



**INVESTIGATION OF BLACK LIQUOR RHEOLOGY AND PARAMETERS  
AFFECTING ITS VISCOSITY**

Lappeenranta–Lahti University of Technology LUT

LUT School of Energy Systems

Masters's Programme in Bioenergy Systems

2023

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## **ABSTRACT**

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### **Investigation of Black Liquor Rheology and Parameters Affecting its Viscosity**

Master's thesis

2023

80 pages, 36 figures and 15 tables

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Keywords: Black liquor, Viscosity, Rheology, Shear rate, Lignin, Dry solids

The paper and pulp industry generates a useful by-product from the pulping process called black liquor, which is often considered as a renewable fuel. The combustion of black liquor in the recovery boiler allows the recovery of chemicals from the pulping process and energy production. Understanding the rheological properties of black liquor is important in the optimization of its handling, transportation and combustion process in the recovery boiler.

The objectives of this master's thesis were to study the rheological properties of black liquor and the influence of factors such as lignin removal, temperature, shear rate and dry solids content on black liquor viscosity.

The methodology of this study was based on an extensive literature review of research papers, scientific articles, conference papers and other scholarly material. A systematic search approach was utilised to identify relevant literature on black liquor from reputable databases and sources. The selected material was critically analysed to extract key information on black liquor.

Some key findings from this investigation show how black liquor viscosity decreased when temperature, shear rate or lignin removal increased. The study also show that an increase in dry solids content in the black liquor resulted in an increase in viscosity. Going forward, in order to enhance the research on the rheological properties of black liquor, future studies can focus on experimental work in the laboratory and/or on the other factors, which were not in the scope of this work such as the effect of pH on black liquor viscosity.

## **ACKNOWLEDGEMENTS**

I would like to express my gratitude to my supervisors Professor, D.S. Esa Vakkilainen and Researcher, D.Sc. Jesus Nuncira for their invaluable expertise, guidance and patience during the course of this work.

My heartfelt appreciation to my beloved family; Patience, Desmond, Puella and Takudzwa, Mr and Mrs Mushosho's family, Pekka, Rennie, Risto and my amazing friends during my time at LUT University, I appreciate the love and encouragement as I worked on this thesis.

I would like to express my deepest thank you to my God-mother Riitta, for her love and full-support through-out my studies and journey in Finland. Kiitos paljon!

I am forever grateful for this opportunity and praise be to God.

## **ABBREVIATIONS**

ABL	Acidified Black Liquor
BKBL	Bamboo Kraft Black Liquor
BL	Black Liquor
Cc	Carbon content
DBL	Diluted Black Liquor
DSC	Dry Solids Content
HHV	Higher Heating Value
IEA	International Energy Agency
LLBL	Lignin Lean Black Liquor
LUT	Lappeenranta University of Technology
sBL	strong Black Liquor
T <sub>b</sub>	bulk droplet temperature
T <sub>g</sub>	gas temperature
VIE	Volumetric Isothermal Expansivity
wBL	weak Black Liquor

## Symbols

$\rho$	Density	$\text{kg/m}^3$
$\rho_{25}$	Density of black liquor at 25°C	$\text{kg/m}^3$
$\gamma$	Shear rate	$\text{s}^{-1}$
$\lambda$	Thermal conductivity of black liquor	$\text{W/m}\cdot\text{°C}$
$\lambda_{\text{H}_2\text{O}}$	Thermal conductivity of water	$\text{W/m}\cdot\text{°C}$
$\eta$	Viscosity	$\text{m}\cdot\text{Pa}\cdot\text{s}$
$X$	Dry solids concentration	$\text{kg dry solids/kg}$

## Table of Contents

Abstract

(Acknowledgements)

(Symbols and abbreviations)

## Contents

1	Introduction .....	1
2	Bibliographic Review .....	3
2.1	Black Liquor.....	3
2.1.1	Chemical Composition .....	4
2.1.2	Physical Properties.....	5
2.2	Recovery Boiler .....	11
2.2.1	Black Liquor Combustion.....	12
2.3	Rheology .....	15
2.3.1	Influence of Lignin Removal.....	17
2.3.2	Influence of Dry Solids Content .....	18
2.3.3	Influence of Temperature.....	18
2.3.4	Influence of Shear Rate.....	18
3	Research Methodology .....	20
3.1	Digital Sources of Information.....	20
3.1.1	Google Scholar .....	20
3.1.2	Scopus.....	21
3.1.3	Science Direct .....	21
3.1.4	Web of Science .....	21
3.2	Physical Sources of Information .....	22
3.3	Expert Interview .....	22
4	Results .....	24
4.1	Black Liquor Metrics .....	26
4.2	Black Liquor Viscosity .....	29
4.2.1	Lignin Removal .....	29
4.2.2	Temperature .....	36

4.2.3	Dry Solids Content.....	42
4.2.4	Shear Rate .....	47
4.3	Discussion .....	53
4.3.1	Articles Summary .....	55
5	Conclusions .....	66
	References.....	68

## Figures

Figure 1. Distribution of black liquor organics (Alen et al., 1994)

Figure 2. Weak black liquor (Clay, 2000)

Figure 3. Effects of temperature and dry solids content on black liquor viscosity (E. Vakkilainen, 2008)

Figure 4. Boiling point increase as a function of black liquor dry solids (E. Vakkilainen, 2008)

Figure 5. Density of black liquor to dry solids content (Korpinen et al., 2008)

Figure 6. Black liquor thermal conductivity as a function of dry solids content (E. Vakkilainen, 2008)

Figure 7. Recovery Boiler (E. Vakkilainen, 2008)

Figure 8. Recovery Boiler lower furnace (E. Vakkilainen, 2008)

Figure 9. Simple shear flow with Cartesian coordinates (Osswald, 2015)

Figure 10. Black liquor articles from four different digital databases

Figure 11. Search results of Lignin removal articles related to black liquor viscosity

Figure 12. Search results of temperature articles related to black liquor viscosity

Figure 13. Search results for dry solids articles related to black liquor viscosity

Figure 14. Search results for shear rate articles related to black liquor viscosity

Figure 15. Variation of viscosity different black liquor samples with variable lignin content at different temperatures (Moosavifar et al., 2006)

Figure 16. Effects of black liquor lignin removal on liquor viscosity (Wallmo et al., 2015)

Figure 17. Influence of lignin concentration on viscosity (Machado et al., 2023)

Figure 18. Apparent viscosity of black liquor vs shear rate of four black liquor samples with varying lignin content (Chen et al., 2023)

Figure 19. Viscosity as a function of lignin concentration (Zaman & Fricke, 1996)

Figure 20. Apparent viscosity as a function of temperature data from an Arrhenius model (Singh et al., 2015)

Figure 21. Influence of temperature on black liquor viscosity with different solids concentration (Moosavifar et al., 2006)

Figure 22. Viscosity of thermally untreated black liquor and thermally treated black liquor as a function of temperature (Nassar et al., 2016)

Figure 23. Viscosity of wheat straw black liquor as a function of temperature and dry solids content (Singh et al., 2021)

Figure 25. Black liquor viscosity as a function of temperature (Y. Xu et al., 2015)

Figure 26. Variation of black liquor viscosity with dry solids content (Llamas et al., 2007)

Figure 27. Viscosity of black liquor as a function of dry solids content (Moosavifar et al., 2009).

Figure 28. Viscosity of wheat straw black liquor as a function of dry solids concentration (H. Xu et al., 2021)

Figure 29. Viscosity of rice-straw black liquor vs solids content and temperature (Zhang & Chen, 2016)

Figure 30. Viscosity of Eucalyptus black liquor content with different solids content (Santos Leite et al., 2011)

Figure 31. Apparent viscosity of black liquor as a function of shear rate (Alabi et al., 2012)

Figure 32. Black liquor viscosity as a function of shear rate (Costa et al., 2011)

Figure 33. Viscosity changes in wheat straw soda black liquor as a function of shear rate (Singh et al., 2015)

Figure 34. Apparent viscosity of BKBL as a function of shear rate (Yue et al., 2017)

Figure 35. Viscosity of *Eucalyptus grandis* black liquor samples from Mill A as a function of shear rate (Cardoso et al., 2009)

Figure 36. Viscosity of bamboo black liquor from Mill F as a function of shear rate (Cardoso et al., 2009)

## **Tables**

Table 1. Composition of black liquor dry solids from kraft pulping of birch (E. Vakkilainen et al., 2000)

Table 2. Dry solids composition of black liquor (Clay, 2000)

Table 3. Heating values of black liquor and black liquor constituents (Adams et al., 1988)

Table 4. Stages in black liquor combustion (E. Vakkilainen, 2008)

Table 5. Effects of different properties on black liquor viscosity

Table 6. Comparison of the digital tools

Table 7. Document type search results on Scopus

Table 8. Black liquor samples in the experiment (Moosavifar et al., 2006)

Table 9. Black liquor samples (Wallmo et al., 2015)

Table 10. Black liquor samples from the experiment (Machado et al., 2023)

Table 11. Black liquor samples and the percentage of lignin removed (Chen et al., 2023)

Table 12. Wheat straw black liquor samples at varying dry solids content (Singh et al., 2015)

Table 13. Softwood black liquor samples with varying dry solids content (Moosavifar et al., 2006)

Table 14. Black liquor samples (Santos Leite et al., 2011)

Table 15. Summary of the black liquor articles

# 1 Introduction

Renewable fuels are in demand now more than ever before with the recent global energy crisis (World Energy Outlook, 2022). With fossil fuels still the dominant energy source, there is a need for alternative energy sources; which are sustainable and environmentally friendly to use in generating energy whilst cutting down emission levels. The International Energy Agency (IEA); states that Finland's goal is to decarbonise its economy by 2035 and renewable fuels will play a major role in fulfilling these targets. In this sense, bioenergy is an important source of renewable energy and currently accounts for nearly 10 percent of global total primary energy supply (International Energy Agency, 2023).

Biomass is renewable organic material that comes from plants and animals. In Finland, wood biomass is the most common source of biomass and accounts for roughly 85 % of the renewable energy used in the country (International Energy Agency, 2023). Wood biomass is also of major importance in the paper and pulp industry (Holmberg & Gustavsson, 2007) and it generates a useful by-product called black liquor (BL), which is classified as a renewable fuel.

Black liquor is produced from kraft pulping process and in the early years of the 20<sup>th</sup> century, it used to be discarded as waste. It only began to be used for energy generation and chemical recovery of cooking chemicals in the 1930's (E. K. Vakkilainen, 2017a) and as of 2018 black liquor was the leading fuel used for heat generation by UPM-Kymmene Oyj, Finland (Statistic\_Upm-Kymmene-Oyj, 2018). According to Statistics Finland 2021, the production of electricity with renewable fuels amounted to 10.9 TWh in 2020 of which 6.0TWh was produced with black liquor (Statistics Finland, 2021).

Black liquor combustion occurs in the recovery boiler, which is an important and complex unit of the kraft pulping process. Inside the recovery boiler, production of energy and recovery of chemical from the cooking process occurs simultaneously (Adams et al., 1988). In subchapter, 2.2 the processes in black liquor combustion are analysed and chemical reactions, which take place, are presented.

Among the diverse properties of black liquor, viscosity is of great interest since it affects the effectiveness of other major operational units in the recovery cycle such as for example evaporators, concentrators, storage tanks and also the firing and combustion into the recovery boiler (Fricke et al., 1999). Black liquor viscosity is affected by different variables such as temperature, shear rate, dry solids content and lignin content among others (Yue et al., 2017). There are also other properties, which affect the viscosity of black liquor; however, they are not part of the scope of this work.

In this study, an investigation on the rheological properties of black liquor and the parameters, which affect its viscosity, was performed. Data from studies already reported was utilised to analyse the properties of black liquor, its rheology, the combustion in the recovery boiler and its viscosity. To gather the information, tools such as digital databases, physical sources and an expert interview were utilised during the course of this work. The objective of this Master's thesis is to present an analysis of the factors within the scope of this work that affect the rheology of black liquor, which can be utilised in future works in this field.

## 2 Bibliographic Review

This chapter provides a description about black liquor, giving details of its general chemical composition, physical properties, combustion process and the rheology.

### 2.1 Black Liquor

Black liquor is a useful by-product produced from the kraft pulping process. It has both organic and inorganic constituents. The organic composition of black liquor contains lignin, polysaccharides and hemicellulose, whilst the inorganic composition contains inorganic chemicals from the cooking process such as sodium hydroxide (NaOH), sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>), and other sodium salts. Black liquor also has some minor amounts of impurities such as phosphorus, calcium and non-process elements such as silicon, aluminium and iron (Adams et al., 1988; Cardoso et al., 2009; E. Vakkilainen, 2008).

It should be noted that, the composition of black liquor varies depending on pulping conditions, treatment after pulping, and on the type of raw material used in the pulp process like for example softwood (*pine*) or hardwood (*eucalyptus*) (E. Vakkilainen, 2008). The Figure 1 below shows the different distribution of black liquor organics from softwood and hardwood. The figure displays that softwood generally has a higher lignin content than hardwood, whilst the hydroxyl acids are nearly the same for both samples.

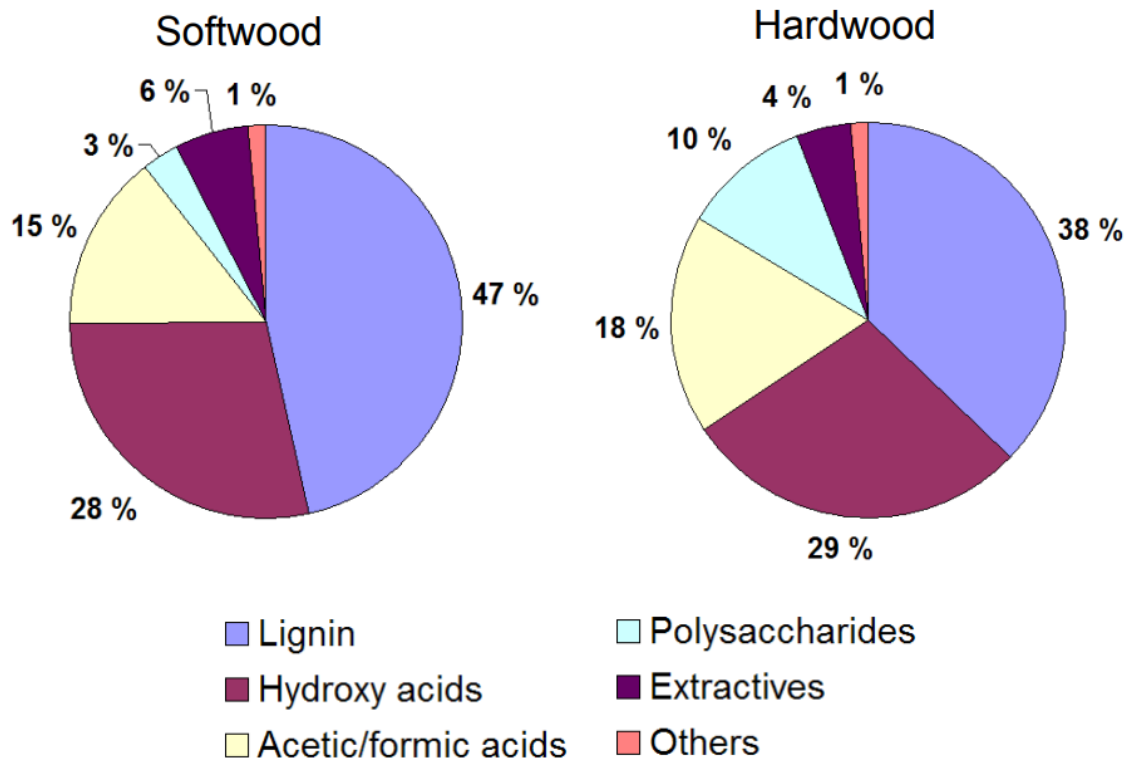


Figure 1. Distribution of black liquor organics (Alen et al., 1994)

### 2.1.1 Chemical Composition

Black liquor contains spent chemicals from the pulping process, dissolved wood and water. The chemical components of kraft black liquor are lignin, hydroxyl acids, extractives, acetic acid, formic acid, sulphur and sodium (Adams et al., 1988). The typical percentages of the organic and inorganic components are shown in the Table 1.

Table 1. Composition of black liquor dry solids from kraft pulping of birch (E. Vakkilainen et al., 2000)

<b>Organics, percentage by weight (wt.%)</b>	<b>78</b>
Degraded lignin including Na and S,	37.5
Isosaccharinic acids, including Na,	22.6
Aliphatic acids, including Na,	14.4
Resin and fatty acids, including Na,	0.5
Polysaccharides,	3.0
<b>Inorganics, % by weight (wt. %)</b>	<b>22</b>
NaOH,	2.4
NaHS,	3.6
Na <sub>2</sub> CO <sub>3</sub> and K <sub>2</sub> CO <sub>3</sub> ,	9.2
Na <sub>2</sub> SO <sub>4</sub> ,	4.8
Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> , Na <sub>2</sub> SO <sub>3</sub> and Na <sub>2</sub> S <sub>x</sub> ,	0.5
NaCl,	0.5
Non-process elements (Si, Ca, Fe, Mn, Mg, etc.),	0.2

### 2.1.2 Physical Properties

The physical properties of black liquor are important and depend on how the liquor was produced and the specific composition of the liquor. The first physical property to be discussed is the dry solids content, which is defined as the ratio of dried black liquor to wet black liquor before drying (E. K. Vakkilainen, 2017a). The black liquor produced after the cooking process is termed as weak black liquor (wBL) as it has a small dry solids concentration ranging from 15% - 18%. It is not efficient to combust this weak liquor in the recovery boiler, so the dry solids content are increased by using multiple effect evaporators to form a strong black liquor (sBL) with high solids content. Figure 2 below shows the composition of a weak black liquor (Clay, 2000).

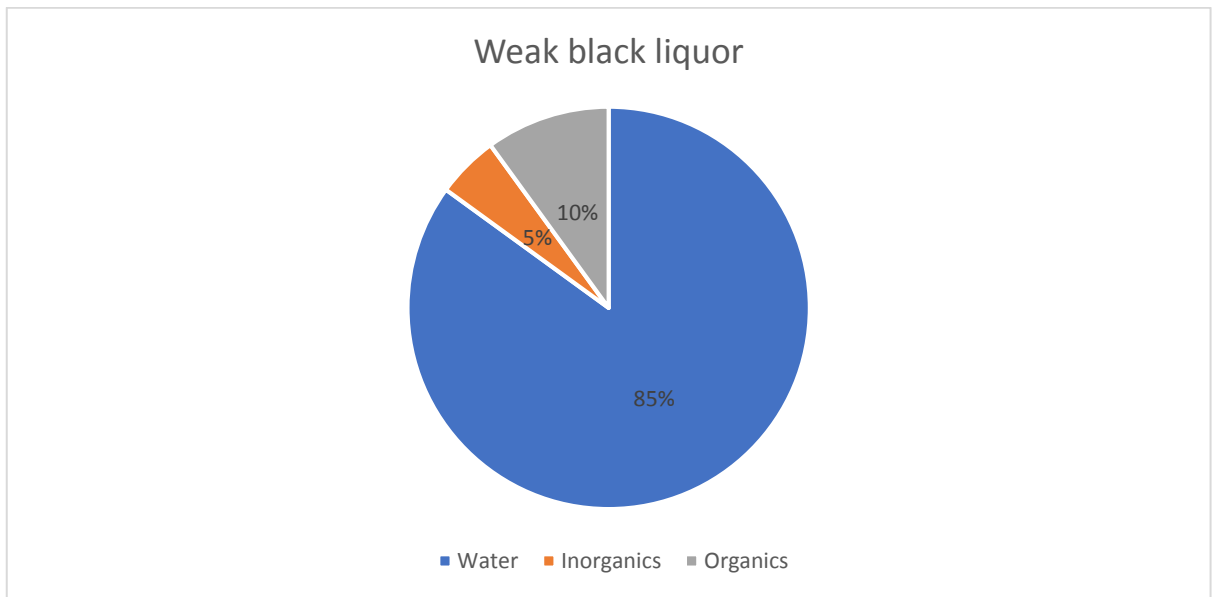


Figure 2. Weak black liquor (Clay, 2000)

The dry solids content basis of black liquor are listed in Table 2 (Clay, 2000)

Table 2. Dry solids composition of black liquor (Clay, 2000)

Dry solids	Weight (wt.%)
Alkali lignin	30-45
Wood acids and polysaccharides	30-45
Inorganic salts	30-45
Resins and fatty acids	3-5

Temperature is an important parameter when handling black liquor as it affects properties like black liquor viscosity, chemical composition and solids content (Yue et al., 2017). It is essential to establish how the viscosity changes when temperature rises. The correlation of temperature and viscosity is highlighted in Figure 3 for black liquor with different dry solids content ranging from 67 % - 75.7%. As observed in the figure, the viscosity drops rapidly when the temperature of black liquor increases (E. Vakkilainen, 2008).

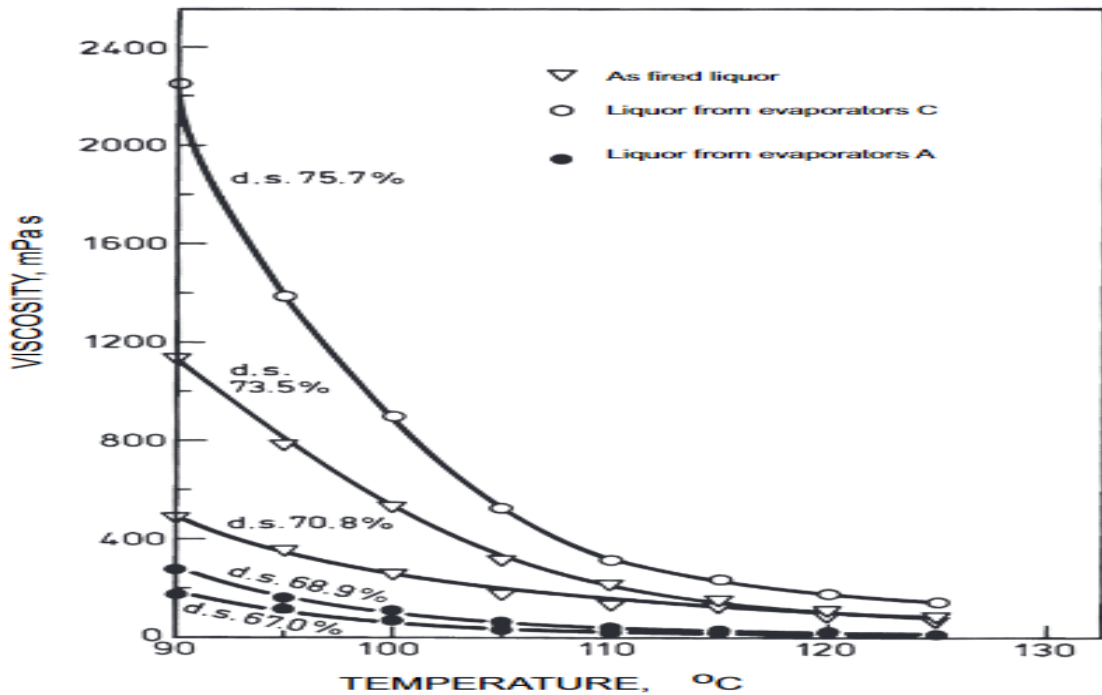


Figure 3. Effects of temperature and dry solids content on black liquor viscosity (E. Vakkilainen, 2008).

Boiling point rise is the term used to describe the difference between the boiling point of an aqueous solution and the boiling point of water. In the case of black liquor, the boiling point rise is dependent on factors such as the dry solids content and the inorganic content in the liquor among other factors (Clay, 2000). In a recovery boiler, when strong black liquor with high dry solids content is fired, the boiling point increase ranges from 12% - 30% (Järvinen, 2015). The relationship between dry solids content and boiling point rise is such that when the dry solids content increase, the boiling point rise temperature also increases and Figure 4 below demonstrates this relationship perfectly (E. Vakkilainen, 2008).

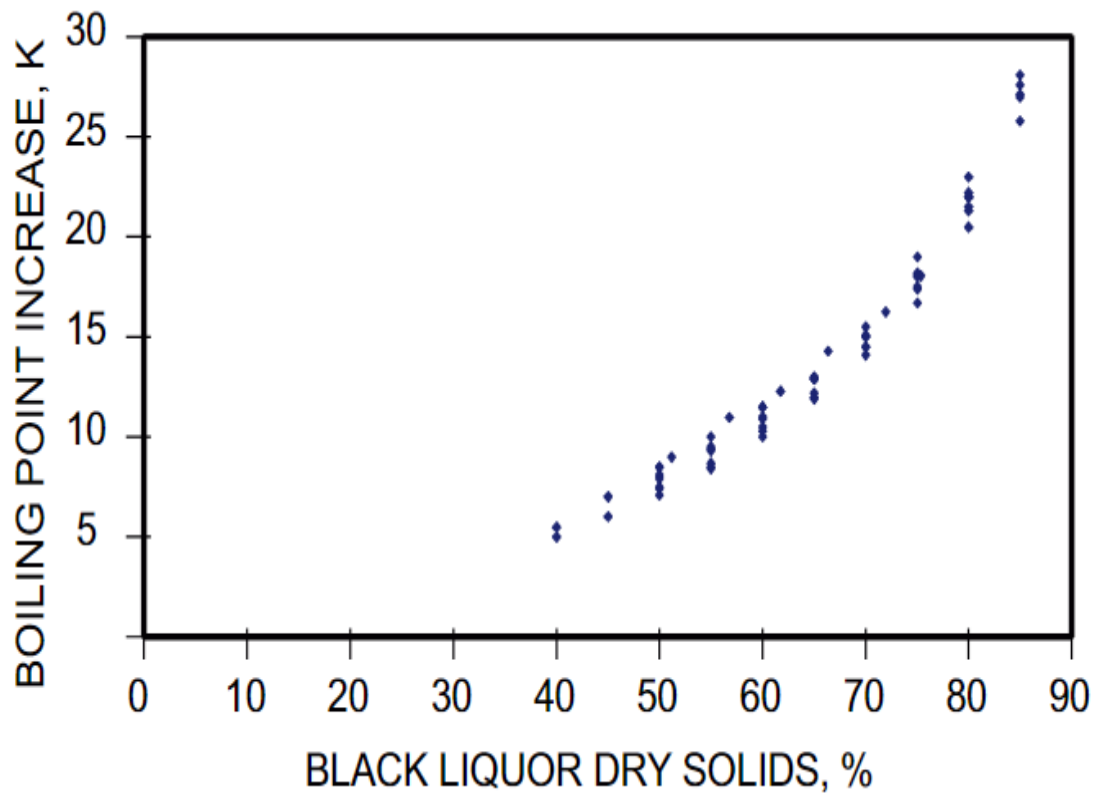


Figure 4. Boiling point increase as a function of black liquor dry solids (E. Vakkilainen, 2008)

According to Adams et al (1988), the density of black liquor is important when dealing with flow characteristics calculations. Weak black liquor with low solids content have density values, which are similar to that of water, provided the temperature is the same. The correlation now between dry solids content and density is such that when the dry solids content increase, the inherent density of the black liquor increases. The inorganic fraction has a strong influence on the overall density of the black liquor (Adams et al., 1988). The model for calculating the density of a black liquor sample with up to 50% dry solids content, at 25°C is given by Equation (1) (E. Vakkilainen, 2008).

$$\rho_{25} = 997 + 649X \quad (1)$$

where  $\rho_{25}$             Density of black liquor at 25 °C, [kg/m<sup>3</sup>]  
 $X$                     Concentration of dry solids, [kg dry solids/kg]

Figure 5 below show the relationship between dry solids content and the density of black liquor.

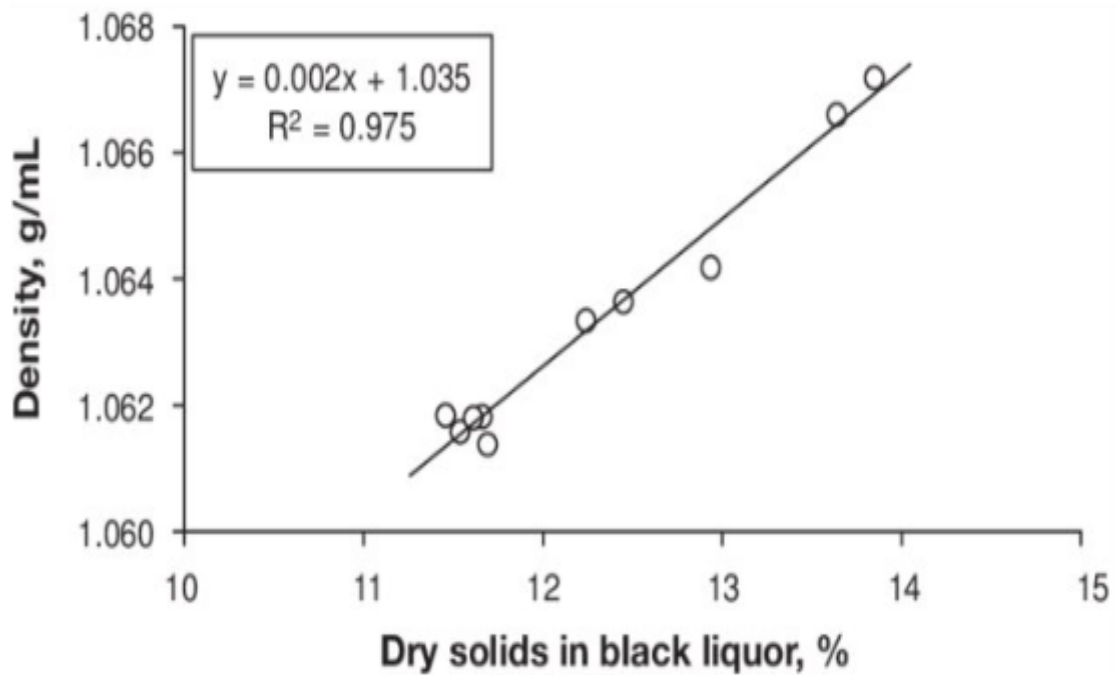


Figure 5. Density of black liquor to dry solids content (Korpinen et al., 2008).

Heating value is the heat produced by a fuel during the combustion process. A higher heating value represents the maximal chemical energy released. Higher Heating Value (HHV) is dependent on the carbon content in the dry solids of the black liquor. When the carbon content of the dry solids is given, the Equation (2) is utilised to calculate the higher heating value of black liquor. Coefficients of the equation are 29.35 and 3.959. This equation is applicable for Northern hardwoods and softwoods within this range;  $\pm 0.4$  MJ/kg dry solids (E. Vakkilainen, 2008).

$$HHV = 29.35(Cc) + 3.959 \pm 0.42 \quad (2)$$

where HHV Higher Heating Value, [MJ/kg dry solids]

Cc Carbon content, [kg C/kg dry solids]

Typical heating values of black liquor and black liquor constituents are in Table 3.

Table 3. Heating values of black liquor and black liquor constituents (Adams et al., 1988)

<b>Component</b>	<b>Heating values Kj/kg</b>
Softwood lignin	26 900.0
Hardwood lignin	25 110.0
Carbohydrates	13 555.0
Resins, Fatty acids	37 710.0
Sodium sulfide	12 900.0
Sodium thiosulphate	5 790.0

The thermal conductivity of black liquor is dependent on temperature and concentration of dry solids. The relationship is such that, when the dry solids content increases, the thermal conductivity decreases and when temperature increases; the thermal conductivity increases (E. Vakkilainen, 2008).

$$\lambda = \lambda_{H_2O} (1 - X) + aX + bX^2 \quad (3)$$

where	$\lambda$	Thermal conductivity, [W/m·°C]
	$\lambda_{H_2O}$	Thermal conductivity of water, [W/m·°C]
	X	Concentration of dry solids, [kg dry solids/kg]
	T	Temperature of the black liquor, [°C]
	a	variable calculated by $a_1+a_2T$
	b	variable calculated by $b_1+b_2T$

This Equation (3) enables the calculation of thermal conductivity of black liquor.

Figure 6 below shows the variation of thermal conductivity with respect to the temperature change and dry solids content change (E. Vakkilainen, 2008).

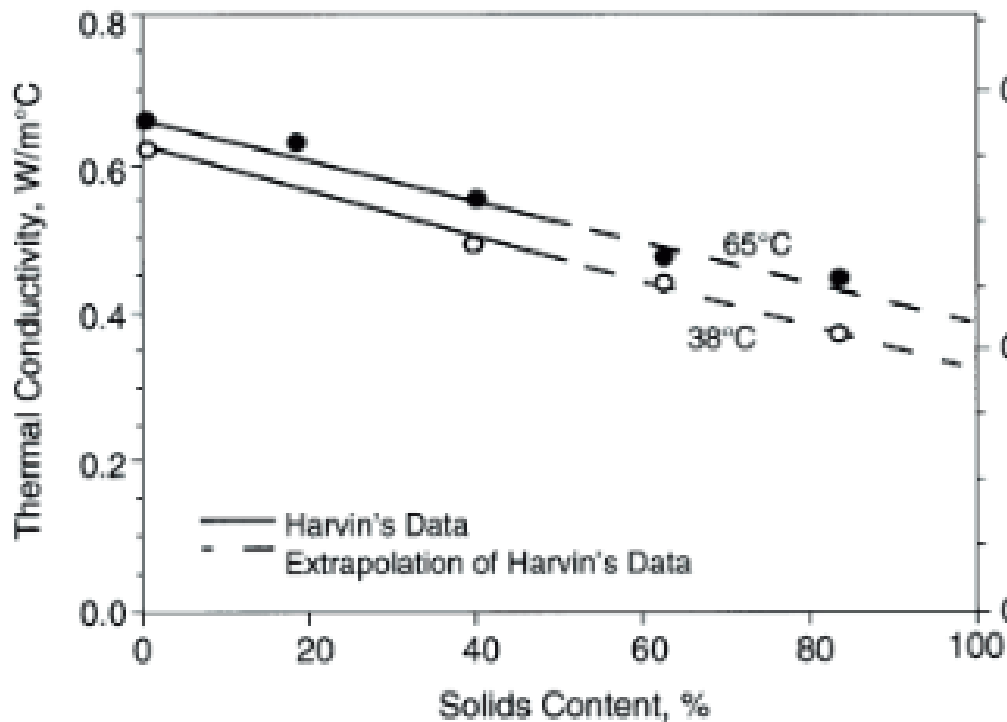


Figure 6. Black liquor thermal conductivity as a function of dry solids content (E. Vakkilainen, 2008).

Viscosity is a measure of fluids resistance to flow. In the case of black liquor, its viscosity is dependent on different factors such as solids concentration, shear rate, temperature amongst others (Alabi et al., 2012). The viscosity of a weak black liquor with 15% dry solids is twice that of water at the same temperature. Now when the dry solids content increase in quantity, the viscosity tends to increase as well. One way of reducing BL viscosity is by increasing the temperature (Adams et al., 1988).

## 2.2 Recovery Boiler

The combustion of black liquor occurs inside the recovery boiler. The main functions of the recovery boiler are to burn the organic matter in black liquor for steam and heat production, regeneration of inorganic chemicals in black liquor and reducing waste discharge streams in an ecologically sound way. The recovery boiler has different specialised equipment

integrated to it such as super-heaters, liquor guns, soot blowers, char bed and smelt sprouts among others, which help in executing its functions in the most efficient way possible.

The recovery boiler has different sections such as the furnace section, the convective heat section and the char bed. Nozzles mounted on the walls spray the black liquor into the boiler and the mixing of the black liquor with air and combustion occurs in the furnace section. According to Adams et al (1988), around 40 % of the heat transfer from combustion gas is completed in the furnace. Figure 7 shows the profile of a recovery boiler layout and the specialised equipment (Adams et al., 1988; E. Vakkilainen, 2008).

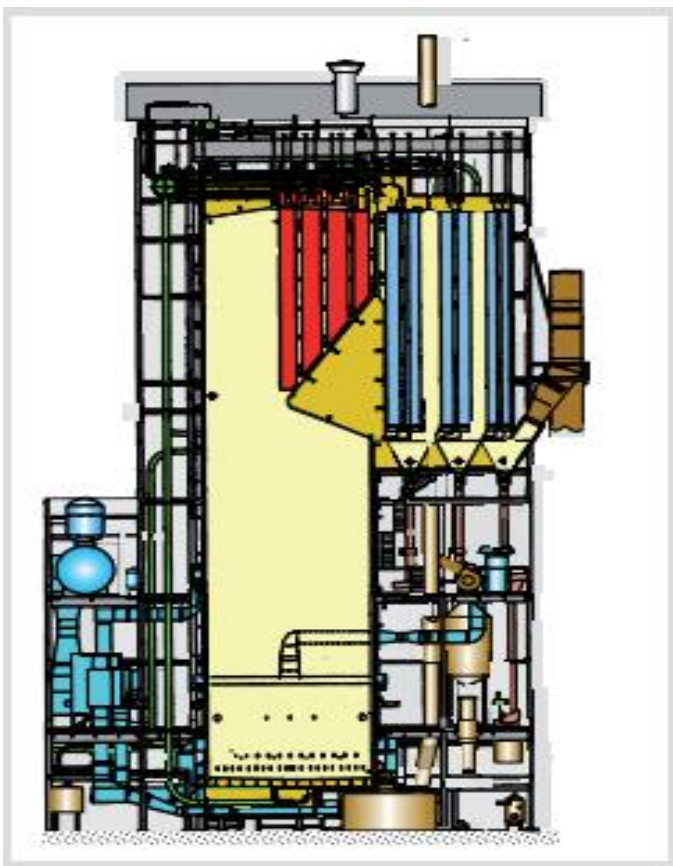


Figure 7. Recovery Boiler (E. Vakkilainen, 2008)

### 2.2.1 Black Liquor Combustion

Black liquor combustion takes place by spraying black liquor droplets through liquor guns into the furnace of the recovery boiler. The size of the droplets is crucial as it can affect the

combustion processes, so droplets are usually between 0.5 to 5 mm. Black liquor droplets smaller than 2mm are significantly affected by gas flow patterns in the boiler and as a result they dry and devolatize in flight. In the case of larger droplets, they travel directly to the walls or char bed, and they devolatize more slowly as compared to the smaller droplets (Adams et al., 1988). Table 4 shows the stages in black liquor combustion in the recovery.

Table 4. Stages in black liquor combustion (E. Vakkilainen, 2008)

<b>Stage</b>	<b>Characterised by</b>	<b>Time scale in furnace for a 2mm drop formation</b>
Drying	Water Evaporation Constant diameter after initial swelling	0.1 - 0.2 s
Devolatilization	Appearance of flame, ignition Swearing of droplets Release of volatiles	0.2 - 0.3 s
Char burning	Disappearance of flame Decreasing diameter Reduction reactions	0.5 - 1 s
Smelt	Constant or increasing diameter Reoxidation	Long

The black liquor combustion process is divided into different stages with the first one being drying, which is the process of water evaporation from black liquor droplets. Heat is required for the evaporation of water and the speed at which the black liquor dries depends on the rate at which heat is transferred to the droplet. The drying rate is difficult to predict and one of the simpler models for predicting drying of black liquor droplets is shown below in Equation (4). One assumption when using the model is that drying is controlled by the rate of heat transfer both to and within the black liquor (Adams et al., 1988).

$$\frac{dQ}{dT} = \frac{T_g - T_b}{R_{tot}} \quad (4)$$

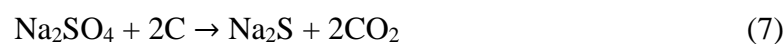
where	$\frac{dQ}{dT}$	Overall rate of heat transfer, [W]
	$T_g$	gas temperature, [°C]
	$T_b$	bulk droplet temperature, [°C]
	$R_{tot}$	Overall resistance to heat transfer, [°C/W]

The second stage in the combustion process is devolatilisation. According to Adams et al (1988), the rate and yield of devolatilisation determines where burning occurs and where heat is released in the heater. During this stage, black liquor droplets undergo significant swelling and volatile gases such as sulphur dioxide (SO<sub>2</sub>), and hydrogen sulphide (H<sub>2</sub>S) are released from the droplet. During devolatilisation, there is a visible flame and the total heat input needed to devolatise a completely dry droplet is given by the Equation (5) below (Adams et al., 1988).

$$Q_{tot, devol} = m_{bls} \cdot C_p \cdot (T_{devol} - T_{dry}) + (m_{bls} - m_{char}) \cdot \Delta H_{devol} \quad (5)$$

where	$Q_{tot, devol}$	Total heat to devolatize the droplet, J
	$m_{bls}$	mass of black liquor solids in the droplet, kg
	$C_p$	Specific heat capacity
	$T_{devol}$	Temperature of devolatilisation
	$T_{dry}$	Temperature of dry droplet
	$m_{char}$	mass of char at the end of devolatisation, kg
	$\Delta H_{devol}$	Enthalpy of devolatisation, J/kg

The third stage is char combustion, which begins when the volatile gas release ends. A solid char forms which contains fixed carbon from the organic matter and it forms a mixture with inorganic salts. During char combustion, there is no visible flame. Reduction reactions happen at this stage and the chemical reactions are shown in the equations below (Adams et al., 1988; E. Vakkilainen, 2008).





The formation of smelt is the fourth stage in the combustion process. The smelt is produced from the inorganic component of black liquor and it is composed of compounds of sodium sulphide, sodium carbonate, and other dissolved inorganic substances. It collects at the bottom of the recovery boiler and the smelt exits through smelt sprouts. This allows the recovery of cooking chemicals from smelt, which are reused in the kraft pulping process thus reducing the need for fresh chemicals and minimizing waste (Vakkilainen, 2017). Figure 8 shows black liquor droplets being sprayed into the lower furnace of the recovery boiler and the smelt exiting through the smelt sprouts (E. Vakkilainen, 2008).

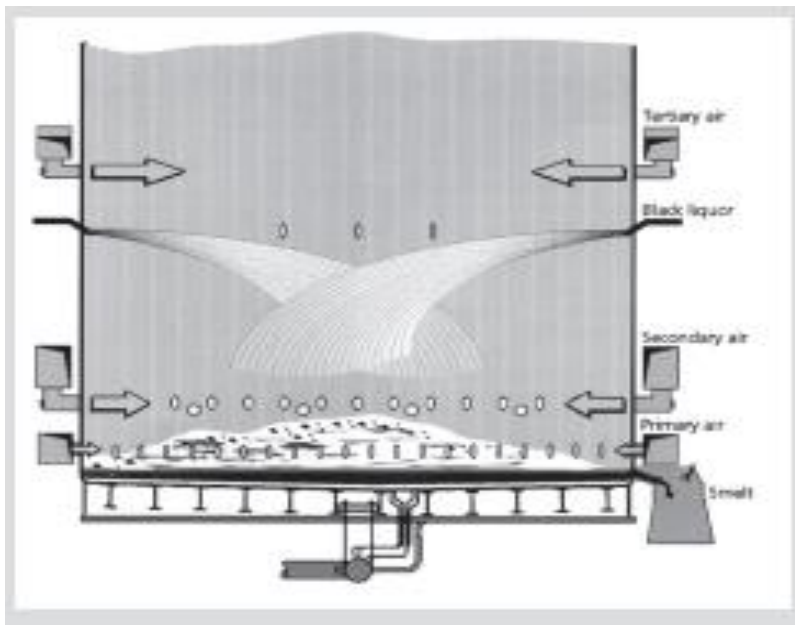


Figure 8. Recovery Boiler lower furnace (E. Vakkilainen, 2008)

### 2.3 Rheology

Rheology is the behaviour of fluids undergoing stress, and the deformation can be in the form of shear or elongation. In the 17<sup>th</sup> century, Sir Isaac Newton formulated the initial hypothesis regarding the resistance to motion experienced by deforming fluids. This flow resistance in deforming fluids, is a physical property called viscosity and understanding how viscosity varies under different conditions is important when dealing with fluids. Viscosity is affected by different parameters such as pressure, temperature, shear stress and molecular weight among others (Carreau et al., 2021; Osswald, 2015).

The relationship between viscosity and shear stress is expressed by Newton's law of viscosity, which states that, the shear stress between adjacent fluid layers is proportional to the velocity gradients between the two layers.

$$\tau \propto \frac{du}{dy} \quad (9)$$

where  $\tau$  shear stress  
 $\frac{du}{dy}$  velocity gradient

For a fluid between two adjacent planes as shown in Figure 9, the simple shear flow is expressed in Equation (10)

$$\frac{F}{A} = \eta \cdot \frac{u}{h} \quad (10)$$

Where  $F$  Force required to maintain the motion  
 $A$  Surface area of the plane  
 $\eta$  Viscosity  
 $u$  velocity  
 $h$  distance between the planes

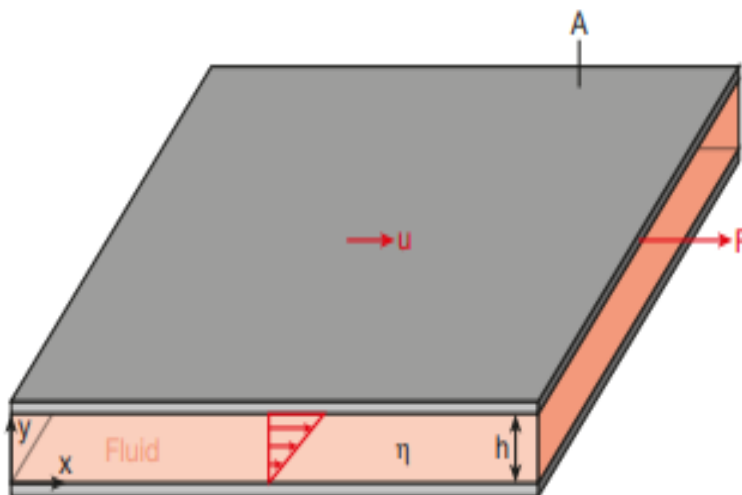


Figure 9. Simple shear flow with Cartesian coordinates (Osswald, 2015)

$$\tau_{xy} = \eta \cdot \gamma_{xy} \quad (11)$$

where	$\tau_{xy}$	Shear stress
	$\eta$	Viscosity
	$\gamma_{xy}$	Shear rate

The viscosity of fluid varies according to different conditions and their behaviour is termed as Newtonian and non-Newtonian behaviour. Fluids which show a constant viscosity at a given temperature and pressure are termed Newtonian fluids. However, for non-Newtonian fluids, the viscosity is variable as a function of the rate of deformation (shear stress). Non-Newtonian fluids behaviour of fluids include pseudoplastic and thixotropic behaviour. According to Adams et al (1988), pseudoplastic behaviour occurs when shear forces disturb long polymer molecule chains from their preferred conformation. This behaviour is described as reverse shear thinning. For thixotropic behaviour, a decrease of viscosity as a function of time is observed when a sample is under a constant rate of shear. This decrease in viscosity is due to the change in structure from the applied shear rate (Adams et al., 1988; Carreau et al., 2021).

For the most part, black liquor is considered under certain conditions as a non-Newtonian fluid. However, at low shear rates, the viscosity is constant and black liquor exhibits Newtonian fluid behaviour. According to Adams et al (1988), the nature of the organic components such as colloidal state and molecular weight are important when determining the viscosity of a particular liquor (Adams et al., 1988; Sanders et al., 1998). Overall, the viscosity of black liquor is important as it affects different characteristics such as black liquor flow, droplet formation, drying and swelling in the furnace among others (Adams et al., 1988). Below will be discussed the main parameters affecting the viscosity of black liquor.

### 2.3.1 Influence of Lignin Removal

The overall viscosity of black liquor is affected by the lignin content. According to Chen et al, a decrease in lignin content leads to a decrease in the network structure and as a result black liquor with lower lignin concentration also has lower viscosity values. The volumetric isothermal expansivity (VIE) of the black liquor was found to be directly proportional to the lignin content (Chen et al., 2023). Moosavifar et al also performed a study on the effects of lignin removal on kraft black liquor and noted that for black liquor samples with lignin

removed and dry solids content above 40 %, the viscosity could be reduced up to about 90 % (Moosavifar et al., 2009).

### 2.3.2 Influence of Dry Solids Content

Controlling the dry solids content of the black liquor is important in achieving the desired rheological properties. Higher dry solids result in an increase in the viscosity. Black liquor with high solids content produces more heat when combusted, but pumping the viscous black liquor poses challenges resulting in more energy used (Sjostrom, 1993). It is also noted that when the dry solids content is low, black liquor behaved as a Newtonian fluid and when the dry solids increased the behaviour changed to non-Newtonian with an exponential rise in the viscosity as well (Singh et al., 2015).

### 2.3.3 Influence of Temperature

The viscosity of black liquor is affected by a change in temperature, with an increase in temperature resulting in a decrease in viscosity. The decrease in viscosity as temperature was increased is due to the increase in inter-molecular mobility in the black liquor (Singh et al., 2021). Work by Zaman and Fricke demonstrated that the dynamic viscosity changed drastically whenever the temperature or dry solids contents was altered (Zaman & Fricke, 1995).

### 2.3.4 Influence of Shear Rate

Shear rate is the rate of deformation of a fluid and is mathematically expressed as the derivative of the shear angle with respect to time. The units for shear rate is reciprocal seconds and changes in shear rate affect the rheological behaviour of fluids (Carreau et al., 2021). In the case of black liquor, the viscosity is influenced by a change in the shear rate and according to Singh et al (2015), the viscosity as a function of shear rate curves demonstrate a pseudo-plastic non-Newton behaviour as shear rate increases. Generally, at low shear rates, the lignin macromolecules in the black liquor can interact easily and as a result, the viscosity is much higher. An increase in shear rate, results in the lignin

macromolecules aligning together thus reducing the resistance to flow and the overall effect is a decrease in viscosity (Singh et al., 2015).

A summary on how lignin removal, dry solids content, temperature and shear rate affects black liquor viscosity is given in the form of Table 5.

Table 5. Effects of different properties on black liquor viscosity

<b>Property</b>		<b>Effect on Viscosity</b>	<b>Reference</b>
Lignin content	↓	↓	(Chen et al., 2023b)
Dry solids content	↑	↑	(Sjostrom, 1993)
Temperature	↑	↓	(Zaman & Fricke, 1995)
Shear rate	↓	↑	(Singh et al., 2015)

## 3 Research Methodology

This chapter will cover the research methods and tools, which were used in collecting information. Digital and physical sources were utilised to search for articles on black liquor rheology done in the past years.

### 3.1 Digital Sources of Information

Four different digital sources were utilised during the course of this work to varying extents. Each source provides different search methods and the number documents produced from the search results is always different even with the same keywords are applied across all the platforms.

#### 3.1.1 Google Scholar

Google scholar is a web search engine, which is freely accessible containing different scholarly literature from various disciplines. It is classified as a bibliographic database and the scholarly material on this database is available in different publishing formats like academic journals, peer reviewed papers, books, theses, dissertations, abstracts, technical reports and patents. Registration is optional and users can search for digital copies of articles or other scholarly material. On google scholar, the results, which appear first, are the ones with the keywords used in the search, with other relevant studies related to the keywords appearing as well. Some search results provide only abstracts and citation details to the full article in the case of journal articles behind a paywall and are only accessible after paying a fee (Wiki Google Scholar, 2023.)

### 3.1.2 Scopus

Scopus is the second data base which was used to search for papers. Scopus is an academic site with scholarly literature across a wide variety of discipline. It contains a well-curated abstract and citation database and all the journals appearing on scopus are reviewed. Material is available in 40 languages and the temporal coverage starts from 1788 to the present date.. Scopus has different options to search for papers and to find the relevant documents the search is done in three ways, which are document search, authors and affiliations. The site is updated daily and whilst other journals have an open access requires a paid admission to get full-text access to journals (Wiki Scopus, 2023).

### 3.1.3 Science Direct

Science direct is the third site which was used and it is a platform which contains scientific and technical articles and journals. The search options are divided into two, with the first one you can search for documents using keywords or authors, and the second option is termed the advanced option were you can search by combining the keywords, authors, author affiliation, volume of the book and year (Wiki Science Direct, 2023).

### 3.1.4 Web of Science

The final digital database used was Web of Science. For access to this digital platform, a subscription is required. On Web of Science, there is a wide collection of academic journals, conference proceedings and other scholarly material (Wiki Web of Science, 2023). Access to Web of Science during the course of this thesis was through LUT Primo, which is a digital platform for LUT students.

## Summary of the scholarly literature databases

Table 6. Comparison of the digital tools

<b>Digital platform</b>	<b>Launched</b>	<b>Temporal period</b>	<b>Access</b>
Google Scholar	2004	1791-present	Free
Scopus	2004	1788-present	Free and Paid
Science Direct	1997		Free and Paid
Web of Science	1997	1900-present	Paid

### 3.2 Physical Sources of Information

The LUT library at the Lappeenranta campus was the source of all the books, journals and other physical sources used in this thesis work. The scholarly material in the library is available for all students of the university and a system of shelf classification is utilised in grouping books in the same field on similar shelves. Use of a LUT primo, which is a digital platform where a student can login and search the availability of books and which section the books are located in is the best way of searching books. Other methods also include asking for assistance from the librarians stationed inside the library and a self-search using guidance maps inside the library. After collecting a book, a student can self-checkout the book from the library and each loan lasts a fortnight unless if you renew the book loan through LUT primo.

### 3.3 Expert Interview

As part of this master's thesis on the subject of black liquor, I conducted an expert interview with a distinguished professional in the field. This interview aimed to shed light on the pulping process, wood science and black liquor viscosity. The interview was conducted with Clara Mendoza, a Post-doctoral researcher at LUT University in the Laboratory of Sustainable Energy Systems with many years of expertise in industrial processes related to bioenergy technology and sustainability. The interview was conducted online via Google

Meet and key takeaways from the interview are explained in detail in the following paragraphs.

During the interview, Clara provided several significant deductions in the context of kraft and sulphite pulping processes in Finland. The key information I gathered was, kraft pulping is the dominant method and the pulp produced is usually brownish in colour due to less lignin removed as compared to sulphite pulping. The kraft pulping process produces versatile pulp, which is suitable for various paper grades such as cardboard. For sulphite pulping, the key takeaways were that it produces a whiter pulp due to more lignin removal, has lower temperature operating conditions and the pulp produced is used processes such as manufacturing toilet paper.

In terms of the wood species the key takeaways were, softwood such as *pine* and *spruce* are commonly used in Finland, and they are sustainably sourced from forests. Softwood fibres are noted for their strength and long fibres, making them ideal for products such as industrial paper and packaging materials. For hardwood such as *eucalyptus*, which is commonly used in Brazil, the fibres are weaker and shorter making them suitable for printing and writing paper. In terms of black liquor produced from both these wood species, it was noted how softwood black liquor typically has higher levels of lignin, which contribute to its higher heating value and energy content.

Now on black liquor, key findings were that after concentration in the multiple evaporator units it becomes a highly viscous substance, which presents challenges during its handling and combustion. Clara explained how viscosity of black liquor is influenced by different factors such as temperature and concentration of dry solids. It was highlighted how higher viscosity black liquor requires more energy for pumping and therefore it is essential for pulp and paper mills to carefully manage the viscosity of black liquor in order to optimise the mill operations.

## 4 Results

In this chapter the results from the use of the digital databases and the articles on black liquor rheology are presented. Google scholar, Science, Direct, Scopus and Web of Science provided a wide range of articles on black liquor rheology, some of these articles have been analysed, and the results are discussed in this chapter.

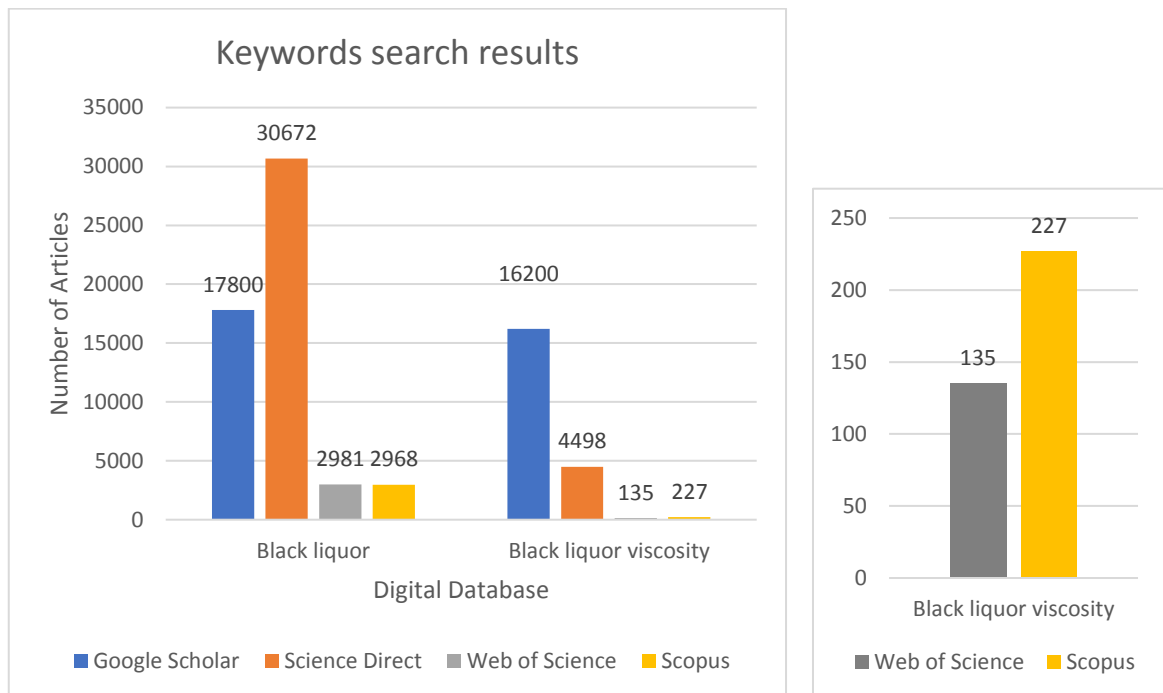


Figure 10. Black liquor articles from four different digital databases

Using Google scholar, the first keywords used are “black liquor” and the time range of the papers was from 2000 to 2023. The search produced 17 800 results of papers with those keywords. To filter the results to within the scope of this thesis work another key word was added and the search for black liquor viscosity produced 16 200 results related to the viscosity of black liquor. These results are classified by relevance with the most cited papers appearing at the top and the language used for the search was English. Patents are excluded from these search results and the review articles from the black liquor viscosity search were only 2760.

In the second search Scopus was used with the same keywords “black liquor” and the result was 2968 documents appearing from the search for the time range 2000 to 2023. The table

below shows the different documents and their respective search numbers on the Scopus database when using the keywords black liquor.

Table 7. Document type search results on Scopus

<b>Document Type</b>	<b>Search Results</b>
Articles	1916
Conference Papers	875
Review	106
Conference Review	32
Book chapter	27
Short survey	6
Note	5
Book	1

Addition of another keyword, the search results for “black liquor viscosity” produced 227 results within the same time range as before. There is a filter option for the results from Scopus by using author name, subject area, document type, keywords, publication stage, language and many other options. This gives well-detailed search results and makes searching of specific documents more efficient.

For Science Direct, maintaining the same keywords “black liquor” the search produced 30 672 results which was the most when compared to all the other databases. Research articles accounted for 20 041 documents and book chapters at 4 063 documents. When another key word was added to the search, “black liquor viscosity” produced only 4 498 results.

When using Web of Science, the keywords “black liquor” were produced 2 981 results for the time range of January 2000 to April 2023. The classification of the search results for these different categories, highly sorted papers, review articles, early access, open access, associated data and enriched cited references. There was an added option to search within the results, and when another keyword was added, the search results for “black liquor viscosity” was only 135 results.

## 4.1 Black Liquor Metrics

In this sub-chapter, results from searching different key terms from four digital databases are shown. The search results varied from articles, book chapters, conference papers, patents and review articles. The terms for the search were linked to black liquor viscosity and results are presented in the form of graphs and literature to explain the data collected.

Using the key term 'black liquor lignin removal', the google scholar database produced the highest number of search results with 30 100 documents, and from that number review articles were 2900 and patents accounted for 4800 results. For Science Direct, 3 922 documents were shown after the search with 2076 results being research articles, 570 review articles and 762 book chapters amongst other types of documents. Web of Science produced smaller results with 290 results, with articles having 260 documents, 21 proceeding papers and 1 book chapter amongst other documents. Scopus produced almost similar search results to Web of Science with 264 documents, which were divided into 194 articles, 39 conference papers, 1 book chapter and 18 conference reviews amongst other documents. The figure below is a comparison of the number of articles on lignin removal in black liquor from Google Scholar, Science Direct, Web of Science and Scopus, other documents like patents, conference papers and book chapters have been excluded from the figure.

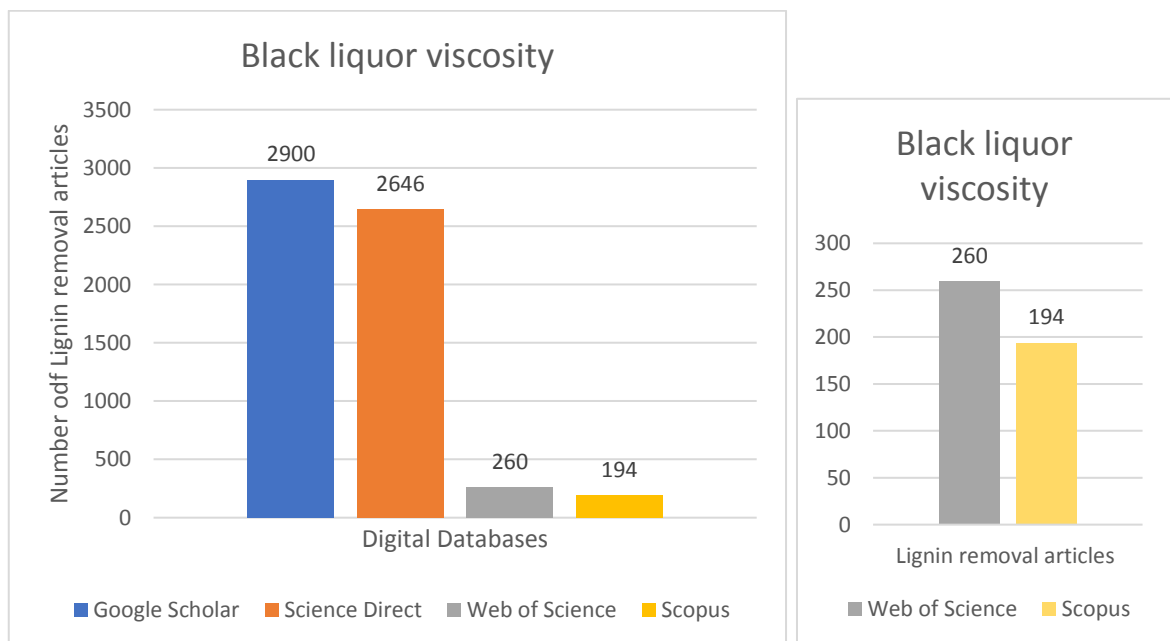


Figure 11. Search results of Lignin removal articles related to black liquor viscosity

The second key phrase for the search using the same digital databases was ‘black liquor viscosity temperature’ and Google Scholar produced the highest results with 35 800 documents. Patents accounted for 8 000 documents and review articles were 2 680. Using Science Direct, the search produced 4 326 results, with 1 105 book chapters, 154 conference abstracts, and 2 548 research and review articles amongst other documents. For Scopus the search results were much lower with only 116 documents divided into 83 articles, 32 conference papers and 1 book chapter. The least number of results from using the key phrase ‘black liquor viscosity temperature’ was from Web of Science which had 84 results, with articles accounting for 66 results and the rest of the documents being proceeding papers and book chapters. The figure below presents a comparative analysis of the temperature articles, which are linked to black liquor viscosity, other documents like patents and book chapters, are excluded from the figure.

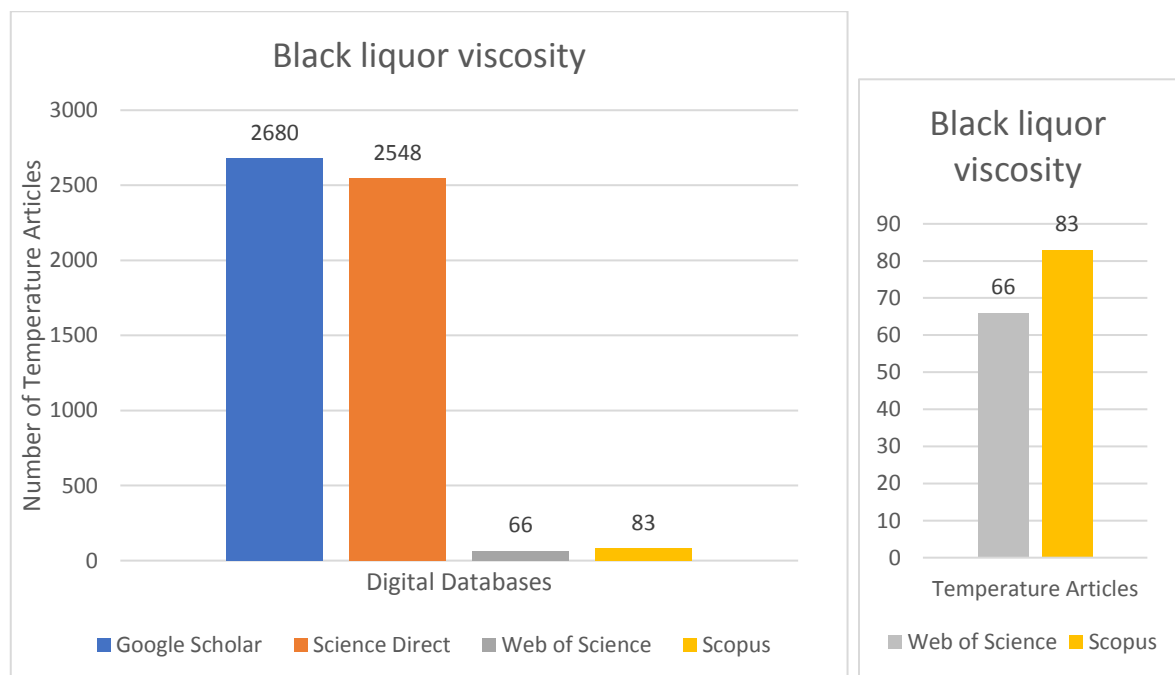


Figure 12. Search results of temperature articles related to black liquor viscosity

The third key phrase search using the digital databases was ‘black liquor viscosity dry solids’ and Google Scholar had the highest results with 29 800 documents. Review articles comprised of 15 900 documents and patents were only 2700 amongst other documents. Science Direct had the second highest results with 3 230 documents, with 937 being book

chapters, 101 conference abstracts, and 1 483 research and review articles amongst other documents. Web of Science had much lower results from the search with only 27 results divided into 22 articles, 6 proceeding papers and 1 book chapter. Science Direct had the least results amongst the four digital databases with 24 results divided into 19 articles, 4 conference papers and 1 review.

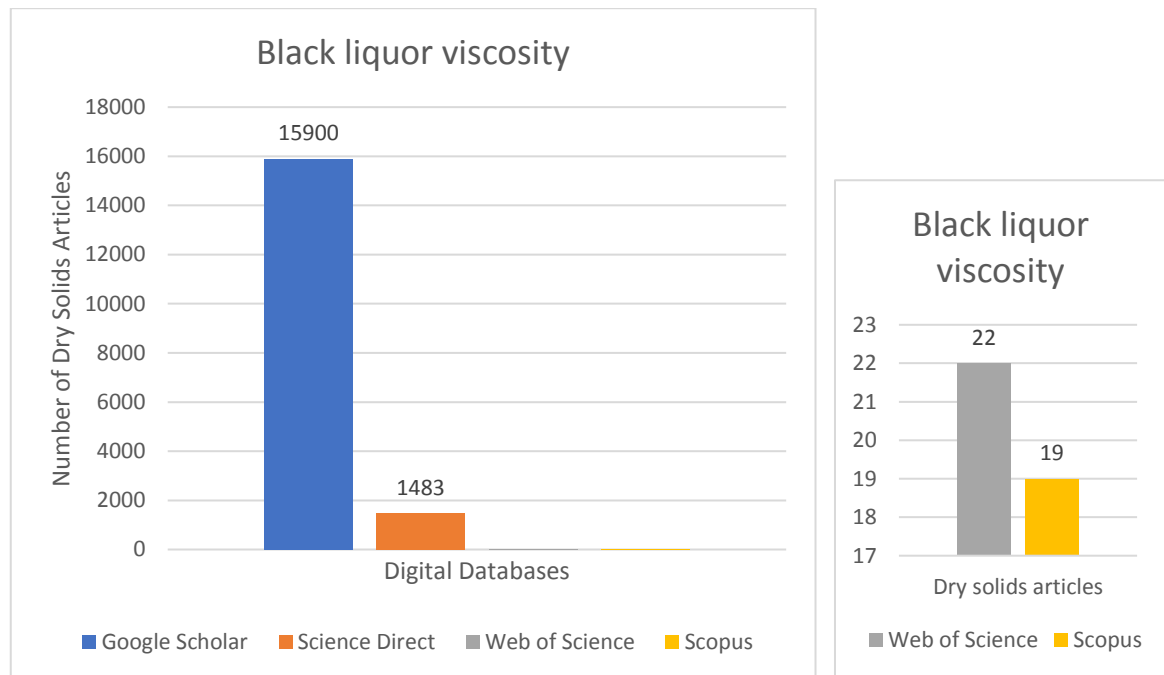


Figure 13. Search results for dry solids articles related to black liquor viscosity

The final search phrase utilised was ‘black liquor shear rate’ and Google Scholar produced 22 400 results with review articles being 8 410 documents and 1 500 patents amongst other documents. Science Direct had the second highest number of results with 1 346 documents divided between 404 book chapters, 70 conference abstracts and 688 review and research articles amongst other documents. Scopus produced much lower results when the same phrase was used with 24 documents divided into 18 articles and 6 conference papers. The least number of search results was from Web of Science with 17 documents, which were comprised of 14 articles and the rest being proceeding papers.

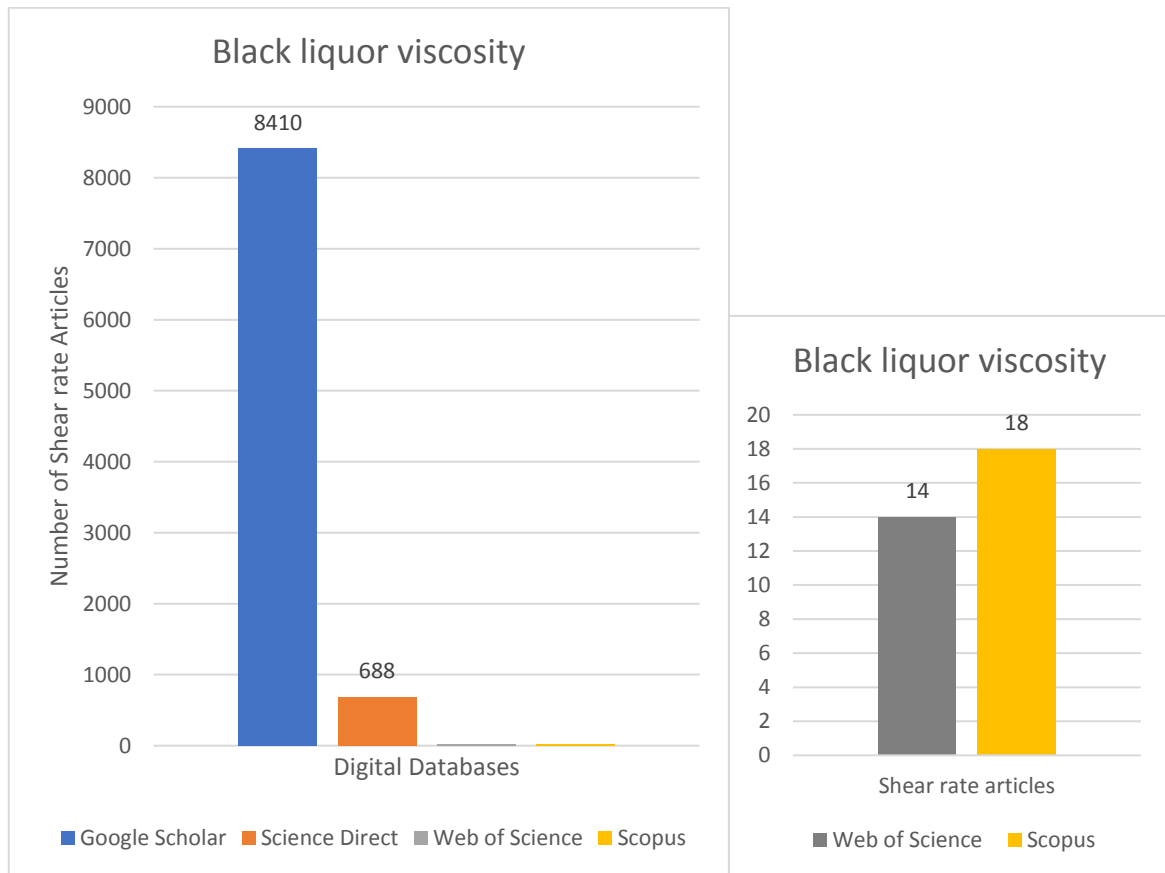


Figure 14. Search results for shear rate articles related to black liquor viscosity

## 4.2 Black Liquor Viscosity

In this sub-chapter, parameters that affect the viscosity of black liquor will be discussed in detail. The effects of lignin removal, temperature, shear rate and dry solids content of black liquor is analysed from articles of previous works on black liquor viscosity.

### 4.2.1 Lignin Removal

Moosavifar et al in 2006 reported a work in which they extracted a fraction of lignin from black liquor to observe the changes on the viscosity. A Swedish pulp mill provided the softwood black liquor utilised in the experiment. The main black liquor from the pulp mill were classified into two categories; thin black liquor and filtrate. Lignin was removed from the liquor in the lignin extraction plant section of the pulp mill. The thin black liquor acted as a reference and had the normal lignin concentration, whilst the filtrate had lignin removed

by a lignin precipitation process. The other samples of the black liquor used in the experiment were a mixture of the thin black liquor and filtrate classified as, mixture 1 which comprised of 25% filtrate+75% thin liquor and mixture 2 which comprised of 50% filtrate and 50% thin liquor. Table 8 shows the different black liquor samples with their respective dry solids content (Moosavifar et al., 2006).

Table 8. Black liquor samples in the experiment (Moosavifar et al., 2006)

<b>Type of black liquor</b>	<b>Dry solids content %</b>
Thin (BL)	14.0
Filtrate (F)	22.4
Mixture1(25%F & 75%TL)	16.1
Mixture2(50% F & 50%TL)	18.2

In the study, Moosavifar et al used the 4 black liquor samples in Table 6 to conduct the experiment. The samples were evaporated to get black liquor with 49% - 52% solids content. From the chemical analysis, lignin content in thin black liquor was four times higher than in the filtrate. A Bohlin rheometer CS50 was used to measure viscosity and, shear rate during the experiment was between 0-300 s<sup>-1</sup>. Results from the experiment showed that at similar solids content, viscosity was highest in samples with higher lignin content. Thin black liquor had the highest viscosity, followed by mixture1, mixture 2 and then the filtrate. The conclusion from the experiment was that removing lignin from black liquor decreases the viscosity of the black liquor. Figure 15 shows variation of viscosity of 4 different black liquor samples with variable lignin content at different temperatures (Moosavifar et al., 2006).

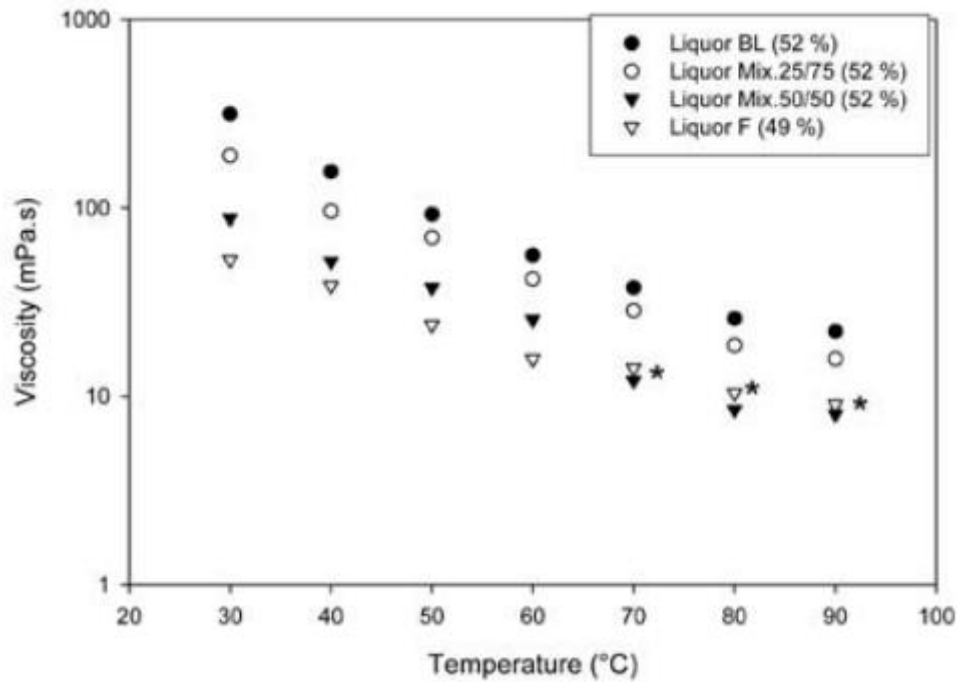


Figure 15. Variation of viscosity different black liquor samples with variable lignin content at different temperatures (Moosavifar et al., 2006).

Wallmo et al in 2015 did an experiment on evaporation of lignin lean black liquor, and part of that work focused on effects of removing lignin on BL viscosity. Softwood kraft BL from Swedish pulp mills was used and four samples of black liquor with varying lignin content were utilised. Lignin was removed through the LignoBoost process in Bäckhammar, Sweden. The first sample had no lignin removed and acted as the reference, second sample had 5% lignin removal rate, third sample had 21% lignin removal rate and the last sample had the maximum lignin removal rate of 60%. Table 9 shows four black liquor samples, lignin removal rate and their dry solids content.

Table 9. Black liquor samples (Wallmo et al., 2015).

Black liquor sample	Lignin removal rate	Dry solids content %
Ref	0 %	31.4
5.5	5.5% lignin removal rate	29.0
21	21% lignin removal rate	27.1
60	Max 60% lignin removal rate	23.2

According to Wallmo et al, the BL viscosity change for the four samples were described through an exponential behaviour of actual lignin outtake. The results from the experiment showed that at similar dry solids content, viscosity of reference black liquor was the highest, whilst the black liquor with maximum lignin removal rate displayed the lowest viscosity. The conclusion from the experiment was that black liquor viscosity is highly affected by the lignin content. Figure 16 shows viscosity of different liquor samples at varying solids content (Wallmo et al., 2015).

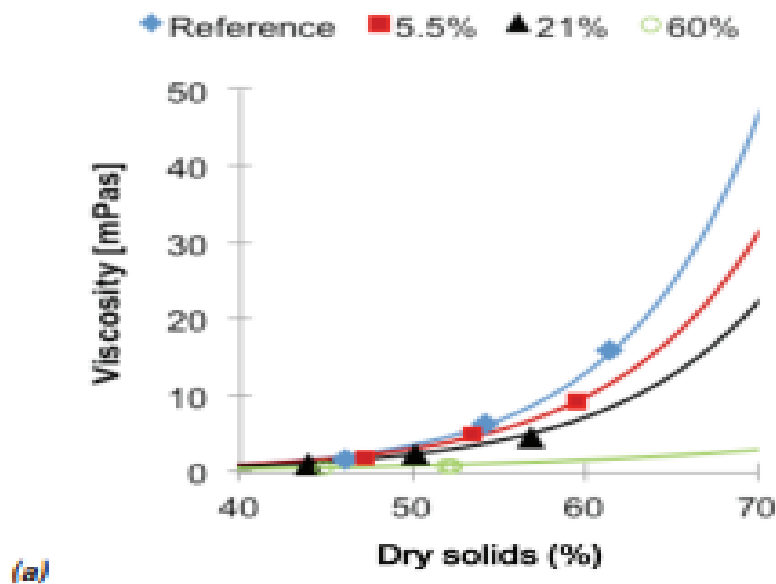


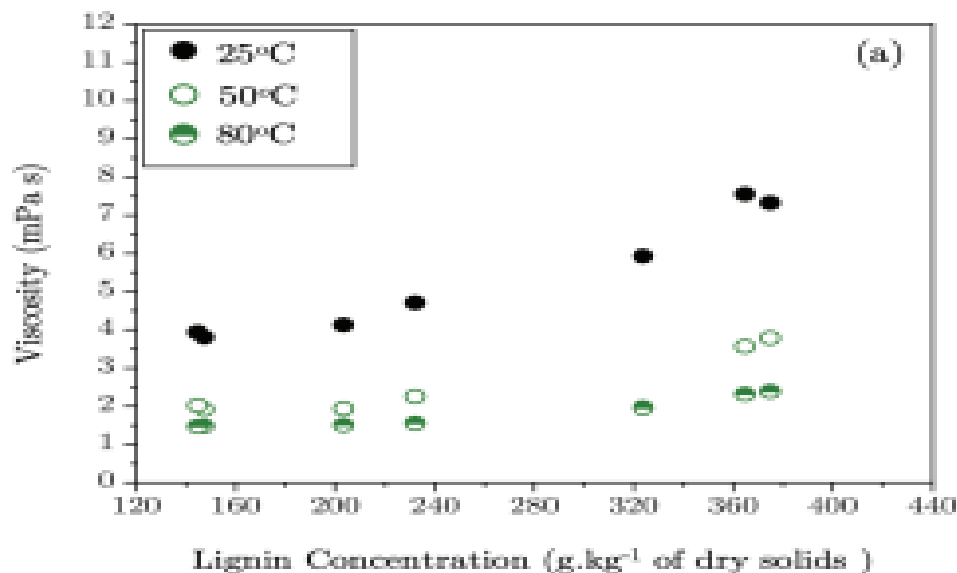
Figure 16. Effects of black liquor lignin removal on liquor viscosity (Wallmo et al., 2015).

Machado et al in 2023 performed a study on different properties of hardwood black liquor from *Eucalyptus*. Black liquor was obtained from a pulp mill in São Paulo, Brazil and different samples were prepared by acidification. Carbon dioxide was used for the acidification process in the experiment. The original black liquor without acidification was termed diluted black liquor, the acidified samples were termed acidified black liquor and the last sample where the lignin was fully precipitated by the acidification was termed lignin lean black liquor. Table 10 shows the black liquor samples and their respective lignin content (Machado et al., 2023).

Table 10. Black liquor samples from the experiment (Machado et al., 2023)

Black liquor sample		Lignin g/kg of dry solids
Diluted black liquor	(DBL)	374.9
Acidified black liquor	(ACL)	232.2
Lignin lean black liquor	(LLBL)	144.6

A Haake Mars III rheometer was used to measure viscosity of black liquor samples, with shear rate for the experiment between 10 - 2000  $s^{-1}$ . The results showed that diluted black liquor sample with the highest lignin content displayed the highest viscosity values and the lignin lean black liquor exhibited the lowest viscosity in the experiment. The conclusion from the experiment was that lignin removal significantly affects the viscosity of *eucalyptus* hardwood black liquor (Machado et al., 2023). Figure 17 below shows the variation of viscosity of three black liquor samples with respect to lignin concentration. From the results in Figure 17 it can be seen that as lignin concentration increased, the value of viscosity also increased.



Diluted black liquor ● Acidified black liquor ○ Lignin lean black liquor

Figure 17. Influence of lignin concentration on viscosity (Machado et al., 2023)

Chen et al in 2023 performed a study on rheological properties of black liquor with low lignin content. Guizhou Chi-tianhua Ltd, in China, provided bamboo kraft black liquor for the experiment. Low lignin bamboo kraft black liquor samples were prepared by using sulphuric acid ( $\text{H}_2\text{SO}_4$ ) to precipitate lignin out from original black liquor sample. The precipitation process lasted for one hour at a temperature of  $80^\circ\text{C}$ . For solids content, a vacuum drying oven at  $80^\circ\text{C}$  was used to concentrate black liquor samples to 80% solids content. The rheological properties of the bamboo kraft black liquor were measured by a dynamic rheometer AR2000ex, TA and shear rate was between  $0 - 100 \text{ s}^{-1}$ . BKBL samples used in the experiment are shown in Table 11 (Chen et al., 2023).

Table 11. Black liquor samples and the percentage of lignin removed (Chen et al., 2023)

<b>Black liquor sample</b>	<b>Percentage of lignin removed %</b>
Original BKBL	0.0
BKBL <sub>90</sub>	10.0
BKBL <sub>80</sub>	20.0
BLBL <sub>70</sub>	30.0

The experiment to measure the effects of lignin content on apparent viscosity was done at a temperature of  $98^\circ\text{C}$ . Results for the experiment showed that Original BKBL with no lignin removed had the highest viscosity, whilst BKBL<sub>70</sub> registered the lowest viscosity values, indicating that viscosity decreased as lignin content decreased. The conclusion from the study was that, removal of lignin from bamboo kraft black liquor weakens the network structure of lignin, which results in a decrease in viscosity. Figure 18 shows variation of viscosity of four BL samples as shear rate increases (Chen et al., 2023).

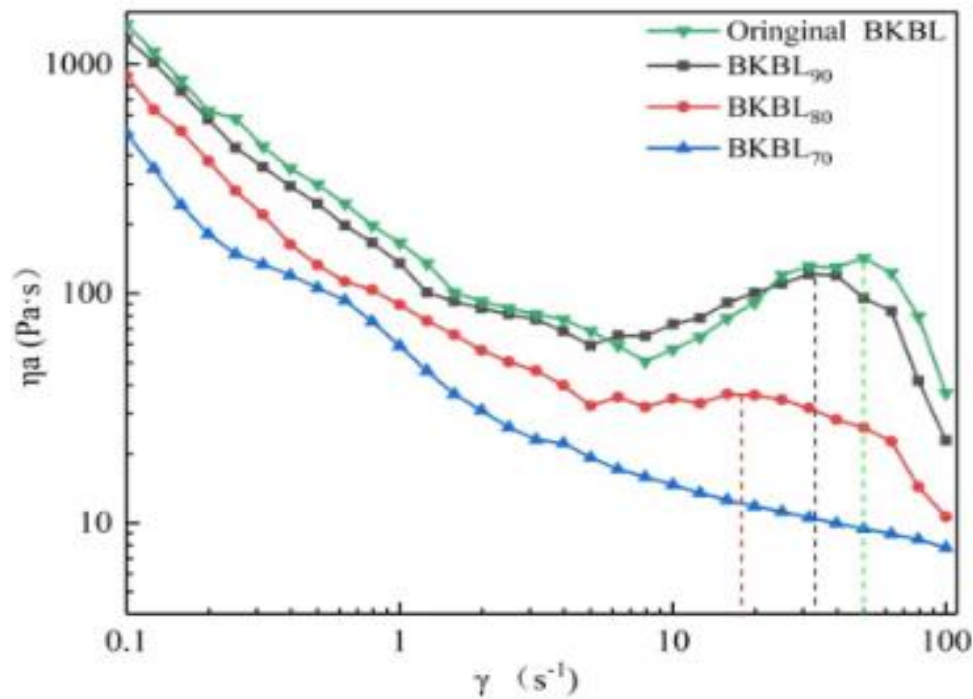


Figure 18. Apparent viscosity of black liquor vs shear rate of four black liquor samples with varying lignin content (Chen et al., 2023).

Zaman and Fricke in 1996 performed a study on effects of black liquor composition on viscosity. For their experiment, softwood slash pine black liquor from Florida, America was used and effects of lignin concentration on BL viscosity were analysed. The viscosity measurements for slash pine black liquor samples with high solids content and at high temperatures were made by an Instron capillary viscometer. Black liquor samples were concentrated to 80% solids content in a small-scale evaporator (Zaman & Fricke, 1996).

Results for viscosity of slash pine black liquor at 120 °C, showed that viscosity is directly proportional to lignin concentration. Figure 19 shows when lignin concentration was low, the viscosity was also low for the samples in the experiment with different effective alkali and sulfidity levels. Conclusion from the experiment was lignin concentration and lignin molar mass have a significant effect on viscosity of high solids concentration softwood BL (Zaman & Fricke, 1996).

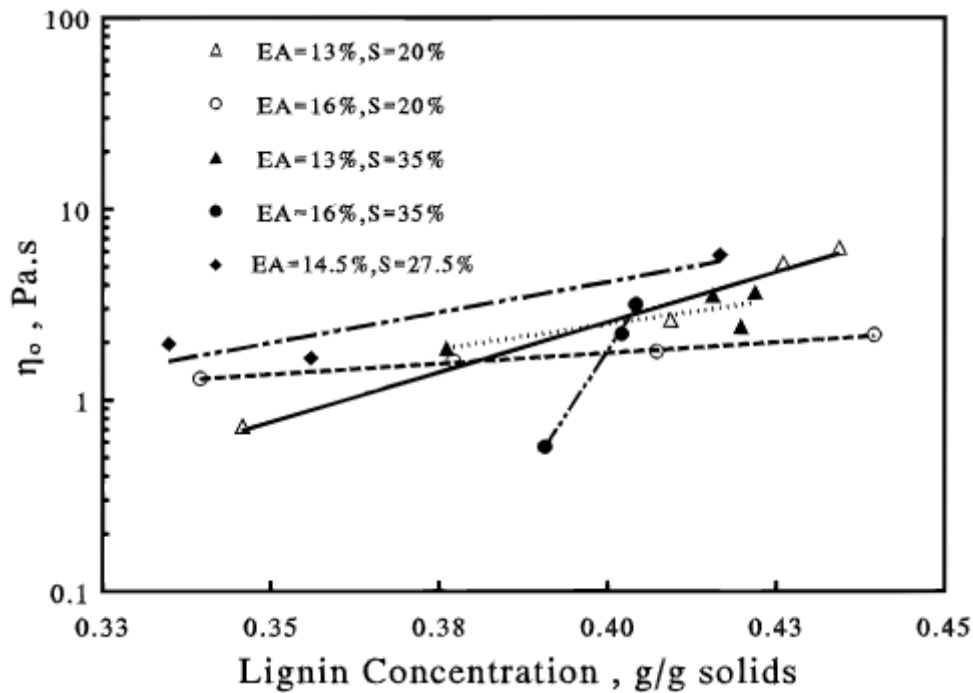


Figure 19. Viscosity as a function of lignin concentration (Zaman & Fricke, 1996).

#### 4.2.2 Temperature

Singh et al in 2015 performed a study on rheological properties of black liquor. An agro based pulp mill in India supplied wheat straw BL used in their experiment. Different samples with varying dry solids content were prepared by evaporating water in wheat straw black liquor through a vacuum rotary evaporator. For the rheological characterisation, a Physica MCR 100 rheometer was used. Shear rate during the experiment varied from  $10 - 1000 \text{ s}^{-1}$ . The black liquor samples were analysed at varying temperatures by running them through a cone plate geometry. A thermostatic bath was used to control the temperature with  $10^\circ\text{C}$  temperature increment from the initial temperature of  $60^\circ\text{C}$  until the maximum temperature of  $100^\circ\text{C}$  (Singh et al., 2015). Table 12 shows the different wheat straw soda black liquor samples.

Table 12. Wheat straw black liquor samples at varying dry solids content (Singh et al., 2015)

Wheat straw soda black liquor	Dry solids content %
Sample 1	36.0
Sample 2	42.0
Sample 3	47.0
Sample 4	52.0

The results of the experiment showed that as temperature increased, apparent viscosity of wheat straw black liquor decreased and this was true for the four different samples with varying solids content. The conclusion from the work by Singh et al was that black liquor exhibits a non-Newtonian pseudo-plastic behaviour when reconstituted with water. The Arrhenius relationship displayed the temperature dependency of viscosity and figure 20 below illustrates the variation of the apparent viscosity at different temperature points for the four black liquor samples (Singh et al., 2015)

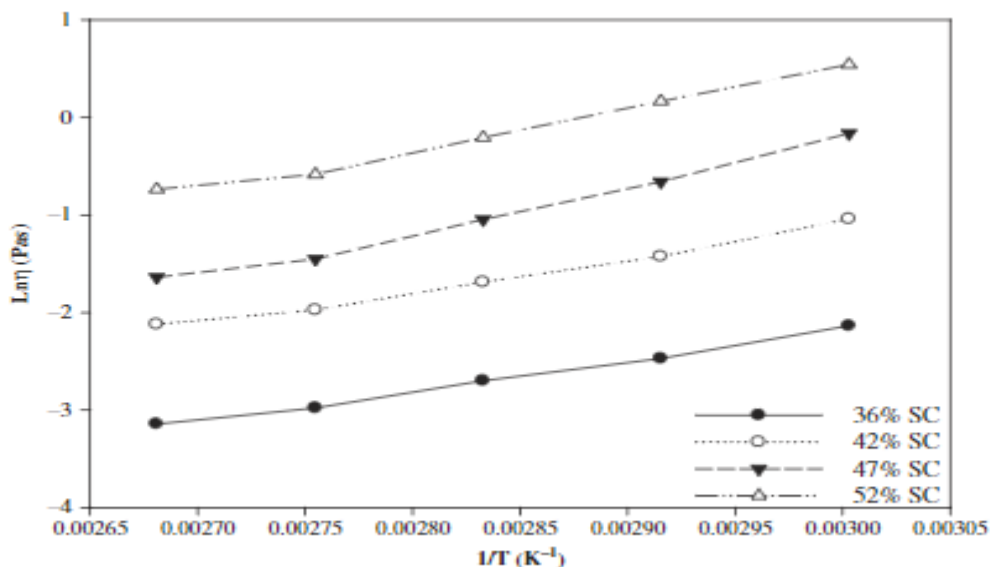


Figure 20. Apparent viscosity as a function of temperature data from an Arrhenius model (Singh et al., 2015)

Moosavifar et al in 2006 performed a study on viscosity of black liquor and part of their work focused on influence of temperature on BL viscosity. Softwood black liquor from a

Swedish pulp mill was utilised during their experiment. Viscosity of black liquor was studied for temperatures in the range between 30 – 90 °C. Shear rates were between 0-300 s<sup>-1</sup> and a Bohlin rheometer CS50 was used for the viscosity measurements. The rheometer had an integrated bath, which was used to control the temperature for the experiment (Moosavifar et al., 2006) Table 13 shows the softwood black liquor samples with varying dry solids content which were utilised in the experiment.

Table 13. Softwood black liquor samples with varying dry solids content (Moosavifar et al., 2006)

<b>Softwood black liquor sample</b>	<b>Dry solids content %</b>
Sample 1	14.0
Sample 2	31.6
Sample 3	41.0
Sample 4	52.8
Sample 5	61.1

Results from the study by Moosavifar et al showed that as temperature increases, viscosity of softwood black liquor decreases. The change in viscosity due to temperature was more apparent in BL sample 5 with highest dry solids concentration and figure 21 shows clearly these variations. The conclusion from the work was temperature has a significant influence on black liquor viscosity, and these effects are greater for black liquor with high solids content (Moosavifar et al., 2006)

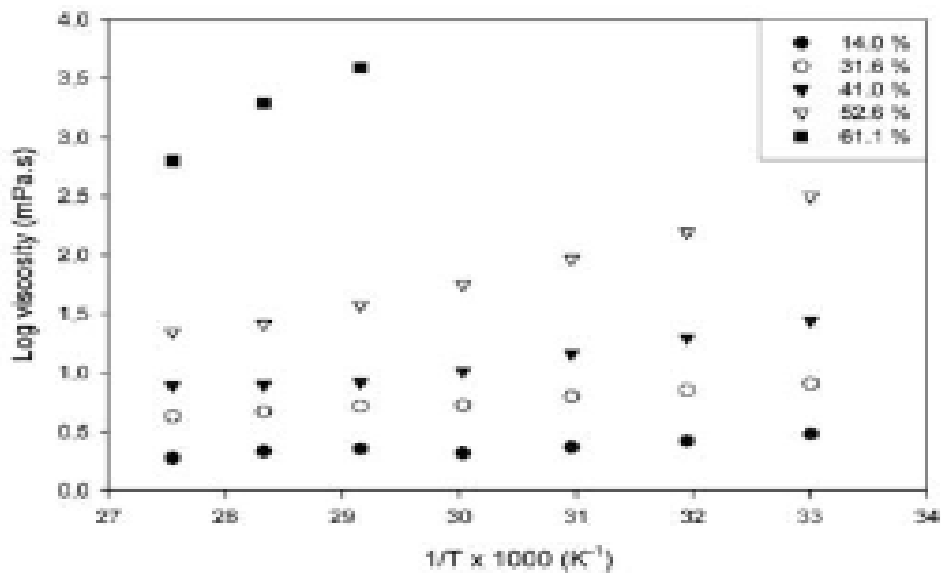


Figure 21. Influence of temperature on black liquor viscosity with different solids concentration (Moosavifar et al., 2006)

Nassar et al in 2016 performed a study on viscosity control of bagasse black liquor. Kous pulp mill located in Egypt produced the black liquor for their experiment from kraft pulping of bagasse. Samples with varying solids content were prepared. A rotational viscometer Brookfield DV-II+Pro was used to measure the viscosity at different temperatures. The temperature range for the experiment was between 70°C and 120°C (Nassar et al., 2016).

Results for the experiment showed that for both the thermally untreated and thermally treated black liquor, the viscosity dropped as the temperature increased. This effect was more noticeable for the thermally treated black liquor for the different samples with varying solids content. At 80°C, thermally untreated black liquor had higher viscosity values when compared to the thermally treated black liquor and this viscosity decreased as the temperature increased to 110°C. The significant decrease in BL viscosity after thermal treatment was due to the depolymerization of BL during the heat treatment process. The conclusion from this study was, heat treatment of BL significantly reduces its viscosity (Nassar et al., 2016).

Figure 22 shows the graphs of the reduction in viscosity of the black liquor as the temperature increased for different liquor samples with variable dry solids content. The first graph represents thermally untreated black liquor and the second one represents thermally treated black liquor.

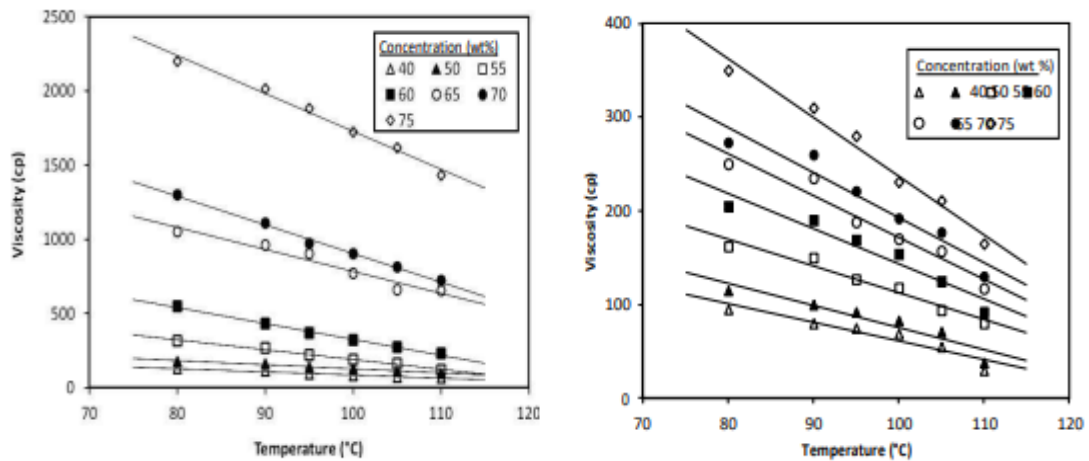


Figure 22. Viscosity of thermally untreated black liquor and thermally treated black liquor as a function of temperature (Nassar et al., 2016).

Singh et al in 2021 performed an experiment on effects of temperature on rheological properties of black liquor. Wheat straw black liquor for their study was obtained from a pulp mill in India. A thermostatic bath was used to control the temperature during the experiment. For the viscosity measurements, a Physica MCR 100 rheometer was utilised and the applied shear rate was between  $10 - 1000 \text{ s}^{-1}$ . For analysis of data, Singh et al connected the rheometer to a computer equipped with the Physica US 200 software (Singh et al., 2021).

Response Surface Methods (RSM) was used for the analysis of data. The results from the experiment showed that when temperature increased, viscosity of black liquor decreased. Temperature range during the experiment was between  $60 - 80 \text{ }^{\circ}\text{C}$ . Conclusion was temperature has a significant effect on black liquor viscosity. Figure 23 shows response surface and contour plots representing effect of temperature and dry solids concentration on wheat straw BL viscosity (Singh et al., 2021).

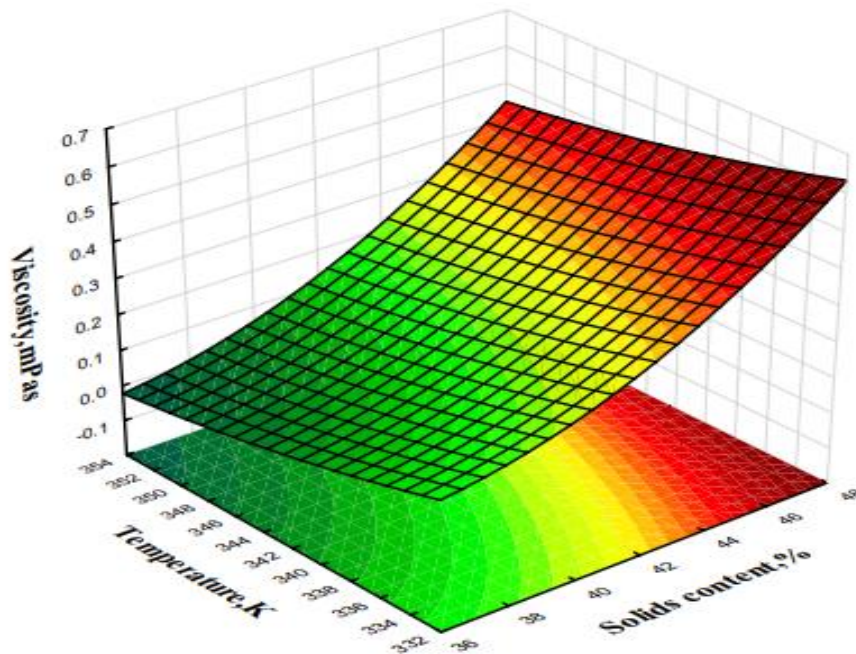


Figure 23. Viscosity of wheat straw black liquor as a function of temperature and dry solids content (Singh et al., 2021).

Xu et al in 2015 performed a study on wheat straw black liquor and in their work; they investigated the effects of temperature on BL viscosity. A pulp mill in China supplied the thick black liquor for the experiment with 54.12 wt.% solids content. The viscosity measurements were done at a shear rate of  $2 \text{ s}^{-1}$  in the temperature range between 70 – 120 °C. Original black liquor and four other black liquor samples containing small percentages of aluminium sulphate were used in the experiment (Y. Xu et al., 2015).

Results from the experiment showed that as temperature increased, viscosity of BL decreased for most of the samples in the experiment with the exception of a BL sample with 3% aluminium sulphate. Figure 25 shows this variation in viscosity as temperature increases from 70 – 100 °C. The conclusion from the experiment was an increase in temperature has significant effects in reduction of black liquor viscosity (Y. Xu et al., 2015).

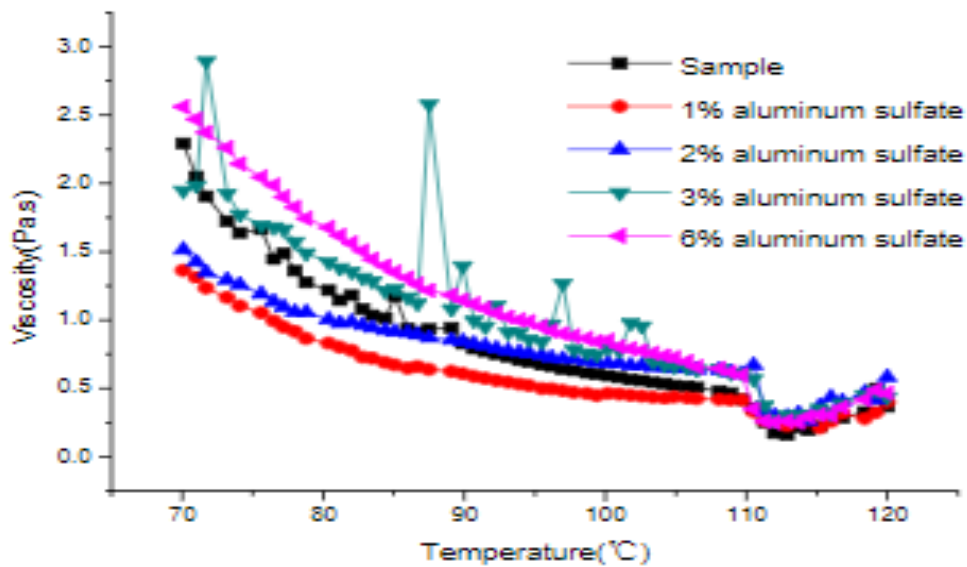


Figure 25. Black liquor viscosity as a function of temperature (Y. Xu et al., 2015).

#### 4.2.3 Dry Solids Content

Llamas et al in 2007 performed a study focused on viscosity reducers of black liquors with high dry solids concentration. Hardwood *Eucalyptus* black liquor obtained from a mill in Spain was used during the experiment. The rheological conditions in their study were such that, temperature of the black liquor was kept below 90°C by a thermal fluid circulated in a jacket cell and a Haake VT500 viscometer was used for viscosity measurements. The applied shear rate was between 0-550 s<sup>-1</sup> (Llamas et al., 2007).

Results from the experiment showed that viscosity of BL is directly proportional to dry solids content and Figure 26 displays this effect with 4 black liquor samples at different shear rates showing an increase in viscosity as the dry solids concentration increased. The conclusion from the study was black liquor behaves like a Newtonian fluid at low solids content and at high solids content they exhibit non-Newtonian fluids behaviour (Llamas et al., 2007).

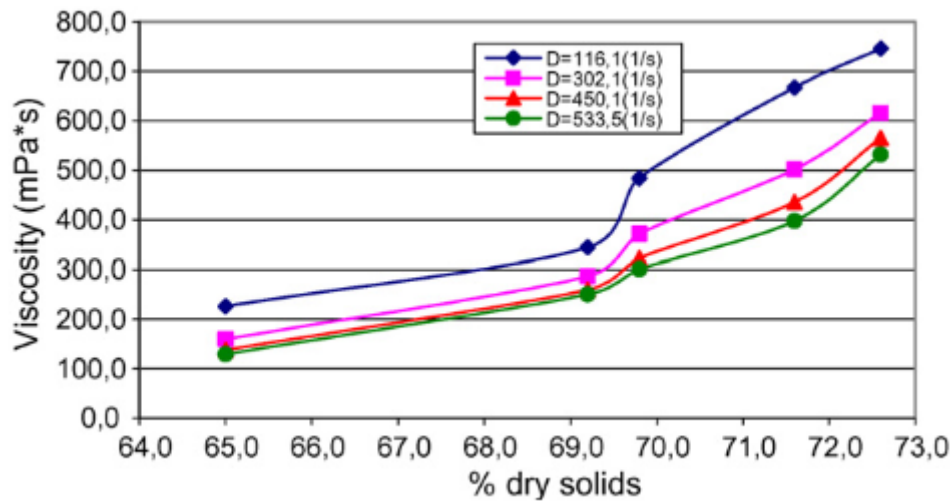


Figure 26. Variation of black liquor viscosity with dry solids content (Llamas et al., 2007).

Moosavifar et al in 2009 performed an experiment on changes in viscosity with part of their work focusing on effects of dry solids on BL viscosity. Black liquor for their experiment was sourced from several Swedish pulp mills. For viscosity measurements, a Bohlin rheometer CS50 was used and the shear rate for this study was between 3 and 300  $s^{-1}$  (Moosavifar et al., 2009).

Results from the experiment from a softwood black liquor sample showed that a rise in dry solids concentration increased viscosity. Figure 27 below shows a black liquor sample subjected to different temperatures and when solids content increased, viscosity followed the same pattern. From the figure, the viscosity rise was sharper for solids content above 50% compared to the viscosity change in dry solids content below 50% (Moosavifar et al., 2009).

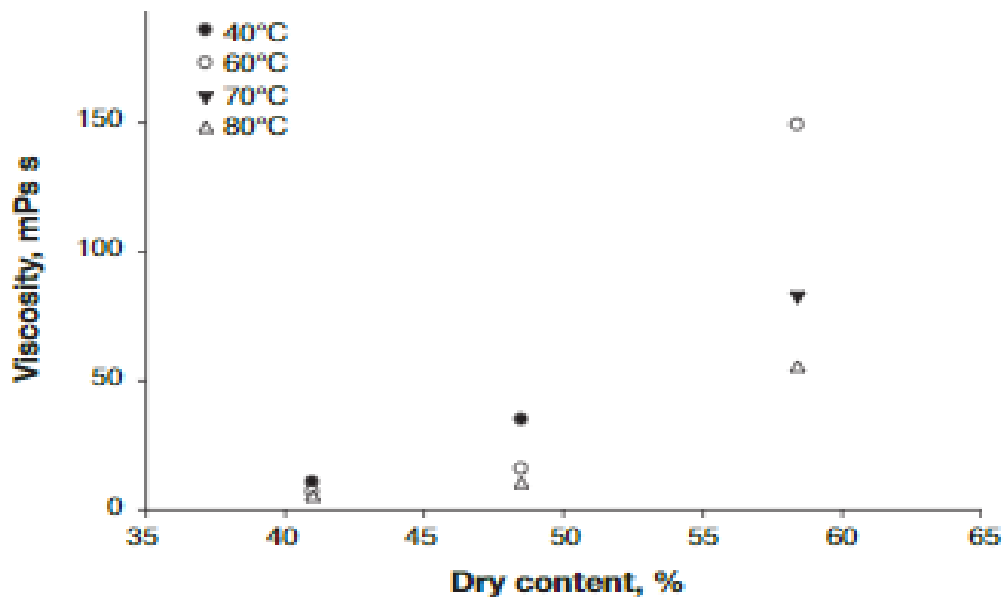


Figure 27. Viscosity of black liquor as a function of dry solids content (Moosavifar et al., 2009).

Xu et al in 2021 performed an experiment on viscosity reduction in wheat straw black liquor. In their work, effect of dry solids concentration on BL viscosity were analysed. Black liquor for the experiment was obtained from Shandong Province, China. A SNB-1 viscometer was used for the viscosity measurements and the temperature during the experiment was maintained at 90°C (H. Xu et al., 2021).

Results show that viscosity of black liquor increased as the solids content increased. Between 10 to 45 % solids content there was a slow rise in viscosity and after 45% solids content, the viscosity increased significantly with a slight increase in solids content. BL samples with higher solids concentration displayed higher viscosity values. Figure 28 shows variation of viscosity of black liquor samples as total solids concentration increased (H. Xu et al., 2021).

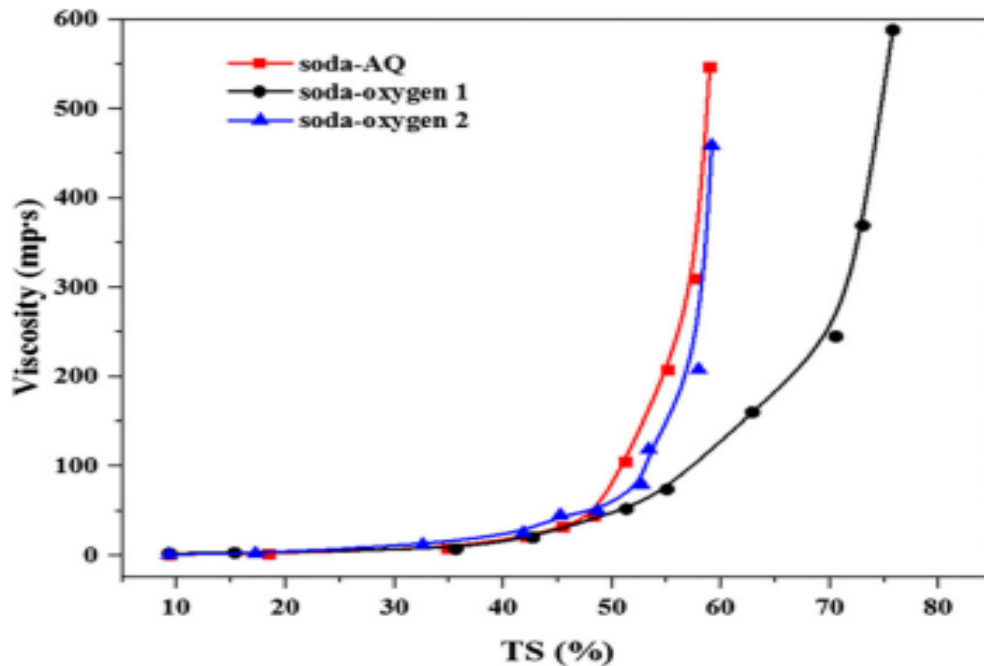


Figure 28. Viscosity of wheat straw black liquor as a function of dry solids concentration (H. Xu et al., 2021)

Zhang and Chen in 2016 performed a study on properties of black liquor. The alkali-oxygen pulping of rice straw at Pulping and Papermaking Research Center of Yunnan Province, China provided BL for the experiment. Black liquor solids content was concentrated by drying BL in an electric oven at 105 °C temperature. A SNB-1 viscometer was used for the viscosity measurements for temperatures between 50°C - 90°C (Zhang & Chen, 2016).

Results for the experiment by Zhang and Chen showed that viscosity of rice straw black liquor increased as dry solids content in black liquor increased. Figure 29 shows the variation in viscosity of BL. At lower dry solids 30 wt.%, viscosity is low and slightly rising with increased solids content. From dry solids content of 45 wt.% to 60 wt.% there is a sharp rise in viscosity as the solids content increase. This trend is the same for all the temperature ranges in the experiment (Zhang & Chen, 2016).

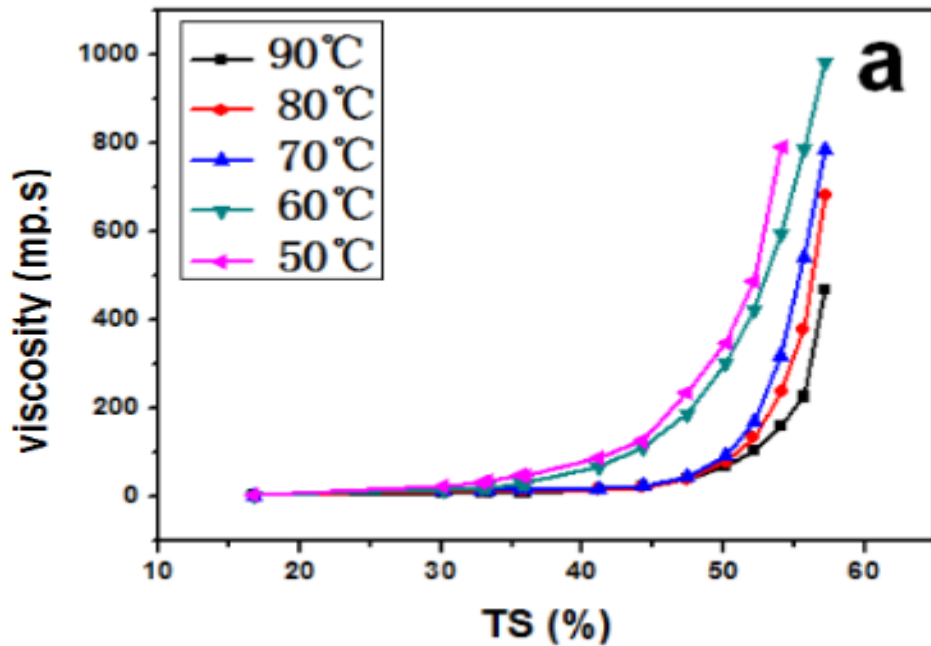


Figure 29. Viscosity of rice-straw black liquor vs solids content and temperature (Zhang & Chen, 2016).

Santos Leite et al in 2011 performed a study on viscosity of *Eucalyptus* black liquor. An industrial mill recovery unit in Brazil provided black liquor samples for the experiment. Table 14 shows dry solids content and different collection points in an evaporation plant for the BL samples (Santos Leite et al., 2011).

Table 14. Black liquor samples (Santos Leite et al., 2011)

Black liquor sample extraction point/ Process stream	Abbreviation	Solids content of the samples
Evaporation plant inlet stream	EPI	Low
6 <sup>th</sup> effect recirculation stream	6ER	Medium
2 <sup>nd</sup> effect outlet stream	2EO	High

For viscosity measurements, Santos Leite et al used a Brookfield LV viscometer. Shear rate was changed by varying the rate of spindle rotation of the viscometer and viscosity values were obtained at a fixed temperature. Results for the experiment showed that viscosity increased as the solids content in black liquor samples increased. Black liquor viscosity was highest for samples from the 2<sup>nd</sup> effect process stream 2EO with high solids concentration

and viscosity decreased as solids content decreased Figure 30 shows the different viscosity values for black liquor samples. (Santos Leite et al., 2011).

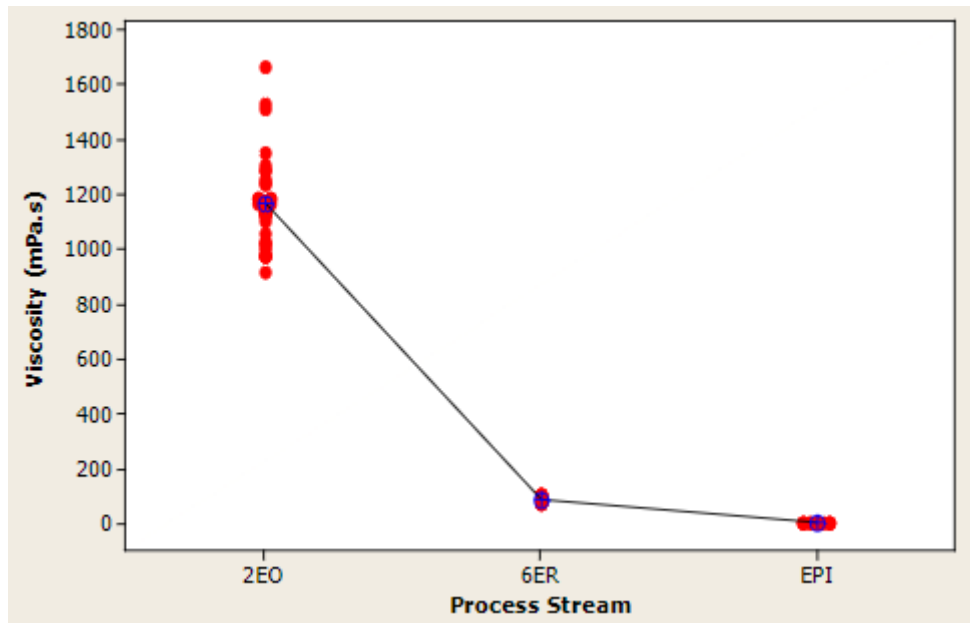


Figure 30. Viscosity of Eucalyptus black liquor content with different solids content (Santos Leite et al., 2011).

#### 4.2.4 Shear Rate

Alabi et al in 2012 performed an experiment on non-Newtonian behaviours of black liquor. The black liquor for their experiment was obtained from a mill in Kinleith, New Zealand. The BL samples were composed of 92.5% softwood and 7.5% hardwood. For the viscosity measurements, a Haake Rotovisco RV20 rotational viscometer was used. Temperature during the experiment was between 0 - 115°C and the applied shear rate was between 200 - 1000 s<sup>-1</sup> (Alabi et al., 2012).

Results from the experiment showed that as shear rate increased, apparent viscosity of BL decreased. The viscosity was highest when the shear rate was 250 s<sup>-1</sup>, and it dropped significantly with every increase in shear rate as shown in Figure 31. From the experiment, when apparent viscosity was above 4000 mPa.s, the black liquor sample exhibited thixotropic behaviour. Figure 31 below show the variation in viscosity as the shear rate changes, for a BL sample with solids concentration of 64.4% and at 40°C (Alabi et al., 2012).

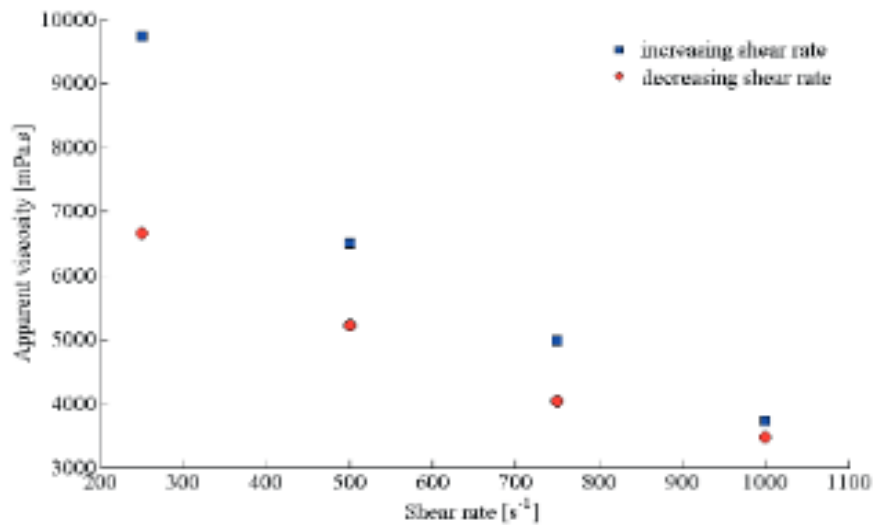


Figure 31. Apparent viscosity of black liquor as a function of shear rate (Alabi et al., 2012)

Costa et al in 2011 performed a study on the rheology of *Eucalyptus Globulus* kraft black liquor. A pulp mill in Portugal provided the black liquor for the experiment. The viscosity measurements were done by a controlled stress rheometer Haake model RS<sub>1</sub> and a shear between 0 – 2000  $s^{-1}$  was applied during the experiment. The temperature range was between 25 – 65 °C (Costa et al., 2011).

Results from the experiment showed a reduction in viscosity when the shear rate increased. A BL sample with 59.5 solids content and at a temperature of 65 °C showed a significant viscosity dropped as the shear rate changed from 0 to 200  $s^{-1}$ . At 250  $s^{-1}$ , when shear rate increased, the change in viscosity was small as shown in Figure 32. The conclusion from the experiment was, at low shear rates the black liquor observed a pseudo plastic flow and if shear rate continues increasing a Newtonian plateau can be reached. Figure 32 below shows the changes in viscosity of *Eucalyptus globulus* BL at 65°C and 59.5% solids content as a function of shear (Costa et al., 2011).

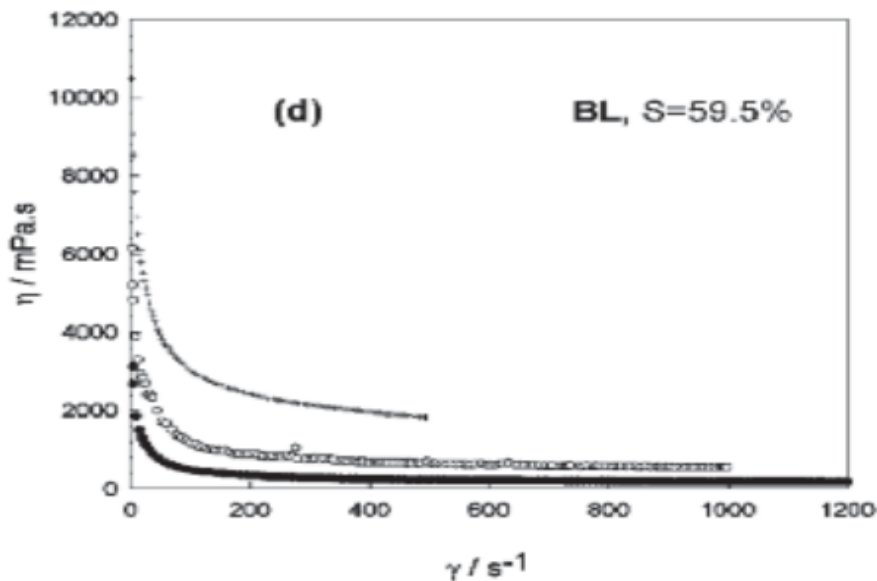


Figure 32. Black liquor viscosity as a function of shear rate (Costa et al., 2011).

In 2015, Singh et al performed a study on wheat straw black liquor with part of their work focusing on the effects of shear rate on BL viscosity. An agro based pulp mill in India provided the black liquor for the experiment. For viscosity measurements, a Physica MCR 100 rheometer was used and the applied shear rate was between  $10 - 1000 \text{ s}^{-1}$ . The temperature during the experiment was in the range of  $60 - 100 \text{ }^\circ\text{C}$  (Singh et al., 2015).

Results showed that when applied shear rate was low, the apparent viscosity of black liquor was high due to the lignin macromolecules in the BL interacting more easily at low shear rates. Increasing this shear rate would cause the viscosity to lower. When the shear rate increased from  $0 \text{ s}^{-1}$  to  $200 \text{ s}^{-1}$ , there was a significant drop in viscosity. After that drop, the change in viscosity was now gradual until it reached a plateau stage. The conclusion from this study was wheat straw BL present a pseudo-plastic non-Newtonian behaviour (Singh et al., 2015). Figure 33 below shows the viscosity changes of a sample of black liquor as a function of shear rate. The black liquor sample had 52 % solids content and was under different temperatures in the range of  $60 - 100 \text{ }^\circ\text{C}$ .

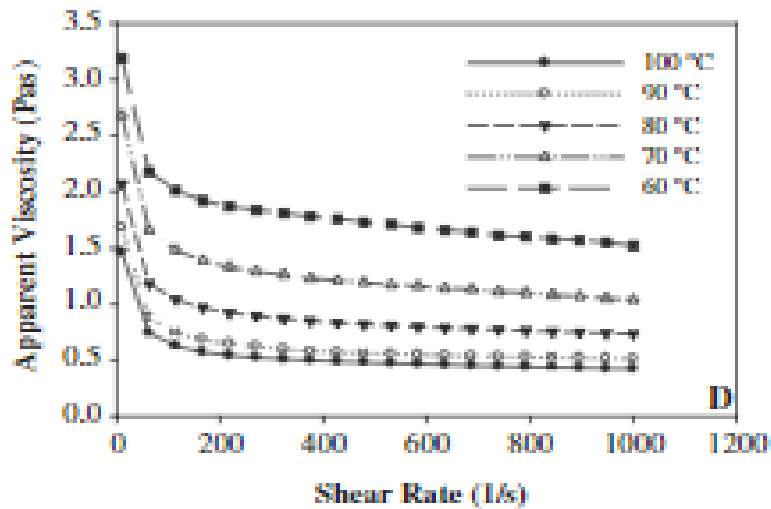


Figure 33. Viscosity changes in wheat straw soda black liquor as a function of shear rate (Singh et al., 2015).

Yue et al in 2017 performed a study on rheological properties of thick kraft black liquor and in their study, the effects of shear rate on BL viscosity were analysed. Chitianhua Pulp and Papermaking Company in Guizhou China supplied the bamboo kraft black liquor (BKBL) which was utilized in the experiment. In order to evaporate the water in the BKBL, Yue et al used a vacuum drying oven at 80°C and this increased the dry solids concentration. The black liquor samples for the study had 70.19 wt.% and 79.19 wt.% solids content. For the viscosity measurements, an AR2000ex rotational rheometer was utilised at temperature 70°C and 98°C, with the shear rate between 0.1 – 100 s<sup>-1</sup> (Yue et al., 2017).

Results from the experiment show that an increase in applied shear rate caused the apparent viscosity of the BKBL to decrease. Figure 34 shows this trend for the black liquor samples with 70.19 wt.% and 79.87wt.% at temperature of 70°C, when the shear rate increased from 0.1 s<sup>-1</sup> to 10 s<sup>-1</sup>, the apparent viscosity dropped significantly. From 10 s<sup>-1</sup> to 100 s<sup>-1</sup>, there was a steady decline in viscosity to an almost constant state as the shear rate increased and this area was described as the Newtonian zone. An almost similar trend was observed at 98°C until shear rate reached 30 s<sup>-1</sup> and a shear thickening phenome appeared in the BKBL. The conclusion from the study was BKBL exhibits pseudo-plastic behavior with Newtonian zones, and changes in shear rate and temperature has a significant effect on apparent viscosity (Yue et al., 2017).

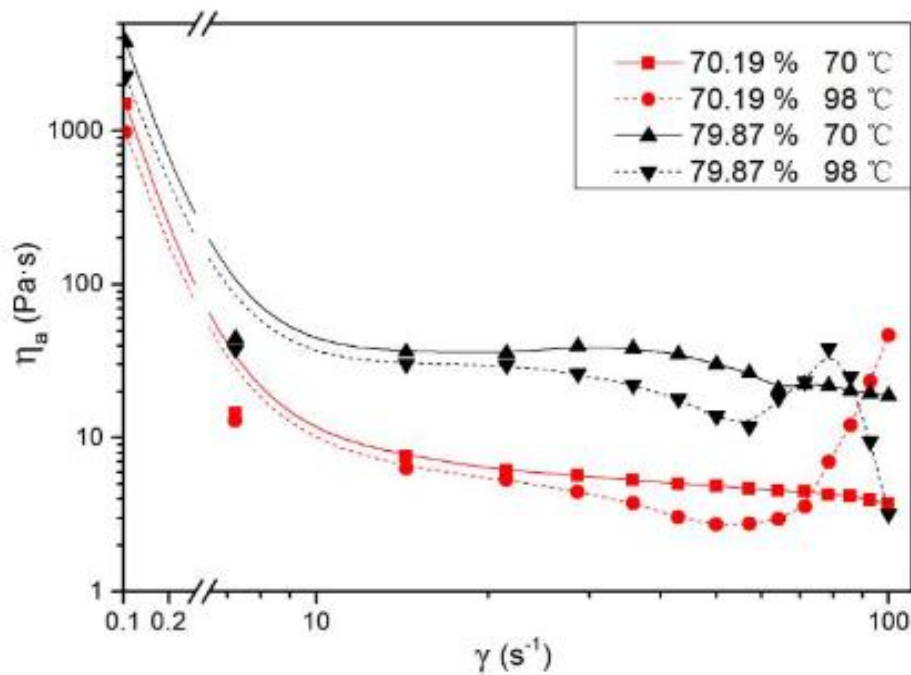


Figure 34. Apparent viscosity of BKBL as a function of shear rate (Yue et al., 2017).

Cardoso et al in 2009 performed a study on black liquor composition and physical properties. In their work, parameters that affect black liquor viscosity such as shear rate were investigated. The BL was supplied by different Brazilian mills, with five mills supplying hardwood *Eucalyptus grandis* black liquor and one mill supplying bamboo black liquor. A rotational Cole-Parmer viscometer was used for viscosity measurements at different temperatures and shear rate. The temperature range for the viscosity measurements was between 29.5 – 69.5 °C and the shear rate range was between 0 – 20 s<sup>-1</sup> (Cardoso et al., 2009).

Results for the experiment show the correlation between shear rate and viscosity, which highlight that as the shear rate, increased, the apparent viscosity for eucalyptus decreased. The black liquor sample with 49.3% solids content and at 35.3 °C had a sharp decrease in viscosity when shear rate was increased from 0 – 5 s<sup>-1</sup>, and from 5 – 10 s<sup>-1</sup>, the viscosity change was almost constant as the shear rate was increased. The sample with 40.5 % solids content and at temperature 31.5 °C had a low viscosity, which remained constant when shear rate increased. Figure 35 shows the variation of *Eucalyptus* black liquor viscosity as a function of shear rate for samples with different solids content and different temperature (Cardoso et al., 2009).

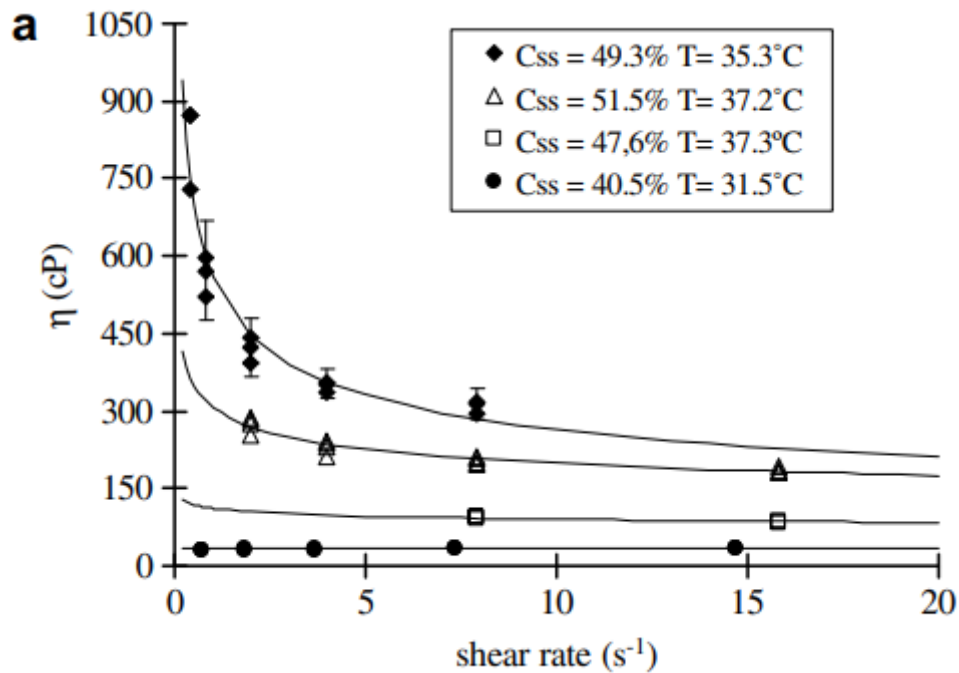


Figure 35. Viscosity of *Eucalyptus grandis* black liquor samples from Mill A as a function of shear rate (Cardoso et al., 2009).

For bamboo BL from mill F, the same effect of a decrease in viscosity when shear rate increases was noted. Figure 36 shows the variation of the viscosity as shear rate increased. The conclusion from the study was that, the presence of silicon and a higher lignin molar mass in bamboo black liquor resulted in the viscosity for bamboo black liquor samples being much higher than those from *Eucalyptus*. From the experiment, it was also observed that, higher viscosity values at low shear rates were due to lignin macromolecules entangling more easily and increasing shear rates aligns macromolecules together, which reduces the viscosity of both samples of black liquor (Cardoso et al., 2009).

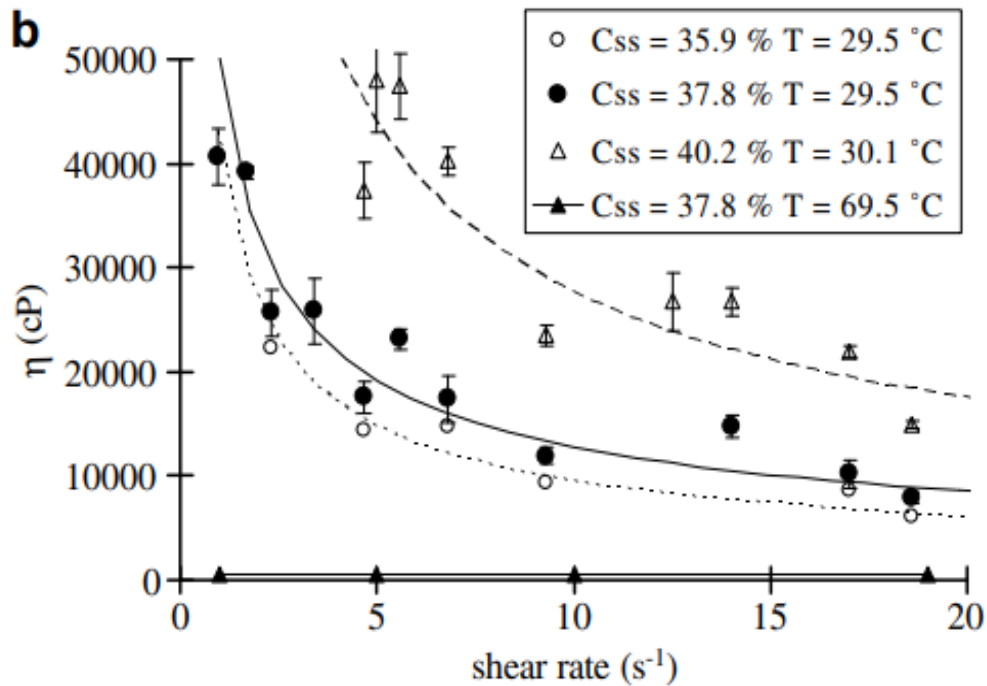


Figure 36. Viscosity of bamboo black liquor from Mill F as a function of shear rate (Cardoso et al., 2009).

### 4.3 Discussion

In this section, the discussion focuses on the key findings related to black liquor, and the articles related to black liquor viscosity. The literature used in this chapter were on the effects of lignin removal, temperature, dry solids content and shear rate on the viscosity of black liquor. So a summary of the main ideas, techniques and key observations are presented in the following paragraphs.

The effects of lignin removal were analysed from five different articles related to black liquor viscosity. The earliest paper was by Zaman and Fricke (1996) and the latest one was by Machado et al (2023). Both softwood and hardwood black liquor were analysed. Generally, black liquor with no lignin removed has high viscosity due to the strong network structure formed by the lignin molecules, which interferes with the flow of the liquid. Lignin removal by techniques such as the LignoBoost process results in a decrease in viscosity due to the weakening of the lignin network structure. Therefore pulp and paper mills can lower the

viscosity of their black liquor by a certain degree through lignin removal and optimize their mill operations.

For temperature, articles related to black liquor viscosity were analysed with the earliest one being Moosavifar et al (2006) and the latest one being Singh et al (2021). Black liquor literature on softwood, hardwood and non-wood black were studied to determine the correlation between temperature and viscosity. The relationship between temperature and black liquor viscosity was determined to be such that when the temperature increases, the viscosity decreases. This decrease in viscosity is due to the increase in kinetic energy in the black liquor molecules when the temperature is increased. The result is such that the increased molecular movement reduces the interactions between molecules thus lowering the viscosity of the black liquor.

In terms of dry solids content, their effect on black liquor viscosity was analysed from research articles with the earliest one being Llamas et al (2007) and the latest one being Xu et al (2021). Hardwood, softwood and non-wood black liquor were all analysed in the different research articles to determine the correlation between dry solids content and viscosity. The general conclusion was that black liquors with high dry solids content had higher viscosities when compared to samples with low dry solids content. This effect is due to the presence of more solid particles, which increase the resistance to flow, and as a result, higher viscosities are observed when the dry solids content is high.

For shear rate and black liquor viscosity, their relationship was studied from research articles with the earliest one being Cardoso et al (2009) and the latest one being Yue et al (2017). Softwood, hardwood and non-wood black liquors were studied to determine the variation of viscosity when the shear rate is changed. Generally, black liquor exhibits non-Newtonian behavior, which means that its viscosity changes as a function of the applied shear rate. From the studied literature, it was observed that at low shear rates, black liquor had high viscosity values and when the shear rate was increased, the viscosity decreased. This behavior is termed as shear thinning behavior. The effect of increasing shear rate is such that, there will be shear alignment, which rearranges the structure and entanglements in the black liquor molecules thus reducing its viscosity.

#### 4.3.1 Articles Summary

A table containing the key information from black liquor viscosity articles is attached below. Main data obtained from the papers already cited in the results subchapter 4.2 is presented together with additional papers, which have been only included in the table to maintain the length of this document. The table is has four main sections, which are lignin removal, temperature, dry solids content and shear rate. The papers are arranged in chronological order under each section. The table is composed of 15 columns, starting from reference column, the location of the mill, the main physical and chemical condition of the black liquor, and the main rheological findings and parameters.

Viscosity Reductor	Reference	Mill Origin	Location	Wood Type	BL Type	BL Solids Content	Rheological Tests Temperature	Methodology of Viscosity Reduction	Viscosity Reduction	Viscosity Reduction Principle	Rheometer	Shear Rate Range	Fixed Shear Rate	Main Conclusions
Lignin Removal:														
	<a href="#">Zaman, 1996</a>	Pilot-scale digester operated with liquor circulation	USA	Softwood	Slash pine	80%	40 - 140 °C		Reduction of viscosity in the temperature range of 40 - 120°C was between 2 - 6 orders of magnitude		Haake RV-12 viscometer with normal open cup for Black liquor with solids content in the range 50 - 65 and temperature between 40 - 90 °C. A custom-built pressure cell concentric cylinder viscometer for Black liquor with solids content less than 75 and temperature less than 100 °C with maximum shear rate of 1000 s <sup>-1</sup> . Instroncapillary viscometer Model 3211 for maximum shear rate of 10 000, For Non-Newtonian behavior conditions; RheometricsRMS-800 mechanical spectrometer with a parallel-plate setup at temperatures below 85 °C.	Solids Content less than 50 % - shear rate maximum 1000 s <sup>-1</sup> and for Solids Content above 65% - shear rate maximum 10000 s <sup>-1</sup>	N/A	The viscosity increased as the concentration of lignin increased. At Lignin concentration of 0.44 g/g solids, the apparent viscosity value was higher than at concentration of 0.34g/g solids for the BL samples in the experiment
	<a href="#">Moosavifar, 2006</a>	N/I	Sweden	Softwood	Weak Black Liquor (WBL)	*14% (mill) *14% - 61.1% (tests)	30 - 90°C	Lignin removal by acid hydrolysis with sulphuric acid (H <sub>2</sub> SO <sub>4</sub> ) and CO <sub>2</sub> .	Qualitative	A reduction in the average molecular weight of the lignin will reduce the viscosity of the black liquor. Average weight of lignin is higher for WBL compared to liquor LLBL.	Bohlin Instruments Rheometer CS50 with a concentric cylinder	N/A	180 s <sup>-1</sup>	After lignin precipitation, the lignin content in LLBL (77 mg.g <sup>-1</sup> ) was about 4 times lower than in the WBL (314 mg.g <sup>-1</sup> ) which is related to the reduction in viscosity. LLBL viscosity was the lowest when compared to the other BL samples
				Low-lignin Black Liquor (LLBL)	*22.4% (lignin extraction plant) *49% (tests)	30 - 90°C	Qualitative							
				Mix of 25%LLBL/75%BL	52% (tests)	30 - 90°C	Qualitative							
				Mix of 50%LLBL/50%BL	52% (tests)	30 - 90°C	Qualitative							
	<a href="#">Moosavifar, 2009</a>	Several Pulp Mills	Sweden	Softwood, Hardwood and a mix of Softwood/Hardwood	Not informed	50 w/w% - 70 w/w%	40 - 110 °C	Lignin removal by LignoBoost process and acidification with CO <sub>2</sub> .	Qualitative		Bohlin Instruments Rheometer CS50. The rheometer, equipped with a jacket, was connected to a heating bath through which the temperature was controlled (accuracy ±0.1°C).	N/A	150 s <sup>-1</sup>	The removal of lignin reduces the BL Viscosity, irrespective of the origin of the liquor and raw material. At dry contents above 40%, the viscosity could be reduced up to about 90%. LignoBoost

													process implies that potential improvements can be made in the chemical recovery process, especially in the evaporation plant. A decrease in viscosity should result in an increase in the heat transfer coefficient and a significant decrease in the heat transfer areas in new evaporators (i.e. decrease in investment cost). Also, a decrease in viscosity should result in an increase in capacity of existing evaporators.	
	<a href="#">Wallmo, 2015</a>	Pulp Mill	Sweden	Softwood	Reference Black liquor , 5.5 lignin removal black liquor, 21 lignin removal black liquor, 60 lignin removal black liquor	31.4 % 29.0 % 27.1 % 23.2%	120 °C	Removal of lignin by LignoBoost Process	Viscosity reduction of the black liquor samples with lignin removal at 50 % solids content relative to the reference black liquor; 5.5lignin removal : 20 % reduction; 21 % removal: 38 %reduction; 60 % lignin removal : 75 % reduction	The degree of reduction of lignin concentration in black liquor samples reduces BL viscosity	Not informed	Not informed	N/A	Reducing black liquor viscosity by removal of lignin varies according to the amount of lignin removed, black liquor sample with 60 % lignin removal showed a 75 % reduction in viscosity. After LignoBoost process the solids content of the black liquor samples varied between 23.2 - 31.4 % depending on the degree of lignin removal
	<a href="#">Chen, 2022</a>	Guizhou Chitianhua Company, Ltd.	China	non-wood	Bamboo	* 47.5 wt.% (mill) * 80 wt.% (tests)	98 °C	Removal of lignin by acidification with H <sub>2</sub> SO <sub>4</sub>	Qualitative	The strength of the network structure becomes weaker in low-lignin (70%) black liquor	Dynamic rheometer (AR2000ex, TA, American).	0.1 - 100 s <sup>-1</sup> and 0.1 - 100 rad.s <sup>-1</sup>	N/A	Reducing the viscosity of BL by lignin removal may allow to omit the passivation section in the alkali recovery or at least reduce the passivation times, leading to a reduction in the energy consumption in alkali recovery system.

	<a href="#">Machado, 2023</a>	Pulp Mill	Brazil	Hardwood	Diluted Eucalyptus (DBL), Acidified Eucalyptus (ABL), Lignin Lean (LLBL)	26 - 32.5%	25 - 80 °C	Lignin removal by acidification with CO <sub>2</sub> .	Qualitative	Removal of high molecular weight lignin in LLBL resulted in lower viscosity values as compared to DBL and ABL	Haake Mass III rheometer (Thermo Fisher Scientific; Waltham, MA, USA)	10 - 2000s-1	N/A	The removal of lignin with high molecular mass by precipitation with CO <sub>2</sub> reduces BL viscosity
<b>Temperature:</b>														
	<a href="#">Kobe &amp; McCormack, 1949</a>	Soundview Pulp Company, Washington.	USA	Softwood	Western hemlock	11.2% - 45.6% (tests)	0.2 - 96.8 °C	Increasing BL temperature	Up to 89%	N/I	Ostwald capillary viscometer	N/I	N/I	The reduction in the BL viscosity after increasing the temperature of the BL between 0.2 and 96.8°C was: *85% (at 11.2% and 15.0% solids content) *89% (at 25.6% solids content) *72% (at 45.6% solids content)
		St. Regis Kraft Company, Washington		Softwood	Western hemlock + Douglas fir	14.3% - 47.8% (tests)	0.3 - 97.2 °C		Up to 90%					The reduction in the BL viscosity after increasing the temperature of the BL between 0.3 and 97.2°C was: *87% (at 14.3% solids content) *88% (at 22.8% solids content) *90% (at 26.7% solids content) *48% (at 47.8% solids content)
		Everett Pulp and Paper Company, Washington		Hardwood + softwood	Cottonwood + hemlock	12.4% - 52.5% (tests)	0.3 - 96.1 °C		Up to 89%					The reduction in the BL viscosity after increasing the temperature of the BL between 0.3 and 96.1°C was: *85% (at 12.4% solids content) *86% (at 15.1% solids content) *89% (at 24.1% solids content) *46% (at 52.5% solids content)

<a href="#">Zaman &amp; Fricke, 1996</a>	Pilot-scale digester	USA	Softwood	Slash pine	50 - 85 wt.% (tests)	40 - 140°C		Viscosity of BLs decreased between 2 - 6 orders of magnitude in the temperature range of 40 - 120°C		<p><b>*For SC &gt; 50 wt.%:</b> Haake RV-12 rheometer (for temperature range: 40 ≤ T ≤ 90°C and % solids ≤ 65), and a custom-built pressure cell, concentric cylinder viscometer (for Temperature ≥ 100°C and % dry solids &lt; 75).</p> <p><b>*For SC &gt; 65 wt.%:</b> Instron capillary viscometer (Model 3211) at temperatures up to 120°C</p> <p><b>*For very low shear rates:</b> Rheometrics RMS-800 mechanical spectrometer with a parallel-plate setup at temperatures below 85°C</p>	<p><b>*For SC &gt; 50 wt.%:</b> up to 1000 s<sup>-1</sup></p> <p><b>*For SC &gt; 65 wt.%:</b> 10000 s<sup>-1</sup></p>	At high solids content, BL viscosity is a strong function of both temperature and dry solids content concentration. When temperature is fixed, there is at least 2-6 orders of magnitude change in viscosity as the solids content is increased from 55% to 80% solids	
<a href="#">Moosavifar, 2006</a>	N/I	Sweden	Softwood	Weak Black Liquor (WBL)	*14% (mill) *14% - 61.1% (tests)	30 - 90°C	Increasing BL temperature and lignin removal	Qualitative	N/I	Bohlin Instruments Rheometer CS50	N/A	180 s <sup>-1</sup>	The lignin precipitation process leads to precipitation of the high-molecular weight lignin fractions from BL, and as a result, the filtrate not only has a lower lignin content but also it has low-molecular weight lignin fractions. Lower lignin values were recorded when the temperature was increased.
				Low-lignin Black Liquor (LLBL)	*22.4% (lignin extraction plant) *49% (tests)	30 - 90°C		Qualitative	N/I		N/A	180 s <sup>-1</sup>	
				Mix of 25%LLBL/75%WBL	52% (tests)	30 - 90°C		Qualitative	N/I		N/A	180 s <sup>-1</sup>	
				Mix of 50%LLBL/50%WBL	52% (tests)	30 - 90°C		Qualitative	N/I		N/A	180 s <sup>-1</sup>	
<a href="#">Yang, 2007</a>	Bagasse Pulp Factory	China	non-wood	Bagasse	43 - 68%	45 - 70 °C	Increasing BL temperature	Qualitative	Not informed	Rheometric RFSII rheometer	0.1 - 1000 s <sup>-1</sup>	N/A	Power-law rheological model can be applied to fit the viscosity curves.
<a href="#">Moosavifar, 2009</a>	Swedish Pulp Mills	Sweden	Mix of Softwood/Hardwood	Mix of Softwood/Hardwood	39.1% - 67.3%	40 - 80 °C	Increasing BL and LLBL temperature	Qualitative	At high solids content, the polymer organics behave as the continuous phase in black liquor. Above the Tg temperature, the	Bohlin Instruments Rheometer CS50 with three different measurement systems were: a concentric cylinder, a double gap and a concentric high pressure cell.	N/A	150 s <sup>-1</sup>	A viscosity reduction should result in an increase in the heat transfer coefficient and a significant decrease in the
			Mix of Softwood/Hardwood	Mix of Softwood/Hardwood	66.3 w/w% - 73.3 w/w%	90 - 130 °C							
			Hardwood	Hardwood	around 50%	40 - 80 °C							

				Softwood, Harwood and Mix of Softwood/Hardwood	Softwood, Harwood and Mix of Softwood/Hardwood	~50% - ~60%	40 - 80 °C			non-covalent bonds between the polymer chains become weak, so the organic compounds become soft leading to a plastic deformation without fracturing, thus decreasing the viscosity.				heat transfer areas in new evaporators (i.e., decrease in investment cost). Another result due to viscosity reduction is an increase in capacity of existing evaporators. At dry solids content above 40%, the viscosity of BL could be reduced up to about 90%.
				Softwood and Mix of Softwood/Hardwood	Softwood and Mix of Softwood/Hardwood	Around 70%	90 - 136 °C							
<a href="#">Alabi, 2010</a>	Carter Holt Harvey Pulp and Paper Mill	New Zealand	Softwood	Pinus radiata	*52.21% (from the Mill) *15.25% - 44.12% (tests)	25 - 85 °C	Lignin degradation by increasing the BL temperature up to 190 °C in a pressurised autoclave (8 bars) during 8 h	83%	Temperatures above 100 °C in concentrated BL result in lignin degradation, which takes place due to its reaction with residual alkali and this leads to a permanent reduction in the BL viscosity. From the Research reports, the data shows that a temperature range of 180 – 190 °C and exposure time of about 15 min are the optimal conditions for this reaction.	Haake RV 20 rotational viscometer	up to 2000 s <sup>-1</sup>	N/I	After the heat treatment: Solids content of the BL decreased from 52.21% to 51.00% (~1% difference) and this difference is not considered significant enough for the significant drop in the viscosity of BL. Viscosity of the BL drop ~83% (from 818.6 to 140.5 mPa.s) which indicated that the large polymers such as lignin must have been broken down (depolymerised) during heat treatment. pH of the BL decreased from 13.47 to 11.29 which indicated that the alkali was consumed during the heat treatment.	
<a href="#">Costa, 2011</a>	Eucalyptus Pulp Mill	Portugal	Hardwood	Eucalyptus globulus	*13.3% (white liquor) *30% - 59.5% (test)	25 - 65 °C	Increasing BL temperature	Qualitative	Not informed	A Haake, model RS1 controlled stress rheometer	0 - 1200 s <sup>-1</sup>	N/A	Black liquors viscosity increases when the solids content is raised and/or the temperature is decreased, results that are in close agreement with those found by other authors.	

<a href="#">Alabi, 2012</a>	Carter Holt Harvey pulp and paper Mill	New Zealand	Softwood (92.5%) + Hardwood (7.5%)	Pinus radiata (softwood) and a mixture of eucalypt and poplar, in ratio 1:1 (hardwood)	*52.21% (raw BL) *47.91% (raw BL) *50.98% (raw BL) *69.80% (raw BL) *12% (test) *80% (test)	0 - 115 °C	Temperature change	Qualitative		A Thermo Scientific Haake Rotovisco RV 20 rotational viscometer (open-cup) and Contraves Rheomat® RM 115 rotational viscometer (open-cup).	10 - 2000 s <sup>-1</sup>	N/A	BL displayed with solid contents above 40% displayed Newtonian and non-Newtonian behaviour, which were dependent on the operating conditions
<a href="#">Singh, 2015</a>	Agro-Based Paper Mill	India	non-wood	Wheat straw	36% - 52%	60 - 100 °C	Increasing BL temperature	Qualitative	Cohesive forces theory: when there is an increase in temperature, there is a decrease in the cohesive forces between molecules, and as a result, the flow becomes freer. This effect causes viscosities of liquids to decrease as the temperature increases in liquids.	Physica MCR 100 rheometer (Anton Paar, Ostfildern, Germany) equipped with a coaxial cylinder.	10 - 1000 s <sup>-1</sup>	N/A	The viscosity of BL increased with an increase in dry solids concentration and decrease with an increase in temperature. On the other hand, the activation energy E <sub>a</sub> was found to increase with an increase in black liquor concentration. These rheological properties will be of great use in designing of chemical recovery systems for wheat straw black liquors.
<a href="#">Xu, 2015</a>	Paper Mill	China	non-wood	Wheat straw	54.68%	70 - 120 °C	Increasing BL temperature.	Qualitative	An increase in temperature increases the energy of the polymer, and as a result, the polymer molecules move much faster and this reduces intermolecular friction. Increasing the temperature shortens lignin and other long-chain carbohydrate molecules, thus weakening the strength of the network structure of BL.	Not informed	N/A	20 s <sup>-1</sup>	Sodium silicates (Na <sub>2</sub> O) <sub>x</sub> (SiO <sub>2</sub> ) <sub>y</sub> have a high melting point, which cause the consumption of a lot of energy when BL combustion occurs. At temperatures higher than 110 °C, gases compounds such as water and hydrogen sulfide, cause a decrease in BL viscosity.
<a href="#">Xu, 2016</a>	Chitianhua Pulp and Papermaking Company, Ltd	China	non-wood	Bamboo	63.10 - 77.38 wt%	50 - 80 °C	Increasing BL temperature	Qualitative	As the temperature increases, there is a drop in the bonding strength of polymers and therefore the molecular activity free space increases.	Rotational rheometer AR2000ex, 1000 μm; Samples were being run on a cone-plate geometry.	0.1 - 100 rad.s <sup>-1</sup>	N/A	Dynamic viscoelasticity of BL decreases with increasing the temperature. At 80 °C and above 12.59 rad.s <sup>-1</sup> , the viscous component of

													black liquor became dominant which means that black liquor had begun soften.	
	<a href="#">Zhang, 2016</a>	Pulping and Papermaking Research Center of Yunnan Province	China	non-wood	Rice Straw	20% - 60%	50 - 90°C	Increasing BL temperature	Qualitative	A temperature increases resulted in the smaller particles appearing to have higher kinetic energy. Overall, the result was that the viscosity of the filtrated BL at 90 °C approached that without the tiny suspended matter under the same conditions.	SNB-1 viscometer with 60 rd.min <sup>-1</sup> rotor speed.	N/A	60 rd.min <sup>-1</sup>	Viscosity of BL and filtered BL decreased with increasing the temperature from 50 to 90 °C. The viscosity turning point of both BL and filtered BL increased with the temperature, which is beneficial for Alkali recovery.
	<a href="#">Nassar, 2016</a>	Kous Pulp Mill, Quena Paper Industry Company	Egypt	non-wood	Thermally treated Bagasse BL and Thermally untreated Baggase BL	40 - 75 wt%	80 - 110 °C	Thermal treatment of BL	Qualitative	Bagasse BL heated to a temperature above cooking temperature for a specific time and this heat treatment depolymerizes high molecular weight lignin and polysaccharides		Not informed	N/A	Thermally untreated BL had higher viscosity values when compared to thermally treated BL. The significant decrease in BL viscosity after thermal treatment was due to the depolymerization of BL during the heat treatment process.
	<a href="#">Yue, 2017</a>	Chitianhua Pulp and Papermaking Company, Ltd	China	non-wood	Bamboo	70.19 - 79.87 wt%	70 - 98 °C	Thermal treatment by increasing BL temperature	Qualitative	The apparent viscosity was reduced by increasing the temperature.	AR2000ex rotational rheometer (TA Instruments, USA).	0.1 - 100 rad.s <sup>-1</sup>	N/A	A Temperature increase led to a reduction of the apparent viscosity due to macromolecules in BKBL moving faster from the increased kinetic energy.
	<a href="#">Singh, 2021</a>	Agro-Based Paper Mill	India	non-wood	Wheat straw	36 - 48 %	60 - 80 °C	Increasing BL temperature	Qualitative	An increase in temperature results in an increase in molecular mobility and decrease in inter-layer friction	Physica MCR 100 rheometer connected to a computer with Physica US 200 Software	10 - 1000 s <sup>-1</sup>	N/A	Viscosity reduced as the temperature increased for Wheat straw BL due to the increase in molecular mobility.
<b>Dry Solids:</b>														
	<a href="#">Kobe &amp; McCormack, 1949</a>	Soundview Pulp Company, Washington.	USA	Softwood	Western hemlock	11.2% - 45.6% (tests)	0.2 - 96.8 °C	Decreasing BL dry solids content	Up to 95%	N/I	Ostwald capillary viscometer	N/I	N/I	The reduction in the BL viscosity after decreasing the solids content of the BL from 45.6% to

													11.2% was: *42% (at 96.8 °C) *95% (at around 65.0 °C)	
		St. Regis Kraft Company, Washington		Softwood	Western hemlock + Douglas fir	14.3% - 47.8% (tests)	0.3 - 97.2 °C		Up to 94%				The reduction in the BL viscosity after decreasing the solids content of the BL from 47.8% to 14.3% was: *91% (at around 97.0 °C) *94% (at around 80.0 °C)	
		Everett Pulp and Paper Company, Washington		Hardwood + softwood	Cottonwood + hemlock	12.4% - 52.5% (tests)	0.3 - 96.1 °C		Up to 97%				The reduction in the BL viscosity after decreasing the solids content of the BL from 52.5% to 12.4% was: *95% (at around 96.0 °C) *97% (at around 80.0 °C)	
	<a href="#">Llamas, 2007</a>	National Factory of Cellulose	Spain	Hardwood	Eucalyptus	62-72.6%	Below 90 °C	Additives	Qualitative	Injection of additives like dimethylformamide	Haake VT500 viscometer with a coaxial cylinder sensor system consisting of an SV cup with an SV II rotor	0-550 s-1	N/A	Effect of additives in viscosity reduction is more effective in BL with higher solids concentration. There is also a larger reduction in viscosity at higher shear rates
	<a href="#">Moosavifar, 2009</a>	Several Pulp Mills	Sweden	Softwood, Hardwood and a mix of Softwood/Hardwood	Softwood BL; Softwood + Hardwood Mix	50 - 70 %	40 - 100 °C		Qualitative		Bohlin Instrument Rheometer CS50	N/A	150 S-1	BL samples with higher dry solids displayed higher viscosity.
	<a href="#">Leite, 2011</a>	Industry Mill Recovery Unit	Brazil	Hardwood	Eucalyptus	15 - 39%	20 °C		Qualitative		Brookefield LV viscometer with cylindrical spindles and an ultra-low adapter	0-60 rpm spindle rotation	N/A	BL with high solids content showed a significant decrease in viscosity when an increase in spindle rotation is applied
	<a href="#">Xu, 2016</a>	Chitianhua Pulp and Papermaking Company, Ltd	China	non-wood	Bamboo	63.10 - 77.38 wt%	50 - 80 °C	Decreasing BL dry solids content	Qualitative	At low solids content, the polymer network structure in black liquor becomes weaker leading to the reduction in viscosity.	AR2000ex rotational rheometer.	0.1 - 100 rad.s <sup>-1</sup>	N/A	The viscoelastic motion law of BL with high solids concentration (72.26 and 77.38 wt.%) was conforming with the Kelvin model, and for BL with a medium concentration, it followed the Maxwell model.

	<a href="#">Zhang, 2016</a>	Pulping and Papermaking Research Center of Yunnan Province	China	non-wood	Rice Straw	20% - 60%	50 - 90°C	Increasing BL temperature	Qualitative	A temperature increase resulted in the smaller particles appearing to have higher kinetic energy. Overall, the result was that the viscosity of the filtrated BL at 90 °C approached that without the tiny suspended matter under the same conditions.	SNB-1 viscometer with a 60 rd.min <sup>-1</sup> rotor speed.	N/A	60 rd.min <sup>-1</sup>	The apparent viscosity of the original BL and filtered BL with varying solids content decreased as the temperature was increased
	<a href="#">Xu, 2021</a>	Jining, Shadong Province	China	non-wood	Wheat straw	10 - 75%	90 °C	Silicon removal	Qualitative	Silicon removal in the soda pulping process. Centrifugation to remove suspended particles	SNB-1 viscometer	Not informed	N/A	Viscosity of black liquor a major factor in alkali recovery
<b>Shear rate:</b>														
	<a href="#">Cardoso, 2009</a>	Several Pulp Mills	Brazil	Hardwood + non-wood + softwood	Eucalyptus Grandis, Bambosa Vulgaris and Pinus Caribaea	40.5 - 51.5 %	29.5 - 69.5 °C	Increasing Shear rate	Qualitative		Rotational Cole-Parmer viscometer	0 - 250 s-1	N/A	Rheological properties of eucalyptus and bamboo BL are affected by chemical composition and as a result, the behavior of those BL's is different to that of pine BL in the industrial recovery boiler and evaporator. Bamboo BL has lower sulfur concentrations and higher silicon content when compared to eucalyptus and pine BL.
	<a href="#">Costa, 2011</a>	Pulp Mill	Portugal	Hardwood	Eucalyptus globus	30 - 59.5%	25 - 65 °C	Increasing Shear rate	Qualitative	N/I	A Haake model RS1 controlled stress rheometer with a connected thermo controller.	0 - 1200 s-1	N/A	BL displayed a complex shear dependent non-Newtonian behavior
	<a href="#">Alabi, 2012</a>	Kinleith Pulp Mill	New Zealand	Softwood and Hardwood Mix	92.5 % softwood + 7.5 % hardwood	12 - 80 %	0 - 115 °C	Increasing Shear rate			A Thermo Scientific Haake Rotovisco RV 20 rotational viscometer and Contraves Rheomat RM 115 rotational viscometer	10 - 2000 s-1	N/A	BL samples displayed non-Newtonian behavior at high solids content.
	<a href="#">Singh, 2015</a>	Agro-based Pulp Mill	India	non-wood	Wheat straw	36 - 52 %	60 - 100°C	Increasing Shear rate	Qualitative		Physica MCR 100 rheometer (Anton Paar, Ostfildern, Germany) equipped with a coaxial cylinder.	10 - 1000 s-1	N/A	The viscosity as a function of shear rate data followed a good fit to the Power Law
	<a href="#">Yue, 2017</a>	Chitianhua Pulp and Papermaking Company, Guizhou	China	non-wood	Bamboo	70.19 - 79.19%	70 - 98 °C	Increasing Shear rate	Qualitative		AR2000ex rotational rheometer (TA Instruments, USA).	0.1 - 100 rad.s-1	N/A	BKBL was a pseudoplastic displaying shear thinning phenomena

Table 15. Summary of Black Liquor Articles

	<a href="#">Chen, 2022</a>	Guizhou Chitianhua Company, Ltd.	China	non-wood	Bamboo	47.5 - 80 %	98 °C	Shear rate change	Qualitative			0.1 -100 s <sup>-1</sup>	N/A	Apparent viscosity decreased when the shear rate increased
	<a href="#">Machado, 2023</a>	Pulp Mill	Brazil	Hardwood	Diluted Eucalyptus (DBL), Acidified Eucalyptus (ABL), Lignin Lean (LLBL)	26 - 32.5%	25 - 80 °C	Variation in shear rate	Qualitative	Haake Mass III rheometer (Thermo Fisher Scientific; Waltham, MA, USA)		10 - 2000s <sup>-1</sup> and 10 - 250 s <sup>-1</sup>	N/A	Viscosity greatly affected by shear rate, lignin removal and temperature

## 5 Conclusions

The main objectives of this master's thesis were to study the rheology of black liquor and the parameters, which affect its viscosity. The foundation of this work was mainly on the existing body of knowledge in the field of black liquor rheology. Digital platforms such as Science Direct, physical sources such as the LUT Library were key in gathering scholarly work for this study and an interview with an expert in the field was very helpful in better understanding pulping processes and black liquor in general. This thesis work was accomplished by combining all the above-mentioned methods and the valuable insights from this study are summarised in this chapter.

The rheology of black liquor was determined to be complex and the behaviour of black liquor under different conditions was analysed from the literature presented in this thesis.

The influence of lignin on the viscosity of black liquor was determined to be such that, its extraction from black liquor, reduces the viscosity. Black liquor with no lignin removed had high viscosity values due to the strong network structure formed by the lignin molecules, which interferes with the flow of the liquid. Following the previous notion, the removal of lignin results in weakening of the strong network structure, which in turn causes a reduction in the viscosity in black liquor samples with any degree of lignin removal.

For the influence of temperature on black liquor viscosity, the relationship was such that when temperature increased, the black liquor viscosity decreased. This variation in viscosity from the rise in temperature was determined to be due to the increase in kinetic energy in the black liquor molecules. The increased molecular movement resulted in the reduction of the interactions between molecules thus lowering the viscosity of the black liquor.

In terms of dry solids content, their influence on black liquor viscosity was such that an increase in dry solids content, results in an increase in the viscosity. This effect was due to the presence of more solid particles in the black liquor, which increase the resistance to flow, and as a result, higher viscosities are obtained when the dry solids content is high.

The influence of shear rate on black liquor viscosity is such that, at low shear rates, high viscosity values are observed and an increase in the shear rate results in the decrease of viscosity. This effect was due to shear alignment, which rearranges the structure and entanglements in the black liquor molecules when shear rate increases thus reducing its viscosity.

In conclusion, finding the balance in the degree of lignin removal, temperature conditions, applied shear rate and dry solids content is important in obtaining the optimal viscosity of the black liquor, which in-turn ensures better efficiency of the industrial mill processes involving black liquor. The reduction of black liquor viscosity by altering any of the above stated parameters includes benefits such as an increase in the heat transfer coefficient, a significant decrease in the heat transfer areas in new evaporators and an increase in capacity of existing evaporators amongst other benefits. Future research on the subject of black liquor viscosity could focus on an experimental approach and/or on the other parameters, which were not discussed in the course of this thesis.

## References

- Adams, T., Frederick, J., Grace, T., Hupa, M., Lisa, K., Jones, A., & Tran, H. (1988). *Kraft Recovery Boilers*.
- Alabi, S. B., Williamson, C. J., Lee, J., & Lecturer, S. (2012). *Non-Newtonian behaviour of black liquors: a case study of the Carter Holt Harvey Kinleith mill liquor*. <https://doi.org/10.3316/informit.807045179064641>
- Alen, R., Rytkonen, S., & Paterson, M. (1994). *Thermogravimetric behavior of black liquors and their organic constituents*.
- Cardoso, M., de Oliveira, É. D., & Passos, M. L. (2009). Chemical composition and physical properties of black liquors and their effects on liquor recovery operation in Brazilian pulp mills. *Fuel*, 88(4), 756–763. <https://doi.org/10.1016/j.fuel.2008.10.016>
- Carreau, P., De Kee, D., & Chhabra, R. (2021). *Rheology of Polymeric Systems Chapter 2*.
- Chen, S., Xu, Y., Guo, K., & Yue, X. (2023a). Rheological properties and volumetric isothermal expansivity of bamboo kraft black liquor with high solids content and low lignin content. *Scientific Reports*, 13(1). <https://doi.org/10.1038/s41598-023-29350-0>
- Chen, S., Xu, Y., Guo, K., & Yue, X. (2023b). Rheological properties and volumetric isothermal expansivity of bamboo kraft black liquor with high solids content and low lignin content. *Scientific Reports*, 13(1). <https://doi.org/10.1038/s41598-023-29350-0>
- Clay, D. T. (2000). *EVAPORATION PRINCIPLES AND BLACK LIQUOR PROPERTIES*.
- Costa, H. F., Egas, A. P. V., Ferreira, A. G. M., & Lobo, L. Q. (2011a). Rheology of Eucalyptus globulus kraft black liquor. *Applied Rheology*, 21(4). <https://doi.org/10.3933/ApplRheol-21-42533>
- Costa, H. F., Egas, A. P. V., Ferreira, A. G. M., & Lobo, L. Q. (2011b). Rheology of Eucalyptus globulus kraft black liquor. *Applied Rheology*, 21(4). <https://doi.org/10.3933/ApplRheol-21-42533>
- Fricke, A. L., Crisalle, O. D., Anthony Dutka V R Basker Richard A Gibbs, contributors P., & Barbara Speck Santiago Tavares Abbas Zaman James Detamore Steve Beatty Cory Wisniewski Richard Clark Tracy Lambert, J. (1999). *FINAL REPORT-PHASES I, II, 11A, AND 111 Prepared by Under Cooperative Agreement DE-FCO2-93CH10564*.
- Holmberg, J. M., & Gustavsson, L. (2007). Biomass use in chemical and mechanical pulping with biomass-based energy supply. *Resources, Conservation and Recycling*, 52(2), 331–350. <https://doi.org/10.1016/J.RESCONREC.2007.05.002>
- International Energy Agency. (2023, April). <https://www.iea.org/countries/finland>.
- Järvinen, M., K. A., D. B. C. and M. P. (2015). *Vapor pressure and boiling point elevation of black liquor*. . 30(3), 411–416.

- Korpinen, R., Fardim, P., Hultholm, T., & Lonnberg, B. (2008). *Black liquor impregnation of Scots pine sawdust and chip screenings*. <https://www.researchgate.net/publication/230005495>
- Llamas, P., Dominguéz, T., Vargas, J. M., Llamas, J., Franco, J. M., & Llamas, A. (2007). A novel viscosity reducer for kraft process black liquors with a high dry solids content. *Chemical Engineering and Processing: Process Intensification*, 46(3), 193–197. <https://doi.org/10.1016/j.cep.2006.06.003>
- Machado, V., Cruz, V., Vicente, J., & Dangelo, H. (2023). Eucalyptus black liquor properties in a lignin extraction process: density, dry solids, viscosity, inorganic, and organic content. In *TAPPI JOURNAL* (Vol. 22, Issue 3).
- Moosavifar, A., Sedin, M., & Theliander, H. (2009). *Changes in viscosity and boiling point elevation of black liquor when a fraction of lignin is removed -consequences in the evaporation stage*.
- Moosavifar, A., Sedin, P., & Theilander, H. (2006). *Viscosity and boiling point elevation of black liquor: Consequences when lignin is extracted from the black liquor*. 180–187.
- Nassar, M. M., Hassan, K. M., Farrag, T. E., Abd Elrahman, S. A., & Mohamed, H. A. (2016). PHYSICAL PROPERTIES AND VISCOSITY CONTROL FOR STRONG BAGASSE BLACK LIQUOR BY SALT ADDITION. In *International Water Technology Journal, IWTJ* (Vol. 6, Issue 3).
- Osswald. (2015). *Polymer Rheology*.
- Sanders, C., Bakhtiyarov, S. I., & Siginer, D. (1998). *Rheological Characterization of High Percent Solids Kraft Black Liquor*. <https://doi.org/10.13140/RG.2.1.1121.4486>
- Santos Leite, B., Hallak D'angelo, J. V., Andreuccetti, M. T., & Hallak D'angelo, J. V. (2011). *CHARACTERIZATION OF EUCALYPTUS BLACK LIQUOR-SOLIDS AND SODIUM SULFATE CONTENT, DENSITY AND VISCOSITY-AIMING AT THE EVALUATION OF SCALE FORMATION*. <https://www.researchgate.net/publication/289426544>
- Singh, S. P., Bansal, M. C., Singh, S. P., Singh, A. M., & Dixit, A. K. (2015a). Rheological properties and statistical analysis of wheat straw soda black liquor. *Energy Sources, Part A: Recovery, Utilization and Environmental Effects*, 37(24), 2639–2646. <https://doi.org/10.1080/15567036.2011.636140>
- Singh, S. P., Bansal, M. C., Singh, S. P., Singh, A. M., & Dixit, A. K. (2015b). Rheological properties and statistical analysis of wheat straw soda black liquor. *Energy Sources, Part A: Recovery, Utilization and Environmental Effects*, 37(24), 2639–2646. <https://doi.org/10.1080/15567036.2011.636140>
- Singh, S. P., Jawaid, M., Yadav, B., & Sarmin, S. N. (2021). Effect of pH, temperature, and solids content on rheological properties of wheat straw black liquor. *Biomass Conversion and Biorefinery*. <https://doi.org/10.1007/s13399-021-01863-6>
- Sjostrom, E. (1993). *Wood Chemistry—Fundamentals and Applications* (Vol. 2). <https://doi.org/10.1007/978-1-4615-1021-0>
- [statistic\\_id960695\\_fuels-used-for-heat-generation-of-upm-kymmene-oj-in-2018-by-source](https://www.statistic.gov.fi/tat/fi/til/salatuo/2020/salatuo_2020_2021-11-02_tie_001_en.html#:~:text=In%202020%2C%20the%20production%20of%20electricity%20with%20renewable%20fuels%20amounted,with%20other%20wood-based%20fuels). (n.d.).
- Statistics Finland. (2021). [tat.fi/til/salatuo/2020/salatuo\\_2020\\_2021-11-02\\_tie\\_001\\_en.html#:~:text=In%202020%2C%20the%20production%20of%20electricity%20with%20renewable%20fuels%20amounted,with%20other%20wood-based%20fuels](https://www.statistic.gov.fi/tat/fi/til/salatuo/2020/salatuo_2020_2021-11-02_tie_001_en.html#:~:text=In%202020%2C%20the%20production%20of%20electricity%20with%20renewable%20fuels%20amounted,with%20other%20wood-based%20fuels)

- Vakkilainen, E. (2008). *Chemical Pulping Part 2, Recovery of Chemicals and Energy*. Published in cooperation with the Finnish Paper Engineers' Association and TAPPI.
- Vakkilainen, E. K. (2017a). Recovery Boiler. *Steam Generation from Biomass*, 237–259. <https://doi.org/10.1016/B978-0-12-804389-9.00011-3>
- Vakkilainen, E. K. (2017b). Recovery Boiler. In *Steam Generation from Biomass* (pp. 237–259). Elsevier. <https://doi.org/10.1016/b978-0-12-804389-9.00011-3>
- Vakkilainen, E., Suomen Paperi-insinöörien Yhdistys., & Technical Association of the Pulp and Paper Industry. (2000). *Forest products chemistry*. Published in cooperation with the Finnish Paper Engineers' Association and TAPPI.
- Wallmo, H., Andersson, U., Gourdon, M., & Wimby, M. (2015). Evaporation of lignin-lean black liquor. *Tappi*, 14(7), 441–450.
- Wiki Google Scholar. (2023, May 23). *Google Scholar*. [https://en.wikipedia.org/wiki/Google\\_Scholar](https://en.wikipedia.org/wiki/Google_Scholar)
- Wiki Science Direct. (2023, May 23). *Science Direct*.
- Wiki Scopus. (2023, May 23). *Scopus*. <https://en.wikipedia.org/wiki/Scopus>
- Wiki Web of Science. (2023, May 23). *Web of Science*. [https://en.wikipedia.org/wiki/Web\\_of\\_Science](https://en.wikipedia.org/wiki/Web_of_Science)
- World Energy Outlook 2022*. (n.d.). [www.iea.org/t&c/](http://www.iea.org/t&c/)
- Xu, H., Chen, K., Zhang, L., & Wu, Y. (2021). Synchronous silicon removal and viscosity reduction in the soda-oxygen pulping of wheat straw. *Cellulose*, 28(14), 9081–9089. <https://doi.org/10.1007/s10570-021-04078-0>
- Xu, Y., Sun, H., Li, X., Zhang, D., & Tian, Y. (2015). Method of Black Liquor Combustion to Remove Silicon from Wheat Straw Pulping. In *BioResources* (Vol. 10, Issue 2).
- Yue, X., Du, X., & Xu, Y. (2017). Black liquor rheology. In *BioResources* (Vol. 12, Issue 4).
- Zaman, A. A., & Fricke, A. L. (1995). Viscoelastic Properties of High Solids Softwood Kraft Black Liquors. In *Ind. Eng. Chem. Res* (Vol. 34). <https://pubs.acs.org/sharingguidelines>
- Zaman, A. A., & Fricke, A. L. (1996). *Effect of Pulping Conditions and Black Liquor Composition on Newtonian Viscosity of High Solids Kraft Black Liquors*. <https://pubs.acs.org/sharingguidelines>
- Zhang, L., & Chen, K. (2016). *Effects of pH and Suspended Matter on the Physico-Chemical Properties of Black Liquor from Alkali-Oxygen Pulping of Rice Straw*.