# Development and Implementation of an Online Kraft Black Liquor Viscosity Soft Sensor

A thesis submitted in fulfilment of the requirements
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# ABSTRACT

The recovery and recycling of the spent chemicals from the kraft pulping process are economically and environmentally essential in an integrated kraft pulp and paper mill. The recovery process can be optimised by firing high-solids black liquor in the recovery boiler. Unfortunately, due to a corresponding increase in the liquor viscosity, in many mills, black liquor is fired at reduced solids concentration to avoid possible rheological problems. Online measurement, monitoring and control of the liquor viscosity are deemed essential for the recovery boiler optimization. However, in most mills, including those in New Zealand, black liquor viscosity is not routinely measured.

Four batches of black liquors having solids concentrations ranging between 47 % and 70 % and different residual alkali (RA) contents were obtained from Carter Holt Harvey Pulp and Paper (CHHP&P), Kinleith mill, New Zealand. Weak black liquor samples were obtained by diluting the concentrated samples with deionised water. The viscosities of the samples at solids concentrations ranging from 0 to 70 % were measured using open-cup rotational viscometers at temperatures ranging from 0 to 115 $^{o}$C and shear rates between 10 and 2000 $s^{-1}$. The effect of post-pulping process, liquor heat treatment (LHT) on the liquors' viscosities was investigated in an autoclave at a temperature >=180 $^{o}$C for at least 15 mins.

The samples exhibit both Newtonian and non-Newtonian behaviours depending on temperature and solids concentration; the onsets of these behaviours are liquor-dependent. In conformity with the literature data, at high solids concentrations (> 50 %) and low temperatures, they exhibit shear-thinning behaviour with or without thixotropy but the shear-thinning/thixotropic characteristics disappear at high temperatures (>= 80 $^{o}$C). Generally, when the apparent viscosities of the liquors are <= ~1000 cP, the liquors show a Newtonian or a near-Newtonian behaviour. These findings demonstrate that New Zealand black liquors can be safely treated as Newtonian fluids under industrial conditions. Further observations show that at low solids concentrations (< 50 %), viscosity is fairly independent of the RA content; however at solids concentrations > 50 %, viscosity decreases with increasing RA content of the liquor. This shows that the RA content of black liquor can be manipulated to control the viscosity of high-solids black liquors. The LHT process had negligible effect on the low-solids liquor viscosity but led to a significant and permanent reduction of the high-solids liquor viscosity by a factor of at least 6. Therefore, the incorporation of a LHT process into an existing kraft recovery process can help to obtain the benefits of high-solids liquor firing without a concern for the attending rheological problems.

A variety of the existing and proposed viscosity models using the traditional regression modelling tools and an artificial neural network (ANN) paradigm were obtained under different constraints. Hitherto, the existing models rely on the traditional regression tools and they were mostly applicable to limited ranges of process conditions.

On the one hand, composition-dependent models were obtained as a direct function of solids concentration and temperature, or solids concentration, temperature and shear rate; the relationships between these variables and the liquor viscosity are straight forward. The ANN-based models developed in this work were found to be superior to the traditional models in terms of accuracy, generalization capability and their applicability to a wide range of process conditions. If the parameters of the resulting ANN models can be successfully correlated with the liquor composition, the models would be suitable for online application. Unfortunately, black liquor viscosity depends on its composition in a complex manner; the direct correlation of its model parameters with the liquor composition is not yet a straight forward issue.

On the other hand, for the first time in the Australasia, the limitations of the composition-dependent models were addressed using centrifugal pump performance parameters, which are easy to measure online. A variety of centrifugal pump-based models were developed based on the estimated data obtained via the Hydraulic Institute viscosity correction method. This is opposed to the traditional approaches, which depend largely on actual experimental data that could be difficult and expensive to obtain. The resulting age-independent centrifugal pump-based model was implemented online as a black liquor viscosity soft sensor at the number 5 recovery boiler at the CHHP&P, Kinleith mill, New Zealand where its performance was evaluated. The results confirm its ability to effectively account for variations in the liquor composition. Furthermore, it was able to give robust viscosity estimates in the presence of the changing pump’s operating point. Therefore, it is concluded that this study opens a new and an effective way for kraft black liquor viscosity sensor development.

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# Abbreviations*

| | |
|---|---|
| ANN | artificial neural network |
| BM | binomial model |
| CAPE | (department of) chemical and process engineering |
| CD | continuous digester |
| CHHP&P | Carter Holt Harvey pulp and paper |
| DCS | distributed control systems |
| LHT | liquor heat treatment |
| MIMO | multiple-input multiple-output |
| NMR | nuclear magnetic resonance |
| NSSC | neutral-sulphite semi chemical |
| PCA | principal component analysis |
| P&C | process and control |
| VSD | variable speed drive |
| 3D | three dimensional |

* The above list of abbreviations is by no means exhaustive. Common acronyms such as USA/US are not listed. Some abbreviations, which are also used as the names of variables, are not listed. Numerous symbols, variables and parameters used in various equations, tables and figures, are not listed here. Most of them are defined at the appropriate places in the thesis. Trade names such as MATLAB, the terms common to pulp and paper industry, e.g. TAPPI, common chemical formulas such as NaOH, are left as they are or explained at the points of their use in this thesis. Other acronyms and symbols which are used sparingly in the thesis are defined at the appropriate places in the thesis.

# 1.0 INTRODUCTION

## 1.1 KRAFT PULPING PROCESS

Chemical pulping can be divided into two categories: sulphate (kraft) and sulphite pulping. The kraft process, accounting for around 80% of world pulp production is the most common chemical pulping process ([EC] 2001; Hodges et al. 2006; Miikkulainen 2006). The term “kraft” is a German word that means “strong” (Chandra 2004) and it is used in connection with sulphate pulping because of the strong fibre produced by this process while the term “sulphate” is based on the fact that the make-up salt, sodium sulphate is added in the recovery cycle to compensate for any chemical losses. In the kraft pulping process, the fibres are liberated from the wood matrix when lignin is removed by dissolving wood chips in the cooking chemical solution, which contains active chemicals-sodium hydroxide and sodium sulphide, at high temperature in a digester. There are three main reasons why kraft pulping is favoured above other pulping techniques: it produces pulp with superior strength in comparison with pulp produced via the sulphite process, it can be used for all wood species and has efficient chemical recovery systems ([EC] 2001) via that over 90% of the pulping chemicals are regenerated while simultaneously producing steam and electricity for the mill. Sulphite pulping chemicals are difficult to regenerate while the energy consumption in mechanical pulping is very high ([EC] 2001; Walker 2006).

The product coming out from the digester contains both the fibres and the spent cooking liquor called black liquor. Black liquor contains a mixture of inorganic chemicals and a large amount of organic chemicals, chiefly lignin. Black liquor and the pulp are separated; the pulp is bleached and sold directly or processed further into paper while the black liquor that contains about 14-18% dry solids content/concentration is channelled to the steam and chemical recovery unit ([EC] 2001). Here, its high water content of ~ 85%, that makes it unsuitable for direct combustion in the recovery boiler, is removed via a series of evaporators/concentrators in order to obtain a liquor having solids concentration of over 60% (Gagnon et al. 1996).

## 1.2 ENERGY USE AND RECOVERY IN PULP AND PAPER INDUSTRY

Pulp and paper manufacturing is energy and capital intensive (Gagnon et al. 1996; Szladow et al. 2001; Maheshwari and Sahasrabudhe 2006; Walker 2006). Energy costs represent around 30% of the total manufacturing costs for a pulp and paper mill (Rodden 2003). In New Zealand, pulp and paper operations consume about 68% of the energy in the forestry and wood processing sector while it consumes over 60% of this sector's electricity and natural gas (Covec Limited 2006). For Canadian mills, energy represents between 15% and 25% of the total production cost (Grenbaum, 2005). The increase in energy and chemical costs in kraft pulping mills (Grenbaum 2005; Piccione 2005) has pushed mill managements towards the programmes that will lead to efficient use of energy and, optimal energy and chemical recovery schemes.

Black liquor as a fuel plays a significant role in energy production. Helynen and co-workers (cited in Miikkulainen 2006) reported that in Finnish energy production, energy from black liquor corresponds to 11% of the total heat and power generation and 46% of the energy generated from biofuels. In New Zealand, energy from black liquor represents 40% of total energy demand by the pulp and paper sector. For chemical pulping, the majority of energy used is thermal (over 85%), and this is supplied by black liquor and biomass (NZFRIL, 2003). At the Carter Holt Harvey Pulp and Paper Mill, Kinleith, New Zealand where energy cost represents 14% of the total cost of dried product, the energy derived from black liquor is around 60% while energy inputs from electricity and gas account for 27% ([EECA] 2005). Therefore, any procedure that is potentially capable of improving the recovery boiler operation where the pulping chemicals are regenerated, while simultaneously producing steam and energy for the entire mill should be given special consideration.

## 1.3 HIGH SOLIDS CONTENT BLACK LIQUORS AND THE VISCOSITY PROBLEM

The economic success of a kraft pulp mill depends significantly on the operation of its chemical recovery facilities. In a newly installed mill, recovery boiler is the single most expensive component, accounting for roughly 20% of the total installation cost. When combined with the power boiler, turbine generator, recausticising and evaporation plants, the installed cost is roughly 50% of the whole plant investment (Brewster 2007). It is then essential that maximum economic benefits must be realised from this unit. It has been reported that recovery boiler operations can be enhanced by firing black liquor at high solids concentrations (Fricke and Crisalle 1999; Porter et al. 2004) and therefore as shown in Figure 1.1, there has been an increasing trend in the solids concentrations of the black liquor being fired in the recovery boilers. The continual improvements in the design and operation of the evaporators/concentrators and the recovery boilers have favoured this trend (see Olausson et al. 1998). There are a number of operational and economic benefits accruable from firing black liquor in the recovery boiler at high solids concentrations. Such benefits include: improvement in thermal efficiency as shown in Figure 1.2, higher reduction efficiency, reduction in environmental emissions, increased liquor throughput, increased pulping capacity, improved bed stability and control (Brewster 2007; McCabe et al. 2007; Cloutier et al. 2010; Porter et al. 2010).

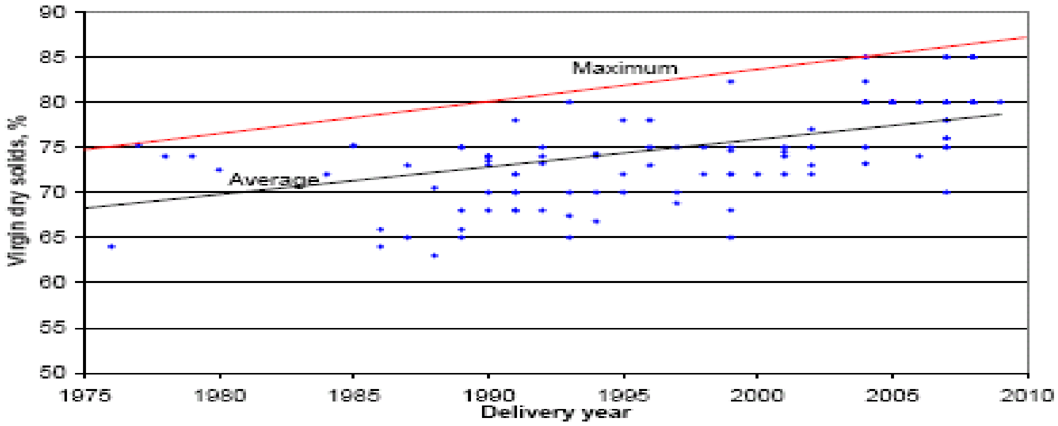


Figure 1.1 Black liquor solids concentration as a function of purchase year of the recovery boiler (Vakkilainen 2007)

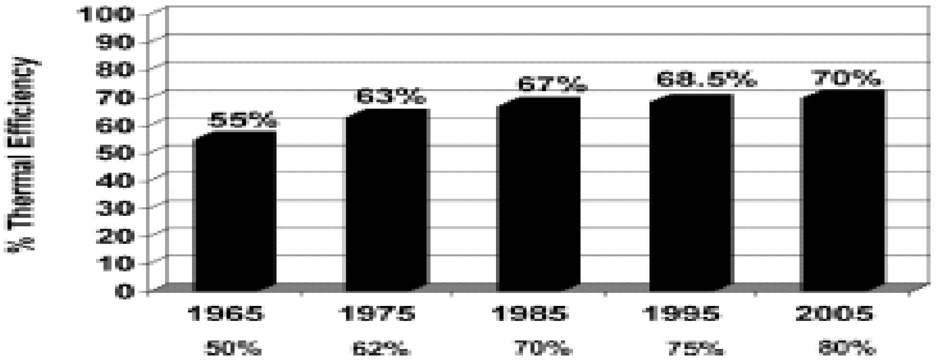
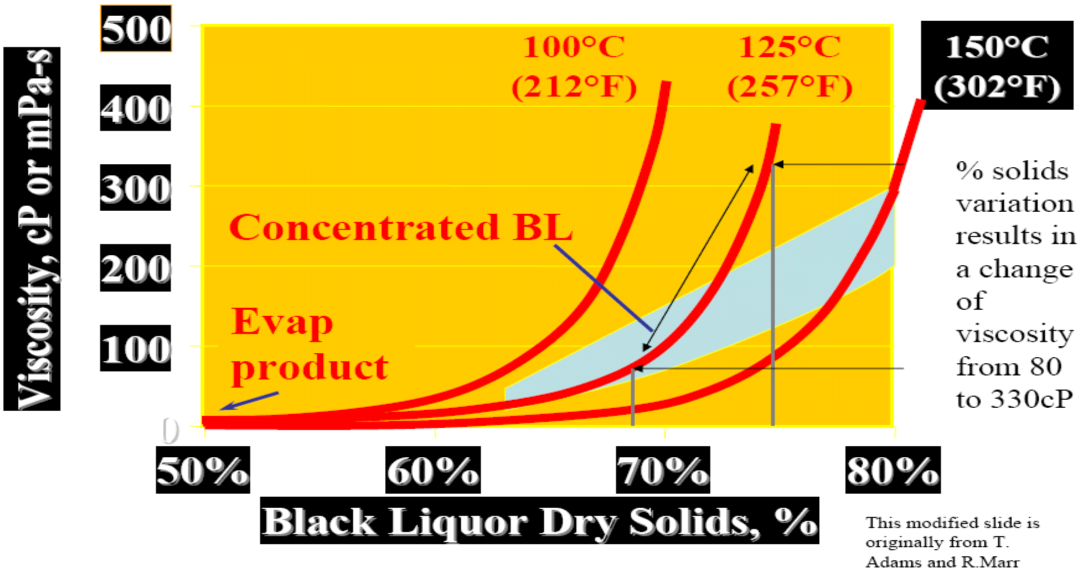


Figure 1.2 Recovery boiler efficiency as a function of black liquor solids concentration (Brewster 2007)

Although it is both economically and operationally beneficial to fire black liquor at high solids concentrations in the recovery boiler, the corresponding increase in viscosity of the liquor is the limiting factor (Olausson et al. 1998). Fricke stated that raising the solids content from 65% to 80% before combustion at a steam economy (kg of solvent evaporated per kg of steam used) of 4:1, the energy savings would be about $760 \times 10^9$ J/day for a typical 1000 ton/day mill (Zaman and Fricke 1994b). Porter et al (2010) reported that steam recovery worth \$680,000/year is possible in a recovery boiler supporting 1000 ton/day mill when solids concentration is increased from 73% to 76.5%. They stated further that improvement in the recovery boiler operation, which leads to a reduction of soot blowers by just one, would lead to \$1.8million/year savings in energy. However, at normal firing temperature, viscosity increases from 90 mPa.s at 73% solids concentration to 190 cP at 75.6% to 600 mPa.s at 80% solids concentration for black liquors taken from a typical north-western USA mill (Fricke and Crisalle 1999). Figure 1.3 shows that under a typical firing condition at 125 $^{o}$C, raising black liquor solids concentration from about 69% to 76%, viscosity increases from around 80 cP to 330 cP (roughly 31% increase in viscosity per 1% increase in solids concentration) for the mill discussed in the work of Porter et al (2010). The strong effect of solids concentration on black liquor viscosity at concentrations above 60% is also emphasized by Clay (2010).



% solids variation results in a change of viscosity from 80 to 330cP

This modified slide is originally from T. Adams and R.Marr

Figure 1.3 Effect of solids concentration and temperature on black liquor viscosity; Marr and Adams (cited in Porter et al. 2004 and modified in Porter et al. 2010)

Viscosity affects the heat transfer in the evaporation units, capacity of pumps and the spray characteristics of the liquor in the recovery boiler (Venkatesh and Nguyen 1992; Moosavifar et al. 2006; McCabe et al. 2007; Porter et al. 2010). Low viscosity can aid the formation of very fine liquor sprays and so be carried over into the super heater regions of the recovery boiler causing fouling and plugging problems. High viscosity can lead to the formation of very large liquor droplets that are too heavy to burn well in the recovery boiler. Consequently, the large droplets that fall into the char bed in the recovery boiler cause the bed to grow. This can lead to increased thermal activity (thermal excursions or temperature spiking) that causes tube cracking and corrosion (McCabe et al. 2007). Because of the rheological problems posed by high solids liquors, many mills operate the recovery boiler conservatively in the interest of safety (Basker et al. 2000). Many mill operations are limited to 72-75% solids, but a black liquor recovery stage can be optimised when the solids content is increased above 75% (Goncalves et al. 2004).

The traditional method of controlling the liquor spray is by manipulating the firing temperature of the liquor. This is usually done manually and by visual observation of the bed shape. In this way, viscosity is managed indirectly and hence liquor sprayed at high solids concentrations (Porter et al. 2010). Unfortunately, since viscosity is an exponential function of solids concentration (Zaman and Fricke 1994b), small variations in solids concentrations can cause large variations in viscosity even if the temperature is held constant and this makes temperature control schemes ineffective (Dutka, Basker et al. 2004). Also, black liquor viscosity depends in a complex manner on many factors. It is possible that at the same temperature and solids concentration, two liquors may differ in viscosity by a factor of at least 4 due to differences in their chemical composition. In fact many factors (including viscosity) reported by Porter et al (2010) that affect the spray characteristics directly affect the liquor viscosity. Therefore it becomes imperative that to be able to optimise the black liquor spray and combustion characteristics in the recovery boiler, adequate online measurement, monitoring and direct control of the liquor viscosity should be adopted.

Unfortunately in most mills black liquor viscosity is not measured (Barrall 1998; Porter et al. 2010). The viscosity of black liquor can be measured directly online by installing a concentric rotational cylinder viscometer but this will require very complex and expensive instrumentation (Chang et al. 1995). An attractive and more economical approach is to use a viscosity soft sensor (software-based sensor). The benefits of soft sensor application are enormous; for example, implementation of an online wood moisture soft sensor can lead to potential mill savings of $100,000/year with a payback period of less than 3 months ([CETC] 2005). It has a fast response time since the prediction of the required response variable will be made available as soon as the input values are obtained. This makes it possible to use the predictions from a soft sensor for real time process control. No additional instruments may be required as long as there are existing instruments to measure the relevant input variables online. In other words, it does not require capital expenditure since this can easily be implemented using the platform of a distributed control system (DCS) ([CETC] 2005) in any mill where there are existing online measuring instruments.

An important aspect of soft sensor application is the development of a predictive model that accurately and reliably describes the relationship between the input variables (variables that can easily be measured online) and the difficult-to-measure variable (e.g. black liquor viscosity in this study) as the response variable. For a homogenous Newtonian fluid, a viscosity model developed purely as a function of temperature may be very adequate for the online implementation. Conversely, for heterogeneous polymeric fluids such as black liquor that can sometimes exhibit non-Newtonian characteristics and whose rheological property varies from liquor to liquor and from time to time in the same mill, the development of models for predicting its viscosity has been a daunting task. Although the literature abounds with models that describe black liquor viscosity as a function of temperature and solids concentration, these models are liquor-dependent and as such useless for online application where black liquor viscosity varies from liquor to liquor due to changes in the liquor composition. In addition, many of these are polynomial models developed where the response variable has been logarithmically transformed and hence suffer loss of accuracy on the actual untransformed scale. Also, due to different rheological behaviours of black liquor over wide ranges of process conditions, it has been a difficult task to develop a single and accurate model that is capable of predicting viscosity over wide ranges of operating conditions. It is apparent that the existing liquor-dependent models may not be directly applicable to New Zealand black liquors. There is scanty viscosity data for the New Zealand black liquors in the open literature. The rheological property of New Zealand black liquors has not been systematically studied and no predictive model is available.

Very few attempts (see  Zaman and Fricke 1995a; Moosavifar et al. 2006) have been made to develop composition-independent black liquor viscosity models; unfortunately the developed models are limited to low solids concentrations that are not applicable in the usual range of process conditions for the real mill operations and their input variables may not be directly measurable online (and where possible may require the use of expensive online analyzers). Fricke and Zaman (1998) reported that at high solids concentrations, black liquor viscosity varies in a very complex manner with the black liquor solids composition but it was difficult to obtain any functional relationship between the viscosity and these factors. The development and online implementation of an accurate and reliable composition-independent black liquor viscosity soft sensor remains a technical challenge to the researchers in this field around the world.

## 1.4 MOTIVATIONS FOR THIS STUDY

- There are economic and operational incentives for firing high solids black liquors in the recovery boiler but the difficulty in being able to manage high viscosity at high solids concentrations has forced many mills to operate conservatively.
- In most mills, black liquor viscosity is not known. Yet, adequate online measurement, monitoring and control of black liquor viscosity are required to be able to optimize recovery boiler operations. A viscosity soft sensor is a preferred alternative to a hardware-based viscometer but it has not been widely adopted.
- Accurate and reliable predictive models are required for successful development and online application of the black liquor viscosity soft sensor; unfortunately, most of the existing models are not reliable because they are composition-dependent. The available composition-independent ones are limited to low solid concentrations, or their input variables will require the use of expensive online analysers or the predictive models suffer a loss of accuracy when utilised with unscaled data.
- In different parts of the world, most especially in the USA, Canada, Finland and Sweden, black liquor rheological properties have been widely studied. Conversely, New Zealand black liquor viscosity data are very scanty in the open literature and no

predictive model has been developed. From the earlier discussions, it is clear that the existing black liquor viscosity models, due to their sensitivities to liquor types, may not be directly applicable to New Zealand black liquors; therefore, a systematic rheological characterization of New Zealand black liquors and subsequent development of relevant predictive viscosity models are important.

## 1.5. OBJECTIVE AND TASKS, SIGNIFICANCE AND SCOPE OF THIS STUDY

### 1.5.1 Overall Objective and Tasks

The overall objective of this study was to develop and implement efficient, robust and reliable online kraft black liquor viscosity sensors at the numbers 4 and number 5 recovery boilers at the Carter Holt Harvey Pulp and Paper (CHHP&P), Kinleith mill, Tokoroa, New Zealand. In order to achieve this overall objective, the following tasks were defined:

- To experimentally investigate the effects of various process conditions/variables such as solids concentration, temperature, shear rate, LHT etc, on the black liquor viscosity.
- To develop predictive viscosity models using different regression modelling tools and artificial neural networks (ANNs).
- To identify the best predictive model(s) and implement them as online viscosity soft sensors at the number 4 and number 5 recovery boilers at CHHP&P Kinleith mill and characterize their performances.

### 1.5.2 Significance of the Study

The significant contributions of this study to knowledge are as follows:

- Through the systematic rheological characterization of New Zealand black liquors, there is now a viscosity database for New Zealand black liquors so that their rheological behaviour under different processing conditions are now better understood; this understanding can be used for the improvement in design and operation of kraft recovery systems including the evaporators/concentrators.

- The successful development and online implementation of the composition-independent, ANN-based, black liquor viscosity soft sensor that covers very wide operating conditions at the recovery boiler section of CHHP&P, New Zealand. Following a further improvement, predictions from the viscosity sensor can be successfully incorporated into an advanced viscosity-based control strategy. Consequently, the economic and operational incentives associated with high solids black liquor firing into the recovery boilers can now be realised without a serious concern for high viscosity.
- One major weakness that plagues many of the existing composition-dependent black liquor viscosity models is that they were built as polynomial regression models whose response variable has been logarithmically transformed; hence they tend to predict inaccurately on actual scale. The composition-dependent models developed in this study addressed this limitation. Also, all the existing black liquor viscosity models are applicable to only limited ranges of process conditions such as solids concentration, temperature and shear rate; this is due to different rheological characteristics manifested by black liquor as these conditions change; it has been a challenge to develop models that are capable of addressing these regimes jointly. For the first time in this study, using ANNs, predictive models that are able to describe the relationship between black liquor viscosity and its influential variables over wide discontinuous regimes were developed.

### 1.5.3 Scope of the Study

Although the effect of black liquor viscosity on the performance of the evaporators and the recovery boilers in any kraft recovery system is well established; the online implementation of the viscosity soft sensor developed in this study is limited to the recovery boiler section. The details of what goes on either in the evaporator or in the recovery boiler is not given prominence in this study, rather the main focus is on the rheological property of the liquor after leaving the evaporators/concentrators and before being fired in the recovery boiler. While the aim of this study was to develop universal black liquor viscosity soft sensor with potential applicability to other liquors around the world, this study has been limited to New Zealand black liquors. There are various post-pulping factors that can cause a significant permanent viscosity reduction in black liquors;

a very prominent one among them is the liquor heat treatment (LHT) approach. While it is possible to investigate various post-pulping operations that affect the black liquor viscosity, LHT was the only post-pulping experiment performed in this work. Finally, due to equipment limitation, the laboratory investigation of the factors affecting the viscosity of black liquors has been limited to solids concentrations up to around 70% and temperature s up to 115 °C under atmospheric pressure. However, centrifugal pump - based viscosity soft sensor was developed in this study using a reference black liquor pump curve, the Hydraulic Institute viscosity correction method and other methods. The sensor is capable of being used with flowing liquors of any solids concentrations and pumping temperatures within the practical pumping limit of about 500 cP.

## 1.6 THESIS OUTLINE

General introduction including discussions on kraft pulping, recovery boiler functions and viscosity problems associated with high solids black liquor firing, of this thesis is presented in this chapter. Readers who are not familiar with these topics may consult the following references for background study: (Adams 1997) and (Gullichsen and Fogelholm 1999).

Chapter 2 presents a detailed review of the existing online viscosity measurement methods for black liquors from different parts of the world including USA, Canada, Finland and Sweden. The strengths and weaknesses of these methods are highlighted. The main conclusion drawn from this review is that the use of a viscosity soft sensor is a preferred option to a hardware-based viscometer.

Chapters 3 and 4 are devoted to the evaluation of the factors influencing kraft black liquor viscosity. Chapter 3 is concerned with the extensive literature review of the factors influencing a variety of liquors around the world while chapter 4 reports in detail the results of the experimental investigations of the factors affecting the viscosity of black liquor samples obtained from a New Zealand kraft pulp and paper mill. The factors considered are solids concentration, temperature, shear rate and LHT as an example of post-pulping factor. Modified approaches for measuring black liquor viscosity at high temperatures in the open-cup rotational viscometer are discussed.

In chapters 5 and 6, the results obtained from chapter 4 and centrifugal pump performance data using black liquor reference pump curve and the Hydraulic Institute viscosity correction procedure are used to build relevant composition-dependent and composition-independent predictive models using multivariate statistical modelling tools and an artificial-neural-network paradigm based on MATLAB® software. Chapter 5 focuses on the model development based on the results obtained from the laboratory investigation of the factors affecting New Zealand black liquor viscosity while chapter 6 concentrates mainly on the utilisation of the centrifugal pump-based performance data obtained via Hydraulic Institute correction method for model development. The effect of pump ageing on the performance of centrifugal pump-based models is discussed.

Chapter 7 discusses the online implementation of the centrifugal pump-based black liquor viscosity sensor at the number 5 recovery boiler at the CHHP&P, Kinleith mill. An overview of the steam and chemical recovery process at the mill, with a particular reference to the recovery boiler is discussed. The results of monitoring, and evaluation of the performance of, the installed black liquor viscosity soft sensor are discussed. Finally, Chapter 8 summarizes the main conclusions drawn from this study and recommendations for future work are presented.

# 2.0 CONTEMPORARY APPROACHES FOR THE ONLINE KRAFT BLACK LIQUOR VISCOSITY MEASUREMENT

## 2.1 INTRODUCTION

What can not be measured can not be controlled. Having established the significant role played by the viscosity in the black liquor processing, it is essential that an effective way of measuring this variable online continuously should be devised before it can be adequately controlled for the subsequent optimization of kraft recovery systems. This chapter focuses on the review of the approaches that are possible for use in the pulp and paper industry to measure black liquor viscosity online. It also reviews the methods, which although not permanently installed at the industrial sites, have undergone either mill or pilot plant trials. The survey includes both hardware and software-based viscosity measurement methods. Finally, measurement methods that utilise pumps as a form of viscometer are examined. The strengths and limitations of the above-stated methods are highlighted. Different viscometers work on different established principles and so these principles are well known; see the following references for background study: (Steffe 1996; Fricke and Crisalle 1999; Leblanc et al. 1999; Bhattacharya 2002; Chhabra and Richardson 2008).

## 2.2. HARDWARE-BASED VISCOMETERS

### 2.2.1 Viscometers Installed and Operating in Mills

An extensive literature survey shows that the use of online viscometers for measuring black liquor viscosity in pulp and paper mills is very limited. An online viscometer was reported to be installed in 1983 and used for black liquor viscosity measurement in Monsteras Pulp mill, Sweden (Herngren et al. 1985; Ljungkvist 1988). Herngren and co-workers (1985) reported that the viscometer was reliable and there were improvements in the plant operation; however, the type of viscometer and how long it was used were not mentioned. Also, there was no information on the response time of this viscometer; yet this is very relevant for efficient online monitoring and control of black liquor viscosity being fired in a complex system such as a recovery boiler where the in-flight time of a 2mm droplet is less than 20 s under typical recovery boiler conditions (Hupa 2010). In addition, the black liquor solids contents reported in their work were all less than 70%; thus, it can not be established that the mentioned viscometer would not have maintenance problems if the black liquor solids concentrations are more than 70%. Apart from the above -mentioned viscometer, no further information was obtained directly from the open literature regarding the permanent online use of a viscometer for black liquor processing units in pulp and paper mills. Barrall (1998) noted, “There appears to be little or no use at present of rheometers or viscometers as process control devices for black liquor recovery. This conclusion is based upon discussions with industry and university experts”. In 1999, Fricke and Crisalle corroborated this assertion. They noted that despite the significance of viscosity in black liquor processing, black liquor viscosity is not routinely measured online in most pulp and paper mills. In addition to the reports of Barrall (1998) and, Fricke and Crisalle (1999), Porter et al (2010) emphasise the need to use viscosity of the liquor to determine the needed temperature of the liquor being fired in the recovery boiler, but stressed that in most mills black liquor viscosity is not known. Fricke and Crisalle (1999) suggested that online viscometers are not available for black liquor processing at the industrial mills because of the economic and technical barriers summarised below:

- Viscometer manufacturers are typically small companies that produce instruments mostly for laboratory use rather than online deployment and so they lack the necessary capital to invest in the cost of developing instruments for new markets. Further, these costs may not be recoverable if they were incurred by a single manufacturer should the market fail,
- The viscometer sensors are required to function in an environment characterised by high temperature, corrosive chemicals and in the presence of suspended solids that can cause fouling and plugging problems,
- Viscosity is temperature-sensitive and so the viscosity sensors require the delivery of very precise temperature control of the fluid and the instrument itself,
- Viscosity, being a transport property, requires that correct flow geometry and measurement conditions be carefully controlled.

Although it is clear that instrument manufacturers and pulp and paper industry would reap benefits from the availability of online viscometers, Fricke and Crisalle (1999) concluded that such technology development would not be possible without external financial support or subsidy. Motivated by these challenges and using the funding provided by the US Department of Energy, a team of researchers led by A.L. Fricke of the University of Florida, some viscometer manufacturers and three mills in the USA and Canada, developed several online viscometers for black liquor processing applications. They carried out pilot plant and mill trials to assess their performances. Detailed discussion on this is presented in section 2.2.2.

In order to find more information about the application of online viscometers to black liquor processing at the mills, Sofraser Instruments (France-based) and Marimex Industries Corp (Canada-based), that specialise in the manufacture of process viscometers for different industrial applications, were contacted via emails. Other relevant information regarding these process viscometers were obtained from other sources. The author's findings based on his communications with Virginie Pinto and Aurélie Isambert, the Sales Assistants at Sofraser Instruments, Dietmar Brand, the owner of Marimex Industries Corp and Mathias Gourdon (a researcher who has made use of Marimex process viscometer at a research evaporator plant at the Chalmers University of Technology, Sweden) are summarised below.

**Sofraser's online vibrating rod viscometer**

Sofraser's online vibrating-rod viscometers are commercially available and have been installed in some mills such as Tembec Tarascon in Canada (for several years0, Papeterie de Gascogne (last order February 2006) and Kruger in Canada (Pinto 2007). The active part of Sofraser's viscometers is a vibrating rod excited by a constant electrical power. The amplitude varies according to the viscosity of the fluid in that the rod is immersed. This sensor can work in most difficult conditions (Pinto 2007). There are different sensor options and where they can be installed in the process plant. Pinto (2007) claims that their process viscometers are highly reliable, rugged and free from maintenance. The Sofraser's Thermoset MIVI 8003, that can measure a large range of viscosities up to 10000 mPa.s, requires electric power and pressurised air up to 7 bars to work. The sensor in this case is not inserted in the main process line but in a by-pass line where the conditions of the measurements are controlled. The response time of the sensor is about 2 to 5mins (Sofraser 2007). For a 2mm black liquor droplet size in a typical recovery boiler conditions, the in-flight time of the droplet is less than 20s (Hupa 2010) and as such the instrument response time (2min) will not be adequate for an efficient operation of the recovery boiler. The instrument is very expensive; the cost (Pinto 2007) is in the range of 40,000-100,000EUR (about $NZ78000-$NZ194235). This will not be an economical choice for an old recovery boiler or in a recovery unit where online viscosity measurement will be required at different locations. Isambert (2010) claims that their standard MIVI viscosity sensor, that is designed to be inserted directly in the process line, has near zero response time. The estimated cost of a standard MIVI sensor plus other accessories and packaging (excluding shipping, installation and start-up etc) is given as 10196EUR (~$NZ19000) (Isambert 2010). Although Isambert (2010) and Pinto (2007) claim that Sofaser's process viscometers are free from maintenance and are not affected by vibrations from other plant machineries, there was no information from any third party (users) to confirm these assertions.

### Marimex viscoscope process viscometer

In using a Marimex viscoscope process viscometer, viscosity is obtained based on the torsional oscillation principle. The changes in frequency and damping decrement caused by the fluid, compared with those in a vacuum depend upon the density and the viscosity of the fluid and on the measurable property of the system. The power required for maintaining the small amplitude and constant shear rate at the resonant frequency of the sensor is a measure of the viscosity. The viscometer does not have moving parts and as such is maintenance free. The accuracy of the sensor is ±2% (Marimex 2009).

Marimex viscoscope process viscometers are available commercially and have been used in the recovery boilers in Europe since the 1990s. They have been sold in Finland, Sweden and to Zellstoff Blankenstein in Germany (Brand 2007). Brand (2010) claims that the viscometer is also being used by a company in Argentina; however, as at the time of communication, he was not too sure if the company's name is Cellulosa. For a black liquor being processed under typical mill conditions, the Marimex viscoscope VA-300L sensor, with necessary electronics and transmitter will cost US$15070 (~$NZ21000 ) free on board in Calgary, Canada. This cost does not include shipping to other parts of the world, installation, start-up etc. This seems to be relatively cheap. Brand (2010) claims further that the instrument has an instantaneous response although the processor takes about 1.5 sec for calculations. Therefore, it could be assumed that the response time is 1.5

sec. A reported downside of the viscometer is that its performance can be affected by plant vibrations. Although special procedures can be used to dampen the effect of plant vibrations, it is recommended that the sensor should be installed as far as possible from motors, agitators, pumps and other strongly vibrating machinery (Marimex 2004); this may restrict the sections of the recovery unit where the viscometer can easily be deployed. Plant vibrations have negligible effects at very high viscosity such as 10,000 mPa.s (Marimex 2004); unfortunately, this is outside the usual viscosity range for flowing black liquor under typical mill conditions.

The information on actual performance of the viscometer at the mills is not available. However, Marimex viscoscope VA-300L was used to measure black liquor viscosity online at a research pilot evaporator (not at the recovery boiler in a mill) at the Chalmers University of Technology, Sweden (see Johansson et al. 2006; Johansson et al. 2009; Gourdon et al. 2010). In email communications with Dr Gourdon (2010) as a third party user of the instrument; the author gathered the following relevant information about the cost and performance of the Marimex viscoscope VA-300L installed at their research evaporator:

- Despite the pilot evaporator plant not normally running for long periods as is common in the industry, there are fouling problems regarding the viscometer probe when operating in a region (solids concentration>50%) where crystallization takes place. Gourdon stated "when scales are formed on the probe the viscometer shows a rapid, almost stepwise increase in viscosity, from for example 10 mPas to 100 mPas. In this solids region I would recommend, if the viscometer is to be installed for constant online measurements that you include either manual or automatic flushing of the probe". This contradicts Marimex's claim that the sensor is maintenance free. It must be noted that black liquor being fired in the recovery boiler is in the range of 65% and above.
- The instruments' response time is almost instant; this agrees with Brand's assertion
- Gourdon stated "We have not seen any indications that it is affected by vibrations created by the circulation pump or any other equipment or activity". This seems to contradict the vibration issues raised in Marimex operator manual (Marimex 2004) regarding the installation of the sensor for online application. However, it might be that special precaution has been taken or that vibration at the pilot plant is not

significant to affect the sensor's performance or vibration problems were not simply noted.

- Their viscometer was purchased towards the end of 2004 from the Sweden-based retailer at an approximate cost (including installation, start-up etc) of 30 000 EUR.

### 2.2.2 Viscometers Used in Pilot Plant and Mill Trials

There were very few reports from late 1990s to date on application of an online black liquor viscometer. The available ones are based on the works of a team of researchers at the University of Florida USA and different viscometer manufacturers. They were tested both at the pilot plants at the University of Florida and different mills (not permanently installed at the recovery boiler or commercialized) in both Canada and USA for the purpose of measuring black liquor viscosity online. Nametre torsional oscillatory, Micro-motion capillary-coriolis and Brookfield cylindrical rotatory viscometers were recommended for industrial applications, but with special conditions attached to them (see Fricke and Crisalle 1999; Basker et al. 2000; Dutka et al. 2004). Their accuracies as compared with standard laboratory viscosity data range between ±10% and ±20%. All the liquors used for testing the performance of the viscometers at both the pilot plant and the mills have less than 80% solids concentrations; this can not be said to have represented the high solids black liquor adequately. Under super concentration conditions (black liquor solids content in the range of 80% and above) (Olausson et al. 1998), it is not clear what the performances of the viscometers will be. Each of the recommended viscometers is now discussed in detail.

#### (i) Nametre torsional oscillatory viscometer

Nametre torsional-oscillatory viscometer was tested at the pilot and industrial plants. It showed good promise; the viscometer was able to track laboratory data at high viscosities to within ±10% when the probe was free of fouling and was not affected by varying flow rates or by secondary phases (such as air) in the fluid. However, the downsides of the viscometer are:

- it has a response delay of about 2 minutes that is not satisfactory for recovery boiler operation where a typical 2mm black liquor droplet arrives at the char bed in less than 20s,

- it is susceptible to fouling starting from 50% (black liquor is fired in the recovery boiler at solids concentration >=60%) solids content for liquors with propensity for precipitation (Basker et al. 2000) and as such may require regular cleaning using steam,
- its performance can adversely be affected by other machinery (see Fricke and Crisalle 1999) at lower viscosities.

### (ii) Micro-motion capillary coriolis viscometer

Dutka et al (2004) specifically reported on the evaluation and performance of the Micro-motion capillary-coriolis viscometer as a candidate for online measurement of black liquor viscosity. Capillary viscometry is based on the Hagen-Poiseuille equation for incompressible Newtonian fluids in fully developed, steady-state, laminar flow conditions in a capillary. The studied viscometer uses a differential pressure cell to measure the pressure drop and the coriolis mass flow sensor to measure both the density and mass flow rate from that the viscosity can be computed. This instrument has a response time of around 30 s. Unless there is no better alternative, this may still be inadequate for recovery boiler operation. The viscometer has the following limitations:

(i) the range of solids concentrations tested was from 34% to 74% and there is no way to justify its suitability for use with liquors with higher solids concentrations,

(ii) Hagen-Poiseuille equation is developed for a straight capillary and fully developed flow but these two conditions do not strictly hold for coriolis sensor (Dutka et al. 2004),

(iii) although the viscosities measured with this instrument track laboratory data reasonably well to within ±10% under laminar condition, unfortunately, the flow condition in the black liquor processing units is not always laminar; the Reynolds number could be as high as 200000 (Adams and Frederick 1988).

### (iii) Brookfield cylindrical rotary viscometer

The performance of a Brookfield cylindrical rotary viscometer (Fricke and Crisalle 1999) was evaluated at the University of Florida pilot plant and Georgia Pacific Corporation (mill), Florida, USA. In the cylindrical rotary viscometer, the fluid whose viscosity is being measured is sheared in the annulus of two concentric cylinders. In the viscometer described in this section, the outer cylinder is rotated at a fixed angular velocity while the inner cylinder (stator) is held stationary by a torsion wire. The viscous drag on the stator induces a deflection of the torsion wire (Fricke and Crisalle 1999). One main assumption that is made in the mathematical analysis of the concentric cylinder system is that there is a steady state laminar flow; although Fricke and Crisalle (1999) assert that the flow through the instrument chamber need not be laminar since only a small portion of the flow enters through the measuring gap between the cylinders. However, the condition in the process line may be turbulent while the computations in the instrument are based on laminar assumption. The viscosity is calculated from the measured torque and the angular velocity. The results from the pilot plant trial of this viscometer show that it is potentially useful for online application: it tracks reliably within ±10% of the laboratory reference viscosity, the viscometer does not suffer fouling, and the instrument response time is around 45s. The downside of the instrument is that at higher flow rates (non-laminar conditions), the instrument readings tended to be lower than the laboratory reference for high viscosity black liquors due to axial flow effects. Also, the instruments' response time of 45 s is not satisfactory for the recovery boiler operation as discussed earlier except where there are no better alternatives. Unfortunately, due to different technical challenges such as instrument damage, pluggage of the side stream lines and some design and installation problems, several months of mill trials were unsuccessful and the mill management refused to continue this project. Consequently, the mill trial was inconclusive.

## 2.3SOFTWARE-BASED VISCOMETER OR VISCOSITY SOFT SENSOR

### 2.3.1 General Background to Soft Sensor Technology

Soft (software-based) sensing or inferential measurement is a technique whereby the control variable or the variable of interest is not measured directly but is inferred or calculated from secondary measurements (Radhakrishnan 2004). A soft sensor can also be defined as the correlation from various raw data sources to create a new source of useful information. It is an empirical model that infers process state and the product quality variables that are difficult to measure online from readily available process measurements (e.g. temperature, pressure, flow etc). Soft sensor technology offers a number of advantages over online, physical sensors and laboratory-based analysers. A major problem in all industries, including the pulp and paper industries, is the lack of real-time measurements of product and process characteristics. A soft sensor provides online, accurate estimates of these variables, eliminating additional energy and production cost associated with out-of-specification production. The infrequent process sample, that may not be representative of the process, is taken to the laboratory and depending on the reference standard being used, the final results may have a typical delay of 20 mins to 1 week ([CETC] 2005). This type of result will not be useful for online application and effective process control. In other words, because of poor control, the process will not be able to operate optimally. Physical analysers are expensive and are highly prone to breakdowns and require regular maintenance, hence an attractive alternative is the application of soft sensor (Radhakrishnan 2004). In summary, a soft sensor is reliable, amenable for online applications, and can give very accurate results if the models used are very accurate. Also, soft sensor technology is now available as a standard option in new distributed control systems (DCS) , or as an add-on option to existing systems ([CETC] 2005). As a result, there may not be any concern for any capital investment or significant implementation issues. Considering the limitations of the online black liquor viscometers discussed earlier, it is obvious that soft sensor technology will be an attractive alternative. While soft sensors have been applied in some other processing industries, including some units in pulp and paper mills (see Radhakrishnan 2004; [CETC] 2005), very limited success has been reported regarding its use for online black liquor viscosity measurements.

### 2.3.2 Nuclear Magnetic Resonance (NMR)-based Viscosity Soft Sensor

An attempt has been made to develop a black liquor viscometer (viscosity meter or sensor) using nuclear magnetic resonance (NMR) spectroscopic method. This is a non-invasive, non-destructive technique based on the interactions of matter with a static and radio-frequency pulsed magnetic field (Fricke and Crisalle 1999; [PNA] 2007). The fluid is passed through the sensor probe that contains a static magnetic field, and a pulsed radio-frequency field is applied, after that the radio-frequency signals re-emitted from the fluid are analysed to determine viscosity based on relevant correlations. Further details on NMR and its application can be found in (Barrall 1995; Draheim and Ragauskas 1997; Barrall 1998).

The potential advantage of an NMR-based viscometer is that there are no moving parts and as such, maintenance is not an issue. In addition, it is not an optical method like near infrared spectroscopy, which requires regular cleaning of the sample cells due to fouling when used with black liquor of high solids concentration. The Southwest Research Institute, USA and various subcontractors, in a cooperative agreement with the USA Department of Energy, have developed and tested an advanced NMR sensor for several industrial applications. In conjunction with Quantum Magnetics, USA, and the team of researchers at the University of Florida, the potential application of the NMR sensor as a black liquor viscosity sensor was tested on different black liquors at the University of Florida (De Los Santos 1997). The results show that a correlation relating relaxation times to black liquor viscosity can be developed for a liquor of constant composition but the condition of constant composition is rare in real mill operations and as such may not be applicable to black liquor under industrial conditions. In comparison with the viscometers discussed earlier, it was concluded that, in light of performance and cost, the NMR-based sensor can not compete effectively for online use in a black liquor recovery system. Unlike the earlier hardware-based viscometers, that were temporarily installed at different industrial sites for mill trials, the NMR sensor was not evaluated beyond what was done at the experimental unit at the University of Florida.

### 2.3.3 Pump-based Viscosity Sensors

#### 2.3.3.1 Indirect pump-based viscosity sensor

A method for measuring black liquor viscosity indirectly online was developed and implemented at Irvin Pulp and Paper Ltd, Canada (McCabe et al. 2007). The procedure was based around the use of the pump current of the recirculating, strong black liquor pump as a measure of viscosity. A new ammeter and current controller were installed and cascaded to the existing temperature controller connected to the black liquor heater. The philosophy here is that the changes in pump current would indicate the changes in black liquor viscosity brought on by changes in solids content, residual alkali, and/or wood species at pumping temperature. Thus, by controlling the pump current (indication of viscosity level) to a desired set point by manipulating the temperature, will keep the recovery boiler operation stable. The report shows that the approach worked effectively as the recovery boiler operators at this mill were able to fire black liquors having solids concentrations up to 76% in the recovery boiler without any problem. However, prior to the use of the pump viscometer and the viscosity index control, the operators were forced to reduce the black liquor solids concentrations to around 70% to avoid fouling, plugging and tube temperature excursions. This was a big economic loss to the company.

The advantages of this approach are:

(i) There was no need to install any hardware-based viscometer, as the pump current from the existing recirculation pump became a measure of viscosity. There was no concern for special capital investment or space issue regarding where to install new analyser,

(ii) Because the current (pump's amperage) readings depend on the overall liquor properties, this approach is robust to changes in liquor type or composition that have a significant effect on black liquor viscosity.

Although this approach improves the recovery boiler operation at this mill, its downsides are that:

(i) Viscosity was not measured directly. The amperage (current) values can not be used for any further computations where the actual value of the viscosity is required e.g. if actual droplet size control is required, a form of correlation will be useful. In some existing black liquor droplet size correlations, dynamic or kinematic viscosity is one of the input variables and its actual value will be required,

(ii) There is no clear indication that the mechanical status of this pump is taken into consideration. As the pump ages, its efficiency deteriorates due to mechanical wear and tear and as such more power(current in this case) will be required to deliver the same flow even when other parameters, including the liquor viscosity, remain the same. It implies that the liquor viscosity (in form of the current) will be over predicted and wrong control action will be taken.

#### 2.3.3.2. Direct pump-based viscosity sensor

An unknown mill duplicated the approach in section 2.3.3.1 with a slight difference (Porter et al. 2010). The basic difference between the indirect pump-based viscosity sensor discussed earlier and the direct pump-based viscosity sensor in this section is that online viscometer readings were compared with pump current for a recirculating strong black liquor tank pump over 1 month trial. Based on the current readings and the actual viscosity, a calculation (model not published) was found; making it possible for the operators to have actual viscosity values for the recovery boiler operation and control rather than pump's current readings as in section 2.3.3.1.

In addition to the two advantages discussed in section 2.3.3.1, the availability of actual viscosity readings is a plus for this method, as this would make further computations, where the actual value of viscosity is required, possible.

In addition to the second weakness associated with the indirect pump-based viscosity sensor, the other downsides of this approach are:

(i) Although there was no need for significant capital expenditure, since pumps are already available as part of the existing plant, the experimental stage of the sensor development requires capital expenditure for the purchase of an online viscometer; however the availability of the hardware-based viscometer may be important for regular checking of the performance of the viscosity soft sensor in the long term,

(ii) It is not clear if the viscosity readings obtained from the viscometer for a month trial represents adequately all possible values of black liquor viscosity that can be encountered under processing conditions in this mill. If this is not the case, the empirical model or equation developed for predicting viscosity will fail when the liquor has a viscosity value outside the original population data used to build the model.

## 2.4 CONCLUSIONS

The currently available methods for the online measurements of the black liquor viscosity have been reviewed. Generally, very limited viscosity sensors have been applied online for the black liquor viscosity measurement at the recovery boilers. Although some viscometers have undergone pilot plant and mill trials, there is no report that they are commercialised or permanently installed at the mills. Two main forms of viscosity sensors working on diverse principles are identified. The hardware-based viscometers are mainly based on fundamental principles and any violation of these principles generally affects their performance. The main issues with the hardware-based viscometers are their cost, maintenance and their slow response time. A soft sensing approach was found to be an attractive alternative due to both economic and technical reasons. They do not require significant capital expenditures but they require good predictive models or correlations. Although an NMR analyser was considered as a potential online black liquor viscometer, it is not recommended for economic reasons; also, it is not robust to changes in the liquor chemical composition. The innovative idea of using the recirculation pump (at the recovery boiler) parameters to develop a viscosity sensor is the most economical method among all the reviewed techniques. It is very robust to variations in liquor composition, and there is no need to purchase a new pump for this purpose since pumps are normally part of a black liquor process system. However, currently, the effect of pump ageing is not taken into consideration, the viscosity data collection method using an online viscometer is an expensive approach in the short term and the model utilised is unknown.

At the Carter Holt Harvey Pulp and Paper (CHHP&P), Tokoroa, New Zealand, viscosity of black liquor being fired into the recovery boiler is currently neither being measured online nor controlled directly. In this study, an attempt was made to develop a generalized, pump-based, black liquor viscosity sensor while taking into consideration the limitations identified above. Details of the approach are discussed in Chapter 6 and its online implementation at the number 5 recovery boiler at the CHHP&P is fully discussed in Chapter 7.

# 3.0 FACTORS AFFECTING KRAFT BLACK LIQUOR VISCOSITY: A REVIEW

## 3.1 INTRODUCTION

Having established in Chapter 2 that using a soft sensor for the online prediction of black liquor viscosity is a preferred choice due to technical and economic reasons, it is essential to build accurate and reliable models to be implemented for this purpose. However the knowledge of the factors that influence black liquor viscosity is required before useful models can be developed. Therefore in this chapter, firstly, the nature of black liquor is discussed. This is followed by a detailed literature review of the factors that influence the rheological behaviour of black liquors obtained from diverse sources. For background study, the suggested references in chapters 1 and 2 are equally relevant to this Chapter.

## 3.2 THE NATURE OF BLACK LIQUOR

Black liquor is a complex mixture of water, inorganic salts and organic matter. The dissolved organic matter in black liquor consists of alkali lignin and the sodium salts of the polysaccharinic acids, resin acids, and fatty acids. The inorganic portion of the liquor consists of the inorganic salts and also the sodium salts of wood acids. The chemical composition of black liquor and the nature of the dissolved organic matter from wood determine its physical and transport properties (Frederick 1997). Black liquor is considered as a polymeric solution since the polymeric lignin composes more than 50% of the organic constituents in black liquor (Zaman and Fricke 1995b). Its solids are composed of about one-third of the spent inorganic cooking chemicals and two-thirds of the organic chemicals extracted from the wood (Boniface 1992; Clay 2010). The relative amount of the components in black liquor and their properties (including the rheological properties) are influenced by the process operating conditions (Frederick 1997). The most important rheological property of black liquor is its viscosity. It is not only dependent on temperature, solids concentration, and shear rate (at high solids concentrations and lower temperatures) but varies from liquor to liquor due to variations in the liquor chemical composition (Nikkanen 1993; Zaman and Fricke 1995b; Zaman and Fricke 1996; Vakkilainen et al. 1999; Torniainen 2007; Cardoso et al. 2009). The composition of black liquor in turn is affected by many factors including types of wood pulped, pulping conditions, post-pulping conditions or processes such as oxidation and liquor heat treatment (LHT), chemical additives, high intensity shearing, and a host of others.

Some of the above-mentioned factors produce reversible changes while some lead to permanent changes in the liquor viscosity. Due to the complex way in that black liquor viscosity depends on many factors, it is essential that, for any kraft mill, the factors that influence its black liquor rheological characteristics must be systematically investigated for improvement in the design and operation of the mill equipment. Generally, the factors affecting the black liquor viscosity can be grouped into four main classes: temperature, solids concentration, shear rate and composition. These factors are discussed in detail in section 3.3.

## 3.3 INFLUENTIAL FACTORS

### 3.3.1 Solids Content and Temperature

The effects of temperature and solids content/concentration on the black liquor viscosity have been well researched and understood. As a result of this, most black liquor viscosity models are developed mainly as functions of solids concentration and temperature. Unfortunately these models are inadequate for real mill applications where liquor viscosity varies with factors other than solids concentration and temperature; therefore large deviations in their predictions are possible (Holmlund and Parviainen 1999). Literature abounds with studies on the effects of solids concentration and temperature on black liquor viscosities from a wide range of sources (pulping type, mode and conditions, and wood types) from different parts of the world such as North America, Australia, Sweden, Finland and a host of others. The viscosity of black liquor is a strong function of solids concentration and temperature. As is common to many liquids, black liquor viscosity decreases as the temperature increases; conversely, the liquor viscosity increases as the solids concentration increases (Vakkilainen 1999), as long as other influencing factors remain fairly constant.

At lower solids concentrations (typically below 50%), the viscosity of black liquor is relatively low (Venkatesh and Nguyen 1992); however at solids concentrations>=60% for as-fired liquor, viscosity is a very strong and exponential function of solids concentration (Sandquist 1981; Venkatesh and Nguyen 1992; Gagnon et al. 1996; Smith et al. 1998;

Clay 2010). Conversely, the results of the work of Scott-Young and Cukier (cited in Vakkilainen 1999) show that, at any fixed solids concentration, viscosity is a strong exponential decay function of temperature at temperatures <=100 $^{o}$C and the degree of exponential dependence on temperature increases with increasing solids concentration. As the temperature increases beyond 100 $^{o}$C (typical firing conditions), the viscosity becomes a weak function of temperature. It seems that because of the strong opposing effects of the solids concentration and temperature on the black liquor viscosity, the main tool that has been used to indirectly control viscosity of the high-solids black liquors until now is temperature. Unfortunately, this method has been found to be ineffective because there are factors other than temperature and solids concentration that are responsible for changes in the viscosity of black liquor (McCabe et al. 2007; Porter et al. 2010). There is also a limit to that temperature can be used to manipulate the viscosity of black liquor since, if the temperature is raised significantly above the atmospheric boiling point of the black liquor, this evaporation of water from the liquor may occur before it reaches the nozzle guns thereby leading to two-phase flow. This phenomenon is termed “flashing” and is known to lead to reduced velocity of the liquor being sprayed at the recovery boiler guns resulting in significantly smaller (than non flashing conditions) droplets that can cause boiler fouling and plugging problems (Roxare 2007). Extensive study on black liquor spray formation under flashing conditions has been reported by Mikkulainen (2006).

### 3.3.2 Shear Rate and Duration of Shearing

Many polymeric fluids exhibit complex rheological behaviours (Bhattacharya 2002; Chhabra and Richardson 2008). black liquor is regarded as a polymeric fluid since it contains high proportion of polymeric lignin and other high molecular weight organic constituents (Hermans 1984).

Black liquor viscosity is dependent on shear rate under certain conditions. Generally, black liquor at low solids concentrations behave as Newtonian fluids (Venkatesh and Nguyen 1992; Ghosh 1993; Llamas et al. 2007). However, most liquors whose rheological behaviours at low solids concentrations, reported in the literature, were tested at temperatures>=25 $^{o}$C. The behaviour of these liquors at lower temperatures needs to be understood, for example, in countries like New Zealand where sometimes temperature can be sub-zero during winter. It is expedient to know if these weak liquors can be pumped and stored under ordinary conditions without causing any rheological problems or require additional heating to keep the liquor thin during storage. Concentrated black liquor is typically not a Newtonian fluid (Vakkilainen 1999). At high solids concentrations (>50%), black liquor exhibits both Newtonian and non-Newtonian characteristics depending on the temperature, shear rate and the liquor composition (Zaman and Fricke 1991). The typical non-Newtonian behaviours exhibited by the black liquor are shear-thinning and sometimes thixotropic behaviours (Soderhjelm 1988; Venkatesh and Nguyen 1992). Softwood liquors have been reported to exhibit shear-thinning behaviour only (Zaman and Fricke 1995b) while hardwood liquors show thixotropic behaviour (Soderhjelm 1988; Frederick 1997) in addition. However, at mill conditions (typically high temperatures), the viscosity of black liquor is low enough that there are no concerns for the manifestation of both shear-thinning and thixotropic behaviours (Adams and Frederick 1988; Ghosh 1993; Zaman and Fricke 1995b; Frederick 1997). The onset of non-Newtonian behaviour at solids concentration< 50% is possible and varies from liquor to liquor but also depends on temperature and shear rate. Adams and Frederick reported that, for most flowing liquors under practical ranges (Table 3.1) of process conditions, black liquor shows only Newtonian behaviour unless the viscosity itself is greater than about 1000 cP. Thixotropic behaviour is typically associated with thick liquors that have significantly higher viscosity values compared with those typical liquors at the same temperature and solids concentration (Adams and Frederick 1988). This seems to have nothing to do with the type of wood pulped or the pulping process conditions. On the other hand, Soderhjelm (1988) shows that at solids concentrations of 65% and 70%, temperature of 110 $^{o}$C and shear rate 98.4 s$^{-1}$, liquors from pulping birch (hardwood) exhibit both strong shear-thinning and thixotropic behaviours at viscosities as low as 100 cP while liquors from softwood pulping, having viscosities as high as 400 cP, show purely Newtonian behaviour. This indicates that hardwood black liquors can show shear-thinning with or without thixotropic characteristics under real mill conditions, even at low viscosities.

Table 3.1 Typical Characteristics of flowing black liquor (BL)
(Adams and Frederick 1988)

| Parameter | Range |
|---|---|
| Pipe diameter(m) | 0.075-0.15 |
| Flow velocity(m/s) | 1-3 |
| BL density(kg/m$^3$) | 1000-1400 |
| BL viscosity(mPa.s) | 1-250 |
| Reynolds number | 300-200000 |
| Shear rate(s$^{-1}$) | 30-4000 |

Tiu et al(1993) studied the viscosity response of a black liquor consisting of a mixture of 47% pine (softwood) kraft and 44% eucalypt (hardwood) kraft and 9% neutral sulphite semi-chemical process(NSSC) liquor over 15-95 $^{o}$C and shear rates between ~10$^{-3}$ and 10$^{3}$ s$^{-1}$ at solids concentrations of 47, 65 and 75%. They found that at 47% solids concentration and low shear rates; the liquor exhibits shear-thinning behaviour even when the actual viscosity is less than 1000 cP. However, the liquors show negligible shear-thinning behaviour when actual viscosity is <=100 cP. The dependence of the liquor viscosity on shear rate is relatively weak even when the actual viscosity is up to 1000 cP at solids concentration=66%. At solids concentration=75%, temperature= 55-95 $^{o}$C, and shear rate ranging from 0.1 to 100 s$^{-1}$, the degree of shear-thinning reported appears ambiguous as shear-thinning behaviour was stronger at higher temperatures(lower viscosities) than at lower temperatures (higher viscosities); this raises a question as to whether there was a problem with the equipment used for these measurements. Generally, for all the results presented, it seems that at all temperatures, and shear rates from around 10$^{-1}$ to 10$^{3}$ s$^{-1}$, the viscosities of the liquors are relatively independent of, or weakly dependent on, shear rate; however, they did not investigate the effect of shear rate on viscosity at higher shear rates. All the results appear to be settling to a constant value as the shear rate approaches 1000 s$^{-1}$ ruling out the possibility of another rheological behaviour beyond this point. Despite the contradictions noticed in Tiu's work, one interesting finding from the work is that, in the regions where they claim that the black liquor viscosity depends on shear rate, the dependence is not uniform across all shear rates or temperature or solids concentrations investigated, which means the viscosity dependence of black liquor on shear rate is a non-linear relationship. Zaman and Fricke(1995b) found a similar relationship for softwood kraft black liquor.

Zaman and Fricke (1995b) carried out extensive rheological tests on black liquors obtained from pulping slash pine in a pilot digester under controlled pulping conditions. The controlled pulping conditions were for liquors at solids concentrations from around 50-84% and shear rate up to 10,000 $s^{-1}$ and temperature up to 140 $^{o}$C using a variety of viscometers. Important results from their work are:

- At lower temperatures and high solids concentrations, the liquors exhibit shear-thinning behaviour. The onsets depend on solids concentration, temperature, shear rate and liquor type,
- The shear-thinning behaviour diminishes or disappears as the temperature is increased or the solids concentration is reduced; at lower solids concentrations and higher temperatures, the liquors exhibit typically Newtonian behaviour,
- A common observation for all the liquors is that, irrespective of the solids concentration or temperature or shear rate, when the actual viscosity is around 1000 cP or less, the liquor behaves as a Newtonian fluid,
- The degree of dependence of the black liquor viscosity on shear rate over the regions where the liquor shows shear-thinning characteristics, are not uniform and vary over different shear rate ranges, solids concentration, temperature and from liquor to liquor.

The study of black liquors from eucalyptus (hardwood) from a Brazilian pulp and paper mill shows that at shear rates <=40 $s^{-1}$, T=30 $^{o}$C and solids concentration= 47.6%, the liquor exhibits weak shear-thinning behaviour (Goncalves et al. 2004) at viscosity values (<100 cP) far less than 1000 cP. Although, the shear-thinning behaviour is weak under the conditions investigated, the observed trends shows that, at much higher shear rates (and possibly lower viscosities than 100 cP), the liquor may exhibit stronger shear-thinning behaviour. They concluded that, transition from Newtonian to pseudoplastic behaviour occurs at lower solids concentrations (40.5-47.6%) for eucalyptus than for pine liquors (at solids concentration>50%). The range of viscosities at which shear-thinning behaviour is manifested for the eucalyptus liquor in their work is far less than the reported range of viscosities at that it occurs for most liquor.

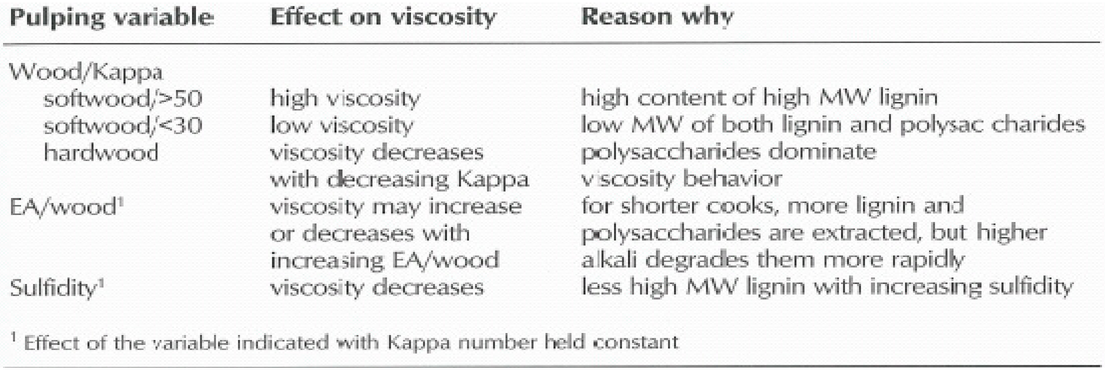
### 3.3.3 Composition

Black liquor as earlier described is a complex mixture of organic and inorganic chemicals. The nature of the organic, its molecular weight and colloidal state, determine the viscosity of particular liquor. These are dependent on the type of wood pulped, pulping conditions and further handling conditions (Soderhjelm and Hausalo 1996; Vakkilainen 1999; Llamas et al. 2007). Black liquor properties (including viscosity) are not constant; they change as black liquor flows from one process unit to another in the mill. Oxidation and LHT have greatest impact on the liquor properties (Vakkilainen 1999). Variation in the liquor composition is primarily responsible for the large differences among liquors from different mills and even in the same mill at different times at the same temperature and solids concentrations. This greatly complicates the development of generalized viscosity correlations for black liquors. For classification purpose, factors responsible for variations in the black liquor composition and its subsequent effect on its viscosity can be grouped into wood types (hard or soft), pulping variables such as effective alkali content, sulfidity, cooking time and temperature, and post-pulping operations mentioned in section 3.2. The pulping conditions and/or the degree of delignification (pulp kappa number) in the digesters ultimately determine the relative amount of chemicals present in the black liquor at the end of cooking and washing operations, before any specialised post-pulping operation come into play.

#### 3.3.3.1 Effect of wood type

Black liquor composition is a function of pulpwood species and cooking conditions (Venkatesh and Nguyen 1992; Empie et al. 1995; Moosavifar et al. 2006; Clay 2010). Black liquors from softwood pulping generally have higher viscosities than black liquors from hardwood pulping at the same temperature and solids concentration within a certain range of alkaline content. However cooking conditions for hardwoods have a dramatic effect on their black liquor viscosity. For example, cooking with low sulfidity white liquor, and using higher effective alkali charges to maintain digester throughput, produced black liquors with viscosities more than two times those seen under normal cooking conditions (Thompson et al. 2007). Frederick claims that the type of wood pulped is less likely to influence viscosity than the degree to which the dissolved organic is degraded to lower molecular weight compounds as shown in Table 3.2.

Table 3.2 Effects of pulping variables on black liquor viscosity (Frederick 1997); (EA=effective alkali, MW=molecular weight)

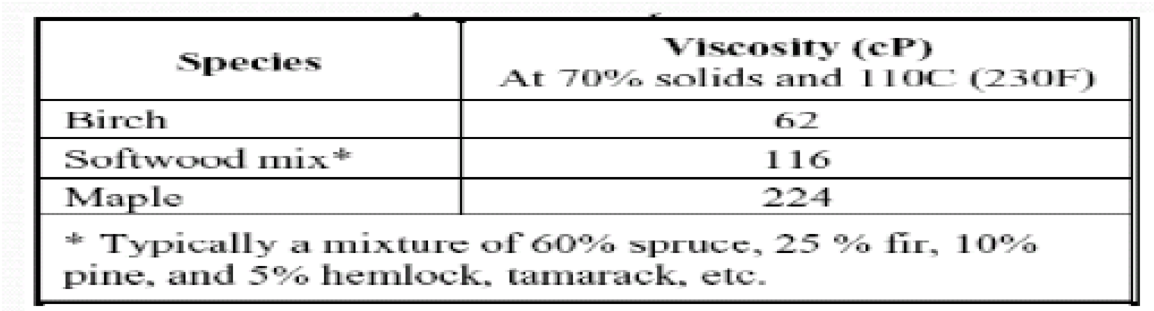


| Pulping variable | Effect on viscosity | Reason why |
|---|---|---|
| Wood/Kappa | | |
| softwood/>50 | high viscosity | high content of high MW lignin |
| softwood/<30 | low viscosity | low MW of both lignin and polysac charides |
| hardwood | viscosity decreases with decreasing Kappa | polysaccharides dominate viscosity behavior |
| EA/wood[1] | viscosity may increase or decreases with increasing EA/wood | for shorter cooks, more lignin and polysaccharides are extracted, but higher alkali degrades them more rapidly |
| Sulfidity[1] | viscosity decreases | less high MW lignin with increasing sulfidity |

[1] Effect of the variable indicated with Kappa number held constant

It is observed that pulping softwood to different kappa numbers significantly determine the viscosity while the same effect is observed with hardwood, which shows that increasing kappa number increases the viscosity of the black liquor. Similarly, at constant kappa number, irrespective of wood type, viscosity will vary with effective alkali (EA) charge or sulfidity of the cooking liquor. The suggested reasons are as presented in Table 3.2. Table 3.3 shows viscosity for three types of woods pulped at Irvin Pulp and Paper mill, Canada at the same solids concentration and temperature; however, the effects of factors other than type of wood pulped were not separated in their study. Here, the viscosity of birch (hardwood) is about half that of softwood mix with the composition shown in Table 3.3 while the viscosity of black liquor from maple, another hardwood is about twice that of the softwood and almost four times that of the birch. It is clear that factors other than type of the wood pulped must be responsible for these significant variations. It appears that the effect of wood types is likely to be noticeable when other pulping conditions remain fairly constant but it seems the effect of pulping conditions is

Table 3.3 Viscosity of black liquor from different wood species at Irvin Pulp and Paper Ltd (McCabe et al. 2007)



| Species | Viscosity (cP)<br>At 70% solids and 110C (230F) |
|---|---|
| Birch | 62 |
| Softwood mix* | 116 |
| Maple | 224 |

* Typically a mixture of 60% spruce, 25 % fir, 10% pine, and 5% hemlock, tamarack, etc.

more influential than the effect of wood type as suggested by Frederick, and Thompson and his co-workers. Porter and his co-workers (2010) reported that, in an unnamed mill where they switch between softwood and hardwood, the viscosity of softwood liquors was higher; however, there is no clear indication that the effects of other factors were separated from that of the wood type in their study.

The results of the study conducted by Sandquist (1981) on three black liquors from two Swedish mills do not confirm that wood species have independent effect on black liquor viscosity. In his work, 95% birch (hardwood) and 95% softwood black liquors were obtained from the same mill that uses automatic batch digesters where hardwood is pulped to 18% kappa value and softwood to 33% kappa value. The third liquor was based on 95% softwood pulped in another mill that uses a continuous digester and pulps softwood to 33% kappa value (the same kappa level for softwood in the first mill). The results show that the viscosity of the birch at the same solids concentration and temperature is lower than that of the softwood from the same mill at all solids concentrations, until around solids concentration of 73%, when the reverse is noted. The reason for this change was not given. Lundquist (cited in (Sandquist 1981)) has shown that molecular weight of milled wood lignin from birch is lower than milled wood lignin from softwood and this is the likely reason for the difference in their viscosities. Despite the fact that the softwoods from the two mills are pulped to the same kappa value, their viscosities are significantly different at the same temperature and solids concentration except at around solids concentration=67% where both have approximately the same viscosity. At solids concentrations below 67%, the viscosity of the softwood black liquor from the 2nd mill is typically lower than that of the softwood black liquor from the first mill but the direction changes at solids concentrations above 67%. No reason was given for these changes. Despite having the same kappa number, the softwood liquors produced at different plants have significant differences in viscosity at the same solids concentration and temperature. It was suggested that, this was because the black liquor from the second mill contains more sulphur (higher sulfidity during digesting breaks down lignin more rapidly) but the available data does not show how this influences viscosity as compared with liquor having low sulphur content. The overall deduction from this study is that the type of wood pulped seems not to have a strong and independent effect on the liquor viscosity but the pulping conditions and the degree of delignification seem to have stronger and independent effect as noted earlier by Frederick, and Thompson and his Co-workers.

### 3.3.3.2 Effects of pulping (cooking) conditions

The effects of pulping variables on black liquor viscosities were also extensively studied by Soderhjelm and Sagfors (1994) and Zaman and Fricke (Zaman and Fricke 1995a; Fricke and Zaman 1998). Soderhjelm and Sagfors investigated the effects of the degree of delignification (kappa number of the pulp), effective alkali (EA) charge and sulphidity (S) of the cooking liquor, cooking time and temperature on hardwood and softwood liquors having solids concentrations up to 70%. Their results showed that the viscosity of the black liquors from the hardwood pulping decreases with increasing sulphidity while the influence of sulphidity was less obvious for softwood black liquors; however, these softwood liquors were obtained at higher kappa numbers than that for the hardwood. They stated that the effect of sulphidity is hard to explain. They found that the hardwood black liquor is very sensitive to small changes in the degree of delignification. High EA in the cooking liquor gives high viscosity; however, regardless of the EA content, for sufficiently long cooking time, viscosity is low. The reason suggested for this is that the major part of the polysaccharide in the wood chips is degraded at this point thereby lowering viscosity of the eventual black liquor. The independent effect of cooking temperature on the viscosity of the black liquors was not discussed. Zaman and Fricke (Zaman and Fricke 1995a; Fricke and Zaman 1998) investigated the effects of cooking variables discussed earlier on viscosity of several softwood liquors both at low and high solids concentrations and temperatures up to 140 $^{o}$C (for the high-solids liquors). At low solids concentrations, they found out that at high sulphidity levels, liquor viscosity decreases with increasing EA level while at low sulphidity levels, viscosity increases with the EA level. At lower cooking temperatures, viscosity is an increasing function of cooking time while at higher cooking temperatures; viscosity reduces as cooking time is increased. At high solids concentrations, viscosity of black liquor depends not only on the temperature, but also on shear rate and liquor composition. Zaman and Fricke (Zaman and Fricke 1996; Fricke and Zaman 1998) studied the effect of cooking variables (EA,S, cooking time and cooking temperature) on the zero-shear viscosity (Newtonian viscosity, that is the limiting viscosity of the liquor at very low shear rate) of high-solids softwood kraft liquors, at constant temperature and solids concentration. At fixed low levels of sulphidity and any kappa number, viscosity is a decreasing function of EA. However, at a fixed EA, viscosity variation with sulphidity is a function of kappa number. At lower kappa numbers than 40, viscosity is a decreasing function of sulphidity level; however at kappa values higher than 85, viscosity is an increasing function of sulphidity. Fricke and co-workers (cited by (Zaman and Fricke 1996)) suggested that this behaviour depends on the molecular weight of the lignin dissolved during the kraft pulping process. The lignin dissolved in the initial stage of delignification has a smaller molecular weight than the lignin dissolved during the bulk delignification process. The lignin molecular weight decreases again in the final stage of the pulping process. Generally, viscosity is always a maximum at intermediate kappa numbers and the locations of the maxima vary with EA and sulphidity. An interesting conclusion from their study is that the zero-shear viscosity behaviour of the black liquors at high solids concentrations is extremely complex (Fricke and Zaman 1998). This is a clear indication that at very high solids concentrations, the dependence of black liquor viscosity on pulping conditions (that plays a significant role on black liquor composition) is not unique and so the development of black liquor viscosity-composition correlations has been a daunting task until now.

### 3.3.3.3 Residual effective alkali content

Residual effective alkali is the remaining hydroxyl ion content in the black liquor at the end of the kraft pulping process (Porter et al. 2004). Residual effective alkali present in the black liquor can be expressed as equivalent of $Na_2O$ or NaOH or, $Na_2S$ in g/L or following North American practice, it is normally defined as %$Na_2O$/black liquor solids (SCAN 1994; Porter et al. 2004; Thompson et al. 2007; Torniainen 2007; Roxare 2009; KnowPulp 2010). The residual alkali (RA) content of black liquor is typically defined as residual effective alkali $=NaOH+0.5Na_2S$; however in some reports, the RA contents in the liquors are expressed in terms of either active alkali $=NaOH+Na_2S$ or total titrable alkali $=NaOH+Na_2S+Na_2CO_3$. In this thesis, RA is described in the exact form reported by various researchers in their works. The most important concern in this study is to observe the trend of the effect of RA on the viscosity of black liquor and this can easily be observed based on any of the definitions above. Therefore the definitions are used interchangeably to describe RA. Previous workers have shown that RA has a strong effect on the viscosity of black liquor (Porter et al. 2004; Porter et al. 2010). It can be impacted by changes in the digester process conditions, modifications to the liquor prior to the recovery boiler and a host of other factors. A recovery boiler operator typically doesn't know the RA of the black liquor being fired in the recovery boiler (Porter et al. 2004; McCabe et al. 2007; Thompson et al. 2007). Traditionally, changes in the liquor spray characteristics at high solids concentrations are controlled by temperature. However, changes in RA should provide insight into viscosity upsets that developed due to low or high RAs (Porter et al. 2010) and as such the measurement of RA can be linked into a control strategy at the recovery boiler.

The pH of the aqueous solution affects the degree of association of its colloidal organic contents. This  affects the ease with which layers within the black liquor will slip past each other; it is then expected that its viscosity will be affected by pH or RA from the pulping process(Adams and Frederick 1988). Because the RA acts on the already complex colloidal state of the black liquor organics, the response would be expected to vary with different liquors and conditions (Adams and Frederick 1988). For example, from an operating point of view, viscosity of black liquor at any solids concentration and temperature can be changed by any of the following: addition of alkali, oxidation and storage at high temperatures (Venkatesh and Nguyen 1992). Storage at high temperature can be seen as a form of LHT. Oxidation and LHT will be discussed in more detail later.

Generally, all the three methods depend on the initial RA content of the liquor, thus their corresponding effects on the black liquor viscosity are as shown in Table 3.4. The low or high RA is on either side of about 4% RA as shown in Figure 3.1.

Table 3.4 Effect of operating conditions on the direction of black liquor viscosity change (Venkatesh and Nguyen 1992)

| Condition | Low residual alkali | High residual alkali |
|---|---|---|
| Alkali addition | Decreases | Increases |
| Oxidation | Increases | Decreases |
| Storage at high temperature | Increases | Decreases |

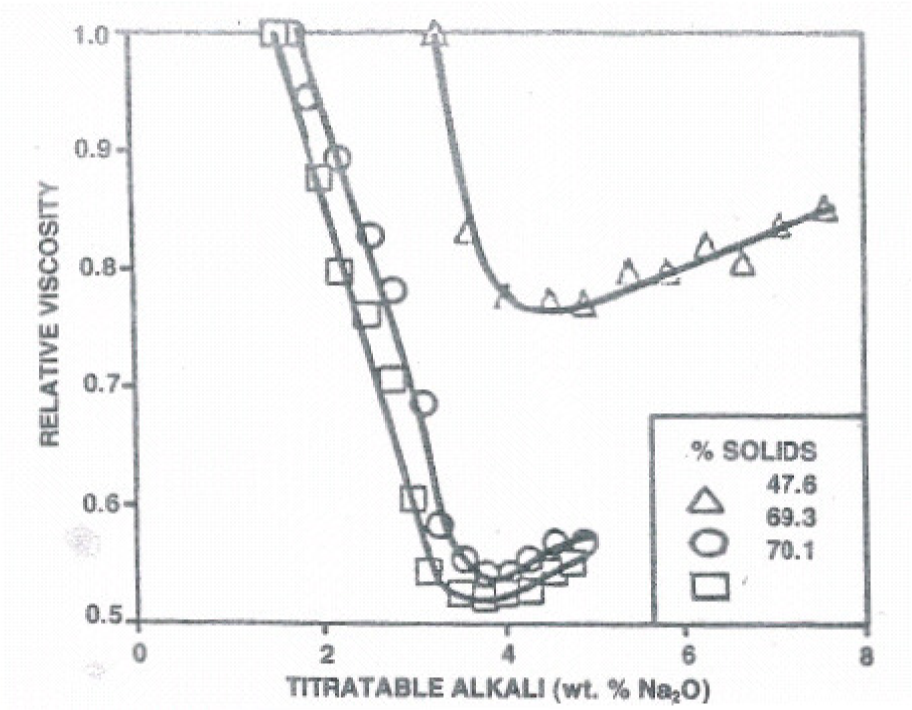


Figure 3.1 Effect of residual alkali on the viscosity of black liquor
Millanova and Dorris (cited in Venkatesh and Nguyen 1992).

From Figure 3.1, it is seen that too low or too high RA will lead to an increase in viscosity (as long as other variables are constant). Also, the effect of RA is very significant at very high solids concentrations (around 70%) but less significant at lower solids concentration (around 48%). However, it is clear that the effect of RA will become increasingly noticeable as solids concentration increases beyond around 48%. Generally, it seems to minimise liquor viscosity, a RA content of around 3% should be adequate. From all the investigations, it seems the combination of RA with temperature, to manipulate the viscosity of black liquor, will enhance the performance of the recovery boiler. This is because using temperature alone can lead to flashing, most especially if the liquor viscosity change is caused by factors other than solids concentration and temperature. Flashing has negative impacts on the recovery boiler performance (Miikkulainen 2006; Roxare 2007). An online approach for measuring RA exists but it is currently limited to weak black liquor (Hodges et al. 2006).

Thompson et al (2007) studied extensively the effect of many variables (including RA) that have significant effects on the viscosity of black liquor obtained from the traditional cooking liquors and modified cooking liquors for different wood types including Jack pine, birch and aspen. They found that, for all the viscosity-residual effective alkali profiles, there was a residual effective alkali value at which the viscosity was a minimum. However, there was a subsequent increase in viscosity to a maximum as the residual effective alkali increases, before it decreases again to a lower viscosity. Frederick (1997) explained that, the amount of RA in black liquor affects the volume occupied by the lignin molecules. At a low RA, the lignin molecules expand and associate to form large complex molecules that increase the apparent molecular weight that results in high viscosity observed when the pH of black liquor is too low. Therefore increasing the RA reduces the black liquor viscosity until a minimum is attained. Millanova and Dorris (cited in Thompson et al. 2007) attributed the minimum point (as viscosity decreases) on the viscosity-residual effective alkali profile to the dissociation of the lignin as the residual effective alkali increases but no reason was given for the rise and the eventual levelling off in the viscosity after the minimum has been reached. These observations show that increasing the alkali content of black liquor does not always guarantee a decrease in viscosity. The viscosity response depends on initial RA as reported in Table 3.4. It is essential to know on the profile where viscosity is being measured (Frederick 1997; Thompson et al. 2007). A typical viscosity-residual effective alkali profile for the Jack pine liquor is given in Figure 3.2. Viscosity reaches minimum at around 2.5% residual effective alkali for both the softwood (Jack pine -North American pine) and hardwood (birch) kraft liquors but around 1.2% for aspen (another hardwood) kraft liquor when compared at 70% solids concentration and temperature=100 $^{o}$C but at different shear rates. There was no report that shear rate had any significant impact on their viscosities at this temperature.

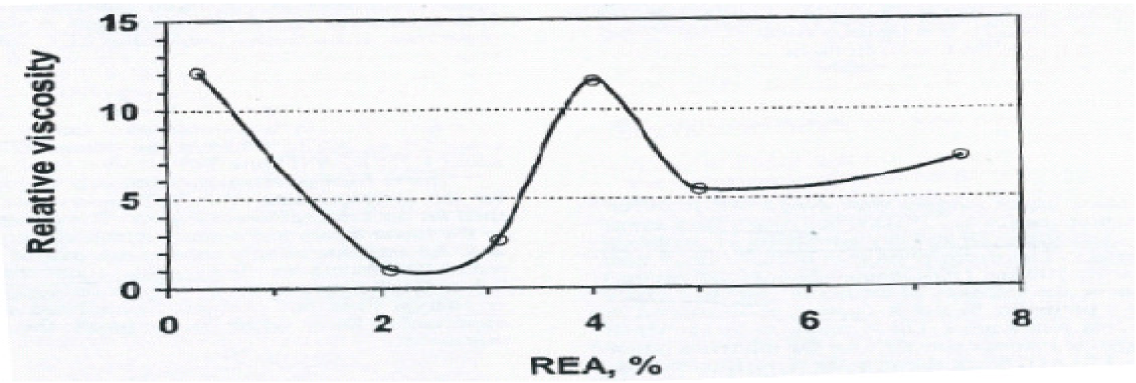


Figure 3.2 Viscosity-residual effective alkali (REA) profile for Jack pine black liquor (Thompson et al. 2007)

When the kraft black liquors obtained from the three woods above were compared with liquors obtained from their corresponding modified pulping liquors, the minima were found to be less than their kraft black liquor counterparts. This suggests that pulping types/conditions/chemicals have significant roles to play in the eventual RA and viscosity of the black liquor. Also, it appears that the effect of RA on the viscosity is nearly independent of wood types. The results also show that the rate at which RA affects the liquor viscosity is liquor-dependent.

Soderhjelm and Sagfors (1994) investigated the effect of RA on viscosity of black liquor obtained from hardwood at two residual effective alkali contents (5g/L and 10g/L). The black liquors discussed in their works at these concentrations have viscosities around 200 cP at solids concentration=~70%. Based on these two RA contents, they concluded that at solids concentrations less than 70%, RA does not have significant effect on black liquor viscosity but at solids concentrations>=70%, its effect can be noticed. Soderhjelm and Hausallo (1996) reported that at 70% solids concentration, black liquor viscosity decreases with increase in RA. This agrees with the report of Ventekash and Nguye (1992) but it is clear from Ventekash's and Nguye's work that RA will have a strong effect on black liquor viscosity even before reaching solids concentration=70% (see Fig 3.1). The direction of viscosity change with respect to alkali addition depends on the initial RA present in the black liquor as shown in Table 3.4. A careful measurement and manipulation of RA of black liquor to control its viscosity may be expedient where recovery boiler and evaporator problems are common due to large viscosity changes attributable to upsets in the RA content rather than solids concentration (Porter et al. 2004; Porter et al. 2010).

### 3.3.3.4 Oxidation

Black liquor oxidation is used to stabilize reduced sulphur compounds for odour control in older kraft recovery boilers. This process prevents the generation and stripping of hydrogen sulphide and other malodorous organic sulphur compounds from black liquor in direct contact evaporators using recovery boiler flue gases(Venkatesh and Nguyen 1992; Vakkilainen 1999). Black liquor viscosity can be affected by oxidation (Herman 1984; Empie et al. 1995; Thompson et al. 2007). Oxidation can lead to an increase or a decrease in viscosity of the black liquor depending on its initial residual effective alkali content and how much it changes during oxidation. The direction of viscosity change depends on the initial RA content in the liquor as presented in Table 3.4.

### 3.3.3.5 Liquor heat treatment (LHT)

The desire to burn higher solids black liquor in the recovery boiler has led to numerous attempts to reduce black liquor viscosity. The LHT approach is notable among these attempts (Porter et al. 2004). Small and Fricke (1985) were the first to report that viscosity of most black liquors decrease with increasing exposure time at temperatures from around 94 to 137 $^{o}$C for liquors of solids concentrations from 60-74%. The rate of this change increases with the exposure temperature and solids concentration (Small and Fricke 1985). Since then, numerous researchers have investigated the factors responsible for this process and the approach has been well developed as LHT process for reducing the viscosity of high-solids black liquors. Generally, LHT is defined as a thermal treatment method whereby RA reacts with dissolved polysaccharides and lignin, and hemicellulose molecules at high temperatures (140-190 $^{o}$C) for a period of time. This leads to the destruction or depolymerization of the high molecular weight compounds and hence a reduced viscosity (Nikkanen 1993; Soderhjelm et al. 1999; Vakkilainen et al. 1999). This viscosity reduction is permanent since the high molecular weight lignin and polysaccharide contents of the liquor have significant impacts on its viscosity, as discussed in the earlier sections. A typical heat-treated liquor viscosity is comparable with the viscosity of the normal liquor having 10% lower solids concentration as shown in Figure 3.3.

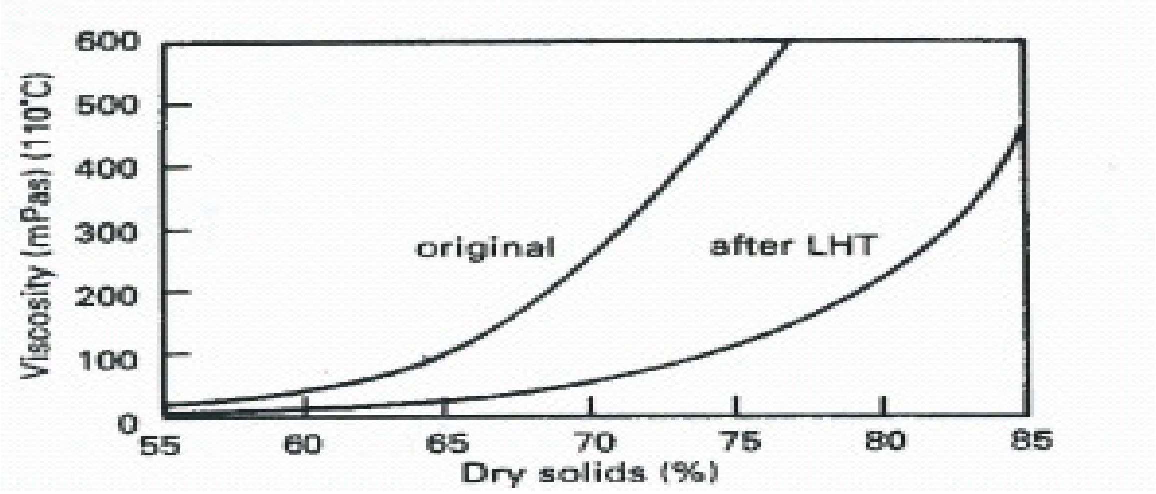


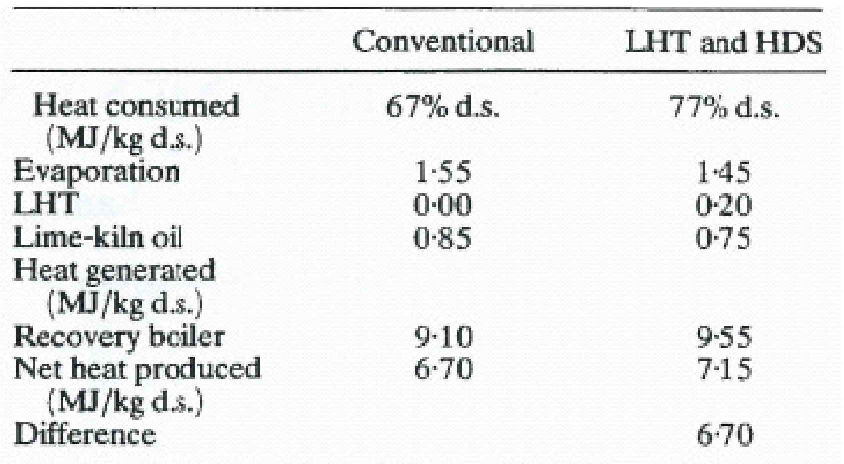
Figure 3.3 Viscosity of heat-treated black liquor (Nikkanen 1993)

Soderhjelm and co-workers (1999) subjected two softwood liquors and one hardwood liquor to heat treatments at either 180 $^{o}$C or 190 $^{o}$C and at different treatment times. At various times, and at a fixed viscosity value of 200 mPas (chosen as limit for easy handling of liquor) and temperature of 110 $^{o}$C, the solids concentrations of the untreated and treated liquors were measured and compared. They discovered that after 15 mins of heat treatment at 180 and 190 $^{o}$C respectively, the heat-treated softwood liquor with 2.2% and 3.0% higher solids concentrations had the same viscosity of 200 mPas at 110 $^{o}$C as the untreated softwood liquor at 70.5% solids concentration. The implication of this is that as-fired black liquor solids concentration can be increased by as much as 3% at constant viscosity via a 15-minute LHT. Increasing the heating duration did not improve the results further. In the case of the hardwood liquor, the LHT continues to improve the results at further higher solids concentrations as the duration increases. This tends to portray that hardwood liquor LHT can further be enhanced if the LHT duration is increased. However, it must be recognised that more heat energy would be required to do this. Major conclusion from their work is that a liquor with a low RA when heat-treated results in an increase in viscosity while a liquor having high enough RA before LHT results in lower viscosity. The former was attributed to lignin polymerization while the latter was attributed to the depolymerization of the lignin and other large molecules. These findings agree with the data in Table 3.4.

Milanova studied hot storage of weak and strong black liquors at low residual effective alkali contents and found that viscosity increased during storage at 120 $^{o}$C (cited in Soderhjelm et al. 1999). This implies that storage of black liquor at high temperatures must be done with caution, and it may be essential to know what the RA content of the liquor is and probably modify this before storage. Porter and co-workers (2004) have stressed that if viscosity reduction methods are to be successfully employed in a mill, it is essential that the RA content of black liquor should be monitored and controlled. Soderhjelm and co-workers (1999) investigated the effect of solids concentration on the LHT of black liquors, they found that the degree of LHT increases with an increase in solids concentration. This was attributed to higher RA content at higher solids concentrations and that it is responsible for more pronounced reaction at higher solids concentrations. Holmlund and Parviainen (1999) discuss the Ahlstrom LHT process in that black liquor at solids concentration of 45% from the evaporator is heated to 180-185 $^{o}$C and maintained at this temperature range for about 30 mins. This approach increases the evaporator capacity as the viscosity is significantly reduced. This liquor at 75-80% can be stored at atmospheric pressure; this would not have been possible without LHT where the limit for atmospheric storage is 73-75%. LHT has been successfully incorporated into the existing recovery areas of some mills in Finland (Nikkanen 1993; Vakkilainen et al. 1999).

Nikkainen (1993) showed that the LHT plus high-dry-solids system is more economical thermally than the conventional firing as reported in Table 3.5 without making any reference to the capital cost and the cost of increased alkali usage. Conversely, McCabe et al (2007), without providing exact economic or energy data, stated that black liquor heat-treated approach was investigated to solve a viscosity problem presented in their work but that it proved to be uneconomical due to high capital costs and increased alkali usage. A complete economic and technical analysis of the process under consideration may be required in order to be able to justify the integration of LHT process unit with existing chemical recovery facilities. It must be noted that LHT can occur during black liquor processing at high temperature, high temperature and high pressure storage or when the depolymerization reaction is well designed for that purpose. Kaila et al (2004) reported that LHT was used for the high solids (80%) black liquor being fired at the Botnia Joutseno mill in Finland. The mill originally operated a batch digestion process.

Table 3.5 Comparison of the heat economies of the LHT/high-dry-solids (HDS) firing and conventional firing (Nikkanen 1993); (d.s.=dry solids)



| | Conventional | LHT and HDS |
|---|---|---|
| Heat consumed (MJ/kg d.s.) | 67% d.s. | 77% d.s. |
| Evaporation | 1·55 | 1·45 |
| LHT | 0·00 | 0·20 |
| Lime-kiln oil | 0·85 | 0·75 |
| Heat generated (MJ/kg d.s.) | | |
| Recovery boiler | 9·10 | 9·55 |
| Net heat produced (MJ/kg d.s.) | 6·70 | 7·15 |
| Difference | | 6·70 |

The liquor from this process did not present any viscosity related problems as the liquor was stored in a pressurised liquor firing tank keeping the liquor at firing temperatures directly.

Since the liquor was stored in a pressurised weak liquor storage tank for extended periods, a certain degree of LHT might have taken place that keeps the liquor viscosity relatively low. However, with the upgrade and the introduction of the continuous digester and the addition of several side-streams to the black liquor, the viscosity of black liquor increased drastically. For example, filtrate from one of the units in the mill is added to the ash loop; residual brine is neutralised in a tall oil acidulation plant and introduced into the system at a point in the process after soap skimming. Consequently, the temperature required to reduce the liquor viscosity caused excessive flashing at the guns. By applying LHT process on the liquor for just 20mins at 175 $^{o}$C, approximately 50% reduction in as fired liquor viscosity was attained (Kaila et al. 2004) and the evaporator capacity was increased. Another mill that has successfully used the LHT process to increase the capacity of their recovery block is Metsa-Sell mill in Finland. They added an Ahlstrom LHT system to their evaporation plant and have been able to achieve many of the benefits associated with high solids black liquor firing as discussed in Chapter 1.

### 3.3.3.6 Other factors

There are other factors reported in the literature that are capable of altering the composition of black liquor and consequently, its viscosity. As black liquor viscosity is strongly dependent on its chemical composition, any process or factor that alters the internal structures of the components of the liquor has a resultant effect on its viscosity. Apart from the factors discussed earlier, high intensity shearing at high temperature (Smith et al. 1998) and cooking method (e.g. batch or continuous cooking with recycle streams or entirely modified pulping) (Ledung and Ulmgren 2000; Kaila et al. 2004; Thompson et al. 2007; Torniainen 2007) are known to affect black liquor viscosity. Further factors that affect black liquor viscosity, due to their effects on the liquor composition are: addition of tall oil soap (Thompson et al. 2007) and the use of salts/chemical additives (Gagnon et al. 1996; Roberts et al. 1996). In a nut shell, any factor that has a potential to alter the chemical composition of the black liquor will definitely have effect on its viscosity that depends strongly on the nature of its chemical constituents.

## 3.4 CONCLUSIONS AND RECOMMENDATIONS

An extensive literature survey of the factors that influence kraft black liquor viscosity was undertaken. It was observed that changes in solids concentration, temperature, shear rate and the composition of black liquor are the four main factors responsible for the changes in the liquor viscosity.

The actual viscosities of the liquors seem to depend more on the pulping variables and other post-pulping operations while the ranges of process conditions (solids concentration, temperature and shear rate) and viscosities at which each liquor manifests Newtonian or/and non-Newtonian ( shear-thinning with or without thixotropy) behaviours are dependent on the wood type. Typically, under mill conditions characterised by high temperatures, black liquors obtained from softwood pulping manifest Newtonian behaviour; this occurs when the liquor viscosity is less than around 1000 cP (500 cP being the typical pumping limit). Concerns about high viscosity supersede the concern for non-Newtonian characteristics under typical process conditions (including pumping and storage). Conversely, it seems hardwood liquors (or liquor having significant percentage based on hardwood pulping) can manifest both shear-thinning with or without thixotropic behaviours under similar mill conditions even at viscosities as low as 100 cP. This is a clear indication that models developed for softwood liquors may not be directly applicable to hardwood liquors for practical applications.

The effects of shear rate, solids concentration and temperature on the viscosity of black liquor are well understood but the relationship between black liquor viscosity and its composition is a very complex one as it depends on a myriad of factors such as wood type, pulping conditions and methods, post-pulping conditions and other recovery operations, etc. The compositional difference is responsible for the wide differences in the viscosities of the black liquors from different sources. It is also responsible for the difficulty encountered in the development of accurate and reliable viscosity models that are applicable to black liquors over a wide range of sources and a wide range of operating conditions. However, the significant effects of RA, oxidation, pulping conditions and the degree of delignification, and LHT on the liquor chemical composition (also viscosity) have been given considerable research attention. The effects of the RA, oxidation and LHT on the viscosity of black liquor are dependent on the initial RA content of the liquor and so a careful analysis, monitoring and control of the viscosity of black liquor may be possible via alkali profiling. Unfortunately, till date, RA is not being measured online for black liquor at high solids concentration where its effect is very significant. It is also clear that RA content manipulation can complement the traditional manipulation of firing temperature for recovery boiler control, most especially where the liquor high viscosity is attributable to factors other than the increase in solids concentration. The research on the effect of chemical composition on the black liquor viscosity is on-going. Given the differences in the rheological behaviours of different liquors even when their solids concentration, temperature and shear condition are the same, it is essential that the rheological behaviour of black liquors obtained from New Zealand kraft pulp mills should first be systematically investigated. Fortunately, this is one of the main tasks of this project and is discussed in detail in Chapter 4.

# 4.0 RHEOLOGICAL CHARACTERIZATION OF NEW ZEALAND KRAFT BLACK LIQUORS

## 4.1 INTRODUCTION

It was shown in Chapter 3 that kraft black viscosity depends on a number of factors including the liquor composition. It was also shown that the liquor composition is primarily responsible for large differences in the rheological behaviours of the liquors obtained from different sources, even when other process conditions are the same. In this Chapter, an overview of pulp and paper mills in New Zealand is given. Detailed description of black liquor production and processing at the Carter Holt Harvey Pulp and Paper (CHHP&P), Kinleith mill, the largest kraft pulp producer in New Zealand, is given. The results of the rheological characterization of the liquor samples obtained from this mill are discussed.

## 4.2 MATERIALS AND METHODS

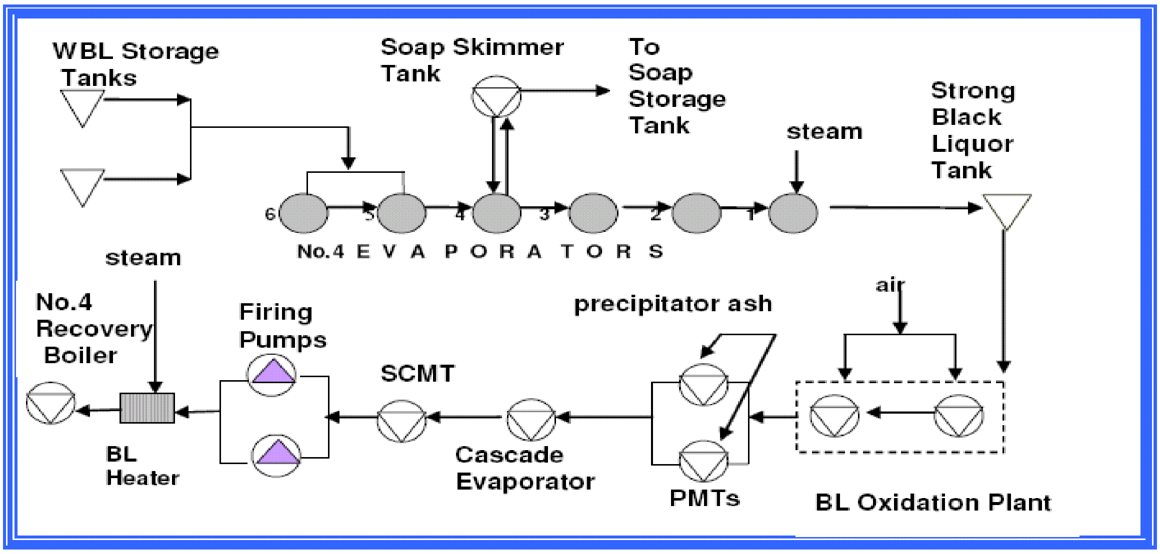
### 4.2.1 Materials

#### 4.2.1.1 Source of fresh black liquors in New Zealand

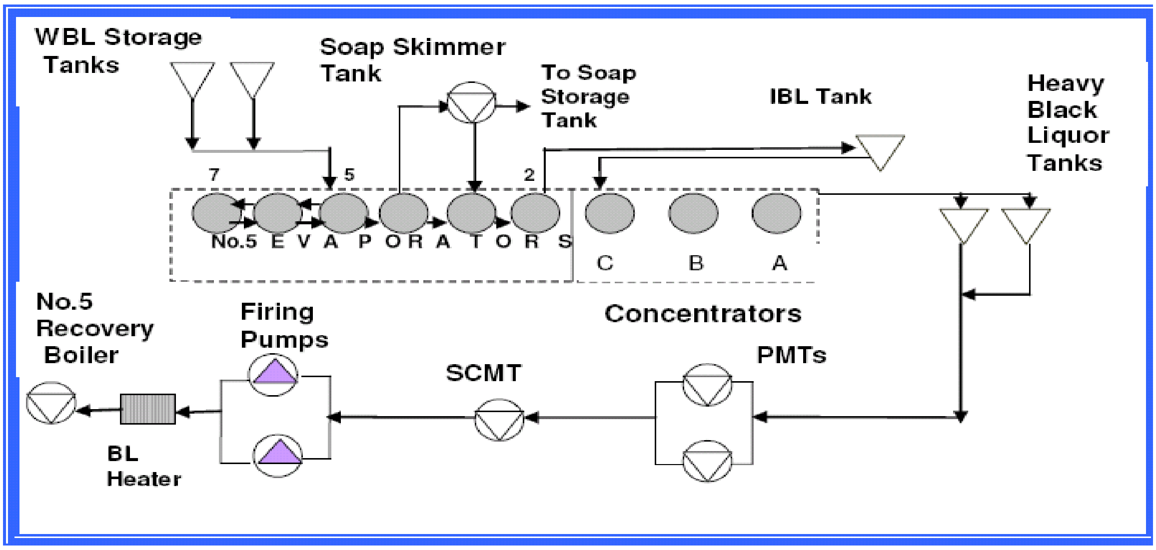
In New Zealand, the companies operating pulp and paper mills are: Carter Holt Harvey, Norske Skog Tasman, Pan Pacific Forest Products and Winstone Pulp International ([NZFRIL] 2003). Carter Holt Harvey Pulp and Paper (CHHP&P) mills (Kinleith and Tasman) utilise mainly chemical methods (CHH 2009) while Norske Skog Tasman utilises mechanical method, Pan Pacific Forest Products utilises thermo-mechanical means and Winstone Pulp International utilises chemi-thermo-mechanical method (NZFRIL, 2003) for their pulp production. CHHP&P is the main producer of kraft pulps in New Zealand thereby making it the major source of kraft black liquors. CHHP&P operates two kraft pulp and paper mills at Kinleith and Tasman sites with the former being larger in production capacity (CHH 2009). The black liquors used in this project were obtained from the CHHP&P Kinleith mill, Tokoroa, New Zealand.

At the Kinleith site, the overall black liquor that is sent to the steam and chemical recovery section comes from different sources. There are two pulp mills producing both bleached and unbleached pulps of combined capacity up to 1600 tonnes/day (Shaw and Sayer 2002).The number 1 pulp mill contains both softwood (radiata pine) and hardwood (eucalyptus and poplar) processes for the production of unbleached pulps using either batch digester or continuous digester (CD) while the number 2 pulp mill is mainly a softwood process and contains a bleach plant that produces bleached pulp. The latter can be used to produce unbleached pulp if required. The number 1 pulp mill produces softwood pulp via kraft process in batch mode. The pulp is washed and the lignin, spent cooking chemicals (mainly NaOH and $Na_2S$) (white liquor) and other materials are removed as black liquor that is recycled to the steam and recovery area to be processed for re-use. However, the hardwood pulp produced in this same pulp mill is obtained in the number 3 CD via neutral-sulphite semi-chemical (NSSC) process (Shaw and Edwards 2002). The NSSC process involves cooking wood chips with a solution of $Na_2SO_3$ and $Na_2CO_3$ as a buffer. The cooking liquor in NSSC process is called pink liquor and the spent liquor obtained from this process after pulp washing is called red liquor. The red liquor is recycled in the steam and recovery area for re-use. In the number 2 pulp mill, number 2 CD is used to obtain softwood pulps by dissolving the wood chips in white liquor. Here also, the pulp is washed to remove the dissolved lignin and spent cooking chemicals. If bleached pulps are required, the unbleached pulps are subjected to a series of oxygen reactions to remove lignin (delignification) further before they are bleached in the bleach plant. The digesters in the two pulp mills are required to pulp the woods to different kappa numbers (measure of the amount of lignin in the pulp (Shaw and Sayer 2002)) depending on the requirements of other process units in the mill. The batch digesters in the number 1 pulp mill pulps mainly radiata pine to kappa number 40-60 while the number 3 CD in the same number 1 pulp mill pulps hardwoods ( eucalyptus and poplar in approximately 1:1 mixture) typically to kappa number 120-140. Lastly, the number 2 CD in the number 2 pulp mill pulps mainly radiata pine to typically kappa number 20-25 (Lysaght 2010). On the average, based on the wood tonnage required per day in all the digesters, 98% of all the wood pulped is softwood.

The black liquor obtained at the end of the wood cooking from the pulp mills is called weak black liquor since it contains low solids concentrations around 10-20% (Lister 2003). As noted above, the liquors are obtained via different pulping methods and cooking different woods and they are stored in weak black liquor storage tanks. These liquors are subjected to different processes before, during and after storage. Definitely, the conditions of these processes change from time to time and as such, the liquor properties including viscosity are expected to change correspondingly. The weak black liquor obtained from the pulp washer of the batch digesters in the number 1 pulp mill is slightly thickened to around 20% solids concentration in the blow heaters before being sent to the weak black liquor storage tanks. The red liquor from the washer of the number 3 CD in the same number 1 pulp mill is also thickened by blow heaters before being sent to mix with the weak black liquor in the weak black liquor storage tanks. The weak black liquor from the washers of number 2 CD in the number 2 pulp mill is not pre-evaporated or thickened before being sent to the weak black liquor storage tanks. Any spilled and reclaimed liquor collected from the designated weak black liquor tanks of the caustic plant is also sent to mix with the other liquors in the weak black liquor storage tanks. The weak black liquor that has been mixed with red liquor and other liquors as mentioned earlier are all stored in the large insulated weak black liquor tanks (Fenton 2010).There are two evaporator sets and two recovery boilers at the Kinleith site. The recovery boiler section will be discussed further in Chapter 7. The weak black liquor from the large weak black liquor tanks is pumped to both the number 4 and the number 5 evaporators. The processes undergone are different between the two evaporator sets and this may lead to differences in the compositions of the product liquors from each evaporator set and subsequently to differences in their rheological properties as discussed in Chapter 3. The liquor in the number 4 evaporators is subjected to the evaporation process to obtain strong black liquor (solids concentrations=40-50%) which is then subjected to oxidation before being mixed with saltcake from the recovery precipitators and then sent through to the cascade evaporator to produce heavy black liquor (solids concentrations=60-70%). This is fed to the saltcake mix tank (currently no saltcake is added) before being fired in number 4 recovery boiler (Fenton 2010). In the number 5 evaporators, the weak black liquor is first passed through a set of evaporators where the intermediate black liquor (solids concentration=~48%) is produced and stored in the intermediate black liquor tank. It is then pumped to a set of concentrators to thicken it to solids concentration around 70% (heavy black liquor). From here, the heavy black liquor is passed through the precipitator and saltcake mix tank before is being fired in the number 5 recovery boiler. Note that no oxidation process takes place in the number 5 evaporators/concentrators. Also, the heavy black liquor obtained in the cascade evaporator in the number 4 evaporators is via direct contact with flue gases from the recovery boiler but heavy black liquor from the number 5 evaporators/concentrators is not obtained this way. Finally the heavy black liquor tank is equipped with electric heat tracing to keep the heavy black liquor from solidifying (Lister 2003). The flow of black liquor from the weak black liquor tanks to the number 4 and number 5 recovery boilers thorough various intermediate processes/units are as shown in Figure 4.1.



(a)



(b)

Figure 4.1 Black liquor systems for the recovery boilers (a) number 4 (b) number 5 (Lister 2003); (BL=black liquor; WBL=weak black liquor;PMT= precipitator mix tank; SCMT saltcake mix tank; IBL=intermediate black liquor)

Based on the discussions above, it is clear that the weak liquors stored in the weak black liquor storage tanks come from different pulping processes (kraft and NSSC) via different pulping modes (batch and continuous) and from both softwood and hardwoods, however, since roughly 98% of the liquors come from continuous pulping of softwood mainly via the kraft process, it seems logical to classify the black liquor obtained from CHHP&P Kinleith mill as kraft black liquor from softwood (mainly radiata pine) pulping.

Another important fact to be borne in mind is that the weak black liquors flowing to both the number 4 and the number 5 evaporators come from the same weak black liquor tanks. It may therefore be safely assumed that, any rheological differences noticed in the liquor processed in the number 4 evaporators and recovery boiler, and the liquor processed in the number 5 evaporators/concentrators and recovery boiler would be due to the difference in the post- pulping processes undergone by the liquors. The main post-pulping processes after the weak black liquor tanks are: evaporation/concentration, saltcake addition, caustic addition at the cascade, de-soaping, steam addition at the black liquor heaters, oxidation, and the direct contact between the flue gases and the black liquor (Fenton 2010).

### 4.2.1.2 Black liquor samples preparation

#### *Fresh samples preparation*

Two batches (E408 from the number 4 evaporators and E508 from the number 5 evaporators) of black liquor samples having the reported solids concentrations and residual alkali (RA) contents (see Table 4.1) were obtained from CHHP&P Kinleith mill in late February 2008. Two more batches (E509A and E509B) of black liquor samples, having the reported solids concentrations and RA contents as shown in Table 4.1, were sent from CHHP&P late December 2008 and were received at the University of Canterbury early January 2009. E509A is an intermediate black liquor sample (from the intermediate black liquor tank, post number 5 evaporators) while E509B is a product sample (from the heavy black liquor tank, post number 5 concentrators) (Fenton 2010). The E509A and E509B batches were treated as a single batch E509.

Table 4.1 Solids concentrations (SCs) and RA contents of the as-received black liquor (BL) samples

| Fresh BL sample | SC (%) | RA(g/L) |
|---|---|---|
| E408 | 52.21 | 10.72 |
| E508 | 47.91 | 12.86 |
| E509A | 50.98 | 24.40 |
| E509B | 69.80 | 28.80 |

By diluting portions of the fresh samples with deionised water, samples of lower solids concentrations as low as 12% were obtained. By concentrating portions of the fresh samples under vacuum in Rotavapour$^{TM}$ (rotary evaporator), samples with solids concentrations as high as 80% and above were obtained. The vacuum operation was adopted due to the water-based nature of black liquor. Under vacuum, the evaporation takes place at reduced temperature thereby preventing both oxidation (due to oxygen presence) and preventing the possibility of LHT at high temperature and large exposure time. All the samples were stored in either plastic or glass bottles in a cool, dry place to prevent any possible reactions that may occur prior to analysis.

### *Liquor heat treatment (LHT) sample preparation*

As noted from the discussions in Chapter 3, when concentrated black liquor is held long enough at a temperature >=100 $^{o}$C, lignin and other large molecular weight organics are broken down (depolymerization) to simpler molecules due to their reaction with RA (when sufficient) in the liquor; this leads to a permanent reduction in the black liquor viscosity. Although the LHT process depends on the amount of alkali present, temperature and duration of exposure, research reports show that a temperature range of 180-190 $^{o}$C and an exposure time of about 15 minutes are the most favourable conditions for this reaction. The LHT process was carried out using an autoclave in the Department of Chemical and Process Engineering (CAPE) at the University of Canterbury. The autoclave is an old piece of equipment that can not be disassembled immediately after the desired LHT duration. Also, raising the temperatures from room temperature to the desired ranges took several minutes or hours and so all the LHT samples in this work stayed for several hours at high temperatures before they were eventually discharged for analysis. The aim of the LHT in this work was not to investigate the effect of LHT duration, but to determine the effect of LHT on black liquor viscosity and this was accomplished whether the samples stayed in the autoclave for 15mins or longer. The schematic diagram of the experimental set-up for the LHT process is as shown in Figure 4.2.

Two samples of LHT black liquors were prepared. First, a trial sample (E4E508) was heat-treated. Wastes obtained from E408 and E508 during different procedures were gathered together as E4E508 sample. The sources of E4E508 include: leftovers from samples used for solids concentrations determination, leftovers from washing and cleaning of the experimental beakers using deionised and tap waters, residuals from the vacuum evaporation of the black liquor, with or without the use of air gun operated up to around 350 °C (that implies oxidation or/and LHT may have taken place to some extent) to melt highly concentrated black liquors, etc. All these were gathered together as dilute waste black liquor, E4E508. Its solids concentration was 12.3% from the procedure outlined in section 4.2.2.1. The original aim of subjecting E4E508 to LHT was to use it as a trial sample before embarking on the investigation of the effect of LHT on high solids concentration liquor; however, it turned out to be a good sample to investigate the effect of LHT on liquors at low solids concentrations.

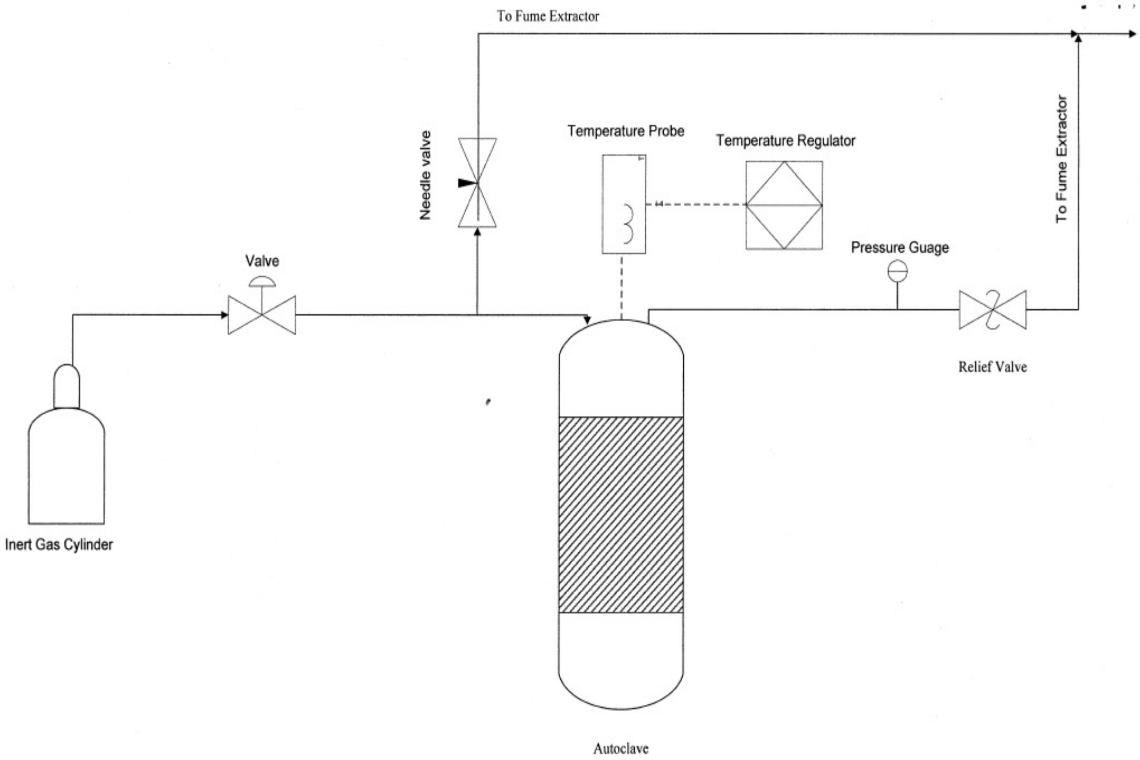


Figure 4.2 Experimental set-up for black liquor heat-treatment process

Approximately 700 ml of E4E508 sample was loaded into the autoclave. The autoclave was pressurised to around 6bars and heated from ~25 °C to ~190 °C over approximately 5hrs. The heating source was turned off and it took several hours for the autoclave to cool down before the LHT liquor was offloaded from the autoclave. A portion of this LHT sample was taken and its solids concentration was determined using the procedure outlined in section 4.2.2.1; the pH of the LHT E4E508 was also determined.

The second sample having high solids concentration (>50%) was taken from E408. Before loading the sample into the autoclave, Nitrogen gas was used to purge oxygen from the system to ensure that no oxidation of black liquor occurred during the LHT process. About 450 ml of E408 at solids concentration=52.21% was loaded into the same autoclave at ~23 °C and pressurised to about 8bars and the temperature was set to 190 °C. Temperature rose to around 220 °C (overshooting the set point by around 30 °C) after about 50 mins despite that a temperature controller was installed on the system. At this juncture, the heat source was turned off and it took around 35 mins to cool down from 220 °C to around 190 °C. It took about 5 hours to cool down from 190 °C to about 50 °C before the sample could be removed from the autoclave. There were some burnt and suspended particles in the LHT sample; these were separated from the sample via filtration. The pH of the fresh and the LHT samples were obtained and compared. The solids concentration of the LHT E408 was determined using the procedure outlined in section 4.2.2.1.

### 4.2.2 Methods

#### 4.2.2.1 Solids concentration determination

In CAPE, at the University of Canterbury, the solids concentrations of the black liquor samples received from the CHHP&P Kinleith mill, those prepared directly from the bulk samples, and those obtained from other procedures including wastes and LHT were determined using a Sartorius Moisture Analyser (MA) 30, which uses infra-red heating. The advantage of using the infra-red based MA 30 over the traditional oven drying is that it is faster. Results are obtained in less than 30 mins while the oven drying method requires about 24 hours. The actual time taken depends on the temperature and the amount of sample being dried. Usually, about 5-10 g sample is sufficient for analysis. The repeatability of the instrument is ±0.05% for initial sample weight >=5 g.

It is worth mentioning that black liquor showed swelling characteristics and uneven drying when concentrated liquors were being analysed. These behaviours may be attributed to the presence of residual alkali in the liquor and also water being trapped in the films of the thick liquors. These problems were overcome by using glass fibre as a surface extender and by diluting the concentrated samples before drying. The dilution ratio depends on the initial concentration of the sample. The aim was to make the sample as watery as possible to avoid swelling that may lead to unequal drying and hence erroneous results. The actual solids concentration was evaluated using Eq (4.1):

$$SC_a\ (\%) = SC_d\ (\%) \times DS/UDS \tag{4.1}$$

Where subscripts 'a' and'd' denote actual and diluted, respectively; DS is the mass (g) of the diluted sample and UDS is the mass (g) of the undiluted (original) sample.

Depending on the environmental temperature and the solids concentration of the liquors, the solids concentration measurements were either done directly on the samples or the samples were preheated before any portions of them were taken for analysis. The liquors having high solids concentrations were first heated in closed glass or plastic bottles in a water bath to make them flow and were shaken thoroughly for proper mixing so that the samples taken were homogenous and representative of the bulk samples. Usually, all the heating was done at temperatures <=100 $^{o}$C. At these conditions, LHT is negligible over short periods.

#### 4.2.2.2 Black liquor viscosity measurement

The viscosities of the E408, E508, E509, E4E508 and the LHT E408 & E4E508 samples were measured using Thermo Scientific Haake Rotovisco® RV 20 rotational viscometer (open-cup) (with M5 measuring head and concentric NV cup/sensor, MV1 cup/sensor and SV1 cup/sensor) and Contraves Rheomat® RM 115 rotational viscometer (open-cup) (with MS DIN 114 and MS DIN 125 sensors). Black liquor viscosity changes by orders of magnitude over wide ranges of process conditions, therefore it was impossible to use a single sensor to measure black liquor viscosity over these wide ranges. For a similar reason, different forms of viscometers, including customised ones, have been reported in the literature to be used for black liquor viscosity measurements because of the nature of black liquor (Zaman and Fricke 1995c; Zaman and Fricke 1996; Fricke and Zaman 1998). Black liquor, being a water-based mixture, suffers evaporation at high temperatures close to its boiling point and so pressurised, instead of open-cup (under atmospheric pressure) viscometers are required under such conditions. Every attempt to obtain a pressurised viscometer in New Zealand and Australia proved unsuccessful. At high solids concentrations such as 80% and above, black liquor becomes very thick and sticky and has very high viscosity; as a result it was very difficult transferring the liquor from the rotary evaporator flask to the viscometer. Some previous researchers had to develop customised evaporation systems that were integrated to a viscometer such that the samples could be directly transferred to the viscosity measurement chamber. However the design, fabrication and commissioning of such customised equipment was not feasible within the current study in that rheological characterization of black liquor was just a fraction of the other main tasks required to be executed within the time available. So all the viscosity data obtained in this study were based on the open-cup viscometers and were limited to solids concentrations up to ~70% although a black liquor sample having solids concentration around 85% was obtained in the vacuum evaporator. The viscosity measurements were carried out under the following conditions: solids concentration=~12-70%; temperature=0-115 $^{o}$C and shear rate=~10-2000 s$^{-1}$. The uncertainty in the viscosity measurements is +/-1.03% of the reported average viscosities (see Appendix B2).

At the CHHP&P Kinleith mill, the key operating parameters for the as-fired black liquor solids are 66% and 70% for the number 4 recovery boiler and the number 5 recovery boiler, respectively and the approximate firing temperature is 123 $^{o}$C (Lister 2003). Although Adams and Frederick (1988) reported that, typical shear rates for the flowing black liquor is 30-4000s$^{-1}$, black liquor viscosity is independent of shear rate under typical firing conditions. Therefore, the viscosity data obtained based on the above-stated experimental conditions, are nearly representative of typical mill conditions. Extrapolation of data to temperatures up to around 125 $^{o}$C should be possible.

Viscosity is temperature-sensitive and so the sensor systems were used with temperature-controlled vessels connected to a thermal liquid circulator to keep the temperature steady during viscosity measurement. In the case of the Haake RV 20, it was connected to Haake F3-C bath that can be operated up to around 150 $^{o}$C. The fluid used typically at T<=100 $^{o}$C is ethylene glycol-water mixture.

The RV 20 viscometer, using NV and MV1 sensors at 20 $^{o}$C was validated using N10 and N1000 standard oils supplied by Paragon Scientific Ltd, England. The maximum absolute relative errors between the measured values and the expected (known) values were 0.52% (for NV and N10 oil) and 1.35 % (for MV1 and N1000 oil). NV sensor is applicable to viscosity measurements up to around $10^{4}$ cP while MV1 can measure up to around $10^{5}$ cP and as such, the above-indicated levels of the instrument accuracies were considered to be adequate for this study. Appendix B1 (Haake Mess-Technik 1988; McGiven and Tuoc 1991) show the ranges of viscosity, shear rate and shear stress within that readings obtained with each sensor is valid, and the dimensions and sample sizes for NV, MV and SV sensors.

As it was done in the solids concentration determination, the black liquor whose viscosity was to be measured was first heated in a closed glass or plastic bottle in a water bath and mixed thoroughly to obtain uniform sample for analysis. The amount of sample used for the analysis depends on the sensor used (see Appendix B1). Once the viscometer was loaded and the required temperature, shear rate ranges and measurement duration were set, the sample was allowed to be brought to thermal equilibrium before the measurement was taken. The whole measurements, computations and results proceeded entirely in an automatic mode.

Having established that black liquor can exhibit shear-thinning and possibly thixotropic characteristics under certain conditions, the up (increasing rate of shear) and down (decreasing rate of shear) runs were performed at each solids concentration and temperature, most especially at low temperatures and high solids concentrations where these characteristics are common. If the viscosity of the sample at the same temperature and solids concentration decreases as the shear rate increases, the sample is said to be a shear-thinning fluid. In addition to the shear-thinning behaviour, if the viscosity readings at the up runs and the down runs approximately coincide or overlap, then the liquor is not thixotropic (time-dependent). But if there is a hysteresis (does not coincide or overlap), then the fluid is thixotropic. Whenever large differences that can not be attributed to shear rate variation or time-dependence factor at fixed shear rate were observed in the viscosities, such samples and their results were discarded and new samples would be analysed. This is because turbulence (at high shear rates) might have set in and some of the sample might have been lost in the process, or evaporation (if temperature is high enough) may have started occurring and as such solids concentration may have changed.

Each sample was sheared for about 30 s at each shear rate (during the up or down runs). At each shear rate, two to four viscosity measurements were automatically taken and the average computed automatically. Once the up and down runs were completed, the temperature was either changed or another sample was loaded and the whole process repeated. Generally, the average total time taken to measure the viscosities of a sample at fixed solids concentration and temperature was about 15 mins. The duration depends on the number of shear rates permissible with a particular sensor. At all solids concentrations and temperatures investigated, there was no concern for LHT for holding a sample for about 15 mins. When no shear-thinning or thixotropic behaviour was observed, the subsequent measurements at higher temperatures were usually done at just a single run, since it was clear that the liquor would be a Newtonian fluid under those conditions. The final results including relevant information about the sensor, temperature, shear rate, shear stress and viscosity could either be stored on the computer or printed.

At high temperatures (>= 80 $^{o}$C), in the absence of a pressurised viscometer, two main procedures were introduced in order to minimize evaporation of the samples so as to obtain accurate and steady viscosity readings. First, the viscometer sensors and the samples were preheated to, or close to, temperatures at which the analyses were to be done and the samples were transferred as quickly as possible into the sensor. This allowed the samples to stay for short periods in the viscometers and the viscosity readings were taken. Second procedure involved the use of very low viscosity silicone oil to cover the surface of the samples so as to minimize evaporation. This was particular helpful when the analysis temperature was close to its boiling point. In order to be able to operate the Haake RV 20 viscometer beyond 100 $^{o}$C, the usual ethylene glycol-water mixture was replaced with BP® THB 32 thermal oil that has a flash point of 204 °C. Incorporating all these measures, viscosity data at temperatures up to 115 °C, shear rates up to 2000 $s^{-1}$ and solids concentrations up to ~70% were obtained. It was difficult to obtain reasonable results beyond 115 °C.

## 4.3 RESULTS AND DISCUSSION

### 4.3.1 Effect of Shear Rate

The effect of shear rate on the viscosities of E408, E508 and E509 was investigated at different solids concentrations and temperatures using the procedures outlined above. All the samples showed shear-thinning behaviours at high solids concentrations (>=50%) and low temperatures. This finding agrees with most of the existing reports on the rheological behaviour of kraft black liquors. For instance, the shear-thinning behaviour of E408 at ~50% and 0 °C is as shown in Figure 4.3. In addition to exhibiting shear-thinning behaviour, as solids concentration increases beyond ~50%, E408 and E508 show significant thixotropy. However, both behaviours decrease dramatically with increase in temperature (exemplified by E508 at 40 °C and 60 °C, at solids concentration=64.39%) as shown in Figure 4.4 and Figure 4.5. Black liquor literature data, as discussed in Chapter 3, corroborate this finding.

The onset of the shear-thinning with or without thixotropic behaviour varies from one liquor to the other as expected since the samples were obtained from different evaporators (different processes) or from the same evaporators at different times such that process conditions must have changed. E408 at solids concentration around 50% and temperature 0 °C shows a strong shear-thinning behaviour as shown in Figure 4.3 while E509 (see Figure 4.6) at around the same solids concentration and temperature is nearly Newtonian over the ranges of shear rates investigated. Comparing both liquors at ~100 $s^{-1}$, E509 has a much lower viscosity (roughly one-tenth) than E408. E408 that was obtained from the number 4 evaporators (including oxidation process) shows appreciable thixotropic behaviour at apparent viscosities>= 6000 cP at solids concentration=~52% and temperature=0 °C as shown in Figure 4.7 but E508 that was obtained from the number 5 evaporators (no oxidation process) shows significant thixotropic effect at apparent viscosities >3500 cP at solids concentration=~64% and 40 °C as shown in Fig 4.4.

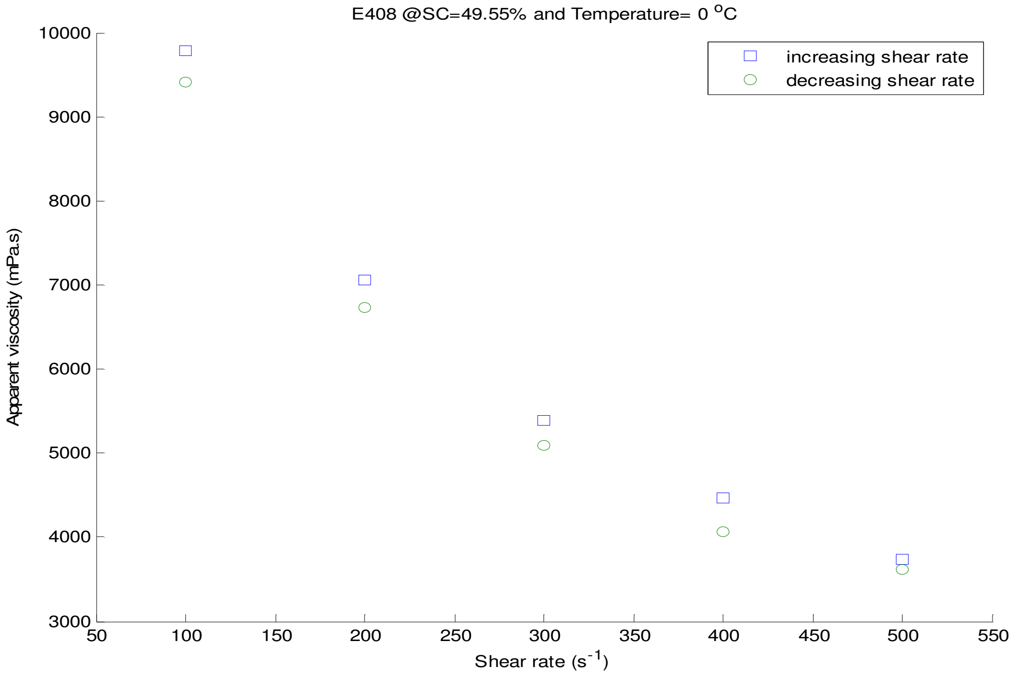


Figure 4.3 Effect of shear rate on the viscosity of E408 @ solids concentration (SC) = 49.55% and temperature = 0 °C

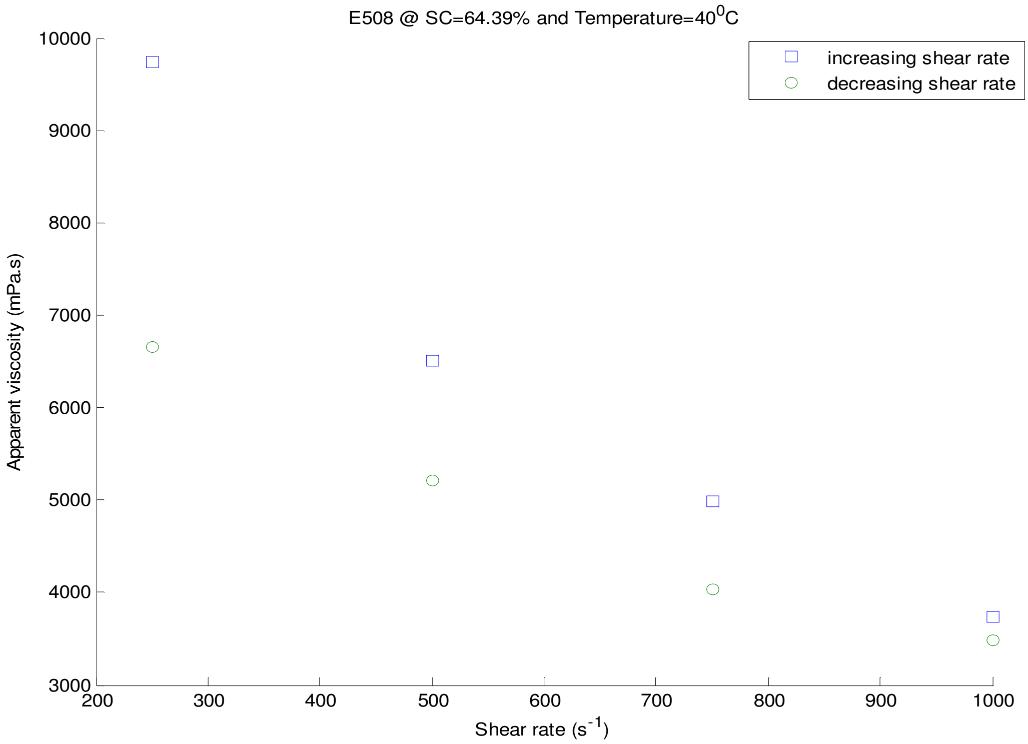


Figure 4.4 Effect of shear rate on the viscosity of E508 @solids concentration (SC) =64.39% and temperature=40 °C

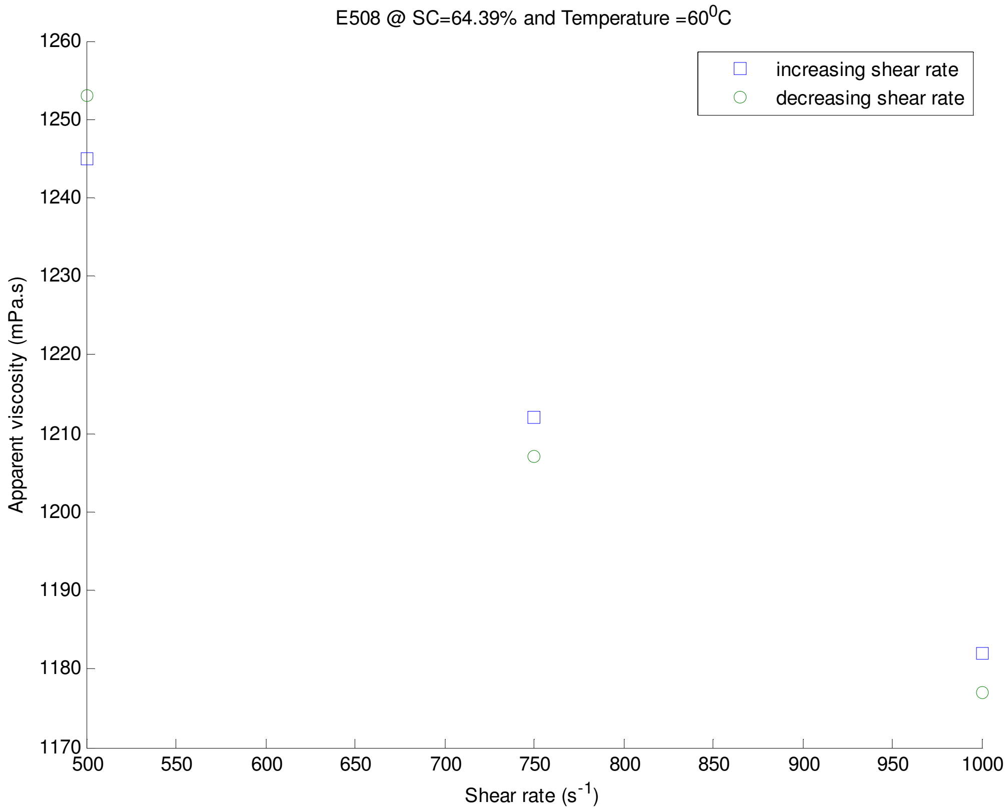


Figure 4.5 Effect of shear rate on the viscosity of E508 @solids concentration (SC) = 64.39% and temperature=60 °C

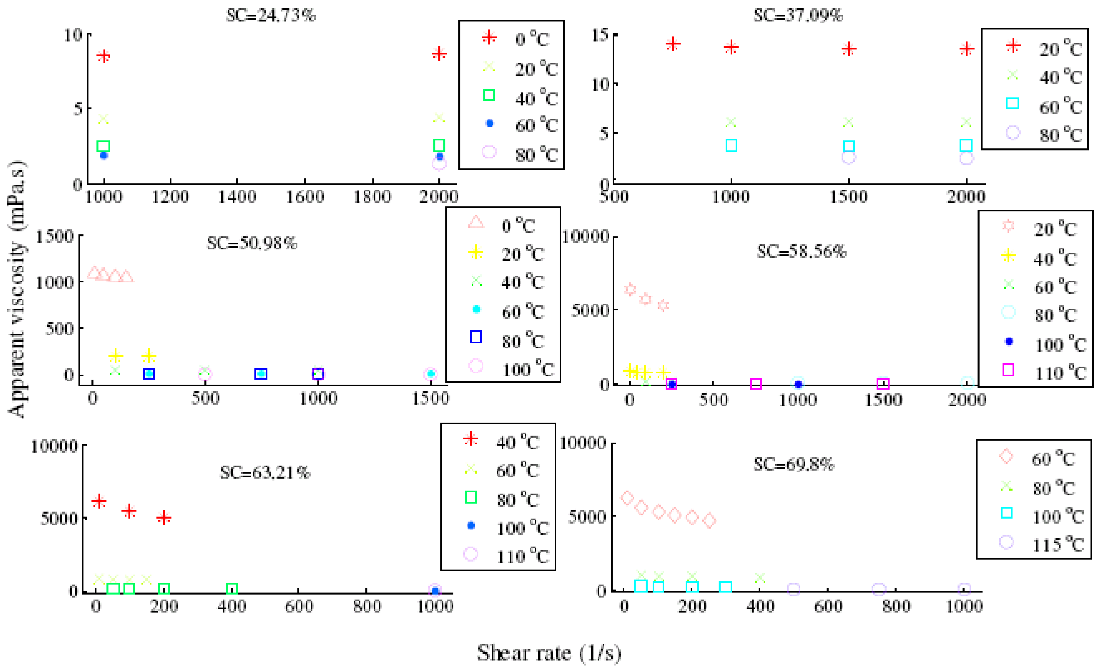


Figure 4.6 Viscosity data for E509 at different process conditions; (SC=solids concentration)

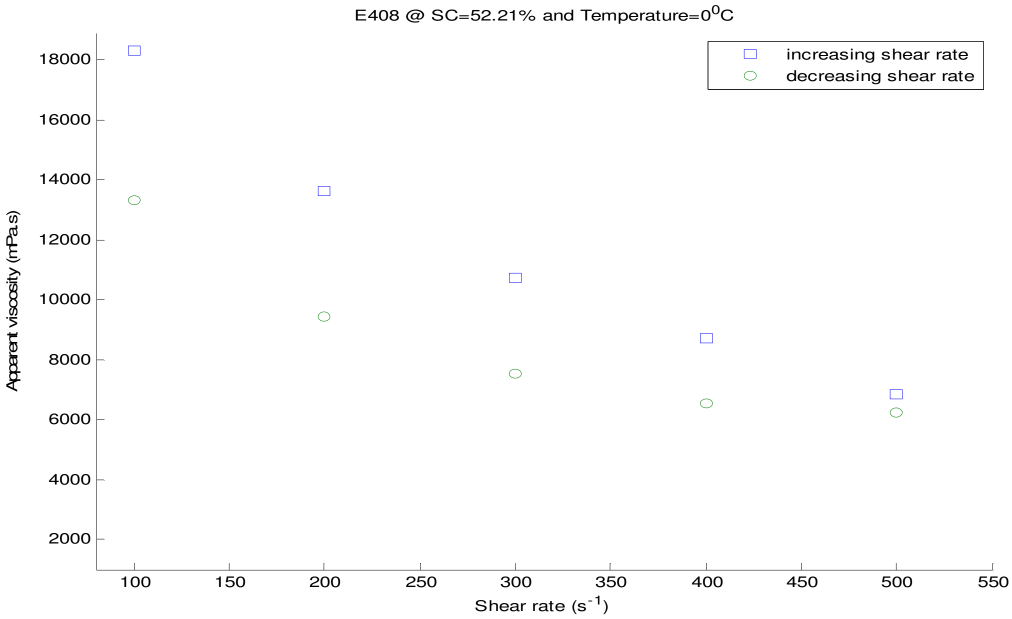


Figure 4.7 Effect of shear rate on viscosity of E408 @solids concentration (SC) =52.21% and temperature=0 $^{o}$C

However, E509 that was obtained about a year later (process conditions may have changed) from the same number 5 evaporators where E508 was obtained does not show thixotropic behaviour even at apparent viscosities above 6000 cP at ~63% and 40 $^{o}$C as shown in Figure 4.8.

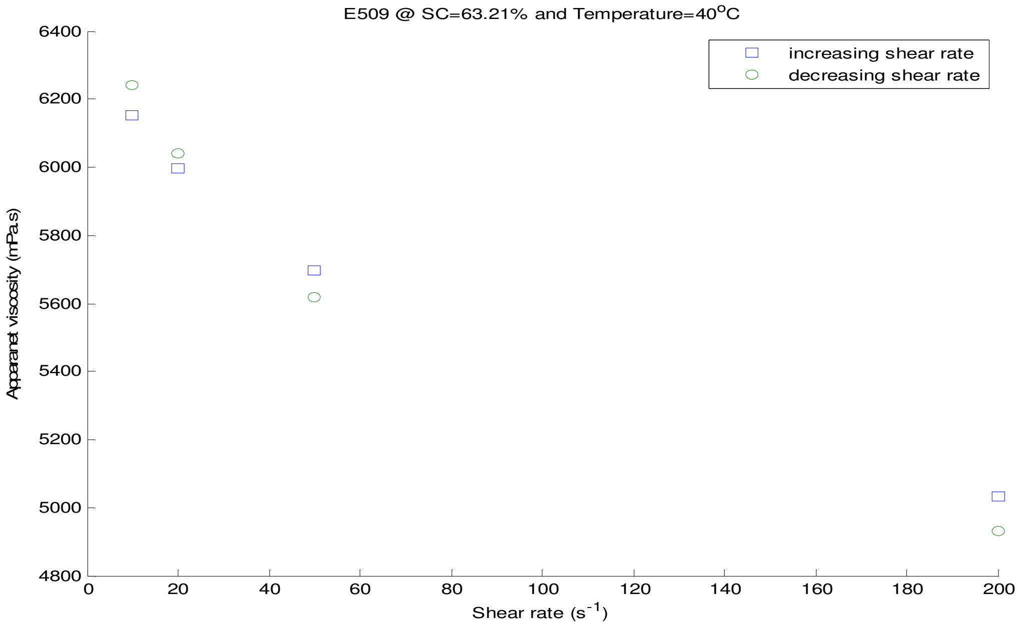


Figure 4.8 Effect of shear rate on the viscosity of E509 @solids concentration (SC) = 63.21% and temperature=40 $^{o}$C

It is possible that E509 may exhibit thixotropic behaviour at higher viscosities but available data are insufficient to establish this. It is interesting to note that none of the three liquors shows an appreciable shear-thinning behaviour at apparent viscosities <=1000 cP (see Figures 4.6, 4.9 and 4.10); this observation agrees with published data for most softwood kraft black liquors. It may then be sensible to take 1000 cP as a threshold viscosity for the onset of shear-thinning behaviours for softwood kraft black liquors for practical applications; however, the apparent viscosity at which thixotropic behaviour is exhibited seems to vary from liquor to liquor.

As discussed in Chapter 3, there are dissenting opinions on the thixotropic behaviour of black liquors. Some researchers claim that softwood kraft black liquors do not show thixotropic behaviour but hardwood kraft black liquors do. Others simply reported that black liquors exhibit shear-thinning with or without thixotropic behaviours at high solids concentrations and viscosities without emphasizing the wood source or pulping conditions. The thixotropic behaviours of the liquors presented in this thesis agree more closely with the reports from the latter group but they seem to contradict the reports of the former group who claim that softwood black liquor does not show thixotropy (even at very high viscosities). It seems unlikely that the thixotropic behaviours of the liquors (almost 100% softwood kraft black liquor) in this work can be attributed to less than 2% liquor obtained from hardwood pulping. As discussed earlier, the onset of shear-thinning behaviour for E408 occurs at solids concentration < 50% and temperature=0 $^{o}$C while E509 does not exhibit significant shear-thinning behaviour until solids concentration > 50% within the limits of experimental conditions. The differences in the onsets of the shear-thinning, with or without thixotropic behaviours of these liquors, can be attributed to the differences in their compositions brought on by differences in the process conditions in the evaporators. The variations in the compositions of the liquors seem to be independent of wood type or pulping conditions since the weak black liquor entering both the number 4 and the number 5 evaporators comes from the same weak black liquor tanks. It may be logical to conclude that any viscosity variations observed for the liquors obtained from the number 4 and the number 5 evaporator sets are dependent on the variations in the processes occurring at the two evaporator sets.

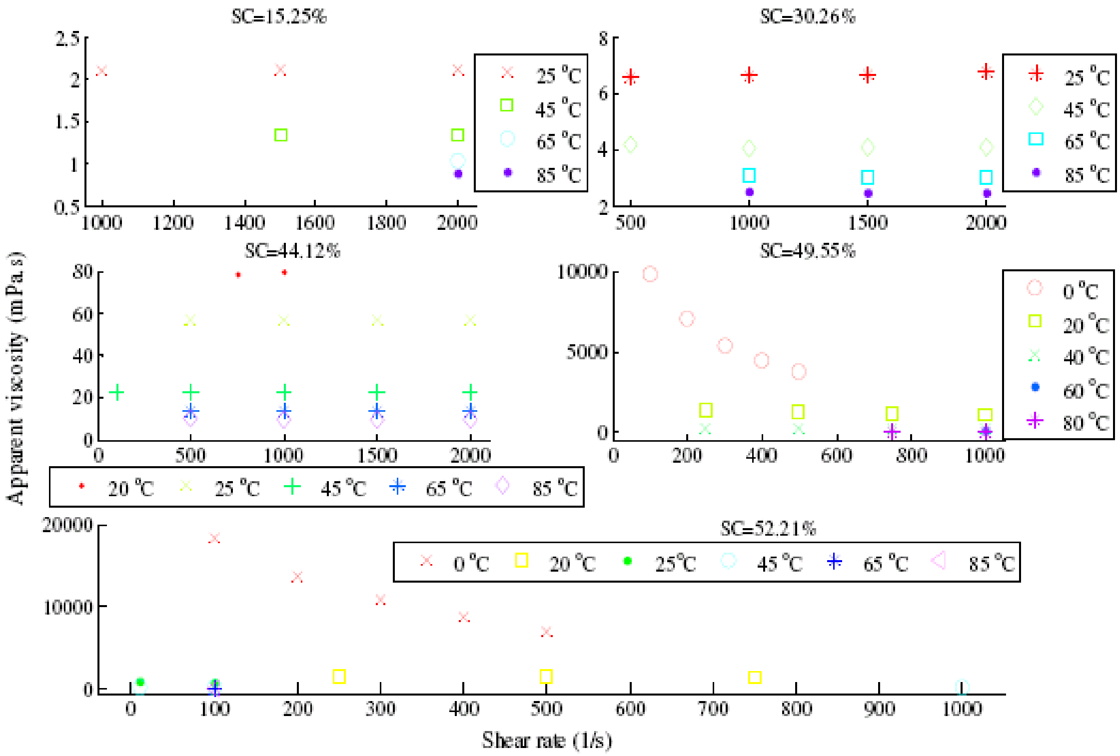


Figure 4.9 Viscosity data for E408 at different process conditions;
(SC = solids concentration)

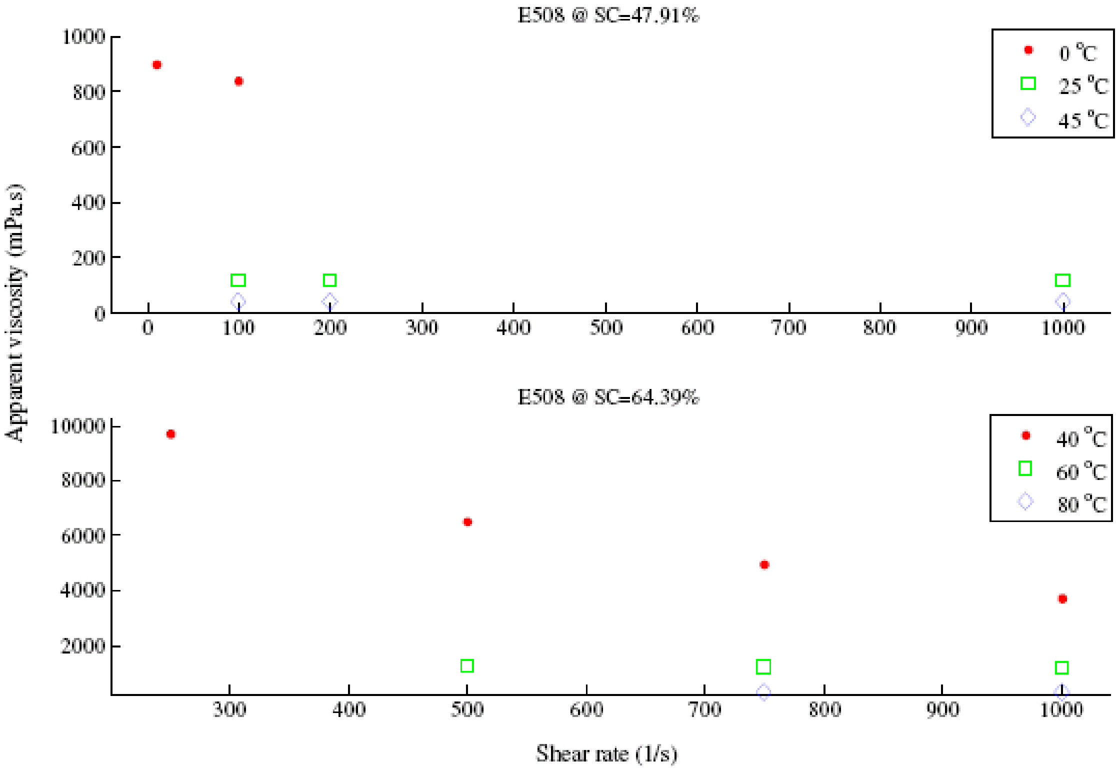


Figure 4.10 Viscosity data for E508 at different process conditions;
(SC=solids concentration)

For example, E408 and E508, having similar RA contents, were obtained around the same time from different evaporator sets. The number 4 evaporators include oxidation process while the number 5 evaporators do not. Although E508 and E509 were obtained from the same number 5 evaporators, the latter having approximately double the RA content in the former, was obtained about a year later. This means changes may have occurred in the process conditions at the evaporators which consequently affect the liquors viscosities.

As noted earlier, temperature has a significant effect on the degree of shear-thinning with or without thixotropic behaviours of the liquors. As temperature increases, the degree of shear-thinning, with or without thixotropic behaviour, reduces dramatically. As shown in Figures 4.6, 4.9 and 4.10, from around 20-25 $^{o}$C upwards, all the samples at solids concentrations <~50% are nearly Newtonian. These findings agree with the works of most previous researchers as discussed earlier in chapter 3. However, as temperature is reduced to below this range, for example, E408@ 0 $^{o}$C and solids concentration=~50% has high viscosities and exhibits strong shear-thinning characteristic. Hitherto, most of the reports on black liquor viscosity are based on room temperature and above, therefore the results of this work are a clear indication of the transition in the rheological behaviours of the black liquor at very low temperature. It simply shows that the Newtonian data obtained at room temperature can not be extrapolated to lower temperature where E408 exhibits shear-thinning behaviour. E509@~50% shows a very weak shear-thinning behaviour at the same 0 $^{o}$C contrary to what is observed for the E408. This is a clear indication that the two liquors are compositionally different. Although only a few data points are available for E508@47.91% and 0 $^{o}$C, it is clear that its characteristic at ~50% may be similar to that of E509 at solids concentration=~ 50% and at 0 $^{o}$C. For all the samples, at all solids concentrations and at very high temperatures (>80$^{o}$C) similar to the ones found in the real mills, all liquor viscosities seem to be independent of shear rate. This finding is supported by the existing reports as discussed in chapter 3. Therefore, the black liquors in this study can be conveniently treated as Newtonian fluids for practical applications in the mill.

Finally, four roughly overlapping rheological regions are observed depending on the solids concentration, temperature and the liquor type:

- the non-Newtonian region of solids concentration <=50% and low temperatures,
- the non-Newtonian region of solids concentration > 50% and low-to-moderate temperatures,
- the Newtonian region of solids concentration < 50% and moderate-to-high temperatures and,
- the Newtonian region of solids concentration > 50% and very high temperatures.

The onsets and the spans of the two Newtonian and the two non-Newtonian regions depend on temperature, solids concentration, shear rate and the liquor composition. The complexity in the rheological behaviours of the black liquors over wide ranges of process conditions for different liquors has posed significant challenges to previous researchers while attempting to model the viscosity of black liquor as a function of its influential variables. The non-Newtonian regions appear to be describable by a power law while the Newtonian regions can simply be modelled as functions of solids concentration and temperature. However, it has been extremely difficult to develop single functional models describing the joint effects of shear rate, temperature and solids concentration to capture all these complexities over wide ranges of the operating conditions; this has been successfully tackled in this project and will be described in more details in Chapters 5 and 6.

### 4.3.2 Effects of Solids Concentration and Temperature

It is observed from Figures 4.6, 4.9 and 4.10 that under similar shear rates, all the samples viscosities increase as solids concentration increases at fixed temperatures while they decrease with increasing temperature at constant solids concentration. The degree of the increase (with respect to solids concentration) or decrease (with respect to temperature) is not obvious. In order to independently observe the temperature or solids concentration dependence of the samples viscosities, averaged Newtonian viscosity data at relevant shear rates are obtained and thus solids concentration-viscosity (at constant temperatures) and temperature-viscosity (at constant solids concentrations) relationships for E509 are presented in Figs 4.11 and 4.12 for illustration. The viscosity data for E509 were chosen because they cover largest ranges of solids concentration (~25-70%) and temperature (0-115 $^{o}$C).

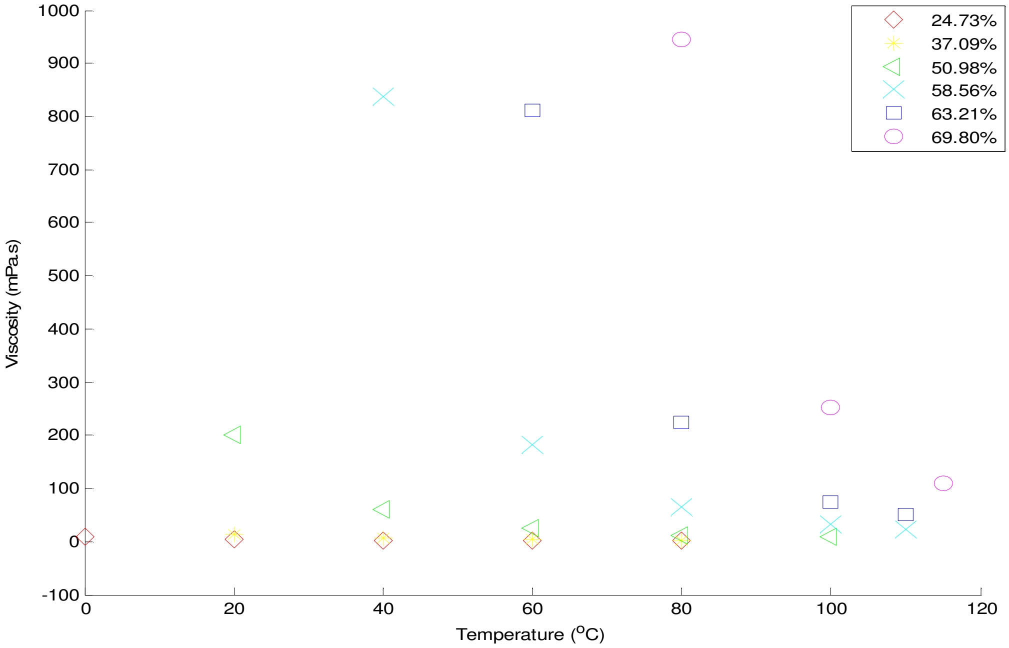


Figure 4.11 Effect of temperature on the viscosity of E509

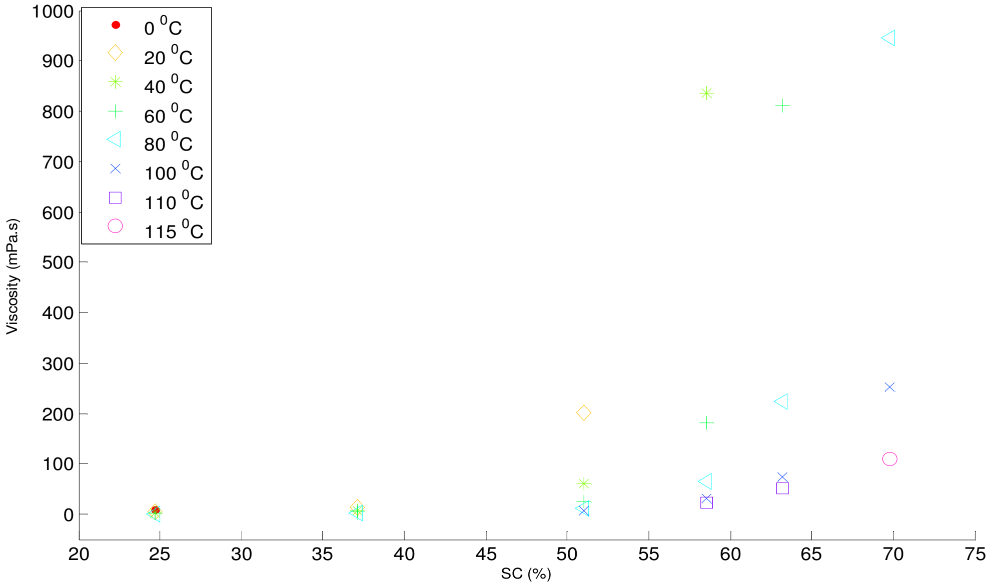


Figure 4.12 Effect of solids concentration on the viscosity of E509

Fig 4.11 shows that at a fixed solids concentration, viscosity decreases with increasing temperature. The effect of temperature on the liquor viscosity is mild at lower concentrations (up to around 50%) but becomes stronger in an exponential form as the solids concentration increases beyond 50%. The observed trend is in agreement with findings published in the literature, as discussed in chapter 3.

Conversely, as shown in Fig 4.12 at any fixed temperature, viscosity is an increasing function of solids concentration. This also is in agreement with the existing reports, as presented in chapter 3. At temperatures >=40 °C and at solids concentrations<~50%, black liquor viscosity is a weak function of solids concentration. However, within the ranges of process conditions investigated, at solids concentrations > 50% and temperatures lower than 100 °C, the effect of solids concentration on the liquor viscosity is very pronounced, typically a strong exponential growth as noted by previous workers (see chapter 3) but the rate of the exponential growth decreases as the temperature increases beyond 100 °C.

As a result of the differences in the rheological behaviours of black liquor over different ranges of solids concentrations and temperatures, it seems a single functional model that describes the joint effects of solids concentration and temperature on black liquor viscosity may be difficult to obtain over these wide ranges of conditions. This agrees with previous researches (to be discussed in detail in chapter 5) where most of the developed models are applicable over limited ranges of solids concentrations and temperatures.

At low solids concentrations (<=50%), black liquors are treated as dilute polymer solutions and models developed for dilute polymer solutions have been used to correlate black liquor viscosity data (Zaman and Fricke 1991). At high solids concentrations (>50%), Masse and Co-workers (cited by (Zaman and Fricke 1994b)) suggested that black liquors behave as polymer continuous materials (solids dissolved in water) and theories developed for polymer melts or plasticized polymers should be applicable to concentrated black liquors.

### 4.3.3 Effects of Residual Alkali (RA) Content or/and Oxidation on the Viscosity of Black liquor

The effects of RA or/and oxidation on the viscosity of black liquors are examined on E408, E508 and E509 at solids concentrations <=~50 % (representing low solids region) and solids concentrations>60% (representing high solids region); the results are presented in Tables 4.2 and 4.3.

Table 4.2 Effects of residual alkali (RA) or/and oxidation on black liquor viscosity at low solids concentration (SC)

| Property | E408 | E508 | E509 |
|---|---|---|---|
| SC (%) | 49.95 | 47.91 | 50.98 |
| RA(g/L) | 10.72* | 12.86 | 24.40 |
| Viscosity (mPa.s)<br>@$0^oC$ , $100s^{-1}$ | ~10000 | ~850 | ~1000 |

Table 4.3 Effects of residual alkali (RA) or/and oxidation on black liquor viscosity at high solids concentration (SC)

| Property | E508 | E509 |
|---|---|---|
| SC (%) | 63-64 | 63-64 |
| RA(g/L) | ~x** | ~2x |
| Viscosity (mPa.s)<br>@$40^oC$ , 200-$300s^{-1}$ | ~10000 | ~5000 |

Comments:

* This is the RA content of E408@ 52.21% and so the actual value for the 49.95% solids concentration (obtained by dilution) should be slightly less than the reported value.

** x was not measured but one could safely assume that x should be greater than 12.86g/L (RA content of E508@ ~50%) since RA increases with solids concentration (if no chemical change occurs for the same liquor). At solids concentration=~50%, RA content of E509 is ~ twice that of E508. Again, one could safely assume that at solids concentration=63-64%, RA content of E509 would be approximately twice that of E508.

At low solids region, despite the fact that RA content in E509 is roughly twice that of E508, the liquors viscosities as measured under the reported conditions are nearly the same. The noticeable difference in their viscosities can be attributed to about 3% difference in their reported solids concentrations. It seems the amounts of RA in these liquors do not play a significant role on their viscosities at low solids concentrations. This agrees with the findings of the previous workers as discussed in chapter 3. In comparison with E408 that was obtained around the same time as E508 but at another evaporator line (number 5), the viscosity of E408 at the condition stated is nearly 10 times that of both E508 and E509. Although it has been reported that at very low or very high RA content, viscosity of black liquor can be very high, the RA contents of E408 and E508 are roughly the same and therefore can not be said to be the factor responsible for this large difference in their viscosities. Also, the difference (~2%) in their solids concentrations can not be the main factor responsible for this very large difference in their viscosities since the strong exponential dependence on solids concentration of viscosity does not occur until solids concentrations >= 50%. E509 has roughly double the RA content of E408 and E508 and yet there was little difference in the viscosities of E508 and E509. Therefore, there must be another strong factor responsible for the marked difference in the liquors (obtained from number 4 and number 5 evaporator sets) viscosities at these low solids concentrations. The inclusion of oxidation process in the number 4 evaporators that is not available in the number 5 evaporator may be responsible for the marked difference observed between the viscosities of E408 and that of E508 & E509. Previous workers have noted that black liquor oxidation can lead to a high viscosity (see Table 3.4). It therefore seems the viscosity of black liquor from the number 4 evaporator is significantly higher than that of the number 5 evaporator because of the oxidation process involved at the number 4 evaporator.

At high solids (solids concentrations=63-64%), the RA has a significant inverse effect on the viscosities of E508 and E509. Both E508 and E509 were obtained from the same number 5 evaporators at about a year interval and did not pass through the oxidation unit; therefore the significant difference in their viscosities under the similar conditions as reported in Table 4.3 can not be attributed to oxidation. It is very likely that the difference in their viscosities is due to the difference in their RA contents. The RA content of E509 is nearly twice that of E508 that yields approximately half of the viscosity of E508 for E509 under similar conditions. The overall findings regarding the effects of RA contents or/and oxidation on the viscosities of low and high solids black liquors agree with the existing reports (see section 3.3.3.3) that the effects of RA on black liquor viscosity is not significant (weak) at lower solids concentrations but becomes increasingly significant (strong) as solids concentration increases to and above 70%.

### 4.3.4 Effect of Liquor Heat Treatment (LHT) on Black Liquor Viscosity

The effect of LHT on black liquor viscosity was investigated at low and high solids concentrations on E4E508 and E408, respectively. The results of the investigations are reported in Tables 4.4 and 4.5.

Table 4.4 Effect of LHT on the viscosity of black liquor at low solids concentration (SC)

| Property | Fresh E4E508 | LHT E4E508 |
|---|---|---|
| SC (%) | 12.30 | 12.31 |
| Viscosity (mPa.s) | | |
| @0 °C, 2000$s^{-1}$ | 3.4365 | 3.4095 |
| @25 °C, 2000$s^{-1}$ | 1.8285 | 1.73 |
| pH | 12.49@13.7 °C | 10.94@14.8 °C |

Table 4.5 Effect of LHT on the viscosity of black liquor at high solids concentration (SC)

| Property | Fresh E408 | LHT E408 |
|---|---|---|
| SC (%) | 52.21 | 51 |
| Viscosity (mPa.s) | | |
| @0 °C, 100s-1 | 18320 | 637.5 |
| @25 °C,100s-1 | 818.6 | 140.5 |
| pH | 13.47@15.7 °C | 11.29@16.8 °C |

At low solids concentration as shown in Table 4.4, the effect of LHT on black liquor viscosity is negligible. Although, there was a decrease in the pH of the fresh liquor after LHT that may signify that depolymerization took place during the LHT process, this does not reflect in the reported values of the viscosities of the fresh and LHT E4E508. However, the difference in the pHs before and after LHT may be attributed to oxidation reaction that may have taken place in the autoclave instead of lignin depolymerization since nitrogen gas was not used to purge the LHT system prior to the LHT process.

At high solids concentrations as shown in Table 4.5, the effect of LHT on the viscosity of the black liquor is very significant. The difference in the reported pHs before and after the

LHT process can be attributed mainly to LHT, which must have led to depolymerization of the large polymers. Oxidation is unlikely to have been a major factor as nitrogen gas was used to purge oxygen from the autoclave prior to the LHT process. This reflects in the large difference observed between the viscosities of the fresh E408 and the LHT E408. The findings as reported for the LHT of the black liquors at both low and high solids concentrations agree with the existing black liquor data where previous workers (see section 3.3.3.5) have observed that the effect of LHT on black liquor viscosity increases with increase in solids concentration, and suggested that there is a more pronounced reaction at higher solids concentration due to an increase in alkali concentration.

## 4.4 CONCLUSIONS AND RECOMMENDATIONS

The effects of shear rate, solids concentration, temperature, and composition on the viscosities of New Zealand black liquors that were obtained via almost 100% softwood kraft pulping process at the CHHP&P Kinleith mill, Tokoroa, New Zealand, were investigated over a wide range of process conditions. The investigation on the effect of composition on the black liquor viscosity was based on the effects of RA content of the liquor and two post-pulping processes, oxidation and LHT.

The results of the study of the effects of shear rate on black liquor viscosity show that at low solids concentrations(<50%) and at moderate to high temperatures similar to those found under recovery boiler firing conditions, the liquors typically are Newtonian (shear-independent) fluids. This agrees with literature data on most softwood black liquor viscosity. However, it is interesting to note that the black liquor viscosity data in the literature are reported at temperatures from around 20-25 $^{o}$C and above and as result, most liquors at low solids concentrations (<50%) are typically treated as Newtonian fluids. The results of this study show that at lower temperatures (0-20 $^{o}$C) and solids concentrations < 50%, black liquor, depending on its composition, can exhibit non-Newtonian behaviour; therefore models developed for low solids concentrations based on Newtonian fluid assumption may fail if the models predictions are extrapolated to temperatures below 20-25 $^{o}$C. Consequently, models that are capable of describing Newtonian or/and non-Newtonian behaviours of black liquors at these low temperatures, for both low and high solids concentrations, are essential. Development of such a model is considered in Chapter 5.

At high solids concentrations (>50%), the liquors show Newtonian or shear-thinning, with or without thixotropic behaviour. The behaviour exhibited depends on the liquor type and process conditions. The degree of shear-thinning behaviour decreases and increases as temperature increases and solids concentration increases, respectively. The shear rate, solids concentration and temperature at which the liquors' rheological behaviour changes from Newtonian to non-Newtonian or from non-Newtonian to Newtonian vary from liquor to liquor (composition-dependent). However, within the ranges of process conditions investigated, the liquors at all solids concentrations show Newtonian behaviour at very high temperatures (>100 $^{o}$C) similar to the recovery boilers' firing conditions and when the actual viscosity value is less than around 1000 cP. This value is double that of the practical pumping limit for black liquors in the mills. It is concluded that New Zealand black liquors can be described as Newtonian fluids for high-temperature practical applications. This is in agreement with findings in the literature for most softwood kraft black liquors (see section 3.3.2).

The investigation of the effects of solids concentration and temperature on the liquor viscosities under shear-independent conditions shows that the liquor viscosities increase with increasing solids concentration (exponentially at solids concentrations>50% and at low temperatures) and decrease with increasing temperature (exponentially at high solids concentrations). These findings agree with literature data on black liquor viscosity (see section 3.3.1).

The results of the investigation of the effects of RA content, LHT, and oxidation on black liquors' viscosities show that all the three factors have significant impact on the viscosities of New Zealand black liquors at fixed solids concentration, temperature and shear rate under certain conditions. Within the ranges of conditions investigated in this study, at solids concentrations <=~ 50%, oxidation increases the liquor viscosity while both an increase in RA content and the application of LHT (at solids concentration=~12%) do not show appreciable effects on the liquors' viscosities. However, both an increase in RA content at solids concentration>60% and the application of LHT at solids concentration>50% decrease the liquor viscosities appreciably; the former by at least ~50% and the latter permanently by~83%. These agree with existing reports (see chapter 3). It is concluded that in addition to shear rate, solids concentration and temperature, viscosities of New Zealand black liquors are sensitive to the effects of RA contents of the high solids concentration liquors, post-pulping processes such as oxidation and LHT and can therefore be used in conjunction with temperature to manipulate the liquor viscosity. This is particularly important in the black liquor processing units where high viscosity problems may be caused by factors other than an increase in solids concentration. Based on the existing reports (see chapter 3), the initial RA content of the black liquor determines the direction of viscosity changes when there is alkali addition, oxidation or LHT; therefore, RA is a very strong variable that determines the extent and direction of viscosity change via any of the above-mentioned post-pulping processes. Although an online approach for measuring and monitoring RA content of weak black liquor exists (Hodges et al. 2006), it is unfortunately not applicable to high-solids (concentrated) black liquors. It may be helpful to devise an online means to continuously measure and monitor RA content of concentrated black liquor. Black liquor RA content can be manipulated in conjunction with temperature for viscosity control where there is high viscosity problem and temperature control alone is causing flashing related problems in the recovery boiler.

Finally, the viscosity data obtained in this chapter is very important for the development of black liquor viscosity models for the improvement in the design and operation of the kraft recovery process units-pumps, evaporators and the recovery boilers. Unfortunately, due to the wide rheological behaviours of black liquors over wide ranges of process conditions, as observed in this study and existing reports, it is clear that it will be very difficult to obtain a single functional model to describe the joint effects of solids concentration and temperature (for shear-independent regions) or solids concentration, temperature and shear rate (for shear-dependent or all the overlapping rheological regions) on viscosity of New Zealand black liquors. Due to this difficulty, existing models are only applicable to limited ranges of process conditions. A data-driven model could be a good candidate for this type of problem and is attempted in chapter 5. Another important observation is that the rheological behaviours of the liquors vary with composition and it has been a daunting task to develop robust composition-independent models; this study addresses this problem in chapter 6.

# 5.0 COMPOSITION-DEPENDENT PREDICTIVE MODELS FOR KRAFT BLACK LIQUOR VISCOSITY

## 5.1 INTRODUCTION

In chapter 4, the rheological behaviour of the New Zealand black liquors were studied over a wide range of process conditions. The liquors exhibit both Newtonian and non-Newtonian behaviours. The transitions from Newtonian to non-Newtonian behaviour depend strongly on solids concentration, temperature, and the liquor composition. However, all the liquors exhibit Newtonian or near-Newtonian behaviour when their apparent viscosity <=1000 cP. In order to be able to translate these rheological data to the form that is useful for process design, analysis and improvement of process equipment in a pulp and paper mill, it is essential to develop accurate and reliable models to describe the relationship between the input variables (factors influencing black liquor viscosity) and the output variable (viscosity). In this chapter, an overview of the existing black liquor viscosity models is presented. The application of some of the existing liquor-dependent models to New Zealand black liquor viscosity data in direct and modified forms is described. Two new models, binomial and artificial neural networks (ANNs), are developed to address the limitations of the existing liquor-dependent models.

## 5.2 BACKGROUND

Literature survey shows that the models relating black liquor viscosity to some or all of its four main influential variables (solids concentration, temperature, shear rate and the liquor composition) are mainly of two forms. In the first form, viscosity is described as a function of a combined solids concentration and temperature (e.g. Ghosh 1993) or combined solids concentration, temperature and shear rate (e.g. Zaman and Fricke 1995b) for specific liquor. The parameters of these models are liquor-dependent and must be correlated with the liquor composition or the factors influencing the composition for them to be suitable for online application. In the second form, viscosity is explicitly correlated with black liquor composition or factors affecting black liquor composition. Although the latter model form is rare in the literature, they are potentially suitable for online application. The downside of the available ones are that they are either limited to low solids concentrations and so are not suitable at the recovery boiler where high solids liquor is being fired or there is no guarantee that the composition variables in the models can adequately describe the effect of composition on the liquor viscosity or can be continuously measured online.

The two model forms described above generally fall into three categories: low solids concentrations (<=50%) (see Zaman and Fricke 1991; Zaman and Fricke 1994a; Zaman and Fricke 1995a; Moosavifar et al. 2006), high solids concentrations (>50%) (see Wennberg 1985; Zaman and Fricke 1991; Zaman and Fricke 1994b; Zaman and Fricke 1995b; Zaman and Fricke 1995c; Zaman and Fricke 1996) and all solids concentrations (see Adams and Frederick 1988; Ghosh 1993; Frederick 1997; Vakkilainen 1999) models. The majority of the models are applicable to limited ranges of solids concentrations (low or high) and the remaining ones that are applicable to a wide range of solids concentrations are limited to a narrow range of other process conditions (temperature and/or shear rate). It is not surprising that none of the existing functional models (linear or non-linear regression) is able to describe the relationship between black liquor viscosity and all its influential variables over a wide range of process conditions because of the complex rheological behaviour of black liquor over such conditions. The literature models, their limitations, applicability (range of process conditions), sensitivities to black liquor composition, the ease of measuring their input variables online and other issues pertinent to these models are summarised in Appendix A.

## 5.3 MODEL DEVELOPMENT

### 5.3.1 Model Form Suitable For Online Application

An important factor to consider before any model can be successfully used as a soft sensor is that its input variables must be continuously measurable or computable online. In most mills under typical operating conditions, softwood kraft black liquor is a Newtonian fluid; therefore, a model that relates black liquor viscosity to solids concentration and temperature can be installed as a soft sensor. Fortunately in most mills, online measurements of solids concentration and temperature of the liquor are routinely done (Ghosh 1993). However, black liquor composition is not constant and the parameters of the above type of model must be correlated with black liquor composition so that it can give robust predictions in the presence of composition variations.

Some hardwood black liquors are known to exhibit shear-thinning behaviour (Soderhjelm 1988) under process conditions and so, the inclusion of shear rate/shear stress as one of the input variables in their viscosity models is expedient. Shear rate or shear stress is not measured directly in the mills but should be computable from the liquor flow rate and pipe dimensions or torque-dependent equipment such as pumps. Many of the composition-dependent models presented in appendix A were developed based on solids concentration and temperature or solids concentration, temperature and shear rate. Take note that none of these models was developed based on the viscosity data obtained at temperatures below 20 $^{o}$C; whereas the data in this study include those obtained at 0 $^{o}$C. In the absence of other models, they were firstly used to fit the data in this study from 0-115 $^{o}$C before the application of the proposed models.

### 5.3.2 Criteria for the Evaluation of Model Accuracy and Adequacy

The accuracy of the models described in this thesis was examined based on two main performance criteria: (i) Coefficient of determination, $R^2$, which is the square of correlation coefficient (R) between the model predictions and experimental observations. $R^2=0$ indicates a poor model while $R^2=1$ is a very good model. (ii) It is known that sometimes, a model with high $R^2$ is not necessarily a very good model (*NIST/SEMATECH* 2010), most especially where the fitted model involves nonlinear transformation of the response variable(s). For example, most of the models described in appendix A involve log-transformed response variable (viscosity or relative viscosity). The parameters of these models were obtained when the viscosity was log-transformed; there is no guarantee that when the model predictions are translated to the actual scale, the level of accuracy attained in the transformed state will also be attained in the untransformed state. Therefore, maximum absolute relative error (MARE (%)) as given by Equation (5.1) was used in addition to $R^2$ to evaluate the goodness of the empirical models described in this thesis. A model having MARE<=5% in addition to a very high $R^2$ (~1) is considered accurate.

$$\text{MARE (\%)} = 100*\text{maximum} \left( \left| \frac{\mu_p - \mu_a}{\mu_a} \right| \right) \tag{5.1}$$

where $\mu_p$ =predicted viscosity (mPa.s) in an untransformed state; $\mu_a$ = actual viscosity (mPa.s) in an untransformed state; $|\cdot|$ =modulus (absolute value) of the terms in the bracket; * is multiplication sign.

The goodness of the model parameter estimates of any model plays significant role in its overall usefulness. A parameter that is poorly estimated or not known precisely may cause the model to perform poorly when exposed to new inputs. The model may fail to generalize or give stable and logical predictions consistently. Where possible in this thesis, the confidence intervals of the parameter estimates were determined based on 95% confidence level (CL). A model whose parameter estimates have narrow  is deemed good and adequate (Motulsky and Christopoulos 2003). Based on the model accuracy criteria and possibly confidence intervals of the model parameter estimates, the developed models were compared. Some of them were then subjected to a preliminary validation (test for model generalization) where possible. The validation procedure is discussed in the calculations, results and discussion section. Detailed statistical modelling principles are beyond the scope of this thesis and readers are referred to the following references for background study (Draper and Smith 1981; Motulsky and Christopoulos 2003; The MathWorks Inc 2007; *NIST/SEMATECH* 2010; Statsoft Inc 2010). The procedures used to evaluate the accuracies and adequacies of the ANNs are discussed in section 5.3.4.2.

### 5.3.3 Data Collection

The data required to develop relevant models depend on the variables involved in the model of interest. The main variables of interest in the composition-dependent models summarised in Appendix A and the proposed models described in section 5.3.4 are solids concentration, temperature, shear rate, shear viscosity, zero shear viscosity, glass transition temperature, viscosity of water, density of water, and density of black liquor. The procedures utilised for obtaining the relevant data for these variables are presented in this section.

#### 5.3.3.1 Shear viscosity and density

It is already established that the black liquor (including New Zealand black liquors) rheological behaviour varies from liquor to liquor and requires different liquor-dependent models. Therefore, only the E509 viscosity data (the largest data) were fitted to the relevant models and the approaches utilized here can be extended to other liquors.

The original E509 viscosity data were obtained at solids concentration=~25-70%, shear rate=10-2000 $s^{-1}$ and temperature=0-115 $^{o}$C, as reported in Chapter 4. The solids concentration of the weak black liquor is usually around 14-18% when it leaves the digester or before entering the evaporators; therefore, viscosity data at solids concentrations < 25% are required to develop models that cover all practical ranges of solids concentrations for black liquor processing. Viscosity data for black liquor at solids concentration = 0% (100% pure water) and the density of water were obtained from the database of the physical properties of water provided by ThermExcel (2003). Viscosities of water were obtained over the temperature range 0-160 $^{o}$C while its density was obtained for the range 4-160 $^{o}$C. The water viscosity ($\mu_w$) and density ($\rho_w$) data were fitted to the models given by Equations (5.2) and (5.3), respectively:

$$\mu_w \text{(mPa.s)}=0.355-0.2053z+0.1006z^2-0.05168z^3+0.02461z^4-0.001536z^5-0.0006853z^6 - 0.003967z^7+0.001774z^8 \quad (5.2)$$

$$\rho_w \text{(kg/m}^3\text{)} = 970.3-29.04y-4.998y^2+0.5187y^3-0.2287y^4+0.0512y^5 \quad (5.3)$$

where z= (T-80)/46.62; y= (T-82)/45.47; T=temperature ($^{0}$C). The performance measures of $\mu_w$ are: $R^2$=1.0 and MARE =0.71% while $R^2$=1.0 and MARE=0.0049% are the performance measures of $\rho_w$. When Eqn (5.3) was used to extrapolate water density to 0 $^{o}$C, the absolute relative error is 0.016%. The levels of the accuracies of Equations (5.2) and (5.3) are considered adequate for this study. Therefore they were used to estimate viscosity and density of water (or black liquor @ solids concentration=0%) where necessary. This eliminates the need for retrieving information from these data points manually and repeatedly.

E509 density was not measured but was estimated using Equation (5.4a) proposed by Fricke (cited in (Frederick 1997) and Equation (5.4b) (Frederick 1997).

$$\rho_{BL}^{25} \text{(kg/m}^3\text{)}=997+649S \quad (5.4a)$$

$$\rho_{BL}^{T} \text{(kg/m}^3\text{)}= \rho_{BL}^{25} (1-3.69*10^{-4}(T-25)-1.94*10^{-6}*(T-25)^2) \quad (5.4b)$$

where $\rho_{BL}^{25}$ is the black liquor density at 25 $^{o}$C ; $\rho_{BL}^{T}$ is the liquor density at temperature, T($^{o}$C); S is the liquor's dry solids mass fraction (0-1).

The parameters of Eqn (5.4b) are relatively insensitive to the liquor composition (Zaman et al. 1994), therefore Eqn (5.4b) was assumed to be applicable to any kraft black liquors. It is valid for temperature range 20-100 $^{o}$C and solids concentrations up to 65 % (Frederick 1997). The model is prone to higher prediction errors at solids concentrations

> 70% (Zaman et al. 1997). Therefore, it is deemed suitable for estimating the density of E509 having largest solids concentration=~70%. Although Eqns (5.4a) and (5.4b) were not defined specifically for temperatures < 20 °C, they were used to obtain black liquor densities from 0-115 °C in this study. The estimation errors are not expected to be pronounced.

At low solids concentrations (<=50%), black liquor exhibits Newtonian behaviour. As shown for E509 in Chapter 4, up to around 50.98% and all temperatures considered, E509 is a Newtonian or nearly a Newtonian fluid. At higher solids concentrations (> 50.98%), it shows shear-thinning behaviour at some process conditions. The variation of the viscosity of a shear-thinning fluid will often reach a limiting value at very low shear rates or at high shear rates where it behaves typically as Newtonian fluid. The limiting viscosity at low shear rates is termed zero shear viscosity (ZSV), $\mu_0$ while the limiting viscosity at very high shear rates is termed infinite shear viscosity, $\mu_\infty$ (Bhattacharya 2002).

$\mu_0$ can not always be measured but must be estimated by extrapolation in some cases (Zaman and Fricke 1994b). Cross model (Cross 1965) given in Eqn (5.5) has been used to estimate zero shear viscosity for black liquor(see Zaman and Fricke 1994b) from viscosity-shear rate data obtained at easily measurable shear rates.

$$\mu_0 = \mu_\infty + \frac{\mu_0 - \mu_\infty}{1 + (C\gamma)^m} \tag{5.5}$$

$\gamma$ is the shear rate ($s^{-1}$), C (sec) is the Cross time constant and m is the dimensionless Cross rate constant (Cunningham 2010). In practice, $\mu_\infty$ may not be attained and so is deemed to be negligible when compared with zero shear viscosity and viscosities at other measurable shear rates. Setting $\mu_\infty$=0.0 and using the nonlinear curve-fitting tools in the MATLAB® optimization toolbox, the parameters (including $\mu_0$) of the model described in Equation (5.5) were obtained from the shear-dependent data presented in Chapter 4. The zero shear viscosity data (where black liquor exhibits non-Newtonian behaviour) obtained above were combined with average viscosity data where E509 exhibits Newtonian or near-Newtonian behaviour to obtain complete Newtonian viscosity data at solids concentration = 0-70%, T = 0-115 °C. These data were used to develop various

Newtonian models described in this Chapter. In order to be able to develop functional models that are capable of predicting both the Newtonian and non-Newtonian behaviours of E509, the average viscosity data obtained above, where E509 behaves typically as a Newtonian fluid, were combined with the shear-dependent data where E509 exhibits non-Newtonian behaviour as discussed in Chapter 4. The complete shear-dependent data were used to develop functional shear-sensitive viscosity models for E509.

In the ANN modelling, the input and response variables data are normally pre-processed so that all the data fall within [-1, 1] or [0, 1] to enhance its training (Demuth et al. 2008; Statsoft Inc 2010). In some cases, where the pattern in the data is exponential or in power law form, it is advisable they are log-transformed before applying the mapping or scaling functions (See Demuth et al. 2008). At zero shear conditions where shear rate tends to zero, log (0) is undefined for the scaling process mentioned above. In order to be able to define low shear conditions for ANN modelling, it was assumed that shear rate($s^{-1}$) =$10^{-4}$ =~0. The zero shear viscosity data were then combined with the above shear-dependent data for the purpose of modelling shear-sensitive ANN based viscosity models for E509. Flowing black liquors typically have shear rates of 30-4000 $s^{-1}$ and so using $10^{-4}$ in place of 0.0 for scaling purposes should have negligible effect on the overall modelling procedures and the models' performances. Chhabra and Richardson (2008) have shown that many materials attain $\mu_0$ at shear rates <= 0.01 $s^{-1}$; therefore taking $10^{-4}$ $s^{-1}$ as the low shear rate value is justified for black liquor.

### 5.3.3.2 Glass transition temperature

It has been shown by Fricke and Masse (cited in Zaman and Fricke 1994b) that from around solids concentrations >=43%, black liquor does not freeze but exhibits glass transition behaviour. Zaman and Fricke (1994b; 1995b) measured glass transition temperatures, $T_g$ (K) of high solids softwood black liquors and found that $T_g$ is approximately a linear function of solids concentration at solids concentrations > 50%. They also found that $T_g$ is weakly dependent on the liquor type. In this study, Tg of black liquor was not measured. Based on Zaman's and Fricke's (1994b) report, it was assumed that black liquor $T_g$ is independent of composition, valid at solids concentrations > 50%, and was therefore modelled as a linear function of solids concentration as shown in Eqn (5.6):

$$T_g = b_1+b_2S \tag{5.6}$$

where $b_1$ and $b_2$ are constants and S is the dry solids mass fraction (0.0-1.0). Therefore, Eqn (5.6) was used to provide an estimate of black liquor $T_g$ wherever they were required.

### 5.3.4 Proposed Models

The various models summarised in Appendix A have some limitations. The limitations of the composition-dependent ones include:

(i) Most of these models are applicable over limited ranges of process conditions,

(ii) No guarantee that most of them will give accurate predictions at temperatures below 25 °C; current E509 data are available down to 0 °C,

(iii) Many of them involve variables such as $T_g$, ZSV, and black liquor density, to be measured or computed. $T_g$ is only applicable at solids concentrations > 50% and ZSV can not always be measured,

(iv) Many of them involve log-transformed response variable and their predictions may not be accurate when transformed to actual viscosity scale.

New models are proposed to address one or more of the aforementioned limitations. First, a binomial model (BM) is proposed to be able to model Newtonian viscosity of black liquor purely as a function of solids concentration and temperature and to attempt to address all or some of the limitations (i)-(iii). Secondly, ANN models that attempt to address all of the limitations are developed.

#### 5.3.4.1 Binomial model

The binomial model (BM) proposed in this study is a multiple linear regression whose terms are obtained from the binomial expansion of solids concentration and temperature. In Chapters 3 and 4, it was established that viscosity is an increasing exponential function of solids concentration and a decreasing exponential function of temperature, respectively. Consequently the binomial terms are defined as exponential functions of solids concentration and reduced temperature. The binomial model is developed to address the situation whereby black liquor exhibits purely Newtonian behaviour.

The binomial model is proposed as follows:

$$Z = \sum_{i=1}^{n} (L + M)^{i} \quad (5.7a)$$

$$\bar{\mathbf{Z}} = \left[\overline{Z_1}, \overline{Z_2}, \ldots\ldots.\overline{Z_q}\right] \quad (5.7b)$$

$$\mathbf{a} = \left[a_1, a_2, a_3, \ldots\ldots.a_q\right] \quad (5.7c)$$

$$\log(\mu_{bl}) = \mathbf{a} \bullet \bar{\mathbf{Z}} \quad (5.7d)$$

where $q = 2+3+4+\ldots\ldots n+1$; $L = \exp(S)$ and $M = \exp\left(\frac{T_r}{T}\right)$; S (or solids concentration) is the dry solids mass fraction (0.0-1.0); T is the temperature (K) and $T_r$ is a reference temperature. $T_r$ can be preset to a definite value or adjusted either in a trial-and-error manner or in an iterative parameter search to obtain the best fit. In this study, Tr was set to 273 K or adjusted in a trial-and-error manner to obtain a more accurate fit than when Tr was preset to 273 K; $\mu_{bl}$ is the black liquor viscosity (mPa.s). The model is obtained as follows: after expanding Equation (5.7a) in an increasing order of M for each i, the coefficients of all the terms are set equal to unity and a vector $\bar{\mathbf{Z}}$ in Eqn (5.7b) containing these terms in that order is formed. A vector **a** is then obtained as in Equation (5.7c) and subsequently the model is obtained as a dot product of **a** and $\bar{\mathbf{Z}}$ given by Equation (5.7d). For example when n=2 (2nd order model), q= 2+3=5; and so $Z = L + M + L^2 + 2LM + M^2$, therefore $\bar{\mathbf{Z}} = \left[L, M, L^2, LM, M^2\right]$ and $\mathbf{a} = \left[a_1, a_2, a_3, .a_4, a_5\right]$ and consequently $\log(\mu_{bl}) = a_1L + a_2M + a_3L^2 + a_4LM + a_5M^2$. This is a 5-parameter 2nd order model. The parameters to be estimated are $\left[a_1, a_2, a_3, .a_4, a_5\right]$.

This model eliminates the need for measurement or computation of black liquor density or glass transition temperature required for some of the existing high solids models. It does not require any fundamental parameter measurement; it is purely empirical.

### 5.3.4.2 Artificial neural network models

**Background to artificial neural network**

Artificial neural network (ANN) is the generalization of the mathematical model of biological nervous system (Abraham 2005). It is a highly parallel system that processes information through modifiable weights, thresholds/biases, and mathematical transfer functions (Rounds 2002). They can model any complex nonlinear relationship and approximate any function (with a finite number of discontinuities)(Aggarwal et al. 2005; Demuth et al. 2008). Therefore, they are deemed suitable to model the complex rheological behaviours of black liquor over a wide range of process conditions. Different architectures for, and training algorithms associated with, ANNs are well discussed in the literature; their details will not be presented in this thesis (see Bulsari 1995; Rojas 1996; Smith 1996; Demuth et al. 2008; Statsoft Inc 2010). This thesis describes only the application of the feedforward multilayer ANN to the modelling of black liquor viscosity.

**Feedforward multilayer artificial neural networks**

A feedforward multilayer architecture is the most commonly used ANN and is usually referred to as a universal approximator due to its ability to model any measurable function with a finite number of discontinuities (Demuth et al. 2008). This makes ANN particularly useful for modelling black liquor viscosity, which exhibits complex behaviours over a wide range of process conditions. In feedforward networks, the signal flow is from the input to the output units, strictly in a feedforward direction. The data processing can extend over one or several layers of neurons, but no feedback connections are present (Abraham 2005). A typical 3-layer feedforward ANN is shown in Figure 5.1. It has inputs and three layers (each layer contains an interconnection of neurons). Each neuron contains weights 'w', biases 'b', a nonlinear sigmoid transfer function '$f$ ', (such as a hyperbolic tangent function in the hidden layer) and usually a linear transfer function in the output layer. The nonlinear sigmoid functions in the network's hidden layer give ANN great computational flexibility and enable it to learn nonlinear and linear relationships between input and output variables (Demuth et al. 2008). In Figure 5.1, layers 1 and 2 are called hidden layers while layer 3 is the output ($\mathbf{a}^3$) layer. Some authors refer to the input(p1,p2,……$p_R$) as input layer or fourth layer and with such notation, ANN is described as having an input layer, one or more hidden layers and the last layer, an output layer. In this thesis, the input layer terminology is not used. The input is described simply as inputs. The number of neurons in the output layer usually corresponds to the number of response variables. The output from layer 1 ($\mathbf{a}^1$ ) becomes an input to layer 2 and output from layer 2 ($\mathbf{a}^2$) becomes an input to layer 3 and so on depending on the number of hidden layers used. The subscript ‘i’ in **a** is associated with the $i_{th}$ neuron in each layer**.**

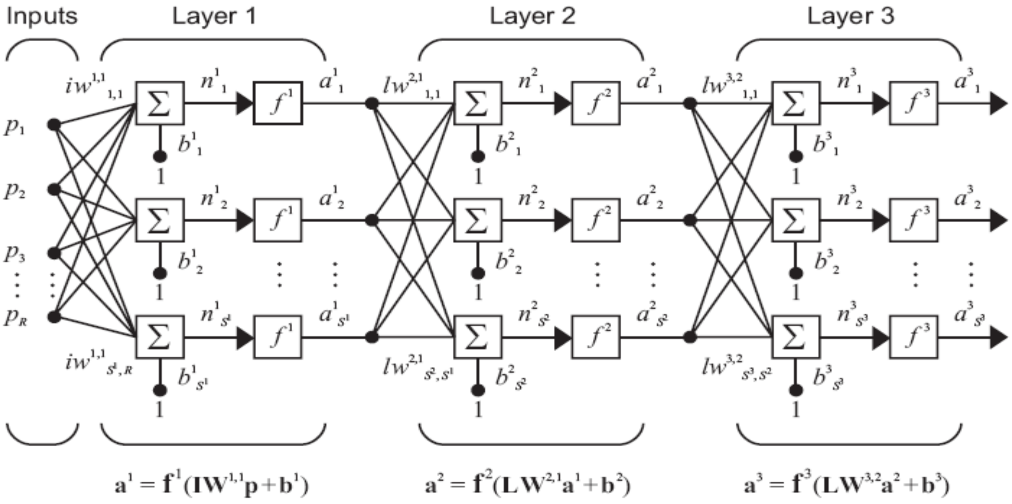


Figure 5.1 A typical 3-layer feedforward ANN (Demuth et al. 2008)

Overall output matrix of the above network is given by Eqn 5.8 (Demuth et al. 2008):

$$\mathbf{a}^3 = \mathbf{f}^3(\mathbf{LW}^{3,2}\mathbf{f}^2(\mathbf{LW}^{2,1}\mathbf{f}^1(\mathbf{IW}^{1,1}\mathbf{p}+\mathbf{b}^1)+\mathbf{b}^2)+\mathbf{b}^3) \tag{5.8}$$

A simplified form of Fig 5.1 is as shown in Figure 5.2.

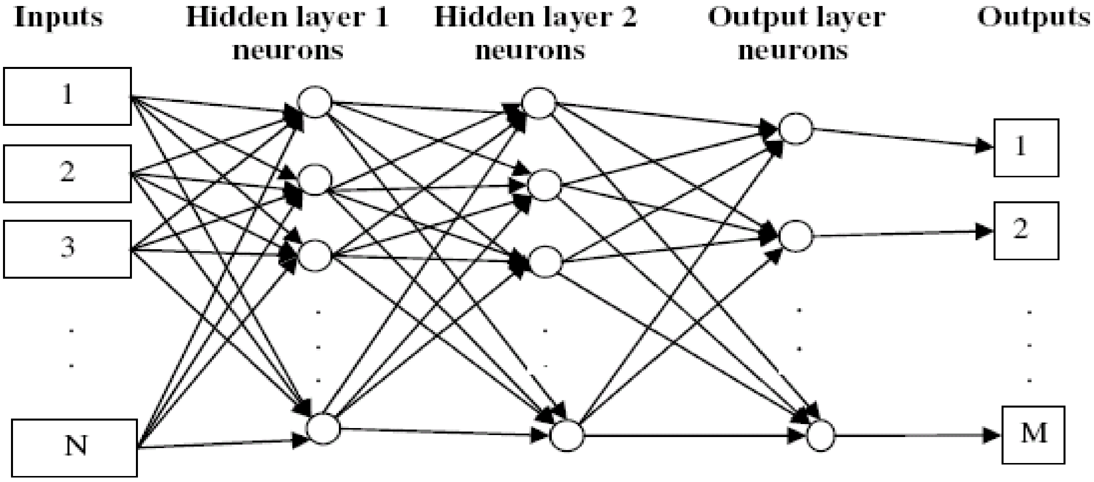


Figure 5.2 A simplified model of a typical 3-layer feedforward ANN

Throughout this thesis, the ANN of the form given in Fig 5.1(or Fig. 5.2) is used. The number of hidden layers used is determined by the complexity of the problem considered. In addition, hyperbolic tangent (tansig) sigmoid transfer function of the form shown in Figure 5.3a and a linear transfer (purelin) function as shown in Fig 5.3b are used in the hidden and output neurons respectively, throughout this study.

(a) Hyperbolic tangent sigmoid transfer function (b) Linear transfer function

Figure 5.3 Transfer functions used in this thesis (Demuth et al. 2008)

### Supervised training of an ANN using Bayesian regularization

An ANN needs to be properly configured so that a set of inputs produces a desired set of outputs (Abraham 2005). The process of configuring the network involves the selection of a network structure, number of hidden and output layers, choice of activation or transfer functions, selecting the number of neurons in each layer and subsequent setting of the network weights and biases. The totality of these steps is called training (Hirschen and Scha¨fer 2006) and is usually done in an iterative manner. In a supervised training/learning, such as the feedforward multilayer ANN trained using backpropagation, the network is trained based on a given set of inputs and desired output sets (Rounds 2002; Abraham 2005). The ANNs reported in this thesis were trained using the automated Bayesian regularization algorithm available in the MATLAB® neural network (neural network) toolbox.

One of the major problems associated with the training of ANN is that of overfitting. During training, the network prediction error can be driven to a very small value as the input and output data are presented to the network. However, when the networks are exposed to new inputs, they perform poorly. One of the most effective methods reported in the literature for addressing this problem is via regularization. In this method, instead of minimising the usual network prediction errors such as mean squared errors (MSE), a modified performance function defined as regularized mean squared error (MSEREG) is minimised. MSEREG is given by Equation (5.9) (Demuth et al. 2008):

$$\text{msereg} = \alpha\,\text{mse} + (1-\alpha)\,\text{msw} \tag{5.9}$$

where '$\alpha$' is the performance ratio, "mse" is the usual mean squared errors of the network predictions and "msw" is the additional objective, mean squared weights and biases.

The automated Bayesian regularization algorithm in the MATLAB® neural network toolbox was used to obtain the weights and biases of the ANNs reported in this thesis. This tool updates the weights and biases of the network according to the Levenberg-Marquardt algorithm. The algorithm minimises the combination of squared errors and weights (including biases) to produce a network that generalises well. The idea behind this approach is that using the modified performance function causes the network to have smaller weights and biases. This forces the network response to be smoother and less likely to over-fit. There is no need to divide the data into training, validation and/or test sets; all the available data are used in the training. This method is very useful where available data is small, as observed for most cases treated in this thesis. The fundamental principles and various applications of Bayesian regularization, as well as other methods that can be used to improve ANN generalization capability, are well discussed in the literature (see Edwards and Murray 1998; Edwards et al. 1999; Burden et al. 2000; Aggarwal et al. 2005; Cawley and Talbot 2007).

### Crucial issues while training artificial neural network

#### *Input-output data processing*

ANN works well when the input and output data are all scaled to identical ranges. In this work, all the variables were scaled to between -1 and +1. Prior to the scaling, variables such as viscosity and shear rate were log-transformed. This was done because the scaling function available in the neural network toolbox gives linear transformation and, considering for example the exponential characteristics of black liquor viscosity with respect to solids concentration or/and temperature, prior logarithmic transformation enhances its linear scaling for efficient ANN training. The architecture chosen is a multilayer feedforward network with 1 or 2 hidden layers and 1 output layer (see Figure 5.1). Each activation or transfer function in the hidden layer is a hyperbolic tangent sigmoid function while a linear transfer function is used in the output layer (see Figure 5.3).

***Parameter search procedures***

Some approaches were adopted in order to minimize the chances of obtaining a network with a local optimum or a network that is too large. First, the training begins with a network with 1 hidden layer and 1 hidden neuron and then increased gradually until the most acceptable network was obtained based on the accuracy criteria outlined in section 5.3.2 and those described in this paragraph are met. Secondly, each complete optimization was carried out at least 10 times starting from different initial weights and biases that were chosen at random (automatically done via initialization tools available in the MATLAB® neural network toolbox) for each number of hidden neurons. Starting at different initial values minimised the chances of obtaining a local optimum. During training, the network's parameters as well as its performance criteria were monitored. If the results were not satisfactory after different optimization attempts and starting from different initial parameter values, the number of hidden neurons would be increased and the process repeated until satisfactory performance criteria were obtained.

Given enough of training epochs (depending on the complexity of the problem) e.g. 5000, a true convergence is reached when maximum MU (Marquardt adjustment parameter) is attained, the effective number of parameters (#), sum of squared weights (SSW) and the network prediction errors remain fairly constant over a significant number of iterations (Demuth et al. 2008). This should be the case no matter the size of the given network structure. In addition to monitoring the above-stated indices, the $R^2$ (based on the scaled viscosity data), and MARE (based on actual unscaled viscosity data) were checked at the end of each complete optimization stage. It is desirable to keep the network size as small (in the number of effective parameters and sum of the weights) as possible to avoid overfitting.

Once a network (if one exists) that satisfied all these conditions was found, the training could be terminated. In this thesis, a network with 1 hidden layer (having L neurons) and

1 output layer (having M neurons) is denoted as an [L, M] network. A network with 2 hidden layers (having K neurons in the first hidden layer and L neurons in the 2nd hidden layer) and 1 output layer (having M neurons) is denoted as a [K, L, M] network.

## 5.4 CALCULATIONS, RESULTS AND DISCUSSION

This section describes the computational steps involved in, and the discussion of the results of, the applications of the existing and the proposed models to E509 viscosity data over different ranges of process conditions. First, both the existing and the proposed models were applied to the data over the same ranges of process conditions and secondly, the ANN models were extended to the conditions where both the existing and the binomial models are not applicable. The results are discussed under three sub-headings: models at low solids concentrations (<=50.98%), models at high solids concentrations (>=50.98) and models at all solids concentrations (0-70%). It should be noted that the existing models were classified normally as low solids concentration models at solids concentrations<=50% and high solids concentrations models at solids concentrations>50%. Solids concentration=50.98% was used as transition point here since E509 data used for the modelling exhibits Newtonian or nearly-Newtonian behaviour at solids concentrations=0-50.98% and at temperatures=0-115 °C. Some of the existing models were originally developed for limited temperature ranges; however both the existing and the new models were applied directly to cover the entire temperature range (0-115 °C) in this study.

### 5.4.1 Newtonian Viscosity Models at Low Solids Concentrations (≤ 50.98%)

Based on the Newtonian viscosity data obtained in section 5.3.3.1, the existing models **A** and **B** (see Appendix A), the proposed BM and ANN models were used to fit 23 E509 viscosity (mPa.s) or kinematic viscosity (mPa.s/(kg/m$^3$)) data points at solids concentrations <= 50.98% and temperature = 0-115 °C. According to Zaman and Fricke (1994a), $A_2$ and $B_2$ in model **A** are defined as follows:

$$A_2=A_{20}+A_{21}S \tag{5.10a}$$

$$B_2=B_{20}+B_{21}S+B_{22}S^2 \tag{5.10b}$$

Tr was set =273 K (the minimum temperature) in model **B**. For the BM, Tr was set

=273 K and was used as a search parameter in a trial-and-error manner. Here S is defined as black liquor solids mass fraction (0.0-1.0).

Based on the facts, data, procedures and performance criteria described in section 5.3, the parameters of the linear models were obtained using the linear regression tools in the MATLAB® statistics toolbox while the parameters of the nonlinear models were obtained using the nonlinear curve-fitting tools in the MATLAB® optimization toolbox. The weights and the biases of the ANN models were obtained using the automated Bayesian regularization algorithm in the MATLAB® neural network toolbox.

A 2nd order model **B**, whose $R^2$=0.9904 and MARE=32.71% was obtained. However, its parameter estimate, a1 has a wide confidence interval (CI) (not adequate). With poorly known parameter estimate a1 and having MARE=~33%, the 2nd order model **B** is not deemed suitable for practical application and is not to be discussed further. A 3rd order model **B** (having $R^2$=0.9989), whose accuracy is roughly twice (MARE=16.75% compared to 32.71%) that of the 2nd order model **B,** was obtained. Its parameter estimates were obtained as a1=8.6664, a2=-28.0588 and a3=67.7417. The CIs of these parameter estimates are found to be satisfactory (narrow or moderate). Increasing the order of the model **B** to a higher (than 3rd) one did not result in a significantly higher accuracy but instead resulted in higher uncertainties in the parameter estimates. Variation of Tr does not have any effect on the accuracy of the model.

A 3rd order linear binomial model ($BM^3$) having $R^2$= 0.9999 and MARE=6.61% with the following 9 parameter estimates was found to be accurate and potentially adequate (parameter estimates have moderate CIs) when Tr was obtained in a trial-and-error manner as 1 K: a1=$2.5758*10^6$; a2=$-2.1328*10^6$; a3=$-10.5402*10^3$; a4=$-5.1121*10^6$; a5=$4.2375*10^6$; a6=17.4424; a7=10.4431*103; a8=$2.5364*10^6$; a9=$-2.1048*10^6$. Roughly, a two-fold improvement in MARE (from 11.74 to 6.61%) was observed when Tr was changed from 273 K to 1 K. Although a 2nd order BM having fewer number (5) of parameters, with performance indices as $R^2$=0.9907 & MARE=41.41, and good parameter estimates was obtained, its level of accuracy compared to the 3rd order model makes the latter a preferred choice.

The 6 parameters of the nonlinear model **A** whose $R^2$= 0.99999 and MARE= 41.99%, were obtained as $A_{20}$=1.9568*$10^{-6}$; $A_{21}$=-2.8990*$10^{-7}$; $B_{20}$=2.3645; $B_{21}$=-0.8616 and $B_{22}$=15.2363; and $T_o$=173.0443 K. The practical suitability of this model is discussed later in this section.

For the ANN models, the inputs are solids concentration (i.e. solids mass fraction, S) and temperature (T (K)) while the output is viscosity (V (mPa.s)) that was log-transformed prior to scaling to within [-1, 1]. ANN networks of different sizes were trained according to the procedures described earlier. When the number of hidden neurons was increased from 4 to 6, the SSWs are ~14 while the #s range between ~13 and ~15. The $R^2$s are >=0.99994 and MAREs range between 4.14 and 4.15% indicating true or near true convergence. However, a [3, 1] network having performance indices as SSW=16.7 (~17), effective number of parameters, #=~12/13 (out of 13 tuneable parameters, the model uses approximately 12 for predictions), $R^2$=0.9998 and MARE=4.76% was chosen. This because it gives acceptable (high $R^2$ and MARE<5%) and comparable indices ($R^2$ and MARE) to the [4, 1]-[6, 1] networks; furthermore, it is likely to generalize better than the [4, 1] network with #=~13/17 (having 3 free parameters).

### Comparison of the existing and proposed models for E509 at low solids concentrations

The existing nonlinear functional model **A** having the largest $R^2$ has the worst MARE. This model was original developed for predicting black liquor viscosity at temperatures up to 80 °C; it seems unable to predict viscosity data over a wide range of temperatures accurately in this study. Although all the models have very high $R^2$s, it is clear that only the BM and the ANN developed in this study are able to give very low MAREs, however at the expense of larger numbers of parameters. While a model with a very high accuracy is desirable, a 3-parameter linear model **B** having MARE=16.75% shows that black liquor viscosity can conveniently be modelled at low solids concentrations using the reduced variables (STr/T) philosophy developed for dilute polymers with a little sacrifice for accuracy. A 3-parameter model with MARE=16.75% may be selected in preference to a 10-parameter (including Tr) linear BM with MARE=6.61%. It can also be considered more convenient to use than either a nonlinear model **A** having 6 parameters with MARE=42% or an ANN with #=12 and MARE=4.8%. However, the ultimate choice would depend on the level of accuracy desired, generalization ability of each model and the ease of their online implementation.

On this note, these models were validated by exposing them to the few unseen data points presented in Table 5.1. Their performances are as reported in Table 5.2.

Table 5.1 Preliminary validation data for E509 viscosity models; (SC=solids concentration)

| SC (%) | Temperature ($^{o}$C) | Shear rate (s$^{-1}$) | Viscosity (mPa.s) |
|---|---|---|---|
| 11.95 | 16 | 1000 | 2.138 |
| 11.95 | 16 | 1500 | 2.138 |
| 11.95 | 16 | 2000 | 2.138 |
| 11.95 | 25 | 1000 | 1.773 |
| 11.95 | 25 | 1500 | 1.773 |
| 11.95 | 25 | 2000 | 1.773 |
| 31.85 | 10 | 200 | 10.755 |
| 31.85 | 10 | 400 | 10.755 |
| 31.85 | 30 | 500 | 5.615 |
| 31.85 | 30 | 1000 | 5.615 |
| 31.85 | 30 | 1500 | 5.615 |
| 31.85 | 30 | 2000 | 5.615 |

Table 5.2 Generalization performances of E509 Newtonian viscosity models at low solids concentrations; (T=temperature)

| **Model/Applicable** | **R$^2$** | | **MARE (%)** | | **SSW** | **#** |
|---|---|---|---|---|---|---|
| **process conditions** | **Modelling** | **Generalization** | **Modelling** | **Generalization** | | |
| **A**<br>@ all T | 0.99999 | 0.9948 | 41.99 | 37.67 | - | - |
| **B**<br>@ all T | 0.9989 | 0.9979 | 16.75 | 14.81 | - | - |
| BM$^2$<br>@ all T | 0.9907 | 0.9998 | 41.41 | 38.17 | - | - |
| BM$^3$<br>@ all T | 0.9999 | 0.9966 | 6.61 | 5.14 | - | - |
| ANN ([3,1])<br>@ all T | 0.9998 | 0.9935 | 4.76 | 7.27 | 16.7 | 12/13 |

As observed from Table 5.2, based on modelling MAREs, models **A**, **B**, BM$^2$ and BM$^3$ are less accurate than the ANN. However, all these models show better generalization capability than the ANN, since the generalization error of the latter is higher than its corresponding modelling error. On the contrary, the generalization errors of the other four models are smaller than their corresponding modelling errors. Therefore, the BM$^3$ is the most generalized of all the models despite the fact that the ANN is the most accurate of them all.

Although models **A** and **B** may not be recommended for practical application in their present forms due to their low accuracies, it is clear that they have strong generalization abilities. They would have been the preferred choices since they have very few parameters. If they can be modified to improve their accuracy while retaining their generalization abilities, that would be a plus. Although the ANN is less generalized than the BM$^3$ in this study, the level of its generalization is still very good for practical applications assuming that its performance would not deteriorate further at other conditions not tested. The [4, 1] network mentioned earlier was also validated but its generalization MARE (14.81%) is worse than that of [3, 1] network as anticipated. Therefore, it was not considered further.

### 5.4.2 Viscosity Models at High Solids Concentrations (>=50.98%)

Black liquor behaves either as a Newtonian fluid or shear-thinning fluid at high solids concentrations depending on the temperature, shear rate and the liquor type. In order to be able to develop a model that is capable of describing the rheological behaviour of black liquor at high solids concentrations over a wide range of temperatures, two model forms were developed. The first form is a set of Newtonian or zero shear viscosity models applicable only at low shear conditions where black liquor behaves typically as Newtonian fluid. The second model form incorporates the joint effects of shear rate, solids concentration and temperature on the liquor viscosity.

#### 5.4.2.1 Newtonian viscosity models at high solids concentrations

The existing linear **I** and nonlinear **K** models as described in Appendix A, and the proposed BM and ANNs were applied to E509 Newtonian viscosity data reported in section 5.3.3.1 based on similar procedures and tools utilized in obtaining the models at low solids concentrations above. The parameter estimates of the models were obtained for E509 firstly at solids concentrations >=50.98% (21 data points) and secondly at solids concentrations >= 58.56% (15 data points). The potentially useful modelling results are as reported in Table 5.3. At solids concentrations >=50.98%, no reliable model **I** was obtained. The $R^2$ values from 1st to 3rd order (higher orders were not possible as the inputs became rank-deficient) **I** model increase from 0.911 to 0.933; conversely, their corresponding MAREs increase from 244% to 411%. This model was not analysed further due to the unreliable trend in its MAREs. A possible reason for the poor performance of model **I** is that it was originally developed for black liquors at solids concentrations > 50% and temperatures >=40 °C. However, in this study, it was attempted to include viscosity data at lower temperatures and solids concentration = 50.98% (that is not sufficiently different from 50%). This was confirmed as there was a substantial improvement in the model performances when it was used to fit E509 viscosity data at solids concentration >= 58.56% (sufficiently>50%) where its $R^2$s increased from 0.967 to 0.9835 and the corresponding MAREs dropped from 108.82% to 62.18% from 1st to 3rd order models. The $R^2$ and the MARE for the 3rd order **I** model are reported in Table 5.3. It seems the model is particularly suited to concentrated black liquors having solids concentrations that are sufficiently higher than 50%. Another possible reason for the

Table 5.3 E509 functional Newtonian viscosity models at high solids concentrations; (SC=solids concentration, SR=shear rate, T=temperature)

| **Model/Applicable process conditions** | **$R^2$** | **MARE (%)** |
|---|---|---|
| **I**<br>@ SC>=58.56%,<br>low SR, all T | 0.9835 | 62.18 |
| **K**<br>@ SC>=58.56%,<br>low SR, all T | 0.99998 | 9.00 |
| $BM^3$<br>@ SC>=50.98%,<br>low SR, all T | 0.9990 | 13.78 |
| $BM^3$<br>@ SC>=58.56%,<br>low SR, all T | 0.9994 | 10.79 |
| $BM^2$<br>@ SC>=58.56%,<br>low SR, all T | 0.9966 | 27.68 |

observed performances is that the model response variable was log-transformed when the model parameter estimates were obtained. While the high $R^2$ gives an impression that the model fits the data well in the transformed state, the model performed poorly on the actual scale as revealed by its high MARE. The CIs of the parameter estimates of the model **I** are extremely wide, indicating poor estimates. Therefore, this model was not considered further due to its poor accuracy and its inadequate parameter estimates. Note that by evaluating this model based on the high $R^2$ value alone, it could be wrongly chosen to be suitable for practical application. Zaman and Fricke (1991) had reported very high $R^2$ values for the models presented in their work without explaining how the model performed on an untransformed scale. The parameter estimates (reported in Table 5.4) obtained for the E509 data at solids concentrations >= 58.56% when fitted to a 2nd order model **I** were compared with those obtained for the mill liquor presented in Zaman's and Fricke's(1991) paper, they are found to be similar though not exactly the same.

Table 5.4 Comparison of the binomial and Zaman and Fricke (ZF) models

| Model | a0 | a1 | a2 | $R^2$ |
|---|---|---|---|---|
| ZF | 24.2399 | $-6.9167*10^4$ | $4.15023*10^7$ | 0.988 |
| $BM^2$ | 29.1854 | $-7.7144*10^4$ | $4.4686*10^7$ | 0.983 |

This should be expected as the parameters are sensitive to the liquor type. Both models have high $R^2$ values that may lead one to wrongly assume that the models are accurate. However, as shown in this study (high MARE value on the actual scale), high $R^2$ is not sufficient to arrive at such a conclusion.

According to Zaman and Fricke (1994b), expressions for the parameters A and B in the nonlinear model **K** (see Appendix A) are given in Equations (5.11a) and (5.11b) while they recommend that C can be fitted as a parabola. Therefore, C is given by equation (5.11c). $T_g$ is given by Eqn (5.6) while To is given by Eqn (5.12).

$$A=\exp(A_1+A_2S) \tag{5.11a}$$

$$B=B_1+B_2S \tag{5.11b}$$

$$C=C_1+C_2S+C_3S^2 \tag{5.11c}$$

$$T_o = b_3T_g \tag{5.12}$$

**K** is a 10-parameter nonlinear model. Using the nonlinear curve-fitting approach described earlier, the nonlinear model **K** was fitted to the E509 Newtonian viscosity data first at solids concentrations >=50.98% and secondly at solids concentrations >=58.56%. At solids concentrations >= 50.98%, model **K** performances are not reliable. Despite having high $R^2$=0.9986, **K** has a high MARE=85.4% and some of the parameter estimates are not reliable. In particular, obtaining $b_2$=~0.0 nullifies the fact that $T_g$ is approximately a linear function of solids concentration and making $T_o$ in the **K** model unreliable. The probable reason for the poor estimation of b2 is the inclusion of the viscosity data at solids concentration=50.98% (not sufficiently higher than 50%) in the computations. This finding is similar to the poor performance of the linear model **I** at solids concentrations>=50.98% as observed earlier.

At solids concentrations >= 58.56%, the parameter estimates of the **K** model whose performances are as reported in Table 5.3 were obtained as: $A_1$=-29.5516; $A_2$=33.1184; $B_1$=10795.1; $B_2$=-12400; $C_1$=-13.3688; $C_2$=40.6350; $C_3$=-29.05415; $b_1$=59.3406; $b_2$=126.434; $b_3$=2. These parameter estimates seem logical and reliable having $b_2$=126.434 (as opposed to 0.0 for the data which included solids concentration = 50.98%). Similar to the observed improved performance of model **I** when applied to the viscosity data at solids concentrations >=58.56% (compared to when applied at solids concentrations >=50.98%), a substantial improvement in the performance of model **K** (from MARE 85.4% to 9%) was noticed when it was fitted to data at solids concentrations >=58.56%. It may be safely concluded that model **K** is valid at high solids concentrations where $T_g$ is valid. For a nonlinear model to require 10 parameters before its accuracy value can be driven down to MARE=9% (target is <=5%) is an indication that the relationship between black liquor viscosity and its inputs, solids concentration and temperature, is highly nonlinear at high solids concentrations. The complexity seems to be compounded by modelling the data over a wide range of temperatures. Although the model is able to describe black liquor viscosity accurately at high solids concentrations (sufficiently higher than 50%), it is not able to provide prediction continuity to a model developed for low solids black liquors if they are implemented online since it is not reliable around solids concentration=50% which is the upper limit of the model at low solids concentrations. Another issue of concern is that only 15 data points were available to obtain the 10 parameters for the nonlinear functional model **K**. Although it has a high

$R^2$ and a moderate MARE=9%, there is no guarantee that the model would generalize well when exposed to unseen data. Independent data would be required to confirm this.

The BM was used to fit E509 Newtonian viscosity data first at solids concentrations >= 50.98% and secondly at solids concentrations >= 58.56% following the procedures described earlier. At solids concentrations >=50%, a 10-parameter (including Tr) 3rd order binomial model ($BM^3$) having $R^2$ and MARE reported in Table 5.3 was obtained. The Tr was obtained in a trial-and-error manner as 6.5Tdatamax where Tdatamax=388 K. This further confirms that using Tr as a search parameter (rather than pre-setting it to the data minimum temperature) improves the performance of the BM. Although $BM^3$ has a high $R^2$=0.999 and moderate MARE=13.78 % (target<=5%), it is not certain that this model would generalize well, as many of the CIs of its parameter estimates are moderately or very wide (indicating high uncertainties). This would require independent data to confirm its generalization capability. A less accurate model whose parameter estimates are more certain should be potentially more useful but it was difficult to obtain one based on the procedures used in this study.

When the BM was used to fit the data at solids concentrations >=58.56%, a 10-parameter $BM^3$ whose $R^2$ and MARE are as reported in Table 5.3 was obtained. The Tr was obtained in a trial-and-error manner as 2.28Tdatamax. Although $BM^3$ has a very high $R^2$=0.9994 and moderate MARE=10.79% (target <=5%), there is no guarantee that it would generalize well as the CIs of many of its parameter estimates are very wide. A 6-parameter 2nd order BM ($BM^2$) whose parameter estimates have narrow and moderate CIs was obtained. Its $R^2$=0.9966 and MARE=27.68% are as reported in Table 5.3. Tr=2Tdatamax. Although this is less accurate than the $BM^3$, it is potentially able to generalize (satisfactory CIs) better than the $BM^3$.

No matter how accurate and adequate the BMs developed based on solids concentrations >=58.56% are, there is no guarantee that they can be satisfactorily used to provide Newtonian viscosity estimates for E509 at solids concentrations < 58.56%. This makes it unsuitable to function as a complementary online model to the models developed for low solids liquor whose upper limit of applicability is around solids concentration=50%. A generalized high solids model with lower limit at solids concentration=50.98% with similar accuracy as that of its companion low solids model would be desirable to provide prediction continuity.

Based on the procedures described earlier in section 5.3, ANNs of different sizes and configurations were trained to predict E509 Newtonian viscosities as a function of solids concentration and temperature firstly at solids concentrations >=50.98% and then at solids concentrations >=58.56%. At solids concentrations >= 50.98%, two ANNs were obtained and their performances are as reported in Table 5.5. Increasing the networks sizes beyond [4, 1] or [4, 2, 1] did not yield any significant improvements over the reported results. This shows that the algorithm truly converged however at different solutions for the two different network configurations. The [4, 2, 1] network having #=~18 is more accurate than the [4, 1] network having # =~14. The convergence of Bayesian trained networks seems to be dependent on the network configuration. This shows that if a correct network and configuration is not chosen, the algorithm may yield unreliable solutions. Although it is clear that the higher accuracy of the [4, 2, 1] network is dependent on having a larger number of #, the degree of improvement of [4, 2, 1] network over the [4, 2] network, as noted in their MAREs, justifies the extra 3 parameters in the [4, 2, 1] network. Although Bayesian algorithm is theoretically able to guarantee that the resulting model would generalize well, over-fitting can still occur (Edwards and Murray 1998; Edwards et al. 1999) as it was observed when the low solids ANN model validated earlier gave

Table 5.5 ANN-based Newtonian viscosity models for E509 at high solids concentrations; (SC=solids concentration, SR=shear rate, T=temperature)

| **Model/Applicable process conditions** | **$R^2$** | **MARE (%)** |
|---|---|---|
| ANN [4,1] @ SC>=50.98%, low SR, all T | .9996 | 10.29 |
| ANN [4,2,1] @ SC>=50.98%, low SR, all T | 1.0 | 3.69 |
| ANN [3,1] @ SC>=58.56%, low SR, all T | .9997 | 11.45 |
| ANN [3,2,1] @ SC>=58.56%, low SR, all T | 1.0 | 3.44 |

generalization error higher than its modelling error. Considering the fact that # (18) in the [4, 2, 1] network is nearly the same as the data size (21) although with small SSW (~13), it can not be concluded that the network would generalize well. Some independent data points might be required to confirm its generalization capability. It is important to note that having this large number of parameters and also a network comprising of 2 hidden layers before a very high accuracy could be attained is an indication that the viscosity of black liquor depends on the solids concentration and temperature over the ranges of data modelled, in a complex manner; this may explain why the functional statistical models described above find it extremely difficult to describe the underlying relationship between black liquor viscosity and solids concentration & temperature accurately and reliably at high solids concentrations. The [4, 2, 1] network (obtained at solids concentrations >=50.98%) has a comparable level of accuracy as the [3, 1] network obtained at solids concentrations <=50.98% (see Table 5.2). The two models have MAREs=3.69% and 4.8%, respectively. Subject to further confirmation, the two networks are potentially able to serve as companion online models for each other provided they have acceptable comparable generalization capabilities.

At solids concentrations >=58.56%, a [3, 1] ANN having #=~10 and small SSW=~8 was obtained. Its performances are as reported in Table 5.5. Effort was made to improve the accuracy of the model by increasing the number of tuneable parameters (by increasing the number of neurons in the hidden layer from 3 to 5), the Bayesian algorithm ensures that the above performances and indices reported for the network in Table 5.5 remain nearly the same, indicating that the algorithm has truly converged. However, in order to obtain a more accurate (lower MARE) network than the [3, 1] network, a 2-hidden layer (configuration change) ANN was searched and the optimum network was obtained as [3, 2, 1] having #=~13 (data size=15) and SSW=11. The network's $R^2$ and MARE are as reported in Table 5.5. Although further attempts were made to improve the performance of the [3, 2, 1] network by increasing the network size from [3, 2, 1] through [5, 2, 1] (by increasing the number of neurons in the first hidden layer thereby increasing the number of tuneable parameters), all the performance indices including the reported # and SSW remain approximately the same. This shows that true convergence was also attained. Similar to the earlier observations, the Bayesian algorithm converged at different solutions for different network configurations and/or sizes, indicating that the algorithm does not guarantee a unique or global solution.

Generally, the results show that it is relatively easier for the ANNs to model the data at solids concentrations >= 58.56% than at solids concentrations >=50.98%. For the [L.M] and [K, L, M] configurations, an extra neuron was required at the hidden and the 1st hidden layer of [L, M] and [K, L, M] configurations, respectively at solids concentrations >=50.98% to obtain comparable MAREs to those obtained at solids concentrations >=58.56%. This shows that the wider the range of operating conditions, the more difficult it becomes to model the data, even with the application of ANNs. Also, that it requires a 2-layer network to drive the models accuracies to acceptable levels is an indication of the degree of the complexity of the relationship between black liquor viscosity and solids concentration & temperature at high solids concentrations. Considering the fact that the data size is 15 and #s are~10 and ~13 in the above networks, independent datasets would be required to determine their generalization capabilities.

### 5.4.2.2 Non-Newtonian viscosity models at high solids concentrations

The existing modified Cross model **L** (see Appendix A) developed by Zaman and Fricke (1995b; 1995c), and applicable to high solids (>50%) black liquors, was used to fit E509 non-Newtonian viscosity data obtained for functional modelling in section 5.3.3.1. The 3 most accurate zero shear viscosity (ZSV) functional models ($BM^3$ having MARE=10.79% obtained for E509 at solids concentrations >=58.56%; $BM^3$ having MARE=13.78% obtained at solids concentrations>=50.98% and the Zaman & Fricke nonlinear model **K** having MARE=9% obtained at solids concentrations>=58.56) discussed earlier were used to provide ZSV estimates while fitting the shear-sensitive viscosity data to the Cross model **L**. Equations (5.6) and (5.12) provided the $T_g$ and $T_o$ estimates respectively in the William-Landel-Ferry (WLF) equation as reported in Appendix A. Although the original application of the modified Cross model to black liquor viscosity modelling was limited to temperatures >=40 $^oC$, it was used to fit the data in this study from 0 $^oC$ to 115 $^oC$.

Having defined all necessary expressions, the search for the parameter estimates ($\lambda$, m, b1, b2 and b3) was conducted at all temperatures and shear rates first for the viscosity data (size=65) at solids concentrations >=50.98% and secondly for the viscosity data (size =47) at solids concentrations >=58.56% using the nonlinear curve-fitting tools in the MATLAB® optimization toolbox. At solids concentrations >=50.98%, the best modified Cross model parameter estimates: b1=42.5521; b2=132.7024; b3=2.76; $\lambda=3.8282*10^{-9}$; m=0.1626 were obtained when $BM^3$ having MARE=13.78% was used to provide ZSV estimates. The best modified Cross model performance indices, $R^2$ and MARE are as reported in Table 5.6. It is not surprising that, when the other two more accurate ZSV models were used to provide ZSV estimates, the modified Cross models obtained were less accurate since they were obtained based on data at solids concentrations>=58.56%. This indicates that they can not be used to extrapolate the ZSV to solids concentration=50.98% accurately. On the application of the above three ZSV models to provide ZSV estimates for E509 at solids concentrations>=58.56%, so as to obtain the parameters of the modified Cross model **L**, all the results obtained are more accurate than the results obtained at solids concentrations>=50.98%. The most accurate results were obtained when the $BM^3$ obtained at solids concentrations>=50.98% was used; its performance indices are as reported in Table 5.6. The parameter estimates of the best model **L** are: b1=70.1894; b2=238.0196; b3=1.5783; $\lambda=6.8072*10^{-9}$; m=0.146.

Table 5.6 Non-Newtonian viscosity models for E509 at high solids concentrations; (SC=solids concentration, SR=shear rate, T=temperature)

| **Model/Applicable process conditions** | **R2** | **MARE (%)** |
|---|---|---|
| **L**<br>@ SC>=50.98%,<br>all SR, all T | .9965 | 44.12 |
| **L**<br>@ SC>=58.56%<br>all SR, all T | .9987 | 24.60 |
| ANN [6,1]<br>@ SC>=50.98%,<br>all SR, all T | 1.0 | 4.68 |

The improved performance of the modified Cross models obtained at solids concentrations>=58.56% over the ones obtained at solids concentrations>=50.98% is expected since the model is dependent on $T_g$ that is very effective at solids concentrations sufficiently greater than 50%. However, despite the fact that all the three ZSV models are adequate to provide ZSV estimates for the modified Cross models at solids concentrations>=58.56%, it is not clear why the BM$^3$ obtained at solids concentrations>=50.98% (other two were obtained at solids concentrations>=58.56%) having the largest MARE among the three ZSV models led to the best modified Cross model at solids concentrations>=58.56%. There should be no concern for overfitting since the modified Cross model has just 5 parameters as compared to 47 data points utilised in the modelling. Also, the level of accuracy (minimum MARE=24.6%) attained does not signal to a model that has been over-fitted the. However, this model may not be able to function accurately as a complementary model to a model developed for low solids black liquor going by its accuracy level of MARE=44.12% (at solids concentrations>=50.98). Its more accurate (MARE=24.6%) counterpart may suffer extrapolation problem since it is applicable at solids concentrations>=58.56%. Moreover, the level of the accuracy (MARE=~25%) obtained in this study may not be the best for product quality monitoring and process control applications.

The functional model **L** developed above relies on zero shear viscosity estimates that require another model to provide. Model **L** is also dependent on $T_g$ and as such, limits its accurate application to solids concentrations sufficiently higher than 50% as shown above. ANN was attempted to fit the E509 non-Newtonian viscosity data obtained in section 5.3.3.1 for ANN modelling. Viscosity (log-transformed prior to scaling to [-1, 1] range) was modelled as a function of solids concentration (as dry solids mass fraction), temperature (K) and shear rate ($s^{-1}$), which was log-transformed prior to scaling to [-1, 1] range. The ANN models neither require a separate ZSV model nor $T_g$ model which limits the applicability of model **L** to solids concentrations sufficiently greater than 50%. Therefore, using Bayesian regularization algorithm as described earlier, ANN based viscosity model was developed for E509 at solids concentrations >=50.98%. This was done to allow for an approximate comparison with the functional shear-sensitive models developed above.

At solids concentrations>=50.98% (86 data points), different sizes of [L, M} networks were searched. It was difficult to attain true convergence. Therefore, the search was terminated when a [6, 1] ANN (see Table 5.6) having #=~29 and SSW=~84, $R^2$=1.0

which satisfies the target MARE<=5% and $R^2$=1 criteria was obtained. It is possible that, the difficulty encountered by the ANN in learning the underlying relationship between black liquor viscosity and its input factors- solids concentration, temperature and shear rate, might be due to the presence of repeated shear-independent viscosity data. This situation is discussed further in section 5.4.3.2. Since the ANN does not require $T_g$ and ZSV models which are essential in the functional Cross model **L,** and is purely empirical, it can easily be used to predict viscosity for black liquor at all shear rates and other process conditions where the functional models failed.

## 5.4.3 Viscosity Models for E509 at All Solids Concentrations (0-70%)

It was shown in Chapter 4 that E509 exhibits a Newtonian or non-Newtonian behaviour at solids concentrations from 0 to 70%, temperatures between 0 and 115 $^{o}$C and shear rates up to 2000 $s^{-1}$. In this section, two model forms are attempted to describe the rheological behaviours of E509 over a wide range of process conditions. The first form assumes that shear rate is relatively low and so the liquor at all temperatures and solids concentrations is treated as Newtonian fluid. The second form involves the explicit incorporation of the shear rate factor. The literature abounds with the first form but there is no published report on the second form. Therefore, in this section, the existing and the proposed functional, and ANN based viscosity models were used to model the Newtonian viscosity data. The proposed ANN was used further to model the black liquor rheological behaviours over the entire data points as obtained in section 5.3.3.1, as a combined function of solids concentration, temperature and shear rate.

### 5.4.3.1 Newtonian viscosity models for E509 at all solids concentrations (0-70%)

The existing models **D, E & F** (see Appendix A)**,** and the binomial & ANN models proposed in this study, were used to fit the Newtonian viscosity data (size=38) reported for E509 at solids concentrations=0-70%, T=0-115 $^{o}$C in section 5.3.3.1 according to the procedures utilised to develop separate models for the low and high solids E509. The only exception here was the use of the nonlinear curve-fitting tools in the MATLAB® statistics toolbox for the nonlinear models **E** and **F** as opposed to the use of the nonlinear curve-fitting tools in the MATLAB® optimization toolbox mentioned earlier. The former is able to compute CIs together with parameter estimates directly. Before the curve-fitting was done, in the model **D**, Tr was set equal to 273 K (minimum temperature in this study) as Ghosh(1993) did not report the value of Tr used in his work. In models **E** and **F**, Tr was set to 373 K as recommended by the Authors (Adams and Frederick 1988; Frederick 1997) while in the BM, Tr was set to 273 K. As the order of the model **D** was increased from 2 to 4, the CIs of their parameter estimates become increasingly very wide without any significant improvements in their MAREs (109.69%-90.4%); although all have $R^2$s>=0.9736. Considering the unsatisfactory levels of the models (2nd to 4th order) accuracies (high MAREs) and inadequacies of their parameter estimates, these models were not considered further. It is clear that model **D** can not adequately fit black liquor viscosity data over a wide range of process conditions. Ghosh(1993) in his paper used model **D** to fit different black liquor viscosity data over a wide range of process conditions and reported very high $R^2$s >=0.85 for the models and used these to judge their suitability for practical application. It is evident from this study that, it would be inappropriate to evaluate the accuracy and possibly the practical suitability of **D** model based on its $R^2$ alone.

Just as model **D** is unable to adequately describe black liquor viscosity over a wide range of process conditions, the BM proposed in this study, which had been applied separately to both the low and high solids contents liquors, do not have the capability of fitting the entire data jointly. The best BM obtained in terms of parameters adequacies (narrow CIs) is a 5-parameter (excluding Tr) 2nd order model having $R^2$=0.9756 but poor MARE=112%. Attempt was made to improve the model accuracy but the parameter adequacy deteriorated as the model order was raised from 2nd (5-parameter model) to 3rd (9-parameter model). The 3rd order model have performances, $R^2$=0.9915 & MARE=74.66% with parameter estimates whose CIs are either moderate or wide. While significant improvements ($R^2$=0.9915-0.9996;MARE=74.66%-14.15%) were observed as the order of the BM was increased from 3rd to 5th, there was a drastic deterioration in the adequacies of the parameter estimates as their CIs became extremely wide, indicating poorly estimated parameters. The BM was not analysed further due to the adequacy limitation. It seems the BM is not suitable for fitting black liquor viscosity data over a wide range of process conditions. Judging by $R^2$ (close to 1.0) alone, the inaccurate and inadequate BM would have been chosen erroneously for practical application. While the model seemed to perform well when the response variable was log-transformed, it did not perform as well on actual scale as indicated by high MARE.

The applications of the nonlinear models **E** and **F** to the E509 viscosity data result in model **E** having $R^2$=.9807 & MARE=80.75%, and model **F** having $R^2$=0.9913 and MARE=65.73%. These two models have high $R^2$s that would erroneously indicate they are accurate but the examinations of their MAREs indicate otherwise. The adequacies of these models were examined by checking the CIs of their parameter estimates. While the confidence interval of parameter c in model **E** is very narrow (indicating adequate parameter), the confidence interval of its parameter b is extremely wide (indicating poor estimate). The CIs of the parameter estimates c and d in model **F** are extremely narrow (indicating very good estimates). It is clear that the nonlinear model **F** describes black liquor viscosity more accurately and adequately than the nonlinear model **E** over a wide range of process conditions. Despite its (**F**) low accuracy level, in the absence of a better (regarding accuracy and adequacy) functional model, model **F** is preferred to model **E.** It is particularly desirable because it has a fewer number (just 2) of parameters, c =0.2996 and d=-0.2850. These parameters are different from the ones (c=0.679 and d=-0.656) obtained for the data presented in the work of Frederick (1997) where the model was used to fit the black liquor viscosity data from a wide range of sources. This should be expected as these parameters are liquor-dependent.

Different configurations and sizes of ANNs were trained to model E509 Newtonian viscosity data over all the solids concentrations=0-70% and temperatures=0-115 $^{o}$C based on the training approaches described earlier for ANN. Here, solids concentration is expressed in fractional form (0-1.0) while temperature is expressed in K. Viscosity was log-transformed prior to scaling to [-1, 1] range. An [8, 1] network with SSW=56.75; #=~25, $R^2$=0.9998 and MARE=10.09% was obtained. Increasing the size of the network did not improve or change any of the above performances; this indicates that the algorithm has truly converged and so, the [8, 1] network was selected. In order to improve the network performance via a change in the network configuration, different sizes of 2-hidden layer networks were searched. By fixing the first hidden layer number of neurons as 2, the best network obtained is [2, 5, 1]. Increasing the number of 2nd layer neurons from 5 to 6 did not change its performance indices and so, [2, 5, 1] network having SSW=46.59; #=~24; $R^2$=1.0; MARE=6.4% was chosen. Fixing the 1st hidden layer neuron as 3; a [3, 8, 1] network was obtained having smallest (among the three networks) SSW=36.19 but highest (compared with the [8, 1] and [2, 5, 1] networks) #=~31. The network's $R^2$=1.0 and its MARE=3%. Increasing the number of neurons in the 2nd hidden layer did not change the reported performances; this indicates a true convergence for this configuration. Similar to the earlier observations, the results show that the effectiveness of the algorithm depends on the networks configuration as the three different networks had true convergences at different solutions. However, a close observation of the results shows that the complexity of the ANN required to attain a high accuracy increases as the range of operating conditions widens. This is clear from the #s and the network configuration required in modelling the data at low solids concentrations and high solids concentrations (as reported earlier) and all solids concentrations. It is worth mentioning that the structural flexibility of the ANN enhances its performance. It was able to accurately model complex relationships that are difficult for the functional models and can take on as many parameters as possible. However, caution must be exercised to avoid developing a model that would not generalize.

Table 5.7 Performances of E509 Newtonian viscosity models at all solids concentrations; (SR=shear rate, T=temperature)

| **Model/Applicable process conditions** | **R2** | | **MARE (%)** | | **SSW** | **#** |
|---|---|---|---|---|---|---|
| | **Modelling** | **Generalization** | **Modelling** | **Generalization** | | |
| **F**<br>@ low SR, all T | 0.9913 | 0.9986 | 65.73 | 25.34 | - | - |
| ANN [8,1]<br>@ low SR, all T | 0.9998 | 0.9982 | 10.09 | 12.49 | 56.75 | 25/33 |
| ANN [2,5,1]<br>@ low SR, all T | 1.0 | 0.9994 | 6.40 | 12.63 | 46.59 | 24/27 |
| ANN [3,8,1]<br>@ low SR, all T | 1.0 | 0.9994 | 3.00 | 5.61 | 36.19 | 31/50 |

Therefore, the nonlinear model **F** and the three ANNs discussed above were exposed to the unseen data reported in Table 5.1. The results of the test are as reported in Table 5.7. Surprisingly, the results show that the least accurate (in terms of MARE) 2-parameter model **F** was able to generalize better than all the three ANNs as it gives generalization error that is less than half of its corresponding modelling error. If model **F,** having the fewest numbers of parameters could be modified in order to substantially improve its level of accuracy while retaining its strong generalization property, it could be recommended for practical application. The two most accurate networks among the three ANNs lack generalization capability since their generalization errors are roughly 2 times larger than their corresponding modelling errors. On the contrary, the modelling and the generalization errors of the least accurate [8, 1] network are comparable (just ~2.5% difference). However, if the generalization error, 5.6% (~2ce its corresponding modelling error) of the [3, 8, 1] network would not deteriorate further on exposure to other unseen data, it is clearly the most accurate and should be adequate for online application over a wide range of conditions.

The less accurate and simpler network [8, 1] seems to generalize better than the more complex and more accurate [2, 5, 1] network, as the former gave slightly lower generalization error than the latter. Although the simpler network has more # and larger SSW than the more complex network, it seems the effect of structural complexity supersedes the effect of # and weights distribution on a network performance.

### 5.4.3.2 Non-Newtonian viscosity models for E509 at all solids concentrations (0-70%)

There is no model reported in the literature that describes the combined effects of solids concentration, temperature and shear rate on black liquor viscosity over a wide range of solids concentrations (low to high solids). This finding is not surprising. In Chapters 3 and 4, the complexity in the rheological behaviour of black liquor over a wide range of process conditions has been shown. In this Chapter, it has also been shown how difficult it is to describe the relationship between black liquor viscosity and its input variables-solids concentration, temperature and shear rate using functional models applicable only at high solids concentrations. Furthermore, as reported earlier, modelling black liquor viscosity over the entire process conditions as a function of solids concentration and temperature alone, is a daunting task. This is even without the inclusion of shear rate as an additional input variable. However, by virtue of the computational flexibility of ANN, it was used to model the entire data including the shear rate factor, in this study. The inputs to the ANN are solids mass fraction, S, temperature (K), and shear rate ($s^{-1}$), which was log-transformed prior to scaling to [-1, 1] range). The output is viscosity (mPa.s), which was log-transformed prior to scaling to [-1, 1] range.

Following the ANN training procedures described in section 5.3.4.2, different ANN structures and sizes were searched. Although in all cases, maximum MU was attained, true convergence in terms of #, SSW and SSE was not attained the way it was, for most of the zero shear viscosity models described earlier. For example, for 1-hidden layer network, increasing the number of hidden neurons from 7-10 did not bring any appreciable difference in the $R^2$s (all =~1) and MAREs (decreases from 8.1 to 6.3%) of the networks. However, # increases substantially from 33 to 45 and SSW decreases from 265.13 to 173. Therefore, a [7, 1] network was selected pending further performance evaluation tests. With less than 7 hidden neurons, the networks obtained have less #s and SSWs (except for 1 hidden neuron) but are less accurate in terms of MAREs (15-105%) despite having $R^2$s>0.98. Since the overall target was to have a network with $R^2$=~1 and MARE<=5%, the search was terminated when a network having 11 hidden neurons with #=52; SSW=481.4; $R^2$=1.0 and MARE=3.38% was obtained. Attempt was made to search for a 2-hidden layer network to model the entire data. The non-convergence trend similar to the one observed while training the 1-hidden layer network was observed. Therefore, the training was terminated when a [4, 4, 1] network having #=38, SSW=183, MARE=4.7% (target <= 5%) and $R^2$=1.0 was obtained.

A probable factor responsible for the lack of true convergence to a unique solution is that the ANN may be having difficulty learning the relationship between black liquor viscosity and the three input variables, solids concentration, temperature and shear rate, under the conditions where shear rates do not affect the liquor viscosity. At solids concentrations<=50.98%, E509 viscosity is independent of shear rate as reported in chapter 4. At higher solids concentrations (>50.98%), the E509 viscosity is independent of shear rate at high temperatures; however, at lower temperatures and/or high shear rates, the liquor shows shear-dependence behaviour. It is very likely that ANN sees shear rate as a redundant variable under the Newtonian conditions and therefore, this made its learning difficult. The lack of unique convergence of the solutions were also noticed when ANN was used to separately model shear-dependent behaviours of the E509 at either low or high solids concentrations. The results of the search and training of ANNs at high solids concentrations was discussed in section 5.4.2.1. While it is clear that at the

Newtonian regions, black liquor viscosity is independent of shear rate, this is not so at the non-Newtonian regions. Therefore, in order to develop a model that incorporates the two zones jointly requires shear rate as an input factor. Despite suffering the redundancy problem, it is clear that ANN is potentially able to accurately model the joint Newtonian and non-Newtonian behaviours of black liquor over a wide range of process conditions. It seems the conventional multilayer feedforward ANN structure trained using Bayesian regularization algorithm can not handle effectively this type of behaviour. A network with internal classification ability (beyond the scope of this current study), trained using other training algorithms, may be more effective.

In order to ascertain the generalization ability of the three shear-dependent ANNs obtained above, they were exposed to the independent data reported in Table 5.1. The performances of the networks are as shown in Table 5.8. It is observed that [7, 1] network, the least accurate among the three networks, has a generalization error smaller than, and comparable (difference<2%) with its modelling error. This indicates good generalization ability. Conversely, the 2 larger and more accurate networks have generalization errors that are roughly 3 times larger than their corresponding modelling errors, indicating that they have poor generalization abilities. On comparing the [11,1] and [4,4,1] networks, the more accurate [11,1] network, having larger SSW and more # than the [4,4,1] would have been expected to generalize less than the [4,4,1] network; but the generalization results proved otherwise. It seems logical to say that the better performance of the [4, 1] network over the [4, 4, 1] network depends more on its simpler (1-hidden layer) structure/configuration rather than the number of parameters or size of SSW. This agrees with the findings on the ANN based models reported earlier for Newtonian viscosity models for E509 at all solids concentrations.

Table 5.8 Performances of the ANN-based non-Newtonian viscosity models for E509 at all solids concentrations; (SR=shear rate and T=temperature)

| **Model/Applicable** | **R2** | | **MARE (%)** | | **SSW** | **#** |
|---|---|---|---|---|---|---|
| **process conditions** | **Modelling** | **Generalization** | **Modelling** | **Generalization** | | |
| ANN [7,1]<br>@ all SR, all T | 1.0 | 0.9943 | 8.08 | 6.45 | 265.13 | 33/36 |
| ANN [11,1]<br>@ all SR, all T | 1.0 | 0.9952 | 3.38 | 9.56 | 481.43 | 52/56 |
| ANN [4,4,1]<br>@ all SR, all T | 1.0 | 0.9997 | 4.70 | 13.73 | 183.10 | 38/41 |

Conversely, for the networks of the same configuration (1-hidden layer), the more accurate [11, 1] network with the larger SSW and more #, is less generalized than the [7, 1] network, as expected. It seems logical to conclude that, the [7, 1] network's generalization ability is a function of its SSW. Although it was difficult to obtain a unique Bayesian-trained multilayer feedforward ANN model for black liquor viscosity over a wide range of process conditions (including shear rate as an input variable), it is evident that, for practical application, the least accurate (MARE=8.1%), but most generalized (MARE=6.45%) [7, 1] network obtained in this study, may be suitable.

### 5.4.4 Model Consideration for Practical Applications

A variety of conventional and ANN-based viscosity models were developed for predicting black liquor viscosity over either a limited range of process conditions (sections 5.4.1 and 5.4.2) or a wide range of process conditions (section 5.4.3). It was shown that models that are applicable to a wide range of process conditions are more suited for practical applications as they eliminate the need for multiple models. Although the generalization capabilities of the Newtonian and non-Newtonian models, which are applicable to a wide range process conditions, have been evaluated based on unseen data at low solids concentrations and viscosities where black liquor behaves typically as Newtonian fluid, it is not clear whether the above models will generalize well at high solids concentrations and viscosities. It has been shown (see Chapters 3 and 4) that at high solids concentrations and high viscosities, black liquor may sometimes show shear-thinning with or without thixotropic behaviours depending on temperature, shear rate and the liquor type. Evaluating the generalization capabilities of these models at these high process conditions is essential to establish the models' true generalization capabilities over a wide range of process conditions. In the absence of experimental data under these conditions, a response surface methodology was used to study the behaviours of the models. The logic of the approach is as follows: predictive models are built as a function of known input and output data points. Hypothetically, a model that adequately describes the underlying relationship between its input and output variables will give accurate estimates of the output variable that will generally fall at the intermediate output levels of the known output data points when exposed to intermediate (within the range of modelling data points) levels of the known input data points . Such model can be said to be general.

#### 5.4.4.1 Generalization performances of E509 Newtonian viscosity models at all solids concentrations

In section 5.4.3.1, based on the generalization tests conducted at low solids concentrations and viscosities, the conventional model **F** (Frederick 1997) and [8, 1] ANN were adjudged to be the most generalized models. It would be interesting to compare the performance of the least accurate ANN model with the most accurate functional model **F** (see Table 5.7) in this section. These models were exposed to input data points reported in Appendix B3. The data points were carefully selected to fall at intermediate levels of known temperatures at constant solids concentrations or intermediate levels of known solids concentrations at constant temperatures. Few data points beyond the ranges of solids concentrations and temperatures used to develop the models were also included to test the extrapolation ability of the empirical models. As a function of solids concentration and temperature, Figures 5.4 and 5.5 show the models' predictions (viscosities) based on actual modelling inputs as surfaces while the actual modelling output(viscosity) data points and the intermediate (and the extrapolated) models' predictions (viscosities) are shown as 3-dimensional (3D) scatter points.

It should be recalled that both the **F** and ANN models were developed to describe the relationship between black liquor viscosity and solids concentration & temperature spanning two rheological (Newtonian and non-Newtonian) zones jointly. The non-Newtonian zone was approximated by the limiting high zero-shear (Newtonian) viscosity segment, at low shear rates.

From the regions of low to moderate and moderate to high viscosities, it is observed that the ANN model has a smoother continuous prediction surface (Fig. 5.5) that covers both rheological regions, than the model **F** (Fig. 5.4). While all the modelling data fall smoothly on the ANN prediction surface, some of the modelling data at both moderate viscosity of ~1000 mPa.s (at solids concentration=~51%; temperature=0 $^{o}$C) and very high viscosity (>12000 mPa.s) are off the prediction surface of the **F** model. This shows that ANN is a better predictive viscosity model for black liquor than model **F** over a wide range of process conditions.

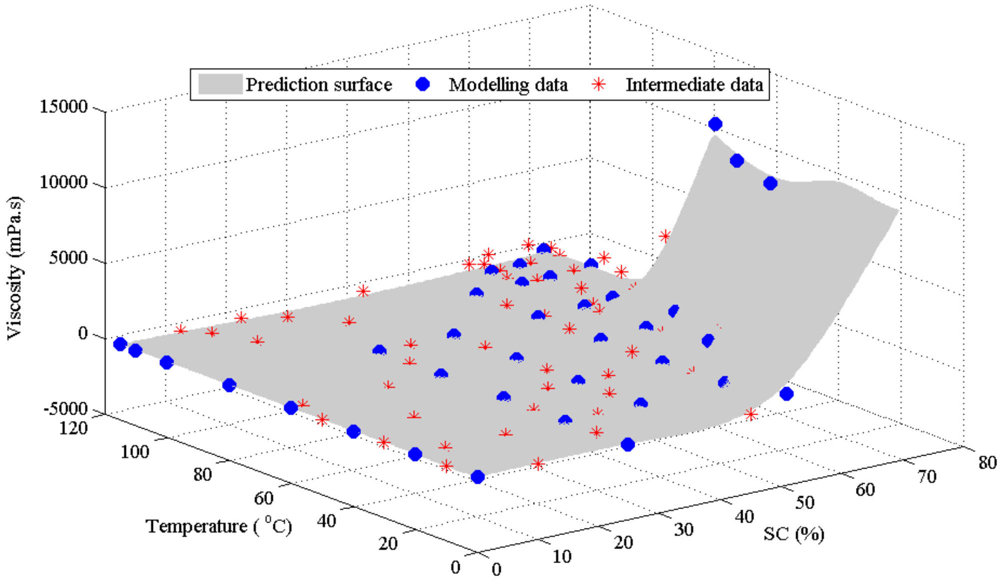


Figure 5.4 Generalization performance of the Newtonian **F** model for E509 at all solids concentrations (SCs)

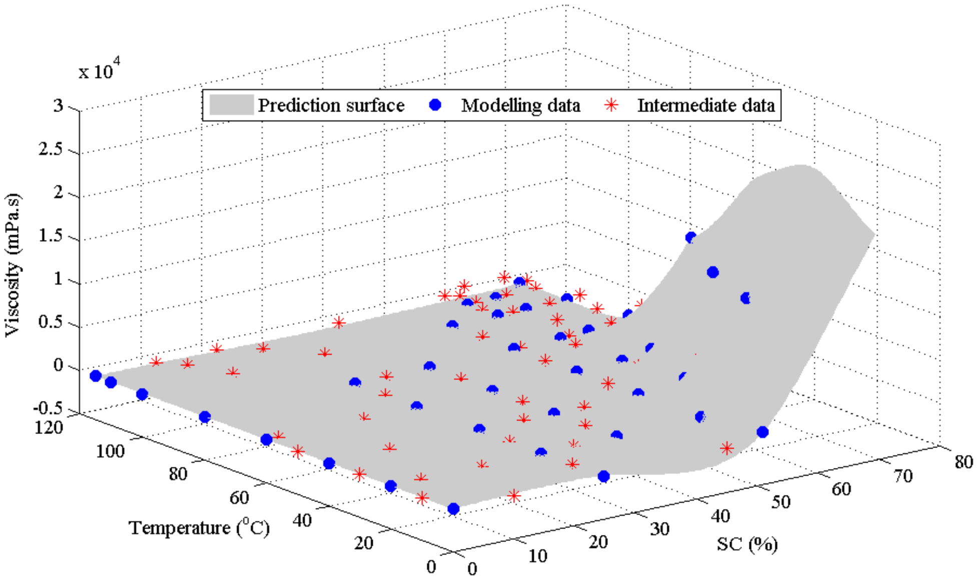


Figure 5.5 Generalization performance of the Newtonian [8, 1] ANN for E509 at all solids concentrations (SCs)

As observed from Figs 5.4 and 5.5, with the exception of a few data points that are slightly off the models' prediction surfaces at the intermediate process conditions investigated, the models' predicted outputs generally fall smoothly on their predictions' surfaces at the intermediate levels of the known modelling outputs. This shows that the two models are able to generalize well to unseen inputs. However, both models should be used with caution for extrapolation purposes as the predicted outputs, with the exception of 1 or 2 data points, are noticeably off the model prediction surfaces when inputs outside the range of modelling input data (solids concentration=~0-70%; temperature=0-115 $^{o}$C) were used. This type of limitation is typical of empirical models. Overall, within the range of modelling data, ANN is found to be more accurate and generalized than model **F** for the purposes of describing the relationship between black liquor viscosity and solids concentration & temperature over a wide range of process conditions at low shear rates.

#### 5.4.4.2 Generalization performances of E509 non-Newtonian viscosity models at all solids concentrations

Three ANN-based non-Newtonian models were developed for predicting the viscosity of black liquor of a known composition as a function of solids concentration, temperature and shear rate, over a wide range of process conditions in section 5.4.3.2. The generalization capabilities of the three networks were evaluated using independent data points limited to low solids concentrations and viscosities where the liquor behaves typically as Newtonian fluid. It is not clear what the models' behaviours will be at high solids concentrations and high viscosities where black liquor is known to exhibit non-Newtonian behaviour. To be able to evaluate the performances of the three networks [7,1], [11,1] and [4,4,1], they were exposed to input data-solids concentrations and temperatures at carefully selected intermediate values of the known modelling input data points for shear rates spanning more than three decades (see Appendix B4). Following the procedures in section 5.4.4.1, prediction surfaces, multiple 3D scatter plots of the modelling and intermediate outputs are obtained at each shear rate for the three networks.

At 10 s$^{-1}$, as observed from Figure 5.6, the modelling outputs from all the three networks fall smoothly on their prediction surfaces, indicating that the models are able to accurately predict their outputs from known inputs. However, only the [7, 1] and [11, 1] networks are able to predict intermediate outputs, which all fall on their respective surfaces at appropriate intermediate positions between the modelling outputs. The [4, 4, 1] network with the most complex architecture among the three networks predicts very low viscosity of 281 mPa.s at solids concentration=61% and temperature=40 $^{o}$C , as opposed to viscosity > 2000 mPa.s predicted by [7, 1] and [11, 1] networks at the same conditions. Consequently, as shown in Fig 5.6, only the predictions from [7, 1] and [11, 1] networks are large enough to be noticed on their respective surfaces. This result shows that [4, 4, 1] network over fitted its training data, and hence failed to generalize to new inputs at 10 $s^{-1}$ and high viscosity.

At 100, 1000, 1500 and 2000 $s^{-1}$, the networks performances were also evaluated using the data in Appendix B4 following the procedures utilised at 10 $s^{-1}$. Figure 5.7 shows the models' generalization performances at 1000 $s^{-1}$. At all process conditions, modelling and the intermediate outputs from all the three networks fall smoothly on their respective prediction surfaces while the intermediate outputs fall at appropriate intermediate positions between the modelling outputs. This finding demonstrates that all the networks are accurate and have strong generalization capabilities at 1000 $s^{-1}$. The models' performance results at 100, 1500 and 2000 $s^{-1}$ are found to be similar to their performances at 1000 $s^{-1}$. It is concluded that over wide ranges of solids concentrations, temperatures, shear rates, and viscosities, [7, 1] and [11, 1] ANNs would give accurate black liquor viscosity estimates when used with known and new input data. Since a model with a low complexity is usually desirable, a [7, 1] network is deemed suitable for practical application over a wide range of process conditions for a liquor of known composition.

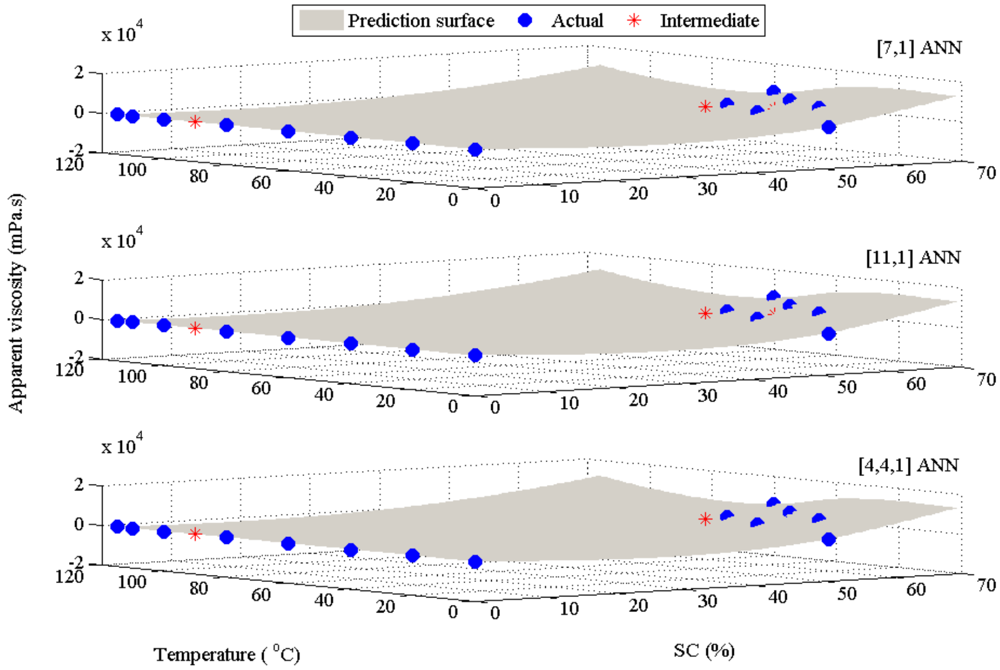


Figure 5.6 Generalization performances of three non-Newtonian ANNs for E509 at 10 $s^{-1}$; (SC= solids concentration)

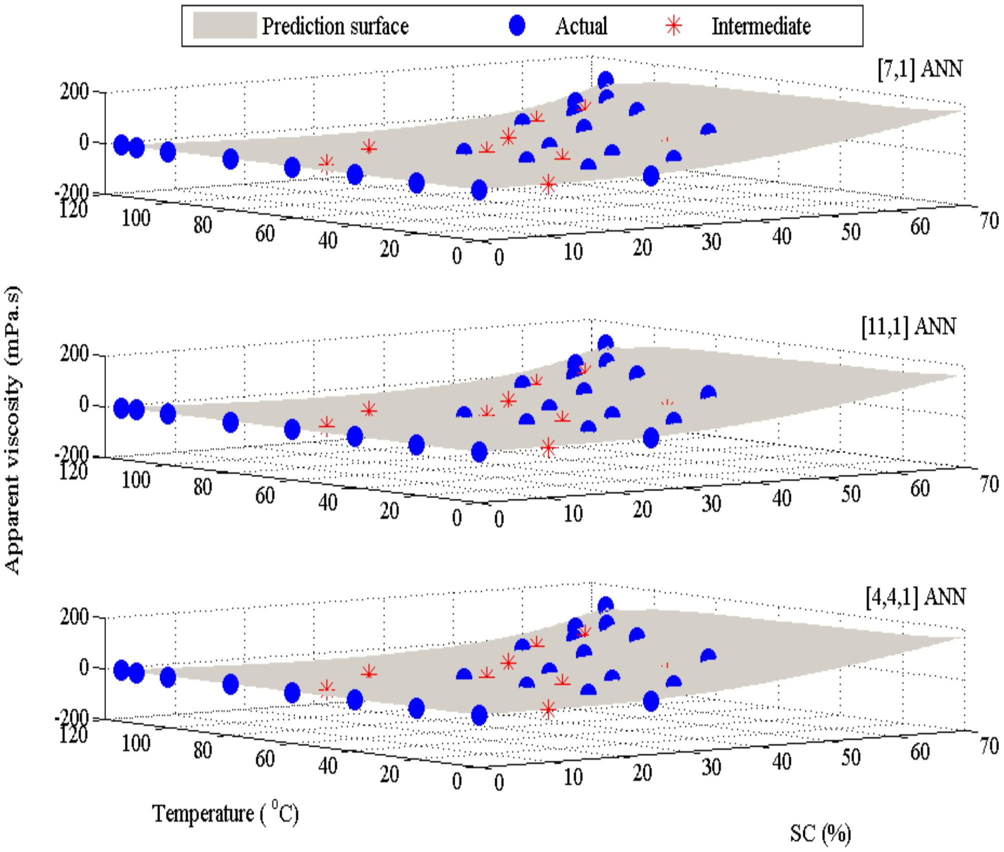


Figure 5.7 Generalization performances of 3 non-Newtonian ANNs for E509 at 1000 $s^{-1}$; (SC= solids concentration)

## 5.5 CONCLUSIONS AND RECCOMENDATIONS

A variety of the existing functional, the proposed functional binomial and ANN based composition-dependent models that are applicable at different process conditions were used to describe the relationship between viscosity and its influential factors for a New Zealand black liquor, E509. The approaches are applicable to other liquors under similar conditions. The models were classified based on the ranges of solids concentrations at which they are applicable viz: low solids (<=50.98%) models that are applicable mainly to Newtonian black liquor, high solids (>=50.98%) models & all solids (0-70%) models, which are applicable to a Newtonian black liquor mainly at low shear rates, and a non-Newtonian black liquor at all shear rates. Since many of the models are applicable to limited ranges of solids concentrations, the practical suitability of the high solids models as complementary models to the low solids models was considered.

At low solids concentrations, while the existing linear model **B** and nonlinear model **A** with fewer numbers of parameters than the 10-parameter 3rd order binomial model show strong generalization ability, the latter that was developed in this study outperformed the 2 existing models in terms of both accuracy and generalization ability. Although the [3, 1] ANN, trained via Bayesian regularization and having 12 effective parameters, is the most accurate among all the models, it shows a poor generalization. It is therefore concluded that, the 3rd order binomial model, is the most suitable for practical application based on its level of accuracy and generalization at low solids concentrations.

At high solids concentrations, the existing Newtonian models **I** and **K,** developed by Zaman and Fricke (1991;1994b), were found to be unreliable at solids concentrations>=50.98%. Although they were effective at sufficiently high solids concentrations (>=58.56%), model **I** is both inaccurate and inadequate for practical application. The high accuracy level (MARE=9%) and the effectiveness of model **K** under this condition was linked with the fundamental parameter, black liquor glass transition temperature (Tg) that was found to be valid only at solids concentrations sufficiently higher than 50%. Therefore, it is concluded that the existing model **K** is not suitable for practical implementation where it would be required to function as a complementary model to the low solids models that have upper limit of solids concentration applicability around 50%. However, if it is to be utilised as a stand-alone model at sufficiently high solids concentrations, subject to an acceptable generalization performance, it is potentially suitable for practical application. Although no adequate BM was obtained at solids concentrations>=50.98%, an adequate but moderately accurate (MARE=27.68%) 2$^{nd}$ order BM was obtained at solids concentrations>=58.56%. It is clear that the BM can not be used as a complementary model to the low solids model; however, it can be used as a stand-alone model at sufficiently high solids concentrations if no better generalized model is available.

Accurate ANN-based Newtonian models were obtained at both solids concentrations>=50.98% and solids concentrations>=58.56%. While it has been theoretically shown that ANNs trained via Bayesian regularization would not over-fit, it has been reported in the literature, and also shown in this study that, this is not always true. Therefore, the suitability of the reported high solids ANN based models for practical application either as a stand-alone or complementary model to the low solids models should be based on its performance based on generalization test.

The existing functional shear-dependent model **L** that requires the use of Newtonian viscosity model and Tg model was used to fit the combined Newtonian and non-Newtonian viscosity data at both solids concentrations>=50.98% and solids concentrations>=58.56%. The results show that the Tg-dependent **L** models obtained at solids concentrations>=58.56% are more accurate than those obtained at solids concentrations>=50.58%. At solids concentrations>=50.98%, the most accurate **L** was obtained when the Newtonian viscosity model obtained from the data at solids concentrations>=50.98% (compared with Newtonian models obtained from the data at solids concentrations>=58.56%) was used to provide zero shear viscosity estimates. It is therefore concluded that, the Newtonian viscosity models obtained at sufficiently high solids concentrations, can not be used to extrapolate to lower solids concentrations. The best model **L** (MARE=24.60) may be used for practical applications as a stand-alone model at sufficiently high solids concentrations if there are no better alternatives. However, it can not function as a good companion model to a low solids model as it is applicable only at solids concentrations>=58.56%.

In lieu of the functional model **L** that is dependent on Tg, thereby making it applicable only at sufficiently high solids concentrations, an accurate (MARE=4.68%) shear-sensitive [6, 1] ANN was obtained based on the data at solids concentrations>=50.96%. This eliminates the need for the use of Tg and zero shear viscosity models. It is concluded that, the [6, 1] network is potentially suitable for practical application either as a stand-alone model or a complementary model to the low solids models, given an acceptable generalization performance.

The viscosity data at all solids concentrations (0-70%) were fitted to two different kinds of model. The first model form assumes that the shear rate is low enough such that the liquor, even at high solids concentrations and low temperatures, shows a Newtonian behaviour. The second form incorporates the direct effect of shear rate on the liquor viscosity. No suitable existing linear model or the binomial model developed in this study was found to describe the relationship between the black liquor viscosity and its input variables-solids concentration and temperature over a wide range process conditions. It is clear that the underlying relationship, over this wide range of process conditions, is nonlinear and has finite discontinuities, as was shown by having separate models over limited ranges of solids concentrations. This finding agrees with the observations of many previous workers. However, it contradicts Ghosh (1993)'s claim that the linear model **D** developed in his study and whose performance was evaluated based on $R^2$ alone is suitable for practical application. An important observation is that many of the existing models (including Ghosh's model) and those developed in this study involve the cases whereby the response variable, viscosity has undergone logarithmic transformations. While many of them have high $R^2$ values on the transformed scale, the adequacy of the models were not discussed. It has been shown in this study that many of them have poor parameter estimates; they also have high MAREs on the untransformed scale. It is concluded that the existing linear model **D** and the linear BM developed in this study are not suitable to model black liquor viscosity over a wide range of process conditions at low shear rates.

Consequently, the performances of the existing nonlinear functional model **F** and the [8, 1] ANN developed and used in this study, to describe the relationship between E509 Newtonian viscosity and solids concentration & temperature over a wide range of process conditions, were evaluated using response surface methodology. The results show that although both models have strong generalization capabilities, the ANN gives more accurate viscosity predictions than the model **F**. However, both models show poor extrapolation abilities. This is a common problem with empirical models. It is concluded that for practical applications, the [8, 1] ANN is deemed suitable for the prediction of black liquor Newtonian viscosity over a wide range of process conditions. This is particularly important as it could replace the need for complementary models where relevant models have been built based on limited ranges of solids concentrations.

Hitherto, there has been no published model, which has the capability of modelling all the rheological behaviours of black liquor jointly over all process conditions, including where shear rate plays a significant role. This is understandable as the underlying relationship between black liquor viscosity and its influential factors over a wide range of process conditions is highly nonlinear. Three ANNs [7, 1], [11, 1] and [4, 4, 1] were used to describe the relationship between E509 viscosity (output) and three input variables solids concentration (0-70%), temperature (0-115 $^{o}$C) and shear rate (0.0001-2000 $s^{-1}$). The training results show that the three networks are capable of providing accurate ([7, 1] ANN has worst MARE =8.08%) viscosity estimates over all the process conditions investigated. A response surface methodology was used to evaluate the models' generalization performances. The results demonstrate that both [7,1] and [11,1] ANNs are able to generalize well while [4,4,1] network with the most complex architecture failed to generalize at a shear rate of 10 $s^{-1}$ and a high viscosity, giving an indication of a network that has been overfitted. It is concluded that either the [7, 1] or [11, 1] (having MARE=3.38%) ANN could be considered for practical application over a wide range of process conditions depending on the level of accuracy desired. Interestingly, the non-Newtonian [7, 1] ANN outperformed the Newtonian [8, 1] network described above despite that the Newtonian zones described by [8, 1] network is a subset of all the rheological zones covered by the non-Newtonian [7, 1] network. The [7,1] ANN addresses all the limitations of the above models as it is applicable to the wide ranges of shear rates, temperatures and solids concentrations described in this study. However, it should be noted that the parameters of all the models developed in this Chapter are liquor-dependent and therefore must be correlated with black liquor composition before they can be fully utilised in practice.

Finally, the results of the multilayer feedforward ANNs developed in this chapter, based on the automated Bayesian regularization algorithm, show that Bayesian algorithm true convergence is sensitive to the network configuration. It is also clear that where there are redundant variables that are essentially part of the system under consideration just as found in this study, the training algorithm (Bayesian in this study) may not converge. A network with internal classification ability is suggested.

# 6.0 COMPOSITION-INDEPENDENT PREDICTIVE MODELS FOR KRAFT BLACK LIQUOR VISCOSITY

## 6.1 INTRODUCTION

In this Chapter, an overview of composition-independent black liquor viscosity models is presented. The development, strengths and limitations of a multiple-input multiple-output (MIMO) artificial neural network (ANN) model using shear stress as composition indicator are reported. A variety of centrifugal-pump based black liquor viscosity models using Hydraulic Institute viscosity correction procedures are described; their strengths and limitations are highlighted. Finally, performances of these models are evaluated, conclusions are drawn regarding their suitability for practical application and recommendations are made.

## 6.2 AN OVERVIEW OF THE LITERATURE COMPOSITION-INDEPENDENT BLACK LIQUOR VISCOSITY MODELS

A variety of rheological models that describe the relationship between black liquor viscosity and its influential factors (solids concentration, temperature and shear rate) were reported in Chapter 5. While some of these models are potentially suitable for practical applications, their parameters are sensitive to black liquor composition. It is imperative that these parameters must be correlated with the liquor composition or the factors that influence the liquor composition before they can be used for online applications.

It is difficult to fully model the liquor viscosity as a function of the factors that affect its composition, as the factors are numerous and some of them are difficult to measure online. A limited number of composition-independent models(**C**, **G** and **N**) reported in the literature are as shown in Appendix A. Models **C** (Moosavifar et al. 2006), **G** and **N**(Zaman and Fricke 1995a; Zaman and Fricke 1996) were developed in a bid to describe the effect of changes in the liquor composition on black liquor viscosity. **C** and **G** are limited to low solids concentrations (<50%) and pulping temperatures; thus they are not suitable for the recovery boiler operation where high solids liquors are fired. In model **G**, the parameter $a_1$ is treated as a constant while $a_2$ is expressed as a function of pulping variables (effective alkali, sulphidity, cooking time and cooking temperature) or a function of composition (lignin molecular weight, $L_m$; lignin concentration, $L_c$; sodium ion concentration and concentration of all other inorganics). There is no guarantee that the composition variables can be measured in real time under industrial conditions. Also, factors other than pulping variables affect black liquor viscosity after it has left the digester and/or before being eventually fired at the recovery boiler. These make the composition-independent correlations which rely on the pulping variables inadequate for practical application. While model **N** is applicable to high solids liquors, it is limited to low shear rates and pulping temperatures. In addition, its parameter estimates vary with solids concentrations, effective alkali concentration and the sulphidity of the cooking liquor. It is apparent that none of the reported composition-independent black liquor viscosity models is suitable for online application. Motivated by this difficulty, the subsequent approaches were attempted to develop composition-independent black liquor viscosity models in this study.

## 6.3 MULTIPLE-INPUT MULTIPLE-OUTPUT ARTIFICIAL NEURAL NETWORK-BASED MODEL

### 6.3.1 Three-input Two-output Artificial Neural Network Development

Unlike the literature models discussed in section 6.2, the MIMO ANN-based modelling approach presented here focuses on the measurable or computable effect of the changes in the liquor composition on its physical properties such as viscosity. This is contrary to the direct focus on the constituents of the black liquor or the direct effect of the pulping variables on the liquor viscosity. It is known that black liquor viscosity is dependent on solids concentration and temperature and can be dependent on shear rate under certain conditions (Venkatesh and Nguyen 1992; Zaman and Fricke 1995c; Vakkilainen 1999). MIMO ANN approach assumes that if two liquors are compositionally similar, at the same solids concentration and temperature, they will have the same viscosity. This implies that when the liquors are subject to the same shear stress, they will experience the same rate of shear. However, if the liquors are compositionally different, even at the same solids concentration and temperature, they will have different viscosities and probably different shear-dependent behaviours. Consequently at the same shear rate, they will have different shear stresses or vice-versa. The underlying philosophy of the approach is mathematically illustrated below:

Viscosity= function (solids concentration, temperature, shear rate, liquor heat treatment, oxidation, residual alkali, chemical modification, wood type, pulping variables, high intensity shearing, etc) (6.1)

Black liquor composition=

function (liquor heat treatment, oxidation, residual alkali, chemical modification, wood type, pulping variables, high intensity shearing, etc) (6.2a)

Equation (6.2a) is summarised as:

Black liquor composition =

function (pre-pulping factors, pulping factors and post-pulping factors) (6.2b)

By substituting Eqn (6.2b) into Eqn (6.1), a generalized black liquor viscosity model can be described as:

Viscosity =

function(solids concentration(SC),temperature (T), shear rate (SR), composition (C))(6.3)

The relationship between viscosity and the first three factors (SC, T and SR) are well defined and various models describing their relationships have been presented in Chapter 5 and Appendix A. However, there is no straight forward approach to relating the overall effect of the change in the liquor composition on its viscosity as discussed earlier.

It is known that:

Viscosity (V) =shear stress/shear rate=SS/shear rate (6.4)

For two hypothetical liquors having the same SC (%), T ($^{o}$C), SR($s^{-1}$), and C (unit depends on the variable involved):

$$V_1=f\,(SC, T, SR, C) \qquad (6.5a)$$

$$V_2=f\,(SC, T, SR, C) \qquad (6.5b)$$

Since all operating conditions (including the liquor composition) are equal, then Eqn (6.5a) =Eqn (6.5b), i.e. $V_1=V_2=V$. Substituting for V and shear rate in Eqn (6.4) yields $SS_1=SS_2$.

However, if $C_1 \neq C_2$ while other operating conditions are the same for the two liquors, then from Equations (6.5a) and (6.5b), $V_1 \neq V_2$; consequently from Eqn (6.4), $SS_1 \neq SS_2$.

Therefore, SS as a single variable, if it can be computed can be used as a measure of effect of change in the liquor composition on black liquor viscosity. Therefore, a MIMO model of the following form was proposed as shown in Equation (6.6).

$$[V, SR]=f\,(SC, T, SS) \tag{6.6}$$

Based on the findings presented in Chapters 3 and 4, hardwood liquors tend to manifest shear-dependent behaviour at much lower viscosities than softwood liquors. The latter generally have their shear-dependence onsets at viscosities around 1000 cP and above. Utilising E509 as a case liquor, and assuming that when viscosity >=1000 cP, black liquor will exhibit shear-thinning behaviour, a composition-independent multiple-input multiple-output (MIMO) ANN (see Chapter 5 for the architecture and other details), which is applicable to liquors that exhibit shear-thinning behaviour at viscosities >=1000 cP, was developed. The network inputs are solids concentration, temperature and shear stress while the outputs are viscosity and shear rate. This model is applicable to both Newtonian and non-Newtonian liquors. The input shear stress serves two purposes: (i) it expresses the liquor viscosity dependence on shearing condition when the liquor exhibits shear-thinning behaviour and (ii) it serves as a composition indicator as noted earlier. The approach eliminates the need to focus on the composition or the factors that directly affect the composition of black liquor; rather, it focuses on the effects of these factors as reflected in the difference in the shear stresses on the liquor under similar solids concentration, temperature and shear rate.

Shear stress data was computed from the viscosity and shear rate data reported in Chapters 4 and 5. The approaches utilised for the ANN modelling as described in Chapter 5 were utilised to obtain the parameters of the MIMO ANN presented above. A [15, 2] network having an effective number of parameters #~=87, sum of squared weights SSW~=355 and performance indices: $R^2$=1.0 & MARE=3.51% for viscosity and $R^2$=1.0 & MARE=4.95% for shear rate was obtained.

While the reported accuracy levels are considered satisfactory for practical application, the final suitability of the model will be highly dependent on the availability of the online and real time measurements of its input parameters. Solids concentration and temperature are routinely measured in pulp and paper mills but shear stress is not and so must be accurately computed. The original aim was to estimate shear stress from the pump torque or from the pressure drop across a given length of a pipe conveying black liquor in the mill. None of the two approaches was eventually pursued due to the limitations posed by the available pipe flow theories and the complex flow dynamics in the pump internals. These are discussed in the following subsections.

### 6.3.2 Pipe Flow Theory Regarding MIMO ANN-based Viscosity Model

Fluid flow in a pipe can either be laminar or turbulent or may even be in the transition zone. While the laminar flow theory is well developed for a Newtonian fluid in fully-developed flow, a rigorous theoretical analysis is as yet not possible for turbulent flow (Munson et al. 2010). The MIMO ANN described above was built based on the laboratory viscosity data obtained from a rotational viscometer that gives steady readings under laminar conditions. Although the pressure drop across a given pipe length from which shear stress can be calculated based on Equation (6.7) is applicable to both laminar and turbulent conditions, the relationship between shear stress and shear rate (velocity profile) in the laminar flow is completely different from that in the turbulent flow zone (Munson et al. 2010). For a Newtonian fluid in laminar flow, shear stress is simply proportional to the shear rate but the shear stress dependence on the velocity profile in turbulent flow is very complex and does not lend itself easily to theoretical analysis. The implication for the black liquor flow is that under similar process conditions such as the same solids concentration, temperature and viscosity, pressure drop during a laminar flow will be completely different from that of the turbulent flow, as they would have different shear stress and velocity profiles.

$$\Delta P = 4L \times SS_w / D_p \tag{6.7}$$

L (m) is length of the pipe; $SS_w$ (N/m$^2$) is wall shear stress and $D_p$ (m) is the pipe's diameter and $\Delta P$ (Pa) is the pressure drop across L.

Typical black liquor under processing conditions has Reynolds number (Re) in the range 300-200000(Adams and Frederick 1988). Its flow regimes cover laminar, transition and turbulent zones and these zones can change from time to time depending on the prevailing process operating conditions. It is apparent that the MIMO ANN built purely on laminar data can not be implemented online in its current form by using only the well known laminar pipe flow equations. Appropriate black liquor pipe flow experiments and the subsequent building of an empirical model that addresses the specific recovery boiler or any aspect of the mill under consideration where the model is to be used may be required. This approach was not explored in this study.

### 6.3.3 Fluid Flow in the Pump Internals

The idea of computing shear stress online from the installed centrifugal pump parameters (particularly torque measurements) was frustrated based on similar difficulty discussed for the pipe flow theories in regards to black liquor flow. The nature of the flow in the pump internals is very complex. Two types of shear actions are possible inside a pump, particularly the vane cascade type. The first type occurs within the vanes of the pump impeller and the flow is usually turbulent while the second form occurs within the clearance between vanes and the casing, as well as between the flanks of the vanes for open impellers that are typical for pulp and paper, and the wear plates. Treating the clearance as a boundary layer (viscous layer), the shear rate in this layer is reported to be several thousand times higher than what would be ordinarily found in pipe flow under laminar condition (Pumping Machinery 2009). Further to the above complexity, the shaft torque required to maintain a particular pump speed is also impacted by other factors (including fluid viscosity) and is not a pure viscous torque. This torque is a function of the impeller size, fluid properties, pump capacity, friction within the pump mechanical components, etc. Under industrial conditions, the torque measurements obtained from the electric motor/drive or the torque delivered to the impeller shaft is a total torque and so resolving this torque to its individual components is not a simple task. It is clear that the shear stress or the velocity profile (often turbulent flow) in the pump internals is completely different from the pure laminar condition used for obtaining the laboratory viscosity and shear stress data that were used to build the MIMO ANN model developed in this study. To be able to use the installed pump parameters, particularly the torque measurements, explicit and direct pilot scale pump experiments over a wide range of flow conditions (from laminar through transition to turbulent) may be required to effectively relate the viscosity of black liquor to the pump parameters. This approach was not explored in this study.

## 6.4 CENTRIFUGAL PUMP-BASED BLACK LIQUOR VISCOSITY MODELS

### 6.4.1 Motivation

Due to the limitation of the composition-independent MIMO ANN discussed in section 6.3, a straight forward approach would be to conduct a series of actual pumping and/or pipe flow experiments in a pilot or an industrial plant under both laminar and turbulent flow conditions. These experiments could be undertaken in conjunction with either systematic laboratory or online hardware-based viscosity measurements. An empirical viscosity model could then be developed in relation to the flow variables or pump parameters for online implementation. However, apart from reliability concerns regarding the use of an online hardware-based viscometer, a large amount of experimental data would be required to build a reliable model. This could be time consuming and may be economically unfavourable. Motivated by the time factor and possible economic implications of conducting actual and extensive experiments, the idea of obtaining centrifugal pump viscous performance data using a well known Hydraulic Institute viscosity correction method was attempted in this study. The use of centrifugal pump parameters as an indirect online measure of black liquor viscosity(McCabe et al. 2007) or their direct correlation with actual black liquor viscosity (Porter et al. 2010) for the online prediction of black liquor viscosity is not new, as discussed in Chapter 2. The novelties in this study are the utilization of Hydraulic Institute method to minimize the amount of, or eliminate the need for, actual experimental data for a specific pump, and the direct incorporation of the effect of pump age in the resulting black liquor viscosity models.

### 6.4.2 Centrifugal Pump-based Modelling Philosophy

This section discusses a novel predictive modelling method in which black liquor viscosity is correlated with centrifugal pump parameters. It takes advantage of the changes that occur in the performance of the centrifugal pump as the viscosity of the pumped fluid changes at the pumping conditions. It does not require the installation of any new equipment as centrifugal pumps are an integral part of the installed pulp and paper mill. This method should minimise the amount of, or eliminate the need for, actual experimental data that has been historically required to develop predictive models for black liquor viscosity. It takes advantage of the existing generalized large database for rotodynamic pump (also known as centrifugal pumps) performance data, gathered by the Hydraulic Institute over several decades(ANSI/Hydraulic Institute 2004).

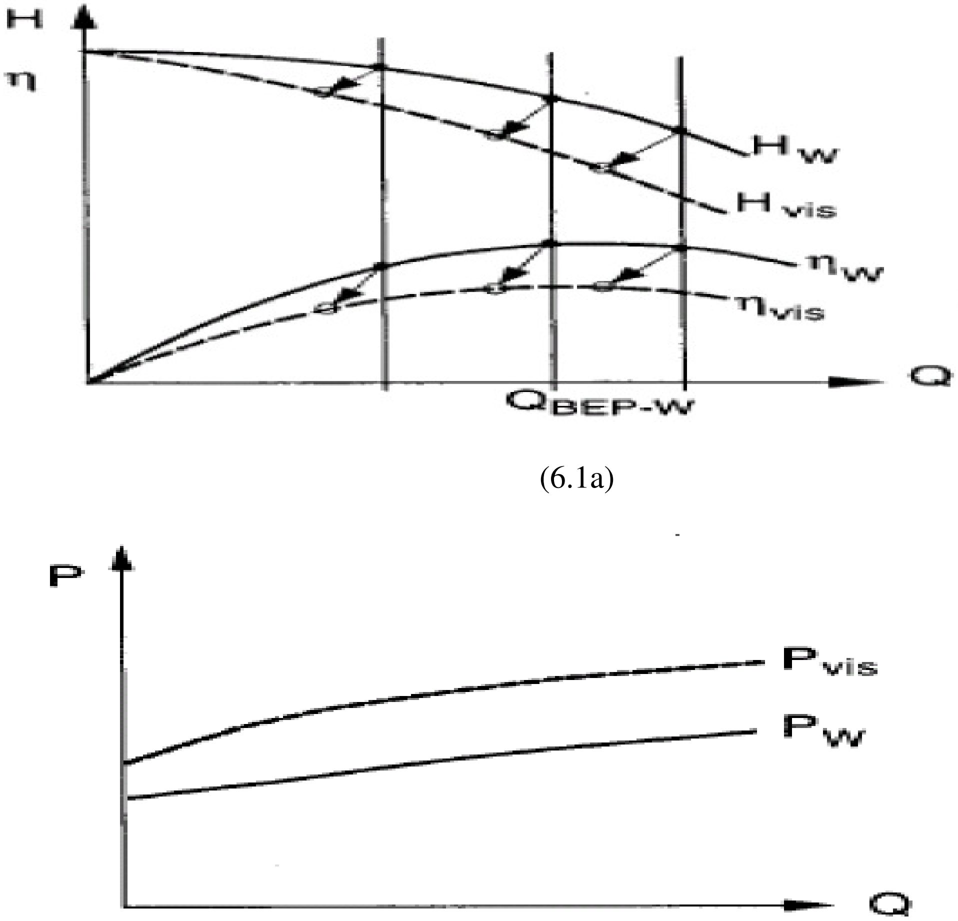
The Hydraulic Institute viscosity correction method was developed mainly for centrifugal pump design when it is to be used to pump liquids that are significantly more viscous than water. For the first time in this study, the method was extended beyond the usual pump design. It was used to estimate pump performance data at a defined range of the anticipated black liquor viscosities for a fixed impeller size of a given centrifugal pump model. The data was subsequently used to build predictive viscosity models that could be used for online black liquor viscosity measurements, monitoring and/or control.

The torque (TQ (m)) required to maintain the shaft speed (N (RPM)) of the pump impeller depends on different factors, including the liquor viscosity. Changes in the liquor viscosity due to the changes in liquor solids content, composition, pumping temperature, and other factors will reflect in the values of measured torque and the capacity (Q ($m^3$/s)) of the pump accordingly. Hence, viscosity models built using the pump's parameters as inputs should be robust to variations in the liquor composition. The Hydraulic Institute pump performance database is based on a wide range of operating conditions for a variety of rotodynamic pumps. It is therefore anticipated that the resulting models would be insensitive to the nature of black liquor flow (laminar or turbulent) in the pump internals, thereby making it potentially able to address the weakness of the MIMO ANN model presented earlier.

## 6.4.3 Centrifugal Pump and the Flowing Black Liquor

### 6.4.3.1 Effect of viscosity on centrifugal pump efficiency

Although pump vendors usually supply the pump performance curves based on water roughly at kinematic viscosity of 1 cSt and density of 1 g/$cm^3$, the actual process liquid does not always have viscosity close to that of water. Increase in viscosity reduces the head (H (m)), Q and the pump efficiency ($\eta$ (%)) but increases the brake horse power (BHP (W)) (more power will be required to pump a more viscous liquid) of the pump. BHP is the power delivered to the shaft of the pump impeller by the electric motor. The performance of a pump chosen based on water performance deteriorates as the process liquid viscosity increases significantly above that of water. For a rotodynamic pump, the typical shifts in H, η and BHP due to an increase in viscosity are shown in Figure 6.1. The subscript “vis” denotes viscous liquid and “w” stands for water, while ‘P” stands for power (BHP); BEP indicates best efficiency point.



(6.1a)

(6.1b)

Figure 6.1 Performances of a centrifugal pump when pumping water and more viscous liquid (ANSI/Hydraulic Institute 2004) ( —— Water ---- Viscous liquid )

### 6.4.3.2 Criteria for the application of Hydraulic Institute method

The Hydraulic Institute viscosity correction method (ANSI/Hydraulic Institute 2004) provides a means of determining the performance ($H_{vis}$, $Q_{vis}$ and $\eta_{vis}$) of a rotodynamic pump handling viscous liquid when its performance on water is known. This is an approximate method and is not exact for any pump since it is a generalized method based on empirical data obtained from diverse rotodynamic pumps over a wide range of operating conditions. The Hydraulic Institute method is applicable to:

- pumps of hydraulic design with essentially radial impeller discharge (e.g. centrifugal pumps),
- fully open, semi-open and closed impellers,
- Newtonian liquid having kinematic viscosities between 1 and 3000 cSt,
- Q =3-260 $m^3$/hour at best efficiency point (BEP) for water and H per stage=6-130 m.

Flowing black liquor is typically Newtonian; its viscosity is usually in the range, 1-250 cP and density in the range, 1000-1400 kg/$m^3$ (Adams and Frederick 1988). The practical centrifugal pumping limit for black liquor is around 500 cP (Adams and Frederick 1988; Holmlund and Parviainen 1999) and so, for practical consideration, the upper limit for the black liquor kinematic viscosity was estimated as 360 cSt. The centrifugal pumps being used for black liquor and the black liquor being processed under normal industrial operating conditions satisfy the criteria outlined above. Therefore, the Hydraulic Institute method is considered suitable for estimating the required performance data for the viscous black liquor. However, it should be noted that some hardwood black liquors can exhibit shear-thinning with or without thixotropic behaviour at viscosities as low as 100 cP (Soderhjelm 1988). For such liquors, the procedure developed in this study can only be applied to them up to the maximum viscosity where they behave as Newtonian fluids.

#### 6.4.3.3 Viscous performance data estimation for the number 5 recovery boiler firing pumps at the CHHP&P Kinleith mill, New Zealand

Two identical heavy black liquor firing pumps, which are used alternately at the number 5 recovery boiler (see Chapter 7 for further process description) section at the Carter Holt Harvey Pulp and Paper (CHHP&P) Kinleith mill, New Zealand, were chosen for a case study. They are Ahlstrom-made THP-10 centrifugal pumps having outer impeller diameter 360 mm (see Appendix C1). The design and the selection of the above pump and its associated motor/driver were based on the worst case black liquor viscosity (500 cP) at solids concentration=73% and pumping temperature =110 °C in the recovery boiler house (Ayers and Clarihew 1988). Design calculations show that specific gravities of black liquor at 65% D.S (dry solids), 90 °C and 73%, 110 °C are 1.37 and 1.4, respectively. It seems logical for estimation purposes to choose a specific gravity value in the range 1.37-1.4 for heavy black liquor at ~70% and 110 °C. Ayers and Clarihew

(1988) states that "Ahlstrom supplied graphs gave 70 cP at 65% D.S., 110 $^{o}$C", therefore, it was assumed that the pump curve as shown in Appendix C2 represents the performance of any of the two identical THP-10 firing pumps while pumping heavy black liquor at 70 cP .

The manufacturer's (Ahlstrom) water-based pump curve, HT 10P72 was used for the design and selection of the electric motor and the THP-10 pump required to transfer black liquor at number 2 effect of the number 5 evaporator set to the intermediate black liquor tank. The same reference curve was used for estimating the viscous performance data of the same pump model (THP-10) at the number 5 recovery boiler, where heavy and viscous liquor is processed. The design data for the low viscosity (4 cP) liquor at pumping temperature (111 $^{o}$C), specifications of the pump impeller, and the motor/driver are reported in Appendix C3 while the associated water-based pump curve HT 10P72 used for the design is as shown in Appendix C4. For the low viscosity black liquor, no viscosity correction is required. The curve is applicable to THP-10 pump model with impeller sizes ranging from 270 to 390 mm at a pump speed N=960 RPM. Since the outer diameter (D) of the impeller of the same pump model being used to pump heavy viscous liquor at the number 5 recovery boiler is 360 mm, all data were estimated from the reference curve HT10P72 at D(m)=0.360 (360 mm).

At fixed N and D, the centrifugal pump operating point varies with changes in Q and subsequently leads to changes in $\eta$ even at a constant viscosity. Although the liquid viscosity may remain constant, the BHP and TQ are increasing function of Q at a fixed N. In order to be able to obtain performance data that covers different flow conditions (FCs) or pump operating points, data were obtained from 0.2 to $1.4Q_{BEP}$ (at intervals of 0.2, thereby giving rise to 7 flow conditions FC1-FC7; FC1=0.2 and FC7=1.4). Although effort is usually made to operate the pump at or near BEP, due to changes in the production demands, Q may be adjusted to meet these demands either at a constant N or at varying N. In a situation, whereby a centrifugal pump is being driven by constant-speed motor, flow adjustments via a valve may be inevitable to meet different production or operational demands. This procedure will shift the operating point of the pump even at a constant viscosity. With a variable speed drive (VSD) motor, the pump can be made to operate at a definite operating point; however, the choice of operating point may vary from mill to mill due to technical, economic or production reasons.

The aim of this study was to develop predictive models that can be used in the presence of deliberate or non-deliberate changes in the centrifugal pump operating points and with or without VSD motor. Therefore, in order to be able to obtain a predictive model that is robust to changes in centrifugal pump operating points at any constant viscosity, it is essential to cover the practical ranges of FCs. Although Qs below $0.6Q_{BEP}$ may be a conservative choice, they have been included in this data collection and modelling for completeness sake. The number of operating points chosen for the model development is purely arbitrary; but it is advisable that the operating points other than the BEP should be considered, as this will be able to accommodate changes in the normal operating point of the pump due to process upsets. Inclusion of operating points other than the BEP in the model development will also be useful when there is a plan to change the operating point of the pump or where the operating point changes due to plant modifications. This eliminates the need to rebuild the predictive model that might have been installed as a soft sensor.

For each operating point or FC at 960 RPM, $H_w$ (m), $Q_w$ ($m^3/s$), $\eta_w$ (%) were obtained from the reference liquor pump curve HT10P72 (see Appendix C4). Having known the centrifugal pumping practical limit ( viscosity =500 cP) for black liquor processing, the centrifugal pump performance data ($H_{vis}$, $Q_{vis}$, and $\eta_{vis}$), based on user pre-defined viscosities ranging from 5 to 552 cP, were estimated for the viscous liquor using the Hydraulic Institute viscosity correction method (ANSI/Hydraulic Institute 2004; IDC Technologies 2009; Campbell 2010; Whitesides 2010). The Hydraulic Institute method is a well-established procedure and well discussed in the literature and so the readers are referred to the cited references for further details on the method. Based on the estimated performance data for viscous liquor, $BHP_{vis}$ (kW) and $TQ_{vis}$ (Nm) were estimated from Equations (6.8) and (6.9):

$$BHP_{vis}\,(kW) = 0.001\rho_{vis} g Q_{vis} H_{vis} / \eta_{vis} \qquad (6.8)$$

$$TQ_{vis}\,(Nm) = 9.548 BHP_{vis}\,(W) / N\,(RPM) \qquad (6.9)$$

where $\rho_{vis}$ is the viscous liquor density (kg/m$^3$) and $g$ is the acceleration due to gravity = 9.8 m/s$^2$. Other parameters are as defined earlier. The average density of the heavy viscous black liquor at anticipated ranges of pumping temperature was taken as 1.38 g/cm$^3$ (1380 kg/m$^3$). Note that while the pump's H-Q and $\eta$-Q relationships are not affected by the variations in the liquor density, the BHP-Q relationship is dependent on density; thus, TQ-Q relationship will be affected by the density variation. However, the viscous performance data obtained here is limited to heavy (at solids concentration=~70% and pumping temperature=~110 $^o$C) viscous black liquor and the effects of any variations (from the assumed 1.38 g/cm$^3$) in the liquor density on the BHP and/or TQ should be negligible. In a situation whereby a wide range of densities is anticipated, the explicit effect of density on BHP-Q and TQ-Q relationships must be considered.

The available online measurements, from the installed motors/ VSDs connected to the number 5 recovery boiler firing pumps at the CHHP&P Kinleith mill, are given as the percentage of the nominal motor/VSD torques at definite Ns and Qs and other process conditions. Therefore, the ratio (in percentage form) of torque developed by the motor ($TQ_m$ (Nm)) at any process condition to the nominal torque ($TQ_{nom}$ (Nm)) developed at the motor-rated output power and speed is given by Equation (6.10):

$$TQ_p\ (\%) = 100TQ_m/TQ_{nom} \tag{6.10}$$

$TQ_{nom}$ (obtained as 357.3 Nm) is based on 55 kW motor at the rated 1470 RPM (see Appendix C1). It was assumed that the torque ($TQ_m$) developed at the motor/drive unit is completely transmitted to the pump shaft as $TQ_{vis}$ in Equation (6.9) so that $TQ_m$=~$TQ_{vis}$ for estimation purposes.

After obtaining the estimated viscous performance data at 960 RPM, affinity laws (see Menon 2004; Claverton Energy Research Group 2009) were used to obtain more performance data ($H_{vis}$, $Q_{vis}$ and $BHP_{vis}$) at each flow condition and each viscous condition at other pump impeller shaft speeds, between 300 and 1800 RPM. The data (modelling set) collected above was used to build the relevant predictive viscosity models.

Following the same procedures above, another independent data set (batch) that covers 6.9-345 cP over 500-1600 RPM was obtained. This is a preliminary validation set. This was obtained at 0.6-1.2$Q_{BEP}$ (at intervals of 0.2). The first batch of data was used to build the models presented in subsection 6.4.4 while the second independent batch was used for a preliminary model validation. The two data sets were based on new pump performance and are designated modelling and preliminary validation data sets. The purpose of model validation at this stage was to find out if the developed models, assuming the estimated data are a true representation of the pump's performance, could adequately describe the relationships established among the relevant variables based on the estimated performance data. Assuming the developed models describe the underlying relationships between the variables well, a final validation that would establish whether the estimated data is appropriate to replace full scale laboratory or online viscosity measurements should be based on actual experimental data.

### 6.4.3.4 Data analyses and explorations

A series of explorations were performed on the modelling data set using the exploratory functions in MATLAB® statistics toolbox in order to identify the underlying relationship among the variables associated with the pumping operation and the liquor viscosity at different FCs or pump operating points. Note that the variables involved in the data analysis and modelling have been normalised and as such, are treated here as dimensionless variables. When any variable is mentioned from this point forward, it refers to a normalised variable unless otherwise stated.

It was found that using $V_n$ (normalised viscosity V) as a grouping variable, across all the FCs and at constant $V_n$ as shown in Figure 6.2, a clear and consistent relationship exists between TQNN (normalised torque $TQ_p/N^2$) and QN (normalised flow Q/N). Prior to the normalisation of the variables and the subsequent modelling, the units of $TQ_p$, N, Q and V are %, RPM, L/min, and cP respectively while the FC is dimensionless ($Q/Q_{BEP}$). Subscript "vis" has been omitted for convenience. Note that the variables were only normalised for proprietary reason; the pattern observed between the normalised variables as shown in Figure 6.2 is expected to also hold if the variables were not normalised.

Variables normalisation was done using zscore function in the MATLAB® statistics toolbox or Equation (6.11):

$$z=(y-y_m)/y_{std} \qquad (6.11)$$

where y is the variable (e.g. $TQ_p/N^2$, Q/N and V) to be normalised; $y_m$ is the mean of y and $y_{std}$ is the standard deviation of y and z is the normalised y. During modelling, different forms of V were attempted and so the ys, $y_m$s and $y_{std}$s used to normalise V differ. For example, when viscosity data was used directly in its raw form, $z=V_n=(V-V_m)/V_{std}$ but when the logarithm of V was attempted, $V_n=(\log(V)-\log(V)_m)/\log(V)_{std}$, etc. Table 6.1 is a summary of the statistics of the variables based on the modelling data set.

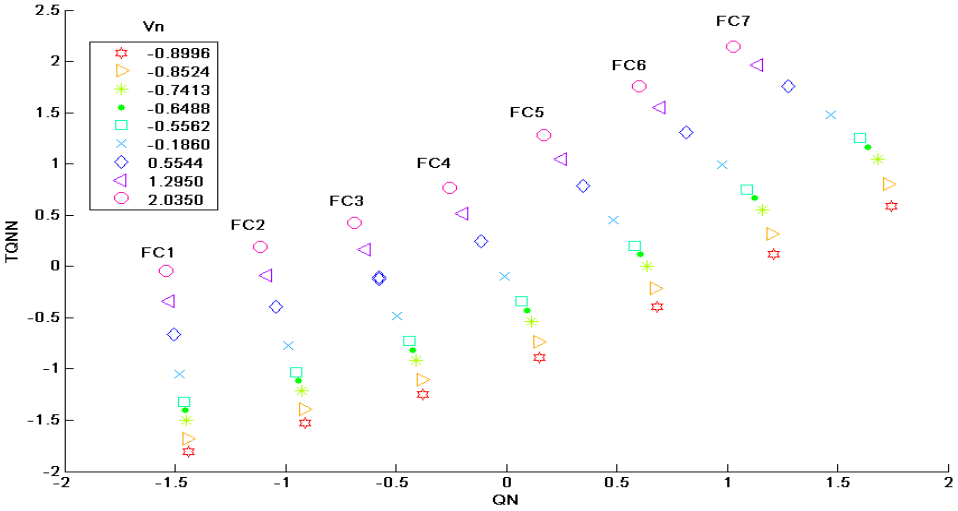


Figure 6.2 Relationship between the normalised flow (QN) and the normalised torque (TQNN) at different viscosities and FCs

Table 6.1 Statistics of the input and output variables based on the new pump data

| | Variables | | | | |
|---|---|---|---|---|---|
| Statistics | Q/N (L/min/RPM) | $10^5$ TQp/$N^2$ (%/$RPM^2$) | V (cP) | log(V) (cP) | $V^{0.5}$ ($cP^{0.5}$) |
| Minimum | 0.3030 | 1.938 | 5.000 | 1.609 | 2.236 |
| Maximum | 2.625 | 4.658 | 552.0 | 6.314 | 23.49 |
| Mean | 1.394 | 3.181 | 172.7 | 4.316 | 11.06 |
| STD* | 0.7069 | 0.6894 | 186.4 | 1.490 | 7.107 |
| Range | 2.322 | 2.720 | 547.0 | 4.704 | 21.26 |

* Standard deviation

As observed in Fig 6.2, along each FC (FC1-FC7), TQNN increases while QN decreases as $V_n$ increases (from -0.8996 to 2.035). Alternatively, looking across all FCs simultaneously at any constant $V_n$, TQNN is observed as an increasing function of QN, and so, the evolving models will have parameters that are clearly dependent on $V_n$. It is important to note that all the three variables $V_n$, TQNN and QN are dependent (correlated) on one another. The ultimate desire is to treat $V_n$ as a dependent variable while TQNN and QN are treated as independent variables. Different approaches could be adopted in developing the relevant models; e.g. partitioning the data into different FCs so that different models can be obtained for each FC. This may not be very useful for applications where a constant-speed motor is being used and FC is not anticipated to remain fixed even at a fixed viscosity, as discussed in the earlier sections. In addition, processes are modified from time to time in a plant, thereby changing the overall system pumping requirements that in turn changes the operating point of the pump. Another approach that could be adopted is to develop robust models that are capable of predicting the liquor viscosities across all FCs jointly. In this study, the latter approach was adopted. This is particularly useful since FCs can be changed for production or technical reasons and there will be no need to modify the existing model. Furthermore, there is no guarantee that the pump will actually operate at its BEP, there may be some fluctuations around (either side of) the BEP. It appears that a more logical approach is to develop a model, which is robust to the changes in FCs at constant viscosity, and will work with a centrifugal pump being driven by either a constant-speed or VS motor.

## 6.4.4. Linear Predictive Models

### 6.4.4.1 Principal component analysis-based linear regression model

*Preamble*

Principal component analysis (PCA) is the first statistical step in principal component regression modelling when dealing with correlated variables in multivariate statistics. In PCA, the correlated explanatory variables represented by columns of matrix X are transformed to uncorrelated orthogonal variables (latent variables or the principal components (PCs)) represented by columns of matrix XX, that are linear combinations of the original correlated explanatory variables. The standard assumption is that the explanatory variables are linearly correlated; however, this is not always the case. The PCA step is followed by the conventional multiple linear regression modelling involving the PCs (in place of the original explanatory variables) and the original response variable(s), Y. There are two main reasons for regressing a response variable on the PCs rather than directly on the correlated explanatory variables (Filzmoser 2010):

(i) due to the correlation between the explanatory variables, the ordinary least squares regression may lead to poor regression coefficient estimates; this can be avoided by using the uncorrelated PCs instead of the correlated explanatory variables,

(ii) the dimensionality of the regressors is reduced by taking only a subset of the PCs for prediction.

Although PCA is a powerful tool, there are conditions under which it may not be effective; one such condition is where the explanatory variables are non-linearly related and as such, a non-linear PCA may be required (Kruger et al. 2007; Scholz et al. 2007). Since usually, a subset of PCs is used, the ones that contribute significantly to the total variations in the original regressor variables are retained while discarding the less significant PCs. However, there are cases where the widely believed less-important PCs are strongly important to the predictive ability of the eventual model; and another case where the neglected PC (that contributes less than 1% variability in the original variables) is most important (Jolliffe 1982; Hadi and Ling 1998; Hwang and Nettleton 2003; Filzmoser 2010).

Some researchers have argued that there is no strong justification for using PCA under the conditions where the explanatory variables are correlated. They argued that, simply removing superfluous variables would have removed the computational difficulty due to them (Hadi and Ling 1998). However, one must appreciate the fact that where there are many variables and, it is not obvious how to analyse their effects on the dependent variable, PCA may be a good tool to handle such condition.

This thesis does not intend to prove or disprove the effectiveness of PCA; rather, the focus was on its application as a useful statistical tool for deriving relevant predictive models based on the data obtained in this study. In addition, the aim of using PCA was not to reduce the number of input variables but to obtain uncorrelated input variables before applying standard regression tools. For this reason, the usual variance analysis, which is a part of PCA for identifying the PCs that contribute significantly to the total variance in the original regressor variables, was neither incorporated nor explored. Instead, PCA was used with the ultimate aim of eliminating the correlation between TQNN and QN. Detailed mathematical analysis, strengths, weaknesses and other applications of PCA are beyond the scope of this thesis; interested readers are referred to the cited references and the references therein for further details.

### *Parameter estimation of principal component analysis-based linear models*

Using the available PCA functions in the MATLAB® statistical toolbox, two principal components $PC_1$ and $PC_2$, each as a function of QN and TQNN were obtained. Having obtained two independent and orthogonal variables, a model describing the relationship between $V_n$ (dependent variable) and independent variables ($PC_1$ and $PC_2$) were developed by utilizing the surface fitting function in the MATLAB® curve fitting toolbox. Based on 95% confidence level (CL), a PCA-based linear cubic model was obtained; this is given by Equation (6.12):

$$V_n = a0+a1\ PC_1+a2\ PC_2+a3\ PC_1^2+a4\ PC_1\ PC_2+a5\ PC_2^2+a6\ PC_1^3+a7\ PC_1^2\ PC_2 +a8\ PC_1\ PC_2^2+a9\ PC_2^3 \tag{6.12}$$

where $V_n$ is the normalised $V^{0.5}$; $PC_1$ and $PC_2$ are the principal components obtained as functions of QN and TQNN, as shown in Equations (6.13a) and (6.13b):

$$PC_1 = 0.7071QN+0.7071TQNN \tag{6.13a}$$

$$PC_2 = -0.7071QN+0.7071TQNN \tag{6.13b}$$

The parameter estimates (a0-a9) and their respective lower and upper limits are as reported in Table 6.2. The PCA-based cubic model performances are: Sum of squared errors (SSE) =0.6297 and R-square statistic ($R^2$) =0.9983.

As observed in Table 6.2, the parameter estimates have narrow confidence intervals (CIs), indicating that the parameters are very certain and should be reliable. Although, there was an improvement in the model performances as the order of the model was raised to 4, some of the model parameters became highly uncertain (have large parameter intervals based on 95% confidence level (CL)). Using such models for predictive purposes can lead

Table 6.2 Parameter estimates of the linear PCA-based cubic model

| Parameter | Mean | Lower limit | Upper Limit |
|---|---|---|---|
| a0 | 0.1547 | 0.1460 | 0.1634 |
| a1 | 0.06257 | 0.05284 | 0.0723 |
| a2 | 2.080 | 2.058 | 2.103 |
| a3 | -0.1062 | -0.1092 | -0.1033 |
| a4 | 0.05384 | 0.04472 | 0.06297 |
| a5 | 0.1329 | 0.1112 | 0.1547 |
| a6 | 0.02692 | 0.02444 | 0.0294 |
| a7 | -0.04829 | -0.05559 | -0.041 |
| a8 | 0.09193 | 0.07384 | 0.1100 |
| a9 | -0.2519 | -0.2918 | -0.2121 |

to unstable predictions. It is clear that a higher order linear model with a larger number of parameters may be required for higher accuracy; however, a less accurate but stable model is preferable and so the best model obtained using the above tools was as reported in Equation (6.12).

### 6.4.4.2 Quartic linear regression model

Not all readers are familiar with PCA, but many engineers and scientists are well grounded in using standard least squares regression procedures where the actual (not transformed via PCA) explanatory variables are used in the regression analysis. Here, the modelling proceeded without de-correlating the correlated variables (QN and TQNN) as done while developing the PCA-based model in Equation (6.12). Different linear regression models were searched; the best model obtained using the surface fitting function in the MATLAB® curve fitting toolbox is of order 4 (order 3 in QN and order 4 in TQNN). Effort was made to improve the performance of the model by raising the order of QN to 4, but this led to high uncertainty in the coefficient of $QN^4$ (based on 95% CL) without a significant improvement in the model performance. Thus, a model having highest degrees=3 and 4 in QN and TQNN, respectively was finally chosen as reported in Equation (6.14):

$$V_n = a0 + a1x + a2y + a3x^2 + a4xy + a5y^2 + a6x^3 + a7x^2y + a8xy^2 + a9y^3 + a10x^3y + a11x^2y^2 + a12xy^3 + a13y^4 \qquad (6.14)$$

where: x=QN; y=TQNN; and $V_n$ is normalised log (V). The quartic linear model performances are SSE=0.347 and $R^2$=0.9991. Table 6.3 summarises the parameter estimates (a0-a13) and their associated CIs.

Table 6.3 Parameter estimates of the linear quartic model

| Parameter | Mean | Lower limit | Upper Limit |
|---|---|---|---|
| a0 | 0.5258 | 0.5177 | 0.5339 |
| a1 | -1.098 | -1.112 | -1.084 |
| a2 | 1.115 | 1.1 | 1.13 |
| a3 | -0.6467 | -0.6576 | -0.6358 |
| a4 | 0.8881 | 0.8623 | 0.9139 |
| a5 | -0.6254 | -0.6455 | -0.6053 |
| a6 | -0.1887 | -0.2 | -0.1774 |
| a7 | 0.6672 | 0.6345 | 0.6999 |
| a8 | -0.8014 | -0.8405 | -0.7624 |
| a9 | 0.4458 | 0.4282 | 0.4635 |
| a10 | 0.206 | 0.1804 | 0.2315 |
| a11 | -0.3215 | -0.3769 | -0.2662 |
| a12 | 0.3175 | 0.2678 | 0.3672 |
| a13 | -0.138 | -0.155 | -0.121 |

### 6.4.4.3 Performance evaluation of the linear predictive models

Some crucial questions must be answered concerning any model to be considered for online prediction, monitoring or/and control purposes; two such questions are:

(i) Can the models give logical, accurate and consistent predictions in the presence of changing process operating points such as FCs in this study? This is a question of model robustness.

(ii) Can the models perform well when they are exposed to other input data different from the ones used to build them? This is a question of model generalization.

#### *Model robustness*

To answer the first question, both the PCA-based cubic and conventional quartic regression models in Eqns (6.12) and (6.14) were firstly applied to the same original input data used to build them, the scatter diagrams of their normalised predicted viscosities and the actual viscosities grouped by FCs are shown in Figs. 6.3 and 6.4, respectively. For a

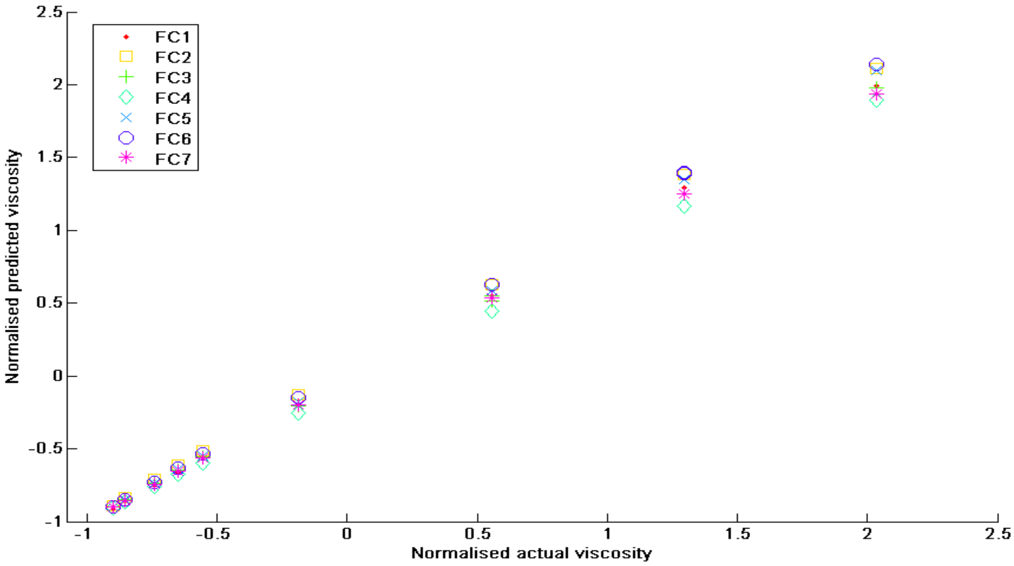


Figure 6.3 Black liquor viscosity predictions using the PCA-based cubic model with the original modelling data

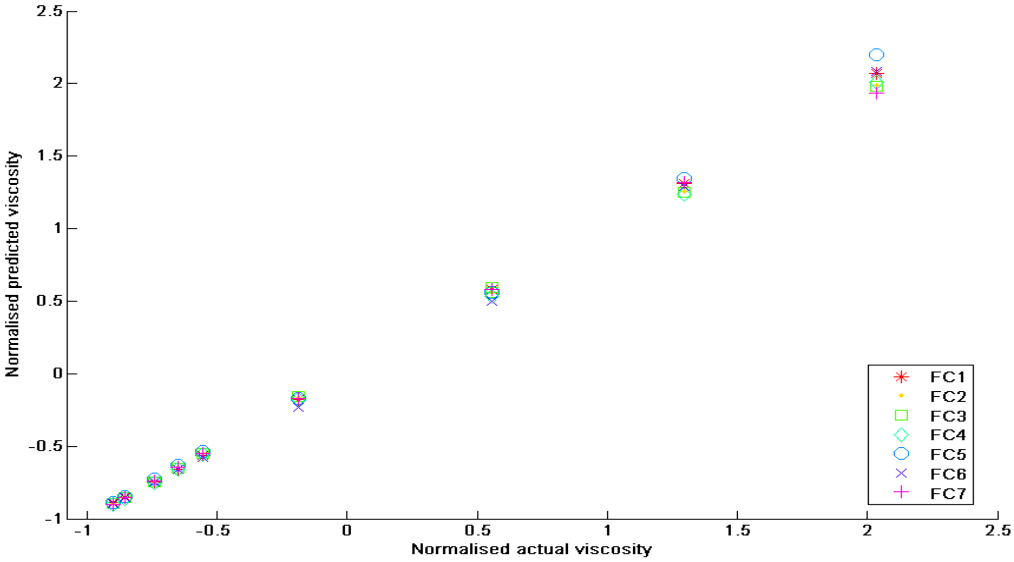


Figure 6.4 Black liquor viscosity predictions using the quartic model with the original modelling data

fair comparison (since the models have different forms of $V_n$s), the predictions from both models were firstly converted to unnormalised Vs and then normalised using $V_m$ and $V_{std}$ of the raw data (see Table 6.1). It is expected that the predictions from the models across all the FCs should be approximately the same if they are robust to changes in the pump's operating points.

It is observed that the two models give strong robust predictions at low viscosities. At moderate to high viscosities, they are moderately sensitive to changes in the process operating conditions (FCs) as their predictions fall within moderate bands. However, by comparing the prediction bands from the two models, generally, the quartic model is found to be more robust to changes in FCs than the PCA-based cubic model as the predictions from the former fall within narrower bands, except at the maximum viscosity where the predictions from the two models fall within similar but large bands. It seems the quartic model may be more useful for general process monitoring where moderate sensitivity to changes in process characteristics may not be an issue. For process control purposes, predictions that fall within very narrow bands would be desirable and a more robust model than the quartic model should be sought. Although the quartic model outperformed the PCA-based cubic model in this study, it is clear that its superiority is dependent on having a larger number of parameters (14 vs. 10) than the PCA based cubic model. This is confirmed by comparing the performance data (SSE=1.516) of the best conventional cubic model (having 10 parameters) with the PCA-based cubic model (also having 10 parameters) having performance data as SSE=0.6297.

It seems the degrees of accuracy of the predictions of the two models are strongly dependent on having large numbers of parameters. This is an indication that the underlying relationships among the variables are much more complicated than linear models can describe accurately. This seems to also be a probable factor responsible for the ineffectiveness of PCA, which is purely a linear statistical tool.

### *Model generalization*

Pending further modifications and improvements, having ascertained the degree of robustness of the quartic model in this study and its potential application for general process monitoring, there was a need to ascertain if it has a generalization capability. On this note, the quartic model was exposed to new independent data set (preliminary validation data), that contain viscosities between 6.9 and 345cP, across four FCs: FC3-FC6 and N=500-1600 RPM. Grouped by FCs, the normalised predictions from the quartic model and the actual viscosities are as shown in Figure 6.5.

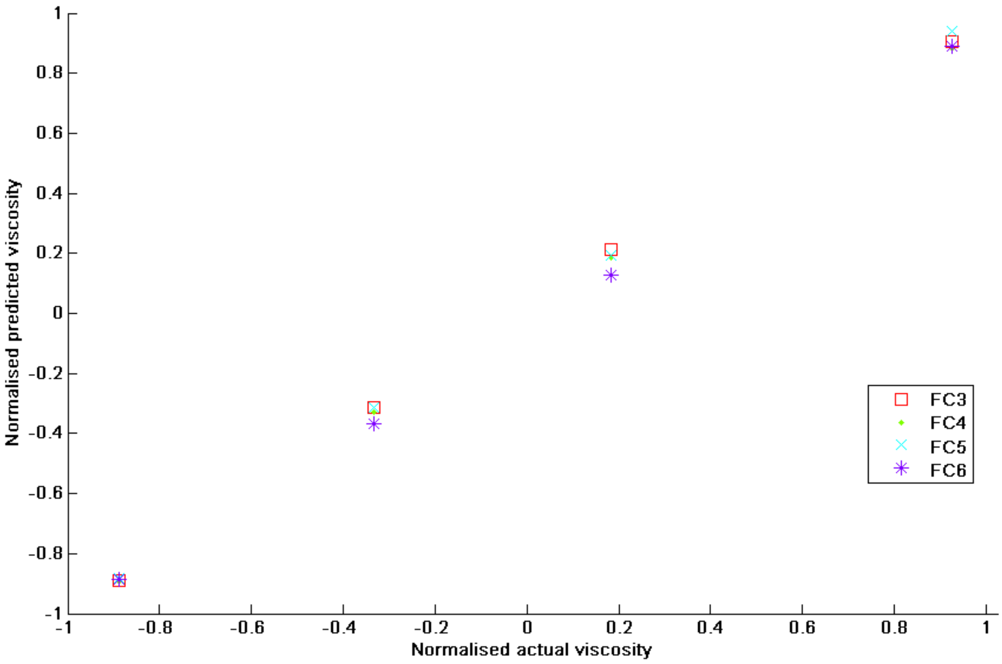


Figure 6.5 Black liquor viscosity predictions using the quartic model with the preliminary validation data

It is observed that the model gives fairly accurate predictions that fall within very narrow (at low viscosities) to moderate (at higher viscosities) bands; this performance is similar to its performance on the original modelling data. This gives an indication that the model has a good generalization capability although with some degree of sensitivity to changes in the operating points of the pump.

### 6.4.4.4 Conclusions and recommendations on linear predictive models

14-parameter quartic and 10-parameter PCA-based cubic linear models have been proposed in this subsection to describe the relationship between black liquor viscosity and the centrifugal pump parameters, QN and TQNN. Despite the large numbers of the parameters of these models, they could not model the relationship between V (response variable) and QN & TQNN (predictor variables) accurately across different FCs jointly. It is concluded that, there is an underlying nonlinear relationship among these variables, which the linear models fail to capture accurately and adequately. The quartic model outperforms the PCA-based cubic model in terms of robustness to changes in the operating point of the pump and shows strong generalization capability in the presence of new input data. In the absence of a more accurate and robust model, the quartic model may be used for general monitoring of the black liquor viscosity in the presence of changes in pump operating points. For process control applications, where a higher level of robustness would be desirable, three approaches may be adopted. The first approach may involve the use of a nonlinear PCA to capture the underlying nonlinear relationship between QN and TQNN across all FCs, thereby yielding nonlinear PCs. Thereafter, standard linear or nonlinear regression methods may be applied to model the relationship between the eventual nonlinear PCs and $V_n$. In the second approach, the linear PCA may be applied to QN and TQNN in order to obtain the traditional linear PCs first. A nonlinear functional model or a data-driven nonlinear model such as artificial neural network (ANN), which correlates $V_n$ with the linear PCs, can subsequently be developed. In the third approach, a complete non-PCA-based nonlinear modelling technique may be attempted. The two latter approaches were attempted in the subsequent subsections to address the problems of non-linearity.

### 6.4.5 Nonlinear Data-Driven Predictive Models

#### 6.4.5.1 Motivation for the choice of ANN

In subsection 6.4.4, linear models were used to describe the relationship between black liquor viscosity and the centrifugal pump parameters, QN and TQNN. Unfortunately, they were unable to accurately and adequately describe the relationship between the variables due to an underlying non-linearity whose nature has yet to be investigated.

A closer look at Figure 6.2 (reproduced below) shows that across the lower flow conditions FC1-FC3, the relationship between QN and TQNN is linear at constant $V_n$. Across higher FCs, FC4-FC7, similar linear relationship between QN and TQNN is observed at constant $V_n$. However, there is a sharp curvature (nonlinear behaviour) between F3 and F4. Within each flow region (lower and higher), two main viscosity regions are identified. A closer look across FC1-FC7 shows that there are two roughly linear regions at each FC. Regions of low-to-moderate $V_n$ (-0.8996 to -0.7413) and that of moderate–to-high $V_n$ (-0.6488 to 2.035) are observed. Between -0.8996 and -0.7413, at each FC there is a curvature (non-linearity) that increases or becomes sharper as FC increases. On a casual look, it seems the relationship between QN and TQNN can be described as a quadratic surface across all FCs at each $V_n$ and that the parameters of the

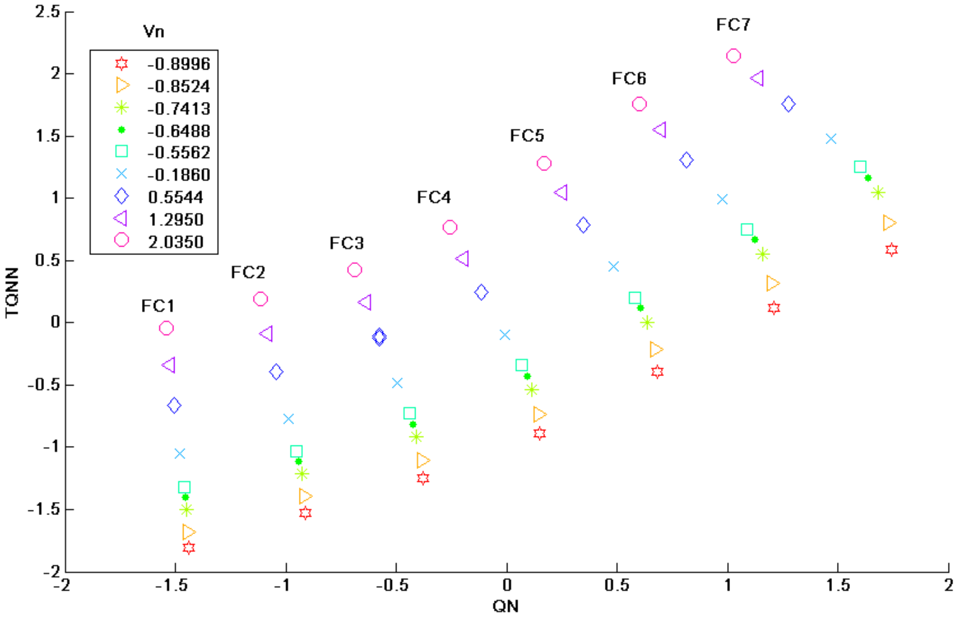


Figure 6.2 Relationship between the normalised flow (QN) and the normalised torque (TQNN) at different viscosities and FCs

quadratic model can be related to $V_n$. Unfortunately, as discussed above, there are roughly four unique discontinuous linear sections with sharp curvatures (one demarcating the region of low-to-moderate $V_n$ and moderate-to-high $V_n$ and the other demarcating the regions of low and high FCs). While linear models may be able to describe the linear sections reasonably, it is clear that they will suffer grossly around the identified curvatures. This may be the reason why the linear quartic and PCA-based cubic models developed in subsection 6.4.4 could not give good robust predictions at moderate-to-high viscosities. There are at least three ways to solving this problem:

(i) develop linear models for each of the 4 linear segments and find a means of relating their parameters to FCs and $V_n$,

(ii) Develop a nonlinear functional model $V_n$=f(QN,TQNN) spanning all the FCs jointly,

(iii) Develop an ANN-based model spanning all the FCs jointly.

It is obvious that the first two options may not be easy tasks. The first option will require that four different linear models must be installed for the online prediction of black liquor viscosity; this will require switching commands to identify FC or/and $V_n$. Even if a way of linking all the models together is found (multi-phasic modelling), one will still be faced with the implementation problems as to know when each segment of the model should dominate during operation. Although it may be relatively easier to identify FC e.g. in a variable speed drive (VSD) pumping, or preset this for online implementation; it doesn't seem to be feasible to identify and preset $V_n$, the response variable in advance.

It is also obvious that the second option may not be a good choice. From the earlier analysis, there are definite linear sections demarcated by nonlinear curvatures or discontinuities. If it is assumed that the degrees of nonlinearity across FCs and those across $V_n$ at each FC are fairly the same (that is clearly not the case, so two different nonlinear models may be required), the nonlinear model may be able to tackle the curvatures problem but may fail at the linear sections. Two other problems that may attend this option is the task of identifying the best mathematical form the nonlinear model should assume and the choice of good starting values for the parameters of the nonlinear model being searched in an iterative procedure (See Draper and Smith 1981; *NIST/SEMATECH* 2010).

ANN is regarded as a universal approximator because of its ability to model any function even in the presence of discontinuities (Demuth, Beale et al. 2008) such as those observed in Figure 6.2. Therefore, ANN is considered as a suitable modelling tool to address the underlying nonlinearity that makes the above linear models inadequate. Relevant ANN concepts that are applicable to this study have been presented in Chapter 5. The methods described therein using the automated Bayesian regularization algorithm in the MATLAB® neural network toolbox were also utilised here to obtain the parameters of the ANNs developed in this subsection.

### 6.4.5.2 ANN-based black liquor viscosity model

#### *ANN selection and training*

A feedforward ANN, with just one hidden layer having two inputs $TQ_p/N^2$ and Q/N, and one output, viscosity (V), was used to describe the relationship between the black liquor viscosity and the centrifugal pump parameters. The modelling data set that was used to develop the linear models presented in subsection 6.4.4 was also used to build the ANNs in this subsection. Two types of ANN were attempted. In the conventional form, TQNN, QN and $V_n$ that are the normalised forms of $TQ_p/N^2$, Q/N and V (in log (V) form) respectively, were obtained using Equation (6.11) or zscore function in the MATLAB® statistics toolbox. They were then scaled to within [-1, 1] prior to the ANN training according to the approaches discussed in Chapter 5. In the non-conventional (PCA-based) form, after obtaining TQNN and QN, principal components (PCs), $PC_1$ and $PC_2$ were obtained as functions of QN and TQNN using Equations (6.13a) and (6.13b). The PCs and $V_n$ were then scaled to within [-1, 1] before training the ANNs following the methods described in Chapter 5. The scaling of the relevant variables to [-1, 1] range was done using mapminmax function in the MATLAB® neural network toolbox or Equation (6.15):

$$B= -1+ 2(A-A_{min})/A_{range} \tag{6.15}$$

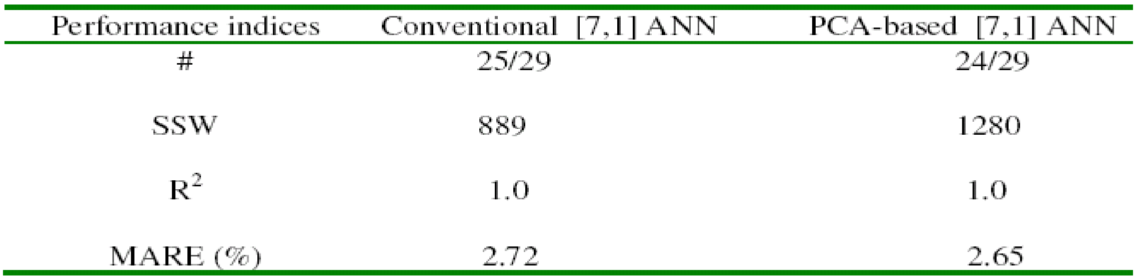
where: B is the new variable in the range [-1, 1]; A, $A_{min}$ and $A_{range}$ are the original variable, minimum of A and range of A, respectively.

## *Computations, results and discussion*

### Parameter estimation for the conventional and the PCA-based ANNs

Conventional and PCA-based ANNs were trained using the algorithms described in Chapter 5. The best networks obtained and their performances are as shown in Table 6.4. It is observed from Table 6.4, that the two models have similar performances ($R^2$=~1.0 and MARE=~2.7%). There should be no concern about overfitting if any of the models is chosen for practical application since the two networks are considerably small in size ([7,1]) and the number of data points (378) used for modelling are considerably larger than the models' #s (24-25). Although the conventional ANN model has a slightly larger (25 vs. 24) effective number of parameters # (each of the two models has 29 tuneable parameters) than the PCA-based model, the former has a smaller sum of squared weights

Table 6.4 The performance indices of the age-sensitive ANNs



| Performance indices | Conventional [7,1] ANN | PCA-based [7,1] ANN |
|---|---|---|
| # | 25/29 | 24/29 |
| SSW | 889 | 1280 |
| $R^2$ | 1.0 | 1.0 |
| MARE (%) | 2.72 | 2.65 |

(889 vs. 1280) than the latter. This makes the former potentially better in terms of generalization capability.

### Robustness of the conventional ANN model

The conventional ANN model was exposed to the original modelling data and the responses were obtained across all the FCs jointly. The scatter of the normalised predicted and the actual viscosities are as shown in Figure 6.6. It is observed that the ANN (nonlinear) model gives robust predictions across all FCs at all viscosities within the practical range of black liquor applications. It is clear that ANN outperforms the linear quartic model (see Fig 6.4) in terms of accuracy and robustness. Without the use of PCA, a linear statistical tool, the conventional ANN is able to robustly predict the viscosity of black liquor across all the FCs despite the underlying nonlinear relationship between the variables. This shows that, the effect of nonlinearity supersedes that of the variables dependency on the performance of centrifugal pump-based black liquor viscosity models. This finding confirms why the linear predictive models (with or without PCA) described in subsection 6.4.4 could not robustly predict black liquor viscosity across all the FCs. Therefore, in terms of robustness, the ANN is considered adequate for process control application. However, one must ensure that the model can perform well in the presence of unseen inputs.

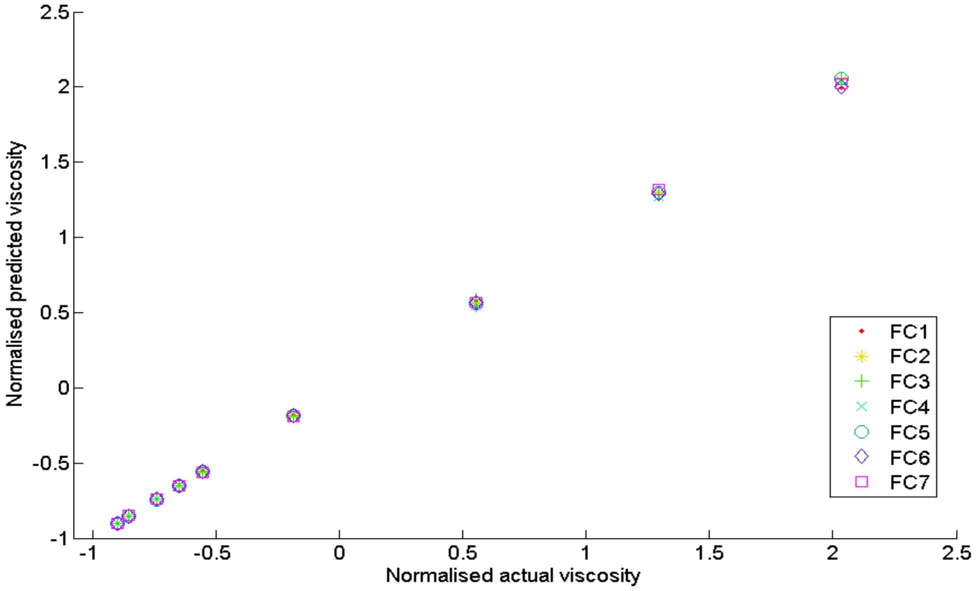


Figure 6.6 Black liquor viscosity predictions using the conventional ANN model with the modelling data

### Conventional ANN generalization

A Bayesian regularized ANN is potentially able to generalize well but can fail in some circumstance as discussed in Chapter 5. It therefore would be helpful to confirm the predictive ability of the conventional centrifugal pump-based ANN developed in this subsection when exposed to unseen (not used in the training) inputs. The predictive ability of the conventional ANN in the domain of the training or modelling data was studied via a response surface approach. In Figure 6.7, the network predictions are shown as the prediction surface while the modelling and the preliminary (pre) validation outputs (normalized viscosities) are shown as the 3-dimensional (3D) scatter points across all the operating points (FCs) of the pump. The outputs from the training data fall smoothly on the prediction surface. The same observation is noted for the pre-validation outputs at the intermediate points between the modelling outputs. It is obvious that the network is very robust and has a strong generalization capability.

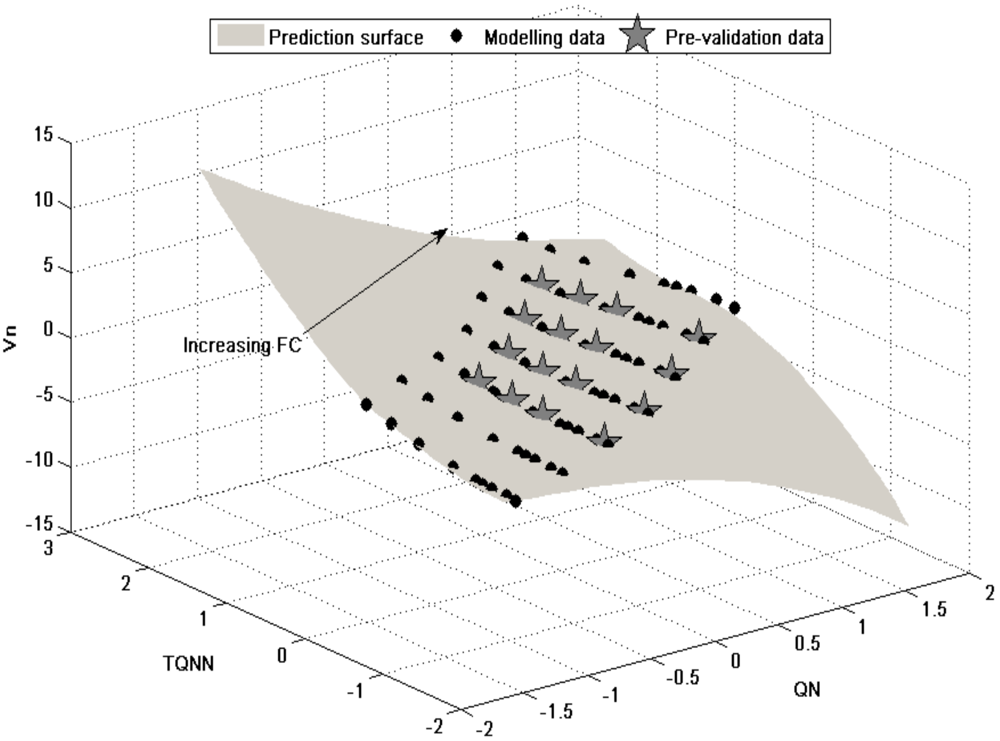


Figure 6.7 Generalization performance of the conventional [7, 1] ANN; (QN=normalised flow; TQNN=normalised torque; $V_n$=normalised viscosity; FC=flow condition)

### Effect of pump age on the performance of centrifugal pump-based viscosity model

The efficiency of a centrifugal pump at a given operating condition depends on a number of factors including the pump model and geometry, piping system, fluid properties, degree of wear and tear of the pump's mechanical components, etc. The models developed above (linear and nonlinear) have effectively taken into consideration the first three factors but have assumed implicitly that the installed pump is new. The implicit assumption is that the pump's water and viscous performances were obtained at the same condition of wear and tear of the mechanical components of the pump. Since the viscosity correction is usually done during the design and selection of a new pump, it implies that pump performance curve based on water is based on the new pump. Unfortunately, as the installed pump ages, the wear and tear of its mechanical components reduces the efficiency of the pump and thereby increases the shaft power under similar pumping conditions compared to the new pump. It is not technically logical to stop the operation of an installed pump after some years, test its performance on water, and then obtain its viscous estimates at other viscous conditions via the Hydraulic Institute or other methods. Since the model developed above is based on torque (that depends on BHP), as the pump ages, higher torque will give erroneous indication of higher viscosity and the above ANN will fail under such circumstance. It was shown in Chapter 2 that the idea of using centrifugal pump parameters as a direct or an indirect measure of viscosity is not new but one of the conclusions therein was that the existing approaches will fail as the mechanical components of the pump wear with use. The serious implication on the existing models is that from time to time, full and explicit actual experimental data would be required to rebuild the predictive model that has been installed as a soft sensor.

Figure 6.8 shows a typical trend in the pump efficiency deterioration, as the pump mechanical components age. The effect of the reduction in the efficiency of the pump due to wear and tear on the centrifugal pump performance has neither been included in the above models, nor taken into consideration in the existing centrifugal pump-based black liquor viscosity models. In Figure 6.8, it is observed that over a period of about 25 years, the efficiency deterioration follows a minimum, an average, or a maximum trend. Intermediate or non-uniform trends are likely.

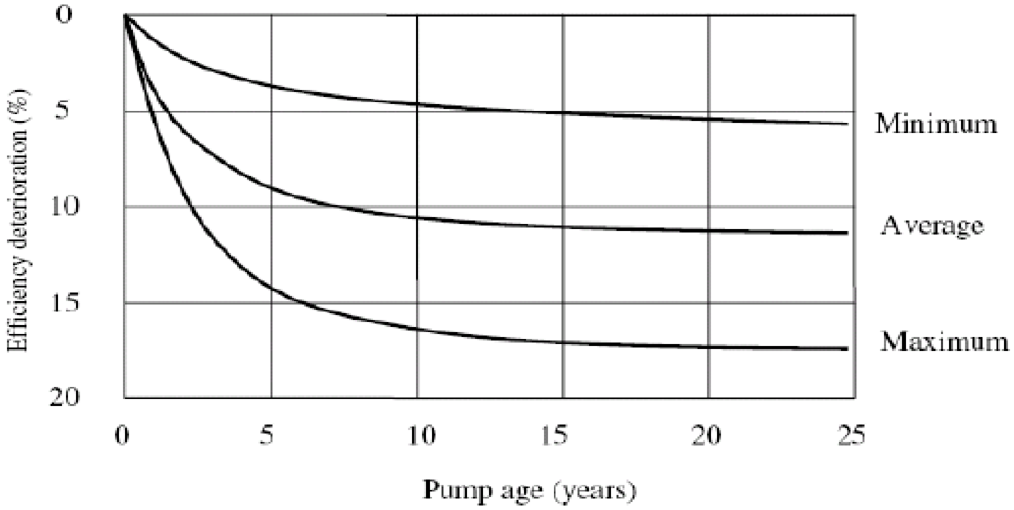


Figure 6.8 Typical trends in efficiency deterioration of an ageing pump (Claverton Energy Research Group 2009)

Based on the new pump condition and the worst-case conditions of the efficiency deterioration trends in Fig 6.8, four hypothetical pump ages (PAs) were defined as: PA=1 (new pump condition at 0% efficiency deterioration), PA=2 (at ~6% efficiency deterioration), PA=3 (at ~12% efficiency deterioration) and PA=4 (at ~18% efficiency deterioration). Based on this definition, the performance data (modelling and preliminary validation) of the THP-10 centrifugal pump model, which was obtained in section 6.4.3.3 based on PA=1, was used (as basis) in combination with Equations (6.1)-(6.3) to obtain the pump performance data across all FCs at PAs=2-4. The earlier performance data (at PA=1) was combined with ageing pump performance data (at PA=2-4) to obtain complete modelling and preliminary validation data. They were designated ageing modelling data (at PA=1-4) and ageing preliminary validation data (at PA=1-4) for the analysis of the pump throughout its entire lifespan.

The study of the effect of PA on the performance of the conventional ANN (developed purely using the new pump data at PA=1) followed two steps. First, based on the means and standard deviations of Q/N, $TQ_p/N^2$ and V of the new pump data (see Table 6.1), QN, TQNN and $V_n$ at all PAs (PA=1-4) were obtained from the ageing modelling data using Equation (6.4). A response surface approach was then used to study the effects of the inputs on the model's predictions at different PAs as shown in Figure 6.9.

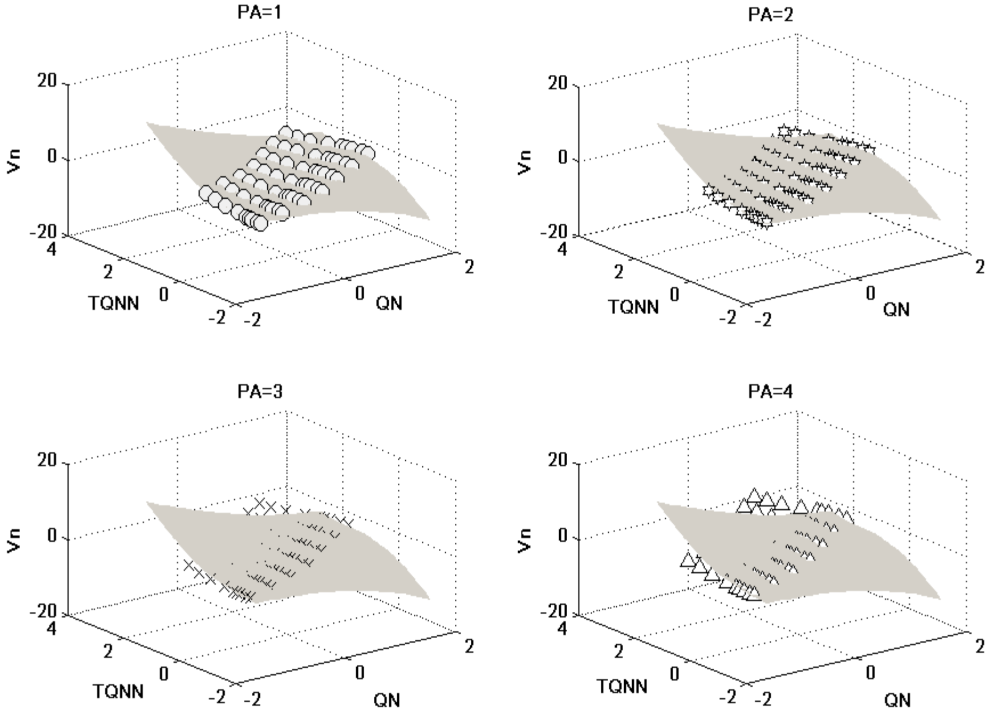


Figure 6.9 Effect of PA on the performance of the centrifugal pump-based black liquor viscosity model built from the new pump data; (PA=pump age, QN=normalised flow, TQNN=normalised torque; $V_n$=normalised viscosity)

The network's predictions based on the training inputs are shown as the surface while the actual performance outputs at different inputs and each PA are shown as 3D scatter points. As expected, at PA=1, which corresponds to the new pump data (training data domain), the model predicts the viscosity accurately at all inputs. At PAs=2-4, some of the outputs fall outside the prediction surface of the model. The number of outputs that the model fails to predict accurately increases as the PA increases. This should be expected since the pump's efficiency reduces, as the degrees of wear and tear increase, thereby leading to increase in TQ (and BHP) while other process conditions remain the same. As can be seen, the model (based on new pump data) over-predicts or under-predicts the viscosity as the pump ages.

Although the conventional ANN model developed in this study is robust to changes in the operating points of the pump when its mechanical status does not change appreciably and has a strong generalization capability within the domain of its training data, it is unreliable as the pump ages significantly. A model that can adequately account for the significant variations in the pump efficiency due to mechanical wear and tear is expedient.

### 6.4.5.3 Age-independent centrifugal pump-based ANN for black liquor viscosity

#### *Age-independent ANN selection and training*

In subsection 6.4.5.2, a robust conventional ANN model with a strong generalization capability was obtained. It was deemed suitable for online prediction of viscosity of heavy black liquor. Despite its ability to address the limitations of the linear model described in subsection 6.4.4, it is sensitive to significant variations in the mechanical status (degree of wear and tear of the components) of the pump. This concern was not addressed in the existing centrifugal pump-based models discussed in Chapter 2. However, comparatively, the approach developed here around the Hydraulic Institute viscosity correction procedure is more general than the existing modelling methods. Moreover, it is potentially able to minimize the amount of experimental data required to build such models. In order to avoid a situation whereby detailed modelling will be required each time the mechanical status of the pump changes significantly, an ANN model that directly incorporates the effect of PA was proposed. In this way, whenever the pump mechanical status changes significantly, it is anticipated that a few experimental data could be used to set the PA. This would greatly simplify the recalibration procedures. A three-input one-hidden layer one-output PCA-based ANN model was attempted. The three inputs to the network are Q/N, $TQ_p/N^2$ & PA, and the output is viscosity, V (cP). See Chapter 5 for details on ANN architecture and training procedures used throughout this thesis.

#### *Calculations, results and discussion*

Based on the ageing modelling data (1512 data points), Q/N, $TQ_p/N^2$, PA and V (in log (V) form) were normalised using Equation (6.4), resulting in QN, TQNN, $PA_n$ (normalised PA) and $V_n$, respectively. Utilizing the PCA functions in the MATLAB® statistics toolbox, three principal components (PCs) $PC_1$, $PC_2$ and $PC_3$ were obtained as functions of QN, TQNN and $PA_n$ as follows:

$$PC_1=0.6431QN+0.7071TQNN+0.2941PA_n \tag{6.16a}$$

$$PC_2= -0.4159QN-9.411*10^{-11}TQNN+0.9094PA_n \tag{6.16b}$$

$$PC_3= -0.6431QN+0.7071TQNN-0.2941PA_n \tag{6.16c}$$

$PC_1$, $PC_2$, $PC_3$ and $V_n$ were then scaled to fall in [-1, 1] range using Equation (6.15) prior to the ANN training. Following the procedures outlined in Chapter 5, different ANN sizes were searched. The best network obtained is a PCA-based [11, 1] ANN. Its performance indices are as reported in Table 6.5. As observed from Table 6.5, the ANN obtained is very accurate, as it gives high $R^2$ and MARE values. It is a relatively simple network with just 11 hidden neurons. In terms of consideration about over-fitting, there should be no concern as the data size (1512) is approximately 30 times larger than the effective number of parameters #=52 (out of 56 tuneable parameters). In addition, its SSW (2920) seems moderate in size when compared with the SSW (1280) of the PCA-based [7, 1] ANN obtained from new (PA=1) pump data, which is exactly one-fourth of the entire data over all PAs (1-4). The performance indices of the PCA-based [11, 1] model, as reported in Table 6.5, show that it is potentially able to describe the relationship between black liquor viscosity and the centrifugal pump parameters Q/N, $TQ_p/N^2$, and the mechanical status PA of the pump reasonably well. However, there is a need to take a closer look at the actual behaviours of this model at different operating conditions (FCs) at all PAs as well as check whether it can generalize to unseen inputs.

Table 6.5 Performance indices of the age-independent ANN

| Performance indices | Age-independent PCA-based [11,1] ANN |
|---|---|
| # | 52/56 |
| SSW | 2920 |
| $R^2$ | 1.0 |
| MARE (%) | 3.97 |

### Robustness of the age-independent PCA-based [11, 1] ANN

The above model was exposed to the original training (ageing modelling) data used to build the ANN at all FCs of the pump and at all PAs. The normalised predicted and actual viscosities are as shown in Figure 6.10. It is observed that, across all the FCs and all the PAs, it gives robust predictions. It is clear that if appropriate PA of the pump can be determined, the model should be able to perform excellently when in use for online predictions. It has an added advantage over the age-sensitive [7, 1] ANN model in that its mechanical status can be defined in advance to capture the current degree of wear and tear in the mechanical components of the pump.

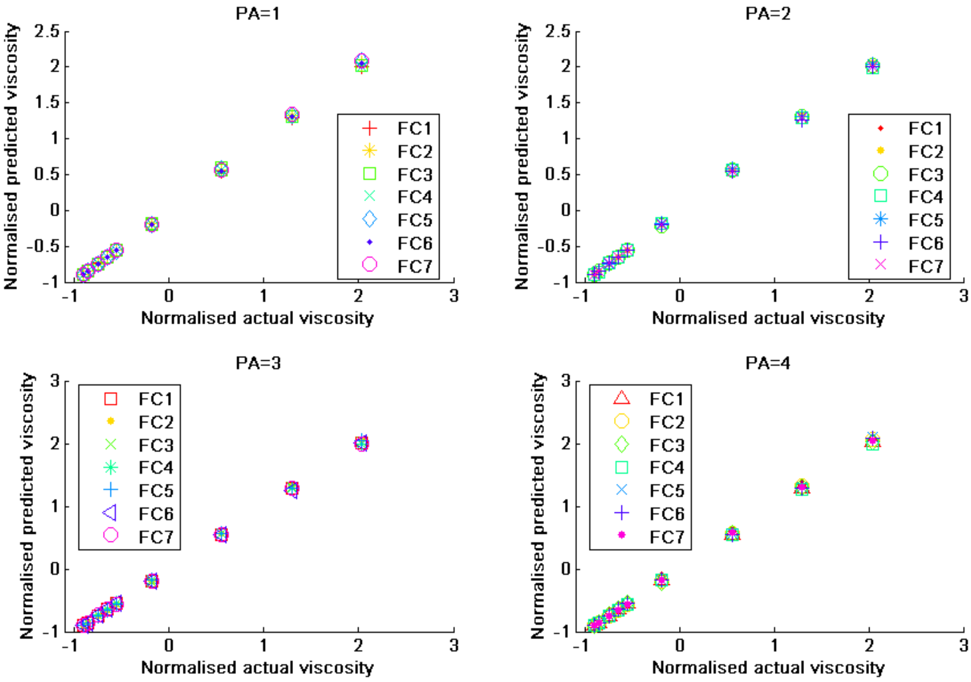


Figure 6.10 Robust performance of the age-independent centrifugal pump-based ANN; (PA=pump age)

### Age-independent PCA-based [11, 1] ANN generalization

A robust model may not eventually generalize. However, a well-trained Bayesian-regularized ANNs usually generalize well. In addition, the model performance indices reported in Table 6.5, do not portray an over-fitted model. For double assurance, a response surface method was used to study its generalization capability when exposed to unseen inputs. The model's predictions based on the domain of the training data (all PAs and FCs) are shown as the surface in Figure 6.11. The 3D scatter points of the ageing

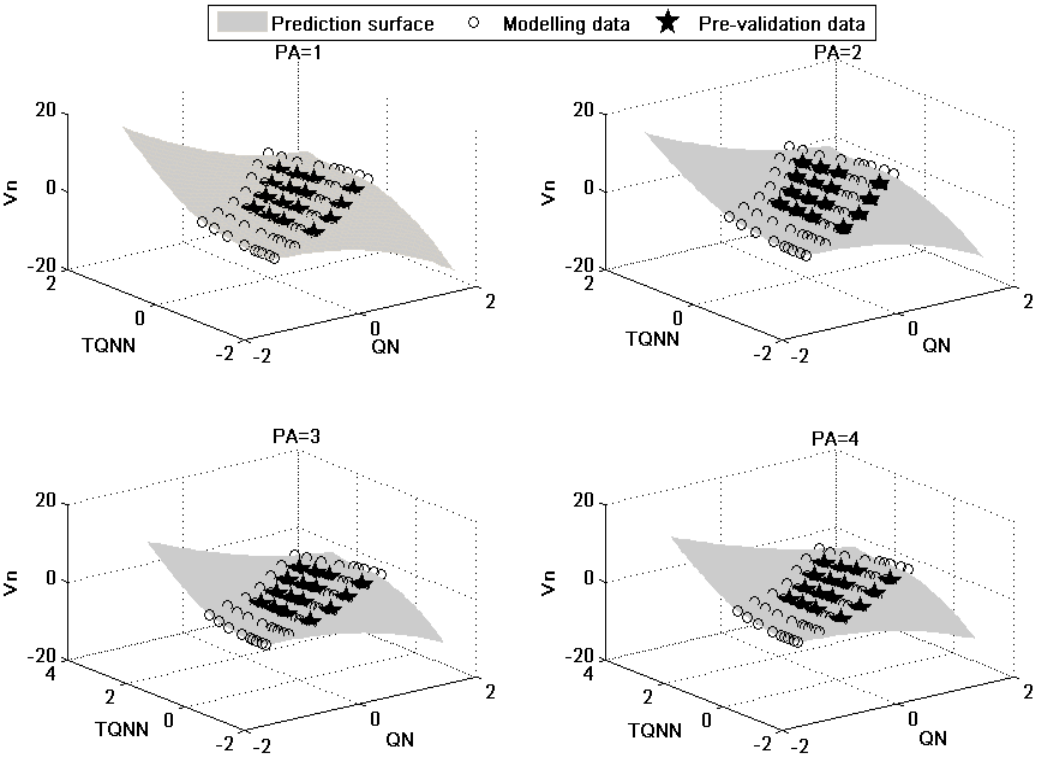


Fig 6.11 Generalization performance of the age-independent centrifugal pump-based ANN; (QN=normalised flow, TQNN=normalised torque, PA=pump age, $V_n$=normalised viscosity)

modelling data and the ageing preliminary validation data set are also shown on the same Figure 6.11. Unlike the off-prediction surface scatter points observed in Figure 6.9 for the age-sensitive [7, 1] ANN at PAs=2-4, it is seen in Figure 6.11 that, all the modelling and the preliminary validation scatter points fall smoothly on the prediction surface of the age-independent PCA-based [11, 1] ANN at all FCs, as well as all PAs. This indicates that the latter is insensitive to PA and has a very strong generalization capability. The age-independent model should be able to perform well for online application, due to its ability to address the changes in PA. Therefore, as the pump ages significantly, it should be easier to use a few experimental data to adjust the PA rather than starting the whole data collection/estimation and model development afresh.

## 6.5 CONCLUSIONS AND RECOMMENDATIONS

In this chapter, a variety of composition-independent linear regression and ANN-based models were proposed for the prediction of kraft black liquor viscosity. These are opposed to the composition-sensitive models described in chapter 5.

A multiple-input multiple-output (MIMO) ANN model, having solids concentration, temperature, and shear stress as the inputs and, viscosity and shear rate as the outputs, was built based on the laboratory data collected under laminar condition. The shear stress serves a dual purpose: (i) as a measure of the shear-thinning characteristics of the liquor at high viscosities and (ii) as an indicator of the liquor composition. While this model is robust to changes in the liquor composition, it is not considered adequate for online application where black liquor processing can occur under turbulent flow condition. It is therefore concluded that if the model can be built based on data collected over the flow conditions ranging from laminar to turbulent, the model can be deployed for an online black liquor viscosity prediction. The shear stress may be successfully computed online from the pressure drop-shear stress relationship applicable to piping system.

The idea of using centrifugal pump parameters to model black liquor viscosity or viscosity index is not new. The novelties of the approaches utilised in this study are:

- Rather than conducting extensive laboratory, or pilot scale or industrial scale experiments that may be time consuming and economically unfavourable, the Hydraulic Institute viscosity correction method was used to address specific pump and system under consideration. The Hydraulic Institute method relies on the existing generalized experimental performance data obtained from a wide range of rotodynamic pumps operated over a wide range of flow conditions,
- The models developed here have wider applications than the existing ones, as they can work with variable–speed or constant-speed motors, and can be made functional over wide ranges of pump's operating conditions,
- The age-independent model developed here has a potential of being used throughout the entire lifespan of the pump where the pump age should be adjustable using few actual experimental data.

Centrifugal pump-based linear regression and ANN-based viscosity models were developed using the Hydraulic Institute viscosity correction method. The linear models though have strong generalization capability, lack desirable robustness in the presence of changing operating points of the pump. Therefore, it is concluded that, they can only be used for general process monitoring where accurate predictions are not an issue. An age-independent ANN having better performance than the linear model and the age-sensitive

ANN was developed. Since it gives robust predictions in the presence of changing pump's operating points, generalizes well to new inputs, and even incorporates the direct effect of changes in the pump age, it is concluded that it can be used for the online prediction of black liquor viscosity.

Although a model that incorporates the pump age (PA) has been developed in this study, PA does not change automatically; it must be adjusted periodically via actual experimentation. It is anticipated that PA can be set via a few experimental data once a significant drift is noticed in the pump mechanical status. This seems to be better than a full-scale experimentation that may be required for recalibrating the existing models, as well as the age-sensitive ones developed in this study. Future work should include how to change this variable automatically, as the pump ages; and how to make the model applicable to any centrifugal pump model.

Finally, it should be noted that, the centrifugal pump-based models developed here, have only be subjected to partial validation since they were based on the estimated data obtained from the Hydraulic Institute generalized database. The validation here, only confirms that, if the estimates are correct, the model describing the relationship among the resulting variables is logical. Since the estimates gave rise to robust and generalized models, it is clear that, the Hydraulic Institute viscosity correction method is useful to providing pump's performance data at a defined range of viscosities. Therefore, it is concluded that the method will be useful to minimise the amount of actual experimental data required for black liquor viscosity modelling. However, some experimental data specific to the particular pump and process under consideration may be required to confirm that the model's estimate is accurate or whether further modifications to the model is required.

# 7.0 ONLINE IMPLEMETATION OF THE KRAFT BLACK LIQUOR VISCOSITY SOFT SENSOR

## 7.1 INTRODUCTION

In this Chapter, an overview of the number 5 recovery boiler section of the Carter Holt Harvey Pulp and Paper (CHHP&P) Kinleith Mill, New Zealand is presented. This is followed by the description of the approach used to refine the age-independent centrifugal pump-based black liquor viscosity model described in Chapter 6. The online implementation of the model as a viscosity sensor at the number 5 recovery boiler using the Distributed Control Systems (DCS) platform, and the subsequent evaluation of the sensor's performance are reported.

## 7.2 AN OVERVIEW OF THE NUMBER 5 RECOVERY PROCESS

### 7.2.1 Process Description

Two (number 4 and number 5) recovery boilers, manufactured by Combustion Engineering$^{TM}$ Canada, were installed and operating at the steam and chemical recovery section at CHHP&P Kinleith Mill, New Zealand. This thesis focuses on the number 5 recovery boiler. The number 5 recovery boiler, which was designed for a maximum continuous rating of 218.4 tonnes of steam per hour at 4500 kPa but at 1350 tonnes/day black liquor solid firing conditions (i.e. operating conditions), produces approximately 170-175 tonnes/hour steam (including 10 tonnes/hour soot blowing steam) at 400 °C, was commissioned in 1985/86(Lister 2003). The firing solids concentration range of the heavy black liquor at the number 5 recovery boiler is 68-72%. In the original design, heavy black liquor at solids concentration of ~70% is passed through the precipitator mix tank where the ash from the recovery precipitator is mixed with the liquor to be reprocessed. It is then passed through the saltcake mix tank where saltcake ($Na_2SO_4$) is used to replace chemical losses in the liquor circuit before being fired in the recovery boiler. In addition, the fume containing mainly sodium, potassium, sulphur compounds and unburnt carbon (Fenton 2010; Gatti 2010) from the recovery furnace is collected as chemical ash in the economiser hopper and is mixed with the liquor in the saltcake mix tank (Combustion Engineering 1989). However, saltcake is no longer added in the saltcake mix tank or to the liquor circuit. Various upgrades over the years has seen a reduction in chemical loses from site, with the mill now considered to be sulphur-positive with the sum of sulphur inputs from neutral sulphite semi chemical (NSSC) liquor and crude tall oil brine that is predominantly saltcake (sodium sulphate) being greater than the total losses from the site. Caustic is added to the white liquor clarifiers for white liquor sulphidity control. The main function of the saltcake mix tank now is to act as a feed tank for the heavy black liquor firing pumps and receives ash from the economizer of the number 5 recovery boiler (Fenton 2010). The details of the original black liquor flow at the number 5 recovery boiler is given in the process and control (P & C) diagram as shown in Appendix D.

A primary direct steam heater is installed in the saltcake mix tank before the firing pumps to decrease the liquor viscosity to optimum pumping level. Originally, the product liquor (a mixture of recycled black liquor from the firing rail, ash from economiser hopper and fresh black liquor) from the saltcake mix tank, is transferred through a variable speed heavy black liquor firing pump into the recovery boiler or burner firing rail via a secondary direct steam heater. This is to raise the liquor temperature to a proper level for spraying and drying in the furnace (Combustion Engineering 1989). There are two identical firing pumps (driven by two identical variable speed motors) as shown in Appendix D but one is used at a time and the other being on stand-by (Lister 2003).

Recently, the number 5 recovery boiler piping system was modified. The current black liquor flow loop at the number 5 recovery boiler section is as shown in Figure 7.1. It is seen from the new piping system that the fresh black liquor, from the number 5 evaporator heavy black liquor (that has passed through the precipitator mix tank) storage tank, is firstly mixed with ash from the economiser hopper (as shown in the original design in Appendix D) in the saltcake mix tank. The saltcake mix tank temperature is maintained at around 110-113 $^{o}$C using direct steam injection. The liquor from the saltcake mix tank is then mixed with hot recycled liquor from the firing rail, and with a small amount of red oil at around ambient temperature before being pumped through a secondary black liquor heater that raises its temperature to around 123-126 $^{o}$C depending on the liquor solids concentration and the furnace conditions. The liquor is subsequently fired in the recovery boiler via the liquor guns that are equipped with beer can nozzle systems while the excess is then recycled as the process continues in a recirculation mode

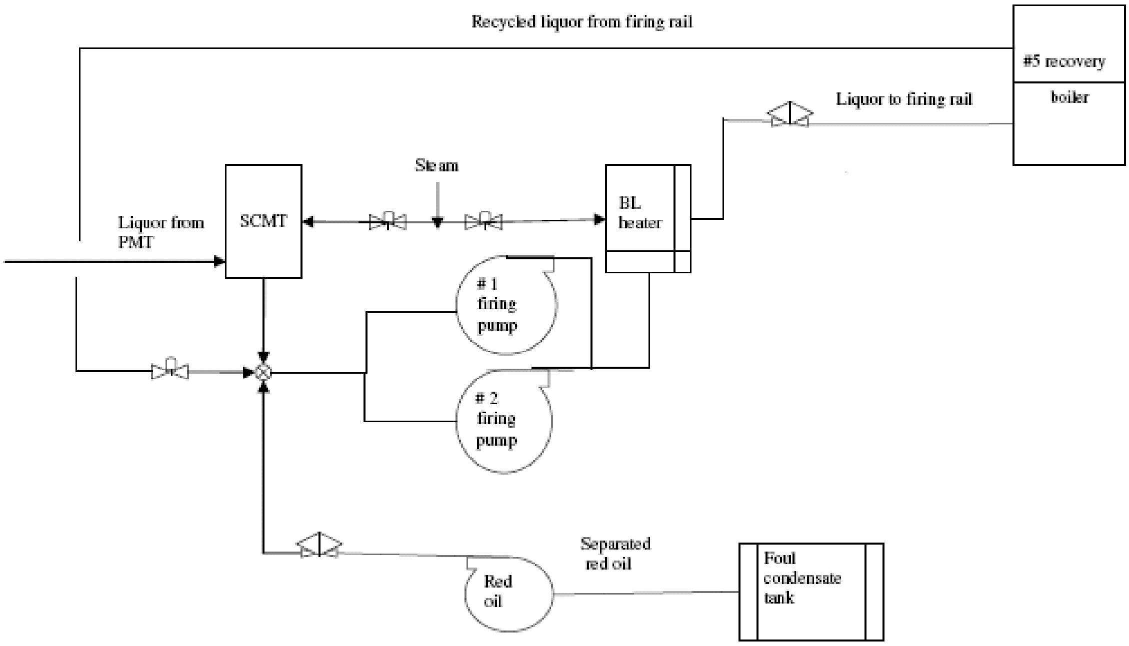


Figure 7.1 Black liquor flow loop at the number (#) 5 recovery process;
(BL=black liquor, PMT=precipitator mix tank, SCMT=saltcake mix tank)

(Fenton 2010). Red oil is a mixture of beta-pinene, mercaptans and other sulphur-containing compounds; it is added to the black liquor to be burned in the recovery furnace for environmental reasons-specifically, to incinerate the malodorous compounds in it (Gatti 2010).

### 7.2.2 Operational Issues

The recovery boiler production rate, which is given in tonnes of dry solids per day (TDS/day) of black liquor flowing into the furnace, depends on the fuel (black liquor available from the evaporator) and the green liquor (smelt) levels, and is set by the operator (Talauta 2010). Once the production rate is set, depending on the density of the liquor, the motor/pump parameters (speed and torque) will automatically be adjusted by the variable speed drive (VSD) to deliver the required flow rate, Q (L/min). The pressure in the ring header (liquor firing rail) will generally track the flow rate; however, the furnace conditions (including variables at the guns) are believed to be among the factors responsible for the changes in ring header pressure and so, temperature compensation is considered to be effective in keeping the furnace variables at desirable conditions (Gatti 2010). This is in addition to the manipulation of temperature of the liquor after the secondary heater in response to the changes in the liquor solids concentration; since increase in solids concentration increases the viscosity and the boiling point elevation of the liquor. It is obvious that different variables such as temperature, solids concentration, composition (due to red oil, ash, and fresh black liquor from the evaporator) within the number 5 black liquor flow loop may cause continuous changes to the liquor properties, including viscosity. This should reflect in the viscosity of the liquor, which in turn will reflect on the firing pump parameters. Consequently, at any conditions of the black liquor, changes in the pump speed and torque generally track changes in the liquor flow rate. Likewise, the change in the liquor temperature after the heater follows the liquor's solids concentration trend; when solids concentration increases, the temperature will be increased and vice-versa. The above operating procedures show that the effect of liquor temperature on the viscosity of the black liquor may not be observable independent of solids concentration but may have to be studied jointly. It must also be borne in mind that the observed flow rate, pump speed and the torque required at the pump's shaft are most likely a reflection of the changes in the liquor properties brought on by the changes in the liquor solids concentration, temperature and most importantly the liquor composition. Since the pump parameters also depend on one another, it seems logical to study their relationships jointly regarding the performance of the installed soft sensor.

### 7.2.3 Crucial Factors for Black Liquor Viscosity Sensor Performance Evaluation

Based on the number 5 recovery process described in section 7.2.1, it is obvious that the overall properties of the liquor being pumped through the secondary heater will keep changing in composition, as there is a continuous inflow of large amount of fresh black liquor from the number 5 evaporator heavy black liquor storage tank. This is expected to be true even if the flow rate or the solids level of the heavy black remain constant. Also the amount of, and the pH of, the ash from the economiser hopper may change from time to time. As discussed in Chapters 3 and 4, pH has a strong effect on the black liquor viscosity. Furthermore, a small quantity of red oil (0.5 – 3.0 L/min) is often added to the black liquor at the suction of the pump. This may influence the liquor properties, including viscosity. All these will mean that the viscosity of the black liquor may keep changing and may require a control action to keep it steady or within a narrow range to keep the furnace condition steady, assuming other variables are at optimal conditions.

It should be noted that the solids concentration of, volumetric flow rate of and the temperature of, the liquor from the heavy black liquor tank might all be variable and controllable. Similarly, the composition of black liquor, as it flows from the digester through the evaporators and other processes in the mill, may also be variable but not easy to control. This variability in the liquor composition will influence the properties of the liquor being fired in the recovery boiler (number 5 in this study) (see Chapters 3 and 4 for more details on this). The above shows that the liquor properties at the pump suction may keep changing due to the continuous changes in the liquor variables such as solids concentration, temperature and in particular composition. The overall effect of these variations should reflect in the pump's capacity (flow rate), shaft speed and torque as indicated by the liquor viscosity, which is a lumped measure of the liquor properties. Although viscosity is a physical property of black liquor but since it depends strongly on the liquor chemical composition, it then seems reasonable to evaluate the liquor properties in terms of its viscosity. The liquor combustion in the furnace could then be improved through optimisation of liquor firing conditions with respect to the liquor property, viscosity.

## 7.3. IMPELEMENTATION ISSUES

### 7.3.1 Validity of the Potential Soft Sensor

Before a model is installed as a soft sensor, it should have undergone a full experimental validation based on the actual system data. Alternatively, data from a full laboratory or pilot plant study that can be scaled up could also have been used to evaluate the model's performance. The above procedures were not followed in this study. It should be recalled that the empirical approach, based on Hydraulic Institute viscosity correction, utilised in the development of the centrifugal pump based models described in Chapter 6, does not depend on actual experimental data that are specific (except for the pump's water performance) to the system under consideration. Rather, it depends on the estimated data obtained from a generalized database developed from a variety of rotodynamic pumps' performances.

The preliminary validation done in Chapter 6 was to see whether the models can reliably track the pump's estimated performance data assuming they were true for the specific pump and system under consideration. The final validation ought to be done to ascertain that the model truly and accurately describes the real system. There are various ways to address the actual validation concern. Two such ways involve the use of online and laboratory viscosity measurements. A hardware-based process viscometer can be installed online from which viscosity measurements at different process conditions can be obtained. Apart from a concern about its reliability, the use of an online hardware-based viscometer is not economically favourable except if it was to be used long term. The use of a laboratory viscometer may be a cheaper option but will require accurate measurements of the samples' viscosities at the pumping conditions. From the process description given in section 7.2.1, it is known that the pumping temperature is >=110 $^{o}$C and so, to measure accurately the samples' viscosities in the laboratory would require the use of a pressure cell that is not available at the industrial site.

In the absence of these methods, a quick but logical approach is to compare the model performance or the estimated performance data to known pump performances at definite viscosities. The logic behind this approach is as follows: pump vendors usually supply a performance curve for the pump based on its actual operation using water at approximately 1 cP and 1 g/cm$^3$. It is on this basis that Hydraulic Institute method was used to estimate the pump performance at viscosities other than 1 cP. If pump curves based on actual performances of the same pump model at viscosities other than water viscosity are available, then Hydraulic Institute estimates can be compared with them. If they are nearly the same, then the model can be said to be able to describe the actual pump performance but if there are significant differences, it could mean that the Hydraulic Institute method has overestimated or underestimated the pump performance at the viscous conditions or that some underlying assumptions are incorrect.

### 7.3.2 Adjustment of the Hydraulic Institute Estimates using 70 cP Pump Curve

Ayers and Clarihew(1988) states that "Ahlstrom-supplied graphs gave 70 cP at 65% D.S., 110 $^{o}$C", therefore, it was assumed that the pump curve shown in Appendix C2 represents the performance of any of the two identical THP-10 firing pumps while pumping heavy black liquor at 70 cP. The pump performance shown in Appendix C2 is given at a rated speed of 1470 RPM. The Hydraulic Institute viscosity correction (approximate method) combined with affinity laws (approximate method) have been utilised to obtain the data used to build the models presented in Chapter 6. Since the actual pump curve is available at 70 cP and 1470 RPM, it seems logical to compare the nearest estimates to the actual data and so, Table 7.1 shows the Hydraulic Institute estimates for 69 cP data (according to the methods described in Chapter 6) and actual data at 70 cP. Actual break horsepower, BHP (kW); torque, TQ (Nm) and percentage torque, $TQ_p$ (%) were calculated based on their relevant equations as presented in Chapter 6.

Table 7.1 The number 5 recovery boiler firing pump performance data at 70 cP; (HI=Hydraulic Institute, AR=adjustment ratio)

| Parameter | Pump curve | HI/Affinity method | AR | Correction suggested? |
|---|---|---|---|---|
| Speed (RPM) | 1470 | 1500 | 0.98 | No |
| Capacity(L/sec) | 44 | 45.07 | 0.98 | No |
| Head (m) | 37 | 37.56 | 0.99 | No |
| Efficiency (%) | 63 | 54.64 | 1.15 | Yes |
| BHP(kW) | 34.95 | 41.95 | 0.83 | Yes |
| TQ(Nm) | 227.02 | 267.05 | 0.85 | Yes |
| TQp(%) | 63.54 | 74.74 | 0.85 | Yes |

Table 7.1 shows that the performance data, capacity (Q) and head (H) at best efficiency point (BEP) estimated via Hydraulic Institute method are nearly the same for the actual pump curve since both 69 cP and 70 cP are nearly the same and 1470 RPM and 1500 RPM are nearly the same. However, the Hydraulic-Institute estimated efficiency (54.64%) is significantly different from the actual efficiency of 63%. It appeared the Hydraulic Institute method underestimated the pump efficiency ($\eta$); consequently, it had led to the overestimation of BHP, TQ and $TQ_p$. It seems 1 cP difference between the actual and the estimated viscosities could not have been responsible for the large deviation in the reported efficiencies. Hence, an adjustment ratio, AR (equation 7.1) was defined at the BEP to adjust all the Hydraulic-Institute estimated ageing modelling data obtained in Chapter 6. H, Q, N were left as they were, as their ARs are approximately 1.0

while the efficiency, BHP, TQ and $TQ_p$ were all adjusted since their ARs are significantly different from 1.0.

$$AR=\text{Actual pump data/Hydraulic Institute estimated data} \tag{7.1}$$

After the data were adjusted, it was observed that the adjusted efficiencies were logical for data at viscosities >=51.75 cP but illogical at viscosities below this value, as they gave efficiencies greater than ~68% (maximum efficiency for the pump performance on water as shown in Appendix C4). Hence, at all ages, the adjusted data at viscosities below 51.75 cP were discarded. However, in order to be able to have data at low viscosity, performance data for 4 cP liquor were obtained based on the information presented in Appendices C3 (4 cP and 1.24 g/cm$^3$ data) and C4 (Ahlstrom's water based pump curve). No viscosity correction was needed for H, Q and $\eta$ since the pump's water performances ($H_w$, $Q_w$ and $\eta_w$) are approximately the same with its performances while pumping 4 cP liquor. BHP, TQ and $TQ_p$ depend on density and so, the relevant equations presented for these variables in Chapter 6 were used to obtain their data based on the liquor density of 1.24 g/cm$^3$ for the 4 cP liquor at the pumping conditions. The data for 4 cP liquor and the adjusted Hydraulic Institute data at viscosities >= 51.75 cP were combined into a new database over all ages, as adjusted ageing modelling data. The ageing prevalidation data obtained in Chapter 6 were also adjusted based on the ARs above to obtain adjusted ageing validation data. The adjusted ageing modelling data ranging from 4 to 552 cP and adjusted ageing validation data ranging from 110.4-345 cP were used to develop and validate respectively, the new age-independent models.

### 7.3.3 The Modified Age-independent Centrifugal Pump-based ANN

Based on the procedures explained in Chapters 5 and 6, using the adjusted data obtained in section 7.3.2, robust (based on the adjusted ageing modelling data) and generalized (based on the adjusted ageing validation data) age-independent conventional [7, 1] ANN having $R^2$=1.0, MARE=4.74%, SSW=49,800 and #=35/36 was obtained. The inputs are Q/N, $TQ_p/N^2$ and PA while the output is viscosity, V (log-transformed prior to its normalisation and the network training). The structure of the above ANN is given in section 7.4.2 while its weights and biases are as given in Table 7.2.

Table 7.2 Weights and biases of the installed ANN-based black liquor viscosity model

| Input j<br>j=1-3 | Hidden neuron i, i=1-7 | | | | Output neuron k, k=1 | | Output k, k=1 |
|---|---|---|---|---|---|---|---|
| | $weight^{*}_{i,j}$ | | | $bias^{*}_{i}$ | $weight^{*}_{l,k}$, $l = i$ | $bias^{*}_{k}$ | |
| Q/N | 1.513 | -0.1087 | 0.009689 | 0.4572 | 0.5361 | -49.59 | Viscosity |
| | -98.61 | 131.1 | -25.42 | 59.89 | 0.2997 | | |
| | -0.2251 | 1.695 | -0.1469 | 1.112 | -1.044 | | |
| $TQp/N^2$ | -0.5630 | 0.5713 | -0.2604 | 1.231 | 3.304 | | |
| | -1.517 | -0.7971 | 0.1637 | -0.03007 | 0.4392 | | |
| | -0.3318 | 1.067 | -0.08671 | 2.390 | 48.36 | | |
| PA | 27.14 | -99.63 | 12.84 | -54.82 | -0.2973 | | |

* Weights and biases are applicable to inputs and outputs scaled to [-1, 1] range

It was assumed that the adjustment done via the 70 cP pump curve would shift the predictions of the model closer to actual viscosities. However, considering the fact that the firing pumps together with their associated variable-speed driven motors have been installed and operating since 1985 without any record of refurbishments, it is difficult to make a pronouncement on their present mechanical and electrical/electronic status. Therefore, it seems logical to firstly study the general performance of the model online in the presence of the variables whose effects are included in the model and those parameters not included in the model but that may or may not influence the performance of the sensor under real industrial conditions. This way, the ability of the soft sensor to give consistent rather than accurate predictions will firstly be evaluated. Once this is established, it may then be worthwhile to consider further actual experimentation to ascertain and possibly improve the accuracy of the sensor's predictions.

## 7.4 DCS IMPLEMENTATION OF THE SOFT SENSORS

### 7.4.1 Online Instruments, Locations and Accuracies

The black liquor viscosity model described in section 7.3.3 was derived as a function of three variables: pump age (PA), Q/N and $TQ_p/N^2$. PA is not measurable online and so must be set in advance. The other two variables were obtained from three variable-speed motor/pump parameters N, Q and $TQ_p$, which are continuously being measured online.

Although solids concentration and temperature are not directly included in the model, they play significant roles on the liquor viscosity, which ultimately reflects in the pump parameters that were used to develop the model. It is therefore essential to have an idea of how accurate the measured variables are, as they will affect the viscosity estimates obtained from the soft sensor. Available information on the relevant instruments shows that there are no concerns with respect to their accuracies. For example, Q measurements obtained from the flow sensors are accurate to within +/-1% while those from the pressure sensors are accurate to within +/- 0.5% and the temperature sensors (resistive temperature device types) are accurate to within +/-0.5% (Verhaegh 2010). The refractometer for measuring the solids concentration is accurate to within +/- (1-2%) of the TAPPI-based laboratory measurements (Hope 2010). The speed and the load (measured as $TQ_p$) on the motor are obtained from variable speed drive (VSD). The controller unit of the VSD is responsible for manipulating the operation of its power electronic converter where the voltage, frequency and/or the current sent to the motor are adjusted. The regulation of these variables results in the motor speed that matches the load on the motor (Emadi 2005). The algorithms that measure and control the motor speed and torque are a part of the VSD located in the switchboard room; the outputs including N and $TQ_p$ from the VSD are linked with or sent to the distributed control systems (DCS) for relevant control actions to be taken. The black liquor process and control (P&C) diagram given in Appendix D shows the locations of the VSDs/motors/pumps (units from which N and $TQ_p$ are obtained continuously) and the flow sensor/transmitter from which Q is obtained continuously. The VSDs associated with the firing pumps number 1 (M745-5078) and number 2 (M745-5079) are linked with flow transmitter (FT 041/1), which is linked to the DCS where relevant computations are performed and the motor control actions are taken.

### 7.4.2 Soft Sensors Installation

The ANN-based model described in section 7.3.3 was installed in the DCS. The block diagram showing the soft sensor implementation in the DCS and its relationship with process instruments is as given in Figure 7.2.

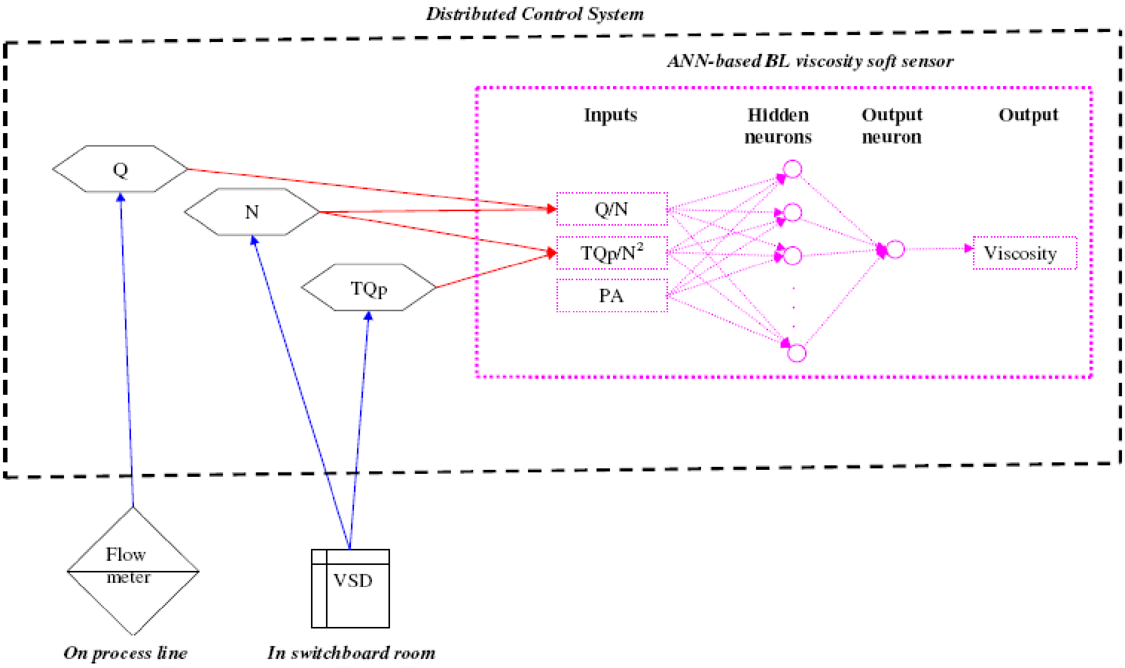
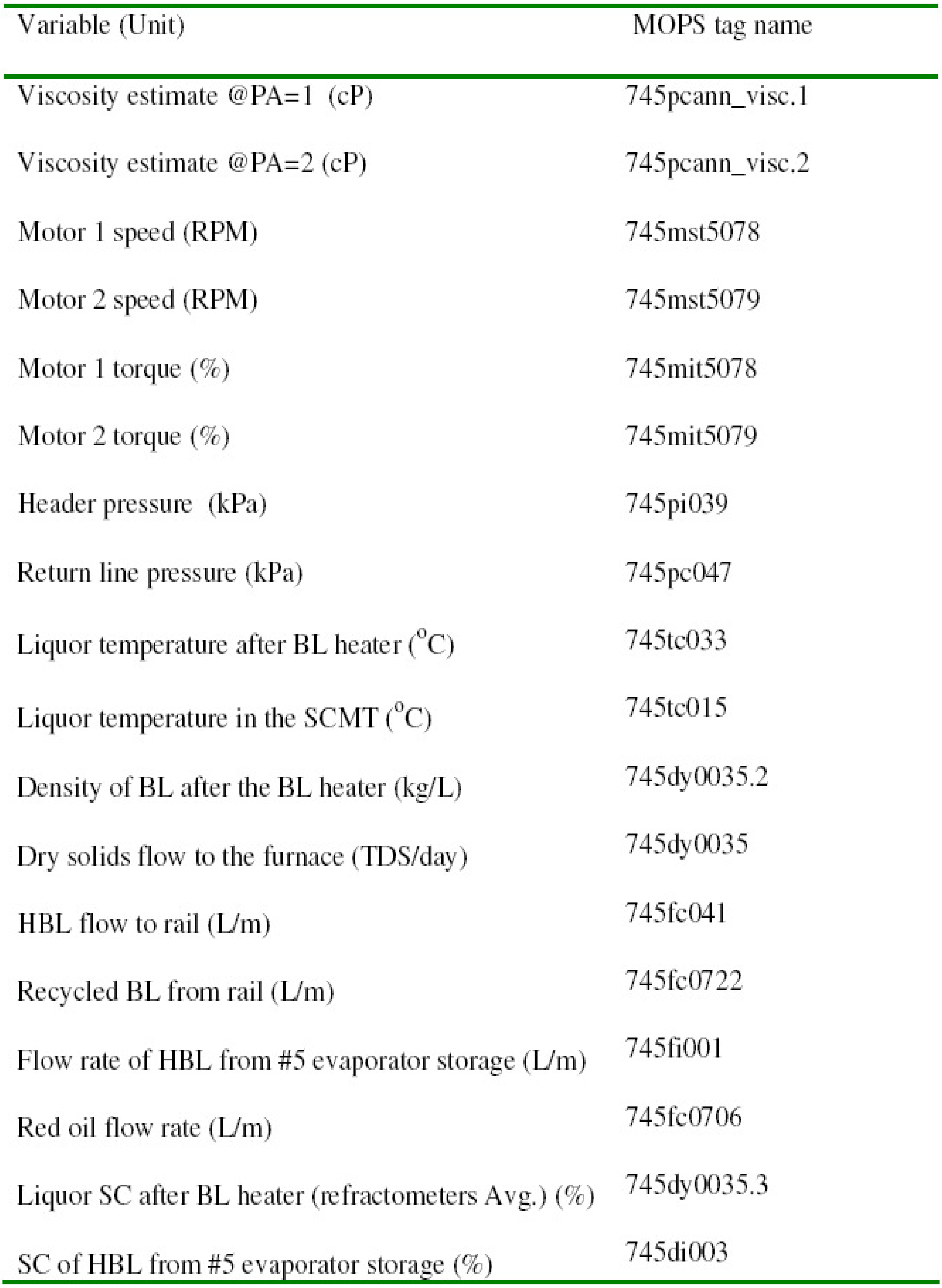


Figure 7.2 The interface between the DCS-implemented black liquor viscosity soft sensor and the process instruments at the number 5 recovery boiler

The actual age or the mechanical status of the pump is currently unknown, therefore two soft sensors, one with PA preset to 1.0 assuming the pumps are operating as they were in 1985(new) and the other at PA=2 (assuming about 6% deterioration in the pump's efficiency due to ageing), were installed. The first sensor hereby called soft sensor 1 has a tag name 745pcann_visc.1 while the second soft sensor hereby called soft sensor 2 has a tag name 745pcann_visc.2 as reported in Table 7.3, which contains the list of relevant process variables considered for the evaluation of the soft sensors' performances.

It is seen from Figure 7.2 that the variables N, Q and $TQ_p$ are continuously being obtained from the DCS and the soft sensor (installed ANN-based predictive model) instantly computes the viscosity from these variables thereby making the values available in real time. It can be seen that it does not require the installation of any additional hardware as it makes use of the measurements from the normally installed flow meter and the VSD that controls the speed of the motors used to drive the firing pumps.

Table 7.3 Variables used to monitor the performances of the installed viscosity soft sensors; (SC=solids concentration, BL=black liquor, HBL=heavy black liquor, #5=number 5)



| Variable (Unit) | MOPS tag name |
|---|---|
| Viscosity estimate @PA=1 (cP) | 745pcann_visc.1 |
| Viscosity estimate @PA=2 (cP) | 745pcann_visc.2 |
| Motor 1 speed (RPM) | 745mst5078 |
| Motor 2 speed (RPM) | 745mst5079 |
| Motor 1 torque (%) | 745mit5078 |
| Motor 2 torque (%) | 745mit5079 |
| Header pressure (kPa) | 745pi039 |
| Return line pressure (kPa) | 745pc047 |
| Liquor temperature after BL heater (°C) | 745tc033 |
| Liquor temperature in the SCMT (°C) | 745tc015 |
| Density of BL after the BL heater (kg/L) | 745dy0035.2 |
| Dry solids flow to the furnace (TDS/day) | 745dy0035 |
| HBL flow to rail (L/m) | 745fc041 |
| Recycled BL from rail (L/m) | 745fc0722 |
| Flow rate of HBL from #5 evaporator storage (L/m) | 745fi001 |
| Red oil flow rate (L/m) | 745fc0706 |
| Liquor SC after BL heater (refractometers Avg.) (%) | 745dy0035.3 |
| SC of HBL from #5 evaporator storage (%) | 745di003 |

## 7.5 VISCOSITY SOFT SENSORS' PERFORMANCE EVALUATION

### 7.5.1 Evaluation Focus

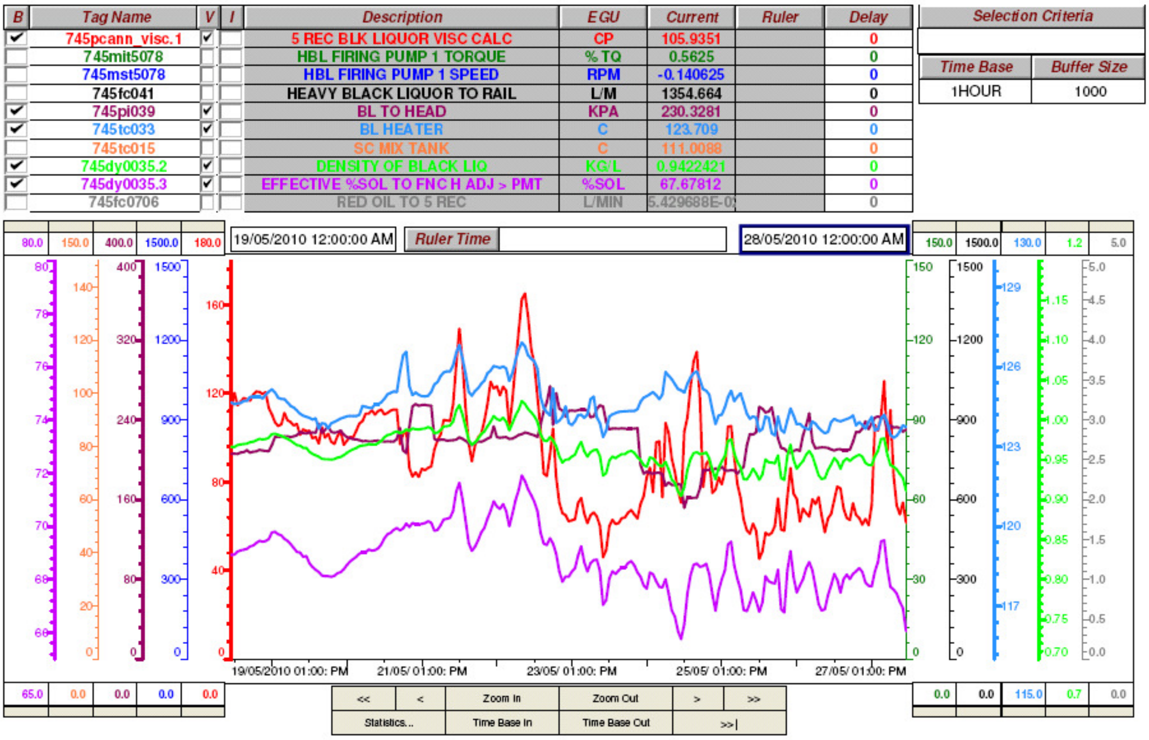
The aim of the present evaluation of the installed viscosity sensors performances was not to determine how accurate their predictions are but to ascertain whether the soft sensors can give consistent predictions in the presence of changing process variables. The model of the sensors was developed based on different underlying explicit and implicit assumptions, e.g. viscosity is not affected by pressure (rather, pressure drop across a given length of pipe for a given flow should indicate viscous condition of the liquor), the heavy black liquor density at pumping conditions is approximately constant at 1.38 g/cm$^3$ and so, should not contribute to the variation in the power consumed by the motor, etc. It is therefore important to evaluate the effect of the changes in pressure on the sensors predictions, check whether the liquor density varies sufficiently while the soft sensor is operational and evaluate the effects of variations of other process variables on the soft sensor's performance.

Many variables listed in Table 7.3 are potentially able to affect and/or reflect in the performances of the installed soft sensors. It was difficult to jointly analyse the independent or interdependent effects of all of these variables on the sensors' performances. Therefore, the sensors' performances were analysed at the suction and the discharge sections of the recirculation (the firing) pump. It is clear that the properties (including viscosity) of the liquor at the suction of the pump will be the same or nearly the same as the properties of the liquor at the pump discharge (before black liquor heater). It was already established (see Chapters 3 and 4) that solids concentration, temperature and the composition of the liquor at pumping conditions determine the liquor viscosity at any instant, which eventually is reflected in the N, Q and $TQ_p$ of the variable-speed driven motors connected to the pumps. In light of the foregoing, the evaluations of the sensors' performances under different process conditions are presented in the following sections, taking into consideration when each pump was operational. The prediction trends of the soft sensors in the presence of changes in process variables were studied through the online window-based application, MOPS™ (i.e. Mill-wide OPtimization System) that provides timely, clear and accurate information about client's process (in this case, CHHP&P, Kinleith Mill, New Zealand).

## 7.5.2 Soft Sensor 1 Performance Based on the Post-pump Variables

### 7.5.2.1 Solids concentration and temperature

The effects of the liquor temperature after the black liquor heater, solids concentration and header pressure on soft sensor 1 predictions were studied using process data from both number 1 and number 2 pumps. For pump 1, a 10-day performance of the soft sensor is as shown in Figure 7.3 while for pump 2; a 20-day performance of the soft sensor is as shown in Figure 7.4. Alongside the above variables, liquor density trends were evaluated. From Figs 7.3 and 7.4, it is observed that changes in the temperature of the liquor tracks changes in its solids concentration; this should be expected since boiling point elevation increases with solids concentration(Frederick 1997) and as such, increase in solids concentration would require an increased temperature compensation and vice-versa. Although changes in the viscosity estimates track changes in both solids concentration and temperature, it is clear that the effect of changes in solids concentration on black liquor viscosity dominates that of temperature change. As can be seen, when there is a decrease in solids concentration (should lead to a decrease in viscosity), despite a decrease in temperature (should lead to viscosity rise), a resultant viscosity reduction was observed and vice-versa. This confirms that simply manipulating liquor temperature in response to changes in solids concentration may not be adequate to compensate for the changes in the liquor properties, represented by viscosity here. While it may be possible to keep increasing temperature to compensate effectively for any increase in solids concentration, there is a boiling point elevation constraint. Beyond a certain boiling point elevation, there will be liquor flashing (two phase flow) at the guns; this is not desirable for proper operation of the furnace (Miikkulainen 2006).



| B | Tag Name | V | I | Description | EGU | Current | Ruler | Delay |
|---|---|---|---|---|---|---|---|---|
| ☑ | 745pcann_visc.1 | ☑ | ☐ | 5 REC BLK LIQUOR VISC CALC | CP | 105.9351 | | 0 |
| ☐ | 745mit5078 | ☐ | ☐ | HBL FIRING PUMP 1 TORQUE | % TQ | 0.5625 | | 0 |
| ☐ | 745mst5078 | ☐ | ☐ | HBL FIRING PUMP 1 SPEED | RPM | -0.140625 | | 0 |
| ☐ | 745fc041 | ☐ | ☐ | HEAVY BLACK LIQUOR TO RAIL | L/M | 1354.664 | | 0 |
| ☑ | 745pi039 | ☑ | ☐ | BL TO HEAD | KPA | 230.3281 | | 0 |
| ☑ | 745tc033 | ☑ | ☐ | BL HEATER | C | 123.709 | | 0 |
| ☐ | 745tc015 | ☐ | ☐ | SC MIX TANK | C | 111.0088 | | 0 |
| ☑ | 745dy0035.2 | ☑ | ☐ | DENSITY OF BLACK LIQ | KG/L | 0.9422421 | | 0 |
| ☑ | 745dy0035.3 | ☑ | ☐ | EFFECTIVE %SOL TO FNC H ADJ > PMT | %SOL | 67.67812 | | 0 |
| ☐ | 745fc0706 | ☐ | ☐ | RED OIL TO 5 REC | L/MIN | 5.429688E-0 | | 0 |

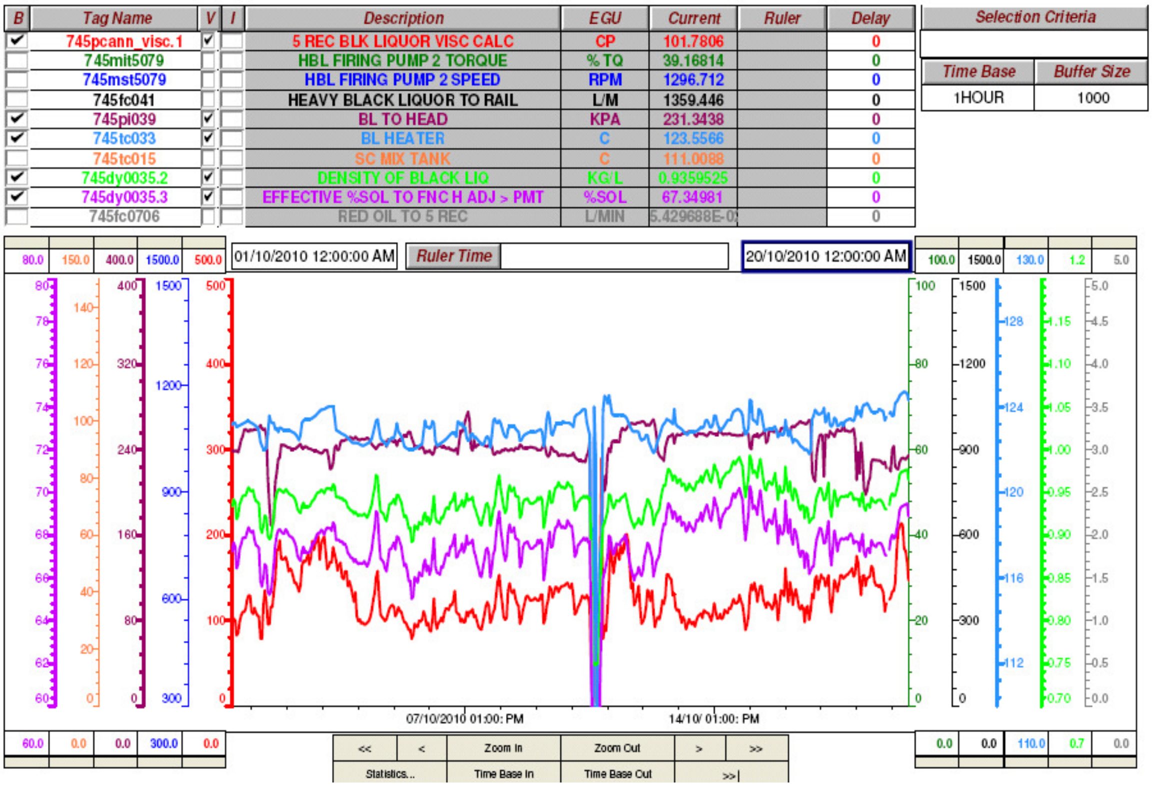
Selection Criteria

| Time Base | Buffer Size |
|---|---|
| 1HOUR | 1000 |

19/05/2010 12:00:00 AM

28/05/2010 12:00:00 AM

Figure 7.3 Effects of the post-pump process variables on soft sensor 1 performance when the number 1 motor/pump was in operation



| B | Tag Name | V | I | Description | EGU | Current | Ruler | Delay |
|---|---|---|---|---|---|---|---|---|
| ☑ | 745pcann_visc.1 | ☑ | ☐ | 5 REC BLK LIQUOR VISC CALC | CP | 101.7806 | | 0 |
| ☐ | 745mit5079 | ☐ | ☐ | HBL FIRING PUMP 2 TORQUE | % TQ | 39.16814 | | 0 |
| ☐ | 745mst5079 | ☐ | ☐ | HBL FIRING PUMP 2 SPEED | RPM | 1296.712 | | 0 |
| ☐ | 745fc041 | ☐ | ☐ | HEAVY BLACK LIQUOR TO RAIL | L/M | 1359.446 | | 0 |
| ☑ | 745pi039 | ☑ | ☐ | BL TO HEAD | KPA | 231.3438 | | 0 |
| ☑ | 745tc033 | ☑ | ☐ | BL HEATER | C | 123.5566 | | 0 |
| ☐ | 745tc015 | ☐ | ☐ | SC MIX TANK | C | 111.0088 | | 0 |
| ☑ | 745dy0035.2 | ☑ | ☐ | DENSITY OF BLACK LIQ | KG/L | 0.9359525 | | 0 |
| ☑ | 745dy0035.3 | ☑ | ☐ | EFFECTIVE %SOL TO FNC H ADJ > PMT | %SOL | 67.34981 | | 0 |
| ☐ | 745fc0706 | ☐ | ☐ | RED OIL TO 5 REC | L/MIN | 5.429688E-0 | | 0 |

Selection Criteria

| Time Base | Buffer Size |
|---|---|
| 1HOUR | 1000 |

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Figure 7.4 Effects of the post-pump process variables on soft sensor 1 performance when the number 2 motor/pump was in operation

### 7.5.2.2 Header pressure

It seems there is no unique relationship between viscosity and pressure, as there is between viscosity and solids concentration & temperature in Figs 7.3 and 7.4. This should be expected as pressure was not anticipated to have any effect on viscosity at absolute pressure less than 400 kPa (around 230 kPa guage) in the liquor line.

### 7.5.2.3 Liquor density

Although black liquor density is expected to remain fairly constant at typical pumping and firing conditions but as observed in Figs 7.3 and 7.4, there is some variation at the prevailing process conditions. As expected, changes in density track changes in solids concentration and temperature closely just as viscosity does, since both variables are functions of solids concentration and temperature. However, density is considered to be less sensitive to liquor composition variations than viscosity (see Zaman et al. 1994;Zaman and Fricke 1996). As can be seen from Fig 7.4 (for pump number 1), over the same ranges of solids concentration and temperature, density varies from around 0.905 to 1.024 kg/L (905-1024 kg/m$^3$) while viscosity varies from around 45 to 165 cP. There are three concerns about this observation:

(i) About 100 kg/m$^3$ variation in density appears to be significant and may probably influence $TQ_p$ on which one of the soft sensor's input variables depend. However, it is not clear at this stage if this amount of variation (about +/-5% based on average density of ~960 kg/m$^3$) can have significant effect on $TQ_p$ and subsequently on the estimated viscosity.

(ii) Going by the level of this density variation for just 10 days of operation, with a likelihood of larger variation in future, it appears that using a constant density in the model may not be adequate for obtaining consistent and/or accurate viscosity estimates. It may be more appropriate to include the effect of density on $TQ_p$. The existing centrifugal pump-based viscosity and viscosity index models described in Chapter 2 assume that changes in the pump amperage can be solely attributed to viscosity change but the observation above shows that significant variation in density would violate that assumption.

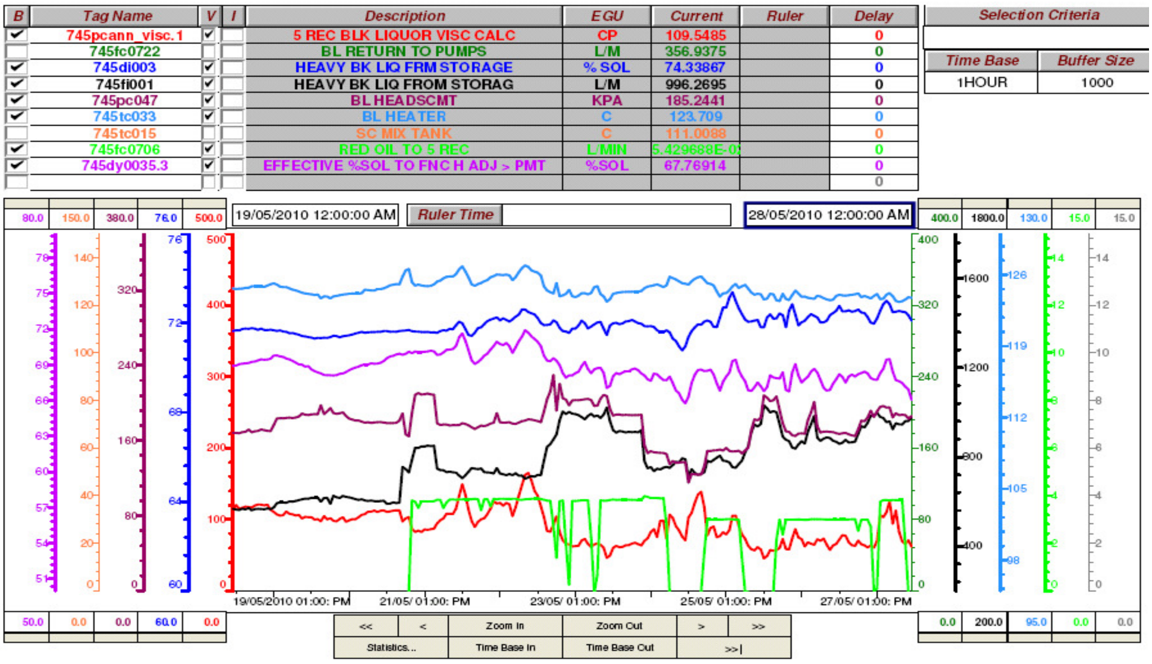
(iii) Black liquor density is an increasing and decreasing function of solids concentration and temperature, respectively. Therefore, the minimum density of the liquor being fired in the number 5 recovery boiler over the 10 days operations of pump 1 as reported earlier would occur at minimum solids concentration of 65.76% and maximum firing temperature of 126.9 $^{o}$C. In Chapter 5, Equations (5.4a) and (5.4b), valid for a variety of kraft pine black liquors (similar to the liquor under consideration), were used to describe the relationships between black liquor density and solids concentration & temperature and are relatively insensitive to the liquor composition (Zaman et al. 1994; Zaman et al.1997) . Applying the equations to the liquor here at the stated boundary conditions gives the minimum density of the liquor being fired during the 10-day operation of pump 1 as ~1342 kg/m$^3$. This seems appropriate for liquor at 65% and 126 $^{o}$C. Pumping temperature is lower than the firing temperature and the liquor solids concentration under pumping condition is slightly higher than that at the firing condition, therefore, liquor density greater than 1342 kg/m$^3$ should be expected. It seems logical that the average liquor density under pumping conditions was chosen as1380 kg/m$^3$ for the sensor development as discussed in Chapter 6. However, the liquor density (under firing conditions) data reported above, ranges between 905 and 1024 kg/m$^3$, indicating that corresponding density at the pumping conditions will be significantly less than 1380 kg/m$^3$; this seems to be extremely low. This causes a concern regarding the accuracy and reliability of the heavy black liquor density correlation being used at the number 5 recovery boiler at the moment. The reported values look like the densities of a weak black liquor (solids concentrations<20%) rather than heavy black liquor. The actual density value used in the current soft sensor model does not appear to have a significant effect on the sensor's ability to predict consistently. However, since liquor density plays a significant role in the black liquor production rate calculations in the recovery boiler, it may be advisable for the steam and recovery plant Management at the CHHP&P Kinleith mill to review the correlation currently being used to compute heavy black liquor density online. In addition, in the event of including a density factor in the soft sensor model, a more reliable density correlation would be required.

Overall, the soft sensor performance seems to be reasonably consistent even when density varies by as much as +/-5% from the average value observed. However, to improve the consistency of its predictions, the effect of density on $TQ_p$ should be incorporated in further work on the soft sensor improvement. Further performance evaluations to determine whether the variations in the viscosity can be attributed to composition, density or operating point of the pump are described in section 7.5.5.

### 7.5.3. Soft Sensor 1 Performance Based on the Pre-pump Variables

According to the black liquor flow diagram shown in Figure 7.1, three streams of fluid namely fresh black liquor from the number 5 evaporator heavy black liquor storage tank, red oil and recycled black liquor from the firing rail were mixed before the suction of the firing pump. Fresh liquor from the number 5 evaporator passed continuously through the precipitator mixed tank and mixed with ash from the economiser hopper in the salt cake mixed tank where its temperature is raised before being mixed with the recycled black liquor and red oil. In addition, it should be noted that composition of fresh liquor depends on the pulping conditions, which do not remain fixed. Since the amount of fresh liquor in the recirculation loop is about 3 times that of the liquor in the recycled stream, it is clear that it would have largest influence on the properties of the liquor at the pump suction.

Taking the above facts into consideration, the overall impact of the three streams on the soft sensor 1 performance was examined. The examination was based on the solids concentration and flow rate of the fresh heavy black liquor from storage, solids concentration and temperature of the recycled liquor, red oil flow rate, and pressure in the recycle line when pumps 1 and 2 were operational for 10 days and 20 days, respectively. The soft sensor 1 viscosity trends, together with the trends of its influential variables, are as shown in Figures 7.5 and 7.6. From both Figs 7.5 and 7.6, it is observed that the changes in the solids concentration of the recycled liquor tracks the changes in the solids concentration of the fresh liquor from storage and the recycled liquor temperature tracks the solids concentrations of both liquors. This should be expected, as the fresh liquor properties dominate the properties of the mixed liquor at the pump suction. In addition, changes in the viscosity estimates track changes in solids concentrations of both the fresh and the recycled liquors, and the temperature of the recycled liquor; this is in agreement with the earlier discussions. This shows that the soft sensor is able to track the variations in the pre-pump process variables.



| B | Tag Name | V | I | Description | EGU | Current | Ruler | Delay |
|---|---|---|---|---|---|---|---|---|
| ☑ | 745pcann_visc.1 | ☑ | ☐ | 5 REC BLK LIQUOR VISC CALC | CP | 109.5485 | | 0 |
| ☐ | 745fc0722 | ☐ | ☐ | BL RETURN TO PUMPS | L/M | 356.9375 | | 0 |
| ☑ | 745di003 | ☑ | ☐ | HEAVY BK LIQ FRM STORAGE | % SOL | 74.33867 | | 0 |
| ☑ | 745fi001 | ☑ | ☐ | HEAVY BK LIQ FROM STORAG | L/M | 996.2695 | | 0 |
| ☑ | 745pc047 | ☑ | ☐ | BL HEADSCMT | KPA | 185.2441 | | 0 |
| ☑ | 745tc033 | ☑ | ☐ | BL HEATER | C | 123.709 | | 0 |
| ☐ | 745tc015 | ☐ | ☐ | SC MIX TANK | C | 111.0088 | | 0 |
| ☑ | 745fc0706 | ☑ | ☐ | RED OIL TO 5 REC | L/MIN | 5.429688E-0 | | 0 |
| ☑ | 745dy0035.3 | ☑ | ☐ | EFFECTIVE %SOL TO FNC H ADJ > PMT | %SOL | 67.76914 | | 0 |
| ☐ | | ☐ | ☐ | | | | | 0 |

Selection Criteria

| Time Base | Buffer Size |
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| 1HOUR | 1000 |

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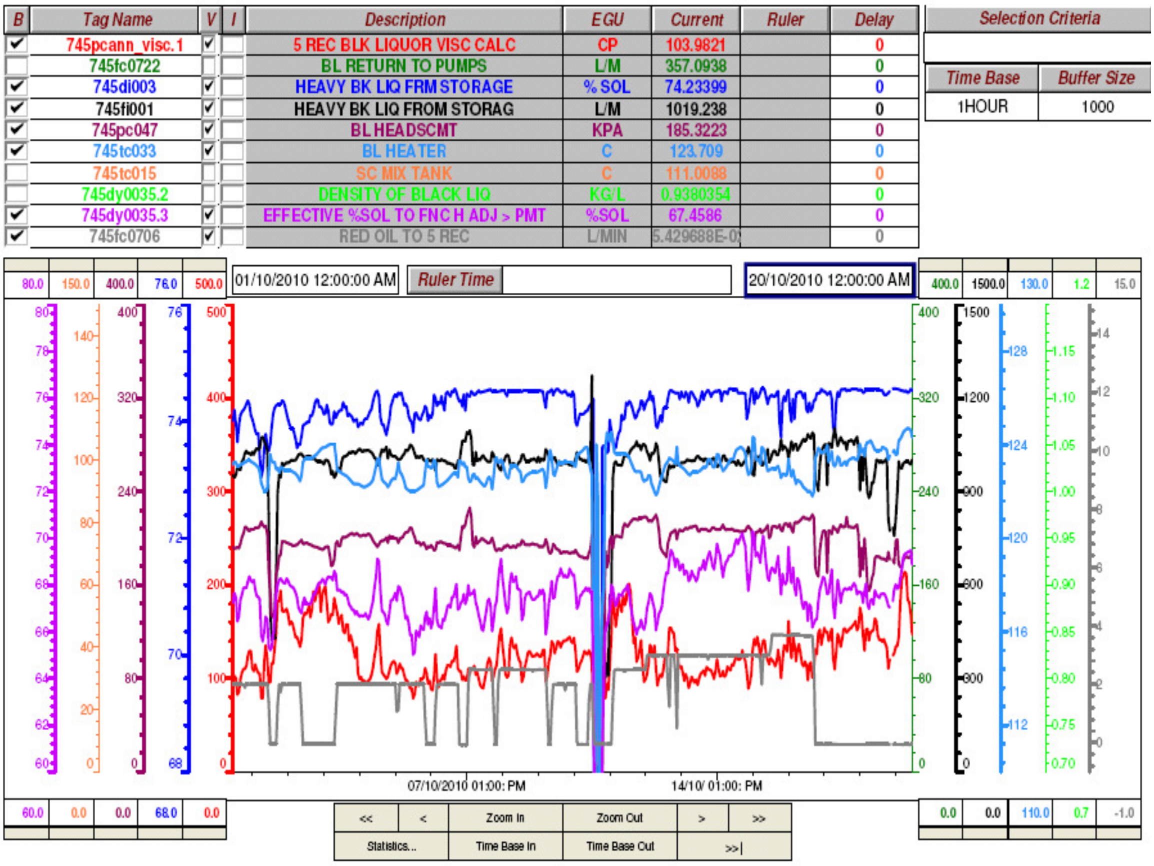
Figure 7.5 Effects of the pre-pump process variables on soft sensor 1 performance when the number 1 motor/pump was in operation



| B | Tag Name | V | I | Description | EGU | Current | Ruler | Delay |
|---|---|---|---|---|---|---|---|---|
| ☑ | 745pcann_visc.1 | ☑ | ☐ | 5 REC BLK LIQUOR VISC CALC | CP | 103.9821 | | 0 |
| ☐ | 745fc0722 | ☐ | ☐ | BL RETURN TO PUMPS | L/M | 357.0938 | | 0 |
| ☑ | 745di003 | ☑ | ☐ | HEAVY BK LIQ FRM STORAGE | % SOL | 74.23399 | | 0 |
| ☑ | 745fi001 | ☑ | ☐ | HEAVY BK LIQ FROM STORAG | L/M | 1019.238 | | 0 |
| ☑ | 745pc047 | ☑ | ☐ | BL HEADSCMT | KPA | 185.3223 | | 0 |
| ☑ | 745tc033 | ☑ | ☐ | BL HEATER | C | 123.709 | | 0 |
| ☐ | 745tc015 | ☐ | ☐ | SC MIX TANK | C | 111.0088 | | 0 |
| ☐ | 745dy0035.2 | ☐ | ☐ | DENSITY OF BLACK LIQ | KG/L | 0.9380354 | | 0 |
| ☑ | 745dy0035.3 | ☑ | ☐ | EFFECTIVE %SOL TO FNC H ADJ > PMT | %SOL | 67.4586 | | 0 |
| ☑ | 745fc0706 | ☑ | ☐ | RED OIL TO 5 REC | L/MIN | 5.429688E-0 | | 0 |

Selection Criteria

| Time Base | Buffer Size |
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| 1HOUR | 1000 |

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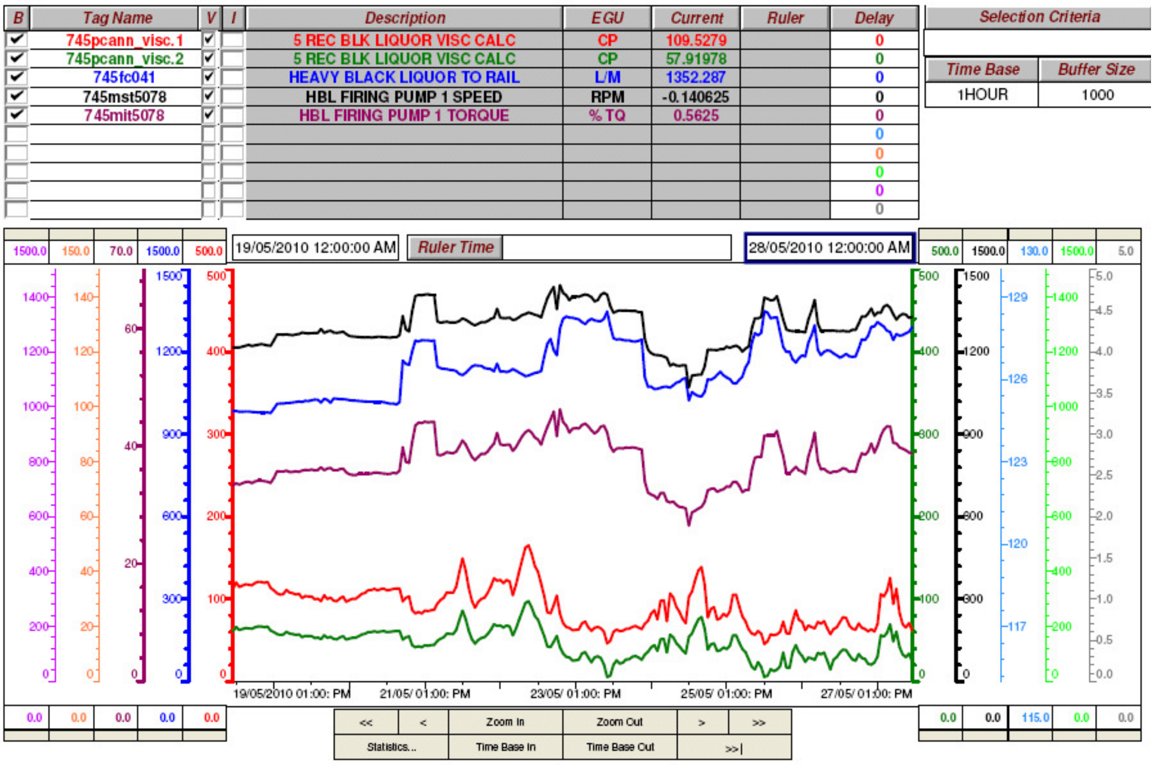
Figure 7.6 Effects of the pre-pump process variables on soft sensor 1 performance when the number 2 motor/pump was in operation

A close look on the viscosity trends in both Figs 7.5 and 7.6 do not show there is a definite relationship between the sensor's predictions and pressure in the recycle line. Similar situation is observed with the red oil. It can be concluded that, the sensor gives consistent predictions in the presence of changing pre-pump process variables. In essence, the sensor is able to effectively and consistently account for the variations in these variables. In addition, despite the continuous changes in the composition of the fresh black liquor, the soft sensor is able to consistently estimate the liquor viscosity. This would not have been possible with composition-dependent models described in Chapter 5.

### 7.5.4 Effect of Pump Age on the Soft Sensors' Performances

The performances of the soft sensors 1 (PA=1) and 2 (PA=2) were examined when each of the pumps was in operation. Figures 7.7 and 7.8 show the sensors' predictions together with the trends of the motors/pumps parameters when pump 1 and pump 2, respectively, was in operation. It is observed from both Figures 7.7 and 7.8 that for each pump in operation, both sensors give identical estimates that are only different in terms of their magnitudes. This shows that the soft sensors can work effectively irrespective of any of the pumps in operation.

There are different ways of interpreting the results shown in Figures 7.7 and 7.8. On the one hand, if the pump mechanical component has deteriorated with use but a model has been built and installed based on the new pump data (PA set to 1.0 in the installed age-independent model), then the sensor will overestimate the liquor viscosity (soft sensor 1 outputs). On the other hand, despite many years of use, if the pump has been well maintained, it may be assumed that its operation is close to that of a new pump. If the sensor is installed on the assumption that the pump has aged significantly by setting PA=2 in the installed age-independent model, then the sensor will underestimate the liquor viscosity (soft sensor 2 outputs). This shows that it is important to establish the approximate mechanical condition of the pump via a few actual experiments if accurate viscosity estimates are desirable.



| B | Tag Name | V | I | Description | EGU | Current | Ruler | Delay |
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| ☑ | 745pcann_visc.2 | ☑ | ☐ | 5 REC BLK LIQUOR VISC CALC | CP | 57.91978 | | 0 |
| ☑ | 745fc041 | ☑ | ☐ | HEAVY BLACK LIQUOR TO RAIL | L/M | 1352.287 | | 0 |
| ☑ | 745mst5078 | ☑ | ☐ | HBL FIRING PUMP 1 SPEED | RPM | -0.140625 | | 0 |
| ☑ | 745mit5078 | ☑ | ☐ | HBL FIRING PUMP 1 TORQUE | % TQ | 0.5625 | | 0 |
| ☐ | | ☐ | ☐ | | | | | 0 |
| ☐ | | ☐ | ☐ | | | | | 0 |
| ☐ | | ☐ | ☐ | | | | | 0 |
| ☐ | | ☐ | ☐ | | | | | 0 |
| ☐ | | ☐ | ☐ | | | | | 0 |

Selection Criteria

| Time Base | Buffer Size |
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| 1HOUR | 1000 |

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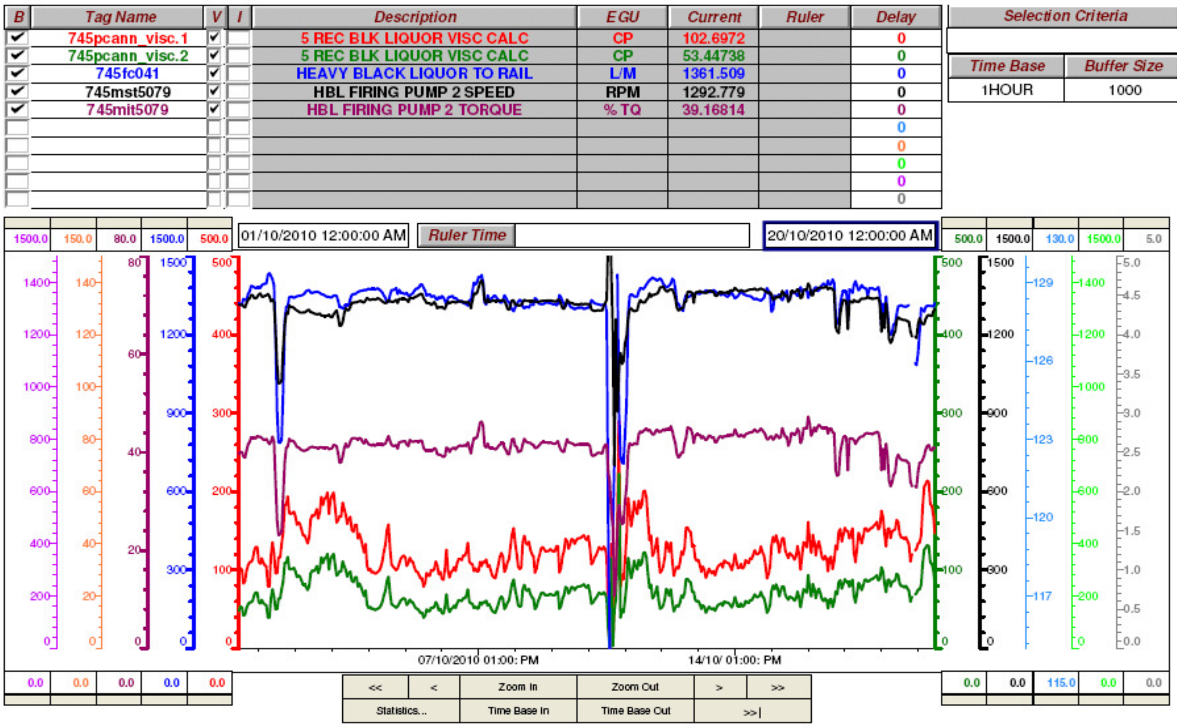
Figure 7.7 Effect of pump age on the performances of the soft sensors when the number 1 motor/pump was in operation



| B | Tag Name | V | I | Description | EGU | Current | Ruler | Delay |
|---|---|---|---|---|---|---|---|---|
| ☑ | 745pcann_visc.1 | ☑ | ☐ | 5 REC BLK LIQUOR VISC CALC | CP | 102.6972 | | 0 |
| ☑ | 745pcann_visc.2 | ☑ | ☐ | 5 REC BLK LIQUOR VISC CALC | CP | 53.44738 | | 0 |
| ☑ | 745fc041 | ☑ | ☐ | HEAVY BLACK LIQUOR TO RAIL | L/M | 1361.509 | | 0 |
| ☑ | 745mst5079 | ☑ | ☐ | HBL FIRING PUMP 2 SPEED | RPM | 1292.779 | | 0 |
| ☑ | 745mit5079 | ☑ | ☐ | HBL FIRING PUMP 2 TORQUE | % TQ | 39.16814 | | 0 |
| ☐ | | ☐ | ☐ | | | | | 0 |
| ☐ | | ☐ | ☐ | | | | | 0 |
| ☐ | | ☐ | ☐ | | | | | 0 |
| ☐ | | ☐ | ☐ | | | | | 0 |
| ☐ | | ☐ | ☐ | | | | | 0 |

Selection Criteria

| Time Base | Buffer Size |
|---|---|
| 1HOUR | 1000 |

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Figure 7.8 Effect of pump age on the performances of the soft sensors when the number 2 motor/pump was in operation

An interesting observation about the similarity in the estimates obtained from the two sensors is that the ratios of their outputs would remain fairly constant at all points and the constant would be proportional to PA. It then seems logical to see PA as a tuning variable rather than just the mechanical status parameter of the pump. By virtue of this, it is clear that the overall prediction trajectory of the sensor can be shifted uniformly by just a single value PA. Theoretically, a single accurate experimental data may just be enough to update the installed viscosity soft sensor. In addition to other advantages highlighted earlier in Chapter 6, the centrifugal pump-based viscosity soft sensor developed and installed in this study would require minimal experimental data to update its performance trajectory, should the mechanical status of the pump shifts significantly. There is no guarantee that the existing centrifugal pump-based methods described in Chapter 2 can be updated in a similar manner, should the pump deteriorates significantly.

Overall, the performances of the sensors as observed in Figs 7.7 and 7.8 show that the sensors can give consistent estimates even when the mechanical conditions of the pumps have changed considerably. However, it must be noted that the analysis above does not conclude that any two new identical pumps will age at the same degree. As a result, for an improved performance, PA for each pump should be determined.

Nevertheless, if the actual viscosity estimates are not required for any further computations, the consistent viscosity estimates in this study could be related to the recovery boiler performance indicators. An optimal viscosity range can then be established. This can subsequently be integrated with the existing control schemes for the optimization of the overall recovery boiler operation.

### 7.5.5 Effect of the Changes in the Liquor Composition and/or the Operating Point of the Pump

#### 7.5.5.1 Effect of composition

It was shown in section 7.5.2 that the viscosity estimates obtained from the installed viscosity soft sensor were able to track the changes in the liquor solids concentration and temperature consistently. However, black liquor viscosity is strongly dependent on the liquor composition. In order to ascertain whether the soft sensor is able to account for the changes in the liquor composition, viscosity estimates obtained from the soft sensor 1 during a 10-day operation of the pump 1 were analysed as a function of the reduced solids, $S_r$ (%). The reduced solids is obtained from Equation 7.2:

$$S_r\ (\%) = \text{solids concentration} \times T_{ref}/T \qquad (7.2)$$

where $T_{ref}$ is the reference temperature given as 373 K; T (K)= liquor temperature and solids concentration is the liquor solids concentration (%).

The expectation is that if the liquor composition remains fairly constant, at any value of $S_r$, the viscosity estimates should remain approximately the same. The scatter plot of viscosity against reduced solids is given in Figure 7.9. It is observed that, with the exception of $S_r$s>=66%, the estimated viscosities seem to depend on factors other than solids concentration and temperature. This should be expected, as there is a continuous inflow of fresh liquor from the number 5 evaporator, whose composition depends strongly on the pulping and post-pulping conditions that do not remain the same. This finding shows that the black liquor viscosity models (existing and those in this work) developed purely as functions of solids concentration and temperature would not be

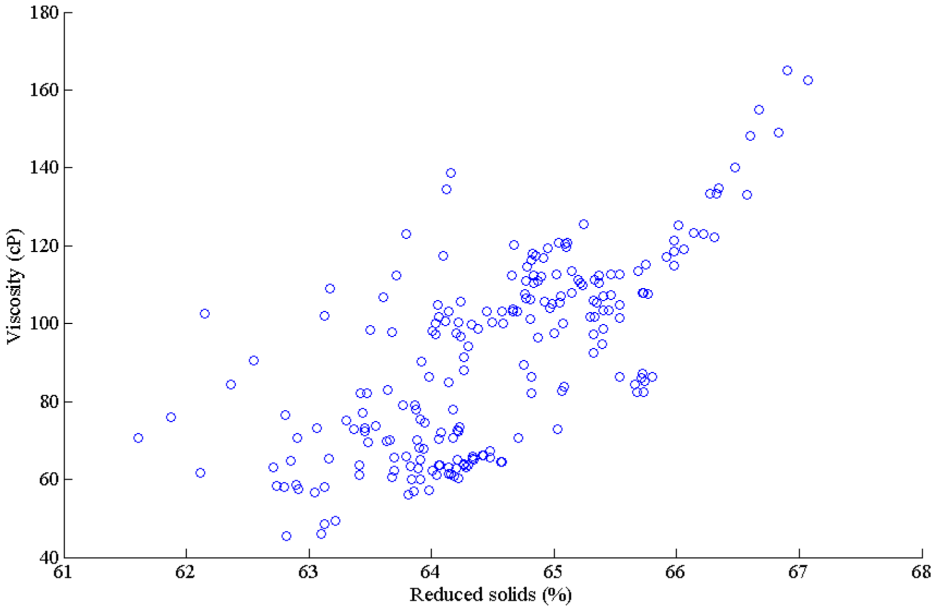

Figure 7.9 Effect of the liquor composition on the soft sensor performance when the number 1 motor/pump was in operation.

adequate for practical application unless their parameters are correlated with the liquor composition, as concluded in Chapter 5. However, it is not obvious at this stage what the other factors are. The observed differences in the viscosity estimates at the same $S_r$ may be due to variation in the liquor composition and/or the sensitivity of the sensor to the changes in the operating point of the pump, or to the variations noticed in the liquor density that was expected to be constant (see section 7.5.2.3). Even if the +/-5% variation observed in the average liquor density has some effect on the performance of the sensor (since $TQ_p$ is a function of density), it is unlikely that this level of variation would have been responsible for the significant differences in the viscosity estimates observed at the same $S_r$ as shown in Figure 7.9.

### 7.5.5.2 Pump's operating point

The effect of the changes in the operating point of the pump on the performance of the soft sensor was explored. It would be recalled that the model installed as a soft sensor has the ability to adapt to changes in the operating point of the pump. Subsequent analysis was undertaken to assess whether the soft sensor's performance as depicted in Fig 7.9 was likely due to variations in the composition of the liquor or the weakness of the model to account for changes in the pump's operating point. It was shown in Figure 6.2 (reproduced below) that at any operating point (FC) of the pump, TQNN increases with QN as $V_n$ increases while at any constant $V_n$ and across different FCs (changes in pump operating point), TQNN is an increasing function of QN. The expectation is that, if the soft sensor performances at any FC or across FCs have similar implications as those described in Figure 6.2, then the soft sensor can be said to be working satisfactorily. The differences in the viscosity estimates at the same $S_r$ as shown in Fig 7.9 ($S_r$ vs. Viscosity) may therefore not be due to the sensor's sensitivity to the changes in the pump operating point. Rather, viscosity variations observed at similar $S_r$s seem to show the ability of the sensor to respond effectively to the changes in the liquor properties and at the same time. The normalised performance data (TQNN vs QN, grouped by $V_n$) of the sensor during a 10-day operation of pump 1 is as shown in Fig 7.10. There are more than 40 different $V_n$s

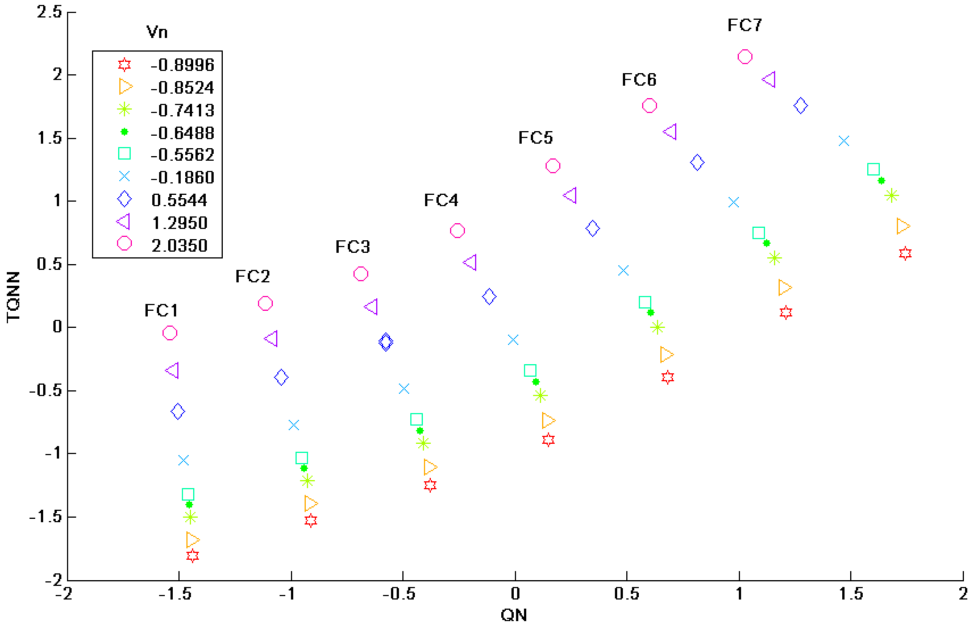

Figure 6.2 Relationship between the normalised flow (QN) and the normalised torque (TQNN) at different viscosities and FCs

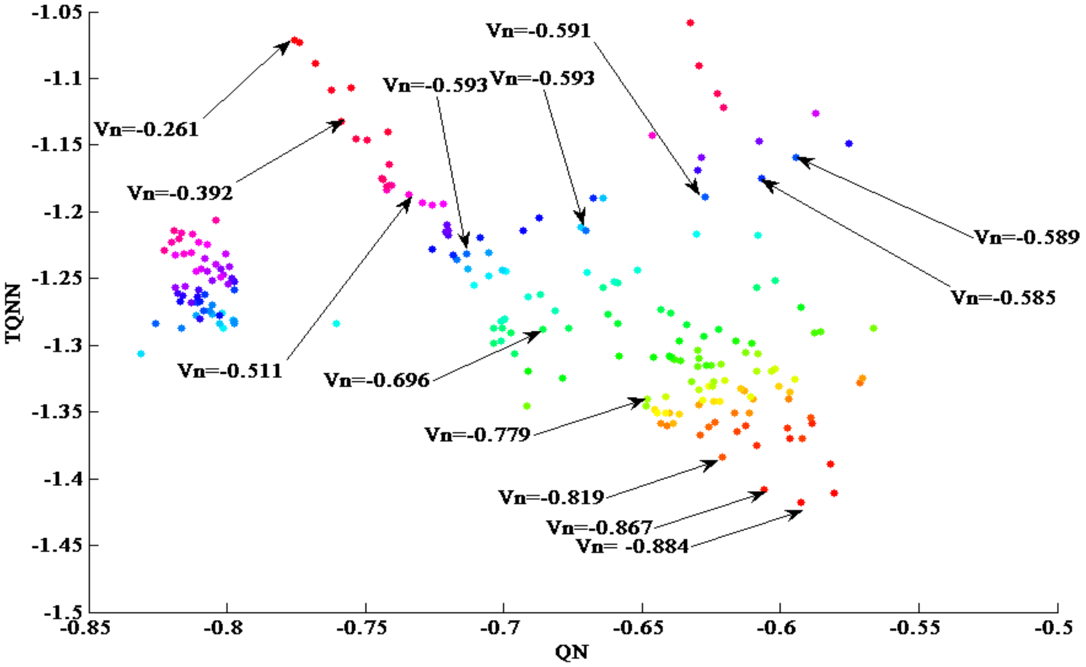

Figure 7.10 Effect of changes in the pump's operating point on the soft sensor performance when the number 1 motor/pump was in operation; (QN=normalised flow; TQNN=normalised torque; $V_n$=normalised viscosity)

and so, the large legend is not shown. However, two strategic sections of the grouped scatter plot were selected for illustration as shown with arrows. It is observed that along the direction of an increasing $V_n$ at an approximate FC, TQNN increases as QN decreases. Along an approximately constant $V_n$=0.59 (rounded to 2 significant digits), TQNN is an increasing function of QN. Other data points were checked and found to have similar trends. This finding is similar to the expected performance trend as shown in Fig 6.2. This shows that while there are changes in the pump's operating point, the sensor is able to give fairly consistent viscosity estimates. Similarly, at any approximate pump operating point, the sensor was able to give consistent viscosity estimates. It is obvious, based on the above findings, the significant variations in the viscosity estimates obtained from the soft sensor at the same $S_r$ can not be attributed either to the sensitivity of the sensor to the changes in the operating point of the pump or the variation in the liquor density. The variations in the liquor viscosity estimates at the same $S_r$s are most likely due to the variations in the liquor composition, brought on by a variety of factors upstream of the firing pump. Therefore, it can be concluded that the soft sensor is able to give consistent viscosity estimates in the presence of the changes in the liquor composition and /or the changes in the pump's operating point.

## 7.6 CONCLUSIONS AND RECOMMENDATIONS ON SOFT SENSOR IMPLEMENTATION

An age-independent centrifugal pump-based black liquor viscosity model, which was obtained using the Hydraulic Institute viscosity correction method, was installed as a viscosity soft sensor at the number 5 recovery boiler at the Carter Holt Harvey Pulp and Paper (CHHP&P) Kinleith mill, New Zealand, where its performances in the presence of different and changing process variables were evaluated. The evaluation was done to determine whether the sensor could give consistent viscosity estimates in the presence of the prevailing and changing process conditions.

Results show that the soft sensor was able to give consistent changes in the viscosity estimates, which track the changes in the liquor solids concentration and temperature, as expected. Although both the temperature and the solids concentration of the liquor track each other as expected, the effect of the liquor solids concentration on the viscosity estimates dominates that of the temperature, indicating that conventional temperature control that is closely associated with the changes in the liquor solids concentration may not be adequate. Excessive manipulation of temperature can lead to liquor flashing at the guns. Hence, it is suggested that in addition to temperature control, other variables such as residual alkali content of the liquor can be used to manipulate the liquor viscosity to compensate effectively for the changes brought on by solids concentration and other factors, on the liquor viscosity.

The idea of correlating centrifugal pump parameters with black liquor viscosity or viscosity index is not new. The advantages of the approach described in this study over the existing ones lie in their ability to account for the significant changes in the pump age, PA and the use of PA as a tuning variable in updating the model installed as a soft sensor based on a few experimental data. The present approach depends extensively on the use of the Hydraulic Institute-estimated data, as opposed to the traditional use of actual experimental data in the existing centrifugal pump-based black liquor viscosity modelling. Furthermore, there is no guarantee that the existing centrifugal pump-based viscosity sensors can give robust viscosity estimates in the face of changing pump's operating points, as done by the soft sensor developed in this study.

Black liquor density is anticipated to remain fairly constant under real mill pumping or firing conditions. Therefore, it should not contribute to the changes in the torque (utilised by the model) developed by the motor connected to the relevant recirculation or firing pump. It was however shown in this study that, black liquor density can vary by as much as +/-5% from the actual average density and higher variations may be possible. It is suggested that for an improved performance, the present soft sensor should be updated by incorporating the effect of the changes in the black liquor density on the motor torque, which in turn affects the viscosity estimates. Although black liquor density prediction is outside the scope of this work and its effect on the present evaluation seems not pronounced, it is expedient to reconsider the heavy black liquor density estimates obtained from the current black liquor density correlation since the black liquor solids flow to the recovery furnace depends partly on these density estimates.

The outputs from the currently installed soft sensor could be taken as a consistent measure of the liquor viscosity or if the actual and accurate viscosity estimates are desirable, the installed model should be modified by obtaining the best PA using few experimental data. The choice would depend on the ultimate goal of the management of the steam and recovery plant at the CHHP&P, Kinleith mill, New Zealand.

Since it has been shown that the present temperature control may not be adequate to address the overall changes in the liquor properties as indicated by viscosity, it is recommended that viscosity control by temperature manipulation in addition to other viscosity-influencing parameters should be attempted to improve the liquor combustion characteristics in the furnace.

The installed viscosity sensor at the number 5 recovery boiler is pump-specific and dependent on the pump's size as well as the motor size. In order to be able to install similar viscosity sensors at the number 4 recovery boiler or other parts of the mill where required without the need to go through all the computational steps outlined in this study, the generalization of the current approach to centrifugal pump of any type and size, and any motor size should be considered.

# 8.0 FINAL CONCLUSIONS AND RECOMMENDATIONS

## 8.1 INTRODUCTION

Factors influencing the viscosity of New Zealand kraft black liquors have been experimentally identified. A variety of composition-dependent models based on traditional regression modelling tools and artificial neural network (ANN) paradigm were used to describe the relationships between the liquor viscosities and their identified influential factors. These models whose parameters must be correlated with the liquor composition in order to be suitable for online application provide basic relationships between the liquor viscosity and its influential variables. Conversely, a centrifugal pump - based black liquor viscosity sensor was developed and subsequently implemented at the number 5 recovery boiler at the Carter Holt Harvey Pulp and Paper (CHHP&P), Kinleith mill, New Zealand. The results of its trial evaluation show that it is capable of providing consistent viscosity estimates in the presence of variations in the liquor composition and/or pump operating points. While this study focussed on a recovery boiler application, the methodology used here could also be applied to other black liquor processing units in the mill. The main conclusions drawn from this study and recommendations for future work are presented in the following sections.

## 8.2 FINAL CONCLUSIONS

Hitherto, the knowledge of the rheological behaviours of New Zealand black liquors that were obtained mainly from the chemical pulping of radiata pine (softwood) and a small percentage of hardwood such as eucalyptus was limited. Systematic investigations of the factors influencing the viscosity of New Zealand black liquors were performed in this study; the results show that the viscosities of New Zealand black liquors are strongly dependent on solid concentrations, temperature, shear rate, and the liquor composition such as the concentration of the residual alkali in the liquor. The liquors exhibit complex rheological behaviours-Newtonian and shear-thinning with or without thixotropy, over the ranges of process conditions investigated. The onset of the Newtonian or non-Newtonian behaviour depends on the prevailing process conditions, the liquor type and the apparent viscosity of the liquor. Interestingly, irrespective of the liquor type, it was found that when their viscosity is <=1000 cP, which is approximately double of the practical centrifugal pumping limit for black liquors, they behave typically as Newtonian fluids. This finding indicates that the design, analysis and operation of softwood kraft black liquor processing systems can be simplified by treating the liquor as Newtonian fluid whose rheological behaviour is well understood.

It was found that the high-solids liquor viscosity can be permanently and significantly reduced by at least a factor of 6 via the post-pulping operation called liquor heat treatment (LHT). It was shown further that the liquors' viscosities are very sensitive to their residual alkali contents. These results will find useful application in the mills where high viscosity has been a limiting factor to black liquor processing.

It is noteworthy that, the rheological behaviours of New Zealand black liquors, which are found to be similar to those of other softwood liquors around the world, are now better understood. There is now a well defined viscosity database for New Zealand black liquors. This suggests that the tools and technologies developed for other softwood liquors around the world can easily be adapted to the New Zealand black liquors and vice-versa.

For process analysis, design, simulation and control, accurate models for describing numerical relationships between two variables are indispensable. Two forms of models namely composition-dependent and composition-independent ones were developed in this study. Although the composition-dependent models are not in the final forms for practical application due to the sensitivity of their parameters to liquor composition, they provide a simple basis for describing the direct relationships between black liquor viscosity and its input variables-solids concentration, temperature and shear rate.

A variety of composition-dependent predictive models including the existing and those proposed in this study have been used to fit the rheological data obtained in this work. For several decades, attempts to model black liquor viscosity have been based on the traditional linear and nonlinear regression models. Although this study began with the use of these traditional methods, it moved on to nonlinear data-driven model based on ANN paradigm. While the traditional models were found to be fairly accurate and adequate to describe the relationship between the liquor viscosity and its influential factors over limited ranges of process conditions, they were found to be grossly inadequate over wide ranges of process conditions. This is not surprising, as the relationship between black liquor viscosity and the input variables are nonlinear when the range of process conditions widens. In many cases as shown in this study, the traditional models built on data obtained over limited ranges of process conditions were not able to satisfactorily complement each other since they failed to provide prediction continuity. The main success of this project lies on the development of accurate and adequate ANN-based kraft black liquor viscosity models, not just applicable to limited ranges of process conditions but also to all practicable ranges of process conditions, despite the liquors' different rheological behaviours over wide ranges in process conditions. This is particularly important, as this new modelling approach eliminates the need for multiple models.

Composition-dependent black liquor viscosity models were easier to obtain but are not directly suitable for practical application since their parameters are liquor-dependent. Although few researchers have attempted to develop black liquor viscosity models that are able to directly account for the variations in the liquor composition, the available ones are not adequate for practical application, as they are either limited to low-solids liquors. In the cases where they are applicable to high-solids liquors, they are limited to specific liquor composition or process conditions and there is no guarantee of obtaining real time measurements of their input variables.

For the first time in Australasia, this study developed a centrifugal pump-based black liquor viscosity model using the Hydraulic Institute viscosity correction method. The model was installed as a viscosity soft sensor at the number 5 recovery boiler at the Carter Holt Harvey Pulp and Paper (CHHP&P), Kinleith mill, New Zealand, where its performance was evaluated to determine whether it could give consistent rather than accurate viscosity estimates in the presence of the prevailing and changing process conditions.

Results show that the soft sensor was able to give consistent changes in the viscosity estimates, which track the changes in the liquor solids concentration and temperature as expected. Although the temperature and the solids concentration of the liquor track each other, the effect of liquor solids concentration on the viscosity estimates dominates that of temperature, indicating that conventional temperature manipulation that is closely associated with the changes in the liquor solids concentration, and being used to control liquor combustion characteristics in the recovery boiler, may not be adequate. The sensor's performance results confirm its ability to effectively account for variations in the liquor composition. In addition, it was able to give robust viscosity estimates in the presence of changing pump's operating point.

The idea of correlating the centrifugal pump parameters with the black liquor viscosity or the viscosity index is not new, as similar approaches have been used in two mills in North America. The advantages of the approach described in this study over the existing ones lie in their ability to account for significant changes in the pump age (PA) and the potential use of PA as a tuning variable in updating the model installed as a soft sensor based on a few experimental data. The approach presented in this thesis relies extensively on the use of Hydraulic-Institute estimated data, as opposed to the use of actual experimental data in the existing centrifugal pump-based black liquor viscosity modelling. Furthermore, there is no guarantee that the existing centrifugal pump-based viscosity sensors can give robust viscosity estimates in the face of changing pump's operating points as done by the soft sensor developed in this study. It is concluded that the centrifugal pump-based black liquor viscosity sensor developed in this study can provide consistent black liquor viscosity estimates at the recovery boiler. Since it is composition-independent, it can be used with any other softwood kraft black liquors in either New Zealand or other parts of the world.

## 8.3 FINAL RECOMMENDATIONS

Black liquor is a water-based polymeric mixture that is prone to evaporation at very high temperatures. The rotary evaporator used to concentrate weak or intermediate black liquor to high solids concentrations in the neighbourhood of 80% was stand-alone equipment; it therefore was difficult to transfer the highly concentrated black liquor to the open cup viscometer, which is also stand-alone equipment where the viscosity measurements were obtained in this study. Therefore, the viscosity measurements of the New Zealand black liquor samples were limited to liquors at solids concentration=0-70% and temperature

=0-115 $^{o}$C due to equipment limitations. It is known that firing black liquors in the recovery boilers at high solids concentrations (significantly higher than 70%) is economically and environmentally beneficial and so, the accurate knowledge of New Zealand black liquor rheological behaviours at higher solids concentrations (>70%) and temperatures (>115 $^{0}$C) would be essential for future process upgrades and improvements. In order to be able to study the rheological characteristics of New Zealand black liquors at solids concentrations above 70% and temperatures above 115 $^{o}$C, it would be helpful to utilise a pressurised viscometer integrated with an evaporator such that the concentrated liquor can be continuously transferred to the viscometer at the measurement conditions.

It has been shown, based on the liquors studied, that both an increase in residual alkali (RA) content of the liquor and the application of LHT at high solids concentrations result in a significant decrease in the liquor viscosity. The existing reports corroborate this finding. Although an online approach for measuring and monitoring the RA content of weak black liquor  exists (Hodges et al. 2006; Porter et al. 2010), unfortunately it is not applicable to high-solids (concentrated) black liquors. In addition, it has been shown that the conventional temperature manipulation in response to the variations in the solids concentrations of the liquor being fired at the recovery boiler guns may not be effective, it would be helpful to devise an online means to continuously measure and monitor RA content of concentrated black liquor so that it may be manipulated in conjunction with temperature for viscosity control at the recovery boiler. This will be expedient where recovery boiler problems can be traced to high viscosity and where the use of traditional temperature control has been shown to be ineffective, for example, where excessive high temperature has caused liquor flashing at the recovery boiler guns. Where a recovery boiler is running at reduced solids concentration due to concern for rheological problems, the use of a LHT unit should be considered.  This unit would help to optimise recovery boiler operations through eliminating the high viscosity problems while increasing liquor solids concentration.

For the first time in this study through the use of ANN, an accurate and a generalized model, which describes jointly the Newtonian and non-Newtonian behaviours of black liquor over a wide range of process conditions, was developed as a function of solids concentration, temperature and shear rate. The resulting multilayer feedforward ANN that was trained using an automated Bayesian regularization algorithm had difficulty learning the relationship between the viscosity and its input variables, as the algorithm failed to converge to a unique solution. The training had to be stopped by focussing on additional criteria such as $R^2$ statistic and maximum absolute relative error (MARE) between the predicted and measured viscosities. It was suspected that, because there are two distinct but overlapping rheological regions-Newtonian and non-Newtonian, modelled simultaneously, the network finds it difficult to learn the relationship between its output and the inputs. A network with internal classification ability trained with other algorithms should be attempted to enhance the training and the eventual performance of the resulting network.

A centrifugal pump-based black liquor viscosity soft sensor, which incorporates the effect of pump age (PA) on its performance has been developed, installed and undergone trial evaluation in this study. The PA must be periodically set and adjusted manually via a few experimental data once a significant drift is noticed in the pump mechanical status. Future work should seek to automatically adjust PA. Alternatively, an approach that is completely robust to the changes in PA should be attempted.

Black liquor density was anticipated to remain fairly constant under the real mill pumping and firing conditions and therefore, should have negligible contribution to the changes in the torque developed by the motor connected to the relevant recirculation or firing pump. It was observed in this study that, black liquor density can vary by as much as +/-5% from the actual average density, and higher variations may be possible. It is suggested that for an improved sensor performance, the present soft sensor should be updated by incorporating the effect of changes in the black liquor density on the motor torque to eliminate potential sensitivities of the viscosity soft sensor to the variations in the liquor density.

The installed viscosity sensor at the number 5 recovery boiler is dependent on the model and size of the installed centrifugal pump, as well as the installed motor size. The generalization of the present approach to centrifugal pump of any type and size, and motor of any size should be considered. This will facilitate the installation of similar viscosity sensor at the number 4 recovery boiler and/or other parts of the mill where required, without the need to go through all the computational steps outlined in this study.

The approach developed here assumes that black liquor is a Newtonian fluid under all practical situations up to the practical pumping limit of 500 cP. It has been reported that some hardwood black liquors can exhibit non-Newtonian behaviours at viscosities as low as 100 cP. Furthermore, the Hydraulic Institute viscosity method is applicable only to Newtonian fluids. It would be worthwhile to consider the extension of the approach here to accommodate black liquors that exhibit non-Newtonian behaviours.

It will be interesting to consider other alternatives to a centrifugal pump-based black liquor viscosity soft sensor. Such alternatives may include the use of pipe flow theories in which the pipe dimensions and the easily measurable flow parameters such as flow rate and pressure drop can be correlated with black liquor viscosity.

Previous researches have shown that black liquor spray and combustion characteristics in the recovery furnace are affected by black liquor physical (including viscosity) and chemical properties. Existing reports also show that black liquor viscosity is affected by its chemical composition. This study confirms that in addition to other factors that affect black liquor viscosity, the liquor composition plays a major role. This shows that black liquor viscosity is a good indicator of the resultant changes in the liquor physical and chemical properties. Previous Investigators have shown that, controlling the viscosity of high-solids black liquor being fired in the recovery boiler resulted in economic, technical and environmental benefits. These benefits could be realized at the CHHP&P, Kinleith mill, New Zealand if the current viscosity soft sensor predictions can be improved and then used in a viscosity-based control strategy that is fully integrated with the existing number 5 recovery boiler control systems. The following steps are suggested to achieve this purpose:

- Study the effects of the recovery boiler firing parameters and the liquor properties, including black liquor viscosity (obtained from the soft sensor) on the number 5 recovery boiler performance indicators (e.g., thermal efficiency, smelt reduction efficiency, opacity, etc). This will help to establish the relationship between the recovery boiler performance indicators, and the liquor optimal firing parameters and liquor properties (including best viscosity range),

- Currently, viscosity control is achieved indirectly by temperature manipulation. The current focus is on temperature manipulation, in response to the variation in the liquor solids concentration. This approach would be ineffective where the increase in liquor viscosity is due to the factors other than solids concentration. Excessive high temperature for viscosity control could lead to liquor flashing at the recovery boiler guns. This study has shown that, the residual alkali content of the liquor can be manipulated in conjunction with temperature, to control the liquor viscosity. To achieve this, a relationship between the viscosity, and the RA content and temperature should be established, and potential economic implication of alkali usage should be evaluated,
- Finally, a viscosity-based control algorithm that utilises temperature (existing control variable) and the RA content as an additional control variable could then be developed. But at the moment, there is no online approach to continuously measure the RA content of heavy black liquor, and therefore, if the use of RA content is found to be economically feasible and technically favourable, firstly, an online method of measuring and regulation of RA content of heavy black liquor should be devised.

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# APPENDIX A EXISTING BLACK LIQUOR VISCOSITY MODELS

| Researcher /Location /Wood type | Model description | Limitations | Temperature range/upper limit(°C) | Dependence on shear rate ($s^{-1}$) | Sensitivity to composition variation | Variables measurable online? |
|---|---|---|---|---|---|---|
| Zaman & Fricke(1994a) / USA /Softwood | (A) $\eta_{bl}= A_2 T^{1/2} \exp\left(\frac{B_2 T_0}{T - T_0}\right)$<br>where $A_2$, $B_2$=f(S), To is related to the freezing point of the liquor; $\eta_{bl}$=kinematic viscosity (cm2/s) of BL, T (Temperature (°K) | Limited to SCs<=50% | Up to 80 | No | Yes | Yes |
| Zaman & Fricke(1991) / USA /Softwood | (B) $\log(\eta_R)=\sum_{i=1}^{n} a_i \left(\frac{ST_r}{T}\right)^i$<br>S=solids mass fraction; T=temperature ($^0K$); i = model order; $a_i$=parameter estimate;$T_r$=reference temperature;<br>$\eta_R = \frac{\eta_{bl}}{\eta_w}$ is the kinematic viscosity of BL relative to that of water at the same temperature. | Log-transformed response variable; accuracy of the actual prediction not guaranteed.<br>Limited to SCs<=50% | >=25 | No | Yes | Yes |
| Moosavifar et al(2006)/ Sweden/ softwood | (C) $\log\left(\frac{\mu_{bl}}{\mu_w}\right)=KS^{1.5}+B\left(\frac{1}{T-250}\right)$<br>K and B are constants to be evaluated. S is replaceable with lignin concentration,$L_c$ ; $\mu_w$ =viscosity of water (mPa.s). | Log-transformed response variable; accuracy of the actual prediction not guaranteed.<br>Limited to SCs<50% | 30-90 | No | Yes (sensitive to factors other than lignin concentration) | Yes (for weak BL) |

Appendix A continued

| Researcher /Location /Wood type | Model description | Limitations | Temperature range/upper limit(°C) | Dependence on shear rate ($s^{-1}$) | Sensitivity to composition variation | Variables measurable online? |
|---|---|---|---|---|---|---|
| Ghosh (1993)/ Softwoods & hardwoods from diverse origins | **(D)**<br>The same form as model **B** but includes i=0 and applicable to all SCs | Log-transformed response variable; accuracy of the actual prediction not guaranteed. | 20-140 (for lumped viscosity data) | No: at low shear rates | Yes | Yes |
| Adams & Frederick (1988)/USA/ different sources | **(E)**<br>$\log\left(\frac{\mu_{bl}}{\mu_w}\right)=1.51\text{x}10^{-2}\left(\frac{ST_r}{T}\right)+b\left(\frac{ST_r}{T}\right)^c$<br>$\mu_{bl}$ =BL viscosity (Pa.s); $\mu_w$ =water viscosity (Pa.s); $T_r$ =373°K; b and c are the parameter estimates; S=SC(%);T(°K) | Log-transformed response variable; accuracy of the actual prediction not guaranteed. | Not specific | No: at low shear rates | Yes | Yes |
| Frederick (1997)/USA/ different sources | **(F)** $\log\left(\frac{\mu_{bl}}{\mu_w}\right)=\frac{ST_r/T}{c+d\frac{ST_r}{T}}$<br>c and d are the parameters to be estimated; S=solids mass fraction; other parameters are as defined in **(E)** | Log-transformed response variable; accuracy of the actual prediction not guaranteed. | Not specific | No: at low shear rates | Yes | Yes |
| Zaman & Fricke (1995a) /USA/ softwood | **(G)** $\log(\eta_R)=\sum_{i=1}^{n}a_i\left(\frac{S}{T}\right)^i$<br>the parameters are as defined in **(B)** except that $a_i$ is correlated with BL composition/pulping conditions | Limited to SCs<=50%<br>Log-transformed response variable; accuracy of the actual prediction not guaranteed. | Pulping temperatures | No | Yes & No (Depends) | Not certain |

Appendix A continued

| Researcher /Location /Wood type | Model description | Limitations | Temperature range/upper limit(°C) | Dependence on shear rate ($s^{-1}$) | Sensitivity to composition variation | Variables measurable online? |
|---|---|---|---|---|---|---|
| Vakkilainen (1999)/Finland/softwood , hardwood, etc | **(H)** $\log(\eta) = A + \frac{B}{T^3}$<br>$\eta$ is the kinematic viscosity ($mm^2/s$) of the liquor; S is the dry solids mass fraction (0-1) and T is temperature (°K); $A=A_{H20}+a_1S+a_2S^2+a_3S^3$; $B=B_{H20}+b_1S+b_2S^2+b_3S^3$; $A_{H20}$, $a_1$, $a_2$, $a_3$, $B_{H20}$, $b_1$, $b_2$ and $b_3$ are the parameter estimates. | Log-transformed response variable; accuracy of the actual prediction not guaranteed. | Near or actual operating condition | No | Yes | Yes |
| Zaman & Fricke (1991)/USA /softwood | **(I)** $\log(\mu_0) = \sum_{i=0}^{n} a_i \left( \frac{S}{S+1} \frac{1}{T} \right)^i$<br>where: S=solids mass fraction(0-1); T=temperature($^0K$); $\mu_0$=zero shear viscosity; $a_i$=parameter estimate. | Limited to SCs>50%. Log-transformed response variable; accuracy of the actual prediction not guaranteed. | 40-130 | No | Yes | Yes |
| Wenberg (1985)/Sweden/ softwoods mainly | **(J)** $\log(\mu_0) = \frac{(A+BY)10^{10}}{T^4}$ -C<br>where Y=S/(1-S); S, T, and $\mu_0$ have the same interpretations and units as they are model **I**. | SCs=68-88%<br>Response variable log-transformed; accuracy of the actual prediction not guaranteed. | 70-170 | No | Yes | Yes |
| Zaman & Fricke (1994b)/USA /softwood | **(K)** $\mu = A\ T^{1/2} \exp\left( \frac{B}{T} + \frac{CT_0}{T-T_0} \right)$<br>where $\mu$ =dynamic viscosity of BL; A, B, C=f(S), $T_0$ is related to glass transition temperature, Tg (having linear dependence on SC) of the concentrated liquor; defined as Tg= $(b_1+b_2S)$; $T_0=b_3Tg$; | Limited to SCs>50% | Up to 140 | No | Yes | Yes |

Appendix A continued

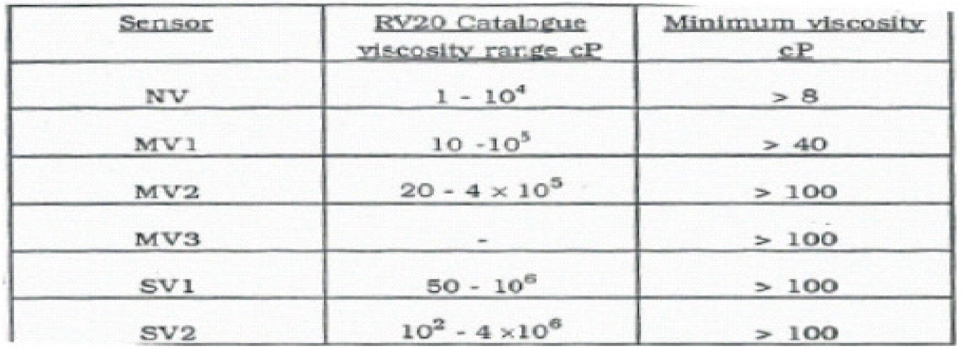
| Researcher /Location /Wood type | Model description | Limitations | Temperature range/upper limit(°C) | Dependence on shear rate ($s^{-1}$) | Sensitivity to composition variation | Variables measurable online? |
|---|---|---|---|---|---|---|
| Zaman and Fricke (1995b,1995c)/ USA/softwoods | **(L)** $\frac{\mu_{bl}}{\mu_0}=\frac{1}{1+(\lambda a_T \gamma)^m}$<br>is the modified Cross model and, | Both models are limited to SCs>50%; | 40 to 140 | Yes | Yes | Yes but shear rate must be computed |
|  | **(M)** $\frac{\mu_{bl}}{\mu_0}=\left[1+(\lambda a_T \gamma)^m\right]^{\left(\frac{n-1}{\alpha}\right)}$<br>is the modified Carreau-Yasuda model both incorporating the temperature and SC effects via WLF equation; $\gamma$ is the SR(s-1); $\mu_{bl}$ and $\mu_0$ are as defined in earlier equations;<br>$a_T=\exp\left[\frac{-26.77(T-T_0)}{104.16+T-T_0}\right]$ is the WLF equation where $T_0$ is related to BL glass transition temperature, Tg which is applicable to high SCs BL; Tg and $T_0$ are as defined for model K; $\lambda$, $a$, m, n, $b_1$, $b_2$ and $b_3$ are the parameter estimates. | Requires $\mu_0$ model;<br>Depends on fundamental parameter, Tg. |  |  |  |  |
| Zaman and Fricke (1996)/USA /softwoods | (N) $\mu_0=aL_M L_C^b$<br>$L_M$ and $L_C$ (g/g solids) are the lignin molecular weight and concentration, respectively; a and b are the parameter estimates. | Limited to specific high SC, temperature and concentrations of effective alkali & sulphidity of cooking liquor | Pulping temperatures | No: at low shear rates | Yes and No (Depends) | Not certain |
| Researcher/ Year/New Zealand (prior to this study) | **(O)** None | - | - | - | - | - |

SC=solids concentration; BL=black liquor; SR=shear rate; WLF=William-Landel-Ferry

# APPENDIX B BLACK LIQUOR VISCOSITY MEASUREMENT

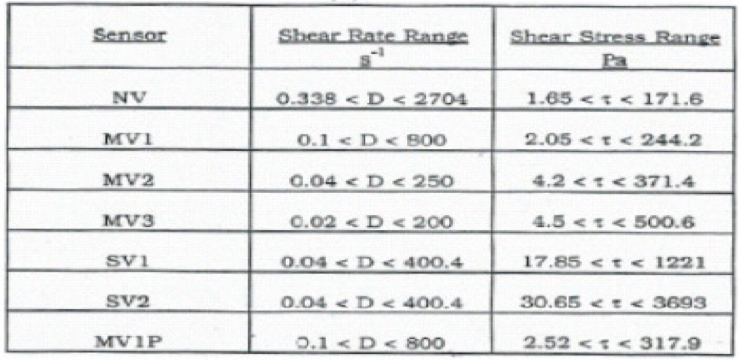
## Appendix B1 Features of Haake RV 20 Sensors (Haake Mess-Technik 1988; McGiven and Tuoc 1991)

(a)



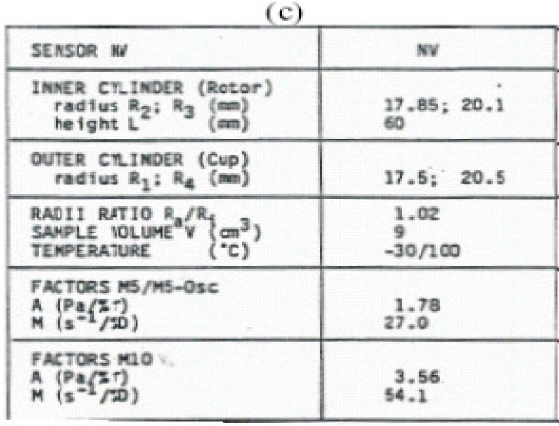
| Sensor | RV20 Catalogue viscosity range cP | Minimum viscosity cP |
|---|---|---|
| NV | 1 - $10^4$ | > 8 |
| MV1 | 10 -$10^5$ | > 40 |
| MV2 | 20 - 4 × $10^5$ | > 100 |
| MV3 | - | > 100 |
| SV1 | 50 - $10^6$ | > 100 |
| SV2 | $10^2$ - 4 ×$10^6$ | > 100 |

(b)



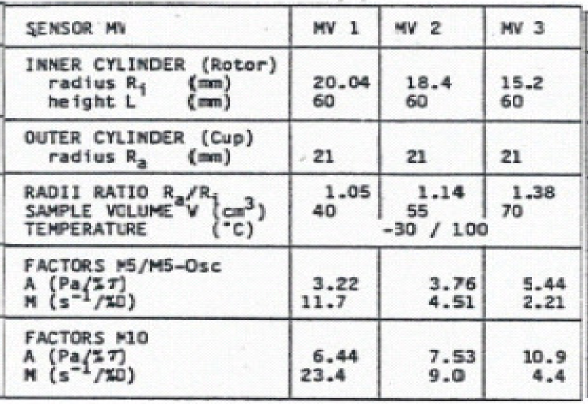
| Sensor | Shear Rate Range $s^{-1}$ | Shear Stress Range Pa |
|---|---|---|
| NV | $0.338 < D < 2704$ | $1.65 < \tau < 171.6$ |
| MV1 | $0.1 < D < 800$ | $2.05 < \tau < 244.2$ |
| MV2 | $0.04 < D < 250$ | $4.2 < \tau < 371.4$ |
| MV3 | $0.02 < D < 200$ | $4.5 < \tau < 500.6$ |
| SV1 | $0.04 < D < 400.4$ | $17.85 < \tau < 1221$ |
| SV2 | $0.04 < D < 400.4$ | $30.65 < \tau < 3693$ |
| MV1P | $0.1 < D < 800$ | $2.52 < \tau < 317.9$ |

(c)



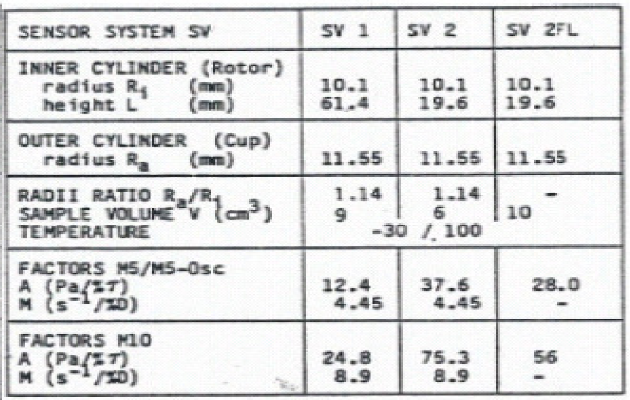
| SENSOR NV | NV |
|---|---|
| INNER CYLINDER (Rotor)<br>radius $R_2$; $R_3$ (mm)<br>height L (mm) | 17.85; 20.1<br>60 |
| OUTER CYLINDER (Cup)<br>radius $R_1$; $R_4$ (mm) | 17.5; 20.5 |
| RADII RATIO $R_a/R_i$<br>SAMPLE VOLUME V ($cm^3$)<br>TEMPERATURE (°C) | 1.02<br>9<br>-30/100 |
| FACTORS M5/M5-Osc<br>A $(Pa/\%\tau)$<br>M $(s^{-1}/\%D)$ | 1.78<br>27.0 |
| FACTORS M10<br>A $(Pa/\%\tau)$<br>M $(s^{-1}/\%D)$ | 3.56<br>54.1 |

(d)



| SENSOR MV | MV 1 | MV 2 | MV 3 |
|---|---|---|---|
| INNER CYLINDER (Rotor)<br>radius $R_i$ (mm)<br>height L (mm) | 20.04<br>60 | 18.4<br>60 | 15.2<br>60 |
| OUTER CYLINDER (Cup)<br>radius $R_a$ (mm) | 21 | 21 | 21 |
| RADII RATIO $R_a/R_i$<br>SAMPLE VOLUME V ($cm^3$)<br>TEMPERATURE (°C) | 1.05<br>40 | 1.14<br>55<br>-30 / 100 | 1.38<br>70 |
| FACTORS M5/M5-Osc<br>A $(Pa/\%\tau)$<br>M $(s^{-1}/\%D)$ | 3.22<br>11.7 | 3.76<br>4.51 | 5.44<br>2.21 |
| FACTORS M10<br>A $(Pa/\%\tau)$<br>M $(s^{-1}/\%D)$ | 6.44<br>23.4 | 7.53<br>9.0 | 10.9<br>4.4 |

(e)



| SENSOR SYSTEM SV | SV 1 | SV 2 | SV 2FL |
|---|---|---|---|
| INNER CYLINDER (Rotor)<br>radius $R_i$ (mm)<br>height L (mm) | 10.1<br>61.4 | 10.1<br>19.6 | 10.1<br>19.6 |
| OUTER CYLINDER (Cup)<br>radius $R_a$ (mm) | 11.55 | 11.55 | 11.55 |
| RADII RATIO $R_a/R_i$<br>SAMPLE VOLUME V ($cm^3$)<br>TEMPERATURE | 1.14<br>9 | 1.14<br>6<br>-30 / 100 | -<br>10 |
| FACTORS M5/M5-Osc<br>A $(Pa/\%\tau)$<br>M $(s^{-1}/\%D)$ | 12.4<br>4.45 | 37.6<br>4.45 | 28.0<br>- |
| FACTORS M10<br>A $(Pa/\%\tau)$<br>M $(s^{-1}/\%D)$ | 24.8<br>8.9 | 75.3<br>8.9 | 56<br>- |

## Appendix B2 Black Liquor Viscosity Measurement Uncertainty Estimation

SC (%) =solids concentration; T ($^{o}$C) =temperature; SR ($s^{-1}$) = shear rate; V (mPa.s) =viscosity; SD =standard deviation RSD (%) = SD/ Average=relative standard deviation.

| Sample | Experimental conditions | | | Run 1 | Run 2 | Run 3 | Run 4 | Average | SD | RSD (%) |
|---|---|---|---|---|---|---|---|---|---|---|
| | SC (%) | T (°C) | SR ($s^{-1}$) | V (mPa.s) | V (mPa.s) | V(mPa.s) | V(mPa.s) | V (mPa.s) | V (mPa.s) | |
| E509 | 69.8 | 60 | 10 | 6296 | 6297 | 6260 | 6308 | 6290 | 20.89 | 0.33 |
| E509 | 69.8 | 60 | 50 | 5632 | 5608 | 5592 | 5576 | 5602 | 23.89 | 0.43 |
| E509 | 69.8 | 60 | 100 | 5322 | 5318 | 5320 | 5310 | 5318 | 5.26 | 0.1 |
| E509 | 69.8 | 60 | 150 | 5119 | 5120 | 5116 | 5115 | 5118 | 2.38 | 0.05 |
| E509 | 69.8 | 60 | 200 | 4970 | 4957 | 4929 | 4938 | 4949 | 18.48 | 0.37 |
| E509 | 69.8 | 60 | 250 | 4812 | 4738 | 4759 | 4750 | 4765 | 32.65 | 0.69 |
| E509 | 69.8 | 60 | 250 | 4744 | 4692 | 4700 | 4708 | 4711 | 22.95 | 0.49 |
| E509 | 69.8 | 60 | 200 | 4798 | 4832 | 4842 | 4855 | 4832 | 24.39 | 0.5 |
| E509 | 69.8 | 60 | 150 | 5011 | 5085 | 5116 | 5100 | 5078 | 46.43 | 0.91 |
| E509 | 69.8 | 60 | 100 | 5304 | 5330 | 5342 | 5354 | 5333 | 21.38 | 0.4 |
| E509 | 69.8 | 60 | 50 | 5645 | 5665 | 5681 | 5693 | 5671 | 20.78 | 0.37 |
| E509 | 69.8 | 60 | 10 | 6177 | 6270 | 6280 | 6396 | 6281 | 89.75 | 1.43 |
| E509 | 69.8 | 80 | 50 | 1015 | 1006 | 1004 | 998.8 | 1006 | 6.75 | 0.67 |
| E509 | 69.8 | 80 | 100 | 984.3 | 980.8 | 979.2 | 976.5 | 980.2 | 3.26 | 0.33 |
| E509 | 69.8 | 80 | 200 | 944.9 | 939.5 | 935.8 | 936.8 | 939.3 | 4.08 | 0.43 |
| E509 | 69.8 | 80 | 400 | 913.1 | 915.2 | 916 | 917.5 | 915.5 | 1.83 | 0.2 |
| E509 | 69.8 | 100 | 50 | 271.1 | 267.2 | 270.5 | 269.7 | 269.6 | 1.72 | 0.64 |
| E509 | 69.8 | 100 | 100 | 254.5 | 254.8 | 255.9 | 258.1 | 255.8 | 1.63 | 0.64 |
| E509 | 69.8 | 100 | 200 | 246.3 | 245 | 244.1 | 243.8 | 244.8 | 1.12 | 0.46 |
| E509 | 69.8 | 100 | 300 | 239.1 | 239.4 | 240.1 | 242.7 | 240.3 | 1.64 | 0.68 |
| E509 | 69.8 | 115 | 500 | 110.6 | 110.2 | 110.3 | 110 | 110.3 | 0.25 | 0.23 |
| E509 | 69.8 | 115 | 750 | 109.7 | 109.3 | 109.2 | 108.9 | 109.3 | 0.33 | 0.3 |
| E509 | 69.8 | 115 | 1000 | 108.5 | 108.4 | 108.2 | 108 | 108.3 | 0.22 | 0.2 |
| E509 | 63.21 | 40 | 10 | 6130 | 6167 | 6156 | 6164 | 6154 | 16.82 | 0.27 |
| E509 | 63.21 | 40 | 100 | 5482 | 5474 | 5476 | 5478 | 5478 | 3.42 | 0.06 |
| E509 | 63.21 | 40 | 200 | 5120 | 5053 | 5016 | 4946 | 5034 | 72.63 | 1.44 |
| E509 | 63.21 | 40 | 50 | 5592 | 5608 | 5632 | 5644 | 5619 | 23.41 | 0.42 |
| E509 | 63.21 | 60 | 10 | 892.5 | 874.4 | 850.9 | 848.7 | 866.6 | 20.81 | 2.4 |
| E509 | 63.21 | 60 | 100 | 792.6 | 792.2 | 792.2 | 790.4 | 791.9 | 0.98 | 0.12 |
| E509 | 63.21 | 60 | 150 | 784.3 | 783 | 780.8 | 782.6 | 782.7 | 1.45 | 0.18 |
| E509 | 63.21 | 80 | 50 | 239.9 | 241.6 | 240.6 | 241.2 | 240.8 | 0.74 | 0.31 |
| E509 | 63.21 | 80 | 100 | 231.2 | 226.8 | 227.6 | 226 | 227.9 | 2.29 | 1.01 |

Appendix B2 continued

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| E509 | 63.21 | 80 | 200 | 219 | 218.2 | 217.8 | 217.9 | 218.2 | 0.54 | 0.25 |
| E509 | 63.21 | 80 | 400 | 211.1 | 210.1 | 209.8 | 209.6 | 210.2 | 0.67 | 0.32 |
| E509 | 63.21 | 100 | 1000 | 74.82 | 74.49 | 74.34 | 74.25 | 74.47 | 0.25 | 0.34 |
| E509 | 63.21 | 110 | 1000 | 52.02 | 51.95 | 51.95 | 51.95 | 51.97 | 0.04 | 0.07 |
| E509 | 58.56 | 40 | 10 | 863.8 | 862.2 | 860.6 | 843.1 | 857.4 | 9.64 | 1.12 |
| E509 | 58.56 | 40 | 100 | 832.1 | 833.1 | 830.2 | 831.4 | 831.7 | 1.22 | 0.15 |
| E509 | 58.56 | 40 | 200 | 823.1 | 822.3 | 821.1 | 820.5 | 821.8 | 1.17 | 0.14 |
| E509 | 58.56 | 60 | 100 | 178.9 | 180.3 | 180.9 | 180.2 | 180.1 | 0.84 | 0.47 |
| E509 | 58.56 | 60 | 250 | 182 | 182 | 182 | 182.3 | 182.1 | 0.15 | 0.08 |
| E509 | 58.56 | 60 | 10 | 184 | 176.8 | 177.9 | 175.6 | 178.6 | 3.74 | 2.09 |
| E509 | 58.56 | 110 | 750 | 22.62 | 22.58 | 22.61 | 22.54 | 22.59 | 0.04 | 0.16 |
| E509 | 58.56 | 20 | 10 | 6354 | 6371 | 6338 | 6410 | 6368 | 30.92 | 0.49 |
| E509 | 58.56 | 20 | 100 | 5764 | 5757 | 5749 | 5749 | 5755 | 7.23 | 0.13 |
| E509 | 58.56 | 20 | 200 | 5383 | 5353 | 5334 | 5318 | 5347 | 27.94 | 0.52 |
| E509 | 58.56 | 100 | 250 | 31.24 | 31.28 | 31.25 | 31.18 | 31.24 | 0.04 | 0.13 |
| E509 | 58.56 | 100 | 500 | 31.3 | 31.27 | 31.23 | 31.14 | 31.23 | 0.07 | 0.22 |
| E509 | 58.56 | 100 | 1000 | 31.15 | 31.15 | 31.12 | 31.06 | 31.12 | 0.04 | 0.14 |
| E509 | 58.56 | 80 | 1000 | 64.82 | 64.75 | 64.63 | 64.63 | 64.71 | 0.09 | 0.15 |
| E509 | 58.56 | 80 | 2000 | 64.85 | 64.9 | 65.01 | 65.22 | 65 | 0.16 | 0.25 |
| E509 | 50.98 | 0 | 10 | 1076 | 1096 | 1097 | 1093 | 1091 | 9.81 | 0.9 |
| E509 | 50.98 | 0 | 100 | 1054 | 1055 | 1056 | 1053 | 1055 | 1.29 | 0.12 |
| E509 | 50.98 | 0 | 150 | 1046 | 1045 | 1045 | 1044 | 1045 | 0.82 | 0.08 |
| E509 | 50.98 | 20 | 10 | 203.7 | 205.7 | 199.3 | 204.8 | 203.4 | 2.84 | 1.4 |
| E509 | 50.98 | 20 | 100 | 199.9 | 200.1 | 200.4 | 199.8 | 200.1 | 0.26 | 0.13 |
| E509 | 50.98 | 20 | 250 | 200.6 | 200.8 | 200.9 | 200.9 | 200.8 | 0.14 | 0.07 |
| E509 | 50.98 | 40 | 50 | 64.49 | 63.44 | 61.86 | 61.36 | 62.79 | 1.44 | 2.29 |
| E509 | 50.98 | 40 | 100 | 60.72 | 60.57 | 60.04 | 60.63 | 60.49 | 0.31 | 0.51 |
| E509 | 50.98 | 40 | 500 | 60.82 | 60.82 | 60.76 | 60.76 | 60.79 | 0.03 | 0.06 |
| E509 | 50.98 | 60 | 250 | 23.75 | 23.65 | 23.87 | 23.91 | 23.79 | 0.12 | 0.5 |
| E509 | 50.98 | 60 | 500 | 24.3 | 24.26 | 24.25 | 24.29 | 24.27 | 0.02 | 0.1 |
| E509 | 50.98 | 60 | 1500 | 24.95 | 24.96 | 25 | 24.98 | 24.97 | 0.02 | 0.09 |
| E509 | 50.98 | 80 | 250 | 12.25 | 12.22 | 12.25 | 12.19 | 12.23 | 0.03 | 0.23 |
| E509 | 50.98 | 80 | 500 | 12.12 | 12.08 | 12.02 | 12 | 12.06 | 0.06 | 0.46 |
| E509 | 50.98 | 80 | 1000 | 12.45 | 12.5 | 12.53 | 12.55 | 12.51 | 0.04 | 0.35 |
| E509 | 50.98 | 100 | 1000 | 7.7 | 7.7 | 7.715 | 7.729 | 7.71 | 0.01 | 0.18 |
| E509 | 50.98 | 100 | 1500 | 7.917 | 7.891 | 7.897 | 7.915 | 7.9 | 0.01 | 0.16 |

Appendix B2 continued

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| E509 | 37.09 | 40 | 1000 | 6.267 | 6.272 | 6.206 | 6.18 | 6.23 | 0.05 | 0.73 |
| E509 | 37.09 | 40 | 1500 | 6.269 | 6.209 | 6.161 | 6.126 | 6.19 | 0.06 | 1 |
| E509 | 37.09 | 40 | 2000 | 6.211 | 6.186 | 6.162 | 6.168 | 6.18 | 0.02 | 0.36 |
| E509 | 37.09 | 60 | 1000 | 3.846 | 3.805 | 3.803 | 3.815 | 3.82 | 0.02 | 0.52 |
| E509 | 37.09 | 60 | 1500 | 3.801 | 3.778 | 3.79 | 3.794 | 3.79 | 0.01 | 0.25 |
| E509 | 37.09 | 60 | 2000 | 3.784 | 3.784 | 3.8 | 3.8 | 3.79 | 0.01 | 0.24 |
| E509 | 37.09 | 80 | 1500 | 2.633 | 2.619 | 2.614 | 2.614 | 2.62 | 0.01 | 0.34 |
| E509 | 37.09 | 80 | 2000 | 2.585 | 2.575 | 2.583 | 2.588 | 2.58 | 0.01 | 0.22 |
| E509 | 37.09 | 20 | 1000 | 13.78 | 13.7 | 13.63 | 13.62 | 13.68 | 0.07 | 0.54 |
| E509 | 37.09 | 20 | 2000 | 13.51 | 13.48 | 13.48 | 13.5 | 13.49 | 0.01 | 0.11 |
| E509 | 24.73 | 0 | 1000 | 8.538 | 8.544 | 8.546 | 8.537 | 8.54 | 0 | 0.05 |
| E509 | 24.73 | 0 | 2000 | 8.756 | 8.766 | 8.781 | 8.766 | 8.77 | 0.01 | 0.12 |
| E509 | 24.73 | 20 | 1000 | 4.4 | 4.342 | 4.374 | 4.368 | 4.37 | 0.02 | 0.54 |
| E509 | 24.73 | 20 | 2000 | 4.41 | 4.392 | 4.398 | 4.387 | 4.4 | 0.01 | 0.23 |
| E509 | 24.73 | 40 | 1000 | 2.503 | 2.466 | 2.445 | 2.436 | 2.46 | 0.03 | 1.21 |
| E509 | 24.73 | 60 | 1000 | 1.913 | 1.925 | 1.91 | 1.956 | 1.93 | 0.02 | 1.09 |
| E509 | 24.73 | 60 | 2000 | 1.871 | 1.858 | 1.855 | 1.871 | 1.86 | 0.01 | 0.45 |
| E509 | 24.73 | 80 | 2000 | 1.316 | 1.315 | 1.318 | 1.327 | 1.32 | 0.01 | 0.42 |
| E509 | 11.95 | 20 | 2000 | 1.93 | 1.94 | 1.947 | 1.956 | 1.94 | 0.01 | 0.57 |
| E509 | 11.95 | 40 | 2000 | 1.432 | 1.432 | 1.42 | 1.437 | 1.43 | 0.01 | 0.51 |
| E509 | 11.95 | 16 | 1000 | 2.101 | 2.072 | 2.093 | 2.09 | 2.09 | 0.01 | 0.59 |
| E509 | 11.95 | 16 | 2000 | 2.189 | 2.189 | 2.189 | 2.189 | 2.19 | 0 | 0 |
| E509 | 11.95 | 25 | 1000 | 1.774 | 1.773 | 1.781 | 1.772 | 1.77 | 0 | 0.23 |
| E509 | 11.95 | 25 | 2000 | 1.793 | 1.773 | 1.777 | 1.764 | 1.78 | 0.01 | 0.68 |
| E509 | 31.85 | 30 | 1000 | 5.514 | 5.504 | 5.516 | 5.503 | 5.51 | 0.01 | 0.12 |
| E509 | 31.85 | 30 | 2000 | 5.698 | 5.709 | 5.702 | 5.703 | 5.7 | 0 | 0.08 |
| E509 | 31.85 | 10 | 200 | 10.69 | 10.66 | 10.6 | 10.58 | 10.63 | 0.05 | 0.48 |
| E509 | 31.85 | 10 | 400 | 10.89 | 10.92 | 10.9 | 10.83 | 10.89 | 0.04 | 0.36 |
| E408T | 51 | 25 | 100 | 138.6 | 139.4 | 139.6 | 137.5 | 138.8 | 0.95 | 0.69 |
| E408T | 51 | 25 | 100 | 146.1 | 141.3 | 141 | 140.3 | 142.2 | 2.65 | 1.86 |
| E408T | 51 | 0 | 100 | 646.2 | 637 | 637.2 | 629.4 | 637.5 | 6.87 | 1.08 |
| E408T | 51 | 0 | 100 | 626.8 | 627.4 | 621.9 | 618.7 | 623.7 | 4.14 | 0.66 |
| E408T | 17.36 | 0 | 2000 | 4.67 | 4.889 | 5.051 | 5.105 | 4.93 | 0.2 | 3.96 |
| E408T | 17.36 | 0 | 2000 | 5.096 | 5.009 | 4.89 | 4.804 | 4.95 | 0.13 | 2.6 |
| E408T | 17.36 | 25 | 2000 | 2.523 | 2.588 | 2.569 | 2.487 | 2.54 | 0.05 | 1.79 |
| E408T | 17.36 | 25 | 2000 | 2.452 | 2.471 | 2.479 | 2.498 | 2.48 | 0.02 | 0.77 |

Appendix B2 continued

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| E4E508T | 12.31 | 0 | 2000 | 3.431 | 3.407 | 3.407 | 3.415 | 3.42 | 0.01 | 0.33 |
| E4E508T | 12.31 | 0 | 2000 | 3.404 | 3.398 | 3.405 | 3.408 | 3.4 | 0 | 0.12 |
| E4E508T | 12.31 | 25 | 2000 | 1.729 | 1.722 | 1.716 | 1.729 | 1.72 | 0.01 | 0.36 |
| E4E508T | 12.31 | 25 | 2000 | 1.734 | 1.736 | 1.739 | 1.733 | 1.74 | 0 | 0.15 |
| E4E508 | 12.3 | 0 | 2000 | 3.434 | 3.426 | 3.429 | 3.425 | 3.43 | 0 | 0.12 |
| E4E508 | 12.3 | 0 | 2000 | 3.436 | 3.444 | 3.441 | 3.454 | 3.44 | 0.01 | 0.22 |
| E4E508 | 12.3 | 25 | 2000 | 1.855 | 1.84 | 1.835 | 1.82 | 1.84 | 0.01 | 0.79 |
| E4E508 | 12.3 | 25 | 2000 | 1.821 | 1.811 | 1.814 | 1.836 | 1.82 | 0.01 | 0.61 |
| E408 | 15.25 | 25 | 1000 | 2.074 | 2.099 | 2.109 | 2.116 | 2.1 | 0.02 | 0.88 |
| E408 | 15.25 | 45 | 1500 | 1.333 | 1.324 | 1.348 | 1.354 | 1.34 | 0.01 | 1.02 |
| E408 | 15.25 | 65 | 2000 | 1.041 | 1.044 | 1.018 | 1.025 | 1.03 | 0.01 | 1.21 |
| E408 | 15.25 | 85 | 2000 | 0.899 | 0.8758 | 0.8758 | 0.8845 | 0.88 | 0.01 | 1.24 |
| E408 | 30.26 | 25 | 1000 | 6.604 | 6.606 | 6.618 | 6.589 | 6.6 | 0.01 | 0.18 |
| E408 | 30.26 | 45 | 1000 | 4.02 | 4.019 | 4.046 | 4.049 | 4.03 | 0.02 | 0.4 |
| E408 | 30.26 | 65 | 2000 | 3.059 | 3.048 | 3.04 | 3.033 | 3.04 | 0.01 | 0.37 |
| E408 | 30.26 | 85 | 2000 | 2.42 | 2.438 | 2.461 | 2.481 | 2.45 | 0.03 | 1.09 |
| E408 | 44.12 | 25 | 2000 | 57.05 | 56.98 | 56.94 | 56.89 | 56.97 | 0.07 | 0.12 |
| E408 | 44.12 | 45 | 2000 | 22.87 | 22.88 | 22.94 | 23.01 | 22.93 | 0.06 | 0.28 |
| E408 | 44.12 | 65 | 2000 | 13.64 | 13.62 | 13.65 | 13.7 | 13.65 | 0.03 | 0.25 |
| E408 | 44.12 | 85 | 2000 | 9.645 | 9.804 | 9.964 | 10.09 | 9.88 | 0.19 | 1.96 |
| E408 | 52.21 | 25 | 10 | 861 | 855 | 849.2 | 858.9 | 856 | 5.18 | 0.61 |
| E408 | 52.21 | 25 | 100 | 821.9 | 817.6 | 817.5 | 820 | 819.3 | 2.11 | 0.26 |
| E408 | 52.21 | 45 | 1000 | 169.3 | 169.7 | 170.3 | 170.4 | 169.9 | 0.52 | 0.31 |
| E408 | 52.21 | 65 | 2000 | 60.46 | 60.42 | 60.11 | 60.57 | 60.39 | 0.2 | 0.33 |
| E408 | 52.21 | 85 | 2000 | 42.61 | 43.06 | 43.87 | 44.65 | 43.55 | 0.9 | 2.07 |
| E508 | 47.91 | 0 | 10 | 945.5 | 879.5 | 856.7 | 911 | 898.2 | 38.61 | 4.3 |
| E508 | 47.91 | 0 | 100 | 847.6 | 842 | 835.4 | 840 | 841.3 | 5.06 | 0.6 |
| E508 | 47.91 | 25 | 100 | 116.8 | 117.6 | 121.5 | 113.6 | 117.4 | 3.25 | 2.77 |
| E508 | 47.91 | 45 | 100 | 42.51 | 38.51 | 41.07 | 38.17 | 40.06 | 2.08 | 5.2 |

Appendix B2 continued

## Pooled RSD Estimation

The above series of viscosity measurements have different sample means (averages) that range from ~1 to 6000 mPa.s and RSDs between 0 and 5%. To be able to estimate the overall uncertainty in the viscosity measurements obtained in this study using Haake RV 20 viscometer, it was assumed that all the measurements (different means) have the same but unknown variability. The unknown variability is estimated as a pooled relative standard deviation ($RSD_p$ (%)) of the individual RSDs using equation (B.1) (IUPAC 2010):

$$\mathrm{RSD_p} = +/- \sqrt{\frac{\sum_{i=1}^{i=n}(N_i - 1)RSD_i^2}{\sum_{i=1}^{i=n}(N_i - 1)}} \qquad \text{(B.1)}$$

where $N_i$ is the number of replicates (taken as the number of runs) for each sample; n is the number of samples.

From the above data, $RSD_p$ =+/-1.03% , which is a measure of the uncertainty associated with viscosity measurements obtained using Haake RV 20 viscometer in this study.

Appendix B3 Intermediate Input Data for E509 Newtonian Viscosity Models

SC (%) =solids concentration

| SC (%) | Temperature (°C) | Model F predictions (mPa.s) | ANN [8,1] predictions (mPa.s) |
|---|---|---|---|
| 0 | 10* | 1.308 | 1.287 |
| 0 | 30* | 0.7979 | 0.7982 |
| 0 | 50* | 0.5471 | 0.5531 |
| 24.73 | 10* | 6.331 | 6.675 |
| 24.73 | 30* | 3.336 | 3.168 |
| 24.73 | 70* | 1.35 | 1.606 |
| 37.09 | 30* | 11.8 | 8.934 |
| 37.09 | 50* | 6.108 | 4.843 |
| 37.09 | 70* | 3.592 | 3.213 |
| 50.98 | 10* | 654.8 | 414.9 |
| 50.98 | 30* | 144.3 | 106.6 |
| 50.98 | 50* | 47.61 | 35.17 |
| 50.98 | 70* | 20.28 | 17.34 |
| 50.98 | 90* | 10.28 | 9.854 |
| 58.56 | 25* | 2880 | 6099 |
| 58.56 | 55* | 217 | 243.1 |
| 58.56 | 75* | 68.54 | 81.82 |
| 58.56 | 105* | 19.41 | 26.89 |
| 58.56 | 117** | 13.02 | 18.52 |
| 63.21 | 50* | 1586 | 2540 |
| 63.21 | 70* | 305.9 | 372.9 |
| 63.21 | 90* | 91.69 | 122.2 |
| 63.21 | 120** | 24.59 | 36.05 |
| 69.8 | 70* | 3676 | 2877 |
| 69.8 | 90* | 589.9 | 457.4 |
| 69.8 | 110* | 156.5 | 140.3 |
| 69.8 | 120** | 91.6 | 86.95 |
| 10* | 0 | 3.024 | 3.37 |
| 45* | 0 | 251.2 | 78.19 |
| 5* | 20 | 1.257 | 1.228 |
| 15* | 20 | 2.184 | 2.193 |
| 30* | 20 | 7.422 | 6.965 |
| 55* | 20 | 1097 | 1297 |
| 10* | 40 | 1.023 | 1.03 |

Appendix B3 continued

| **SC (%)** | **Temperature ($^oC$)** | **Model F predictions (mPa.s)** | **ANN [8,1] predictions (mPa.s)** |
|---|---|---|---|
| 32* | 40 | 4.816 | 4.149 |
| 42* | 40 | 15.86 | 10.58 |
| 61* | 40 | 1702 | 3165 |
| 2* | 60 | 0.5036 | 0.5159 |
| 16* | 60 | 0.9596 | 1.116 |
| 66* | 60 | 1906 | 2421 |
| 30* | 80 | 1.615 | 1.723 |
| 52* | 80 | 16.55 | 15.83 |
| 60* | 80 | 73.41 | 93.59 |
| 67* | 80 | 493.2 | 505.8 |
| 72** | 80 | 3483 | 1756 |
| 15* | 100 | 0.506 | 0.5386 |
| 30* | 100 | 1.146 | 1.009 |
| 61* | 100 | 36.08 | 51.32 |
| 67* | 100 | 134.5 | 153.3 |
| 72** | 100 | 579.3 | 339.7 |
| 12.5* | 110 | 0.4032 | 0.3946 |
| 25* | 110 | 0.7333 | 0.6195 |
| 60* | 110 | 20.56 | 29.73 |
| 65* | 110 | 51.59 | 69.61 |
| 10* | 115 | 0.3455 | 0.3286 |
| 20* | 115 | 0.5323 | 0.453 |
| 40* | 115 | 1.836 | 1.245 |
| 60* | 115 | 17.29 | 25.26 |
| 71** | 115 | 160.8 | 126.8 |

* intermediate data point
** outside modelling data range

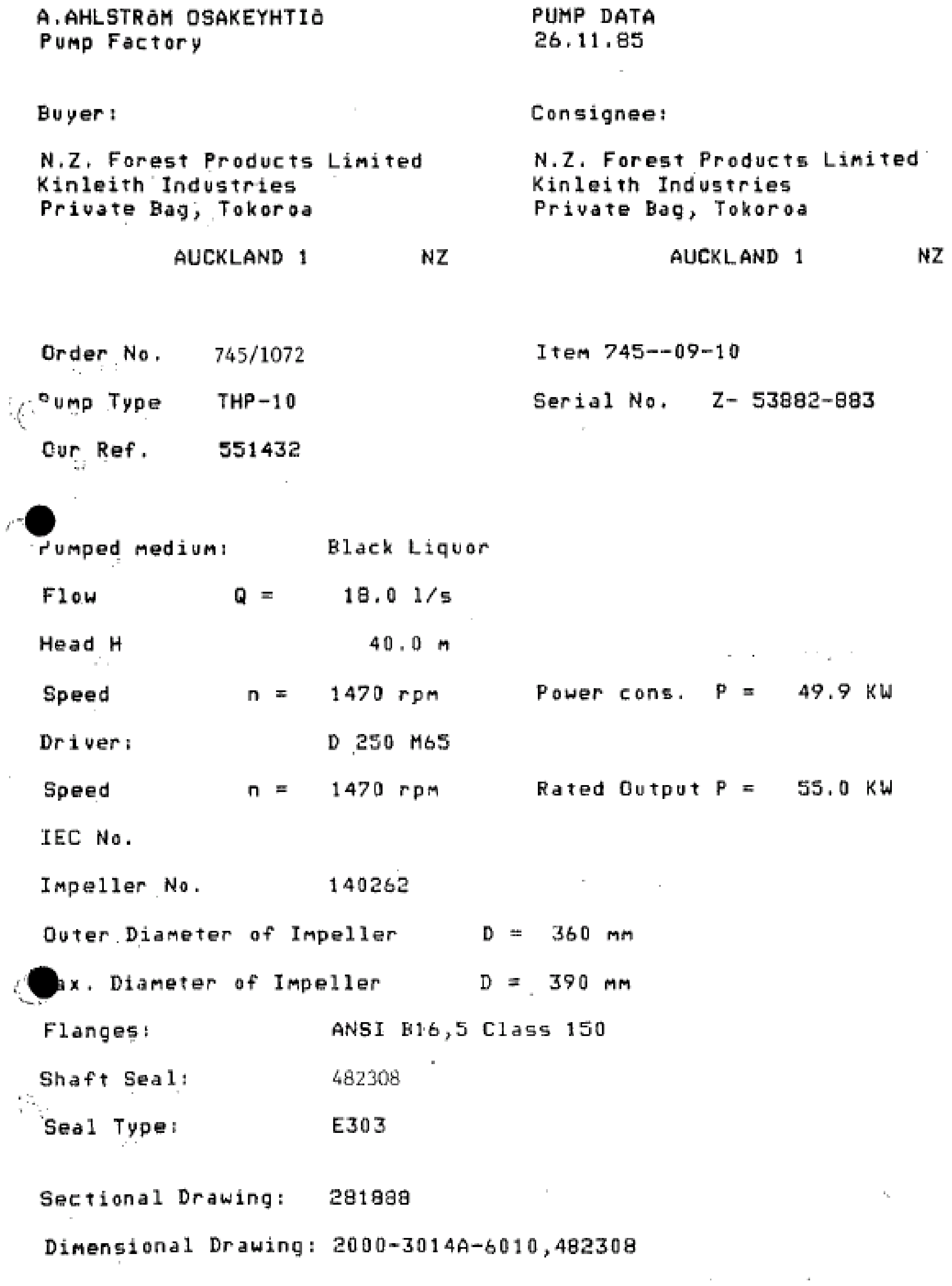
Appendix B4 Intermediate Input Data for E509 Non-Newtonian Viscosity Models
SC=solids concentration

| SC(%) | Temperature ( °C) | Shear rate ($s^{-1}$) | ANN [7 1] predictions (mPa.s) | ANN [11, 1] predictions (mPa.s) | ANN [4,4,1] predictions (mPa.s) |
|---|---|---|---|---|---|
| 0 | 90* | 10 | 0.3155 | 0.3153 | 0.3148 |
| 60* | 60 | 10 | 291.3 | 284 | 352.5 |
| 61* | 40 | 10 | 2257 | 2563 | 281** |
| 66* | 80 | 100 | 396.6 | 469.4 | 544.5 |
| 54* | 40 | 100 | 153.6 | 134.1 | 135.2 |
| 10* | 0 | 1000 | 3.559 | 2.344 | 2.599 |
| 30* | 40 | 1000 | 3.475 | 3.409 | 3.687 |
| 45* | 40 | 1000 | 17.18 | 18.43 | 16.53 |
| 5* | 60 | 1000 | 0.6325 | 0.7531 | 0.6286 |
| 28* | 60 | 1000 | 2.106 | 2.153 | 2.214 |
| 20* | 80 | 1000 | 1.086 | 1.083 | 0.9788 |
| 40* | 80 | 1000 | 3.341 | 3.262 | 3.14 |
| 53* | 100 | 1000 | 10.53 | 10.94 | 11.03 |
| 60* | 100 | 1000 | 42.27 | 41.37 | 40.99 |
| 37.09 | 30* | 1500 | 8.769 | 8.863 | 8.825 |
| 37.09 | 50* | 1500 | 4.68 | 4.705 | 4.695 |
| 58.56 | 95* | 1500 | 37.1 | 36.85 | 37.02 |
| 24.73 | 10* | 2000 | 6.522 | 6.211 | 5.884 |
| 30* | 80 | 2000 | 1.774 | 1.707 | 1.828 |
| 42* | 80 | 2000 | 3.967 | 3.899 | 3.644 |

* intermediate data point
** noticeably off prediction

# APPENDIX C CENTRIFUGAL PUMP-BASED BLACK LIQUOR VISCOSITY MODELLING

## C1 THE NUMBER 5 RECOVERY BOILER FIRING PUMP/MOTOR SPECIFICATIONS (Courtesy, CHHP&P, Kinleith, New Zealand)



A.AHLSTRÖM OSAKEYHTIÖ
Pump Factory

PUMP DATA
26.11.85

Buyer:

N.Z. Forest Products Limited
Kinleith Industries
Private Bag, Tokoroa
AUCKLAND 1 NZ

Consignee:

N.Z. Forest Products Limited
Kinleith Industries
Private Bag, Tokoroa
AUCKLAND 1 NZ

Order No. 745/1072

Item 745--09-10

Pump Type THP-10

Serial No. Z- 53882-883

Our Ref. 551432

Pumped medium: Black Liquor

Flow Q = 18.0 l/s

Head H 40.0 m

Speed n = 1470 rpm

Power cons. P = 49.9 KW

Driver: D 250 M65

Speed n = 1470 rpm

Rated Output P = 55.0 KW

IEC No.

Impeller No. 140262

Outer Diameter of Impeller D = 360 mm

Max. Diameter of Impeller D = 390 mm

Flanges: ANSI B16,5 Class 150

Shaft Seal: 482308

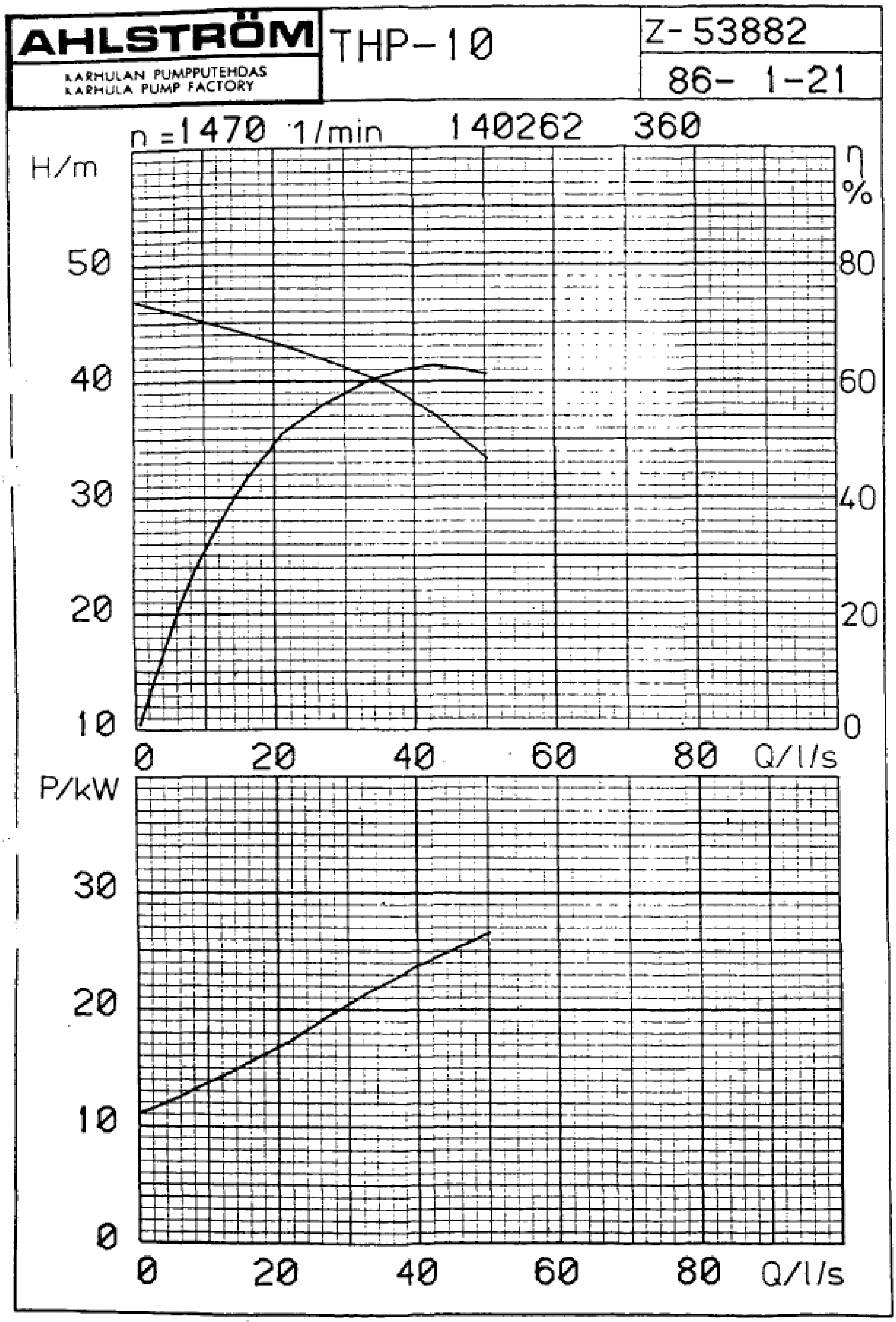
Seal Type: E303

Sectional Drawing: 281888

Dimensional Drawing: 2000-3014A-6010,482308

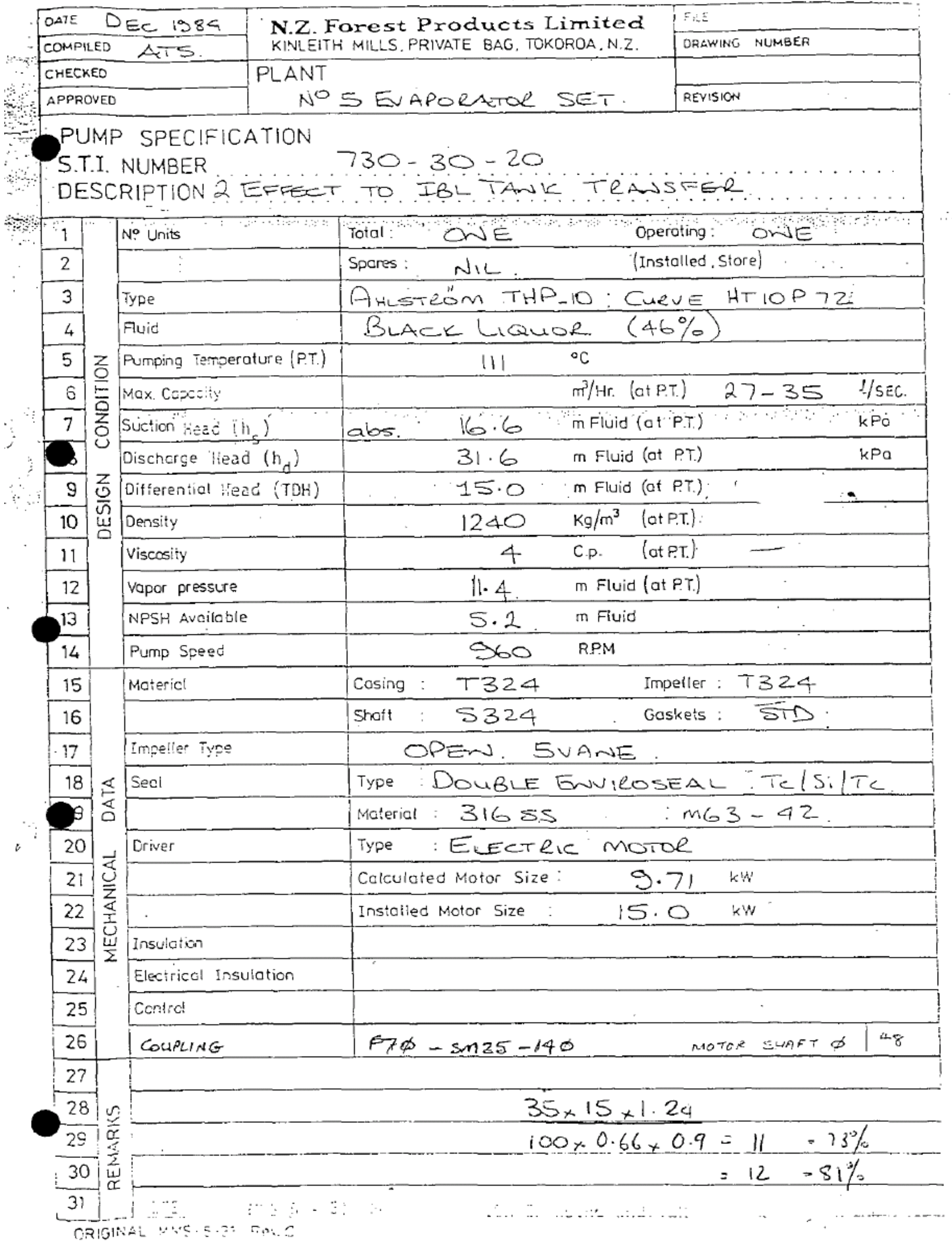
## C2 THE NUMBER 5 RECOVERY BOILER FIRING PUMP PERFORMANCE CURVE

(Courtesy, CHHP&P, Kinleith, New Zealand)
H=head; Q=flow; η=efficiency; n=speed; P=power



# C3 DESIGN DATA FOR LOW VISCOSITY BLACK LIQUOR

(Courtesy, CHHP&P, Kinleith, New Zealand)



| | | |
|---|---|---|
| DATE Dec 1984 | **N.Z. Forest Products Limited**<br>KINLEITH MILLS, PRIVATE BAG, TOKOROA, N.Z. | FILE |
| COMPILED ATS. | | DRAWING NUMBER |
| CHECKED | PLANT | |
| APPROVED | Nº 5 EVAPORATOR SET. | REVISION |

PUMP SPECIFICATION

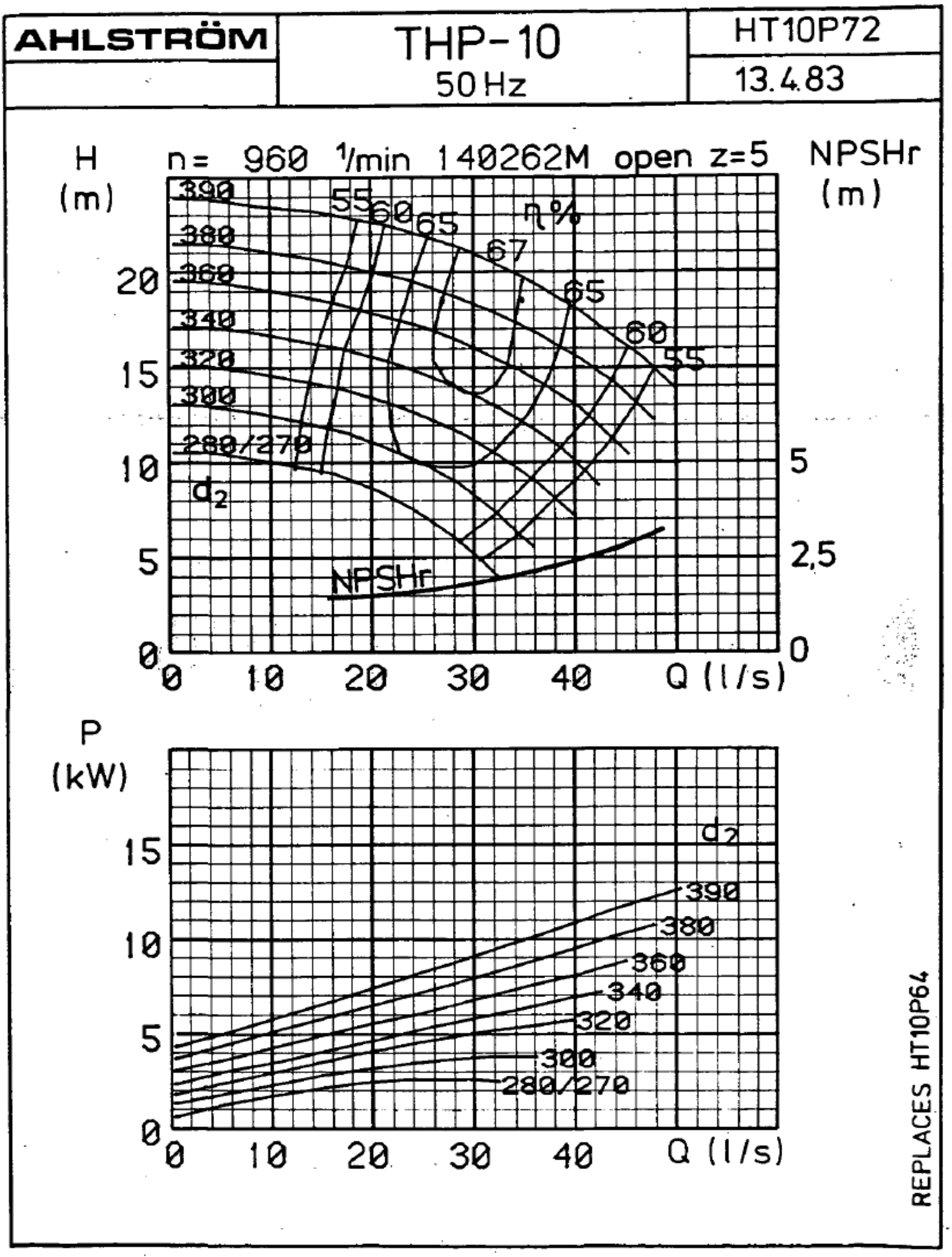
S.T.I. NUMBER 730 - 30 - 20

DESCRIPTION 2 EFFECT TO IBL TANK TRANSFER

| | | | | | |
|---|---|---|---|---|---|
| 1 | DESIGN CONDITION | Nº Units | Total : ONE | Operating : ONE | |
| 2 | | | Spares : NIL. | (Installed, Store) | |
| 3 | | Type | AHLSTRÖM THP-10 : CURVE HT10P72 | | |
| 4 | | Fluid | BLACK LIQUOR (46%) | | |
| 5 | | Pumping Temperature (P.T.) | 111 | °C | |
| 6 | | Max. Capacity | | $m^3$/Hr. (at P.T.) | 27 – 35 l/SEC. |
| 7 | | Suction Head ($h_s$) | abs. 16·6 | m Fluid (at P.T.) | kPa |
| 8 | | Discharge Head ($h_d$) | 31·6 | m Fluid (at P.T.) | kPa |
| 9 | | Differential Head (TDH) | 15·0 | m Fluid (at P.T.) | |
| 10 | | Density | 1240 | Kg/$m^3$ (at P.T.) | |
| 11 | | Viscosity | 4 | C.p. (at P.T.) | — |
| 12 | | Vapor pressure | 11·4 | m Fluid (at P.T.) | |
| 13 | | NPSH Available | 5·2 | m Fluid | |
| 14 | | Pump Speed | 960 | RPM | |
| 15 | MECHANICAL DATA | Material | Casing : T324 | Impeller : T324 | |
| 16 | | | Shaft : S324 | Gaskets : STD | |
| 17 | | Impeller Type | OPEN. 5 VANE. | | |
| 18 | | Seal | Type : DOUBLE ENVIROSEAL | : TC/Si/TC | |
| 9 | | | Material : 316 SS | : M63 – 42. | |
| 20 | | Driver | Type : ELECTRIC MOTOR | | |
| 21 | | | Calculated Motor Size : 9·71 | kW | |
| 22 | | | Installed Motor Size : 15·0 | kW | |
| 23 | | Insulation | | | |
| 24 | | Electrical Insulation | | | |
| 25 | | Control | | | |
| 26 | | COUPLING | F70 – SM25 – 140 | MOTOR SHAFT Ø | 48 |
| 27 | REMARKS | | | | |
| 28 | | | 35 × 15 × 1·24 | | |
| 29 | | | 100 × 0·66 × 0·9 = 11 = 73% | | |
| 30 | | | = 12 = 81% | | |
| 31 | | [illegible] | | | |

ORIGINAL MMS-5-31 Rev.C

C4 AHLSTROM'S THP-10 PUMP CURVE
(Courtesy, CHHP&P, Kinleith, New Zealand)
H=head; Q=flow; η=efficiency; n=speed; P=power



## C5 COMMENT ON THE HYDRAULIC INSTITUTE VISCOSITY ESTIMATES FOR THE NUMBER 5 RECOVERY BOILER FIRING PUMP

The performance data for the number 5 recovery boiler firing pump when pumping liquors more viscous than water were obtained using the Hydraulic Institute viscosity correction method based on the pump curve in Appendix C4. These performance data, coupled with affinity laws and incorporation of pump ageing factor, were used to develop all the relevant models in Chapter 6. Based on the pump curve in Appendix C2, the estimated performance data were adjusted and used to build the refined model that was installed as a viscosity sensor whose performance was evaluated in Chapter 7.

When these data were being estimated and adjusted, Appendix C4 curve had been initially assumed to represent the performance of the pump while pumping low viscosity (4 cP) liquor whose design data are presented in Appendix C3. However, it was taken as water performance since it was assumed that the pump performances on water and 4 cP liquor will be approximately the same. The design statement by Ayers and Clarihew (Ayers and Clarihew 1988) is, “Ahlstrom-supplied graphs gave 70 cP at 65% D.S., 110 $^{o}$C”. The stated conditions are the approximate pumping conditions of the heavy black liquor at the number 5 recovery boiler. It was therefore simply assumed that the pump curve in Appendix C2 is associated with heavy black liquor (with design data in Appendix C1) being pumped at 70 cP. In addition, the pump curve in C2 has a maximum efficiency around 63% while the one in C4 has a maximum efficiency around 68%, thereby leading to an erroneous assumption that the deterioration in the pump efficiency is because it is being used to pump heavy black liquor at 70 cP.

Towards the end of this study and thesis write-up, a closer look on the available pump curves by the author shows that both pump curves in Appendices C2 and C4 actually represent the performances of the THP-10 pump while being used to pump water at the indicated speeds. The design data (see Appendix C1) for heavy black liquor (since the firing pumps are used with heavy black liquor) indicates that the power consumed by the motor was 49.9 kW while the power curve in Appendix C2 indicates significantly lower values at all conditions. This implies that while the sizing of the motor must have been done based on high liquor viscosity at the recovery boiler, the given pump curve C2 simply describes the pump performance while pumping water. If Appendices C2 and C4 are essentially water performance curves for the same pump model, why is there a significant difference in the observed maximum efficiencies? It seems the pump curve in Appendix C4 is the manufacturer's generic pump curve for THP-10 pump model that was used for the design and selection of the required pump and motor based on their pumping requirements as indicated in Appendices C1 and C3. The manufacturer's generic curve was dated 1983; this gives a strong indication that its sole purpose was for pump design and motor sizing before the actual pump was fabricated and tested. Note that number 5 recovery boiler was commissioned in 1985, as stated in section 7.2.1 and the pump curve for the firing pump having a reduced maximum efficiency in Appendix C2 was dated 1986. This indicates strongly that the pump curve in Appendix C2 was specific to the installed pump while the curve in Appendix C4 is a generic manufacturer's curve for the same pump model.

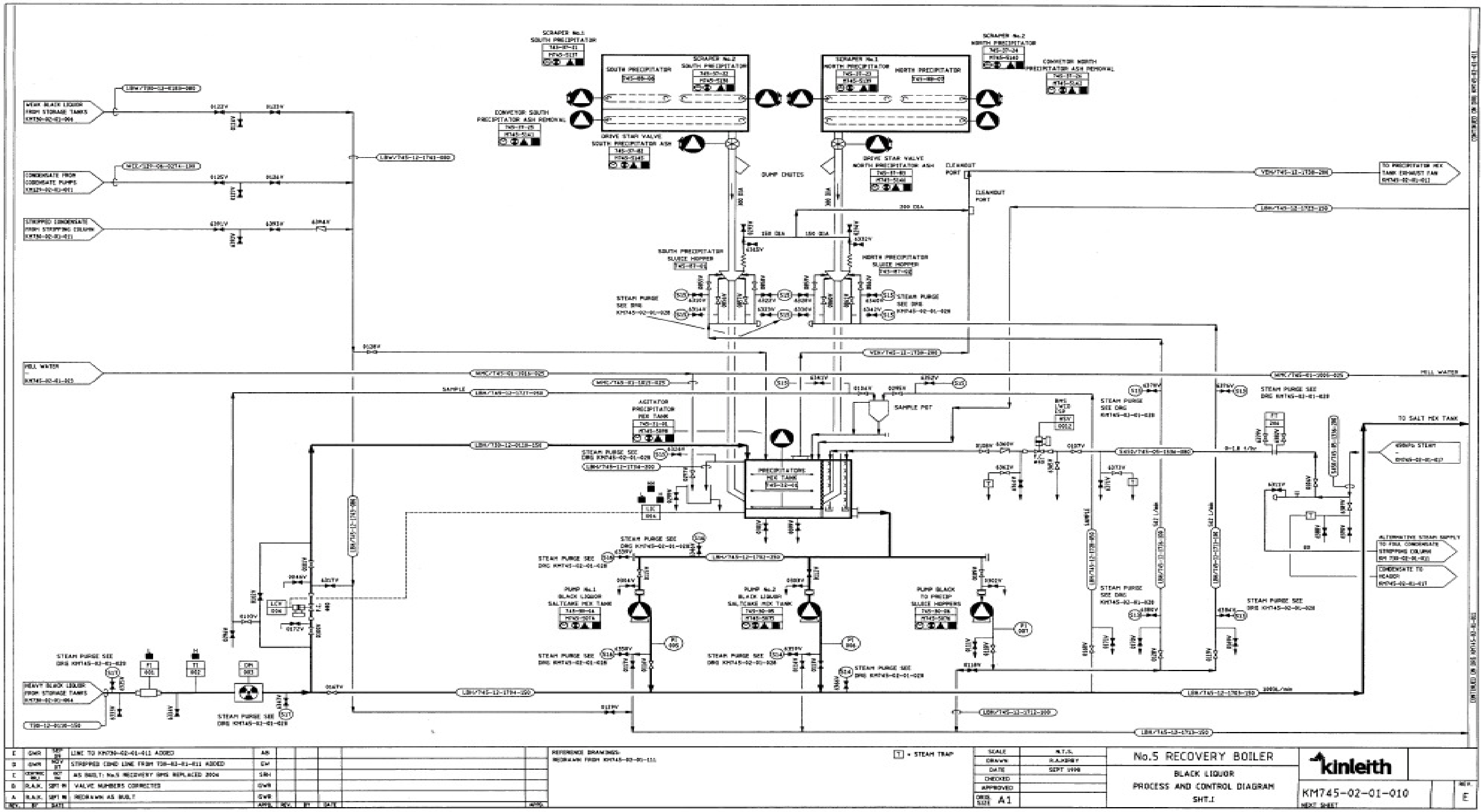
Interestingly, the wrong assumption that the generic pump curve in Appendix C4 was for low viscous (4 cP) liquor but was taken to be directly applicable to water turned out to be true. This is because it is truly a generic curve based on the performance of the pump while pumping water, and has been used to design and select the pump and motor at the number 2 effect to intermediate black liquor tank transfer at the number 5 evaporator (see Appendix C3). Despite that, the pump curve in Appendix C4 describes the pump performance on water on generic basis, a more appropriate water-based curve that ought to have been used with Hydraulic Institute viscosity correction method is the specific pump curve in Appendix C2, which was wrongly assumed as 70 cP curve. Although data adjustment was done based on the wrongly assumed 70 cP curve, with the exception of the performance data at 4 cP that were separately estimated, the adjustment was done on all the other data uniformly. Despite the use of the incorrect pump curves, the resulting viscosity sensor was able to give consistent viscosity estimates as shown in the preceding analyses. This is probably because the errors introduced to the data were uniformly propagated across all data points.

While the flaws reported above are not desirable, they have however shown the strength of the data gathering and modelling strategy adopted in this study. First, it shows that during the actual experimental data collection, which sometimes could be economically prohibitive and time-consuming, instrument's fault and/or wrong calibrations could lead to large amount of inaccurate experimental data being collected. In a worse situation, the errors may not be uniformly propagated, as in the case where the drifts in the instruments' settings may be substantial and non-uniform. In that case, it would be very expensive and time-consuming to perform the actual experiments all over again. Nevertheless, this is not the case in this study where the data collection is purely by estimation. All that would be required to obtain data that are more accurate is computation time. Secondly, for process control applications, consistency is more important than accuracy. Since the errors in the estimated and adjusted data appear to be uniformly propagated and the estimates obtained from the soft sensor are fairly consistent, there may not be any need to do any modification on the installed model unless accurate viscosity values would be required for other purposes. Even if accurate predictions are required, it has been demonstrated that the sensor‘s performance trajectory can be shifted by a single parameter PA (pump age).

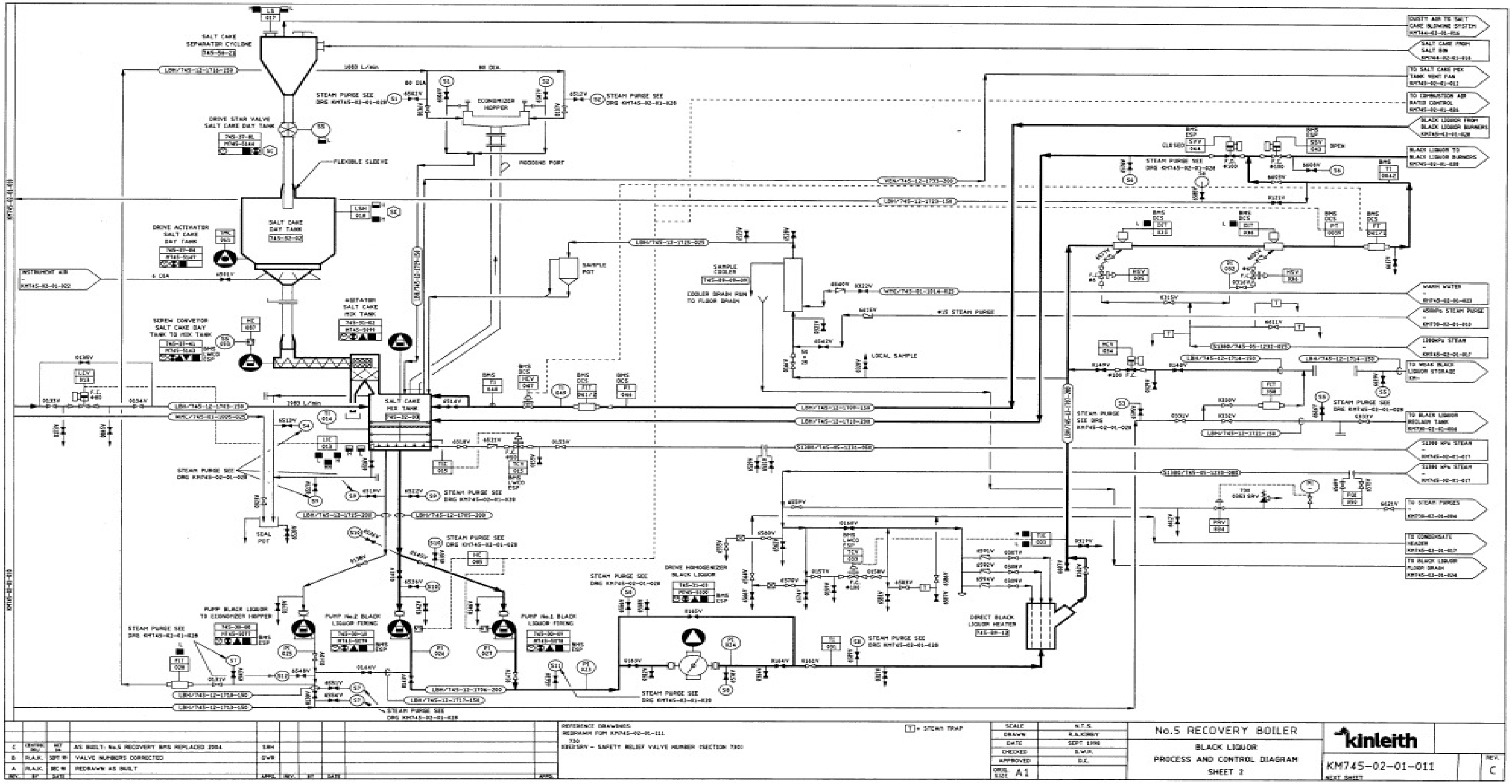
Nonetheless, a new model should be developed using Hydraulic Institute viscosity correction procedures and most appropriate pump curve. The model can then be refined using minimal experimental data to obtain the best PA.

# APPENDIX D THE NUMBER 5 RECOVERY BOILER BLACK LIQUOR PROCESS AND CONTROL DIAGRAM

(Courtesy, CHHP&P, Kinleith, New Zealand)



Appendix D continued



## APPENDIX E PUBLICATIONS FROM THIS STUDY

1. Alabi, S.B., Williamson, C.J. and Lee, J. (2010). Viscosity Models for New Zealand Black Liquor at Low Solids Concentrations. *Asia-Pacific Journal of Chemical Engineering*, **5** (4): 619-625 (earlier version was presented in Chemeca 2009, Perth, Australia).
   URL: http://onlinelibrary.wiley.com/doi/10.1002/apj.444/abstract

2. Alabi, S.B., Williamson, C.J. and Lee, J. (2010). A Novel Quartic Model for Predicting Black Liquor Viscosity using Centrifugal Pump Parameters. Submitted to *Chemical Product and Process Modeling*.