7	1.2	5.1	0.2
9	Kraft, softwood, Scandinavian	26	34.6	3.3	0.07	19.8	1.4	5.2	0.5
10	Kraft, hardwood, Scandinavian	19	33.2	3.3	0.08	20.8	2.6	5.2	0.3
11	Kraft, hardwood (eucalyptus), N. Am.	13	37.3	3.6	0.09	17.3	1.8	3.4	1.6
12	Kraft, softwood, North American	n/a	34.3	3.4	0.06	19.0	3.0	5.2	0.9
15	Soda, straw	n/a	35.4	3.8	0.75	15.8	1.9	1.6	3.6
23	Sulphite, hardwood, Scandinavian	n/a	33.5	4.0	0.2	13.2	1.1	7.6	0.4
28	Kraft, softwood, Scandinavian	n/a	35.3	3.7	< 0.1	18.1	4.0	4.4	0.2
29	Kraft, hardwood, Scandinavian	n/a	33.0	3.4	0.1	19.7	4.3	4.6	0.2

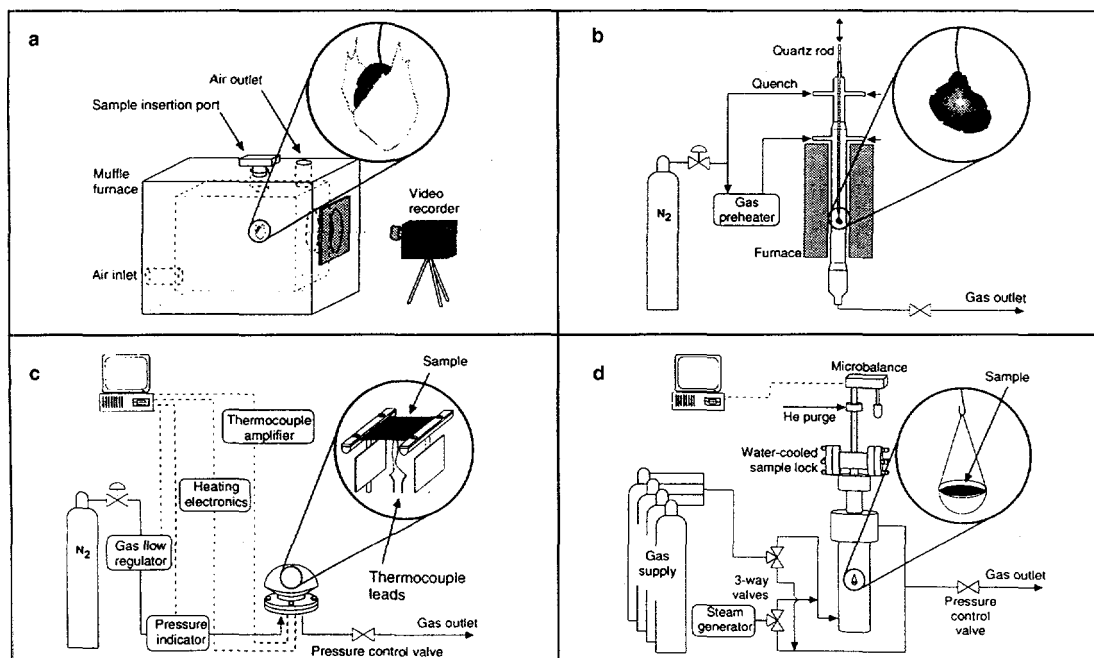


Figure 1. Experimental devices used in this study: (a) single-droplet muffle furnace; (b) single-droplet tube reactor; (c) pressurized grid heater; (d) pressurized thermogravimetric reactor.

behaviour: swelling of the liquor during devolatilization, volatiles yield, relative times for each of the burning stages (drying, devolatilization and char burning) and the reactivity of the char produced. Several tests in various laboratory-scale devices have been performed on each liquor, resulting in data covering a wide range of conditions and being relevant to a variety of applications. From these results, relationships between burning properties have been identified.

BLACK LIQUORS

Fifteen black liquors were used in this study, originating from various wood types, pulping processes and areas of the

world. A brief description of each liquor is provided in Table I, along with the kappa number of the cook, where available, and the composition of the dry material. Thirteen kraft liquors were included, of which nine came from softwood pulping processes and four from hardwood processes. One liquor from a sulphite-based hardwood pulping process and a soda-based liquor from the pulping of straw were also included. The liquors were chosen from a bank of over 40 black liquors, which have been collected specifically for liquor-to-liquor comparison and stored according to strict procedures. Each liquor has been thoroughly characterized by conventional methods, including

elemental analysis and determination of various physical properties (dry solids content, viscosity, etc.). The liquors in this study were chosen based on the completeness of experimental data.

EXPERIMENTAL PROCEDURE

Four laboratory-scale devices were used to perform the experiments in this study: a single-droplet muffle furnace, a single-droplet tube reactor, a pressurized grid heater and a pressurized thermogravimetric reactor. Schematic drawings of the devices are shown in Fig. 1. Each apparatus provides a unique environment for the black liquor, and has similarities to full-

scale units, either existing or proposed. Each is suited to a particular type of experiment, and intrinsic differences in the equipment result in a broad range of temperature-time histories for the liquor. Some experiments involved heating the liquor very rapidly for just a few seconds, while others required longer residence times, of the order of minutes. Descriptions of each device, including experimental procedures and the characteristics measured, are given below. Additionally, for each device an assessment is made regarding how representative it is to full-scale units. The usefulness of the data obtained is also discussed.

Single-Droplet Muffle Furnace

The single-droplet muffle furnace (Fig. 1a) is basically a modified atmospheric pressure laboratory oven. An opening in the top of the furnace allows insertion of black liquor droplets, and a quartz window in the side allows viewing or videotaping of the burning droplets. Air enters the furnace through a port in the side and flows via natural convection through the oven.

Data obtained in this device are most applicable to recovery boilers, where a droplet of black liquor reacts in an oxygen-containing environment. The gas in the muffle furnace is essentially stagnant. This is not the case for a droplet in a recovery boiler prior to entrainment. However, heating of the droplet at temperatures used in this study is driven primarily by radiation, which is also the case in a recovery boiler. The temperatures used in this device were a bit lower than those found in a recovery boiler, but we feel that the differences between the muffle furnace and a recovery boiler are small enough for the muffle furnace data to be relevant to a recovery boiler.

The single-droplet muffle furnace was used to measure the burning stage times and the degree of swelling in air at atmospheric pressure. Two temperatures, 700 and 800°C, were used. To determine the times for each of the stages of black liquor combustion, droplets of concentrated black liquor were videotaped as they were lowered into the furnace on a wire hook and allowed to burn in air. The videotapes were then replayed and boundaries between the stages were defined in the same manner as used originally by Hupa et al. [3]. The appearance of a flame around the droplet signaled the end of the drying stage and the beginning of devolatilization. The disappearance of the flame signified the transition into the heterogeneous char-burning stage. The end of char burning was defined to be the moment when the residue collapses, forming a smelt bead. By noting the time elapsed between the insertion of the droplet and each of the successive burning stages, the times for drying, devolatilization and char burning could be determined. The total combustion time was defined as the sum of the devolatilization and char burning times.

The degree of swelling in air was also

determined from these tests. The droplet diameter was measured both vertically and horizontally at maximum swelling and, based on these values, the volume was estimated. The maximum swollen volume divided by the initial dry mass of the droplet is defined as the specific swollen volume, given in units of cm^3/g . Eight to 10 experiments were performed for each liquor, and the specific swollen volumes reported here are the mean values of the measurements. The procedure for determining the degree of swelling during combustion is described in more detail elsewhere [3,13].

Single-Droplet Tube Reactor

A single-droplet tube reactor (Fig. 1b) was used for pyrolysis tests at atmospheric pressure. It consists primarily of a quartz tube (i.d. 20 mm) positioned vertically inside a tube furnace. The upper portion of the quartz tube extends beyond the furnace, and a special fitting at the top allows a quartz rod with the sample suspended from the bottom to be lowered into the heated part of the reactor. A seal between the fitting and the rod prevents air from entering the reactor when the rod is lowered. Within the fitting is a nitrogen-purged chamber, which keeps the sample in a cool, inert atmosphere both before and after reaction.

The single-droplet tube reactor is representative of devolatilization of a droplet in the lower regions of a recovery boiler where there is little or no oxygen, and data obtained in the device are of value for understanding such environments. Additionally, the data may be relevant to alternative recovery processes in which pyrolysis and subsequent char burning or gasification are carried out independently. However, the droplets are too large for most gasifier concepts.

The single-droplet tube reactor was used to determine the volatiles yield and degree of swelling in nitrogen at atmospheric pressure. Two temperatures, 700 and 900°C, were used. Between 10 and 13 mg of concentrated black liquor was placed on a fine wire at the end of the quartz rod. The sample mass was adjusted based on the solids content so that the sample contained 8 mg of dry solids. The rod was inserted through the top fitting, which was secured to the reactor so that the liquor was in the nitrogen quench chamber. Nitrogen was fed into the reactor at 100 L (STP)/h. After the system had been thoroughly flushed with nitrogen, the sample was quickly lowered into the heated section of the reactor and allowed to remain there for 15 s. It was then lifted back into the quench chamber and allowed to cool. Six replications were performed for each set of conditions.

Volatiles yield was determined by measuring the sample mass both before and after pyrolysis. The percentage of the initial dry solids that volatilized could then be calculated. The specific swollen volume was determined by removing the sample after the experiment was complete and photograph-

ing it next to an object of known size. The diameter of the char was measured in two directions and the volume of the char was estimated based on a spherical particle. The experimental procedure is described more thoroughly by Forssén et al. [27,28].

Pressurized Grid Heater

A pressurized grid heater (PGH) (Fig. 1c) was used to investigate pyrolysis behaviour under pressurized conditions. The PGH is able to achieve high heating rates, up to 3000°C/s, by passing an electric current through a fine wire net on which the sample is placed. A Pt/Pt-Rh thermocouple is welded to the centre of the net and is used both as a sample temperature indicator and as feedback to the heating controller. The pressure, heating rate, final temperature and holding time at maximum temperature are programmed into the controller prior to performing the experiment. The controller then automatically purges the reactor with nitrogen, pressurizes the system, heats the grid, allows it to cool and depressurizes the system. An in-depth description of the PGH device is given by Sorvari et al. [17].

Data from the PGH are of interest for proposed alternative recovery systems that operate under pressurized conditions. The heating rates that can be achieved in this device are comparable to those that relatively large droplets of black liquor would experience upon introduction to a hot environment. Smaller droplets can achieve much higher heating rates, on the order of 10⁵°C/s. The sample in the PGH is in the form of a thin layer rather than a droplet. Therefore, heat transfer through the sample is somewhat different from that in an industrial-scale device. However, the initial sample layer is extremely thin (5–10 μm [17]); conduction through the sample is therefore negligible and the PGH is regarded as a suitable tool for investigation of pyrolysis behaviour under pressurized conditions.

The PGH was used for measurement of the volatiles yield and degree of swelling at 1.0 MPa. Roughly 10 mg of black liquor was painted onto a grid and allowed to dry. The net was weighed and inserted into the device and an electrode was secured to either side. The unit was then tightly closed and the experiment carried out. All experiments in the PGH were performed at 1.0 MPa pressure, with a heating rate of 1000°C/s to the desired temperature, which was held for 5 s. Two temperatures, 850 and 1100°C, were investigated.

Upon completion of the experiment, the net was removed and weighed in order to obtain the volatiles yield. Swelling was determined by viewing the net from the side under a microscope and measuring the thickness of the char formed. By multiplying the thickness by the area of the painted section of the grid, the volume of the char and, hence, the swollen volume, could be calculated. More detail of the experimental procedure is given elsewhere [29,30].

Pressurized Thermogravimetric Reactor

Reactivity and volatiles yield measurements at 2.0 MPa were determined with a pressurized thermogravimetric reactor (PTGR) (Fig. 1d). The heart of the device is a microbalance from which a sample holder is suspended via a long chain. A winch system allows the sample holder to be lowered from a helium-purged, water-cooled sample lock into the reactor. Up to five gases, including steam, can be controlled independently and fed into the reactor or directed through a bypass line. The apparatus has a maximum operating pressure of 10 MPa and the reactor can be heated to 1150°C.

Experiments performed in the PTGR are relevant to proposed low-temperature pressurized gasification schemes. Heating rates in the PTGR are much lower than those found in industrial applications due to the relatively large sample sizes and the geometry of sample holder. Consequently, volatiles yields measured in this device will be somewhat less than what would be expected in a full-scale reactor.

A primary difference between experiments in the PTGR and gasification in a full-scale unit concerns the pyrolysis stage of conversion. While pyrolysis and char gasification occur nearly simultaneously in an industrial-scale unit, these stages were intentionally separated in the experiments performed here, with pyrolysis lasting a total of 400 s.

In the experiments, roughly 35 mg of concentrated black liquor were placed into a small, cylindrical platinum sample holder. The loaded sample holder was placed into the sample lock of the device, which was then pressurized to 2.0 MPa. The reactor was heated to 800°C, and a mixture of nitrogen and 10% carbon monoxide was passed through it. The sample was lowered into the reactor and allowed to remain at 800°C for 200 s. Over the next 200 s, the reactor temperature was allowed to cool to 725°C. After the heat treatment, the gas mixture was changed to 25% H₂O, 20% CO₂, 15% H₂,

TABLE II
EXPERIMENTS TO STUDY BLACK LIQUOR SWELLING

Equipment	Atmosphere	Pressure	Temp.	Specific swollen volume		
				Kraft*	Soda	Sulphite
Single-droplet muffle furnace	Air	1 Atm.	700°C	25.2 – 83.4 (44.8)	32.0	15.4
		1 Atm.	800°C	14.4 – 67.1 (36.4)	26.2	6.8
Single-droplet tube reactor	Nitrogen	1 Atm.	700°C	12.7 – 40.3 (24.8)	6.2	1.8
		1 Atm.	900°C	20.7 – 76.9 (37.6)	16.0	2.2
Pressurized grid heater	Nitrogen	1 MPa	580°C	5.0 – 16.1 (10.1)	6.2	3.6
		1 MPa	1100°C	4.7 – 11.2 (8.4)	6.5	3.9

* The range of measured values is given. Value in parentheses is the arithmetic average.

10% CO, 30% N₂, and the remaining char was gasified. More details of the gasification procedure are given by Whitty et al. [25].

By taking the difference between the initial mass of dry material and the masses of the residue and material gasified, the volatiles yield at 2.0 MPa was calculated. Char reactivity was also determined from the experiments. In this study, the slope of the weight-loss curve at 25% conversion was chosen as the measure of reactivity, and is given in units of %/min based on the amount of gasifiable material remaining in the char. Details of the data reduction are given elsewhere [25,31].

RESULTS AND DISCUSSION

The experimental data were analyzed to determine swelling factors, volatiles yields, burning stage durations and char reactivities. The ranges of values obtained are presented, and the influence of different experimental techniques is discussed with regard to variations in the results. In addition, correlations between the different measured values are identified. To determine whether or not a particular property does correlate with another, a straight line was fit to the data by linear regression, and a global F test was performed using a 95% confidence interval. If the calculated F value was larger than the tabulated limit, it was concluded that a correlation existed. Unless otherwise noted, all correlations presented here are statistically valid.

Comparison between tests cannot be made in all cases due to the large differences in the experimental devices and techniques. Trends in pressure for volatiles yields, for instance, are not determinable from the data because the various tests were performed at different temperatures, had different heating rates and holding times, and used different forms of the black liquor (concentrated liquor vs dry liquor solids).

Swelling

The maximum swollen volume during pyrolysis was measured in three reactors under various conditions, as shown in Table II. The ranges of swollen volumes measured are also indicated. Good correlation was found between swelling measured in the different devices. This can be seen in Fig. 2, which compares swelling measured in the pressurized grid heater at 1 MPa to swelling measured in the single-droplet tube furnace at atmospheric pressure. Variations in the degree of swelling between devices was a result of the different heating methods, heating rates, gas compositions, pressures, temperatures and holding times of the different reactors.

Figure 3 shows the distributions of the specific swollen volumes for pyrolysis in both air and nitrogen under atmospheric conditions at 700°C. Swelling in oxygen was, on average, 80% more than that in nitrogen, which is in disagreement with the results of Frederick et al., who found that

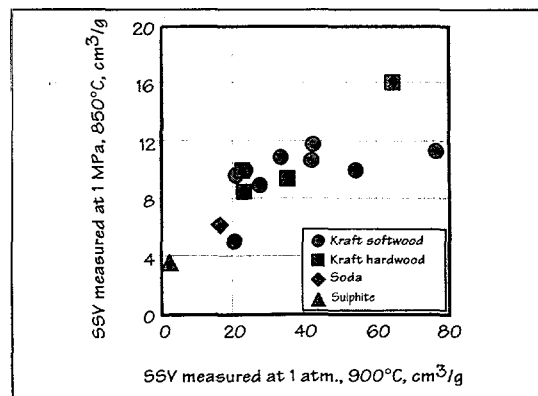


Fig. 2. Specific swollen volumes measured at 1 MPa, 850°C vs atmospheric pressure, 900°C.

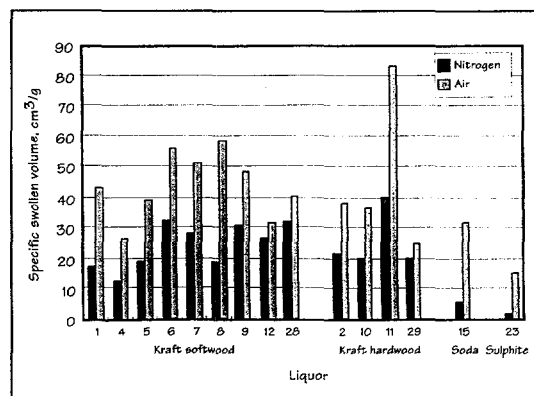


Fig. 3. Distribution of specific swollen volumes measured at atmospheric pressure, 700°C.

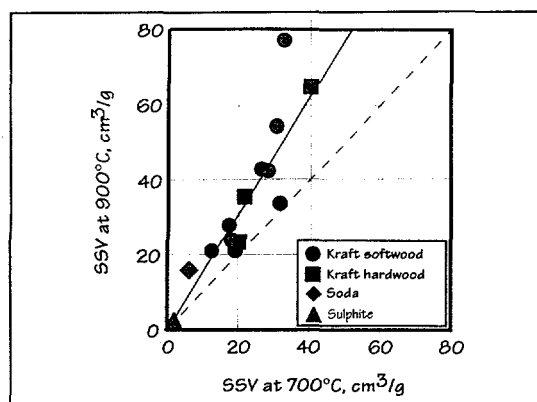


Fig. 4. Effect of temperature on the specific swollen volume (SSV) measured in nitrogen at atmospheric pressure. Solid line: fit by regression to the data. Dashed line: 1:1 relationship.

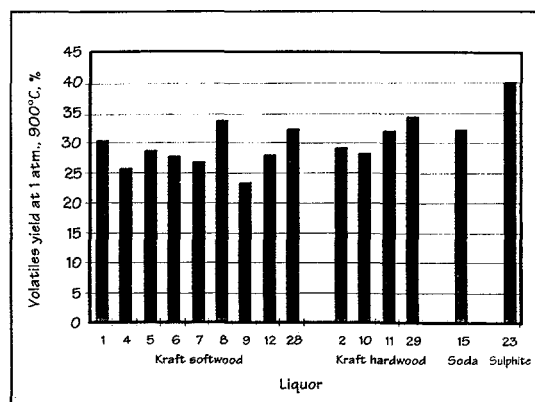


Fig. 5. Distribution of volatiles yields measured at atmospheric pressure, 900°C. Yields given in percent, based on the original mass of dry solids.

swelling in nitrogen was roughly twice that in air at 800°C [14]. However, the results in the current study were obtained using two different experimental devices, which may account for the difference.

For the kraft liquors, swelling was found to vary by a factor of 3.3 in air and 3.2 in nitrogen, which is comparable to ranges found in earlier studies [3,11,12,14]. The liquor from kraft pulping of eucalyptus displayed the highest swelling tendency. The ordering of the liquors is generally the same for both atmospheres, and a correlation was found to exist between swelling measured by these two techniques. The kraft liquors in this study swell significantly more than the sulphite liquor, which is in agreement with results published previously [3,14]. The type of wood pulped appears to have little influence on swelling for the kraft liquors under the conditions studied.

Swelling in air decreased with furnace temperature, i.e. the average specific swollen volume measured at 800°C was 81% of that measured at 700°C for the kraft liquors. This is precisely the value predicted by the equation of Frederick and Hupa for swelling at different temperatures in an oxygen-containing environment [16]. Their expression was based on a study of four kraft liquors. The results from the current study support their analysis, and indicate that their expression is a good generalization for the behaviour of kraft black liquors.

Swelling in nitrogen was measured both at atmospheric pressure in the single-drop tube furnace and at 1.0 MPa in the pressurized grid heater. Two temperatures were investigated in each device. Under atmospheric conditions, the specific swollen volume measured in nitrogen was found to increase with increasing temperature for all of the liquors (Fig. 4). The average increase in specific swollen volume between 700 and 900°C for the kraft liquors was 52% under these conditions. This is opposite what has been observed for swelling in an oxygen-containing atmosphere. Also, these results

TABLE III
EXPERIMENTS TO STUDY VOLATILES YIELDS

Equipment	Pressure	Temp.	Devol. time	Volatiles yields, %		
				Kraft*	Soda	Sulphite
Single-droplet tube reactor	1 Atm.	700°C	15 s	20.0 – 29.6 (25.1)	24.3	39.9
		900°C	15 s	23.2 – 34.3 (29.3)	32.2	40.5
Pressurized grid heater	1 MPa	850°C	6 s	29.9 – 41.6 (36.7)	41.6	41.7
		1100°C	6 s	51.7 – 64.1 (58.2)	62.3	50.5
Pressurized thermogravimetric reactor	2 MPa	800°C	400 s	38.0 – 45.9 (41.1)	43.6	51.6

* The range of measured values is given. Value in parentheses is the arithmetic average.

disagree with those found by Miller et al. [7] for swelling in nitrogen in a similar single-particle reactor. No explanation is offered at this point for these differences, but they may be related to differences in the experimental devices (muffles furnace vs tube reactor) and swelling measurement technique (in situ filming vs measurement after removal from the reactor). Clearly, swelling during pyrolysis is a complex process, and these findings indicate that further study is needed if we are to understand fully the influence of temperature and heating rate in various atmospheres.

Specific swollen volumes measured at 1.0 MPa in the pressurized grid heater were, on average, 27% of those measured at atmospheric pressure at comparable furnace temperatures (Fig. 2, Table II). This is comparable to a previous study in which it was found that liquors pyrolyzed at 1.0 MPa in a pressurized tube reactor have 38% the swollen volume of those pyrolyzed at atmospheric pressure [32]. Specific swollen volume decreased with temperature in the pressurized grid heater, with the average swollen volume at 1100°C being 83% of that measured at 850°C.

Volatiles Yields

During devolatilization of a droplet of black liquor, a number of processes occur simultaneously. Organic molecules are bro-

ken down as a result of heating and tars and lighter gaseous components are released into the gas phase. Within the pyrolyzing particle, these species may recondense onto the solid surface and remain in the char. Additionally, secondary reactions of char inorganic components occur at higher temperatures (>800°C), causing these components to decompose.

In this work, the volatiles yield for each liquor was determined under a variety of conditions, and is defined as the percentage of the initial dry mass released into the gas phase. The conditions used in the various reactors are summarized in Table III, and the measured volatiles yields are also given. Comparison between experimental methods reveals some correlation for the volatiles yield ordering of the liquors. The liquors with the highest and lowest volatiles yields in one device also had these yields in other devices. The liquors that were not at either extreme did not necessarily follow the same ordering between reactors.

The distribution of volatiles yields obtained by pyrolysis for 15 s at atmospheric pressure, 900°C, is displayed in Fig. 5. The kraft liquors have volatiles yields between 23 and 34%, with the yields from hardwood liquors being slightly higher than those from softwood liquors. The yield for the soda liquor was higher than the average for the kraft liquor. The sulphite liquor had

the highest volatiles yield of all under these conditions due to its low inorganic content.

Volatiles yields measured in the pressurized grid heater were higher than those measured in either the single droplet tube furnace or the PTGR, despite the high pressure and shorter pyrolysis time. This is probably due to the higher heating rate obtained in the grid heater. It is of interest to note that, at 1.0 MPa, 850°C, the sulphite liquor had the highest yield of all the liquors while, at 1100°C, it had the lowest. This can be explained by decomposition of the inorganic species in the liquors at higher temperatures. At 1100°C, the kraft liquor carbon reacts with the molten sodium carbonate to release both carbon and sodium, and this release is accounted for in the volatiles yield. Sulphite liquors do not contain sodium carbonate, so this reaction does not occur.

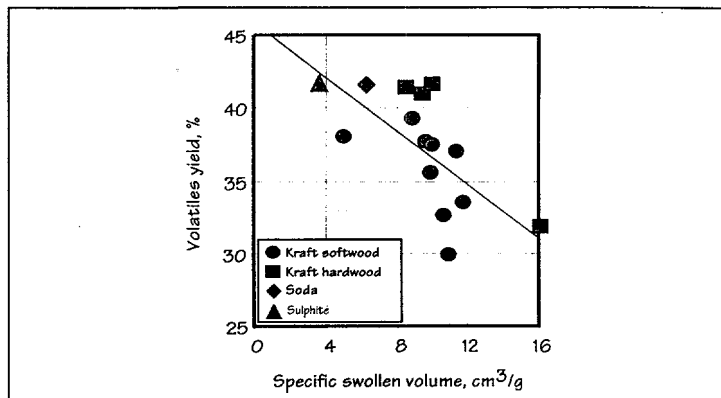


Fig. 6. Volatiles yield vs swelling at 1.0 MPa, 850°C. Nitrogen atmosphere.

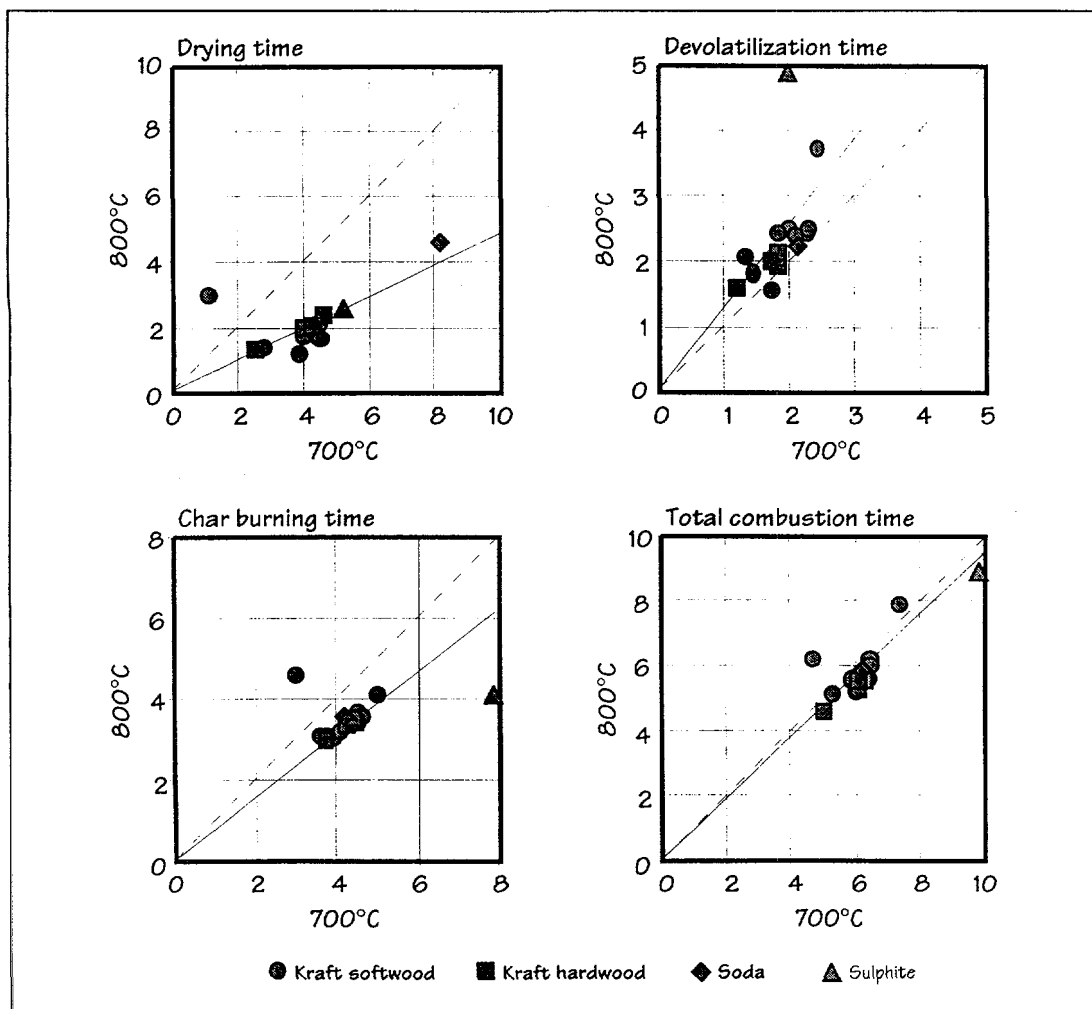


Fig. 7. Burning stage durations, 800 vs 700°C furnace temperature. "Total combustion time" is the sum of the devolatilization and char burning times. Solid line: fit by regression to the data. Dashed line: 1:1 relationship. ● - kraft softwood; ■ - kraft hardwood; ◆ - soda; ▲ - sulphite.

TABLE IV
BURNING STAGE DURATION SUMMARY

Liquor type	Temperature	Drying	Devolatilization	Char burning	Total combustion**
Kraft softwood*	700°C	1.1 – 4.5 (3.7)	1.3 – 2.4 (1.9)	3.0 – 5.0 (4.1)	4.7 – 7.4 (6.1)
Kraft softwood*	700°C	2.5 – 4.6 (3.8)	1.2 – 1.8 (1.6)	3.8 – 4.5 (4.2)	5.0 – 6.3 (5.9)
Soda	700°C	8.1	2.1	4.1	6.2
Sulphite	700°C	5.2	2.0	7.8	9.8
Kraft softwood*	800°C	1.2 – 3.0 (1.9)	1.6 – 3.7 (2.4)	3.1 – 4.6 (3.5)	5.1 – 7.9 (5.9)
Kraft hardwood*	800°C	1.3 – 2.4 (1.9)	1.6 – 2.1 (1.9)	3.0 – 3.5 (3.3)	4.6 – 5.5 (5.2)
Soda	800°C	4.6	2.3	3.6	5.9
Sulphite	800°C	2.6	4.9	4.1	9.0

* The range of measured values is given. Value in parentheses is the arithmetic average.

** Total combustion time is defined as the sum of the devolatilization and char burning times.

Comparison between temperatures at constant pressure reveals that the volatiles yield was consistently higher at the higher temperature. In the atmospheric experiments, comparison of the results at 700 and 900°C reveals that on average, an additional 5% of the liquor solids devolatilized at the higher temperature, corresponding to an additional 2.5% devolatilized per 100°C temperature rise. At 1.0 MPa, 22% more devolatilized at 1100°C than at 850°C, which corresponds to an additional 8.8% per 100°C temperature rise. At a temperature of 1100°C, much of the inorganic fraction of the liquor decomposes by reaction between carbon and molten sodium carbonate, which explains the exceptionally high yields under these conditions.

For all liquors together, volatiles yield seems to correlate weakly with the degree of liquor swelling during pyrolysis measured at 850°C, 1.0 MPa, as seen in Fig. 6. It was found that high-swelling liquors tend to have a lower volatiles yield than those that do not swell as much. For the kraft liquors alone, no such relation was found under these conditions but, at the higher temperature, 1100°C, volatiles yield correlated with specific swollen volume for the kraft liquors. Analysis of the data obtained in the single-droplet tube reactor at atmospheric pressure reveals a similar trend, but statistical analysis indicates that it is not definite enough to conclude that a correlation exists.

Volatiles yield is a function of heat transfer to and within the droplet, and swelling has both a positive and negative effect on heat transfer. A highly swollen particle has a large external surface area available for heat transfer to the droplet via convection and radiation. However, conduction within this particle will be poorer than for a less swollen droplet, and the inside will not experience heating rates as high. The observation that increased swelling leads to lower volatiles yields suggests that this decrease in conduction outweighs the positive effect of increased external surface area. Another factor that may explain this trend is that tars will have more opportunity to recondense onto the interior of a more swollen droplet because the exit path is longer. The data from this study are too limited to make generalizations regarding correlations between vola-

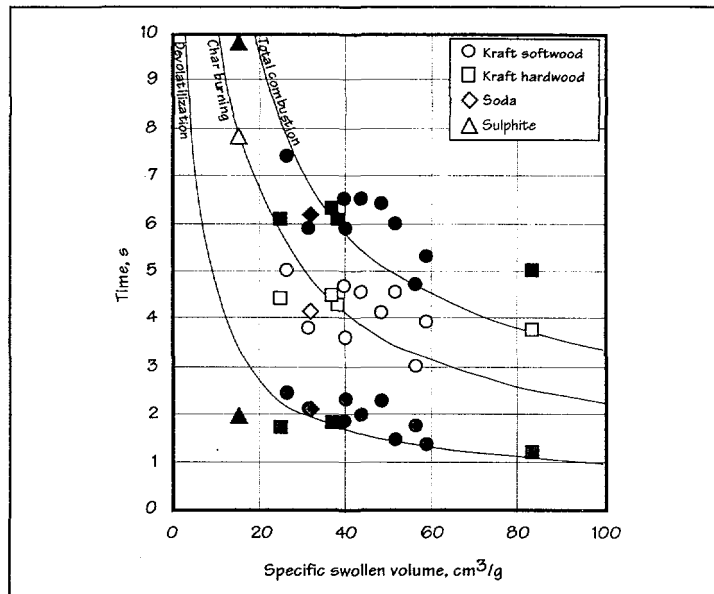


Fig. 8. Burning stage durations vs swelling measured in air at atmospheric pressure, 700°C. Black symbols: total combustion time. White symbols: char burning time. Grey symbols: devolatilization time. Lines are best fits of Eq. (1).

tiles yield and swelling. But clearly some relationship exists and this matter deserves further study.

Burning Stage Durations

Times for drying, devolatilization and char burning were measured at atmospheric pressure, 700 and 800°C for all liquors. A summary of the results is presented in Table IV. The data from the two temperatures correlate well for each of the burning stages, as can be seen in Fig. 7. The range of times for each of the stages is quite narrow due to the fact that the processes are controlled largely by heat and oxygen transfer to the droplet. Drying times at 800°C were observed to be roughly half as long as those at 700°C, and char burning times were about 80% as long. Similar ratios for burning of black liquors and synthetic black liquors have been reported previously [3,15]. Devolatilization times, however, were found to be about 25% longer at 800 than at 700°C. This differs somewhat from

previous studies in which pyrolysis time was found to be nearly independent of furnace temperature [3,15], but is likely due to experimental differences.

The total combustion time, i.e. the sum of the times for the devolatilization and char burning stages, was found to be nearly the same at both 700 and 800°C (Fig. 7). The average total combustion time at 800°C was only 5% less than that measured at 700°C. This results from a combination of the longer devolatilization time and shorter char burning time. Previous studies have found that the total combustion time decreases with increasing temperature [3,15]. The data from the present case confirm this, but indicate that, in general, the decrease is rather slight.

Devolatilization time, char burning time and total combustion time correlate well with swelling during combustion, as can be seen in Fig. 8. Liquors with high specific swollen volumes have shorter pyrolysis and burning times. Such behaviour has

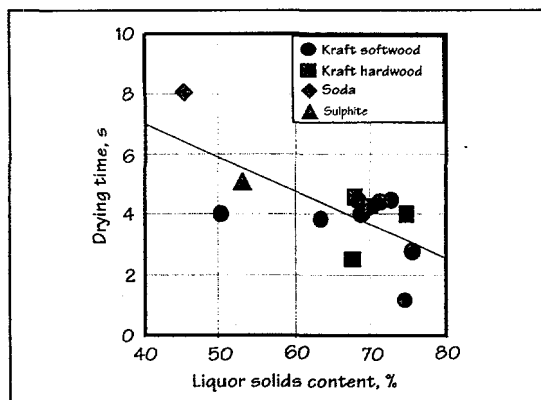


Fig. 9. Drying time at 700°C vs liquor solids content. Line was fit by regression.

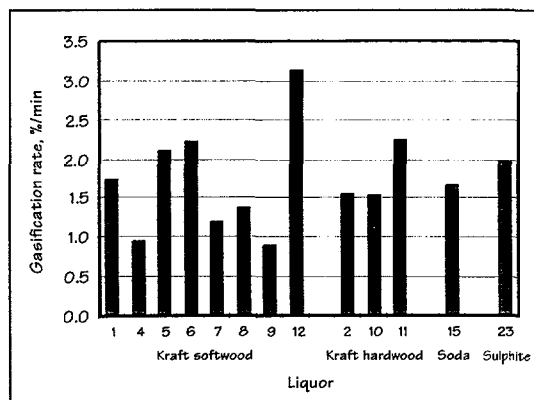


Fig. 10. Distribution of char gasification rates measured for the liquors. Rate given as percentage of remaining gasifiable material reacted per minute, taken at 25% conversion. Gasification conditions: 2.0 MPa, 725°C, 25% H₂O, 20% CO₂, 15% H₂, 10% CO, 30% N₂.

been noted in earlier studies of black liquor combustion as well [3,11,15,33].

Char burning is a mass-transfer-controlled process and the rate of reaction is controlled by the rate at which oxygen can reach the external char surface. Droplets that are highly swollen have more external surface area available for reaction and, consequently, have shorter burning times. The rate of reaction, taken as the reciprocal of the reaction time, is proportional to the external surface area of the swollen particle. For a spherical particle, it can be shown that the relation between char burning time and specific swollen volume is as follows when the rate is controlled by mass transfer:

$$t_{\text{char burning}} = k(SSV)^{-2/3} \quad (1)$$

where t is time measured in seconds, SSV is the specific swollen volume in units of cm^3/g and k is a proportionality constant expressed in units of $\text{s} \cdot \text{cm}^2 \cdot \text{g}^{-2/3}$. This relation was used to fit the curves in Fig. 8 to the data. Statistics indicate that, for the char burning and total combustion times, the equation properly describes the data, even though the droplets never assumed a truly spherical shape. For the measure devolatilization times, however, the equation does not describe the observation suitably. This is not surprising since swelling is part of the devolatilization process and the external surface area is changing drastically during this stage.

As expected, a correlation was found between the drying time and the solids content of the liquor, i.e. liquors with high solids contents (less water) require less time to dry (Fig. 9). Comparison between burning stage durations and other liquor properties (volatiles yield, composition, viscosity) revealed no correlations.

Char Reactivity

In this study, char reactivity is defined

in terms of the gasification rate measured at 2.0 MPa, 725°C, and was measured for 13 of the 15 liquors used in this study. In the experiments, the liquor was first pyrolyzed under pressure to form a char, then gasified under pressurized conditions. A distribution of the resulting reactivities is given in Fig. 10. The slowest and fastest rates differ by a factor of 3.5. The reactivities of the soda and sulphite liquors were within 15% of the average reactivity of the kraft liquors, and the wood type pulped appears to have little influence on the reactivity of kraft liquors under the conditions studied.

The black liquor gasification process is highly catalytic, with sodium and potassium acting as the major species. Alkali species are very efficient catalysts, and the sodium contents of the black liquors in this study varied between 14.2 and 28.6%. Van Heiningen et al. have reported that, for rapid-pyrolysis chars, gasification reactivity increases as the ratio of sodium to organic carbon increases [24]. Analysis was performed to see if this holds true in the current study as well. Compositional data were not available for the chars prior to gasification, so an estimate of the $\text{Na}/\text{C}_{\text{organic}}$ ratio at 25% conversion was made based on the original liquor composition, volatiles yield and release of carbon, sodium and sulphur during pyrolysis at atmospheric conditions. No correlation between reactivity and the $\text{Na}/\text{C}_{\text{organic}}$ ratio was observed. This could be due to several factors, one being that the $\text{Na}/\text{C}_{\text{organic}}$ ratio was estimated rather than measured.

Differences in experimental techniques may also explain the inconsistent results. The method by which chars were formed in this study was quite different from those of van Heiningen et al. In their work, chars were formed by pyrolysis at atmospheric pressure in a grid heater with a heating rate of 715°C/s. Chars used in this study were formed at 2.0 MPa pressure in the

PTGR. The heating rate was estimated to be of the order of 100°C/s at the initiation of pyrolysis, and less as the sample was heated due to a decrease in the temperature difference between the reactor and the sample. In fact, the heating rates of the chars gasified in the current study approach the regime of "slow pyrolysis" as defined by van Heiningen et al. In this regime, they found that the gasification rate and sodium content did not correlate well [24].

In a previous study, in which synthetic liquor chars were formed and gasified under conditions similar to those in the current study, it was found that only a small concentration of sodium is necessary to achieve gasification rates that are orders of magnitude higher than for noncatalyzed material [34]. Beyond that concentration, the reactivity does not continue to increase significantly with further addition of sodium.

Char reactivity did not correlate well with any of the other measured characteristics. The gasification experiments involved a lengthy char preparation technique, with a heat-treatment period of more than 6 min. It is possible that the nature of the char was altered by this pretreatment to such a degree that it was no longer representative of the original liquor.

CONCLUSIONS

The work presented here is the first known study designed specifically to compare a wide range of combustion properties for a wide range of industrial black liquors. Fifteen liquors representing several geographic locations, wood types and pulping processes were subjected to several methods of characterization in order to gain insight into their combustion behaviour and to identify relationships between burning properties. Tests were performed on small samples of the liquors using laboratory-scale equipment to measure volatiles yields, liquor

swelling, burning stage times and char reactivity. Generally, the experimental devices and procedures were found to be suitable for investigation of the characteristics studied, and simulated well the conditions that black liquor would encounter in a full-scale unit. The only exception is the heat-treatment procedure used during the pressurized gasification experiments. Future studies should attempt to limit the amount of time that the char spends in high-temperature atmospheres prior to reaction, to avoid altering the char properties.

The ordering of the liquors with regard to specific swollen volume during pyrolysis varied little between reactors and conditions. For example, the liquors that swell the most in air at atmospheric pressure also swell the most in nitrogen at 1.0 MPa pressure. During combustion at atmospheric pressure and during pyrolysis at 1.0 MPa, the specific swollen volume was found to decrease with temperature. In nitrogen at atmospheric pressure, however, swelling increased with temperature over the range studied, a result which disagrees with all previous studies regarding black liquor swelling. However, little data exist regarding the effect of temperature on swelling in a pure nitrogen atmosphere. More work is necessary before this phenomenon can be fully explained.

Volatiles yields varied by more than a factor of two between experimental devices, due in part to different temperatures used and to differences in the heating method. The ordering of the liquors by volatiles yield was consistent between reactors for the liquors with the highest and lowest yields, but those with intermediate yields did not follow the same order between reactors. As expected, volatiles yield increased with increasing pyrolysis temperature. Particularly notable are the yields measured at 1100°C in the pressurized grid heater. None was lower than 50%, but at this temperature much of the inorganic material in the liquor decomposes by reaction between carbon and molten sodium carbonate to release carbon and sodium.

This study revealed that, for some of the conditions studied, volatiles yield and specific swollen volume correlate weakly with one another. Conductive heat transfer into the centre of a highly swollen droplet occurs more slowly than for smaller droplets, resulting in a lower heating rate. Devolatilization is highly dependent on the heating rate. Therefore, the result is a lower volatiles yield. Recondensation of tars onto the char surface is more likely to occur on a more swollen droplet as well. The data at this point are too limited to safely conclude that volatiles yield always decreases with increased liquor swelling, but further investigation is warranted.

Under the single-droplet burning conditions studied, drying and char burning times decrease with increasing temperature,

while devolatilization times increase somewhat, based on the measurement technique used in this investigation. The total combustion time, however, was found to be essentially the same at both 700 and 800°C. Total combustion time correlates well with the degree of liquor swelling during combustion, with more swelling related to shorter combustion times. This is due to the larger external surface area available for reaction and heat transfer for the more swollen droplets. Numerical analysis of the total combustion time vs the external surface area of the droplet verifies this relationship.

New data were obtained regarding char reactivities under pressurized gasification conditions for a variety of industrial liquors. The reactivities varied between liquors by as much as a factor of 3.5, and did not seem to be dependent on either the pulping method or the wood species. The reactivities did not correlate well with the other measured properties, and better measuring techniques and procedures are required for more reliable and relevant results to be obtained.

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ABSTRACT: Fifteen black liquors were chosen from a special bank, which has been established specifically to make comparisons between liquors. Each liquor was subjected to eight different experiments carried out in four different reactors over a wide range of temperatures and pressures to measure specific burning properties (swelling during devolatilization, volatiles yield, burning stage durations and char reactivity). The ranges of measured values are presented and generalizations are given regarding the behaviour of black liquors with respect to particular burning properties. Additionally, correlations between burning properties are identified and explanations for the observed behaviour are presented.

RÉSUMÉ: Nous avons choisi quinze liqueurs noires dans une réserve spéciale que nous avons constituée spécifiquement aux fins d'études comparatives entre les liqueurs. Chaque liqueur a fait l'objet de huit expériences différentes effectuées à l'aide de quatre réacteurs différents dans une vaste plage de températures et pressions. Nos expériences avaient pour but de mesurer les caractéristiques spécifiques de combustion des liqueurs, notamment le gonflement durant la dévolatilisation, le rendement des matières volatiles, la durée du stade de combustion et la réactivité des résidus de carbonisation. Nous analysons ici les plages des valeurs mesurées et les données générales relatives au comportement des liqueurs noires par rapport à des propriétés de combustion particulières. Nous identifions par ailleurs les relations existant entre les propriétés de combustion et nous fournissons des explications sur les comportements ainsi étudiés.

KEYWORDS: COMBUSTION, GASIFICATION, PYROLYSIS, BLACK LIQUORS, REACTIVITY.



Paper II

Influence of pressure on pyrolysis of black liquor: 1. Swelling

To be submitted.

INFLUENCE OF PRESSURE ON PYROLYSIS OF BLACK LIQUOR: 1. SWELLING

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This is the first part in a series of papers concerning the behavior of black liquor during pyrolysis under pressurized conditions. Two industrial kraft liquors were pyrolyzed in a laboratory-scale pressurized single particle reactor and a pressurized grid heater at temperatures ranging from 650° to 1100°C and at pressures between 1 and 20 bar. The dimensions of the chars produced were measured and the specific swollen volume was calculated. Swelling decreased roughly logarithmically over the pressure range 1-20 bar. An expression is developed to predict the specific swollen volume at elevated pressure when the volume at 1 bar is known. The bulk density of the char increased with pressure, indicating that liquors will be entrained less easily at higher pressures.

1. INTRODUCTION

In the production of pulp for papermaking, wood chips are cooked in an aqueous solution of sodium hydroxide and sodium sulfide. About half the dry weight of the wood, containing lignin and organic acids that bind the fibers together, dissolves into the cooking solution. The fibers that remain constitute the pulp that will eventually become paper. The spent solution from the cooking process, called black liquor, is approximately 15% solids by weight and contains a significant organic fraction from the dissolved wood species. The black liquor is concentrated to 65-85% solids and is burned in a large unit called a recovery boiler which generates steam for mill process and power production. The inorganic cooking chemicals fall to the bottom of the recovery boiler, forming a smelt bed, and are subsequently recovered and recycled to the process.

A black liquor droplet entering the recovery boiler undergoes three stages of combustion: drying, pyrolysis (also called devolatilization) and char burning [1].

These stages are shown schematically in Figure 1. Drying simply involves removal of water from the droplet by evaporation. During pyrolysis organic matter in the liquor degrades, forming various gaseous compounds such as CO₂, CO, H₂, CH₄, other light hydrocarbons, H₂S and other gaseous sulfur species [2-4]. Char burning involves the heterogeneous reaction of oxygen with carbon and other species in the solid char which remains after pyrolysis.

Black liquor is an unusual fuel in the respect that it swells considerably during pyrolysis. For droplets undergoing pyrolysis at atmospheric pressure, volumetric increases by a factor of 50 or more are not uncommon. The tendency of a droplet to swell can be quantified by its specific swollen volume (SSV). The specific swollen volume is defined as the ratio of the volume of the swollen particle to the initial dry mass of the droplet:

$$SSV = \frac{V_{\text{swollen particle}}}{m_{\text{ds},i}} \quad (1)$$

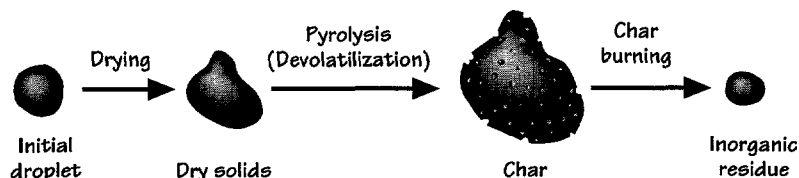


Figure 1. Stages of black liquor combustion.

where $V_{\text{swollen particle}}$ is the volume of the swollen particle, usually measured at maximum swelling and, $m_{\text{ds},i}$ is the mass of dry solids in the initial liquor droplet.

This swelling plays a key role in the combustion of the liquor, and its fate in a recovery furnace. Liquors which have a high tendency to swell burn more quickly than low-swelling liquors due to the larger area available for oxygen transfer to the droplet surface [1,4-8]. Droplets that swell significantly are more likely to become entrained in the upwards moving gas flow and burn in the gas phase while denser, less-swollen droplets will tend to fall to the char bed and burn there.

Indeed, much research has been performed to identify factors which influence swelling and to clarify the swelling mechanism. Hupa *et al.* [1] observed that liquors achieve their maximum swollen volume at the end of the devolatilization stage. Examination of the swelling mechanism suggests that swelling occurs as a result of gases formed during devolatilization and the plastic state of the liquor as it transforms to become char. The volume of the gases is much larger than that of the solid material, and the formation of gaseous bubbles within the liquor causes it to expand, or swell. The result is a very porous material with a high internal surface area.

Research on swelling of biomass pyrolysis oils reveals that swelling continues until surface tension forces holding the droplet together can no longer balance the pressure differential across the liquid surface, and a microexplosion occurs [9]. In discussion of the plastic state of coal during pyrolysis, it is maintained that the effect of surface tension on bubble escape rate is small

compared to viscous forces [10]. The extent to which surface tension and viscous forces influence black liquor swelling is unclear. In a comparative study of black liquor properties of 17 industrial black liquors no correlation was found between either the viscosity or surface tension of the concentrated (ca. 70% solids) liquor and the degree of swelling during atmospheric pyrolysis in nitrogen [8]. In a different study of seven black liquors Söderhjelm *et al.* [11] found that swelling seems to decrease with increasing liquor viscosity at 700°C, but observed no such trend at other temperatures.

Miller *et al.* [12] investigated the influence of composition on swelling of laboratory-prepared black liquors at low temperatures and suggest that bubble formation results from thermal decomposition of sugar acids, and that kraft lignin influences the liquor viscosity. They found that swelling was related to the ratio of kraft lignin to sugar acids, and that a ratio of these components of roughly 1:1 yielded maximum swelling. Alén *et al.* [6] found the same for synthetic liquors pyrolyzed at temperatures more representative of those found in a recovery boiler. Other liquor properties, such as the species pulped and the concentrations of tall oil and hemicellulose, are also known to impact liquor swelling behavior [1,6,8,13,14] though no consensus has been reached on exactly how.

Despite such studies, the relation between a liquor's properties and its tendency to swell is still poorly understood, underscoring the complexity of the swelling process. Research on the influence of furnace conditions has been more successful. Several investigators have observed that swelling decreases with furnace temperature

[1,5,7,13,14]. Frederick and Hupa maintain that the temperature of the particle surface during devolatilization is a key factor for swelling and propose a model to estimate the degree of swelling as a function of furnace temperature and bulk gas oxygen concentration [15].

Many proposed recovery alternatives, such as integrated gasification combined-cycle (IGCC) processes, are planned to operate under pressurized conditions. Such systems promise higher efficiency than conventional technology and can theoretically increase electricity production per unit of black liquor by as much as a factor of two [16,17]. Undoubtedly, liquor swelling will affect the operation of these systems as well. However, little data is available regarding swelling of black liquor under pressurized conditions [8,18], and no known studies have specifically investigated the influence of pressure on liquor swelling during pyrolysis.

The work presented here is the first such study, and aims not only to provide insight about how pressure affects swelling behavior, but to enhance the understanding of the mechanism of swelling. The approach used in this study involved pyrolysis of two industrial liquors was carried out under pressure in two different laboratory-scale reactors. The swelling behavior of the liquors is reported here.

Char yields and component release during pressurized pyrolysis are treated in Part 2 of this series.

2. EXPERIMENTAL

Chars were formed in two devices: a pressurized single particle reactor (PSPR) and a pressurized grid heater (PGH). Pressures between 1 and 20 bar and temperatures between 650 and 1100°C were investigated. The PSPR was used for pyrolysis of single droplets of black liquor. The grid heater is well-suited for investigation of pyrolysis with higher heating rates.

2.1 Liquor samples

Two industrial kraft liquors were used in this. Liquor 1 is a Finnish softwood kraft black liquor with solids content of 73.2%, and was used in some of the experiments in the PSPR. Liquor 2 was from the pulping of a softwood mix at a mill in Finland and was 64.4% solids by weight. Swelling of this liquor was measured in both the PSPR and the PGH. The elemental compositions of the liquors are presented in Table 1.

2.2 Pressurized single particle reactor

Pyrolysis experiments on single droplets of black liquor were carried out in a pressurized thermogravimetric analyzer which was retrofitted to function as a pressurized single-particle reactor (PSPR,

TABLE 1. COMPOSITIONS OF BLACK LIQUORS (WT-%, DRY BASIS)

Element	Liquor 1	Liquor 2
C	34.1	34.9
Na	22.3	20.4
K	1.2	1.4
S	5.5	4.82
H	3.4	3.5
N	0.07	0.062
Cl	0.2	0.35
Other (by difference)	33.2	34.5

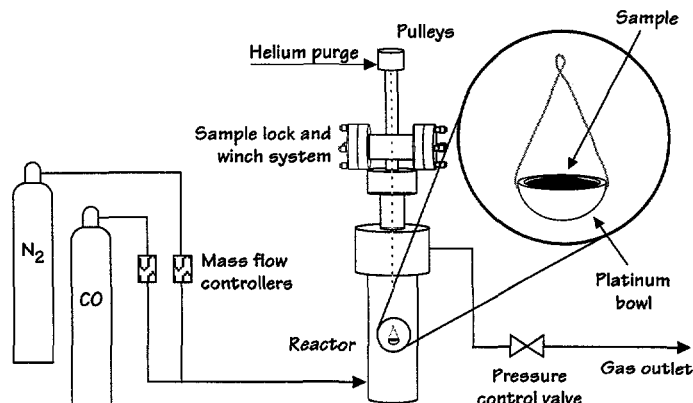


Figure 2. Pressurized single particle reactor showing the sample holder used with Liquor 1.

Figure 2). A winch system allows a small sample holder to be lowered from a helium-purged, water-cooled sample lock into the reactor chamber (i.d. 17 mm), which can be pressurized up to 100 bar and heated to 1100°C. Up to five gases can be independently controlled and fed into the reactor or directed through a bypass line.

In the experiments, a sample holder was filled with concentrated black liquor and placed into the sample lock. Experiments with Liquor 1 used a bowl-shaped platinum sample holder and the sample size was approximately 35 mg. In experiments with Liquor 2 roughly 10 mg of liquor was placed on a platinum wire hook. The device was pressurized and the reactor heated to the desired conditions while a gas mixture of either pure nitrogen or 10% CO in nitrogen was fed into the reactor at 3.0 standard liters per minute. The sample was quickly lowered into the reactor and allowed to pyrolyze for the desired amount of time, after which it was quickly lifted back into the inert sample lock.

To determine the degree of swelling in the PSPR, the resulting char particles were photographed next to an object of known size. From these photographs, the diameter of the particle was measured in either two or three directions and the volume of the swollen particle was calculated from one of the following formulas:

$$V_{\text{swollen particle}} = \frac{\pi}{6} (\sqrt{d_x \cdot d_y})^3 \quad (2)$$

$$V_{\text{swollen particle}} = \frac{\pi}{6} (d_x \cdot d_y \cdot d_z) \quad (3)$$

where d_x , d_y and d_z are the diameters of the particle in the x-, y- and z-directions. The specific swollen volume (SSV) was determined by dividing this volume by the initial dry mass of the sample as shown in Equation 1.

Five pressures were investigated with the PSPR: 1, 2, 5, 10 and 20 bar. The experiments on Liquor 1 were carried out at 650, 750 and 850°C and pyrolysis was allowed to proceed for 30 seconds. For Liquor 2, chars were formed at 900°C by pyrolysis for 15 seconds. Three or four runs were performed at each set of conditions. The values reported here are averages.

2.3 Pressurized grid heater

The pressurized grid heater (PGH, Figure 3) consists of a fine wire grid (3 cm x 3 cm) situated inside a pressure vessel. By resistive heating of the grid heating rates up to 3000 K/s, can be achieved. A Pt/Pt-Rh thermocouple is welded to the center of the grid and is used both as a sample temperature indicator and as feedback to the heating controller. The pressure, heating

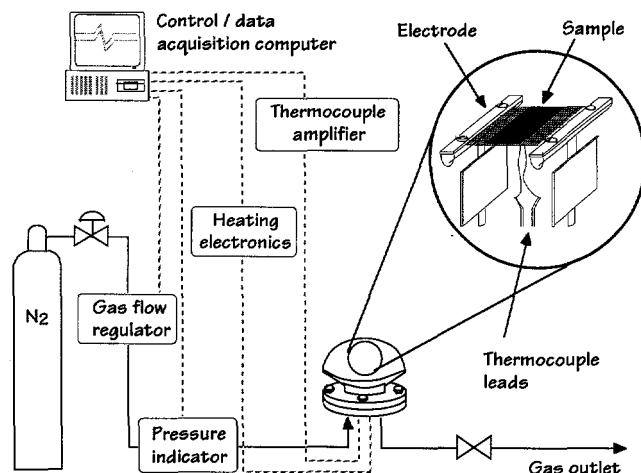


Figure 3. Pressurized grid heater device.

rate, final temperature and holding time at maximum temperature are programmed into the controlling computer prior to performing the experiment. It then automatically purges the reactor with nitrogen, pressurizes the system, heats the grid, allows it to cool and depressurizes the system. An in-depth description of the PGH device and experimental procedure is given by Sorvari *et al.* [19,20].

In the pyrolysis experiments black liquor was painted onto the grid and allowed to dry, resulting in approximately 10 mg dry material in a layer 5-10 microns thick [19]. The grid was then weighed to determine the sample mass and secured between the electrodes of the reactor. The unit was tightly closed, purged and pressurized with nitrogen. The grid was heated at 1000 °C/s to the desired temperature which was held for five seconds, after which the current stopped and the grid quickly cooled.

Upon completion of the experiment, the net was carefully removed. Swelling was determined by photographing the end of the grid through a microscope and measuring the thickness of the char formed. By multiplying the thickness by the area of the painted section of the grid the volume of the char was calculated. The volume of the grid within the swollen char was estimated and

subtracted from the total volume to yield the swollen volume for the char alone. This was divided by the initial dry mass of the liquor to give the specific swollen volume. More detail of the experimental procedure is given elsewhere [18,19,21].

Chars were formed in the PGH at three different temperatures (700°, 900° and 1100°C). At 700° and 1100°C, chars were formed at 1 and 20 bar total pressure. At 900°C five different pressures were used: 1, 2, 5, 10 and 20 bar.

3. RESULTS AND DISCUSSION

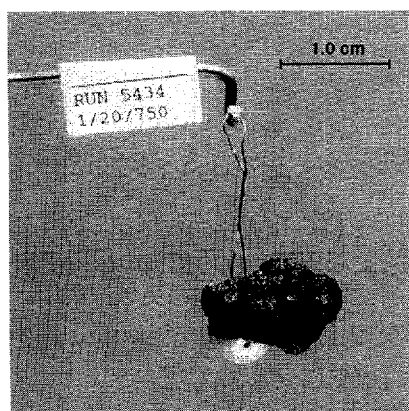
3.1 PSPR results

The influence of pressure on swelling of liquors pyrolyzed in the PSPR can be seen in Figure 4, where chars formed at 750°C and at 1, 5, 10 and 20 bar pressure are shown. Clearly, the size of the resulting char particle decreases with increasing pressure. Between 1 and 20 bar, the average diameter of the char decreases by a factor of 1.6. This corresponds to a decrease in volume by a factor of roughly 4.

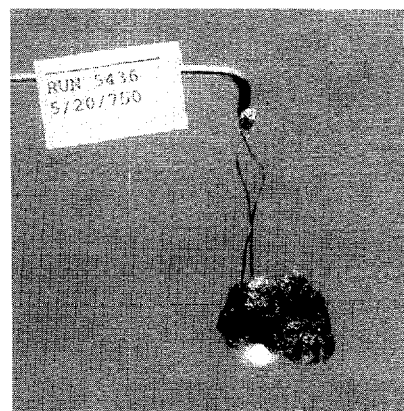
Three or four replications were made at each pressure. The standard deviation of the specific swollen volumes varied between 43% and 8% of the average value, with lower pressures generally yielding

TABLE 2. SPECIFIC SWOLLEN VOLUMES MEASURED IN THE PSPR AT 750°C FOR LIQUOR 1.

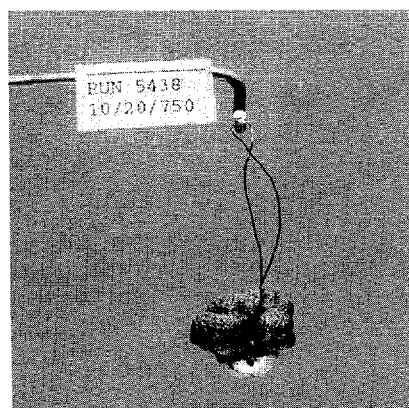
Pyrolysis pressure, bar	SSV, cm ³ /g	Ratio to swelling at 1 bar
1	33.24	1.00
2	27.17	0.82
5	22.68	0.68
10	12.48	0.38
20	8.23	0.25



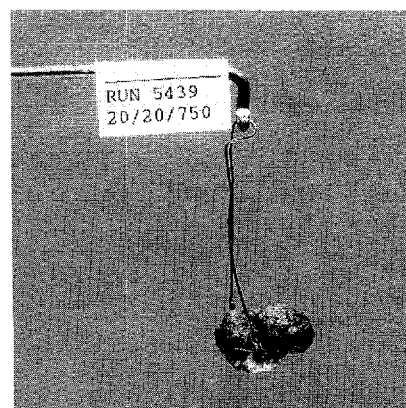
1 bar



5 bar



10 bar



20 bar

Figure 4. Effect of pyrolysis pressure on swelling of chars formed in the PSPR. Chars formed by pyrolysis at 750°C for 30 seconds. The scale in all photos is the same.

TABLE 3. SPECIFIC SWOLLEN VOLUMES OF CHARs FORMED FROM LIQUOR 2, MEASURED AT 900°C.

Pyrolysis pressure, bar	Specific swollen volume, cm ³ /g		Ratio to swelling at 1 bar	
	PSPR	PGH	PSPR	PGH
1	24.76	23.48	1.00	1.00
2	21.77	16.06	0.88	0.68
5	14.63	12.97	0.59	0.55
10	11.76	7.47	0.47	0.32
20	7.04	3.91	0.28	0.17

higher standard deviations. The average specific swollen volumes for Liquor 1 and Liquor 2 chars are given in Table 2 and Table 3, respectively, and are shown as a function of pyrolysis pressure in Figure 5. As noted previously, swelling decreases with increasing pyrolysis pressure, with a more dramatic decrease observed at lower pressures. The specific swollen volume from pyrolysis at 20 bar was roughly one-quarter of that measured at 1 bar.

3.2 Grid heater results

The specific swollen volumes measured for chars formed in the PGH are presented as a function of pressure in Figure 6. The data for pyrolysis at 900°C is given in Table 3. For all three temperatures swelling decreased with increasing pressure, with the swelling at 20 bar averaging 21% of that at 1 bar. The data at 900°C indicates that the decrease is most significant at low pressures. McKeough *et al.* also report having observed qualitatively that pyrolyzed

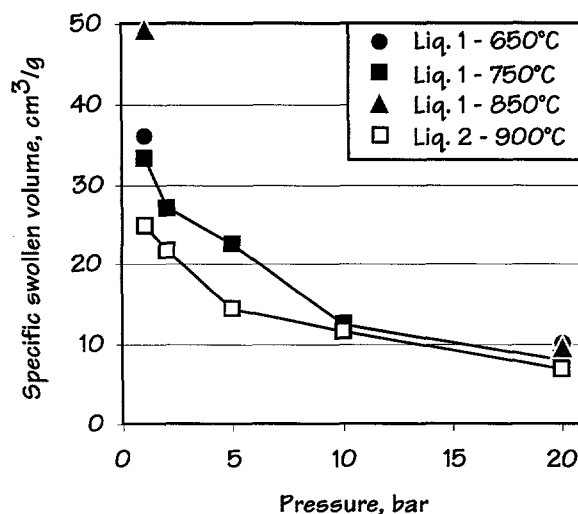


Figure 5. Specific swollen volume versus pyrolysis pressure for liquors pyrolyzed in the PSPR. All values are averages of 3-4 runs.

in a grid heater at 21 bar swell less than those pyrolyzed at 1 bar [22].

Swelling at 1 bar decreased slightly with pyrolysis temperature, while at 20 bar no significant difference was observed. In a previous study performed at 10 bar in the same device, swelling at 1100°C was found to be 83% of that at 850°C. [8] For the data obtained at 1 bar in the current study, the swollen volume at 1100°C is 81% of that at 700°C. The observed decrease in swelling as a function of temperature is inconsistent with the findings of Frederick and Hupa, who determined that swelling of black liquor droplets in oxygen-containing environments decreases with increasing temperature [15]. The inconsistency of these results is likely due to differences in the samples (thin layer on a grid vs droplets), associated heating rates, gas atmosphere (inert vs oxygen-containing) and experimental techniques.

3.3 Comparison of reactors

The specific swollen volume of Liquor 2 pyrolyzed at 900°C was measured in both the PSPR and the PGH over the pressure range 1-20 bar. The values obtained in the PGH are plotted against those from the PSPR in Figure 7, and a straight line has

been fit to the data by regression.

Generally, the values from the two reactors agree well. The specific swollen volumes measured in the PGH were consistently lower than those from the PSPR. The slope of the best-fit line is almost exactly 1.0, indicating that the PGH values are offset from the PSPR values by a specific amount (roughly 3.5 cm³/g) for all pressures, rather than proportional to the PSPR values. The difference could be due to a number of factors. The heating rate in the PGH is roughly 20 times that of the PSPR and the initial diameter, or thickness, of the sample in the PGH was less than 1% of that in the PSPR. As a result, local heating rates within the liquor were much higher for pyrolysis in the PGH than in the PSPR, and the amount of time the liquor was in the plastic state was presumably much less. Differences in the solids content of the liquor in the two devices (100% in the PGH versus 64% in the PSPR) also resulted in higher heating rates in the PGH. The methods for measuring the swollen char were necessarily very different, as well. The ultimate cause for the observed differences between reactors is undoubtedly due to a combination of these factors.

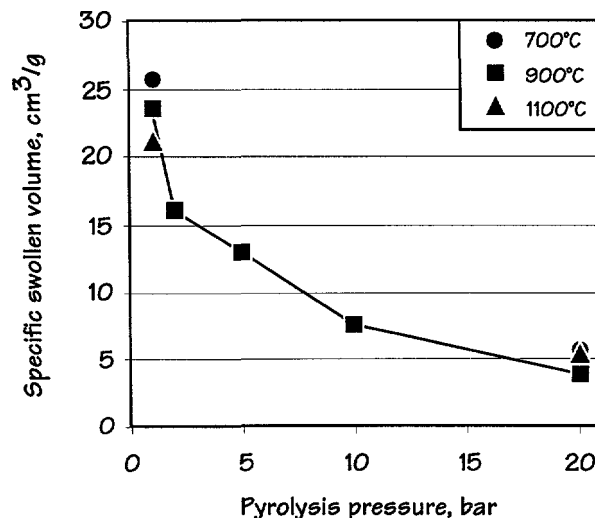


Figure 6. Specific swollen volume versus pyrolysis pressure for chars formed from Liquor 2 in the PGH.

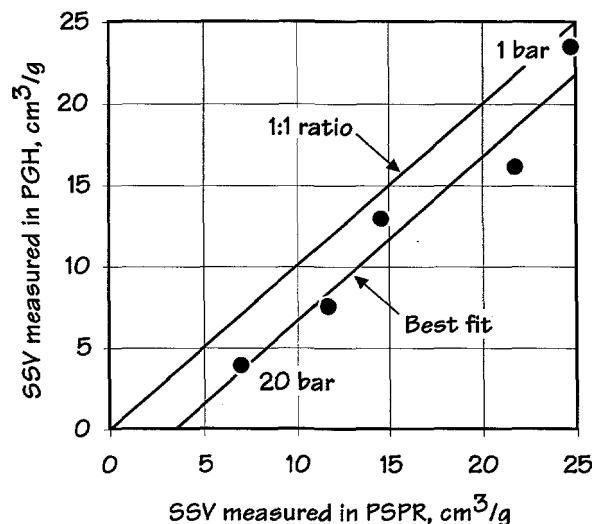


Figure 7. Comparison of swelling measured in two different reactors.
Liquor 2, 900°C.

3.4 Discussion

In this section the mechanism of black liquor swelling under pressure is examined and a model is developed to predict the degree of swelling at elevated pressure.

Analysis of swelling under pressure. For this study, it is clear that the plots of swelling versus pyrolysis pressure for the two reactors (Figure 5 and Figure 6) are strikingly similar. The decrease in swelling with increasing pressure may be explained by the volume of the gas bubbles within the liquor as it undergoes pyrolysis. Ideally, as the pressure is increased from 1 bar, the volume required for a particular quantity of gas decreases by a factor of P , the total pressure of the system. If this volume corresponds to the swollen volume, one would expect the following relation to hold true:

$$SSV_p = SSV_{1 \text{ bar}} \cdot \frac{P_{1 \text{ bar}}}{P} \quad (4)$$

Where SSV_p is the specific swollen volume at the pressure of interest, $SSV_{1 \text{ bar}}$ is the specific swollen volume at 1 bar and P is the total pressure of the system. Alternately, one would expect a plot of

$SSV_p/SSV_{1 \text{ bar}}$ versus $P_{1 \text{ bar}}/P$ to yield a straight line with a slope of 1.0. The rigidity of the solid might seemingly limit the effect of pressure on the volume of the bubbles. One might even argue that the bubbles would not be affected by external pressure because the solid char isolates them from such pressure effects. But during pyrolysis the char is in a soft, plastic state. Therefore we would expect the volume of the bubbles to shrink with increasing total pressure, but to a degree less than that predicted by Equation 4 due to resistance created by the liquor.

In Figure 8 the ratio $SSV_p/SSV_{1 \text{ bar}}$ is plotted versus $P_{1 \text{ bar}}/P$. As noted above, a straight line with slope 1.0 would indicate that the bubbles in the char, and correspondingly the swollen volume of the char, shrink in direct proportion to the pressure of the system. The fact that the data lies above this line indicates that the shrinkage at increased pressures is less than predicted by Equation 4, a result attributed to the resistance of the liquor in its plastic state.

As noted in the introduction, efforts to correlate swelling tendency with other liquor properties have been only marginally successful and despite such efforts no method of estimating swelling based on

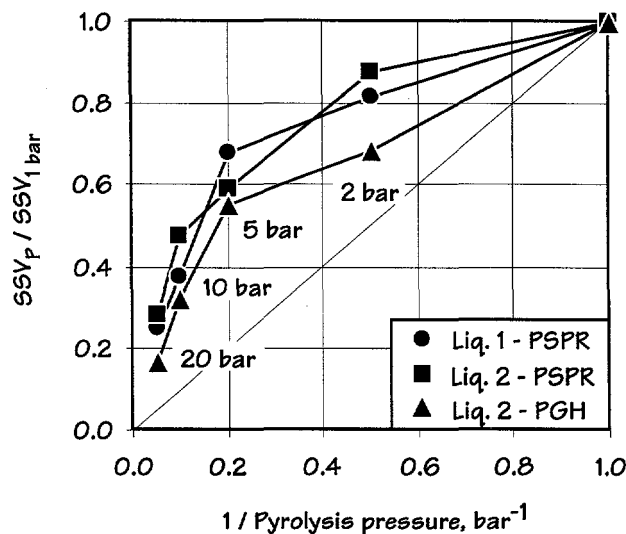


Figure 8. Evaluation of experimental swelling data according to Equation 4.

liquor properties has been proposed. Whitty *et al.* [8] concluded that liquors which display high degrees of swelling at atmospheric pressure also swell more than other liquors under pressurized conditions, and that liquor-to-liquor differences are similar under both conditions. Ultimately, we would like a simple expression which could be used to estimate the degree of black liquor swelling at high pressure.

As previously mentioned, the shape of the swelling-versus-pressure curve is similar for all experiments in this study. In order to normalize the data, the specific swollen volume at a particular pressure was divided by the specific swollen volume at 1 bar. The normalized data for all experiments is shown in Figure 9. The decrease with pressure appears to be roughly logarithmic and fitting a logarithmic expression to the data yields the following equation:

$$\frac{SSV_P}{SSV_{1 \text{ bar}}} = 1 - 0.254 \ln(P/P_{1 \text{ bar}}) \quad (5)$$

where P is the pressure of interest, in bars. The fit of the equation is very good, with a correlation coefficient (R^2) of 0.954.

Multiplying both sides of Equation 5 by $SSV_{1 \text{ bar}}$ results in an expression that can be used to estimate the degree of swelling at high pressure if the specific swollen volume at 1 bar is known:

$$SSV_P = SSV_{1 \text{ bar}} [1 - 0.254 \ln(P/P_{1 \text{ bar}})] \quad (6)$$

Char bulk density. The bulk density of black liquor char is related to its specific swollen volume. Bulk density is defined as the mass of char per unit volume while specific swollen volume is defined as the volume of char per unit mass of *initial dry* material before pyrolysis. Therefore, the two properties are related by the char yield as follows:

$$\rho_{\text{bulk}} = \frac{CY}{SSV} \quad (7)$$

where ρ_{bulk} is the bulk density (g/cm^3) and CY is the char yield, defined as the mass fraction of original material which remains in solid form after pyrolysis. Based on this relation and Equation 6, an expression can be developed to estimate the influence of

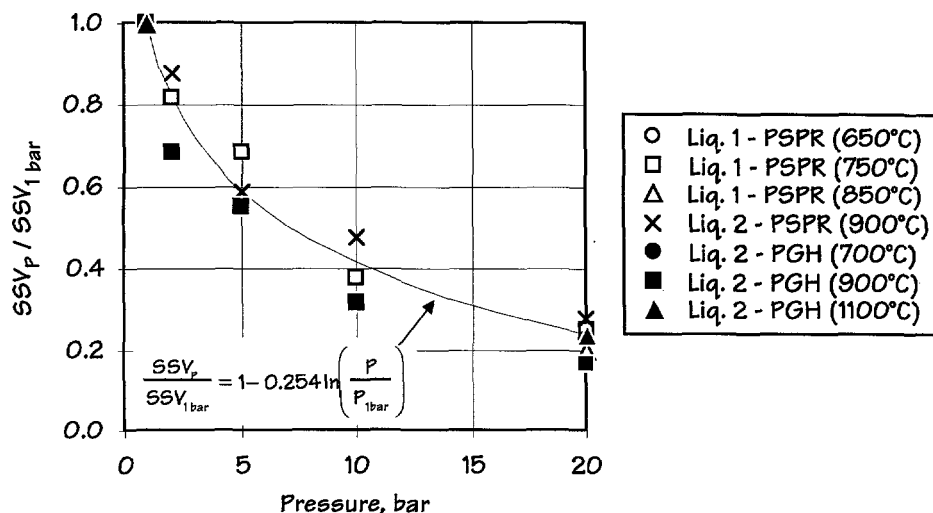


Figure 9. Normalized swelling as a function of pressure.

pressure on the bulk density of chars formed under pressurized conditions:

$$\rho_P = \frac{\rho_{1 \text{ bar}}}{1 - 0.254 \ln(P/P_{1 \text{ bar}})} \left(\frac{CY_P}{CY_{1 \text{ bar}}} \right) \quad (8)$$

The limited data available on the influence of pressure on char yields during black liquor pyrolysis, both from previous studies [22,23] and as discussed in Part 2 of this series, indicate that char yields increase with pressure only at high temperatures ($\geq 850^\circ\text{C}$) and for long holding times (> 5 s). For the case when char yield is not influence by pressure, the rightmost term in Equation 8 can be ignored, resulting in a more simple expression:

$$\rho_P = \frac{\rho_{1 \text{ bar}}}{1 - 0.254 \ln(P/P_{1 \text{ bar}})} \quad (9)$$

The bulk densities of the chars formed in this study were measured directly and a plot of bulk density versus pyrolysis pressure is shown in Figure 10. Also, the bulk density predicted by Equation 9 is shown in the figure, with $\rho_{1 \text{ bar}}$ taken from the data for Liquor 1 pyrolyzed in the PSPR. For all

three cases, the bulk density appears to increase linearly with increasing pyrolysis pressure. The slope of the increase is greatest for Liquor 2 pyrolyzed in the PGH. It would seem that the sensitivity of the bulk density to pyrolysis pressure should be a function of the volatiles yield during pyrolysis, the decrease in gas volume with pressure would be larger for higher amounts of volatiles. This was not found to be the case, however, and the ordering of the slopes in Figure 10 was not the same as the ordering of volatiles yields.

Char bulk density is an important property because it governs how easily a char particle becomes entrained in the gas flow of a reactor and plays a critical role in the amount of carryover in a recovery boiler. Obviously, less dense particles will be more easily entrained. For the chars formed in this study, bulk densities increased by a factor of 4-6 between 1 and 20 bar, indicating that chars formed at high pressure are much less prone to entrainment.

4. CONCLUSIONS

Black liquor chars were formed by pyrolysis under pressures in the range 1-20 bar and at temperatures between 650° and

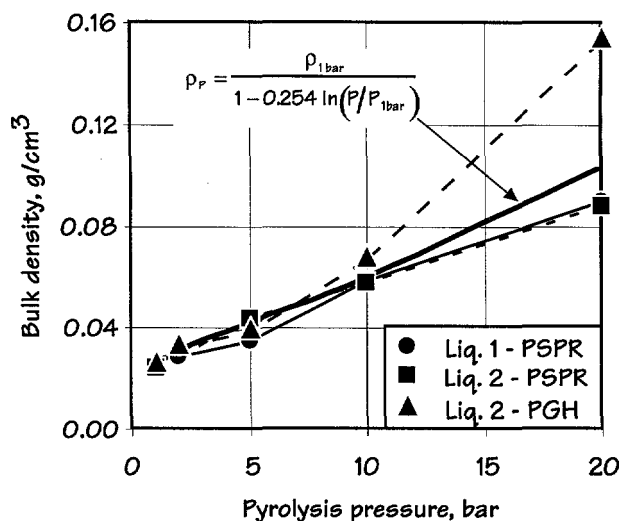


Figure 10. Bulk densities of chars formed under pressure. Thick line is the prediction given by Equation 9 for Liquor 1 in the PSPR.

1100°C. Two laboratory-scale reactors were used: a pressurized single-particle reactor, which allowed investigation of single droplets of black liquor, and a pressurized grid heater which allowed pyrolysis at a higher heating rate. The degree of swelling during pyrolysis was measured for two industrial kraft liquors.

Swelling was found to decrease over the range 1-20 bar with a more dramatic decrease observed at lower pressures between 1 and 5 bar. The specific swollen volume measured at 20 bar was roughly one-quarter of that measured at 1 bar. The decrease was roughly logarithmic with pressure, and an expression has been developed to predict swelling at higher pressures if the specific swollen volume at atmospheric pressure is known.

Char bulk densities increased with pressure by a factor of roughly 4 over the range 1-20 bar, with the increase being roughly linear in this range. Due to the close relation between specific swollen volume and bulk density, the same equation can be used to describe both properties if the variation in char yield with pressure is negligible.

A comparison of specific swollen volumes measured in the two reactors was made. The pressurized grid heater consistently gave lower specific swollen volumes under the conditions studied. The difference between reactors was constant over the pressure range investigated. It is proposed that the observed differences in swelling are due to differences in local heating rates and associated durations of the liquor's plastic state. Swelling measured in the pressurized single-particle reactor more closely represents that which would occur with droplets in an industrial reactor.

There are several practical implications of the results presented here. It is clear that liquor swelling during pyrolysis will still be important in pressurized processes, particularly with regard to entrainment of the particle. Swelling will be less than in atmospheric processes and entrainment will decrease with the pressure of the reactor. It can be expected that relative differences in swelling between liquors will remain consistent at higher pressures, as well.

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Paper III

Influence of pressure on pyrolysis of black liquor: 2. Char yields and component release

To be submitted.



INFLUENCE OF PRESSURE ON PYROLYSIS OF BLACK LIQUOR: 2. CHAR YIELDS AND COMPONENT RELEASE

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This is the second in a series of papers concerning the behavior of black liquor during pyrolysis at elevated pressures. Two industrial black liquors were pyrolyzed under pressurized conditions in two laboratory-scale devices, a pressurized single-particle reactor and a pressurized grid heater. Temperatures ranging between 650° and 1100°C and pressures in the range 1-20 bar were studied. Char yields were calculated and based on analysis of some of the chars the fate of carbon, sodium, potassium and sulfur was determined as a function of pyrolysis pressure. At temperatures below 800°C little variation in char yield was observed at different pressures. At higher temperatures char yield increased with pressure due to slower decomposition of sodium carbonate. For the same reason, sodium release decreased with pressure. Sulfur release, however, increased with pressure primarily because there was less opportunity for its capture in the less-swollen chars.

1. INTRODUCTION

Black liquor is the spent pulping solution resulting from digestion of wood chips in an aqueous solution of sodium hydroxide and sodium sulfide. Conventionally, black liquor is concentrated from roughly 15% solids to 65-85% solids and then burned in a recovery boiler for the dual purposes of energy production and recovery of the pulping chemicals. Pressurized gasification of black liquor is one promising alternative to the recovery boiler, and offers the potential to significantly increase the electrical energy production per unit mass of liquor. However, little data is available regarding the behavior of black liquor under pressurized conditions.

Gasification of black liquor is known to occur in three stages: drying, pyrolysis and char gasification. This paper focuses on the pyrolysis stage, which involves thermal degradation of organic matter in the liquor and release of volatiles to the gas phase. In Part 1 of this series, the swelling behavior of black liquor during pyrolysis under pressure was investigated. In this paper,

char yields and the fate of elements during pressurized pyrolysis are considered.

A number of studies have been performed to characterize pyrolysis of black liquor at atmospheric pressure. It has been found that the primary gaseous products resulting from black liquor pyrolysis are CO₂, CO, H₂O, H₂, CH₄, other light hydrocarbons, tars, H₂S and mercaptans [1,2]. Hupa *et al.* [3] introduced a procedure to measure the durations of the different black liquor burning stages and studied the effects of droplet diameter and furnace temperature on devolatilization time. A number of other studies have investigated the duration of the pyrolysis stage, as well [4-8].

Fewer investigations have focused on char and volatiles yields during pyrolysis. Char yield is defined as the mass percentage of the original dry sample which remains in the solid phase after pyrolysis:

$$\text{Char yield (\%)} = 100 \cdot \frac{m_{\text{char}}}{m_{\text{ds},i}} \quad (1)$$

where $m_{ds,i}$ is the mass of dry solids in the original droplet and m_{char} is the mass of the char remaining after pyrolysis. Volatiles yield is the mass percentage of the dry material which is released to the gas phase during pyrolysis and is equal to 100% - char yield.

Frederick and Hupa [4] considered the influence of liquor- and furnace-specific variables on volatiles yields. Their results indicate that volatiles yields increase linearly over the temperature range 700-1200°C. Volatiles yields were also observed to increase with pyrolysis time, with a dramatic change up to 10 seconds and a slower increase beyond that. Sricharoenchaikul *et al.* [9] went a step further and probed the mechanism of tar and gas evolution during pyrolysis. They concluded that the initial pyrolysis products are tars which immediately degrade to gases. Recently, a great number of studies have considered release of carbon, sulfur and sodium species during devolatilization [1,4,9-25]. Most of these studies were conducted at atmospheric pressure.

As noted earlier, few studies have considered the behavior of black liquor during pyrolysis under pressurized conditions. Kymäläinen [16] measured char yields and release of carbon, sulfur and sodium in a pressurized grid heater. Char yields were observed to increase with

pressure at 1000°C. Sodium release decreased with pressure and sulfur release was observed to increase with pressure. In their studies regarding release of carbon, sodium and sulfur during pyrolysis in a grid heater, McKeough *et al.* included some experiments at elevated pressure [16-19]. Sorvari *et al.* studied sodium release during pressurized pyrolysis, focusing on differences between liquors [25]. Amongst the seven kraft liquors tested sodium release at 850°C and 10 bar pressure varied by a factor of 2.5 and release increased quite linearly with increasing sodium content in the original liquor. Whitty *et al.* also considered differences between liquors, but with regard to char yields during pressurized pyrolysis [26].

In spite of these works, fundamental data on the influence of pressure on char yields and the fate of elements during pyrolysis is still lacking. The purpose of the study reported here was to provide such data. Pyrolysis experiments were carried out on two industrial kraft liquors at pressures ranging from 1 to 20 bar. Char yields were measured and from analysis of the chars and original liquors the release of components was determined.

2. EXPERIMENTAL

Chars were formed in two devices: a pressurized single particle reactor (PSPR) and a pressurized grid heater (PGH).

TABLE 1. COMPOSITIONS OF BLACK LIQUORS (WT-%, DRY BASIS)

Element	Liquor 1	Liquor 2
C	34.1	34.9
Na	222.3	20.4
K	1.2	1.4
S	45.5	4.82
H	3.4	3.5
N	0.07	0.062
Cl	0.2	0.35
Other (by difference)	33.2	34.5

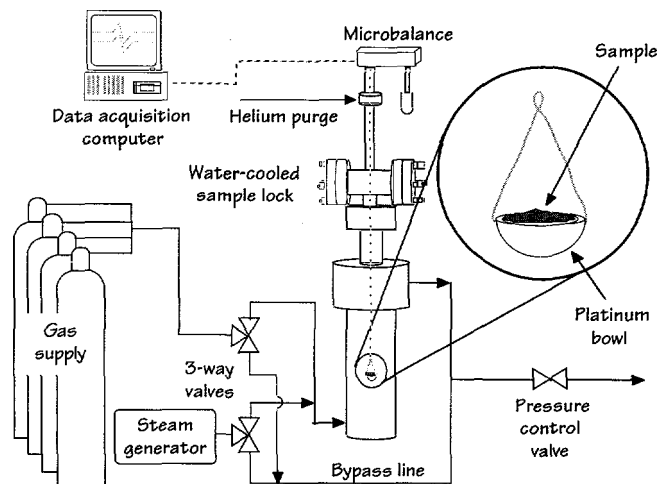


Figure 1. Pressurized thermogravimetric reactor.

Pressures between 1 and 20 bar and temperatures between 650°C and 1100°C were investigated. The PSPR was used for pyrolysis of single droplets of black liquor. The grid heater is well-suited for investigation of pyrolysis at higher heating rates.

2.1 Liquor samples

Two industrial kraft liquors were used in this study. Liquor 1 is a Finnish softwood kraft black liquor with solids content of 73.2%, and was used in some of the experiments in the PSPR. Liquor 2 was from the pulping of a softwood mix at a mill in Finland and was 64.4% solids by weight. Devolatilization behavior of this liquor was measured in both the PSPR and the PGH. The elemental compositions of the liquors are presented in Table 1.

2.2 Pressurized single particle reactor

Pyrolysis experiments on single droplets of black liquor were carried out in a pressurized thermogravimetric analyzer which was retrofitted to function as a pressurized single-particle reactor (PSPR, Figure 1). Details of the device and experimental procedure are provided in Part 1 of this series, but a summary is provided here.

In the experiments, a sample holder was filled with concentrated black liquor and placed into a helium-purged, water-cooled sample lock above the reactor. Experiments used either a bowl-shaped platinum sample holder containing approximately 35 mg of sample or a platinum wire hook upon which was affixed a 10 mg droplet of liquor. The device was sealed shut and pressurized and the reactor heated to the desired temperature. The sample was then quickly lowered into the heated reactor and allowed to pyrolyze for the desired amount of time, after which it was lifted back into the sample lock.

Char yields in the PSPR were determined by weighing the sample before and after the experiment. The carbon, sulfur, sodium and potassium contents of some of the chars was analyzed. Based on this data, the composition of the original liquor and the char yield, the fate of the elements in the liquor could be determined.

Five pressures were investigated with the PSPR: 1, 2, 5, 10 and 20 bar. At some temperatures only 1 and 20 bar were investigated. The experiments on Liquor 1 were carried out at 650, 750 and 850°C

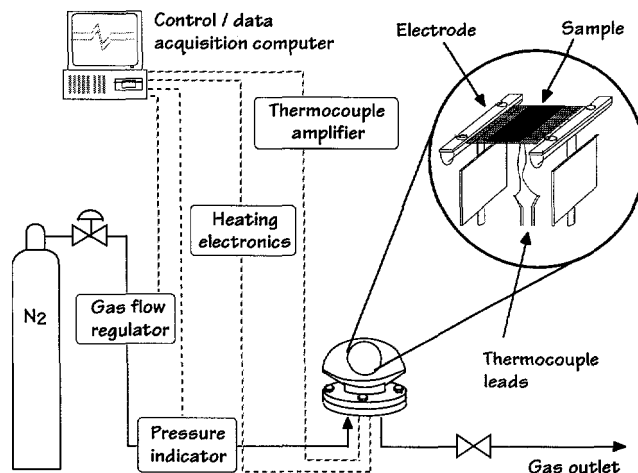


Figure 2. Pressurized grid heater apparatus.

using the bowl-shaped sample holder and pyrolysis was allowed to proceed for 30 seconds. For Liquor 2, chars were formed at 700° and 900°C by pyrolysis for 15 seconds using both types of sample holders. Three or four runs were performed at most conditions. The values reported here are averages.

2.3 Pressurized grid heater

Pyrolysis experiments were also carried out in a pressurized grid heater (PGH, Figure 2). The device and experimental procedure are discussed in detail in Part 1 of this paper, and are summarized here. The grid heater consists of a fine wire grid, 3 cm on a side, that can be heated at rates up to 3000 K/s by passing a current through it. A thermocouple acts as both a temperature indicator and feedback to the heating controller. The grid is situated in a vessel that can be pressurized to 40 bar.

Black liquor was painted onto the grid and allowed to dry, resulting in approximately 10 mg dry material in a layer 5-10 microns thick [27]. The grid was weighed and secured between the electrodes of the reactor. The unit was tightly closed, purged and pressurized with nitrogen. The grid was heated at 1000 K/s to the desired

temperature, which was held for five seconds, after which the current was cut and the grid quickly cooled. Upon completion of the experiment, the net was carefully removed and weighed in order to determine the char yield. As with the experiments in the PSPR, chars were sent for analysis of carbon, sulfur, sodium and potassium. More information about the PGH and experimental procedure is available elsewhere [27-29].

Chars were formed from Liquor 2 in the PGH at 700°, 900° and 1100°C. At 700° and 1100°C, chars were formed at 1 and 20 bar total pressure. At 900°C five different pressures were used: 1, 2, 5, 10 and 20 bar and three measurements were taken for each pressure. The values reported here are averages.

3. RESULTS AND DISCUSSION

The primary goals of this work were to quantify the effect of pressure on char yields and to gain an understanding of the fate of carbon, sulfur, sodium and potassium during pressurized pyrolysis.

3.1 Char yield

In this section char yields are discussed in terms of the different reactors rather than in terms of the different liquors used.

PSPR results. Char yields obtained in the PSPR for Liquors 1 and 2 are presented in Table 2 and Table 3, respectively. The data are also plotted in Figure 3. With the exception of the runs at 650°C and 850°C for Liquor 1, all values are averages of three or four experiments. The standard deviation of the measured char yields was less than 2.5 wt% units.

Char yields decrease with increasing temperature for both liquors. Over the temperature range studied, char yields of Liquors 1 and 2 decreased by 3.9 and 4.8 wt% units respectively, per 100°C temperature increase at atmospheric pressure. Inspection of the data for Liquor 1 reveals a larger decrease between 750° and 850°C than between 650° and 750°C, suggesting that significant degradation occurs at roughly 800°C.

As seen in Figure 3, char yields for droplets pyrolyzed at lower temperatures (<800°C)

did not vary significantly with pressure. While there is some scatter in the data it is not outside the range of experimental error. For experiments conducted at higher temperatures, however, char yields increased with increasing pressure. This is particularly obvious in the experiments conducted with Liquor 2 at 900°C. For the 10 mg droplets char yields increased with pressure up to 10 bar, from 59.5% to 65.6%. The variation is too much to be explained by experimental error, indicating that the observed trend is due to pressure effects.

The unexpectedly low char yield for the 10 mg droplets at 20 bar can be explained by the experimental procedure. These experiments were performed by affixing a small droplet of concentrated black liquor onto an S-shaped platinum wire, towards the top of the wire. When the liquor was pyrolyzed, the char would remain stuck to the wire. This procedure worked well at low pressures. However, at 10 bar and particularly at 20 bar it was observed that the droplet would slide down the wire partway. In fact, two experiments at 20 bar had to be repeated because the sample slid

TABLE 2. CHAR YIELDS FROM LIQUOR 1, MEASURED IN THE PSPR.

Temp. (°C)	Pyrolysis pressure (bar)	Char yield (wt%)	Std. dev. (wt%)
650	1	70.5	n/a*
650	20	68.3	n/a*
750	1	68.7	4.61
750	2	68.8	1.60
750	5	68.1	0.22
750	10	69.4	0.62
750	20	68.5	1.35
850	1	62.7	n/a*
850	20	64.2	n/a*

* Only one experiment was performed at these conditions

TABLE 3. CHAR YIELDS FROM LIQUOR 2.

Temp. (°C)	Pyrolysis pressure (bar)	PSPR*		PGH	
		Char yield (wt%)	Std. dev. (wt%)	Char yield (wt%)	Std. dev. (wt%)
700	1	(71.8)	(0.4)	74.1	n/a**
700	20	(70.8)	(1.7)	72.4	n/a**
900	1	59.5 (62.2)	0.4 (1.1)	66.0	0.6
900	2	61.8	2.4	66.9	2.2
900	5	63.0	2.1	66.3	0.6
900	10	65.6	1.5	64.3	0.7
900	20	61.3 (65.4)	1.6 (1.3)	61.7	2.5
1100	1	—	—	55.0	n/a**
1100	20	—	—	49.9	n/a**

* Experiments with 10 mg droplets. Values with 35 mg droplets shown in parentheses.

** Only one experiment was performed at these conditions

entirely off the wire. The high pressure raises the boiling point of water in the liquor from 100°C at 1 bar to 212°C at 20 bar. At this pressure the droplet took much longer to dry and slid down the hook as the viscosity decreased due to heating of the liquor. It is suspected that at 20 bar, a portion of the liquor fell off the hook, resulting in deceptively low char yields.

A shift in the devolatilization behavior was observed roughly 800°C. The sensitivity of char yield to temperature increased significantly above this temperature. Additionally, pressure had no visible influence on char yields at lower temperatures, but in experiments carried out at higher temperatures char yield increased with pressure. This has been observed by McKeough *et al.* [16-19] as well. In their experiments black liquor was pyrolyzed in a grid heater at 675° and 900°C and at 2 and 21 bar pressure. The low-temperature experiments showed no correlation between char yield and pressure. But at 900°C the char yield at 20 bar was much less than that at 2 bar, particularly at longer holding times.

According to their analysis, the difference is largely due to decomposition of sodium carbonate. Na_2CO_3 reacts with carbon to form volatile sodium, CO and CO_2 [10]. McKeough *et al.* suggest that this reaction is retarded at higher pressure due to an increase in local CO and CO_2 partial pressures near the char surface. Indeed, Kymäläinen [16] analyzed chars formed at 1000°C under different pressures and found that those formed at higher pressure contained more carbonate than those formed at low pressures. In this study the data in Figure 3 are for pyrolysis times of 30 and 15 seconds for Liquor 1 and Liquor 2, respectively, and sodium carbonate decomposition is presumably responsible for the observed behavior.

Grid heater results. The char yields obtained from pyrolysis of Liquor 2 in the grid heater are presented in Table 3 and as a function of pyrolysis pressure in Figure 4. The measured values ranged from 49.9 wt-% to 74.1% within the conditions studied. At atmospheric pressure the char yield decreased from 74.1% at 700°C to 55.0% at

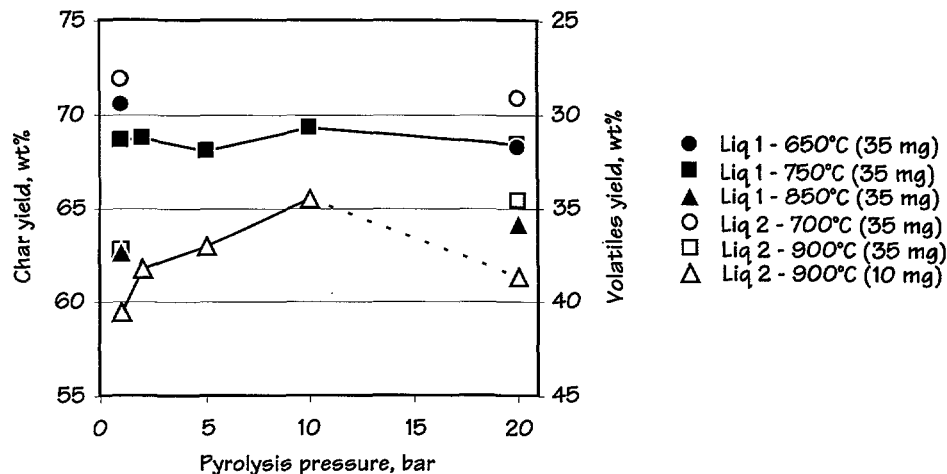


Figure 3. Effect of pressure on char yields measured in the PSPR.

1100°C, or an average of 4.8 wt% units per 100°C increase. This is the same amount of decrease as was found in the PSPR experiments.

In all cases, char yield was observed to decrease with increasing pressure. This result seems counterintuitive in light of the previous discussion, but can be explained. The amount of material volatilized during pyrolysis depends on several factors, both

fuel-specific and condition-specific. Fuel composition, particle size and morphology, reactor temperature, particle heating rate, gas composition and total pressure all may affect how devolatilization proceeds. It is generally understood that high temperatures and heating rates result in a larger release of volatiles due to more intense breakdown of the components within the fuel. The effect of pressure, however, is more involved.

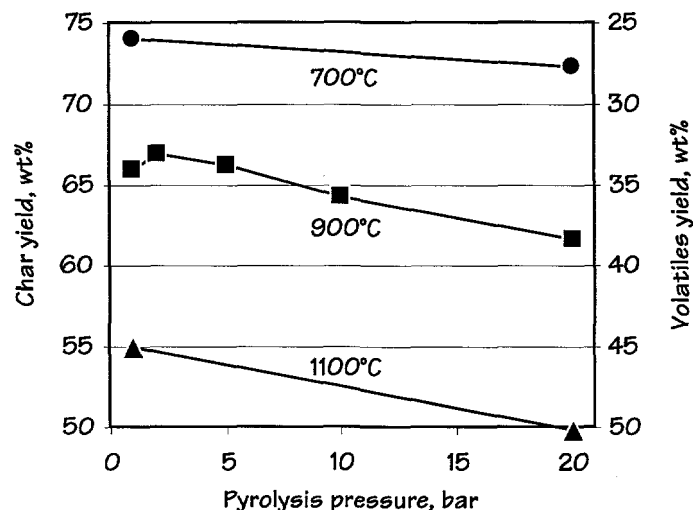


Figure 4. Effect of pressure on char yields measured in the PGH. Liquor 2.

High pressures enhance convective heat transfer, thus increasing the heat flux into the particle and enhancing devolatilization. High pressures may increase the vapor pressure of volatile species, which would reduce their extent of release. Increased pressure decreases gas diffusivity, which can influence the volatiles yield of particles at low heating rates. Chen *et al.* [30] concluded that during low heating rate pyrolysis of biomass particles under pressurized conditions the char yield increases with pressure due to enhanced secondary char formation. Under these conditions, volatile species recondense on the surface of the char before they are able to exit the particle. The phenomenon does not occur at high heating rates, however, where the pressure generated by the volatiles is so large that they are blown out of the particle before they have time to recondense. Fjellerup *et al.* [31] also observed no variation in char yields for wheat straw pyrolyzed under different pressures.

The decreasing char yields as a function of pressure for the data obtained in the pressurized grid heater seems surprising. But it can be explained in terms of the associated swelling during pyrolysis.

Initially, the liquor coats the grid in a fine layer 5 to 10 microns thick. As the liquor heats up, it begins to swell, initially both parallel and perpendicular to the plane of the grid. When the spaces between the wires in the grid become filled, swelling occurs only perpendicular to the plane of the grid. This swelling decreases the release of volatile matter into the gas phase by two mechanisms:

- Decreased heat transfer. Heat transfer in the grid heater occurs both by conduction between the grid and the char and by radiation from the grid. As the liquor swells, the outermost regions become shielded from the grid by the swollen char, resulting in lower heat transfer to these regions. Devolatilization is a function of heating rate and lessens due to the poor heat transfer. The result is a higher char yield.
- Longer gas exit path. Sricharoenchaikul *et al.* [9] demonstrated that devolatilization of black liquor occurs first through the formation of tars, which are then broken down into gaseous species. As the tars and gases exit the particle they may recondense on the surface of the char. This is more likely to occur under high

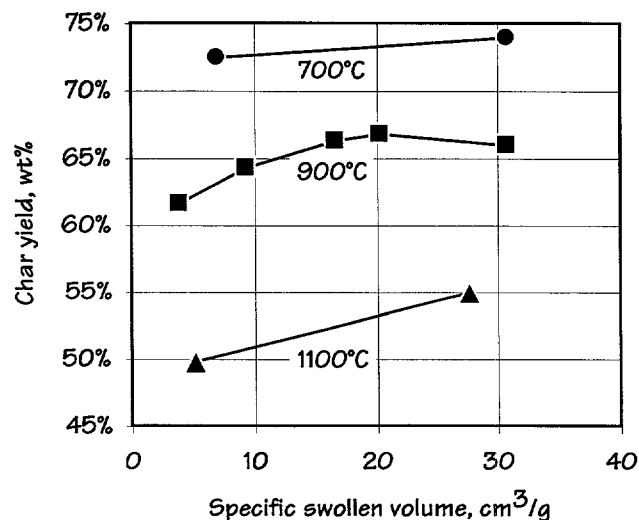


Figure 5. Char yield as a function of measured swelling for chars formed in the pressurized grid heater.

swelling conditions where the exit path is longer. This situation is particularly relevant for volatiles released in the immediate vicinity of the grid, where devolatilization is presumably the most intense. The recondensation results in higher char yields.

The correlation between char yield and swelling for liquors pyrolyzed in the pressurized grid heater is illustrated in Figure 5. Clearly, the more the liquor swells, the higher the char yield. This is likely not to be the case for swelling of black liquor droplets, however. A black liquor droplet in a recovery furnace or single-particle reactor is heated by convection and radiation from the surroundings. In this case, swelling provides a larger surface area for heat flux and thus enhances heat transfer to the particle. However, heat transfer to the center of the particle is reduced by swelling, and the gas exit path for volatiles generated within the droplet will be longer for a swollen particle. These competitive influences of swelling on char yields of black liquor droplets could explain why no variation in char yield was found for chars formed in the PSPR (Figure 6).

Char yields measured in a pressurized grid heater by both Kymäläinen [16] and McKeough *et al.* [17] were observed to increase with pressure. Their experiments were conducted using a folded grid which sandwiched the black liquor. The heat transfer in these experiments was presumably much more efficient than in the current study, so swelling-related influences were minimized.

3.2 Fate of elements during pyrolysis

During pyrolysis, volatile matter in the char is released to the gas phase. Not only is the quantity of material volatilized of interest, but it is important to know the composition of the char and fraction of each component released into the gas phase. We were able to determine the fate of elements in black liquor during the pressurized pyrolysis experiments. The chars formed from Liquor 1 at 750°C in the PSPR were analyzed for carbon, sulfur, sodium and potassium. Similarly, all chars formed in the PGH were analyzed for these components. The results of these analyses are shown in Tables 4 and 5. Additionally, based on the char yields and char analysis the percentage of each component which remained in the char was calculated. The results for pyrolysis of Liquor 1 in the

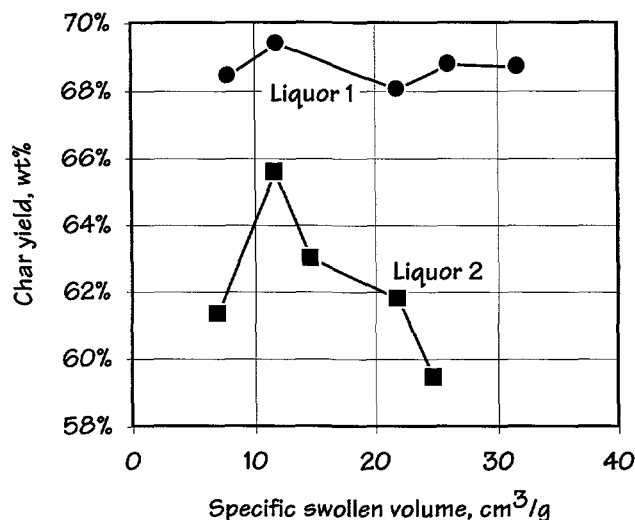


Figure 6. Char yield as a function of measured swelling for chars formed in the PSPR.

TABLE 4. ELEMENTAL ANALYSIS OF CHARs FORMED FROM LIQUOR 1 IN THE PSPR FOR 30 SECONDS AT 750°C. VALUES GIVEN AS WT-%.

Pyrolysis pressure, bar	C	S	Na	K
1	21.91	5.04	28.53	1.43
2	22.87	4.42	28.55	1.48
5	23.47	4.05	30.08	1.44
10	26.57	3.75	29.98	1.45
20	23.36	3.31	30.57	1.48

PSPR are shown versus pyrolysis pressure in Figure 7. A similar plot for pyrolysis of Liquor 2 in the PGH is given in Figure 8. The figures also indicate the release of each element. In this investigation "release" is defined as the difference between the amount retained in the char and the total amount in the original black liquor solids.

Carbon. Unfortunately the carbon analysis technique used in this study was not particularly accurate. Consequently, some values are suspect, particularly that for

pyrolysis at 900°C, 5 bar in the PGH. Nonetheless, we can conclude that roughly half the carbon in black liquor is released during pyrolysis under the conditions used and that there is no significant variation in carbon release with regard to pressure for most conditions. The one exception was for pyrolysis at 1100°C in the PGH. In those experiments it was found that 34% of the carbon remained in the char at 1 bar while 44% remained at 20 bar. McKeough *et al.* [16] found similar results. At 675°C they observed no variation in carbon release

TABLE 5. ELEMENTAL ANALYSIS OF CHARs FORMED FROM LIQUOR 2 IN THE PGH.

Final temp. (°C)	Pyrolysis pressure (bar)	C (wt%)	S (wt%)	Na (wt%)	K (wt%)
700	1	26.72	3.15	21.89	1.77
700	20	27.08	3.32	25.82	2.01
900	1	25.94	3.46	20.81	1.69
900	2	23.64	3.17	22.57	1.61
900	5	18.35	2.76	23.59	1.61
900	10	24.59	2.41	22.93	1.48
900	20	24.51	3.71	26.27	0.75
1100	1	21.53	3.92	18.74	1.81
1100	20	30.66	5.99	19.15	1.48

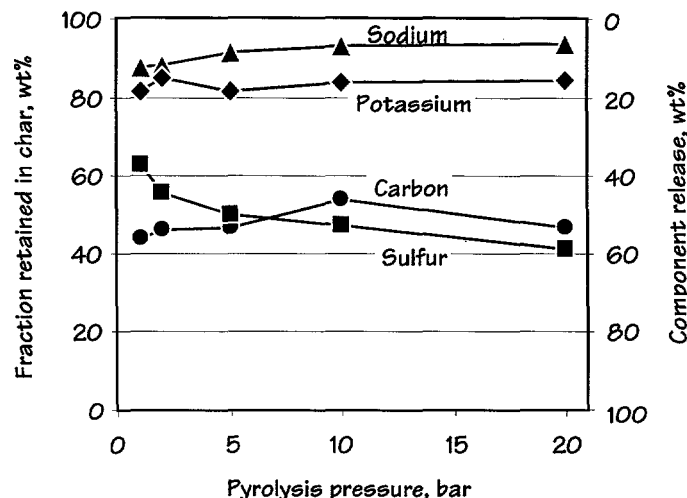


Figure 7. Effect of pyrolysis pressure on the amount of sodium, carbon, potassium and sulfur retained in chars formed from Liquor 1 in the PSPR at 750°C, given as a percentage of the amount initially in the black liquor.

with pressure, but at 900°C less carbon was released at 21 bar than at 2 bar, presumably due to a slower rate of reaction between sodium carbonate and carbon at the higher pressure. Though no such trend was found at that temperature in this study the discrepancy may be due to inaccurate carbon analysis.

Sodium. The fraction of sodium released during pyrolysis increased as the temperature increased, from roughly 10% at 700° to over 50% at 1100°C. Sodium release decreased with pressure for all conditions, but the sensitivity to pressure was higher at higher temperatures. At 900°C the amount released at 20 bar was roughly half that released at 1 bar. At temperatures in this range similar dependencies on pressure were observed by both McKeough *et al.* [18] and Kymäläinen [16]. Again the behavior can be explained by decreased carbonate decomposition. The influence of pressure was more pronounced for the experiments at 900°C in the PGH than for those at 750°C in the PSPR due to the faster kinetics of decomposition at the higher temperature.

Potassium. The majority of the potassium in the black liquor remained in the char during pyrolysis, and potassium release increased with temperature. For pyrolysis at 1 bar in the PGH, potassium release increased from 6% at 700°C to 21% at 1100°C. No influence of pressure on potassium release was observed for pyrolysis at 750°C in the PSPR (Figure 7). Figure 8 shows an apparent decrease in potassium release with pressure. The value at 20 bar seems unreasonably low, however, and it is possible that this value is not correct. The minute sample sizes in these analyses and low potassium content make accurate analysis of this element challenging. For pyrolysis in a grid heater at 1000°C Kymäläinen [16] observed a decrease in potassium release at higher pressures, and one would expect potassium to behave similar to sodium. Apparently more study is needed to clarify the influence of pressure on potassium release.

Sulfur. Sulfur release was in the range 35-70%. As seen in Figure 7 and Figure 8, sulfur release *increased* with pressure in these experiments. The data at 20 bar in the PGH are to be viewed with caution due to the minute sample size analyzed. The data

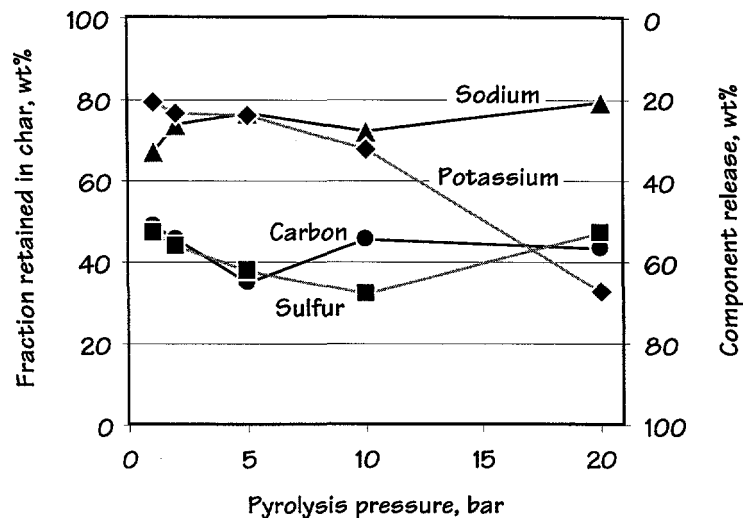


Figure 8. Effect of pyrolysis pressure on the amount of sodium, carbon, potassium and sulfur retained in chars formed from Liquor 2 in the PGH at 900°C, given as a percentage of the amount initially in the black liquor.

of McKeough *et al.* [19] also indicate that sulfur release increases with pressure. In their experiments at 675° and 900°C, the amount of sulfur retained in the char was less for pyrolysis at 15 bar than for pyrolysis at 1 bar. This behavior can be explained in terms of the current understanding of sulfur release.

Previous studies on sulfur release have found that release goes through a maximum at around 500°C [19,24]. Below that temperature conditions are not severe enough to release appreciable quantities of sulfur. Above that temperature, volatilized sodium “captures” the sulfur by reacting with it to form sodium sulfide which remains in the char. McKeough *et al.* [19] were also able to demonstrate that in their experiments the amount of sulfur released during pyrolysis depended on the residence time of the sample in the temperature interval 400-500°C as it was heated. Shorter residence times resulted in less sulfur release.

In this study three factors were identified which could contribute to higher sulfur release at higher pressures:

- **Exit path length.** As shown in Part 1 of this series, swelling of black liquor decreases with pressure. Correspondingly, volatilized sulfur has a shorter exit path from the particle and less opportunity for capture by sodium.
- **Heating rate.** Chars formed at high pressures have more compact structure and more efficient thermal conductivity within the particle. This results in higher local heating rates within the particle and shorter residence times in the critical temperature interval for sulfur release (400-500°C). For chars formed in the PSPR, this is partially offset by the decrease in external surface area and associated decrease in heat transfer to the particle associated with lower swelling.

For liquors containing water, such as those used in the PSPR, the increase in the boiling point of the water with pressure will result in more overlap of the drying and devolatilization stages. Under such conditions the effective heating rate of the sample will be lower in the temperature range critical for sulfur release.

- *Sodium volatilization.* Sodium release was observed to decrease with pressure, so presumably less sodium is available to capture the sulfur.

The degree to which each of these factors influences sulfur release is unknown, but it is believed that the combination of these influences are responsible for the observed decrease with pressure.

The data of Kymäläinen [16] are somewhat different than that reported here. In that study sulfur anions in both the original liquor and chars were analyzed, but total sulfur was not. Sulfur anions in the liquor accounted for roughly 80% of the total sulfur. It was found that the amount of sulfur contained in anions in the char increased slightly with pyrolysis pressure over the range 1.5-20 bar. Unfortunately total sulfur was not known so the results cannot be directly compared to those in this study.

McKeough *et al.* [19] observed that sulfur compounds reacted with the stainless steel grid used in their experiments. In their analysis they concluded that the amount reacted was independent of pyrolysis conditions. It is unknown whether similar reactions occurred between sulfur compounds and the incoloy grid used in this study. It is assumed that the amount of sulfur retained on the grid would not vary with pressure, so that the influence of such reactions would have been the same for all data in Figure 8. The similarity of these data to those from the PSPR, which used a platinum sample holder, also indicate that the influence of such reactions is insignificant.

3.3 Comparison of experimental procedures

Experiments were conducted using both a pressurized single particle reactor and a pressurized grid heater. In this section the devices are compared. The data with Liquor 2 are particularly relevant since that sample was used in both devices.

Char yields. Char yields were generally higher in the PGH than in the PSPR. This may seem surprising in light of the higher

heating rate in the PGH. However, the pyrolysis time was about one-third as long in the PGH as in the PSPR. Secondary pyrolysis reactions, specifically those involving decomposition of inorganic species, had more time to take place in the PSPR resulting in a lower char yield.

The sensitivity of Liquor 2 to temperature was found to be the same in both reactors. Within the range of conditions studied, char yields for this liquor decreased by 4.8 wt% units for every 100°C increase in temperature.

As shown in Figure 5, the char yields measured in the PGH were closely related to the degree of liquor swelling and associated heat transfer. As such, the data on char yields as a function of pyrolysis pressure obtained from this device are not very valuable. It should be pointed out that this relation is specific to the PGH device used in this study. In other studies which use grid heaters, such as that of McKeough *et al.* [16-19], the grid was folded several times and the sample was sandwiched between the folds. This greatly improves heat transfer to the sample and minimizes swelling-related influences.

In the PSPR, experiments carried out on 10 mg droplets resulted in lower char yields than identical experiments with 35 mg droplets. This is due to the higher heating rate of the smaller sample. Three factors contributed to the more efficient heat transfer in these experiments:

- *Smaller sample size.* For a spherical particle, heat flux to the particle per unit mass is inversely proportional to the particle diameter. Smaller particles thus have more efficient heat transfer and higher heating rates than larger particles. Additionally, larger particles have more water that must be evaporated before pyrolysis and the overall heating rate is reduced.
- *Lower swollen volume.* The swollen volume of the char is less for smaller samples. Consequently, conductive heat transfer within the particle is more efficient and the center of the particle will

be heated more quickly. This has been demonstrated by Frederick and Hupa [4].

- *Limited interference by the sample holder.* The bowl-shaped sample holder used in experiments with larger droplets not only had to be heated itself, but it partially shielded the sample from radiation and from convection of the upwards-flowing gas. The platinum wire used with the 10 mg samples caused only limited interference.

Clearly, the experiments with smaller drops are more representative of conditions in an industrial unit. However, these experiments are more challenging to perform, particularly at high pressure. As discussed earlier, the droplets would not always remain on the wire hook.

Fate of elements. Despite differences between liquors and experimental techniques, the observed trends regarding release of carbon, sodium, potassium and sulfur as a function of pressure were remarkably similar in both the PSPR and PGH. Carbon release showed no significant variation with pressure. Sodium release decreased with pressure in both devices and sulfur release increased. Potassium release behaved somewhat differently between devices. No variation was observed with pressure in the PSPR but release increased with pressure in the PGH. This discrepancy is most likely due to the higher temperature used in the PGH.

Chemical analysis of chars formed in the PGH was somewhat more difficult than for those formed in the PSPR. Chars formed in the PGH first had to be removed from, or scraped off, the grid. This was particularly difficult for chars formed at 20 bar due to the low swelling and compactness of the char. In this study analysis of the char formed at 20 bar, 900°C was performed on a 2.4 mg sample, and the possibility of error for such small sample sizes is quite high.

4. CONCLUSIONS

Laboratory-scale investigation of black liquor pyrolysis behavior under pressurized conditions is possible. Of the two devices

employed in this study, the pressurized single-particle reactor is more representative of an industrial scale unit, particularly when small samples are used. The pressurized grid heater is good in the regard that the heating rate can be controlled, but char yields measured in this device were found to be dependent on the degree of liquor swelling. This effect can be minimized by ensuring that heat transfer to the sample is as uniform as possible. Using a folded net is one approach to solving this problem.

A shift in pyrolysis behavior was observed at roughly 800°C. Above this temperature, char yields were very dependent on furnace temperature. Additionally, increasing pyrolysis pressure resulted in higher char yields above 800°C while pressure had little influence in the low temperature experiments. This shift in behavior is due at least in part to decomposition of inorganic species in the char, particularly sodium carbonate, at higher temperatures. The carbonate decomposition reaction is thought to be retarded at higher pressures.

Decomposition of sodium carbonate by reaction with carbon is largely responsible for the fate of sodium during pyrolysis, as well. As temperature increases the rate of decomposition rises so more sodium is released to the gas phase. Similarly, less sodium was released at higher pressure since the decomposition reaction proceeds more slowly. Sulfur release, on the other hand, increased with pressure due to less opportunity for its capture in the less-swollen chars.

The practical implications of these results are that pressurized units operating at relatively low temperatures can be expected to give char yields similar to those from atmospheric units. High-temperature pressurized processes can expect more char production than their atmospheric counterparts. Sodium release should be of no more concern in a pressurized unit than in an atmospheric device, and for high-temperature systems decreased sodium release at higher pressures would be desirable. Under pressurized conditions increased sulfur release during pyrolysis would mean that sulfur enters the gas phase

earlier in the conversion process. This can be desirable for low-temperature gasification processes in which sulfur is recovered from the product gas.

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Paper IV

Influence of char formation conditions on pressurized black liquor gasification rates

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IV

Influence of char formation conditions on pressurized black liquor gasification rates

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Black liquor is a by-product which results from the pulping of wood in a solution of NaOH and Na₂S, and accounts for a significant fraction of the total energy production in papermaking countries. Conventionally, the liquor is concentrated and burned in large recovery boilers, but pressurized gasification of black liquor is a promising alternative. A key concern for pressurized gasification is how char formation conditions affect its resulting reactivity. We studied this and found that prolonged exposure to high temperatures decreases the reactivity by two mechanisms, thermal annealing and, in the presence of CO, soot buildup. Increased pressure during char formation also resulted in lower gasification rates, with chars formed at 20 bar displaying reactivities less than half of that of chars formed at atmospheric pressure. The results also suggest that kinetic behavior observed in previous studies of pressurized black liquor gasification has mistakenly been attributed to reaction kinetics alone, while in fact the char formation technique has influenced its reactivity.

Keywords: Black liquor, gasification, pyrolysis, char, pressure

INTRODUCTION AND BACKGROUND

Black liquor is the aqueous solution which remains after digestion of wood chips in a caustic solution of sodium hydroxide and sodium sulfide, and is inherent in the process of pulping wood for papermaking. During digestion, the organic material binding the wood fibers together dissolves into the solution and the fibers go on to become pulp. The spent pulping solution, the black liquor, is dark brown in color and has a solids content of 10 to 15%. Roughly half the dry weight is dissolved organic material while the other half consists of inorganic species, particularly sodium salts. After the digester, the black liquor is concentrated to 65-85% solids, at which point it is highly viscous and combustible, and then burned in large units called recovery boilers. The function of the recovery boiler is twofold: energy production and recovery of the pulping chemicals for recycle to the process. Black liquor is an important fuel in paper manufacturing countries. In Finland, for

instance, nearly 10% of all energy production comes from combustion of black liquor.

Gasification of black liquor by carbon dioxide or steam is a promising alternative to the recovery boiler. A pressurized gasification system with combined cycle power generation could double the electrical energy production from black liquor. Such a process would also have lower capital costs due to smaller equipment size [1]. However, detailed understanding of black liquor gasification, particularly under pressurized conditions, is limited. This study aims to clarify how conditions during the formation of black liquor char affect the char's subsequent reactivity during gasification under pressurized conditions.

Processes in black liquor gasification

The overall process of black liquor gasification occurs in three stages, as shown in Figure 1. During the drying stage, water in the black liquor evaporates, leaving only

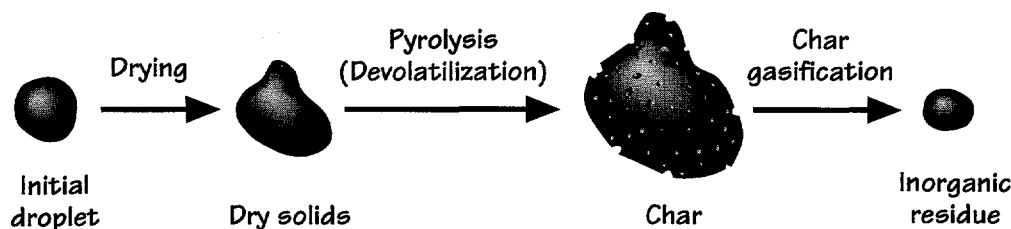


Figure 1. Stages of conversion during gasification of a black liquor droplet.

black liquor solids. During pyrolysis (devolatilization), volatile matter decomposes and is released into the gas phase, leaving a solid residue, or char. The liquor swells considerably during pyrolysis, and the volume of the char that is produced can be 30 or more times the initial volume of the liquor. During the final stage, char gasification, carbon and other species in the char react with CO_2 or H_2O to form gases. Gasification of black liquor char is strongly catalyzed by alkali species in the char, and proceeds at rates several orders of magnitude higher than those of pure carbon. The residue that remains at the end of gasification consists of inorganic salts, primarily sodium carbonate.

Earlier black liquor gasification research

Research into black liquor gasification kinetics began in the mid-1980's, when Li and van Heiningen investigated mass-transfer limitations during the gasification of black liquor char by carbon dioxide at atmospheric pressure [2]. They concluded that external mass-transfer to the char surface and inter-particle diffusion are negligible, but that intra-particle diffusion may limit the gasification rate for large particles and in the char bed of a recovery boiler. They subsequently measured gasification kinetics for gasification of black liquor chars with CO_2 under atmospheric conditions in the temperature range 600-800°C [3,4]. Black liquor chars were found to be much more reactive than coal chars doped with sodium carbonate due to finer dispersion of the sodium, which catalyzes the gasification reactions. The gasification rate could be described by Langmuir-Hinshelwood type kinetics. During the same period Goerg and Cameron measured the rate of CO_2 gasification of kraft char in molten sodium carbonate over the temperature range 927-1010°C [5].

Kinetics of black liquor char gasification with steam under atmospheric conditions have also been studied by Li and van Heiningen [6]. As with CO_2 gasification, it was found that the measured rates could be described by Langmuir-Hinshelwood kinetics. More recently, van Heiningen, *et al.* investigated the influence of pyrolysis rate on the reactivity of the resulting char during atmospheric gasification by steam [7]. The rate of pyrolysis was found to influence the gasification behavior as a consequence of the degree of sodium dispersion in the char.

Gasification of black liquor by carbon dioxide under pressurized conditions has been studied by Frederick and Hupa [8] and Frederick *et al.* [9] over the range 1-30 bar. Whitty *et al.* studied pressurized black liquor gasification by steam [10] and in mixtures of steam and carbon dioxide [11]. Saviharju *et al.* investigated pressurized gasification of chars formed by fast pyrolysis at atmospheric pressure [12]. In all these studies the rate of gasification was found to decrease with total pressure.

Scope of this study

In previous studies of black liquor gasification the focus has been on the reaction of the char with carbon dioxide or steam. To facilitate this, a char was prepared by pyrolysis of black liquor and was then gasified. In many cases the char was prepared in one reactor, then removed and transferred to the gasification device. It has long been recognized for biomass and coal that pyrolysis conditions, particularly pressure, heating rate and holding time dramatically affect the reactivity of the resulting char [13,14]. The results of van Heiningen *et al.* [7], Saviharju *et al.* [12] and Whitty and Sandelin [15] indicate that this is the case for black liquor, as well. Moreover, Chen *et al.* [16] have demonstrated that char produced by pyrolysis of wood in nitrogen is much less reactive during subsequent

TABLE 1. SAMPLE COMPOSITIONS (WT.%)

Element	Liquor #1	Pre-formed char
C	34.6	31.5
H	3.4	2.0
N	0.07	n/a
Na	17.2	18.9
K	3.2	n/a
S	5.4	4.0
Cl	0.3	n/a
Other (by difference)	35.8	43.6

gasification than char which is produced in simultaneous pyrolysis/gasification of wood in the presence of steam.

In industrial scale gasification systems black liquor would presumably not be pyrolyzed in one reactor then later gasified. Rather, the liquor would be introduced directly into the gasifying atmosphere and undergo all three stages of the overall process — drying, pyrolysis and char gasification — in the reactive gas. Hence we make a distinction between *stagewise gasification*, in which pyrolysis and char gasification are carried out separately, and *simultaneous pyrolysis and gasification*, in which all stages of the overall process occur in the reactive gas. The focus of this study is to investigate the effect of pyrolysis conditions on black liquor reactivity under pressurized conditions, particularly with regard to differences between stagewise and simultaneous pyrolysis and gasification.

EXPERIMENTAL

In this study black liquor chars were formed and gasified under various conditions in a laboratory-scale reactor. Gasification was carried out under identical conditions for a particular series of runs in order to identify how char formation conditions affect the subsequent reactivity.

Samples

Three samples were used in this study: two concentrated black liquors and one pre-formed char. One liquor was from a Finnish softwood cook while the other was a softwood/hardwood mix from a mill in the southeastern United States. The liquors were concentrated by heating in an oven at 105°C to 73.2% and 68.6% dry solids, respectively. The pre-formed char was

made from liquor from kraft pulping of hardwood at a mill in the southeastern United States and was formed by pyrolysis in nitrogen at 900°C in a drop-tube reactor [17]. The compositions of one of the liquors and the pre-formed char are given in Table 1. The composition of the other liquor was not available. Note that the sodium content of black liquors is much higher than for other fuels.

Equipment

The experiments in this study were carried out in a pressurized thermogravimetric reactor (PTGR, Figure 2). The PTGR has a maximum operating pressure of 100 bar and a maximum temperature of 1100°C. Up to five gases can be fed into the reactor (17 mm i.d.), and by means of a bypass line around the reactor the gas composition can be quickly changed. A water-cooled, helium-purged sample lock is situated above the reactor, and the sample is placed into the PTGR via an opening in the lock. A small, electrically-driven winch lowers and raises the sample into and out of the heated section of the reactor. Details regarding this device have been published elsewhere [8,10].

Experimental procedure

The experiments involved two phases:

- Phase I: The sample was immersed into a hot, non-oxidative environment containing either pure nitrogen or a CO/N₂ mixture. The concentrated liquors dried and devolatilized (pyrolyzed) during this stage. The pre-formed char experienced some devolatilization beyond that which occurred during its formation.
- Phase II: The sample was in a reactive gas consisting of 20% CO₂, 4% CO and

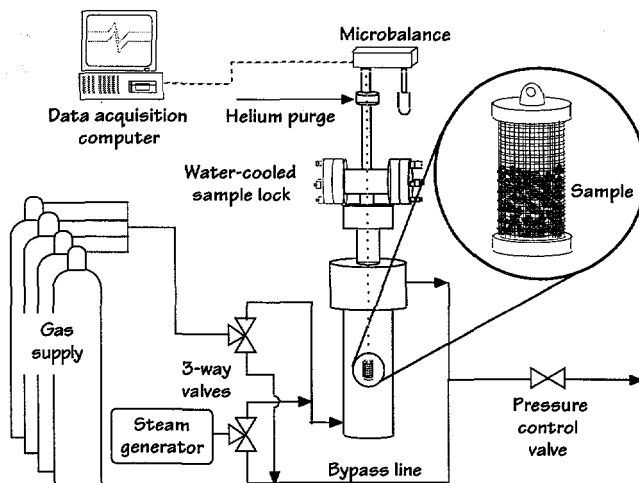


Figure 2. Pressurized thermogravimetric reactor. Max 100 bar, 1100°C.

76% N₂. Gasification of the char took place during this phase. The sample was allowed to react until the weight stabilized, indicating the completion of gasification.

The experiments consisted of either *Phase I* followed by *Phase II*, or just *Phase II* alone. In experiments with *Phase II* alone, the sample was immersed directly into the gasification mixture and simultaneously dried, pyrolyzed and gasified. In experiments which also included *Phase I*, either the sample was removed from the reactor between the phases, or the sample was left in the reactor while the gas composition was changed to that for *Phase II*.

For concentrated liquor samples, 50 mg of the liquor was painted onto the stem of a cylindrical platinum sample holder (Figure 2). The outer netting of the holder was fitted concentrically around the core and the cap was placed on top, thereby forming a "cage" for the sample. This was necessary in order to maintain the shape of the sample as it swelled during pyrolysis. If the sample were to swell outside the boundaries of the sample holder, changes in the shape of the char during subsequent gasification would influence the dynamic buoyancy of the sample, thereby making the weight vs. time data difficult to interpret.

For experiments which started with a pre-formed char, roughly 100 mg of the sample was placed between the core and netting of the sample holder and the cap was installed.

The sample holder was put into the sample lock of the PTGR and the device was sealed shut. The reactor was brought to the desired pressure and temperature and the desired gas mixture was fed through the reactor at 3.0 liters (STP)/min. The sample was rapidly lowered from the sample lock into the hot reactor. Roughly 30 seconds were necessary for the microbalance to stabilize and give a signal after lowering the sample. As a result, no weight-loss data is available for the first half minute of each experiment. The exact amount of time required to obtain a signal was noted for each experiment.

Upon completion of the experiment the sample was lifted back into the sample lock and the device was depressurized. The residue which remained after complete conversion was white and consisted of inorganic material, primarily sodium carbonate. The mass of this residue was recorded.

Analysis of the influence of film mass transfer and pore diffusion effects on the overall rate of gasification in this system was performed in two previous studies [8,10]. In both cases it was concluded that the observed rate of gasification is controlled by the kinetics of the gasification reaction, and that diffusion effects are negligible. The current study involves temperatures lower than those used in these previous studies, so it can safely be assumed that film mass

transfer and pore diffusion do not influence the observed rates in this work.

Data analysis

Figure 3 shows the weight-loss curves for two types of experiments, one involving *Phase I* followed by *Phase II*, and one involving *Phase II* alone. The dashed portion of each curve is a straight line between the initial sample mass and the first data point. For each case, the liquor has been broken down into moisture, volatile material, gasifiable char and inorganic residue. The water content of the initial liquor was determined by drying at 105°C until no further weight loss could be detected. The mass of the inorganic residue is simply the mass of the material that remained after full conversion.

For experiments with *Phase I* followed by *Phase II*, the mass of gasifiable char was determined by taking the difference between the maximum and minimum masses recorded after switching the gases from *Phase I* to *Phase II*, as shown in the figure. The mass of volatile material was determined by difference between the original sample mass and the masses of the moisture, gasifiable char and inorganic residue.

For the case of simultaneous pyrolysis and gasification (*Phase II* only) the initial mass of char was determined from the change in the slope of the weight vs. time curve. The weight-loss curve decreased dramatically during the first 50 seconds or so of the experiment, corresponding to mass loss as a result of drying and devolatilization. After this time the slope of the weight-loss curve

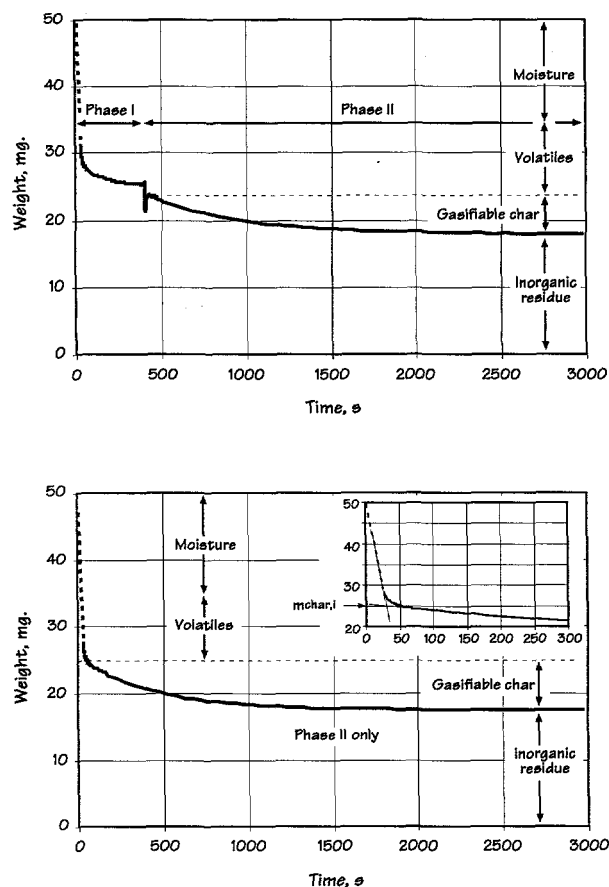


Figure 3. Weight loss curves for the two types of gasification experiments. Upper curve: Phases I and II. Lower curve: Simultaneous pyrolysis and gasification (*Phase II* only). Initial sample mass in both cases was 50 mg.

became much less severe, indicating that pyrolysis was complete and that char gasification had begun. This can be seen in the inset of the lower curve in Figure 3. The initial mass of char was determined by finding the intersection of lines fit to the pyrolysis section of the curve and the initial part of the gasification curve, as shown in the figure. The mass of gasifiable char was determined by subtracting the mass of inorganic residue from the initial mass of char, and volatiles mass was again calculated by difference.

In this work the results are presented as plots of the char gasification rate as a function of conversion for conversions between 10% and 90%. The gasification rate at any particular conversion is defined as the slope of the weight-loss curve at that point divided by the total mass of char gasified and is expressed in units of %/min:

$$\text{rate} = (dm/dt)/m_{gc,i} \quad (1)$$

where m is the mass of the sample at time t and $m_{gc,i}$ is the initial mass of gasifiable char. For every two successive data points the instantaneous rate was calculated. This was plotted versus conversion and a 3rd order polynomial equation fit to the data to form a smooth curve. Correlation coefficients (r^2) for the curve fits were generally above 0.90.

RESULTS AND DISCUSSION

In this study, conditions during black liquor char formation, specifically the duration of heating, CO concentration and total pressure, were investigated with regard to their influence on the char's subsequent gasification rate.

Simultaneous vs. stagewise gasification: Influence of the duration of exposure to high temperature

A key objective of this study was to investigate the reactivity of chars formed during *stagewise* pyrolysis and gasification versus the reactivity of chars formed during *simultaneous* pyrolysis and gasification. Another way of considering this is to study how the char's gasification rate changes with the amount of time the sample is in a hot environment, during which it pyrolyzes, prior to gasification. In this study this corresponds to the duration of *Phase I*. Simultaneous pyrolysis and gasification corresponds to the case where *Phase I* does not exist at all.

A series of experiments was performed in which chars were formed during *Phase I*, which was varied between 0 and 1000 seconds. The gas during this phase was a mixture of 10% CO in nitrogen. The samples were subsequently gasified by CO₂ in *Phase II*. The rate of gasification was determined and plotted as a function of

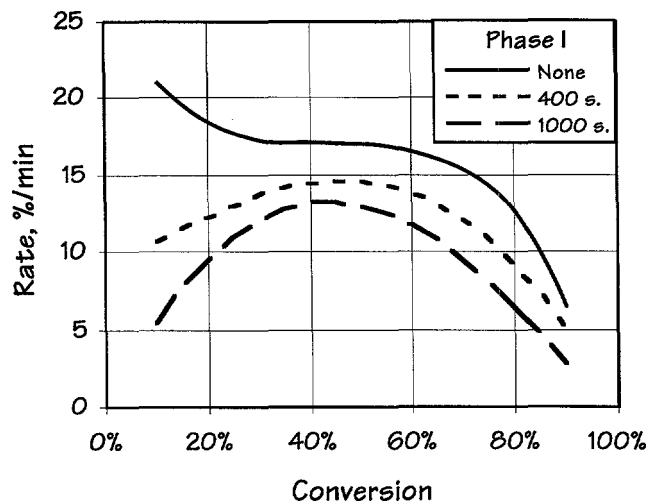


Figure 4. Influence of Phase I duration on char gasification rate when CO is present in the Phase I gas. Phase I: 20 bar, 750°C, 10% CO in nitrogen. Phase II: 20 bar, 750°C, 20% CO₂, 4% CO, 76% N₂.

char conversion. The results for *Phase I* durations of 0, 400 and 1000 seconds are shown in Figure 4. Clearly, the more time spent at high temperatures prior to gasification, the less reactive the char. Conversion was fastest for the case of simultaneous pyrolysis and gasification.

Saviharju *et al.* [12] reported that the presence of carbon monoxide during so-called "hot treatment" of the char, particularly for longer periods of time, results in deposition of soot on the char as a result of the Boudouard reaction:



This soot, in turn, decreases the initial rate of gasification. This effect can be seen in Figure 5, which shows the weight-loss data

for the first 300 seconds of *Phase II*. The initial increase in sample weight is a result of buoyancy effects as the gas composition was changed. The longer the char was exposed to the CO/N₂ atmosphere, the more sluggish the beginning of gasification. This is also discernible from the shapes of the rate vs. conversion curves in Figure 4. Chars which experienced *Phase I* display a low initial rate of gasification whereas the char which was not exposed to the soot-forming environment has the highest rate at the beginning of gasification. The low initial rate is due to the low reactivity of the soot formed on the char. Gasification of this soot is presumably non-catalyzed and therefore is much slower than gasification of the char, which is strongly catalyzed by alkali species.

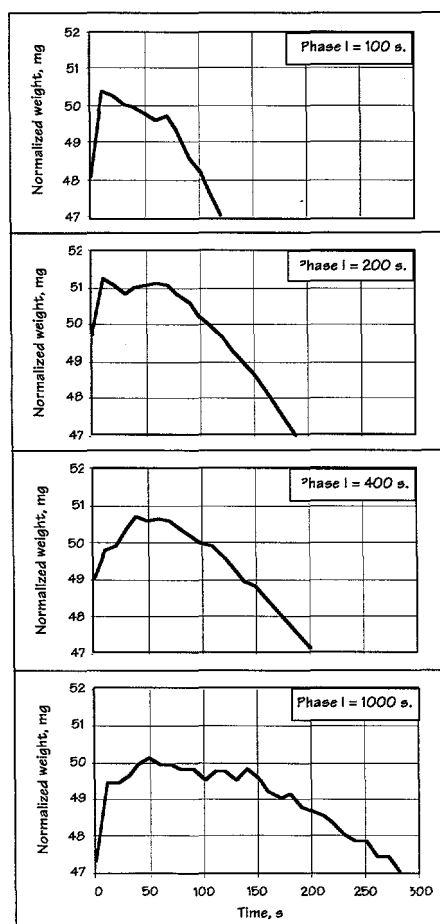


Figure 5. Weight-vs-time data for the first 300 seconds of *Phase II*. *Phase I* conditions: 20 bar, 750°C, 10% CO in N₂. *Phase II*: 20 bar, 750°C, 20% CO₂, 4% CO, 76% N₂. The initial sample mass was normalized to 100 mg.

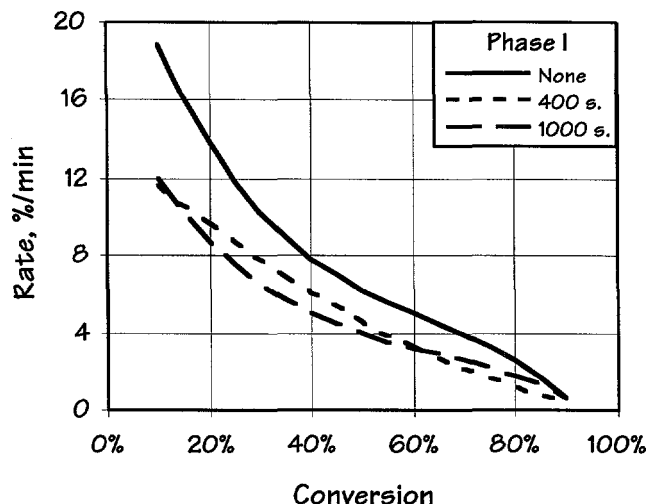


Figure 6. Influence of Phase I duration on char gasification rate when Phase I gas is pure N_2 . Phase I: 20 bar, 725°C, 100% N_2 . Phase II: 20 bar, 725°C, 20% CO_2 , 4% CO , 76% N_2 .

It is desirable to clarify to what extent soot deposition is responsible for the observed decrease in char reactivity, as opposed to possible annealing effects resulting from prolonged exposure to high temperatures. Therefore a series of experiments similar to that described above was carried out, but this time *Phase I* was carried out in pure nitrogen. The results are given in Figure 6, which shows the rates of char conversion for experiments with different durations of *Phase I*. As seen in the figure, chars which spent more time in the hot environment exhibited lower gasification rates. However, the decrease is not as severe as when *Phase I* was conducted in a CO -containing atmosphere (Figure 4). This is particularly notable at lower conversions. This suggests that while thermal effects do decrease the char's reactivity, soot formation during prolonged exposure to high temperatures in the presence of CO has an even larger impact on the gasification rate.

Influence of CO partial pressure

As noted in the previous section, the gas composition during char formation influences the reactivity of the resulting char. In order to study this effect more closely a series of experiments was performed in which chars were formed at the same total pressure, but with different partial pressures of carbon monoxide. The chars were then gasified under identical conditions.

Figure 7 shows the influence of carbon monoxide in the *Phase I* gas. The three samples in the figure were all formed at 20 bar, 750°C for 400 seconds in a mixture of nitrogen and carbon monoxide in the amount shown. Clearly, the higher the partial pressure of CO in the gas the slower the subsequent gasification. The time to reach 50% conversion is roughly half as long for the char formed in pure nitrogen as for the char formed in nitrogen containing 10% CO . The reason for this is again due to soot formation on the char during *Phase I*. As the partial pressure of CO increases, more solid carbon forms to keep the equilibrium of the Boudouard reaction.

A better understanding can be gained from Figure 8, which shows the weight-vs-time curve for the first 500 seconds of *Phase II*. The initial weight of each sample has been normalized to 100 mg. Differences in the sample weights in the figure are a result of higher volatiles yields for char formation in the absence of CO . For the case of pure nitrogen, weight loss occurs immediately. Addition of CO to the gas results in retardation of the initial period of gasification as a result of soot formation on the char. This is also visible in the shapes of the curves in Figure 7. Those samples exposed to the soot-forming environment display a low initial rate of gasification.

Saviharju *et al.* suggest that soot on the char retards the gasification rate up to a certain

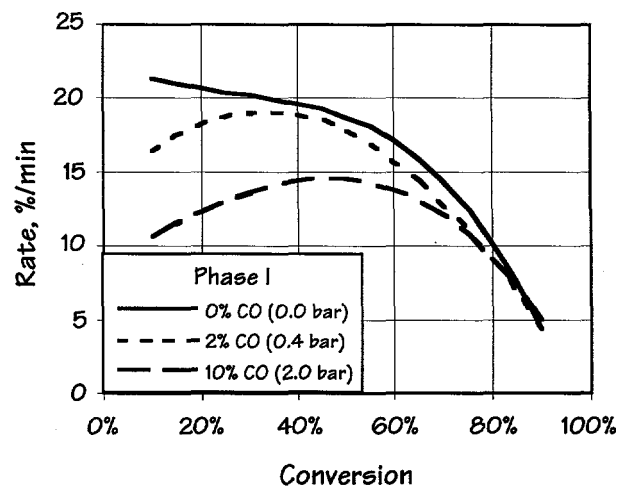


Figure 7. Influence of CO concentration during Phase I on the char gasification rate. Phase I: 20 bar, 750°C, 400 s, N₂ carrier. Phase II: 20 bar, 750°C, 20% CO₂, 4% CO, 76% N₂.

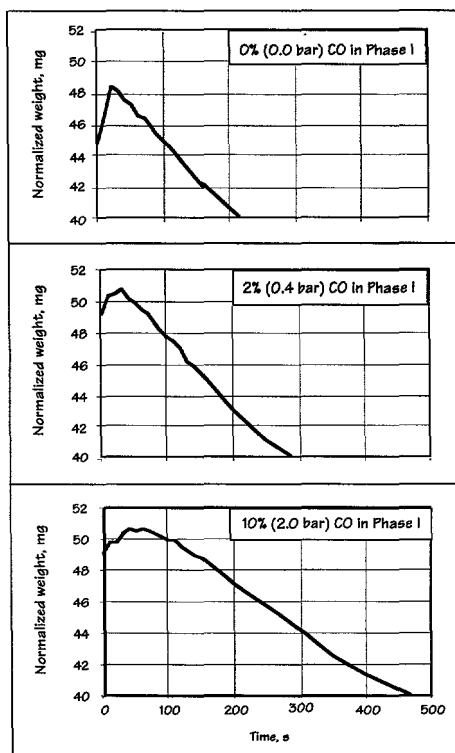


Figure 8. Weight-vs-time data for the first 500 seconds of Phase II after Phase I had varying levels of CO. Phase I: 20 bar, 750°C, 400 s, N₂ carrier. Phase II: 20 bar, 750°C, 20% CO₂, 4% CO, 76% N₂.

conversion, or that perhaps the hot treatment in a CO-containing atmosphere affects the dispersion of that sodium catalyst in the char. Figure 7 supports the first of these contentions. Up to 60% conversion the rates for the experiments are quite different. Beyond 60% conversion, however, the rates are nearly identical. For the three runs in the figure, the time to reach 60% conversion varied by a factor of 1.6. But the times required to proceed from 60% to 90% conversion were within 7% of one another. This indicates that char properties are similar at higher conversions. Differences in dispersion of the catalyst would presumably be noticeable throughout the entire range of conversion. Based on these results the retarding effect of the soot seems a more likely explanation for the observed differences.

Influence of total pressure

In most of the previous studies regarding pressurized black liquor gasification reactivity, the sample material has been black liquor char formed under atmospheric conditions. In a pressurized gasification system, however, the char would be formed under pressure, rather than at atmospheric conditions. We know from previous research that pyrolysis pressure influences the structure of black liquor char, with higher pressures yielding a more compact, less porous char. [15] Moreover, Cai, et al. [14]

have reported that coal char reactivity decreases as the hydrolysis pressure increases over the range 1-20 bar. In light of this, a study was carried out to see how the pressure during char formation affects its reactivity during gasification.

A series of experiments was performed in which black liquor chars were formed by heating for 30 seconds at 750°C under various pressures (1, 2, 5, 10 and 20 bar) in a gas consisting of 10% CO in N₂. The chars were collected and then gasified at 20 bar, 700°C by a procedure involving 200 seconds of *Phase I* followed by *Phase II*. The gas during *Phase I* was 10% CO in nitrogen and during *Phase II* was 20% CO₂, 4% CO and 76% N₂. Though the chars were further exposed to high temperature as a result of this procedure, additional devolatilization was limited by the high pressure and lower temperature and any soot formation would have affected the samples equally. Soot formation during the 30 second char formation period is assumed to be too limited to influence reactivity.

The rates during gasification are shown as a function of conversion in Figure 9. Clearly, chars which are formed at higher pressures are less reactive under gasification conditions. The rate at 50% conversion was over two times faster for the char formed at 1 bar than for the char formed at 20 bar. The gasification rate of chars formed under

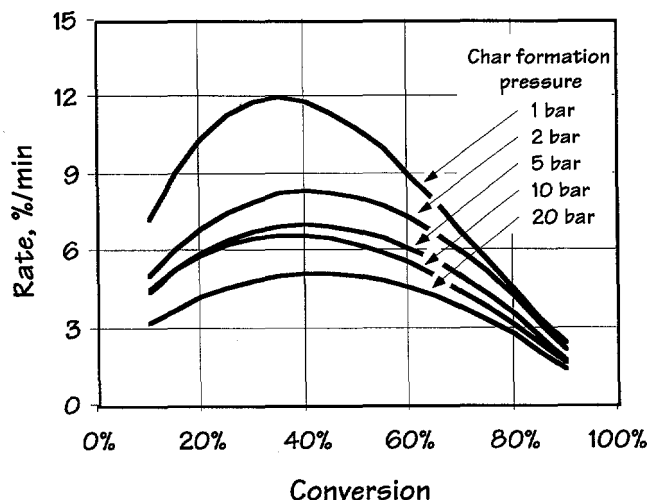


Figure 9. Influence of char formation pressure on char gasification reactivity. Chars formed by exposure for 30 seconds at 750°C at the pressure indicated. All chars gasified at 20 bar, 700°C with 20% CO₂, 4% CO and 76% N₂.

pressure was lower throughout the entire range of conversion, as opposed to having a pressure-dependent latent period at the beginning of gasification, after which all samples display similar reaction profiles. This indicates that the observed differences are due to intrinsic char properties rather than, for example, buildup of an unreactive layer on the char surface.

The reason for the decrease in reactivity as formation pressure increases is thought to be related to structural differences in the chars. It was noted that as the char formation pressure increased the liquors swelled less, and analysis by scanning electron microscopy revealed that the microstructure of the resulting char became less feathery and more compact. Data from van Heiningen, *et al.* [7] indicates that chars produced from liquors with a high tendency to swell during pyrolysis have more internal surface area per unit mass than less swollen chars. This would explain the observed difference in gasification rates. Chars with a higher internal surface area have more area available for reaction and thus a higher overall gasification rate. Unfortunately, the sample sizes in this study were too small to be able to measure the internal surface areas of the chars.

It is also possible that tars which form during pyrolysis more readily recondense on the char surface at higher pressures. This has been observed for biomasses and occurs because the tars are not able to exit the sample as easily at higher pressure due to the lower gas diffusivity. However, if this were the case one would expect to see a change in the char yield as a function of pressure. This was not observed in a previous study performed under conditions similar to those used here. Moreover, one would expect that once the recondensed tars had been reacted off, the resulting chars

would display similar reactivities at higher conversions. This was not observed. Although tar recondensation may increase with increasing pyrolysis pressure, its impact on char reactivity is insignificant.

Reevaluation of previous experimental techniques

The current study demonstrates that char formation conditions can significantly impact the subsequent reactivity of black liquor chars during gasification. Many earlier experimental studies of pressurized black liquor gasification kinetics used a char formed at atmospheric pressure [8-11]. The char was then exposed to high temperature in a CO/N₂ mixture prior to gasification in order to stabilize the weight signal. We decided to check if the pressure during this heating period influenced the rate of char gasification.

Four experiments were performed, each starting with a char formed at 1 atmosphere as in the earlier studies. The pressures of *Phase I* and *II* were varied as shown in Table 2, and the sample was kept in the reactor for the duration of both phases. In cases where the pressures were different, the pressure was changed immediately after the start of *Phase II*. *Phase I* involved treatment at 650°C in a 10% CO / 90% N₂ mixture for 400 seconds at the pressure indicated. *Phase II* was carried out at 650°C in 20% CO₂, 4% CO with nitrogen as a carrier gas.

If the char gasification rate were independent of the pressure during *Phase I*, one would expect experiments 1 and 2 to display similar rates, as well as 3 and 4. Cases 1 and 4 are similar to those that have been used in previous studies that have concluded that the gasification rate decreases by roughly a factor of 3 over the range 1 to 20 bar [8-10].

TABLE 2. CONDITIONS FOR REEVALUATION OF EARLIER EXPERIMENTAL TECHNIQUES

Experiment number	Char formation pressure, bar	Phase I pressure, bar	Phase II pressure, bar
1	1	1	1
2	1	20	1
3	1	1	20
4	1	20	20

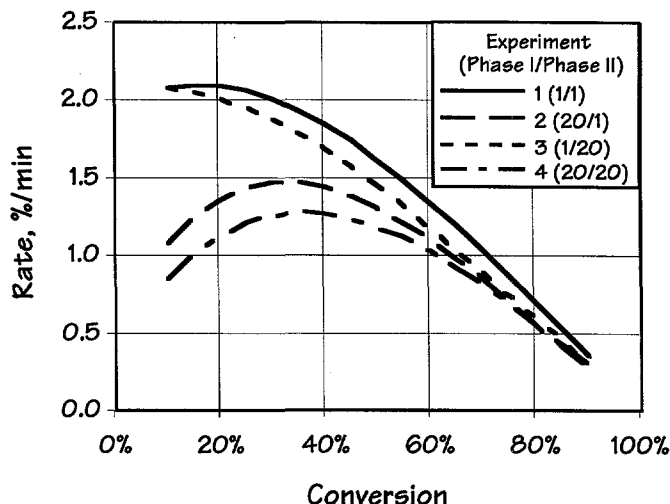


Figure 10. Influence of Phase I pressure on the gasification rate of pre-formed chars. Phase I: 650°C, 400 s., 10% CO in N₂. Phase II: 650°C, 20% CO₂, 4% CO, 76% N₂.

The gasification rates vs. conversion for these experiments are shown in Figure 10. Clearly, experiments 1 and 2 did not behave in the same manner. The char which experienced a *Phase I* pressure of 20 bar had a lower rate than that which experienced a *Phase I* pressure of 1 bar. The same behavior can be seen for experiments 3 and 4. These results indicate that the trends observed in previous studies and attributed to differences in pressure during gasification are actually largely due to pressure differences during the heating period prior to gasification.

A better approach would be to limit the time and number of heating cycles prior to gasification, and to avoid using CO in the heating gas. Experiments 1 and 3 are more suitable for focusing on pressure effects during gasification than are experiments 1 and 4, since pre-gasification treatment has been the same in these. Experiments 3 and 4 would also be suitable, but the *Phase I* pressure of 20 bar surely coated the char with a layer of soot, an effect which is less for experiments 1 and 3. This is evidenced by the initial shapes of the rate curves. Those with *Phase I* pressures of 20 bar initially react more slowly due to the presence of soot.

Considering experiments 1 and 3, it can be seen that although increased gasification pressure does seem to result in slower gasification, the decrease is much less than previously reported. More study is

necessary to clarify the influence of pressure during gasification on the rate of reaction.

CONCLUSIONS

The conditions at which black liquor char is formed greatly impact its resulting reactivity during gasification. Prolonged exposure to high temperatures significantly decreases char reactivity, especially if carbon monoxide is present in the gas. Carbon monoxide reacts to form solid carbon (soot) and carbon dioxide. The soot that is generated over long times coats the surface of the char and must be gasified away before the char itself can begin to gasify. This effect is more pronounced at higher CO partial pressures, where the rate of soot formation is higher. Unlike black liquor char gasification, reaction of the soot layer is uncatalyzed and constitutes a large fraction of the total gasification time, even though the soot itself accounts for a very small fraction of the overall mass.

Prolonged exposure of char to high temperature also reduces its reactivity because of thermal annealing which takes place. The char becomes less porous, resulting in lower surface area available for reaction. The char structure may also undergo some rearrangement on the molecular level, though it is unclear to what extent this occurs and how it affects reactivity. For the conditions studied, the presence of carbon monoxide in the char formation gas contributed more to the

reactivity decrease at longer durations than did thermal annealing of the char.

Increasing the pressure during char formation results in a tighter, more compact char. This char, in turn, exhibits lower gasification rates. Presumably, the compactness and low porosity of the char is correlated to a lower internal surface area available for reaction. Measurement of the internal surface areas of the chars are necessary before this can be proven quantitatively, however.

In previous studies which have reported decreases in gasification rates with higher gasification pressures, the cause was mistakenly interpreted to be due to the kinetics of the gasification reactions. These studies were actually measuring decreases largely resulting from different pressures during heating of the sample prior to gasification. The presence of carbon monoxide during this heating resulted in soot formation which significantly decreased the observed reactivity of the char. The results indicate that the rate decrease due to gasification pressure over the range 1-20 bar is much less than earlier observed. More study is necessary to quantify the influence of gasification pressure on the rate of reaction.

Black liquor pyrolysis conditions will influence the overall performance of an industrial gasifier, particularly with regard to the final degree of conversion achieved for a given residence time. Though prolonged exposure to high temperature has been shown to decrease reactivity, this effect will likely be minor in industrial scale gasifiers where exposure times are only a few seconds. Yet it is an important factor to consider in laboratory-scale investigation of black liquor pyrolysis and gasification behavior.

NOMENCLATURE

m	instantaneous sample mass, mg
$m_{gc,i}$	initial mass of gasifiable char, mg
t	time, s

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Paper V

Morphological studies of black liquor char during formation and conversion

Presented at Finnish-Swedish Flame Days, 3-4 September 1996, Naantali, Finland.

Also presented at the Nordic Seminar on Thermochemical Conversion of Solid Fuels, 4-5 December 1996, Trondheim, Norway.

V

Morphological Studies of Black Liquor Char during Formation and Conversion

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1. INTRODUCTION

Combustion of black liquor is an important industrial process, particularly in the Nordic countries. The annual global production of black liquor is roughly 200 million tons. In Finland, almost 10% of all the energy is derived from black liquor combustion. Also, the black liquor utilization technology is a top know-how area of the Finnish equipment manufacturers. A good third of all recovery boilers sold on the world market in the recent years have been delivered by A. Ahlstrom Corporation and Tampella Power.

Within the past decade or so a number of alternative recovery processes have been proposed for black liquor. The majority have focused on black liquor gasification, in which the liquor is converted by steam or carbon dioxide under reducing conditions rather than by air in oxidizing conditions. Such a system can achieve a higher electrical/thermal energy ratio per unit mass of black liquor than can conventional processes. The gasification schemes fall into two classifications: those that operate above the melting point of the inorganic material in the liquor (high-temperature processes) and those that operate below the melting point (low-temperature processes). Either of these processes may operate under pressurized conditions, which has the advantages of increased electrical/thermal output and lower capital costs due to smaller equipment sizes.

In a gasification system black liquor undergoes three stages of conversion: drying, pyrolysis and char gasification. The char gasification stage is the slowest of the three and at very low temperatures may take several hours for complete conversion [1-4]. Pyrolysis is important since most of the physical changes take place during this stage and conditions during pyrolysis will influence the subsequent reactivity of the char [5,6].

The aim of this study has been twofold. First, the morphology of black liquor after char formation has been studied. This is relevant not only to gasification systems but to conventional combustion systems as well. The second objective has been to investigate how the structure of black liquor char changes as the char is converted by gasification. This information is important for low-temperature gasification schemes where the rate of

conversion is limited by the kinetics of the gasification reaction rather than by mass-transfer. Additionally the data is of significance to lower regions of a recovery boiler in which much of the char conversion occurs through gasification.

2. EXPERIMENTAL

2.1 Black liquor sample

The black liquor used in this study came from the pulping of a softwood/hardwood mix in a mill in the southeastern United States. Prior to performing the experiments the liquor was concentrated from approximately 50% solids to 68.6% solids by heating in a laboratory oven at 105°C.

2.2 Experimental apparatus

The experiments in this study were carried out in a pressurized thermogravimetric reactor (PTGR, Figure 1). The PTGR has a maximum operating pressure of 100 bar and a maximum temperature of 1100°C. Up to five gases can be fed into the reactor (17 mm i.d.), and by means of a bypass line around the reactor the gas composition can be quickly changed. A water-cooled, helium-purged sample lock is situated above the reactor, and the sample is placed into the PTGR via an opening in the lock. A small, electrically-driven winch lowers and raises the sample into and out of the heated section of the reactor. More detail regarding this device is available elsewhere [2,4].

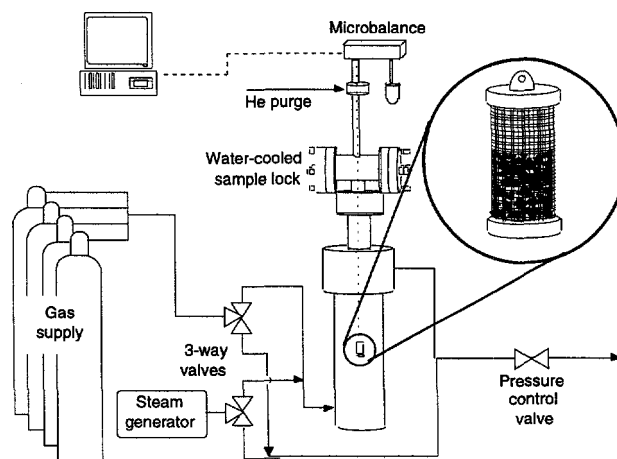


Figure 1. Schematic drawing of the pressurized thermogravimetric reactor. Max. pressure: 100 bar. Max. temperature: 1100°C.

2.3 Experimental procedure

In the experiments, roughly 50 mg of strong black liquor was painted onto the stem of a cylindrical platinum sample holder (Figure 1). The outer netting of the sample holder was installed and the cap was placed on the top, thereby forming a "cage" for the sample. This was necessary in order to maintain the shape of the sample as it swelled during

pyrolysis. If the sample were to swell outside the boundaries of the sample holder it would influence the dynamic buoyancy during subsequent gasification, thereby making the weight vs. time data impossible to interpret.

The sample holder was placed into the sample lock of the PTGR and the device was sealed shut. The reactor was brought to 700°C and pressurized if necessary and a gasifying mixture of 20% CO₂, 4% CO and 76% N₂ was passed through the reactor tube at 3.0 liters (STP)/min. The sample was rapidly lowered from the sample lock into the hot reactor, and over the next 50–60 seconds pyrolyzed to form a char which subsequently began being gasified. After entering the reactor, roughly 30 seconds were necessary for the microbalance to stabilize and give a signal after lowering the sample. After the desired amount of time, the sample was lifted back into the sample lock and the device was depressurized and allowed to cool.

To investigate changes in char morphology during conversion a series of experiments was performed with each being carried out to a different conversion. Because of uncertainty in ascertaining the conversion of the sample *in situ* it was decided to perform each experiment for a predetermined amount of time. This time required to reach a particular conversion was estimated based on an initial run which was allowed to continue to complete conversion. Target char conversions for the experiments were 20%, 40%, 60%, 80% and 100%. Additionally, an experiment was performed in which the sample was kept in the reactor for just 50 seconds and this was considered to correspond to 0% conversion.

2.4 Data analysis

To determine the actual degree of conversion of a particular experiment, the amount of gasifiable material remaining at the end of the experiment was first determined by subtracting the mass of ash from the mass of the residue. The percentage of ash in the original sample was determined in a preliminary experiment in which the sample was completely gasified.

The initial mass of char was determined from the weight vs. time curve for each experiment. The weight-loss curve decreased dramatically during the first 50 seconds or so of the experiment, corresponding to mass loss as a result of drying and devolatilization. After this time the slope of the weight-loss curve became much less severe, indicating that pyrolysis was complete and that char gasification had begun. This can be seen in Figure 2, which shows the first 250 seconds of the mass vs. time curve for a typical experiment. No data was obtained for the first 27 seconds due to the time required for the microbalance to stabilize after lowering the sample, so the dashed portion of the curve is simply a straight line between the initial weight and the first data point. The initial mass of char was determined by finding the intersection of lines fit to the pyrolysis section of the curve and the initial part of the gasification curve, as shown in the figure.

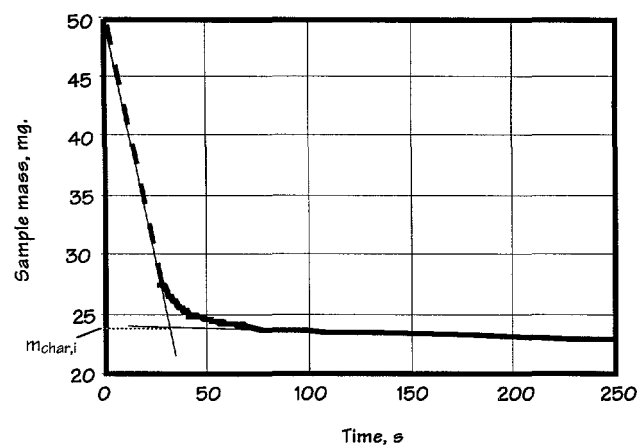


Figure 2. The first 200 seconds of the mass vs. time curve for a typical experiment.

The target and actual conversions obtained for the experiments are shown in Table 1. Generally the true conversion was close to the target conversion, and differences between the target and actual conversions can be attributed to variations between experimental runs. For both the atmospheric and pressurized runs the ordering of conversions is suitable for investigation of changes in char properties during conversion.

Table 1. Actual and target conversions for the experiments

Target conversion	Actual conversion	
	Atmospheric	20 bar
0%	0%	0%
20%	26%	18%
40%	45%	38%
60%	77%	62%
80%	84%	70%
100%	100%	100%

2.5 SEM analysis

Upon completion of an experiment the sample holder was removed from the PTGR and the residue was collected. The microstructure of the char was then analyzed with a scanning electron microscope (SEM). Efforts were made to choose representative samples that were touching neither the net nor the core of the sample holder. The samples were analyzed at two magnifications: 500x and 3000x. Additionally, the distribution of elements in the sample was determined simultaneously by x-ray analysis.

In some instances specific structural features such as granules or fibers were observed on the sample. In these cases a backscattered image of the sample was created to see if the

composition of the special features was different than the rest of the material. Heavier elements appear lighter in color on a backscattered image.

3. RESULTS AND DISCUSSION

The experimental data was collected and analyzed to see what morphological changes occurred during formation and conversion of black liquor char. Most of the results are presented as SEM photos of the samples themselves. Due to necessary scaling of the pictures the magnifications shown in the figures are not correct. Efforts have been made to provide the true magnification in the photos presented here.

3.1 Black liquor char morphology after pyrolysis

Pyrolysis of black liquor is an extremely complex phenomenon, with many physical and chemical processes taking place simultaneously. Heat transfer to and within a black liquor particle, mass transfer within and out of the particle, swelling of the liquor, gas environment and liquor-specific properties all influence the behavior of black liquor during pyrolysis [7]. On account of this it is a challenging phenomenon to study.

The current study focuses primarily on changes in char morphology during conversion by gasification, which by the nature of the experiments in this study also involves pyrolysis. The structure of the char resulting from pyrolysis can be seen in the next section in the cases of 0% char conversion. Pyrolysis as carried out in this study is much more representative of the case in a full-scale unit, where pyrolysis takes place in a reactive gas, than studies in which experiments are performed in an inert atmosphere.

3.2 Morphological changes during black liquor char conversion

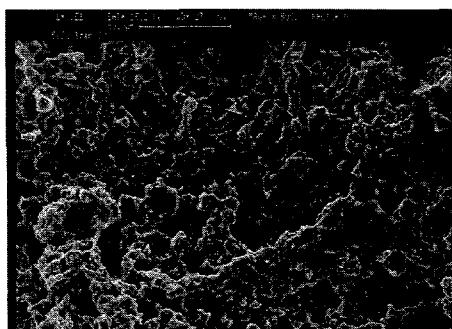
Experiments were performed at both atmospheric and 20 bar pressure and the progression of char conversion was followed for each case. Chars were gasified to different conversions, removed from the experimental reactor and subsequently analyzed through scanning electron microscopy.

3.2.1 Atmospheric pressure

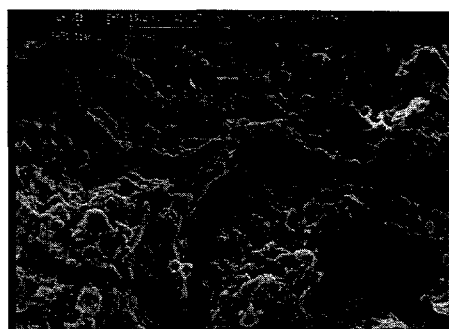
General observations. Figure 3 shows SEM images taken of black liquor char at 280x magnification. The conversion of the char is given under each image. Throughout the range of conversion the chars appear to be quite sponge-like in structure, and are composed of a network of the solid skeletal material. The classes of pores can be identified. Within the skeletal material itself are small pores or holes roughly 2-5 μm diameter. Between crests, or folds, in the skeleton are voids of 10-20 μm . Finally, regions of solid material are separated by open voids with distances averaging 50 μm or more.

Higher magnification reveals that the surface of the skeletal material for some chars is quite bumpy, as can be seen for the char at 45% conversion (Figure 4). In some cases, most notably at intermediate conversions (25-75%) small granules roughly 1 μm in diameter were observed on the surface of the char (Figure 4). X-ray analysis of these granules indicates that they are crystals of sodium carbonate.

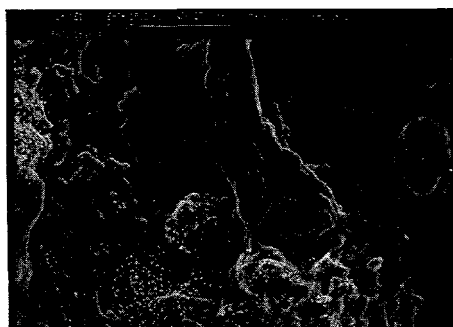
Structural changes during conversion. Following the progression of conversion in Figure 3 one can see that the char becomes less and less porous as it is converted. This is



Initial char



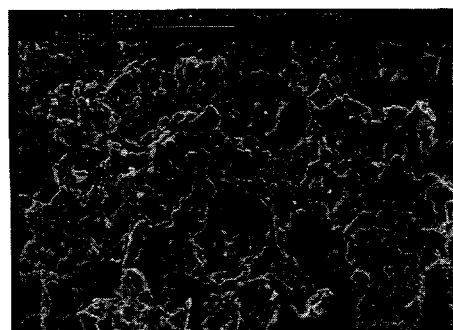
26% conversion



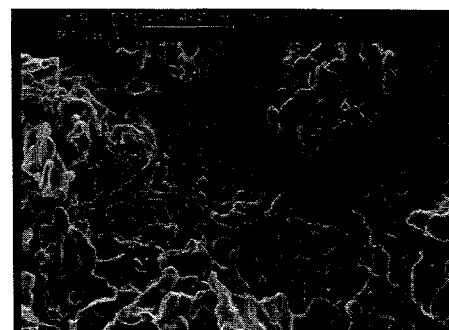
45% conversion



77% conversion



84% conversion



Residue after complete conversion

Figure 3. SEM images of chars in various stages of conversion by gasification at atmospheric pressure, shown at 280x magnification. The scale line in the photos is 50 μm . Experimental conditions: 1 atm., 700°C, 20% CO_2 , 4% CO , 76% N_2 .

particularly notable for the chars at 84% and 100% conversion. In these cases the inorganic content of the char is quite high, and the total volume of the char has decreased significantly.

At 100% conversion the residue appears to have fused together into a uniform mass. This was observed upon removal of the sample from the reactor, as well. Chars that were not fully converted broke apart easily, but the ash that remained after complete conversion could be removed in a few large chunks. Upon closer inspection (Figure 5) it

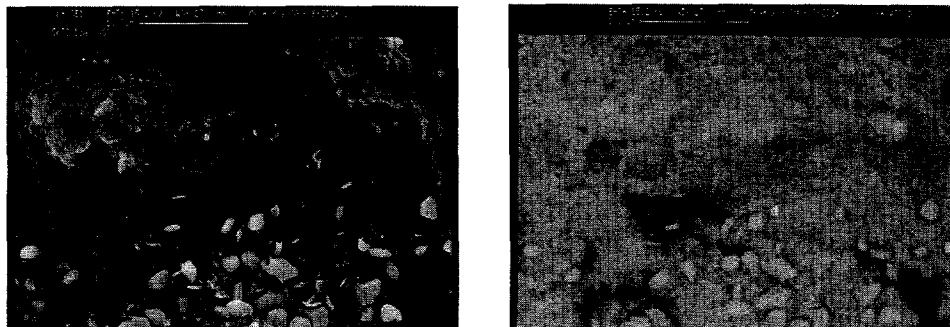


Figure 4. SEM photograph (1700x magnification) and corresponding backscatter scan of black liquor char at 45% conversion during gasification at atmospheric pressure. Lighter areas in the backscattered image indicate the presence of heavier elements.

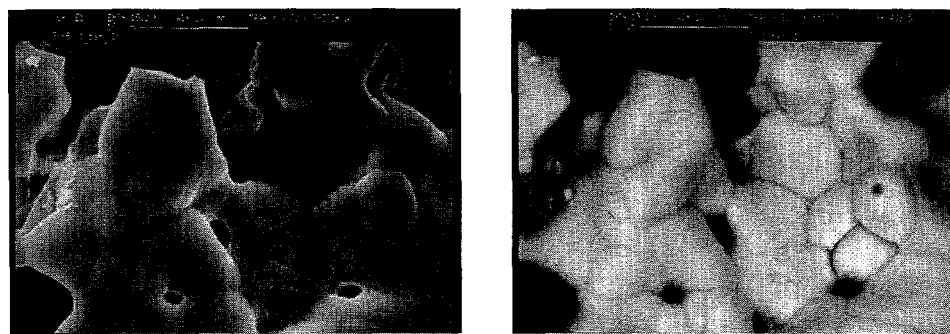


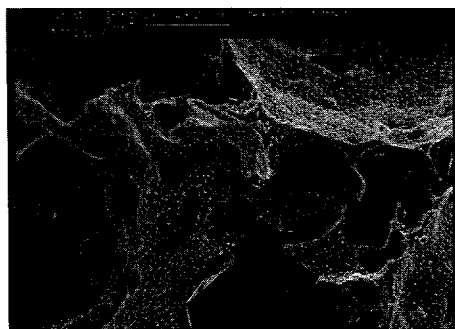
Figure 5. SEM photograph (1700x magnification) and corresponding backscatter scan of the residue remaining after conversion by gasification at atmospheric pressure. The bright area on the left side of the picture was found to be higher in silicon and magnesium than the rest of the sample.

can be seen that the residue consists of many "bubbles" of solid material averaging 5-10 μm in diameter. Scattered about on the residue were areas significantly higher in silicon and somewhat higher in magnesium than the rest of the sample, as determined by x-ray analysis.

3.2.2 20 bar pressure

General observations. The SEM scans in Figure 6, shown at 280x magnification, illustrate the structure of the char at various conversions during gasification at 20 bar pressure. The char appears to be made up of overlapping plates which are feathery at the edges. The surface of the material is quite coarse, covered with bumps averaging 0.5 to 2.0 μm across. The plates themselves have holes 10 to 50 μm across and are separated by distances of 20 μm or more.

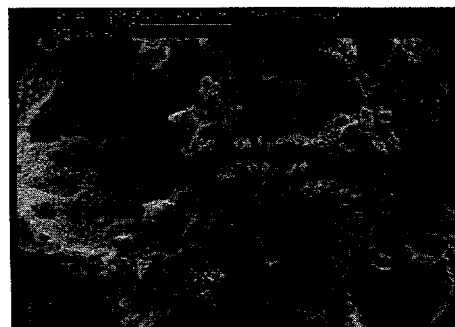
Higher magnification reveals that at intermediate conversions (18-70%) granules of inorganic salts, similar to the case for gasification at atmospheric pressure, exist on the surface of the char (Figure 7). The particles are roughly 1 micron in diameter and x-ray scanning indicates they are composed of sodium carbonate.



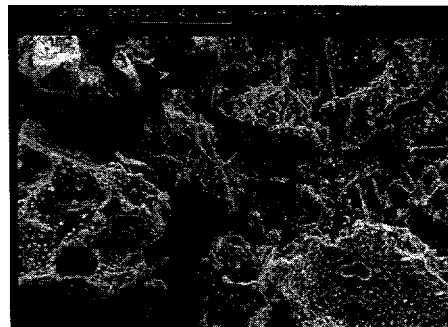
Initial char



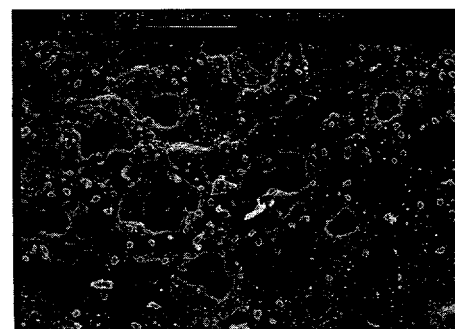
18% conversion



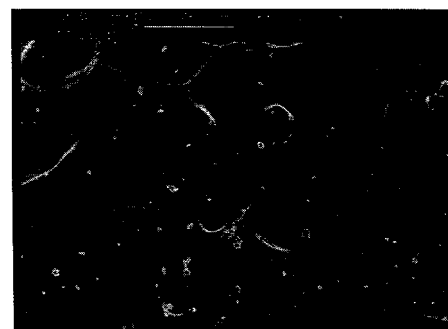
38% conversion



62% conversion



70% conversion



Residue after complete conversion

Figure 6. SEM images of chars in various stages of conversion by gasification at 20 bar pressure, shown at 280x magnification. The scale line in the photos is 50 μm . Experimental conditions: 20 bar, 700°C, 20% CO_2 , 4% CO , 76% N_2 .

Structural changes during conversion. As seen in Figure 6, the nature of the char does not appear to change much up to 70% conversion. At higher magnification it was observed that the “bumpiness” of the char surface decreased with conversion up to 80%. This was particularly noticeable between 0% and 18% conversion, with the bumps at 18% conversion being roughly half the size of those observed on the initial char.

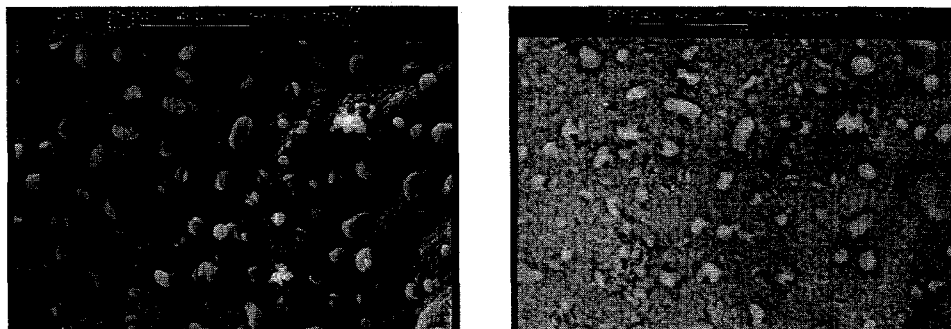


Figure 7. SEM photograph (1700x magnification) and corresponding backscatter scan of black liquor char at 38% conversion during gasification at 20 bar. Lighter areas in the backscattered image indicate the presence of heavier elements.

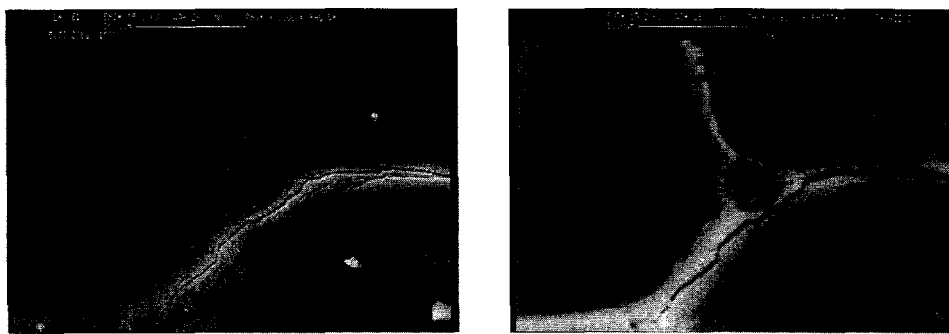


Figure 8. SEM photograph (1700x magnification) and corresponding backscatter scan of the residue remaining after conversion by gasification at 20 bar. The material in the seams of the char is potassium chloride.

The residue which remains at the end of gasification (100% conversion) looks much different, however. It is non-porous and quite smooth in appearance, suggesting that it has melted. As with the case for the experiments performed at atmospheric pressure, it was noted during the removal of the samples from the holder that most could easily be brushed off while the white residue remaining after full conversion had to be scraped off.

The residue remaining after full conversion appears to be made up of solid bubbles roughly 50 μm in diameter. The seams between the bubbles are filled with what appears to have been a molten material (Figure 8). The white color of this material in the backscattered image indicates that it contains a high percentage of heavy elements. A spot x-ray scan on the seam material revealed that it is almost pure potassium chloride.

3.2.3 Comparison of atmospheric and 20 bar pressure

The char which was reacted at 20 bar pressure remained more compact and less porous throughout the range of conversion than that reacted at atmospheric pressure. For both pressures crystals of sodium carbonate formed on the surface of the char at intermediate conversions. The inorganic residue from both chars had a bubble-like morphology, but the diameter of the bubbles were approximately five times larger at 20 bar than at

atmospheric pressure. Some areas high in silicon were found on the residue formed at atmospheric pressure while potassium chloride filled the seams of the bubbles for the residue formed at 20 bar.

3.3 Compositional changes during black liquor char conversion

X-ray scans were performed on each of the samples after reaction in order to estimate the chemical composition of the material. The mass fraction cannot be determined from the scans. Rather, the results are given as ratios between species. It is assumed here that the total amount of sodium in the sample does not decrease during conversion because of the relatively low temperature used, so the amounts of other elements are given in terms of their mass ratio to sodium.

3.3.1 Atmospheric pressure

As expected, the C/Na ratio decreased throughout conversion so that at full conversion very little carbon remained. The S/Na ratio decreased as well, particularly between 45% and 77% conversion, as did the Cl/Na ratio. At 100% conversion neither sulfur nor chlorine could be detected in the sample.

3.3.2 20 bar pressure

As determined by x-ray analysis, the S/Na ratio decreased quite uniformly with conversion, and no sulfur could be detected for samples at or beyond 70% conversion. There was little variation in the Cl/Na ratio for most of the conversion, but the final residue did have a slightly higher value than those of the partially-reacted chars. The K/Na ratio displayed similar behavior, with the highest value existing for the residue remaining after complete reaction.

3.3.3 Comparison of atmospheric and 20 bar pressure

Sulfur decreased with conversion in both cases, to the degree that none was detectable in the residue which remained after conversion. Chlorine and potassium decreased during conversion at atmospheric pressure, but increased slightly during conversion at 20 bar.

4. CONCLUSIONS

Samples of concentrated black liquor were simultaneously pyrolyzed and gasified in a reactive gas consisting of 20% CO₂ and 4% CO in nitrogen. Two pressures, atmospheric and 20 bar, were used and all experiments were performed at 700°C. The samples were reacted to different char conversions and then removed for analysis with a scanning electron microscope. Structure and chemical composition were analyzed.

The microstructure of the char is composed of a network of solid material resembling the structure of a sponge. The solid material itself is porous and the surface is quite bumpy, particularly at lower conversions. The spacing between regions of solid material is quite large, resulting in a highly porous char. Chars formed at atmospheric pressure have larger void volumes than those formed at 20 bar.

As the char is converted it loses its porosity and becomes more compact. This is particularly noticeable at conversions of more than 80%. At intermediate conversions (20% – 70%) small crystals of sodium carbonate, roughly 1 micron in size, form on the

char surface. These are not observed at higher conversions. Finally, when gasification is complete all that remains is a smooth inorganic residue of very low porosity. The residue which results from gasification at 20 bar contains potassium chloride in seams between "bubbles" of the material.

The sulfur content in the char decreases during gasification to the point where none can be detected in the residue. At atmospheric pressure the Cl/Na and K/Na ratios also decrease with conversion. At 20 bar these ratios remain relatively constant until higher conversions, after which they increase somewhat.

5. FUTURE WORK

The work presented here is part of an investigation to gain an understanding of physical and chemical processes that occur during black liquor conversion. The ultimate goal is to understand how the morphology and composition of black liquor change during drying, pyrolysis and char conversion.

A study is planned to follow the physical changes which take place during pyrolysis of black liquor both at atmospheric and pressurized conditions. Previous studies have investigated swelling which occurs, but this study will focus on the microstructure of the material as it is undergoing pyrolysis. Experiments will be carried out in a pressurized grid heater, an entrained flow reactor and a pressurized single-droplet reactor. Short residence times will be used in order to follow conversion. The structure and composition of the samples will be analyzed to see how they change with conversion.

While scanning electron microscopy is a powerful tool for investigation of the microstructure of materials it does not provide any information about the internal surface area of a sample. The rate of gasification is controlled by the kinetics of the reaction and therefore the conversion time is dependent on the surface area available for reaction. Efforts will be made to measure the active surface area of chars and to correlate this with the char formation conditions. Additionally, the progression of active surface area during conversion will be studied. This project proposes a challenge since conventional methods of surface area analysis (e.g. BET) require sample sizes many times larger than can be produced in laboratory-scale pyrolysis equipment.

ACKNOWLEDGMENTS

This work was performed and funded within the project "Single particle studies of black liquor gasification under pressurized conditions" within the LIEKKI 2 combustion research program in Finland. The authors acknowledge Mr. Peter Backman for his skillful operation of the pressurized thermogravimetric reactor and Mr. Clifford Ekholm for his expertise with the scanning electron microscope.

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Paper VI

Gasification of black liquor char with steam at elevated pressures

Journal of Pulp and Paper Science 21(6):J214-J221 (June 1995).

Gasification of Black Liquor Char with Steam at Elevated Pressures

K. WHITTY, M. HUPA and W.J. FREDERICK

The kinetics of the gasification of black liquor char by steam were investigated by means of a pressurized thermogravimetric reactor over the range 600–675°C, 1–30 bar (0.1–3.0 MPa) total pressure. The experiments were performed either with or without one of the reaction products (H₂, CO) present and under conditions such that film mass transfer and pore diffusion did not affect the overall rate. The rate of gasification was found to decrease with increasing pressure, by a factor of 3.5 over the pressure range 2–30 bar (0.2–3.0 MPa). This decrease is presumably due to the increase of inhibiting effects of the products, hydrogen

and carbon monoxide, with increasing pressure. The reaction was found to be of order 0.56 in steam partial pressure. The presence of either hydrogen or carbon monoxide slowed the reaction, with carbon monoxide being the stronger inhibitor. The reaction is very temperature sensitive. The apparent activation energy was found to be 230 kJ/mol, which corresponds to an increase in the rate by a factor of roughly 30 over the temperature range 600–700°C. A comparison with carbon dioxide gasification of black liquor char shows that the rate of steam gasification is 3.8 times higher at equivalent CO₂ versus H₂O partial pressures, with no H₂ or CO present in the reacting gas. The rate of steam gasification could be predicted by means of a model developed for catalytic gasification of carbon.

INTRODUCTION

Gasification of black liquor is one promising alternative for recovery systems in the pulping process. In such a system, carbon in the black liquor char is converted

to gas by reaction with water vapour or carbon dioxide according to the following reactions:



The product gases can then be burned in a gas turbine. A pressurized gasification system would provide many advantages over conventional methods, including higher electrical/thermal energy ratios achieved from black liquor, smaller equipment size and savings in material costs [1–3].

Although much research has been conducted concerning the kinetics of pressurized gasification of carbon and coal chars [4–9], until recently there has been very little effort to study gasification of black liquor char. Previous research has been conducted concerning both atmospheric and pressurized gasification of black liquor char with carbon dioxide [1,10–13]. Atmospheric gasification with water vapour has also been

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studied [14–15]. However, until now there has been very little investigation into pressurized gasification of black liquor with steam. A mathematical expression for the kinetic rate of steam gasification would be a valuable tool. Such a model could aid in the design of recovery furnaces and gasification technologies, as well as provide a basis for comparison with results obtained in other studies of black liquor gasification kinetics.

EXPERIMENTAL Equipment

The gasification kinetics was measured using a pressurized thermogravimetric reactor (PTGR). A schematic drawing of the apparatus is presented in Fig. 1. The PTGR is capable of operating at pressures up to 100 bar (10 MPa) and at temperatures as high as 1100°C. Up to three permanent gases can be supplied to the reactor. In addition, the apparatus is equipped with a steam generator, thereby making it possible to use water vapour as a reacting gas. The steam and permanent gas lines each have a three-way valve which can be switched either to the reactor or to a bypass line. This makes it possible to stabilize the steam flow in the bypass line prior to the start of gasification, thereby eliminating start-up effects associated with the steam generator.

The PTGR is equipped with a water-cooled sample lock placed above the reactor. The sample is loaded into the device via this lock and by means of a small, electrically

driven winch can be lowered into the reacting chamber once conditions have been established.

In a special study to determine the reproducibility of results obtained with the PTGR, it was found that the coefficient of variation between rates (standard deviation divided by average) was 6.5%.

Sample

The char used in the experiments was produced from a North American hardwood kraft liquor. The char was formed by introducing the liquor into a drop tube furnace under pyrolysis conditions at 900°C and atmospheric pressure. The drop tube furnace and experimental procedure is described in more detail by Clay et al. [16]. The char was ground into particles no larger than 200 µm, and was found to have a very low internal surface area, less than 3 m²/g.

Samples of the char used in the experiments were analyzed for carbon, sodium and sulphur content. No determination was made for hydrogen in this char. However, an earlier batch of char from the same mill was analyzed for hydrogen. The results of the analyses of both chars, based on their dry weights, are presented in Table I.

Experimental Procedure

In the experiments, a cylindrical sample holder (Fig. 2) was loaded with approximately 100 mg of crushed char and placed into the sample lock. The reactor was then

TABLE I
ELEMENTAL ANALYSES OF CHARS,
BASED ON DRY WEIGHT

Element	Composition, wt%	
	This Study	Earlier Char
C	31.47	31.22
Na	21.70	18.95
S	4.85	3.99
H	n/a	1.97
Other	41.98	43.87

pressurized and heated to the desired temperature while the steam flow was adjusted and directed through the bypass line. The sample was then lowered into an atmosphere of nitrogen and 5–10% carbon monoxide.

Figure 3 shows the weight versus time curve for a typical gasification run. In region "a", the sample is in the N₂/CO atmosphere and a sharp weight loss is observed. During this period, moisture in the sample is evaporated and volatiles not removed during the previous char formation are pyrolyzed. Also, reduction of sodium sulphate to sodium sulphide may occur.

Once the sample weight stabilizes (generally ~400 s) the gas composition is quickly changed to that for gasification and the flow of steam is switched from the bypass to the reactor. A sharp decrease in the weight signal is observed, followed by an apparent weight increase (region "b"). The weight decreases due to a change in drag force caused by the introduction of steam. The rapid weight increase is presumably due

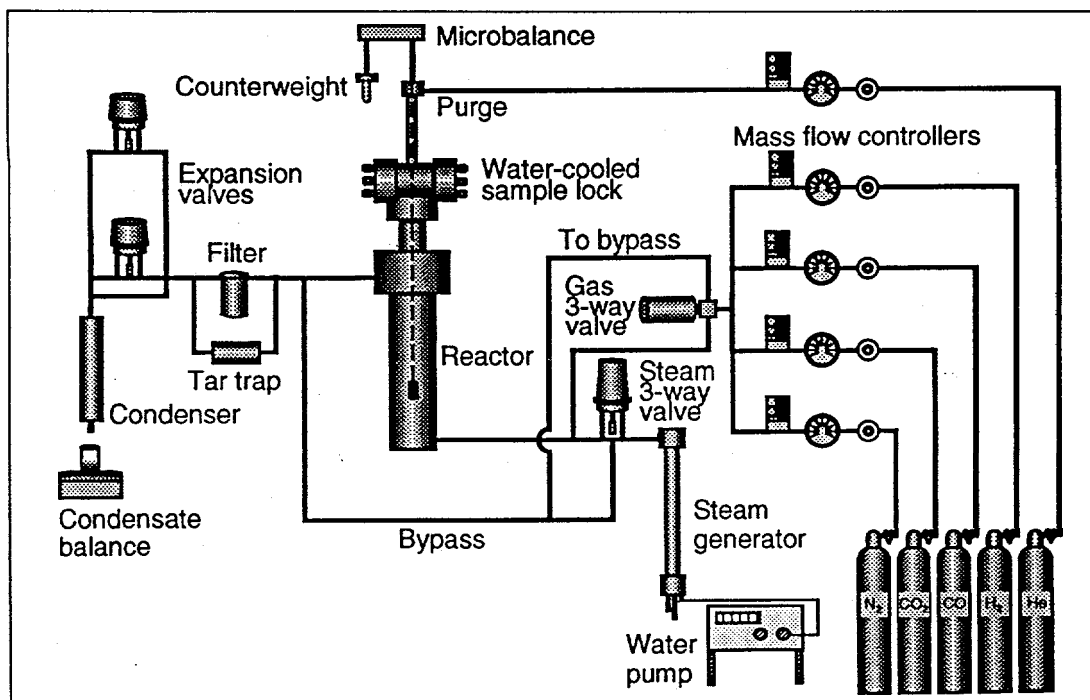


Fig. 1. The Åbo Akademi pressurized thermogravimetric reactor.

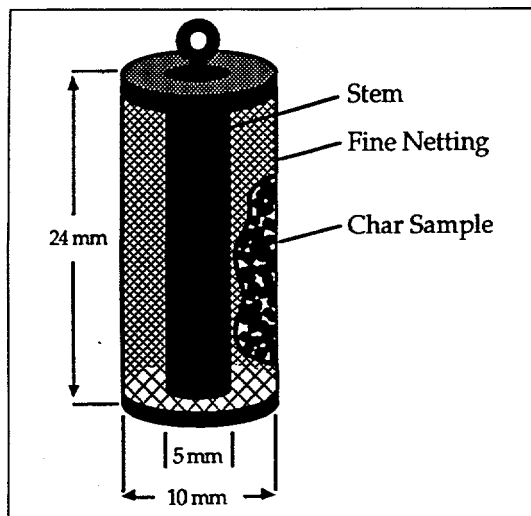


Fig. 2. Sample holder.

to adsorption of H_2O onto the sample [17]. Region "c" depicts the weight loss due to the removal of carbon in the sample by gasification. The reaction begins slowly, then increases in rate due to opening of pores within the char and activation of the catalyst. The rate then decreases as the amount of carbon available for reaction is depleted and as the organically bound sodium catalyst is converted to crystalline sodium carbonate [7]. At the end of the run, the sample was white in colour, as the carbon had been removed by gasification and the remaining material was composed of inorganic salts.

Data Evaluation

The amount of sample gasified, as seen in Fig. 3, is considered to be the difference between the maximum weight after gasification conditions have been introduced and the final weight. This includes the mass of any adsorbed H_2O , but it was decided to include this because (1) it accounted for roughly 10% of the mass gasified, irrespective of gasifying conditions; (2) the fate of the adsorbed water during conversion is unknown; and (3) all experiments were analyzed by the same method, so resulting trends will not be affected. Static buoyancy effects were neglected, as they were found to account for less than 1% of the total gasified weight. In order to evaluate the rate of gasification, the weight loss curve was normalized with respect to the amount of sample gasified. Hence, the rate equation is of the form

$$-r = \frac{1}{m_{C,i}} \frac{dm_{C(t)}}{dt} \quad (3)$$

where $m_{C,i}$ is the initial weight of gasifiable carbon in the char, considered to be the same as the total amount of sample gasified. Based

on this equation, the rate units are s^{-1} .

The slope of the normalized weight loss curve was determined by using regression to fit a polynomial expression to the experimental data and then taking the derivative of this equation. The maximum slope was evaluated using this method and is hereafter referred to as the gasification rate.

In order to determine the reproducibility of the results in this study, four experiments were performed using the same conditions, with the exception that the initial sample weight was different in each case. The results of these experiments are shown in Fig. 4 and Table II.

The runs produced nearly identical results, with the maximum rates being within 4% of one another. This suggests that

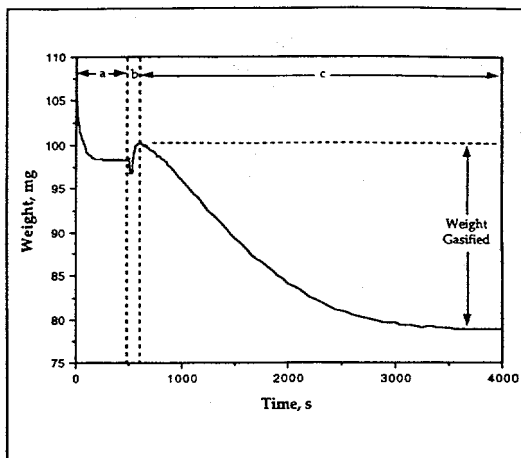


Fig. 3. Typical weight loss curve for a gasification run. The sample is heated in stage "a". In stage "b", the gas composition is changed to that for gasifying and H_2O adsorption occurs. During stage "c" the sample is gasified.

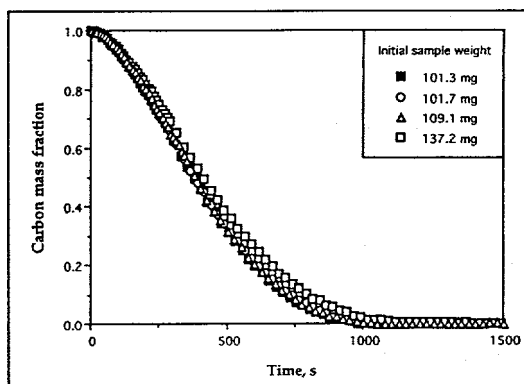


Fig. 4. Normalized weight loss curves (based on gasifiable carbon) for four identical runs. All runs performed at 10 bar (1.0 MPa), $675^\circ C$, 50% H_2O , 2% H_2 , 48% N_2 .

the results obtained in this study are reproducible. Although the rate was lowest for the largest sample (Run 4), it cannot be concluded that sample size affects the gasification rate. The variation between rates is within the reproducibility of the apparatus, and it is apparently coincidental that the rate for the sample with the largest mass was

TABLE II
REPRODUCIBILITY OF EXPERIMENTS

Run no.	Sample Weight	Max. Rate ($\times 10^3$)	Conversion at Maximum Rate	Weight % Gasified*
1	101.3 mg	$17.0 s^{-1}$	38.6 %	19.2 %
2	101.7 mg	$16.8 s^{-1}$	38.2 %	19.4 %
3	109.1 mg	$17.0 s^{-1}$	38.0 %	18.8 %
4	137.2 mg	$15.7 s^{-1}$	37.6 %	19.0 %
Average		$16.6 s^{-1}$	38.1 %	19.1 %
Standard deviation		0.63	0.42	0.26
Coefficient of variation		3.8 %	1.1 %	1.4 %

* Based on original, undried sample weight

lowest. Previous studies by Frederick and Hupa, who studied black liquor gasification with CO₂ [1] and Lisa et al., who studied sulphur capture by limestone in a PTGR [18], have concluded as well that rates of the same magnitude as obtained in this study are not influenced by sample size or geometry.

FILM MASS TRANSFER AND PORE DIFFUSION EFFECTS

Because this study concerns the kinetics of char gasification, it is important to ensure that the results obtained are due purely to chemical kinetics. In the gasification process, there are three processes which can control the overall rate: transport of gaseous reactants and products between the bulk gas and the particle surface (film mass transfer); diffusion of gas within the char bed and the pores of the char (pore diffusion); and the chemical reaction itself. In order to make sure that the chemical reaction is the determining resistance in controlling the rate, the film mass transfer and pore diffusion must occur so rapidly as to make their resistances negligible. Several types of tests, both theoretical and experimental, are available to determine if this is the case.

Frederick and Hupa [1] outlined a procedure which employs the Weisz modulus and mass transfer Biot number to determine the relative importance of the resistances on the overall rate. Using this procedure, five runs representing extremes of the conditions investigated were analyzed, modeling the sample bed as one large particle. Table III summarizes the results of the analysis, and in the worst case it was estimated that film mass transfer and pore diffusion account for just 1.2% of the total resistance for the reaction.

The theoretical time for conversion of a particle of known geometry, assuming only film mass transfer and pore diffusion determine the rate, can be calculated using a procedure described by Levenspiel [19,20]. This was done for the same five experiments as in Table III, and the estimated and ob-

TABLE III
SUMMARY OF MASS TRANSFER LIMITATION ANALYSIS
BASED ON THE PROCEDURE IN [1]

Run	Temp. (°C)	Pressure (bar)	Maximum Rate (mg/mg·s)	Percentage of Overall Resistance Due to	
				Film Mass Tx. + Pore Diffusion	Chemical Reaction
1	600	10	1.68	0.08	99.92
2	650	2	18.60	0.82	99.18
3	650	10	9.55	0.46	99.54
4	650	30	6.90	0.35	99.65
5	675	10	24.90	1.17	98.83

TABLE IV
THEORETICAL AND OBSERVED TIMES TO 90% CONVERSION

Run	Theoretical Time to 90% Conversion (s)		Observed Time to 90% Conversion (s)
	Film Mass Transfer is Limiting Mechanism	Pore Diffusion is Limiting Mechanism	
1	34	21	7220
2	27	20	720
3	33	20	1320
4	37	20	1690
5	32	20	520

served times to 90% conversion are shown in Table IV. In the worst case, the time to 90% conversion, assuming that only film mass transfer and pore diffusion controlled the rate, was only 10% of the observed time, indicating that the chemical reaction was indeed the controlling process.

To experimentally investigate the significance of film mass transfer, two tests were performed at identical conditions, but with different gas velocities. If film mass transfer was a significant resistance, a higher rate would be expected at higher gas velocity. This was not found to be the case, however [21].

Finally, two experiments were performed at identical conditions except that, in one, helium was used as a carrier gas instead of nitrogen. The diffusivity of water vapour in helium is 3.2 times that in nitrogen. Consequently, a higher rate would be expected if pore diffusion or film mass transfer were a significant resistance. However, the results of these experiments were the same within

experimental error [21].

RESULTS AND DISCUSSION Effect of Process Variables on the Reaction Rate Effect of Total Pressure at Constant Gas Composition

In order to determine the effect of total pressure on the gasification rate, several experiments were performed at constant gas composition and temperature over the pressure range 2–30 bar (0.2–3.0 MPa). Figure 5 shows the normalized weight loss curves for runs performed at five different pressures. Clearly, the time for gasification increases with increasing pressure. For these conditions, the time for total gasification at 30 bar (3 MPa) is approximately 2.7 times that at 2 bar (0.2 MPa).

The effect of total pressure on the gasification rate at constant gas composition can be seen in Fig. 6 where the maximum gasification rates of the runs in Fig. 5 are

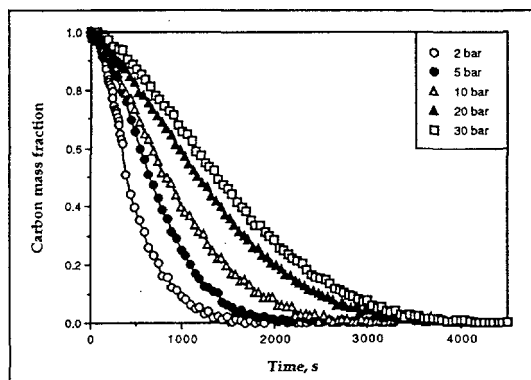


Fig. 5. Effect of total pressure on gasification time at constant gas composition. All runs were performed at 650°C, 20% H₂O, 2% H₂, 78% N₂.

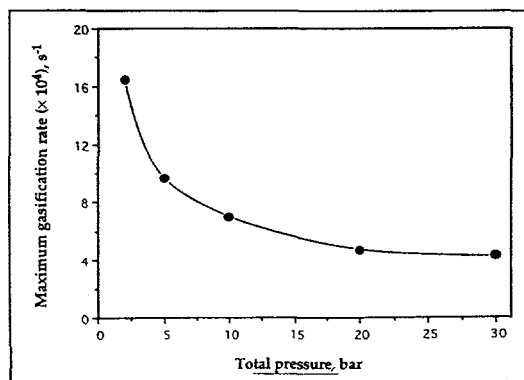


Fig. 6. Effect of total pressure on the maximum gasification rate at constant gas composition. All runs were performed at 650°C, 20% H₂O, 2% H₂, 78% N₂.

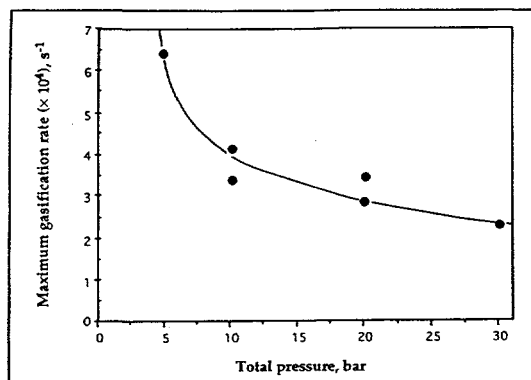


Fig. 7. Effect of total pressure on maximum gasification rate when partial pressures are held constant. All runs were performed at 650°C, with partial pressures of H₂O and H₂ equal to 4.0 and 0.8 bar (0.4 and 0.08 MPa), respectively. Nitrogen was the carrier gas.

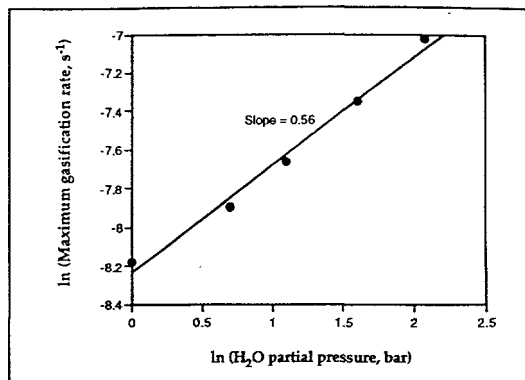


Fig. 8. Effect of H₂O partial pressure at constant total pressure. All runs were performed at 10 bar (1.0 MPa) total pressure, 650°C, 0.4 bar (0.04 MPa) H₂ partial pressure. Make-up pressure was provided by nitrogen.

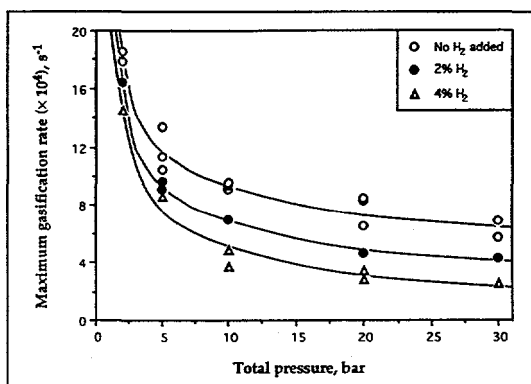


Fig. 9. Effect of H₂ addition on the gasification rate. All runs were performed at 650°C, 20% H₂O, nitrogen carrier.

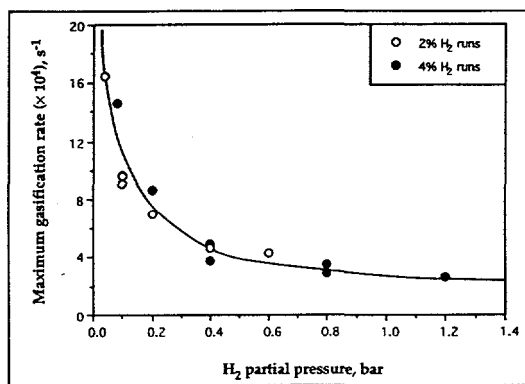


Fig. 10. Maximum gasification rate versus H₂ partial pressure. All runs were performed at 650°C, 20% H₂O, N₂ carrier.

plotted versus total pressure. As the pressure is increased from 2 to 5 bar (0.2–0.5 MPa), the rate decreases dramatically. Above 5 bar (0.5 MPa), the rate continues to decrease with increasing pressure, though not as severely. The ratios of the rates at 5 and 30 bar (0.5 and 3 MPa) to that at 2 bar (0.2 MPa) are 0.48 and 0.29, respectively.

When the total pressure of a system is increased at constant gas composition, the partial pressures of the various constituents also increase. In order to study the effect of total pressure in a system where the partial pressures do not change, a series of experiments was performed over the pressure range 4.8–30 (0.48–3 MPa) bar, with the partial pressures of H₂O and H₂ held constant at 4.0 and 0.8 bar (0.4 and 0.08 MPa), respectively. The effect of total pressure on the gasification rate at these conditions is shown in Fig. 7. As with the case at constant gas composition, increasing pressure decreases the gasification rate when the partial pressures of the reacting species are held constant.

Effect of H₂O Partial Pressure

A series of experiments was performed in which the partial pressure of H₂O was varied from run to run while the hydrogen partial pressure and the total pressure were constant for all runs. The difference between the partial pressures of H₂O and H₂ and the total pressure was made up by nitrogen. Figure 8 shows the results of these experiments. Under the conditions studied, the gasification reaction was found to be of order 0.56 in H₂O partial pressure.

Effect of Hydrogen Addition

Hydrogen was found to strongly inhibit the H₂O gasification reaction. To study the effect of hydrogen addition on the gasification rate, experiments were performed in which 0, 2 or 4% hydrogen was added to the carrier gas. The results of these experiments can be seen in Fig. 9. As the concentration of hydrogen increases, the rate decreases significantly throughout the entire pressure range.

The effect of hydrogen addition can

be seen more clearly in Fig. 10, where the gasification rate is plotted versus the hydrogen partial pressure. Both the data for 2% and 4% H₂ follow the same distinct curve, indicating that hydrogen inhibition is a function of hydrogen partial pressure.

Effect of Carbon Monoxide Addition

Carbon monoxide was also found to be a strong inhibitor to the H₂O gasification reaction, stronger even than hydrogen. In order to study the effects of CO addition, a series of experiments was performed similar to that used to study hydrogen addition. Runs were performed over the pressure range 2–30 bar (0.2–3 MPa) where 0, 2 or 4% CO was added to the carrier gas. The results of these experiments are shown in Fig. 11.

So that the inhibiting effects of H₂ and CO may be compared, the lines for 2% and 4% hydrogen addition from Fig. 9 have been overlaid on Fig. 11. One can see clearly that CO is a much stronger inhibitor than hydro-

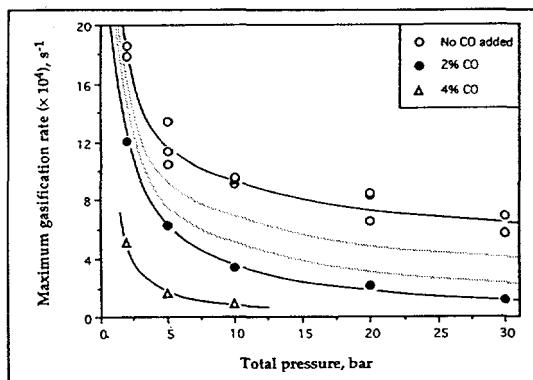


Fig. 11. Effect of carbon monoxide addition on the maximum H₂O gasification rate. The upper and lower grey lines are for 2% and 4% H₂ addition, respectively, and were taken from Fig. 9. All runs were performed at 650°C, 20% H₂O.

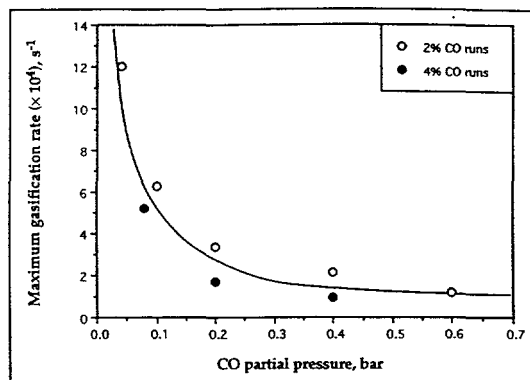


Fig. 12. Gasification rate versus CO partial pressure. All runs were performed at 650°C, 20% H₂O, N₂ carrier.

gen, so much so that 2% CO addition results in a bigger reduction of the rate than 4% H₂ addition.

Figure 12 shows the effect of carbon monoxide partial pressure on the gasification rate. As with the case of hydrogen, the inhibitive effect of carbon monoxide seems to depend on the partial pressure of CO, with both the data for 2% and 4% CO following the same curve.

Effect of Temperature

The rate of gasification is strongly affected by temperature. Figure 13 is an Arrhenius plot of the gasification rates over the

temperature range 600–675°C. The activation energy of the reaction is approximately 230 kJ/mol, which is consistent with values reported in literature for steam gasification of coal. Based on this activation energy, the gasification rate is found to increase by a factor of 27 over the range 600–700°C.

Comparison with CO₂ Gasification

Gasification of black liquor char with steam was found to be much faster than with carbon dioxide. Figure 14 shows the normalized weight loss curves for gasification with H₂O and CO₂. Both runs were performed at

identical conditions, and neither hydrogen nor carbon monoxide was added to either reacting gas mixture.

The times to 90% conversion and gasification rates of the two runs, along with the activation energies for the reactions, are presented in Table V. The gasification rate with steam is approximately 3.8 times faster than that with CO₂. Such values have been reported in literature for gasification of carbon and coal chars.

RATE MODELING OF STEAM GASIFICATION OF BLACK LIQUOR

Several mechanism-based rate models for steam gasification have been proposed for carbon and coal [4–8]. Meijer developed an expression for alkali-catalyzed gasification of carbon after studying the kinetics and mechanism of the gasification of alkali-impregnated peat char [7,8]. Regarding models specific to black liquor gasification, Li and van Heiningen have published a mechanism-based rate expression for steam gasification of black liquor char at atmos-

	Time to Reach 90% Conversion (s)	Gasification Rate (s ⁻¹)	Activation Energy (kJ/mol)
H ₂ O Gasification	1400	9.41	233
CO ₂ Gasification	5100	2.49	205*
Ratio, H ₂ O/CO ₂	0.27	3.8	1.14

* See ref. [1].

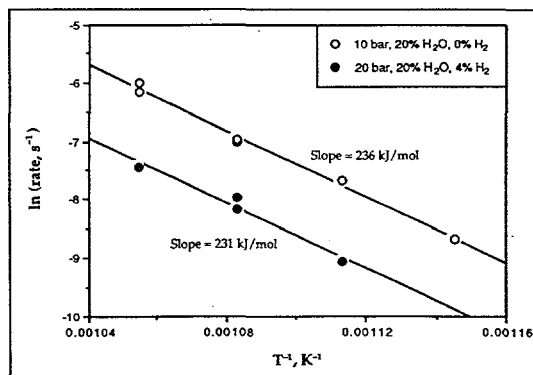


Fig. 13. Arrhenius plot over the temperature range 600–675°C.

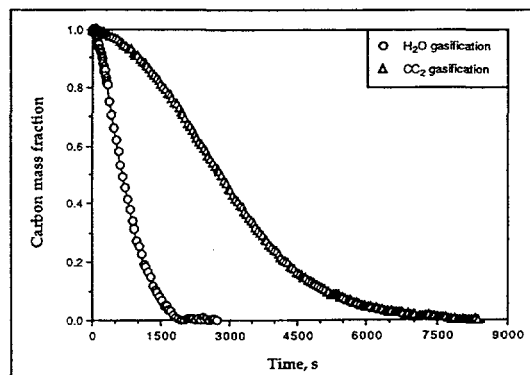


Fig. 14. Comparison of gasification by H₂O and gasification by CO₂. Both runs were performed at 10 bar (1.0 MPa), 650°C. Gas compositions were 20% H₂O, 80% N₂ and 20% CO₂, 80% N₂, respectively.

pheric pressure [14], and Whitty et al. have reported an empirical rate expression for pressurized black liquor char gasification [22].

Eight existing gasification rate expressions were fit to the data obtained in this study by minimizing the sum of the squares of the residuals ($\sum(\text{rate}_{\text{obs}} - \text{rate}_{\text{cal}})^2$). It was found that four of the expressions reduced to a simple Langmuir-Hinshelwood form, such as that reported by Li and van Heiningen, when the constants were forced to be greater than or equal to zero. The best fit, based on the average difference between the calculated and observed rates, was obtained with the rate expression of Meijer:

$$\text{rate} = 10^{-4} \cdot \exp \left[28000 \left(\frac{1}{923} - \frac{1}{T} \right) \right] \cdot \frac{9.01}{1 + \frac{p_{H_2}}{0.449 p_{H_2O}} + 7.09 p_{CO}} \quad (4)$$

where *rate* is the maximum rate of gasification (mg/mg·s), *T* is the temperature (K) and *p_i* is the partial pressure of species *i* (bar) (10^{-1} MPa). The observed and predicted rates are given in Table VI, along with the experimental conditions for the runs. The predicted rate differed from the observed rate by an average of 45%.

This expression accurately reflects the observed inhibitions by product gases but it does not account for the observation that the rate decreases with increasing total pressure, as illustrated in Fig. 7. The latter effect may somehow be related to locally high concentrations of product CO at the char surface but we do not presently have a good explanation for it.

This expression is more suitable than previously published black liquor gasification rates because, in addition to the water vapour term, it takes into consideration the influence of both gasification products, hydrogen and carbon monoxide. The majority of the expressions tested only included terms for water vapour and hydrogen, in spite of the fact that, as was shown previously, carbon monoxide strongly inhibits the gasification reaction at elevated pressures.

CONCLUSIONS

The kinetics of the steam gasification of black liquor char can be investigated successfully by means of the pressurized thermogravimetric apparatus used in this work. The steam gasification reaction is quite temperature sensitive. An Arrhenius plot of the rate over the temperature range 600–675°C results in an activation energy of 233 kJ/mol. Based on this activation energy, the gasification rate is found to increase by a factor of 27 over the range 600–700°C.

A comparison of steam gasification and carbon dioxide gasification of black liquor char shows that the rate of gasification

with steam is 3.8 times higher than with carbon dioxide. This is consistent with findings reported for coal char gasification.

The gasification rate decreases with increasing pressure. This decrease is quite large, with the ratio of rates at 5 and 30 bar (0.5 and 3 MPa) to that at 2 bar (0.2 MPa) being 0.48 and 0.29, respectively. The cause of this decrease is presumably because the inhibiting effects of the products increase more with pressure than the gasification effect.

The rate was found to increase with increasing steam partial pressure, provided that the total pressure and hydrogen partial pressure were held constant. Under the con-

ditions studied, the gasification reaction was found to be of order 0.56 in H₂O partial pressure.

Addition of hydrogen or carbon monoxide slows the reaction. Carbon monoxide is a much stronger inhibitor, and addition of 2% CO decreases the rate more than 4% H₂. The inhibiting effect of either species depends on the partial pressure of that species. No investigation was made into the effect of adding both hydrogen and carbon monoxide to the reaction gas.

The rate of steam gasification can be reasonably estimated by a model developed by Meijer for alkali-catalyzed gasification of carbon.

TABLE VI
RATES PREDICTED FROM EQ. (4) AND OBSERVED EXPERIMENTAL RATES

Temp. (°C)	Pressure (bar)	p _{H₂O} (bar)	p _{H₂} (bar)	p _{CO} (bar)	Observed rate ×10 ⁴ (mg/mg·s)	Predicted rate ×10 ⁴ (mg/mg·s)
600	20.0	4.00	0.80	0.00	0.88	1.10
625	20.0	4.00	0.80	0.00	1.15	2.68
650	1.4	1.00	0.40	0.00	8.83	4.77
650	1.4	1.00	0.40	0.00	12.60	4.77
650	2.0	0.40	0.00	0.08	5.18	5.75
650	2.0	0.40	0.00	0.04	12.03	7.02
650	2.0	0.40	0.08	0.00	14.59	6.23
650	2.0	0.40	0.04	0.00	16.42	7.37
650	2.4	2.00	0.40	0.00	11.82	6.23
650	3.4	3.00	0.40	0.00	10.94	6.95
650	4.8	4.00	0.80	0.00	6.39	6.23
650	5.0	1.00	0.00	0.20	1.70	3.73
650	5.0	1.00	0.00	0.10	6.22	5.28
650	5.0	1.00	0.20	0.00	8.68	6.23
650	5.0	1.00	0.10	0.00	9.10	7.37
650	5.0	1.00	0.10	0.00	9.62	7.37
650	5.4	5.00	0.40	0.00	8.80	7.65
650	5.4	5.00	0.40	0.00	10.24	7.65
650	8.4	8.00	0.40	0.00	9.28	8.11
650	10.0	2.00	0.00	0.40	0.95	2.35
650	10.0	1.00	0.40	0.00	2.79	4.77
650	10.0	4.00	0.80	0.00	3.35	6.23
650	10.0	2.00	0.00	0.20	3.40	3.73
650	10.0	2.00	0.40	0.00	3.72	6.23
650	10.0	1.00	0.40	0.00	3.87	4.77
650	10.0	4.00	0.80	0.00	4.11	6.23
650	10.0	3.00	0.40	0.00	4.69	6.95
650	10.0	2.00	0.40	0.00	4.89	6.23
650	10.0	2.00	0.40	0.00	5.24	6.23
650	10.0	3.00	0.40	0.00	6.32	6.95
650	10.0	5.00	0.40	0.00	6.43	7.65
650	10.0	5.00	0.40	0.00	6.57	7.65
650	10.0	2.00	0.20	0.00	6.95	7.37
650	10.0	5.00	0.40	0.00	7.10	7.65
650	10.0	5.00	0.20	0.00	7.54	8.27
650	10.0	8.00	0.40	0.00	7.54	8.11
650	10.0	8.00	0.40	0.00	8.92	8.11
650	20.0	4.00	0.00	0.40	2.14	2.35
650	20.0	4.00	0.80	0.00	2.86	6.23
650	20.0	4.00	0.80	0.00	3.44	6.23
650	20.0	4.00	0.40	0.00	4.67	7.37
650	30.0	6.00	0.00	0.60	1.17	1.72
650	30.0	4.00	0.80	0.00	2.25	6.23
650	30.0	6.00	1.20	0.00	2.61	6.23
650	30.0	6.00	0.60	0.00	4.32	7.37
675	10.0	5.00	0.20	0.00	14.25	18.41
675	10.0	5.00	0.20	0.00	15.68	18.41
675	10.0	5.00	0.20	0.00	16.79	18.41
675	10.0	5.00	0.20	0.00	16.96	18.41
675	10.0	5.00	0.20	0.00	17.00	18.41
675	10.0	5.00	0.20	0.00	18.69	18.41
675	20.0	4.00	0.80	0.00	5.84	13.87

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ABSTRACT: The kinetics of the gasification of black liquor char by steam were investigated by means of a pressurized thermogravimetric reactor over the range 600-675°C, 1-30 bar (0.1-3.0 MPa) total pressure. The experiments were performed either with or without one of the reaction products (H₂, CO) present and under conditions such that film mass transfer and pore diffusion did not affect the overall rate. The rate of gasification was found to decrease with increasing pressure, by a factor of 3.5 over the pressure range 2-30 bar (0.2-3.0 MPa). This decrease is presumably due to the increase of inhibiting effects of the products, hydrogen and carbon monoxide, with increasing pressure. The reaction was found to be of order 0.56 in steam partial pressure. The presence of either hydrogen or carbon monoxide slowed the reaction, with carbon monoxide being the stronger inhibitor. The reaction is very temperature sensitive. The apparent activation energy was found to be 230 kJ/mol, which corresponds to an increase in the rate by a factor of roughly 30 over the temperature range 600-700°C. A comparison with carbon dioxide gasification of black liquor char shows that the rate of steam gasification is 3.8 times higher at equivalent CO₂ versus H₂O partial pressures, with no H₂ or CO present in the reacting gas. The rate of steam gasification could be predicted by means of a model developed for catalytic gasification of carbon.

RÉSUMÉ: Nous avons étudié la cinétique de la gazéification de la liqueur noire carbonisée par la vapeur en utilisant pour ce faire un réacteur thermogravimétrique sous pression dans une plage de température de 600 à 675°C et dans une gamme de pression globale de 1 à 30 bars (0.1-3.0 MPa). Nos expériences se sont déroulées avec ou sans l'un des produits de réaction présent (H₂, CO) et dans des conditions telles que le transfert massique de la pellicule et la diffusion par les pores n'affectaient pas le taux total. Nous avons observé que le taux de gazéification diminuait avec une augmentation de pression, d'un facteur de 3,5 au-dessus de la gamme de pression de 2 à 30 bars (0.2-3.0 MPa). Cette diminution est sans doute causée par l'augmentation des effets inhibiteurs des produits, hydrogène et monoxyde de carbone, allant de pair avec l'augmentation de la pression. Nous avons noté que la réaction était de l'ordre de 0,56 au niveau de la pression partielle de la vapeur. La présence de l'hydrogène ou du monoxyde de carbone ralentissait le déroulement de la réaction, le monoxyde de carbone agissant alors comme le produit inhibiteur le plus puissant. Cette réaction est très sensible à la température. Nous avons observé que l'énergie d'activation apparente était de 230 kJ/mol, ce qui correspondait à une augmentation du taux d'un facteur d'environ 30 dans la plage de température de 600 à 700°C. Une comparaison avec la gazéification de la liqueur noire carbonisée avec le dioxyde de carbone nous a permis de constater que le taux de gazéification par la vapeur était de 3,8 fois supérieur à un CO₂ équivalent, par rapport aux pressions partielles du H₂O sans la présence de H₂ ou de CO dans le gaz de réaction. Le taux de gazéification par la vapeur peut être prévu au moyen d'un modèle développé pour la gazéification catalytique du carbone.

KEYWORDS: BLACK LIQUORS, CARBON MONOXIDE, DIFFUSION, GASIFICATION, GRAVIMETRY, KINETICS, MASS TRANSFER, PORES, PRESSURE, STEAM, TEMPERATURE.

Paper VII

An empirical rate model for black liquor char gasification as a function of gas composition and pressure

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Symposium Series 90(302):73-84 (1994).*

An Empirical Rate Model for Black Liquor Char Gasification as a Function of Gas Composition and Pressure

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The purpose of this study was to generate an expression for the gasification rate of black liquor char during simultaneous reaction with steam and carbon dioxide under pressurized conditions. Statistical experimental design was used to generate a matrix of thirty experiments with varying concentrations of H₂O, CO₂, H₂, and CO. The gasification rate was then measured using a pressurized thermogravimetric reactor. Regression was used to find an optimum empirical expression which predicts the gasification rate as a function of the partial pressures of the four reacting gases. The calculated rates fit the experimental data well. Based on the model, it was found that for a given gas composition, the rate goes through a minimum as pressure is increased. As the ratio of reductive species (H₂ and CO) to oxidative species (H₂O and CO₂) increases, the gasification rate decreases and the pressure at which the minimum rate occurs increases. The model was applied to a theoretical gasifier, and the gasification time decreased as the air ratio was increased. As the pressure of the reactor was increased, additional air was necessary to maintain the same gasification rate.

There is growing interest worldwide to develop alternate chemical recovery processes for paper mills which are cheaper, safer, more efficient, and more environmentally sound than traditional technology. Pressurized gasification of black liquor is the basis for many proposed schemes and offers the possibility to double the amount of electricity generation per unit of dry black liquor solids. Such technology is also hoped to have capital, safety, and environmental advantages.

Little data exists regarding the kinetics of black liquor gasification, particularly under pressurized conditions. Investigations have been made into black liquor gasification with both steam and carbon dioxide at atmospheric conditions. [1-5] Previous studies at Åbo Akademi have investigated separately pressurized gasification of black liquor char with H₂O and pressurized gasification with CO₂. [6-9] However, no kinetic data exists for a system in which both H₂O and CO₂ gasification occur simultaneously under pressurized conditions.

The purpose of this study was to investigate the kinetics of pressurized black liquor gasification when both steam and carbon dioxide are used as gasifying agents. Linear regression was used to fit a linear rate expression to experimental data obtained by gasifying black liquor char with a mixture of H₂O, CO₂, H₂ and CO. Based on the resulting expression, trends in the gasification rate and changes in the behavior of a pressurized gasification system were predicted.

EXPERIMENTAL

Experimental Approach

The objective of this investigation was to study how the four gases H₂O, CO₂, H₂ and CO affect the char gasification rate under pressurized conditions. It was decided to perform all experiments at one temperature but at several different total pressures. To investigate separately the effects of pressure and gas composition would require an excessively large experimental matrix. Therefore, a statistical experimental design approach was chosen. The experimental parameters were all varied between experiments and linear regression was used to fit a rate expression to the experimental data.

Four parameters were varied: the total pressure and the concentrations of CO₂, H₂ and CO. Seven total pressures varying logarithmically between 2 and 30 bar were used. The concentration of CO₂ was varied between 20% and 60% and the concentrations of H₂ and CO were each varied between 3% and 15%. H₂O provided the remainder of the reacting gas, resulting in a concentration range of 10% to 74%. The limits of the gas concentrations were carefully chosen to avoid carbon formation resulting from the Boudouard reaction ($2\text{CO} \rightarrow \text{C} + \text{CO}_2$).

A Plackett-Burman algorithm was used to generate the experimental matrix [10]. The algorithm generates an experimental plan by minimizing the degree of correlation

between experiments, resulting in a matrix which is highly varied yet which covers the ranges of the parameters well. It was found that 30 experiments were necessary in order to achieve a suitable sampling for all parameters. The conditions for the experiments, as well as the resulting rates, are given in the appendix.

Sample

The char used in the experiments was produced from a North American hardwood kraft liquor by introducing it into a drop tube furnace under pyrolysis conditions at 900°C and atmospheric pressure. The drop tube furnace and experimental procedure is described in more detail by Clay, et al [11].

Samples of the char used in the experiments were analyzed for carbon, sodium and sulfur content. No determination was made for hydrogen in this char. However, an earlier batch of char from the same mill was analyzed for hydrogen. The results of the analyses of both chars, based on their dry weights, are presented in Table 1.

Equipment

The gasification kinetics were measured using a pressurized thermogravimetric analyzer (PTGA). A schematic drawing of the apparatus is presented in Figure 1.

The PTGA is capable of operating at pressures up to 100 bar and the reactor has a maximum operating temperature of 1100°C. Up to four gases can be supplied to the reactor. In addition, the apparatus is equipped with a steam generator, thereby making it possible to use water vapor as a reacting gas. The steam and permanent gas lines each have a three-way valve which can be switched either to the reactor or to a bypass line. This makes it possible to stabilize the steam flow in the bypass line prior to the start of gasification, thereby eliminating startup effects associated with the steam generator.

The reactor consists of a 17 mm i.d. tube wrapped by a heating coil. The sample is suspended in the reactor by a long chain which is connected to a microbalance. The weight signal from the microbalance, as well as the sample temperature, are registered on a data acquisition computer which creates a data file for each experiment.

The PTGA is equipped with a water-cooled, helium-purged sample lock placed above the reactor. The sample is loaded into the device via this lock. By means of a small, electrically-driven winch the sample can be lowered into the reacting chamber once the desired conditions have been established.

Experimental procedure

For each experiment, a cylindrical platinum sample holder was loaded with approximately 100 mg of crushed char and placed into the sample lock. The reactor was pressurized and heated to the desired temperature while the steam flow was adjusted and directed through the bypass line. The sample was then lowered into an atmosphere of nitrogen and 10% carbon monoxide.

Figure 2 shows the weight versus time curve for a typical gasification run. In region "a", the sample was in the N₂/CO atmosphere and a sharp weight loss occurred. During this period, moisture in the sample was evaporated and volatile matter not removed during the char formation was pyrolyzed. Also, reduction of sodium sulfate to sodium sulfide may have occurred.

The sample weight stabilized within 100 to 200 seconds. After 400 seconds the gas composition was quickly adjusted to that for gasification and the flow of steam was switched from the bypass to the reactor. A sharp decrease in the weight signal was observed, followed by a weight increase (region "b"). The sudden decrease was due to a change in drag force caused by the introduction of the gasification mixture. The rapid weight increase was caused by adsorption of gasifying species onto the sample. Region "c" depicts the weight loss due to the removal of carbon in the sample by gasification.

The sample was gasified until the weight became stable, as in the final 500 seconds of the run shown in Figure 2. The steam flow was then turned off and the sample was lifted into the sample lock. After depressurizing the system, the sample was removed and weighed. The remaining material was usually grey or white in color, since the carbon had been gasified and the residue was composed of inorganic salts.

Analysis of the gasification data

In order to evaluate the rate of gasification, the gasification section of the weight loss curve was normalized with respect to the amount of gasifiable material in the sample. Hence, the rate equation is of the form

$$rate = - \frac{1}{m_{gm,i}} \frac{dm_{gm,t}}{dt} \quad (1)$$

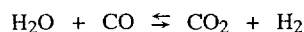
where $m_{gm,t}$ is the amount of gasifiable material remaining in the char at time t and $m_{gm,i}$ is the initial mass of gasifiable material in the char, found in preliminary studies to be 18.0 wt% of the char's starting mass. Based on this equation, the units for the rate are s⁻¹.

The rate of gasification was determined by finding the maximum slope of the normalized weight curve. In this study, this was done by first using linear regression to fit

a polynomial equation to the weight vs. time data. Correlation coefficients were high, generally above 0.999. By differentiating this equation, an equation for rate as a function of time was obtained. The maximum rate was calculated from this equation, and is hereafter referred to as the gasification rate. The relation between rate and char conversion could also be determined from the polynomial equations. A typical rate vs. conversion curve is shown in Figure 3.

GAS EQUILIBRIUM CONSIDERATIONS

The reacting gas for the experiments in the current study was a mixture of H_2O , CO_2 , H_2 and CO . As a consequence of the method by which the experimental plan was generated, the amount of each component for a particular experiment was random. At high temperature, if given time, such a gas mixture will come to equilibrium according to the water-gas shift reaction:



Because this study focuses on the kinetics of gasification as a function of the concentrations of the various species, it is important to ensure that the gas composition reaching the sample is the same as that fed into the reactor, rather than its equilibrium composition.

Preliminary experiments were performed to determine whether the gas mixture was coming to equilibrium prior to reaching the sample. Five groups of experiments were carried out. Each group consisted of three experiments with varying gas compositions, all of which would have the same composition at equilibrium. If the gas mixture were reaching equilibrium prior to reacting with the sample, the same rate would be expected for all three experiments within a given group. It was found that the gasification rates for the three experiments in each group were very different, indicating that the reacting gas was not coming to equilibrium prior to contacting the sample.

MASS TRANSFER CONSIDERATIONS

In this investigation, the kinetics of the chemical reaction itself was focus of study. Consequently, it is of importance to ensure that film mass transfer and pore diffusion provide such small resistances that their contributions to the overall rate are negligible. Several methods, both theoretical and experimental, exist to determine if this is the case. A brief summary of such considerations is presented here. More detailed analyses can be found elsewhere. [6,7,9,12]

Theoretical determination of the roles of resistances

The Weisz modulus and mass transfer Biot number can be used in combination to determine the influence of film mass transfer and pore diffusion on the overall rate.

Frederick and Hupa [7] outline a procedure which employs the Weisz modulus and Biot number to calculate the relative importance of these resistances. Using their procedure, the percentage of the overall rate which is controlled by chemical reaction kinetics was determined for the three fastest experiments in this study, where limitations caused by film mass transfer and pore diffusion would be most likely to occur. In the worst case, film mass transfer and pore diffusion combined account for less than 0.5% of the total resistance, which is negligible.

A second theoretical method to estimate the influences of film mass transfer and pore diffusion considers the case where either of these processes is the sole rate-determining mechanism. The theoretical time for complete conversion can be calculated for either of these cases, based on known parameters of the system. If the calculated time is close to the observed time for complete conversion, it suggests that the overall rate is controlled by film mass transfer or pore diffusion rather than by chemical kinetics.

Such theoretical calculations, to 90% conversion, were performed for the three fastest runs in the study and compared to the observed time to 90% conversion. In the worst case, the sum of the theoretical times for film mass transfer and pore diffusion is 0.9% of the observed time. Hence, the overall rate of gasification is controlled by chemical kinetics.

Experimental methods to investigate the roles of resistances

Several experimental techniques, such as varying the carrier gas and gas velocity, exist to investigate the role of film mass transfer and pore diffusion in the overall gasification process. Earlier studies performed by Åbo Akademi have included such experimental investigations, and in all cases it was concluded that film mass transfer and pore diffusion provide negligible resistance to the overall gasification process [6,7,9].

RESULTS AND DISCUSSION

Development of the gasification rate expression

The 30 experiments yielded a data matrix which included the partial pressures of H_2O , CO_2 , H_2 and CO for each run plus the corresponding gasification rate. Based on this data, the coefficients of linear rate expressions were calculated using a linear regression program. The program optimized the coefficients of the terms in order to minimize the sum of the squares of the residuals. The subroutine could also perform an f-test on each term and remove the insignificant ones so as to simplify the expression. The tested rate equations were chosen with simplicity of the model in mind.

The first model tested was a simple expression of the following form:

$$\text{rate}(\times 10^4) = Z + Ap_{H_2O} + Bp_{CO_2} + Cp_{H_2} + Dp_{CO} \quad (2)$$

where p_i is the partial pressure of species i . Upon regression analysis, the resulting rate expression was:

$$\begin{aligned} \text{rate}(\times 10^4) = & 5.83 + 1.11p_{H_2O} + 0.616p_{CO_2} \\ & - 3.67p_{H_2} - 3.91p_{CO} \end{aligned} \quad (3)$$

The correlation coefficient, R^2 , between the predicted and observed rates for this expression is 0.685. Though the closeness of fit is not very good, analysis of each term provides information as to the behavior of the gasification system. The coefficients of the gasifying species H_2O and CO_2 are positive, suggesting that an increase in the partial pressures of these species contributes to an increase in the rate. H_2 and CO , however, have negative coefficients, indicating that they inhibit the gasification reaction. Based on this expression, one would expect that an increase in the partial pressures of H_2 and CO would result in a decrease in the gasification rate. This trend, as well as the positive effect of H_2O and CO_2 have been reported to be true for pressurized black liquor gasification [7,9].

The magnitude of the coefficient for the H_2O term is nearly double that for the CO_2 term, suggesting that it has a larger impact on the rate. Additionally, the magnitude of both the H_2 and CO terms are larger than those of the H_2O and CO_2 terms. This would suggest that, for a particular gas composition, the rate would decrease with increasing pressure. This has been shown to be true for both carbon dioxide and steam gasification of black liquor char [7,9].

Other forms of the rate expression, including squares, products and inverses of partial pressures were tested and optimized using the regression subroutine. From these models, the most significant terms in the expressions were combined into one large expression. This was then analyzed using the regression subroutine and the insignificant terms were removed one by one until an expression containing just six terms remained:

$$\begin{aligned} \text{rate}(\times 10^4) = & 3.312 + 1.157p_{H_2O} + 0.07119p_{CO_2}^2 \\ & - 2.943p_{H_2} - 3.869p_{CO} + 0.6595\left(\frac{1}{p_{CO}}\right) \end{aligned} \quad (4)$$

It was found that six terms was the least necessary to maintain a high correlation coefficient. For this expression, R^2 is 0.894, and the correlation between the

calculated and observed rates is quite good, as can be seen in Figure 4. This model was chosen to be the most useful due to its simplicity and effectiveness in predicting the gasification rate.

Prediction of gasification behavior based on the model

Based on the above expression, trends in the gasification rate can be predicted. One must bear in mind that the conditions at which the rate is evaluated should be within the limits of those for which the model was developed. Specifically, the rate model is only valid for gasification of the char used in the study at 750°C and with partial pressures of H_2O , CO_2 , H_2 and CO within the limits of those used in the experiments. However, it is likely that the trends hold true for other black liquors as well.

Figure 5 depicts the gasification rate as a function of total pressure for various gas compositions, based on Equation 4. Experimental values are also shown in the figure. Of particular interest is the change in the shape of the curves as the gas composition changes. The rate goes through a minimum as the total pressure increases. As the ratio of reductive species (H_2 and CO) to oxidative species (H_2O and CO_2) becomes larger, the gasification rate decreases, the pressure at which the minimum rate occurs increases, and the curves flatten out.

The model can also be used to estimate the effect of the various gases on the gasification behavior. Figure 6 depicts the effect of carbon dioxide partial pressure on the gasification rate. The model suggests that at lower partial pressures, carbon dioxide does not greatly affect the gasification rate. As the partial pressure increases, the influence of carbon dioxide on the rate becomes more pronounced.

APPLICATION OF THE RATE MODEL

The rate expression given in Equation 4 can be used to study the behavior of a true gasification system. The particular reactor investigated is a hypothetical entrained-flow gasification reactor, shown in Figure 7. Black liquor and air are introduced into the reactor, which is operated isothermally at 750°C. Immediately, the black liquor dries and devolatilizes (zone 1). For the purpose of the model, the simplification is made that the pyrolysis gases and the input air come to equilibrium. This gas then completely gasifies the remaining char (zone 2). As the char is gasified, the gas composition changes, which in turn affects the rate of gasification.

The amount of air introduced into the reactor can be defined in terms of an air ratio, based on the stoichiometric amount required for complete combustion of the black liquor. An air ratio of zero means that no air is fed to the system while an air ratio of 1.0 will result in complete combustion of the black liquor to CO_2 and H_2O .

Typical gasification systems operate with an air ratio of roughly 0.4. The amount of air introduced into the reactor will affect the equilibrium composition of the gases resulting from zone 1 and will consequently affect the gasification rate.

A typical black liquor with a dry solids composition of $C_{10}H_{12.5}O_7Na_{2.4}S_{0.3}$ was used in the calculations. It was assumed that the liquor had been concentrated to 75% dry solids. The composition of the char resulting after pyrolysis, in terms of the original dry solids composition, was $C_{4.67}H_{1.51}O_{4.55}Na_{2.4}S_{0.199}$. Half of the sulfur in the char was assumed to remain in the ash as solid Na_2S . The rest of the sodium was assumed to remain in the form of solid Na_2CO_3 . The remainder of the carbon, sulfur, and oxygen, as well as all the hydrogen, were removed during gasification. It was assumed that the hydrogen and oxygen contents in the char decreased linearly as a function of carbon conversion.

The gasification rate for this reactor has been calculated as a function of the air ratio. Additionally, it has been calculated as a function of char conversion. The equilibrium distribution of gases at a particular conversion was determined based on the composition of the pyrolysis products, vaporized moisture, input air, and gasified char. The gasification rate was then calculated using the partial pressures of these gases.

Figure 8 shows the predicted gasification rate as a function of the stoichiometric air ratio for various pressures. The rates were calculated for the char at 50% conversion. From the figure it can be seen that the gasification rate increases with increasing air ratio. As the pressure of gasification is increased, more air will have to be provided to maintain reasonable gasification rates.

This model is just a first step in the development of a comprehensive model for black liquor gasification. Work is continuing at Åbo Akademi and elsewhere to develop a model which will take into consideration physical and chemical changes which occur as the char is converted.

CONCLUSIONS

An empirical rate expression was developed for gasification of black liquor char as a function of the partial pressures of the reacting gas species. The rates predicted by the model correspond well with the observed experimental rates as measured by the PTGA.

Steam and carbon dioxide both increase the gasification rate with the effect of H_2O being roughly double that of CO_2 . Hydrogen and carbon monoxide both decrease the gasification rate, and their inhibiting effect is stronger than the gasifying effect of H_2O and CO_2 for a particular partial pressure.

Based on the model, it was found that the gasification rate goes through a minimum as a function of pressure at constant gas composition when the ratio of oxidative

species to reductive species is high. As more reductive species are added to the reacting gas, the gasification rate decreases, the pressure at which the minimum rate occurs increases, and the curves flatten out.

The rate expression can be used to predict the behavior of a gasification reactor. The gasification rate increases with as the air ratio increases and as the pressure decreases. As the char is converted, the concentrations of H_2 and CO in the reactor increase. This results in a decrease in the gasification rate.

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Table 1 Elemental analyses of chars, based on dry weight

<u>Element</u>	<u>Composition, wt%</u>	
	<u>This study</u>	<u>Earlier char</u>
C	31.47	31.22
Na	21.70	18.95
S	4.85	3.99
O	(n/a)	38.71
H	(n/a)	1.97
Other (by difference)	(n/a)	5.16

Appendix Conditions and gasification rates for the 30 experiments

Exp. No.	Pressure (bar)	Gas composition (%)				Gasification Rate
		H ₂ O	CO ₂	H ₂	CO	
1	2	74	20	3	3	16.97
2	2	41	50	3	6	11.15
3	2	65	20	6	9	9.73
4	2	32	50	12	6	3.96
5	2	53	20	15	12	7.44
6	3	68	20	3	9	9.33
7	3	22	60	3	15	2.22
8	3	38	50	9	3	9.56
9	3	30	40	15	15	1.18
10	5	22	60	6	12	3.15
11	5	46	30	9	15	2.90
12	5	32	50	12	6	3.86
13	5	33	40	15	12	2.15
14	8	36	40	9	15	1.51
15	8	25	60	9	6	5.51
16	8	26	50	15	9	1.86
17	8	42	40	15	3	5.35
18	12	22	60	6	12	2.92
19	12	59	20	12	9	5.98
20	12	32	50	12	6	3.49
21	12	36	40	15	9	3.00
22	19	61	30	3	6	12.54
23	19	49	30	6	15	1.84
24	19	31	60	6	3	18.15
25	19	22	60	9	9	3.00
26	19	65	20	12	3	8.71
27	30	55	30	3	12	7.65
28	30	61	30	6	3	22.63
29	30	36	40	9	15	0.98
30	30	46	30	12	12	1.68

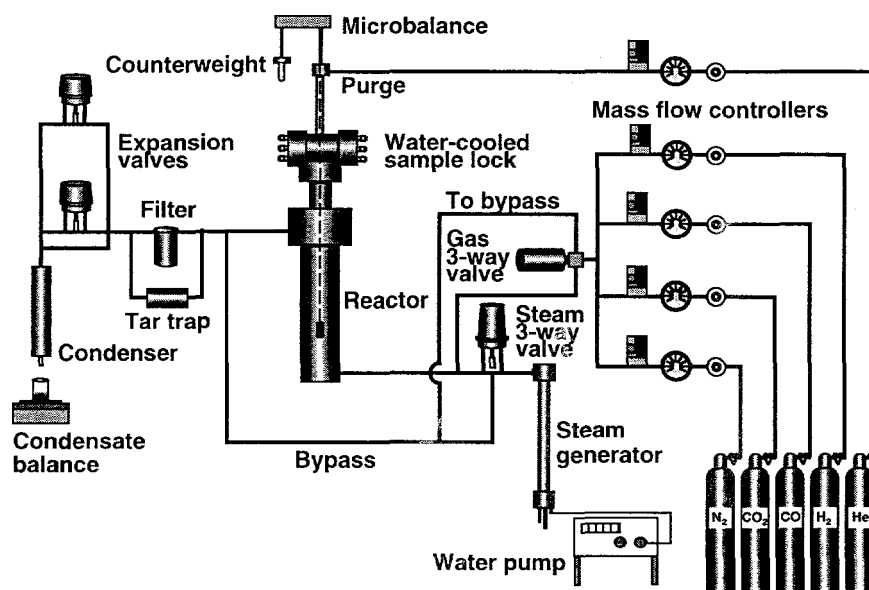


Figure 1 The Åbo Akademi pressurized thermogravimetric analyzer. 1100°C, 100 bar maximum.

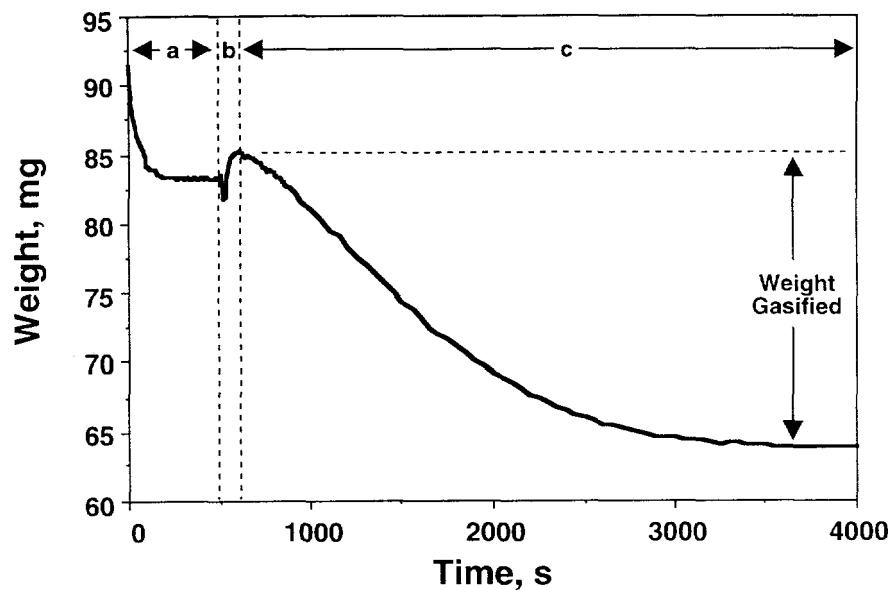


Figure 2 Weight vs. time curve for a typical gasification run.

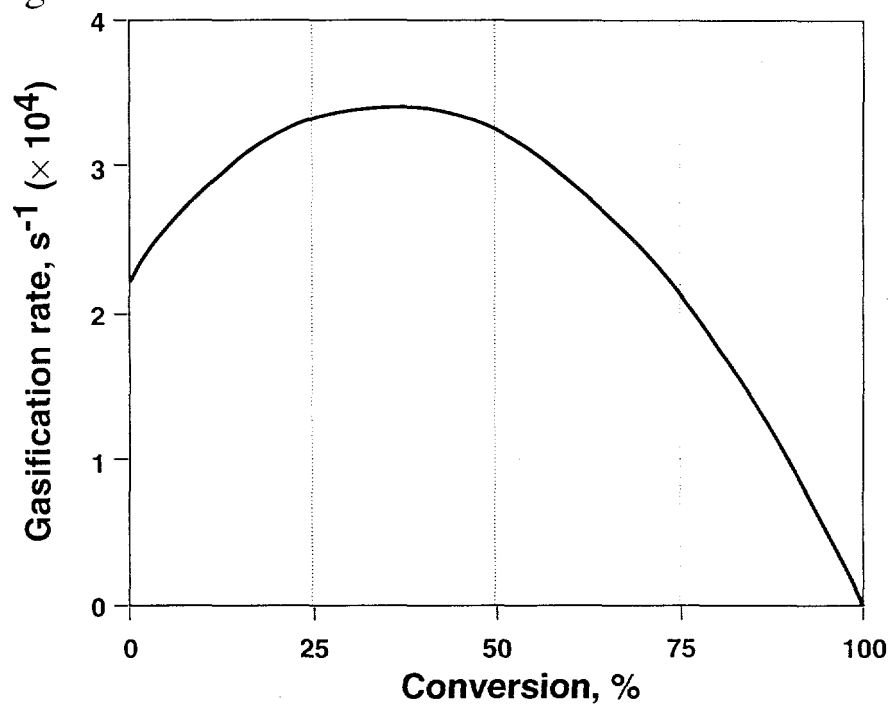


Figure 3 Gasification rate versus conversion for a typical gasification experiment.

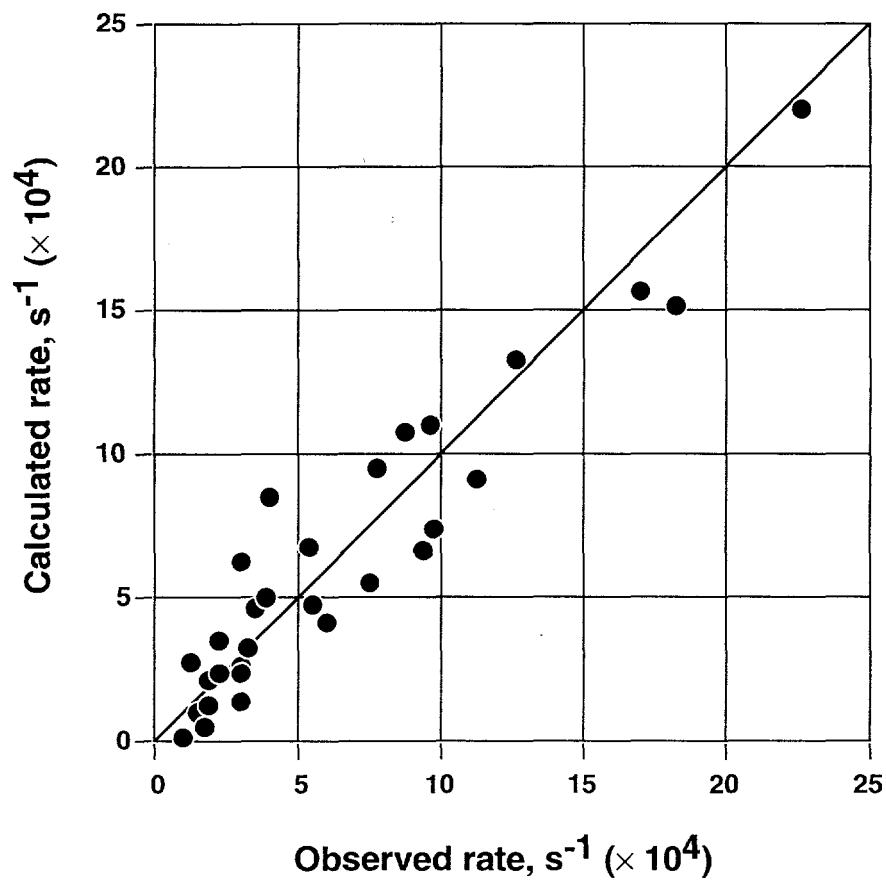


Figure 4 Calculated versus observed rate for the rate expression given in Equation 4.

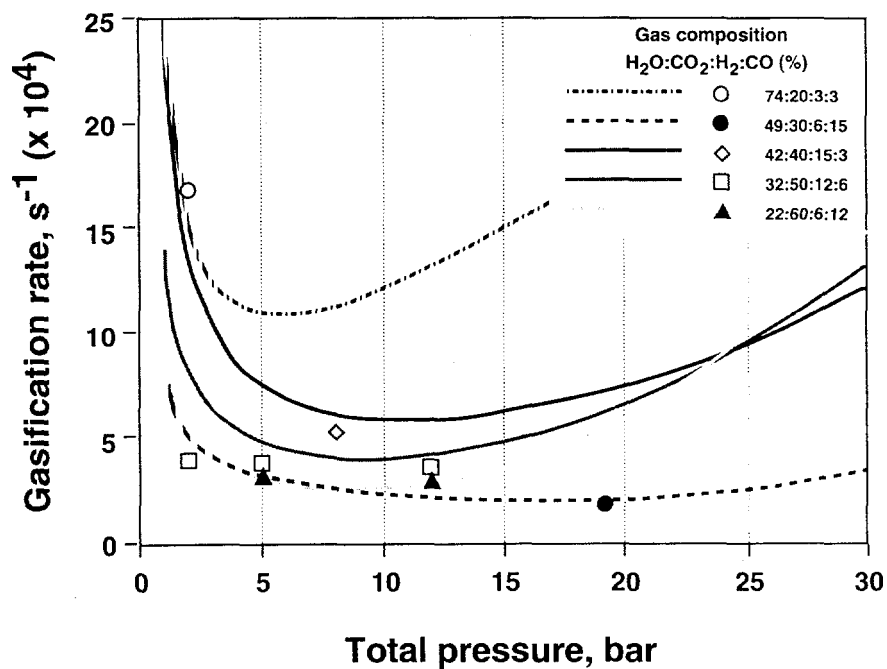


Figure 5 Gasification rate, based on Equation 4, as a function of total pressure for various gas compositions.

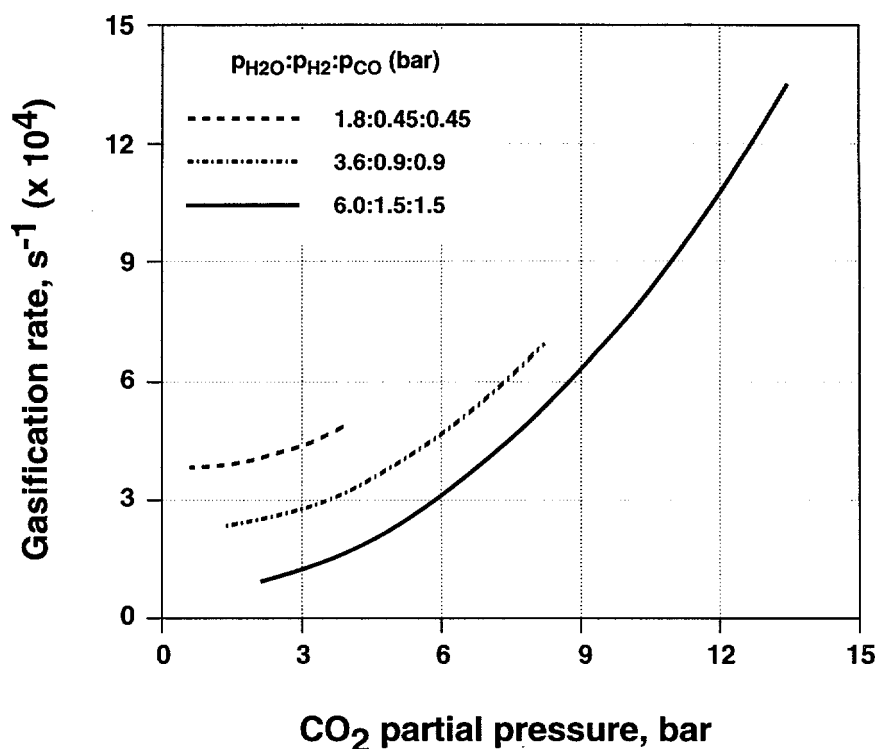


Figure 6 Effect of CO₂ partial pressure on the gasification rate, as predicted by the model given in Equation 4.

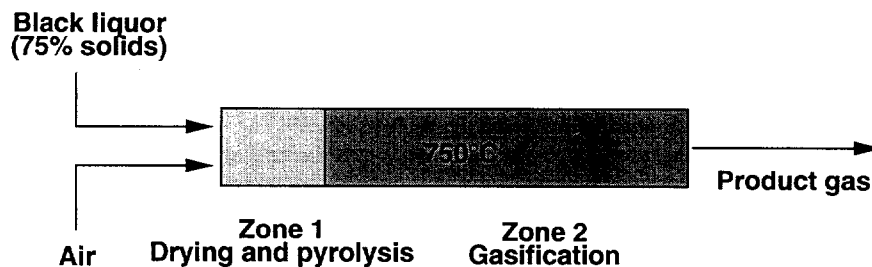


Figure 7 Hypothetical entrained flow reactor for gasification of black liquor.

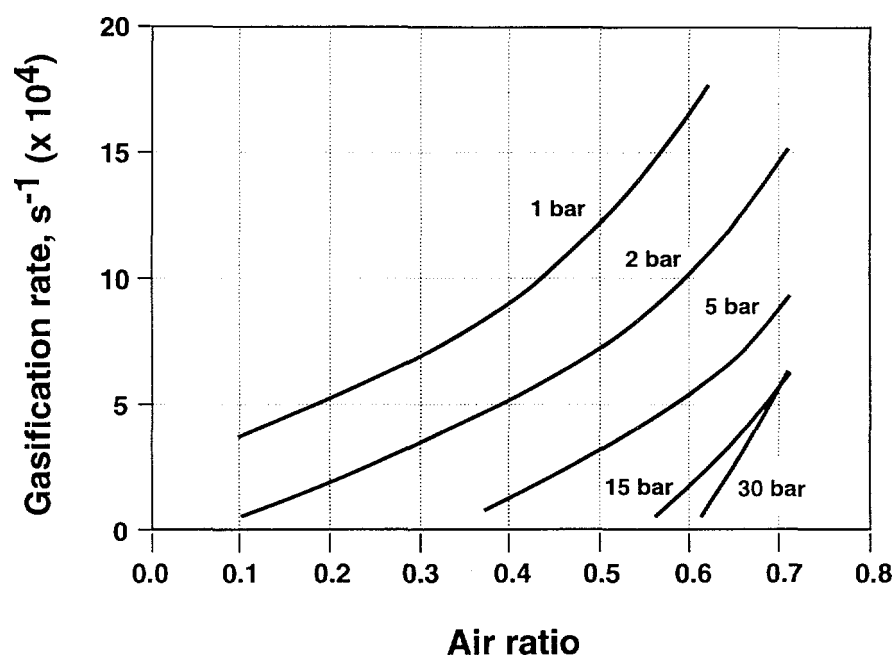


Figure 8 Gasification rate at 50% conversion as a function of air ratio and pressure for the hypothetical entrained flow gasifier. Air ratio is based on complete combustion of the black liquor. Gasification rate is calculated from Equation 4.

Paper VIII

Pressurized gasification of black liquor — Effect of char sodium content

Submitted.

PRESSURIZED GASIFICATION OF BLACK LIQUOR — EFFECT OF CHAR SODIUM CONTENT

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A series of synthetic black liquor chars was produced with varying sodium content. Weight loss during isothermal char gasification, by either CO₂ or H₂O at 800°C and 10 bar, was measured in a thermogravimetric analyzer. For synthetic liquor chars pyrolyzed at 10 bar, both CO₂ and steam gasification rates were found to initially increase with increasing char sodium content. The maximum rate was achieved at 0.20 moles sodium per mole of organic char carbon; the gasification rate decreased for higher sodium loading. Gasification of the highest sodium content char (0.55 mol Na/mol C) was an order of magnitude less than for an industrial kraft liquor char gasified at identical conditions. Liquors pyrolyzed at atmospheric pressure produced more reactive chars than those pyrolyzed at 10 bar. Chars made from dry mixtures of organic solids and Na₂CO₃ gasified at a lower rate than chars made from homogeneous liquid mixtures. Activation energy for CO₂ gasification decreased with synthetic liquor char sodium content.

INTRODUCTION

The composition of black liquor depends on the wood species being pulped, the amount of chemicals added, and the cooking conditions. All black liquors contain three basic components: alkali lignin, aliphatic carboxylic acids, and inorganic sodium compounds. A typical Finnish pine black liquor composition, reported by Alén et al. [1] is presented in Table I. These values were chosen as targets for the synthetic liquor formulations used in this study.

Hydrolysis of wood lignin during the kraft pulping process creates the alkali lignin portion of black liquor; it is present largely as colloidal polymer molecules. The carboxylic acids arise primarily from unwanted degradation of cellulose and hemicellulose. More than half of the sodium present in black liquor is bound to the various ionized organic liquor components [2]. The remaining sodium is present as a mixture of residual active pulping chemicals (NaOH and Na₂S) and reacted, inert species (primarily Na₂CO₃ and Na₂SO₄). Black liquor also contains minor amounts of solvent-extractable compounds and polysaccharides [1], and trace quantities of many inorganic species [2].

Three distinct stages of black liquor combustion have been identified: drying, devolatilization, and char burning [3]. In conventional kraft process chemical recovery operations, nozzles break the concentrated black liquor into a spray of coarse drops. A significant portion of drying and devolatilization occurs as the drops fall to the char bed at the bottom of the recovery boiler; much of the char burning takes place on the char bed [4]. As char carbon is depleted during char burning, the inorganic compounds coalesce as molten smelt. For the purposes of this study, it is necessary only to consider certain processes which occur during devolatilization and char burning.

Char carbon is largely consumed by gasification reactions occurring on the char bed. These heterogeneous reactions are of interest not only for better understanding and control of conventional recovery boiler operation but also for designing more energy-efficient processes, e.g., gasification in pressurized fluidized beds. Gasification reactions are strongly catalyzed by the alkali species present in black liquor char [5]. Much work has been done to study black

TABLE I
BLACK LIQUOR COMPOSITION

Component	Pine liquor [1], mass % dry solids	Synthetic liquor target, mass % dry solids
Lignin	33	35
Aliphatic carboxylic acids	31	30
Inorganics	28 ^a	30
Extractives	5	5
Other organics	3	0

^a Including organically-bound sodium.

liquor char gasification [5-9]; however, a predictive rate model describing the catalytic effect of char sodium content has not been developed.

The objective of this work was to study the effect of sodium on the gasification rate of kraft black liquor char. A series of synthetic liquor chars were produced with varying sodium content, and the rates of gasification by CO₂ and H₂O were separately measured at a set of standard conditions. The rates were compared to those of an industrial kraft liquor (IKL) char, gasified at identical conditions. The main variable of interest in this study was the sodium-to-carbon ratio in the char. Other factors that were expected to affect sodium distribution in the char were also considered; specifically, the method of pyrolysis and the form of the sodium (chemically bound to the organic compounds or physically mixed with the organic solids).

EXPERIMENTAL

Synthetic Liquor Preparation

Synthetic liquors were prepared to produce a set of chars with sodium contents ranging from zero to a level typical of industrial kraft liquor chars. The approximate composition of pine liquor, given in Table I, was used as a model for the liquor formulations. The objective was to maintain a constant organic fraction in the synthetic liquors, both in amount and composition while varying the amount of sodium in the inorganic fraction. The sodium content was varied by dissolving the organic components in aqueous mixtures of NaOH and ammonia solution (NH₄OH). The components used in synthetic liquor preparation are summarized in Table II.

The research sample of acid-precipitated pine lignin (INDULIN AT®) was washed two times to reduce inorganic contamination before using it in the synthetic liquors. Alén

TABLE II
MATERIALS FOR SYNTHETIC LIQUOR PREPARATION

Component	Description	Assay	Source
Lignin	INDULIN AT® kraft pine lignin	> 97%	Westvaco Chemicals
Aliphatic carboxylic acids	GISAL	> 90%	VTT
	lactic acid	88.0%	BDH Lab. Supplies
Extractives	crude tall oil	n.a.	Metsä-Botnia Kemi
Sodium	NaOH	98%	Eka Nobel AB
	Na ₂ CO ₃	99.5%	Riedel-de Haën AG
Base	NH ₃ solution	25%	unknown

et al. [1] found that the combustion behavior of synthetic liquors was not significantly affected by the specific chemical composition of the aliphatic carboxylic acid fraction. However, the presence of lower molecular weight acid components did enhance the extent of swelling. For these reasons a simple, two-component mixture of high and low molecular weight acids was chosen for the synthetic liquors: crystalline α -glucoisosaccharinic acid 1,4 lactone (GISAL), molecular weight of 162.14, and commercial 2-hydroxypropionic (lactic) acid, molecular weight 90.08. The GISAL was isolated from pine black liquor [1]. Crude tall oil (CTO) from a kraft pulp mill was used as a model of black liquor extractives. The low quantity of sodium measured in the sample, 0.74 mg Na per g CTO, indicated that no further purification was required.

Synthetic liquor mixtures, contained in tightly-sealed jars, were stirred and gently heated at 50-70°C for 3-4 days. The completed synthetic liquors contained approximately 7-10% dry material and were stored in a refrigerator at 4-8°C until needed. Details of synthetic liquor preparation are provided elsewhere [10].

Considering the uncertainties caused by the loss of volatile components (ammonia, lactic acid, and CTO) during analysis, there is good

agreement between the estimated and measured sodium contents. The liquor analyses in Table III demonstrate that it was indeed possible to control the sodium content in the synthetic liquor formulations from only trace amounts to levels approaching those of industrial black liquors, i.e., 17-21% of dry solids [2].

Char Formation

Synthetic liquor chars were formed by pyrolysis at 10 bar total pressure in a pressurized thermogravimetric analyzer (PTGA), in situ, prior to beginning each gasification run. Dilute synthetic liquor samples were first freeze dried; it was then possible to load the fine, dry material into the PTGA sample holder.

After pyrolysis for 400 seconds in 90% N₂ and 10% CO at 10 bar and 700-900°C, char samples were either gasified (as described below) or removed for chemical analysis. Char samples required for analysis could be quickly quenched to room temperature within the water-cooled, helium-purged sample lock of the PTGA. They were then removed and weighed in order to determine the pyrolysis yield.

In fundamental studies of catalyzed char gasification, physical mixtures of alkali salts and carbonaceous chars have been frequently

TABLE III
SODIUM CONTENT OF SYNTHETIC LIQUORS^a

Liquor Na target, % liquor solids	Sample ^b	Na content, % liquor solids
0	conc	< 0.03
2	fds	2.39
4	conc	5.17
9	fds	10.4
20	conc	16.1
2(l) ^c	fds	2.23
4(l) ^c	fds	5.49

^a Analysis by Dr. H. Malissa and G. Reuter GmbH, Gummersbach, Germany; given as mass percent of dry liquor solids.

^b Sample type: conc = concentrated liquor; fds = freeze-dried solids.

^c Mixtures of sodium-free freeze-dried liquor solids and sodium carbonate.

used as starting materials [5,11,12]. In order to determine if the form of the sodium in the char precursor (organically bound or physically mixed) has an effect on the catalytic activity of the chars, two dry mixtures of freeze-dried solids and sodium carbonate were made. Predetermined amounts of Na_2CO_3 were added to portions of the sodium-free synthetic liquor solids to produce the desired sodium content (Table III). These mixtures were pyrolyzed in the same manner as the other freeze dried liquor samples.

The IKL sample was previously pyrolyzed in a large drop tube furnace at 900°C and atmospheric pressure, as described by Clay et al. [13]. Additionally, three of the synthetic liquors were pre-pyrolyzed at 1 bar to investigate the effect of pyrolysis pressure on char gasification reactivity. For these samples, a portion of the synthetic liquor was first concentrated in a rotary vacuum evaporator. Char was then formed from the concentrated liquor samples (30-60% solids) by pyrolysis at 800°C in a small tube reactor with a flowing gas mixture of 90% N_2 and 10% CO . A description of the tube reactor is given by Whitty et al. [14]. For this work, batches of approximately 100 mg of liquor were pyrolyzed for 60 seconds in the reactor; the char was then withdrawn into a quench chamber and allowed to cool under a nitrogen flow before removal. All the chars formed at atmospheric pressure were subjected to the 400 s of pyrolytic treatment at 10 bar in the PTGA prior to gasification experiments.

Pressurized Gasification

The usual application of a thermogravimetric analyzer involves slowly heating a sample to identify regions of characteristic weight loss. In these experiments it was more important to measure mass loss during isothermal gasification for a large number of samples. A rapid sample heating method was therefore employed which involved lowering the sample into the preheated reactor tube. Details of the PTGA system are described elsewhere [9,15].

For each pressurized gasification run, freeze-dried liquor solids or pre-formed char was loaded into a platinum sample holder, which

consisted of a cylindrical inner stem surrounded concentrically by a fine platinum net. The material was placed between the stem and the net, resulting in a uniform sample thickness. Due to bulk density variations among the samples, the fully-loaded sample holder contained 60 to 200 mg of material.

The loaded sample holder was placed into the sample lock of the PTGA. The system was pressurized to 10 bar total pressure and purged with a mixture of 90% N_2 and 10% CO ; a total gas flow of 3.0 l/min (STP) was maintained throughout the procedure. Once the reactor had reached the desired gasification temperature ($700\text{--}900^\circ\text{C}$), the sample was quickly lowered, via an electric winch, into the reaction zone. Prior experience has shown that the samples reach constant weight (completion of pyrolysis) in approximately 400 seconds [9]. This heating stage constituted a second pyrolysis step for the char samples initially formed at atmospheric pressure. After 400 seconds, the gas composition was changed to the desired gasifying conditions. One of two gas mixtures was used in each experiment: either 20% CO_2 , 2% CO , 78% N_2 at 10 bar total pressure, or 20% H_2O , 2% H_2 , 2% CO , 76% N_2 at 10 bar total pressure.

During the gasification stage, weight loss was measured by the microbalance and a data file of weight versus time was produced. Whitty et al. [9] and Frederick et al. [8] discuss typical weight loss curves obtained during similar experiments. When the experiment was complete, the holder was lifted into the sample lock and the system was depressurized. The sample was then removed and weighed. Due to time restrictions, some gasification runs were terminated before complete conversion was reached. In experiments that went to completion, the amount of gasifiable material, $m_{gm, \text{tot}}$, was taken as the total weight loss during gasification. The remainder was considered to be inert residual salts. In experiments that did not go to completion, the amount of gasifiable material was estimated from the results of similar experiments in which the amount of gasified material was measured. Fractional conversion (X) was defined as:

TABLE IV
REPRODUCIBILITY OF EXPERIMENTS

Run no.	Liquor Na target, % solids	Char yield, ^a % liquor solids	Gasified material, ^b % liquor solids	$-r_{25\%} \times 10^4, \text{ s}^{-1}$	$-r_{50\%} \times 10^4, \text{ s}^{-1}$
5259	4	38.0	25.7	11.50	9.70
5265	4	36.4	24.3	11.11	7.74
5297	4	36.4	23.9	8.77	6.52
av. ^c		36.9 ± 1.6	24.6 ± 1.6	10.46 ± 2.49	7.99 ± 2.70
5262	2(l)	31.1	22.3	10.17	7.51
5274	2(l)	25.8	21.6	6.16	4.76
5294	2(l)	28.3	23.3	5.43	4.19
av. ^c		28.4 ± 4.5	22.4 ± 1.4	7.25 ± 4.30	5.49 ± 2.99

^a Pyrolysis conditions: 400 seconds in 10% CO, 90% N₂ at 800°C; 10 bar total pressure.

^b Gasification conditions: 20% CO₂, 2% CO, 78% N₂ at 800°C; 10 bar total pressure.

^c Average value \pm 90% confidence limit.

$$X = 1 - \frac{m_{gm,t}}{m_{gm,tot}} \quad (1)$$

where the amount of gasifiable material remaining at time t ($m_{gm,t}$) is the instantaneous sample weight minus the inert residue.

For each measurement time, the rate was taken as the best-fit slope through five points; the instantaneous weight plus two adjacent points on either side. The slope was then divided by the amount of gasifiable material remaining at that time, resulting in the following definition of the rate:

$$-r_x = \frac{dm_{gm,t}}{dt} \times \frac{1}{m_{gm,t}} \quad (2)$$

where r_x is the gasification rate at a given fractional conversion, and $dm_{gm,t}/dt$ is the instantaneous numerical derivative of the weight-versus-time data. A smooth polynomial function was fit to the calculated rate-versus-conversion values. The rate at a particular conversion was determined from this polynomial expression.

Three replicate gasification runs for each of two char samples were conducted to assure reproducibility of the results (Table IV). Both samples were pyrolyzed and gasified

under identical conditions. Reproducibility of gasification rate determined for the char made from synthetic liquor with 4% target sodium content was good. The physical mixture of freeze dried solids and Na₂CO₃ produced more variable results due to inhomogeneous composition of the mixtures. The same degree of variation is reflected in the amount of residue at the end of the gasification runs: 8.8, 4.2, and 5.0% of the liquor solids mass for run numbers 5262, 5274, and 5294 respectively.

Film Mass Transfer and Pore Diffusion Effects

This study concerns the kinetics of char gasification; therefore, it is important that the gasification rate obtained is the actual chemical kinetic rate. In order to ensure that the chemical reaction is the resistance controlling the rate, the film mass transfer and pore diffusion must occur much more rapidly than the overall rate. Several types of tests, both theoretical and experimental, can be used to determine if this is the case.

Frederick and Hupa [16] outlined a procedure which employs the Weisz modulus and mass transfer Biot number to determine the relative importance of mass transfer resistances to the overall rate. Using this procedure, they found

that the rates in their study (up to $15.1 \times 10^{-4} \text{ s}^{-1}$) were controlled by chemical kinetics for a wide range of CO_2 gasification conditions. Similar calculations and verifying experiments were conducted by Whitty [17] to show that chemical kinetics also controlled the faster rates of pressurized steam gasification. In the present set of experiments, the maximum rate of $190 \times 10^{-4} \text{ s}^{-1}$ occurred for steam gasification of IKL char at 800°C . The combined contribution of film mass transfer and pore diffusion was estimated to be approximately 5% of the overall resistance for this run. The remaining rates in this set of experimental results were all less than half of the maximum rate; therefore, the contributions of pore diffusion and film mass transfer were neglected for all runs.

RESULTS

Char Composition

Average char yields from pressurized pyrolysis of five synthetic liquors and two mixtures of sodium-free liquor solids and Na_2CO_3 are given in Table V. Additionally, chars from three synthetic liquors which had been previously pyrolyzed at atmospheric

pressure were investigated. These chars lost a significant amount of material during pressurized heat treatment in the PTGA. Accordingly, the char yields given in Table V were taken as the product of both treatments. Devolatilization of the IKL sample during pre-pyrolysis at 1 bar was not extensive due to short residence time in the large tube furnace [13]. Because the initial char yield of IKL was unknown, only the result of pyrolysis at 10 bar is given, based on the initial mass of the pre-formed char.

Carbon and sodium contents were measured for all chars. Levels of hydrogen and sulfur were expected to be small for synthetic liquor chars; therefore, all samples were not analyzed for these components. Excepting the low sulfur content, the analyses of the highest-sodium-content synthetic liquor chars are similar to that of the IKL, given in Table V, and to those of other chars reported in the literature [5,8].

Figure 1 shows the measured carbon content of all char samples is closely related to the fraction of gasified material in the chars (see Table V). This agreement suggests that less

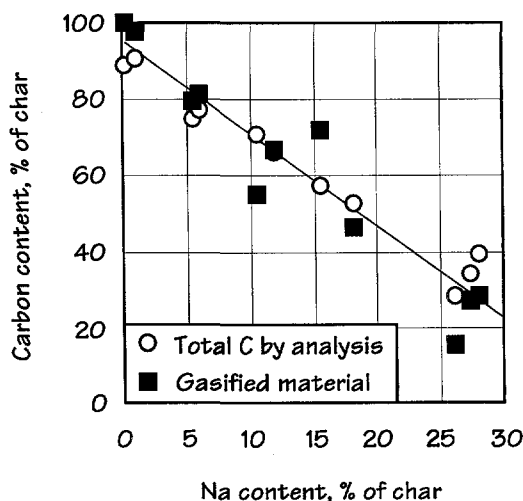


Fig. 1. Synthetic liquor char carbon content by elemental analysis and mass balance from gasification. Pyrolysis at 10 bar in PTGA.

TABLE V
CHAR YIELDS, GASIFIED MATERIAL, AND CHAR COMPOSITION

Liquor Na target, % solids	Pyrolysis pressure, bar	Char yield, ^a % init. mass	Gasified material, ^b % init. mass	Elemental analysis of chars ^c				
				C, % char	H, ^d % char	Na, % char	S, ^d % char	(n_{Na}/n_C) ₀₁ ^e mol/mol
0	10	21.7	20.9	91.06	1.18	1.06	n.d.	0.006
2	10	30.8	23.9	76.89	n.d.	6.05	n.d.	0.039
4	10	36.6	24.3	65.70	0.69	11.90	0.44	0.094
9	10	49.0	21.7	51.72	n.d.	18.20	n.d.	0.208
20	10	54.2	14.4	33.03	0.18	27.45	0.30	0.546
2(l)	10	28.4	22.4	74.38	n.d.	5.53	n.d.	0.034
4(l)	10	37.9	20.8	70.57	0.88	10.65	0.49	0.101
IKL	1 & 10	68.3	10.0	27.50	0.21	26.05	4.16	0.933
0 ^f	1 & 10	10.5	10.5	89.27	n.d.	< 0.3	0.53	0.002
4 ^f	1 & 10	31.1	22.2	56.84	n.d.	15.55	0.48	0.113
20 ^f	1 & 10	54.2	14.7	38.93	n.d.	28.10	0.32	0.541

^a Mass remaining after 400 s pyrolysis at 800°C in 90% N₂/10% CO and 10 bar as percentage of initial mass of liquor solids, except IKL for which char yield is based on initial mass of pre-made char.

^b Measured material loss during gasification as percentage of initial mass of liquor solids, except IKL for which gasified material is based on initial mass of pre-made char.

^c Analysis by Dr. H. Malissa and G. Reuter GmbH, Gummersbach, Germany; given as mass percent of dry char material. Balance assumed to be oxygen.

^d Hydrogen and sulfur analyses were not determined (n.d.) for all chars.

^e Initial molar ratio of char sodium to amount of gasified material.

^f Chars made from concentrated SL at 1 bar were analyzed prior to heat treatment at 10 bar. All other samples were analyzed after pressurized pyrolysis in PTGA.

than 10% of the total synthetic liquor char carbon was present as inorganic carbonate. In keeping with the established convention [7,8], the amount of gasified material ($m_{gm, tot}$) was assumed equal to organic or "gasifiable" carbon and used to calculate the initial molar ratio of sodium to carbon, $(n_{Na}/n_C)_0$. The samples with the lowest sodium contents approach the sodium-to-carbon ratio of alkali-impregnated carbons used in coal gasification mechanistic studies [11]. The minimum $(n_{Na}/n_C)_0$ value for a black liquor char previously reported in the literature (0.34) was obtained by laboratory cooking of wood chips under controlled conditions [7].

Effects of Char Sodium Content on Gasification Rate

The CO_2 gasification rates of the chars made from sodium-free liquors were comparable to those obtained when a metal-free carbon sample was gasified at identical conditions (Fig. 2). The agreement of rates over 10-50% carbon conversion for these samples indicates that gasification of the sodium-free synthetic liquor chars was clearly a case of uncatalyzed gasification.

The effect of char composition on CO_2 gasification rates are summarized in Fig. 3, where the rates at 25% conversion are plotted

against instantaneous molar ratios of sodium to carbon $(n_{Na}/n_C)_X$:

$$\left(\frac{n_{Na}}{n_C}\right)_X = \left(\frac{n_{Na}}{n_C}\right)_0 \times \frac{1}{1-X} \quad (3)$$

A logarithmic scale was used to better show the results for the low-sodium synthetic liquor (SL) chars.

About 6% by mass of sodium in the char resulted in an order of magnitude greater gasification rate than for the lowest-sodium char (Fig. 3). There was a steady increase in gasification rate with increasing sodium content up to the point of $(n_{Na}/n_C)_{25\%} = 0.3$ for the SL chars. However, the highest sodium-content SL char, pyrolyzed at 10 bar, was less reactive than one containing less than half the alkali. In a study of CO_2 gasification of kraft lignin chars, no saturation effects were noted in chars with initial n_{Na}/n_C up to 0.3 for conversions up to 90% [18]. Sams and Shadman [19] found gasification rate of alkali-impregnated chars to increase with n_{Na}/n_C to a level of about 0.1 molar ratio; thereafter, gasification rate rapidly declined with further alkali loading. This effect was attributed to pore blocking by catalyst crystals. Lacking microscopic chemical analysis of the SL chars, it is not certain if

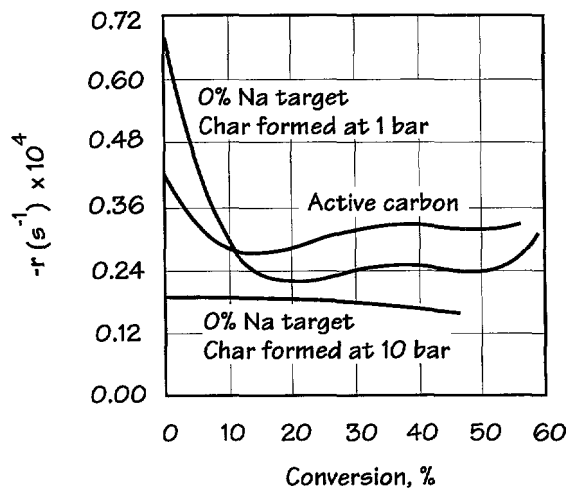


Fig. 2. Gasification rate versus carbon conversion for low-sodium chars and carbon. Gasification conditions: 800°C, 20% CO_2 , 2% CO , 78% N_2 , 10 bar.

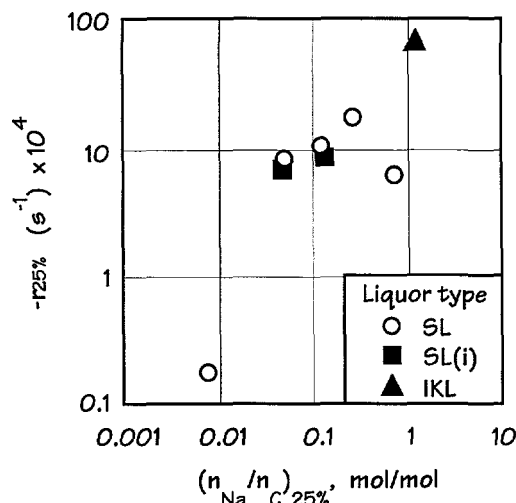


Fig. 3. Effect of char sodium content (as n_{Na}/n_C) and char type on CO_2 gasification rate. Gasification conditions: 800°C, 20% CO_2 , 2% CO , 78% N_2 , 10 bar.

pore blocking was responsible for the decrease in gasification rate observed for the SL chars.

The IKL char contains about 10 times more sulfur than the SL chars; the much higher gasification rate at about the same n_{Na}/n_C ratio may be due to the synergistic effect of sulfur compounds. The results of van Heiningen et al. [7] also showed higher gasification rates for kraft chars over sulfur-free soda chars with similar n_{Na}/n_C ratios. Additional experiments are needed to investigate the effect of sulfur on char gasification rate.

Results in Fig. 3 suggests that, at approximately the same level of $(n_{Na}/n_C)_{25\%}$, the chars made from physical mixtures of sodium-free, freeze-dried solids and Na_2CO_3 are somewhat less reactive than those made from NaOH-containing liquor precursors. The aqueous preparations contained more gasifiable carbon and less residue than the solid mixtures (Table V) which implies there was more sodium present as crystalline carbonate and less available as active catalyst in the solid mixtures. Li and van Heiningen [7] maintain that the organically-bound sodium in black liquor leads to a finer and more uniform distribution of alkali on the surface of chars and allows much higher

n_{Na}/n_C levels without blocking pores in the char. Comparison of gasification rates of coal chars impregnated with sodium carbonate and sodium lignosulfonate lead to similar conclusions by Gokarn and Mühlen [12]. A more uniform dispersion of sodium catalyst may explain the higher reactivities of the chars formed from liquid solutions.

Figure 4 shows that for the synthetic liquor chars, the rate of H_2O gasification is 6-8 times greater than for CO_2 gasification over the range of sodium contents. H_2O gasification was roughly 3 times faster for the IKL char, which agrees with earlier findings [9]. The same decrease in rate at high sodium loadings that was noted in Fig. 3 is evident in the steam gasification results. Van Heiningen et al. [7] reported a nearly linear increase in H_2O gasification rate with sodium over the range $(n_{Na}/n_C)_{25\%}$ from 0.4 to 1.0; the increase appeared to level out at sodium loadings above 1.0.

Effect of Pyrolysis Pressure on Gasification Rate

Figures 5 compares gasification rate versus conversion for the chars initially pyrolyzed at 1 bar in the tube reactor with their corresponding chars formed from pressurized pyrolysis of freeze dried solids.

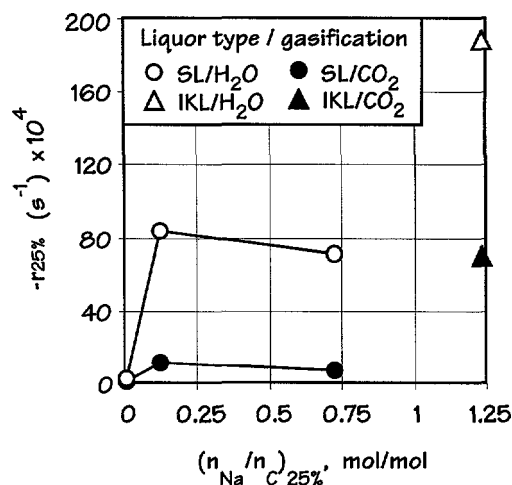


Fig. 4. Effect of char sodium content (as n_{Na}/n_C) and char type on steam gasification rate. Gasification conditions: 800°C, 20% H₂O, 2% H₂, 2% CO, 76% N₂, 10 bar.

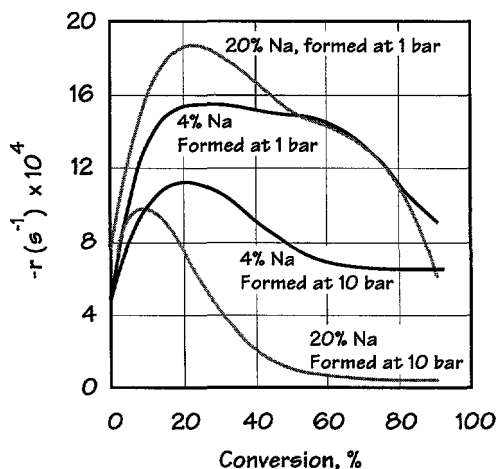


Fig. 5. Effect of char formation pressure on gasification rate for synthetic liquors with 4% and 20% Na target. Gasification conditions: 800°C, 20% H₂O, 2% H₂, 2% CO, 76% N₂, 10 bar.

Not only are the chars formed at 1 bar more reactive than those formed in situ in the PTGA at 10 bar, but they also do not exhibit the reduction in gasification rate at the highest sodium content. It can be concluded that the method of pyrolysis is very important to char reactivity, perhaps due to surface area development [7,11,18]. Due to limited

amounts of the samples, char surface area was not determined in this study.

Effect of Temperature on Gasification Rate

The effect of temperature on CO₂ gasification for two SL chars is illustrated in Fig. 6. The chars are identified by the target sodium level

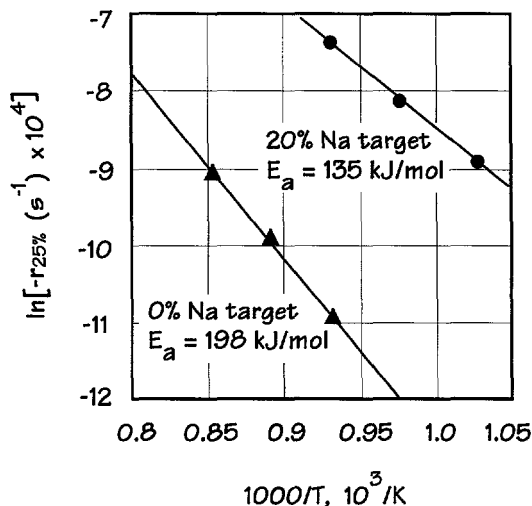


Fig. 6. Effect of temperature on CO₂ gasification rate for synthetic liquor chars with highest and lowest sodium contents. Pyrolysis at 10 bar in PTGA. Gasification conditions: 20% CO₂, 2% CO, 78% N₂, 10 bar.

of their parent liquors; both were pyrolyzed in situ at 10 bar in the PTGA. These results demonstrate the strong dependence of the gasification process on temperature: the rate increased by a factor of 5 over the temperature range 800-900°C for the char made from sodium-free liquor, $(n_{\text{Na}}/n_{\text{C}})_0 = 0.006$, and by a factor of 10 over the temperature range 700-800°C for the high-sodium char, $(n_{\text{Na}}/n_{\text{C}})_0 = 0.546$. The catalytic effect of sodium results in an increase in preexponential factor in the Arrhenius relationship, as indicated by the shift in the plot to the right in Fig. 6.

The slope of the lines in the Arrhenius plot gives the activation energy (E_a) for the CO₂ gasification reaction. An average activation energy of 205 kJ/mol for CO₂ gasification at 3-4 bar over the range 650-800°C was reported by Frederick and Hupa [16]. Li and van Heiningen [5] determined a value of $E_a = 250$ kJ/mol for industrial liquor char gasification with 20% CO₂, 5% CO in He at 1 bar for the temperature range 675-775°C. These are significantly higher than the value determined for the high-sodium char (135 kJ/mol); however, it is difficult to compare activation energies obtained at different reaction conditions. The change in activation

energy between the two SL chars represented in Fig. 6 may indicate a change in gasification mechanism; such a change was not observed in a related study of catalyzed coal char gasification [12].

CONCLUSIONS

By using a novel technique, a series of synthetic liquor chars were produced with sodium contents ranging from nearly zero to levels approaching those of industrial liquors. The results of this study support the proposed mechanism of alkali-catalyzed gasification:

- Gasification rate generally increases with char sodium content; however, pore blocking may hinder gas diffusion and decrease the overall rate at high Na loadings.
- Chars formed from liquid solutions containing NaOH were more reactive than those from physical mixtures of sodium-free organic solids and Na₂CO₃.
- The method of pyrolysis strongly affects gasification rate, probably by surface area development.

Gasification rates were obtained for eight chars containing less sodium than what has been reported in the literature ($n_{\text{Na}}/n_{\text{C}} = 0.002\text{--}0.208$ mol/mol), this catalyst-limited rate data is valuable for developing fundamentally-based models of black liquor char gasification.

Sulfur compounds were found to play an important role in black liquor char gasification. Gasification rate of the highest sodium-content char ($n_{\text{Na}}/n_{\text{C}} = 0.55$ mol/mol) was an order of magnitude less than for an industrial kraft liquor char of similar sodium content, gasified at identical conditions. Additional experiments are required to understand this effect.

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NOMENCLATURE

E_a	activation energy, kJ/mol
$m_{\text{gm,tot}}$	total mass of gasifiable material in the char, mg
$m_{\text{gm,t}}$	mass of gasifiable material remaining at time t , mg
n_{C}	amount of organic carbon in the char, estimated as the material, gasified during the experiments, mol
n_{Na}	amount of sodium in the char, mol
r_X	gasification rate at fractional conversion X , s^{-1}
T	temperature, K
t	time, s
X	fractional conversion of char during gasification, dimensionless

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