Evaporation of Vinasse

Pilot Plant Investigation and Preliminary Process Design

Master's Thesis within the Innovative and Sustainable Chemical Engineering programme

ERIK LARSSON

TOMMY TENGBERG

Department of Energy and Environment
Division of Heat and Power Technology
CHALMERS UNIVERSITY OF TECHNOLOGY
Göteborg, Sweden 2014

MASTER'S THESIS

Evaporation of Vinasse

Pilot Plant Investigation and Preliminary Process Design

Master's Thesis within the *Innovative and Sustainable Chemical Engineering* programme

ERIK LARSSON

TOMMY TENGBERG

SUPERVISORS:

Olle Wennberg (Valmet Power AB)

Malin Larsson (Valmet Power AB)

EXAMINER

Mathias Gourdon

Department of Energy and Environment
Division of Heat and Power Technology
CHALMERS UNIVERSITY OF TECHNOLOGY

Göteborg, Sweden 2014

Evaporation of Vinasse
Pilot Plant Investigation and Preliminary Process Design
Master's Thesis within the *Innovative and Sustainable Chemical Engineering* programme
ERIK LARSSON
TOMMY TENGBERG

Department of Energy and Environment
Division of Heat and Power Technology
Chalmers University of Technology
SE-412 96 Göteborg
Sweden
Telephone: + 46 (0)31-772 1000

Cover: Picture from the research evaporator displaying vinasse flowing on the evaporator tube, at a dry solid content of 70 %.

Chalmers Reproservice
Göteborg, Sweden 2014

Evaporation of Vinasse
Pilot Plant Investigation and Preliminary Process Design
Master's Thesis in the Innovative and Sustainable Chemical Engineering programme

ERIK LARSSON
TOMMY TENGBERG
Department of Energy and Environment
Division of Heat and Power Technology
Chalmers University of Technology

ABSTRACT

The large dependency of fossil fuel have made alternative fuel e.g. ethanol increasingly popular. However, very little research and few publications were found on the after-treatment of the effluent, named vinasse, from the sugar-cane based ethanol production. The vinasse is produced in large quantities, because of the high volume ratio 1:10-15 of ethanol to vinasse and has been labelled an increasing environmental problem in South America.

In a new proposed treatment process for vinasse, evaporation is used to concentrate the vinasse to be able to combust it in a boiler. In this thesis an experimental investigation was conducted on a pilot plant on the evaporation of vinasse. It was found possible to evaporate vinasse to a high dry solid content of at least 70 %. A critical region of particle accumulation and fouling tendencies were established. The most important physical parameters, dry solid content, viscosity, boiling point elevation and the heat transfer coefficient, were closely monitored and assessed in the experiments. For some of the properties, correlations were established as a function of dry solid content and temperature. The heat transfer was tested on a general model used in falling film evaporation, which was proven to not be valid for vinasse. However, a correlation for the heat transfer was developed.

Since vinasse's chemical composition resembles black liquor, these two were compared in this work and it was found that vinasse has lower viscosity and boiling point elevation at the same dry solids content. Thus, the results of the physical properties show that vinasse has better heat transfer and heat economy than black liquor.

Based on the results from the experiments, a preliminary process design of the evaporation plant was established.

Key words: Evaporation, Vinasse, viscosity, boiling point elevation, heat transfer, correlations, Process Design

Indunstning av vinass
Undersökning i pilotanläggning och preliminär processdesign
Examensarbete inom masterprogrammet *Innovative and Sustainable Chemical Engineering*

ERIK LARSSON
TOMMY TENGBERG
Institutionen för Energi och Miljö
Avdelningen för Värmeteknik och maskinlära
Chalmers tekniska högskola

SAMMANFATTNING

Det stora beroendet av fossila bränslen har gjort alternativa bränslen som t.ex. etanol allt mer populära. Det finns emellertid väldigt lite forskning och få publikationer om olika efterbehandlingssätt av restprodukten vinass från sockerrörsbaserad etanolproduktion. Vinass produceras i stora mängder, på grund av det höga volymsförhållandet 1:10-15 etanol till vinass, och anses vara ett växande miljöproblem i Sydamerika.

I en ny efterbehandlingprocess som föreslagits för vinass, används indunstning för att öka torrhalten så att den går att förbränna i en panna. I detta examensarbete har en experimentell undersökning av vinassindunstning i en pilotanläggning genomförts. Undersökningarna visade att det är praktiskt möjligt att indunsta vinass till en hög torrhalt, minst 70 %. En kritisk region för partikelbildning och inkrustering upptäcktes. De viktigaste fysikaliska egenskaper, torrhalt, viskositet kokpunktsförhöjning och värmeöverföring övervakades noggrant och utvärderades under experimenten. För vissa egenskaper fastställdes korrelationer som funktion av torrhalt och temperatur. Värmeöverföringen testades mot en generell modell som används i fallfilmsindunstning, den visade sig emellertid vara otillförlitlig för vinass. En korrelation för värmeöverföringen baserat på mätdata fastställdes.

Vinass kemiska sammansättning liknar den för svartlut. Därför har dessa två produkter jämförts i detta examensarbete och det visade sig att vinass, vid samma torrhalt, har lägre viskositet och kokpunktsförhöjning. Detta medför att vinass har bättre värmeöverföring och värmeekonomi än svartlut.

Baserat på resultaten från experimenten har en preliminär processdesign av indunstningsanläggningen tagits fram.

Nyckelord: indunstning, vinass, viskositet, kokpunktsförhöjning, värmeöverföring, processdesign

Contents

Preface

In this project an experimental study has been carried out on vinasse, which in this case is a residue from sugar-cane based ethanol production in South America. The project was carried out from September 2013 to January 2014. The experiments were conducted on the research evaporated, situated at Chalmers University of Technology, Gothenburg, Sweden. The project was collaboration between the Department of Energy and Environment at the Division of Heat and Power and Valmet Power. The main financer was Valmet Power as a part of their research on new market prospects and applications.

The project has been carried out by Erik Larsson and Tommy Tengberg with the supervision of Olle Wennberg, Malin Larsson and Martin Wimby at Valmet Power. They have been a tremendous help in this project and has guided us with their industrial knowledge. In this project we received invaluable help from our examiner, Assistant Professor Mathias Gourdon. We would also like to sincerely thank Erik Karlsson for aiding us in the operation of the research evaporator.

Finally, we would like to thank the co-workers at Valmet Power and the Division of Heat and Power at Chalmers University of Technology for making us feel welcomed and for all the support and good laughs.

Gothenburg February 2014

Erik Larsson & Tommy Tengberg

Notations

Roman letters

A	Heat transfer area	[m^2]
b	Molality	[mol/kg]
c_p	Heat capacity	[J/K]
d	Tube diameter	[m]
ds	Dry solid content	[%]
g	Gravitational force	[m/s^2]
H_v	Heat of vaporization	[J/kg]
h	Heat transfer coefficient	[W/m^{2}K]
k	Thermal conductivity	[W/mK]
l	Tube length	[m]
$\dot{m}$	Mass flow	[kg/s]
M	Molecular weight	[g/mol]
N	Number of tubes	[-]
Q	Transferred heat	[W]
q	Heat flux	[W/m^2]
R	Ideal gas constant	[atm m^3/kmole/K]
RI	Refractive index	[-]
S	Dry solid content	[%]
T	Temperature	[K]
U	Overall heat transfer coefficient	[W/m^{2}K]
V	Velocity	[m/s]
$\dot{V}$	Volume flow	[m^3/s]
z	Distance from the surface normal to the direction of flow	[m]

Greek letters

Γ	Circulating mass flow rate per unit width	[kg/m·s]
δ	Thickness	[m]
μ	Dynamic viscosity	[Pa·s]
ν	Kinematic viscosity	[m^2/s]
ρ	Density	[kg/m^3]
τ	Shear stress	[Pa]

Dimensionless numbers

Re	Reynold number	[-]
Nu	Nusselts number	[-]
Pr	Prantl number	[-]

Subscript

water	Water
o	Outside
t	Tube(s)
lm	Logarithmic mean
w	Wall
steam	Steam
vinasse	Vinasse
m	Mean
i	Inside
lam	Laminar
turb	Turbulent
BPE	Boiling Point Elevation

bw	Boiling point of pure water
loc	Local
evap	Evaporation
cond	Condensation
loss	Loss
solid	Solid
100	At 100°C

1 Introduction

The world has a steadily increasing demand for energy as more and more countries are becoming developed. The reserves of fossil fuels are limited and only found in certain areas in the world, some of them politically unstable, with increasing prices and uncertain energy supply as result. Fossil fuels also emit carbon dioxide when burnt thus contributing to global warming. So other more sustainable and secure sources of energy are wanted.

In South America the sugar industry has been developed for a long time. When oil prices constantly were increasing and the sugar market was stagnating, the production of sugar shifted its focus towards ethanol production. This more sustainable fuel has played a great role for the economy in many countries in South America (Braunbeck & Cortez, 2000). Like in every process there are by-products. In ethanol production from sugar canes, the main residue is vinasse. Other common denominations of similar by-products, based on different raw materials, are stillage and distillery pot ale. Vinasse is produced in large quantities, normally a ratio of 10-15 l vinasse per produced litre of ethanol, depending on soil quality and distillery process used for producing ethanol (Braunbeck & Cortez, 2000). The characteristics of vinasse is that is has very high water content and it has been used as a moderate fertilizer for soils close to the sugar and ethanol production sites. However, in some regions the spreading of vinasse has caused quite severe eutrophication problems due to its high nutrient content. Another possibly big environmental problem is when vinasse is disposed close to the production site in large quantities; hence the soil struggles to digest it because of the high biological oxygen demand (BOD) and chemical oxygen demand (COD) (Christofoletti, et al., 2013).

One way to reduce the environmental impact of this waste product is to evaporate it, followed by combustion of the residue, in a recovery boiler. The purpose of this operation would be to recover the high content of potassium in vinasse and to produce energy. The potassium is finally reacted with sulphate to form potassium sulphate which can be used and sold as a fertilizer. Similar processing is found in the pulp and paper industry where black liquor is evaporated to recover process chemicals. Evaporation is a well-known separation technology and due to the similar characteristics and properties of vinasse and black liquor, the same separation concept is of high interest.

These are the main reasons why Valmet Power AB in Gothenburg (former Metso Power) is interested in developing the technology and applying it on vinasse. Valmet is a global supplier of technology and services to customers in the process industries, including pulp and paper, fibre, board, tissue and biotechnology. The Gothenburg office has a division specialized in evaporation (but also Lignoboost ® and ash leaching) and is supplying evaporation processes around the world, mainly to paper and pulp industry.

1.1 Objective

This study aimed to investigate the possibility to evaporate vinasse to a dry solid content of 70-75 % in a falling film evaporator. The main objective was to evaluate different operating parameters and how they affected the process and to see what problems that might appear, such as fouling and foaming. During the evaporation, fouling is an anticipated adverse effect, which in the project was closely monitored and measured. The main detrimental effect of fouling is that the heat transfer decreases and thus the efficiency of the evaporation.

The amount of heat transferred is the most important aspect in any heat exchanger, thus also in an evaporation process. It is mainly affected by flow, temperature and viscosity of the fluid and as mentioned before how much incrustation is formed. The heat transfer will be one of the most important parameter to analyse and determine as a foundation for the design and dimensioning of the evaporation plant. Other important objectives are to evaluate the behaviour and property change of vinasse, in a falling film evaporator. The main property changes to observe are viscosity, density and boiling point elevation, BPE (also known as boiling point rise, BPR). The first two properties are temperature dependent and generally decrease with increasing temperature. However, since vinasse is a homogenous, binary solution the dry content increases during evaporation, thus both density and viscosity increases. The goal of this Master's thesis is to evaluate the possibility to evaporate vinasse to high solids content, for it to be economically feasible for combustion, without any major difficulties. If proven successful, it will give guidelines to how the process should be monitored and run and a possible process design will be proposed.

1.2 Method

This master's thesis was based on experiments on vinasse in a single stage research evaporator at Chalmers University of Technology. The first part of the project included a literature study to provide an understanding about the raw material, vinasse, and how it is produced, including the background of ethanol production from sugar canes, based in South America. The literature review also scoped studies on evaporation, to increase the understanding of both theoretical and practical fundamentals involving evaporation processes. Since vinasse has similar composition to black liquor the chemical recovery of black liquor in pulp and paper industry was also studied to a small extent. After that, the first set of experiments was planned to be conducted at the research evaporation plant.

The research evaporation plant is a single stage evaporator originally built by Valmet Power AB for evaporation of black liquor. The vinasse will be concentrated in intervals to increase the solid content, measuring viscosity, density, boiling point elevation and the heat transfer coefficient. The measurements are based on the on-line measurements in the research plant but also extraction of samples for measurements of dry solid content with the scan-method. Some of the extracted samples will also be sent out for more rigorous chemical analysis. A process design will be presented, with the help of a calculation tool used at Valmet Power for calculations and dimensioning of evaporation plants.

1.3 Limitations

This thesis will only focus on the evaporation of vinasse. The sugar and ethanol production are not included, neither is the combustion of the evaporated vinasse in the recovery boiler nor is the crystallization of potassium. Also, this thesis will only investigate the behaviour of vinasse, from sugar cane production, with initial dry contents ranging from about 6.5 – 9.0 % which should be concentrated to about 70 %

ds (dry solid content), based on presumed industrial working conditions for a full-scale plant. Since vinasse origins from seasonal harvesting from different locations with different soil quality, process techniques and equipment, the vinasse can possess a large variety in initial concentration of dry solid contents and in chemical composition. Therefore, all experimental results and conclusions will be based on the vinasse processed within this project, with reservations for possible differences in initial concentration and composition.

Furthermore, all experimental results will be based on the experiments carried out in the pilot evaporation plant at Chalmers, including the dry solid content analysis. However, some samples have been sent out for chemical composition analysis.

2 Background

2.1 Sugar / Ethanol Industry in South America

The sugar cane was introduced in Brazil in the early sixteenth century by the Portuguese and soon spread to different countries in South America and played a great role in the economy for the whole continent. However, the market demand of the sugar has varied over the decades and caused heavy instabilities in the income of the product. Because of this, further processing of sugar cane was investigated in the 1930s but not until early 1970s when Brazil introduced PROALCOOL (Brazilian Alcohol Program) the sugar cane was used to also produce ethanol for fuel as a complement or complete substitute to the oil based fuel (gasoline and diesel) (Braunbeck & Cortez, 2000). In 2012 South America produced 22 million cubic meters of ethanol which corresponds to 27 % of the world market, where Brazil is the world's biggest sugar cane based ethanol producer with 21 million cubic meters (Renewable Fuel Association, 2013).

The big production of ethanol in South America also contributes to a large amount of residue vinasse. The amount of vinasse produced per litre ethanol is between 10-15 litres depending on the soil quality and the process equipment used when producing ethanol (Christofoletti, et al., 2013). Because of the large volume produced and dumped at different sites and the very high pollution potential it possesses (because of its high nutrient content), makes the vinasse pollution an urgent environmental problem.

There are several possible alternatives to process and take care of the residue vinasse e.g. fertirrigation, biodigestion or concentration by evaporation illustrated in Figure 2-1.

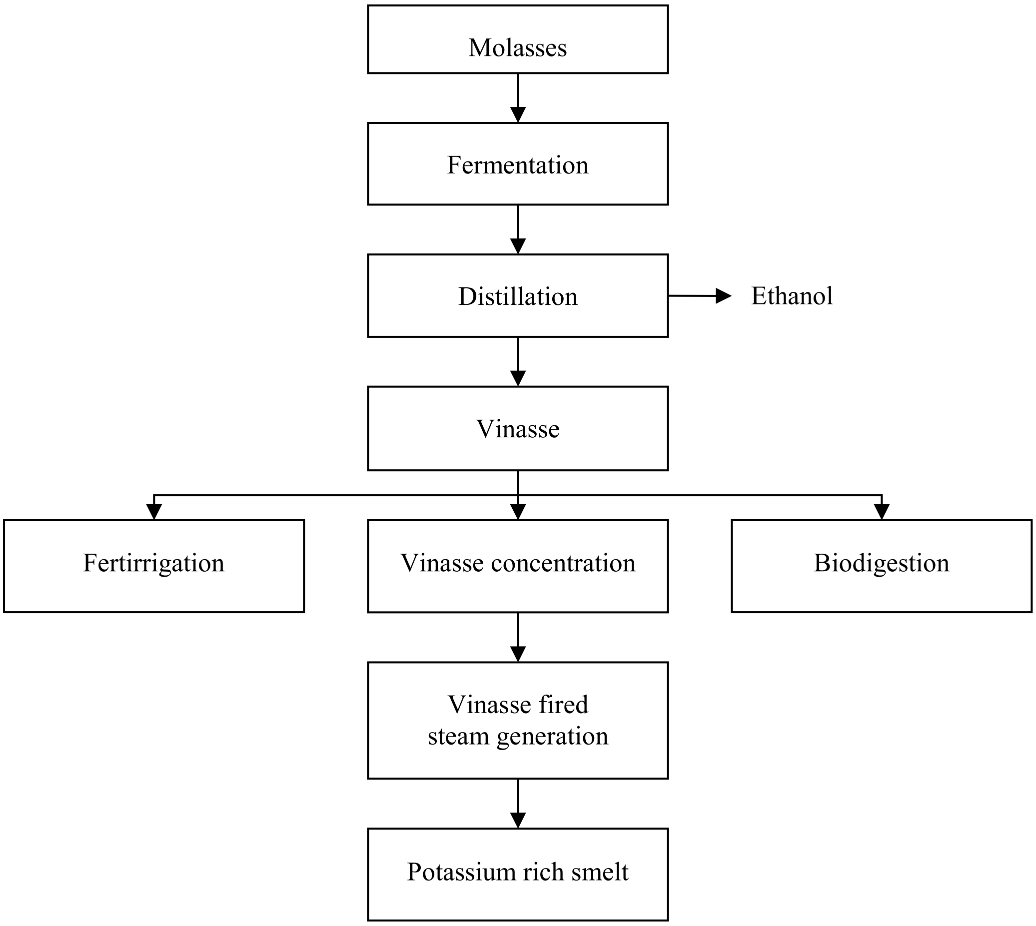

Figure 2-1. General description of how vinasse can be treated and processed

The most commonly used method is fertirrigation, which is basically applying it to agricultural land to utilize vinasse's potential as a moderate fertilizer based on the rich content of potassium and other nutrients. However, this disposal requires good knowledge about the soil composition and nutrient requirement for it to be a sustainable disposal technique. There is also transportation costs connected to the disposal which can be very expensive if the vinasse is un-concentrated, since vinasse often consists of more than 90 % water. The transportation and dumping of vinasse is probably the biggest environmental problems connected to the ethanol production. Because of the big production of vinasse, transportation to different dump sites far from the ethanol plant is very expensive; it is therefore often dumped at the same site close to the ethanol plant. That type of repetitive disposal creates a big surplus of nutrients, inducing eutrophication.

Another major environmental issue is if and when vinasse reaches watercourses and ground water, heavily contaminating them. All this is connected to the restricted knowledge of the long-term effect of the disposal in nature.

Biodigestion treatment of vinasse is another viable option and is adapted in few ethanol distilleries in South America. The basis of this is feeding the vinasse to a bioreactor digesting it during 24 hours, producing biogas (methane) which can be reused in the ethanol process and/or to fuel vehicles. This treatment has the advantages that it creates energy and concentrates the vinasse to some extent, reducing the BOD. However, the technology is expensive and has low conversion and most importantly the disposal problem of the effluent vinasse remains. Despite the increased concentration of the dry solid content, all the nutrients are still present.

Concentration by evaporation as an after treatment will be a very sustainable option both in terms of less environmental impact but also in an economic aspect, compared to fertirrigation, where transportation cost of vinasse is much higher than it will be for concentration by evaporation. This cost decreases because of the much smaller volume. A profit from fertilizer sales is projected in the long run. The proposed design and the basis of this operation is to evaporate the water in vinasse to increase the dry solid content to about 70 % in a multistage evaporator. The concentrated vinasse is then fed to a boiler where it is combusted, producing steam and dissolved inorganic components. The characteristics of the boiler are similar to a recovery boiler in the paper and pulp industry. The purpose is to combust the concentrated vinasse. The inorganic components will form a smelt which is dissolved in water and removed from the process. From the combusted vinasse, the potassium rich smelt is recovered and fed to a crystallizer where the potassium is crystallized with sulphuric acid, producing potassium sulphate (K_2SO_4), which is one of the main nutrients used in modern inorganic fertilizers. Figure 2-2 below, illustrates the general proposed concept of the process.

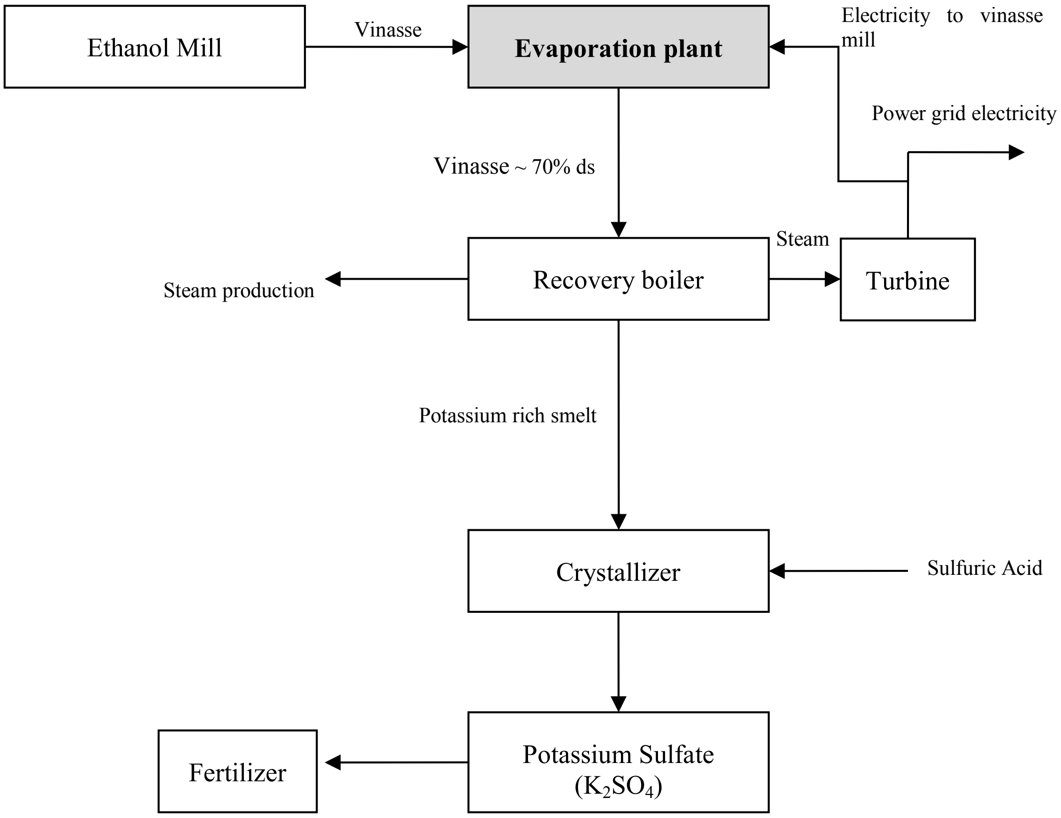

Figure 2-2. General description of the concept of concentration by evaporation, producing potassium fertilizer.

2.1.1 Vinasse – Chemical Composition

Vinasse is as previously mentioned a residue from ethanol production and contains more than 90 % water. The remainder ~10 % is the dry matter and contains dead yeast, non-fermented carbohydrates, unconverted sugars and a variety of inorganic compounds (Braunbeck & Cortez, 2000). It also has a low pH 4-5, which possibly can contribute to acidification of watercourses and ground water. The chemical composition of vinasse varies depending on the harvest method, process equipment used in ethanol production and soil quality, among others.

A chemical analysis of the most prominent nutrients in vinasse is found in the Table 2-1 below.

Table 2-1. Chemical composition of sugarcane vinasse from (Christofoletti, et al., 2013).

Compound	Unit	Value
pH	-	3.9
BOD	mg/L	5046
Potassium	mg/L	2056
Sodium	mg/L	50.2
Sulfate	mg/L	710
Calcium	mg/L	719
Magnesium	mg/L	237
Phosphorus	mg/L	190

As seen from the chemical analysis in Table 2-1, potassium constitutes of a large share of the inorganic material and is one of the key components in fertilizer production.

2.2 Chemical Recovery in Paper Pulp Industry

In the pulp and paper industry the chemical recovery has been used for a long time. Black liquor and vinasse has, as previous mentioned, similarities in composition and the basic principles for recovering chemicals from black liquor can be adopted and applied on vinasse.

The first step in the recovery of black liquor is to increase the concentration of dry solids in the feed flow and this is done by evaporation. There are different kinds of evaporators; one of the most common is the falling film evaporator. Usually, the evaporation is carried out in several different steps or effects mounted in cascade with different temperatures and pressures where the produced vapour in one effect is used as the heat source in the subsequent unit (principle further described in section 3.1.1). After the evaporation the dry solid content is high enough to combust it in the recovery boiler. The valuable cooking chemicals are collected at the bottom of the boiler as smelt, green liquor, and after continued treatment, reused in the process. The boiler also produces steam that is used in the evaporation plant and in other processes. (Theliander, 2008) (Kassberg, 1994)

2.2.1 Comparison of Chemical Composition of Vinasse and Black Liquor

The chemical composition of vinasse is similar to black liquor. In the Table 2-2 below, some of the most important constituents are displayed. For the full chemical analysis see appendix II.

Table 2-2. Comparison of the chemical analysis of vinasse and black liquor (Välimäki, Erkki;, 2012).

	Unit	**Vinasse**	**Kraft**
Dry substance	%	8.44	19.7
In dry matter			
ash	g/kg	329.4	475.6
carbon	g/kg	318	348.8
hydrogen	g/kg	49	33.7
sodium	g/kg	1	200
potassium	g/kg	135	1.1
zinc	g/kg	0.26	0.0023
iron	g/kg	0.67	0.0078
magnesium	g/kg	6.1	0.11
silicon	g/kg	3.8	0.013
phosphorus	g/kg	1.6	0.051
calcium . tot	g/kg	26	0.48
calcium . soluble	g/kg	25	0.43
sulfur	g/kg	31	52
chlorine	g/kg	16	0.44
methanol	g/kg	n.d.	1.2
ethanol	g/kg	54	0.22

n.d = Not detected

The main differences in the inorganic composition between black liquor and vinasse are the calcium and potassium content, which is substantially higher in vinasse, whilst the sodium content constitutes a much higher share in black liquor. Black liquor also has higher concentration of organic substance.

2.3 Fouling

Both vinasse and black liquor have different constituents which can be of great product value. However, they also consist of chemical compounds which can heavily foul the tubes in the evaporators. Fouling is a very important aspect in any heat exchanger, including evaporators. When the heat transfer area gets fouled, subsequently the heat transfer decreases, thus affecting the evaporation efficiency and heat economy. In severe cases the evaporator could stop working completely, forcing a maintenance cleaning of the tube package. This could mean that the evaporator effect or at least one or more sections of it must be taken out of service. This is of course costly and something that should be avoided at all times, within the restriction that health and environmental conditions are withheld. Thus, it is of great importance to know what fouling problems that can be expected when designing an evaporator plant. In paper and pulp industry, fouling of sodium carbonate and sodium sulphate has been a problem for a long time and much research has been conducted to solve those problems. Additional compounds such as calcium carbonate and calcium sulphate is also known to create severe problems in evaporators (Gourdon, 2009).

3 Evaporation

3.1 Evaporators

Evaporation is a unit operation where the purpose is to thermally concentrate a liquid solution by using a heating medium, usually steam. The volatile component is evaporated (in most cases the volatile component is water), leading to an increased concentration of the non-volatile dry solid material. The general principle is illustrated in Figure 3-1 below.

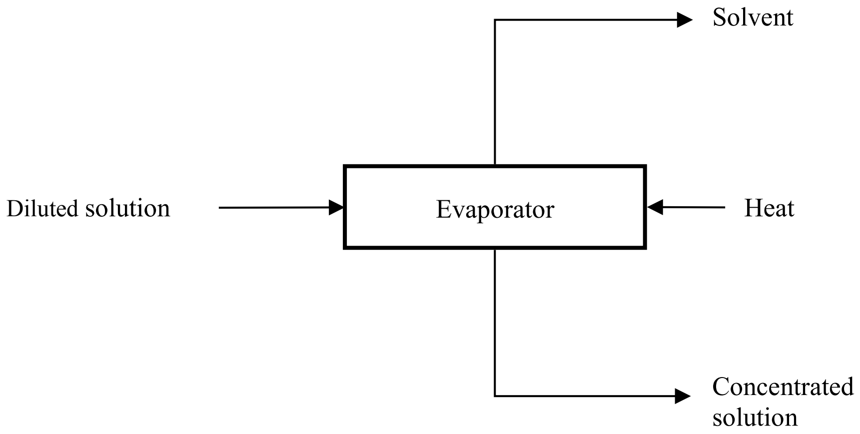

Figure 3-1. General principle for a single stage evaporator

3.1.1 Multi Stage Evaporation

In multistage evaporation the general principle is to utilize the fresh steam effectively, hence improving the heat economy. Fresh steam is only used in the first effect, where the liquid solution is heated to saturation and eventually evaporated. The evaporated vapour is fed to the subsequent effect and used as heating medium, providing that the solution has lower temperature than the evaporated component. This steam sequence characterizes a counter-flow evaporation process, rendering in a pressure drop through each effect (in steam direction), hence the temperature and pressure is highest in the effect where fresh steam is fed. Figure 3-2 below illustrates a general setup of a counter-current, six-stage evaporation process.

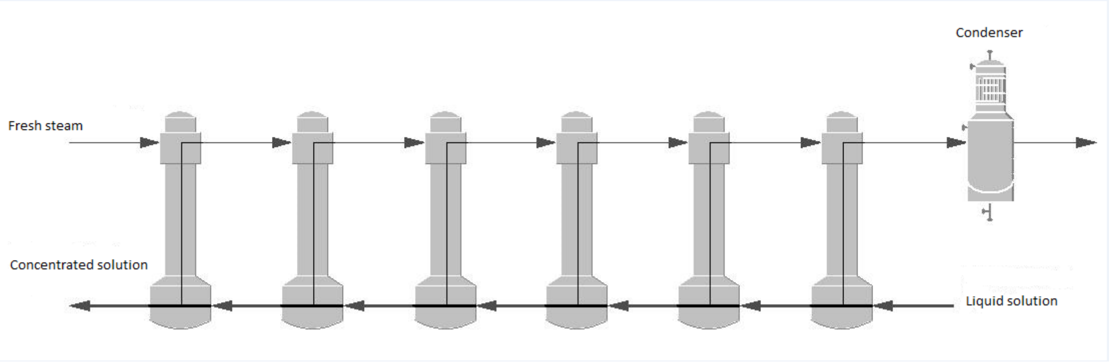

Figure 3-2. A general figure of a counter-current multistage evaporator. The fresh steam is fed to the first effect. In subsequent effects the evaporated solution is used as a heating medium.

3.1.2 Falling Film Evaporators

There are a general distinction between different evaporators in their basic structure and build-up, they are either forced or natural convection. The most common evaporator is the falling film evaporator but there are other types e.g. forced circulation and rising film but they are not discussed further in this thesis.

In falling film evaporators the liquid stream is pumped and enters on top of the evaporator, forcing it to flow downwards, due to gravity. When the fluid is descending down on the tubes it evaporates simultaneously. The normal set-up of falling film evaporators is that the liquid is evenly distributed inside or outside of the tube walls, depending on what dry solid content the diluted solvent possesses i.e. where in the multistage evaporator effect the fluid is located. Another aspect that influences the allocation of the solution is its inclination to fouling.

Characteristic for this type of evaporator is that it has a small liquid hold-up and short residence time, which is of great importance when dealing with heat sensitive materials (Minton, 1986). If the residence time supposedly were longer there is an increased risk of fouling, thus decreased heat transfer. Hence, increased fouling could damage the construction material and erode the pipework (Billet, 1989).

The fluid is distributed on the tubes in the form of a film whilst the steam is fed in the top or bottom of the heating area, also evenly distributed in a co-current or counter-current movement with the solution (Billet, 1989) (Minton, 1986). The heating causes the solvent of liquid film to evaporate on the surface. In the bottom of the heating area the condensate is separated before the liquid reaches the vapour space, located at the foot of the evaporator (Billet, 1989). In modern evaporators there is a possibility to separate clean and contaminated condensate. Depending on the purity of the concentrated liquid, the feed is either led to a subsequent evaporator stage or, if it is pure enough, to a residue tank for storage or further processing. A general illustration is shown in Figure 3-3 below.

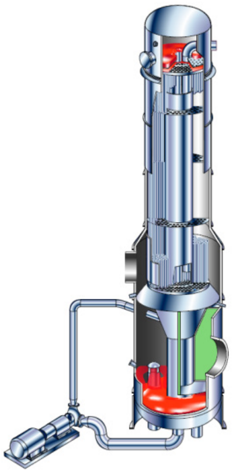

Figure 3-3. The structure of a falling film evaporator where the solution flows on the outside of the tubes (Metso Power AB, 2013).

In falling film evaporation the liquid flowing downwards on the tube surface can be regarded as a thin film, which is utterly dependent on the flow regime that the fluid possesses, either laminar, within the transition region or turbulent. Depending on the flow regime, the fluid will have different velocity profiles, where in the turbulent region the mass and heat transfer will be improved but in the laminar region the heat transfer will decrease, with increased circulation flow. The velocity profiles are dependent on the mass or volume flow of the film but in evaporation processes the common denomination is wetting degree or wetting rate described in Equation (3-1):

$$\Gamma = \frac{\dot{m}}{\pi \cdot d_{o_t}} = \frac{\dot{V}}{\pi \rho d_{o_t}} \tag{3-1}$$

3.1.2.1 Condensate segregation

In each effect condensate is produced. The condensate contains impurities, which often are volatile. Therefore the evaporation effects are designed to segregate the condensate, giving two condensates with different quality. These fractions are divided into one pure and one contaminated condensate stream, as can be seen in Figure 3-4. The foul condensate stream can preferably be further upgraded by using a stripper system. In an evaporation plant where vinasse is evaporated, ethanol will end up in the foul condensate. When using segregation it is possible to remove the ethanol from the condensate and upgrade it in the stripper system. It is then possible to recover the valuable ethanol.

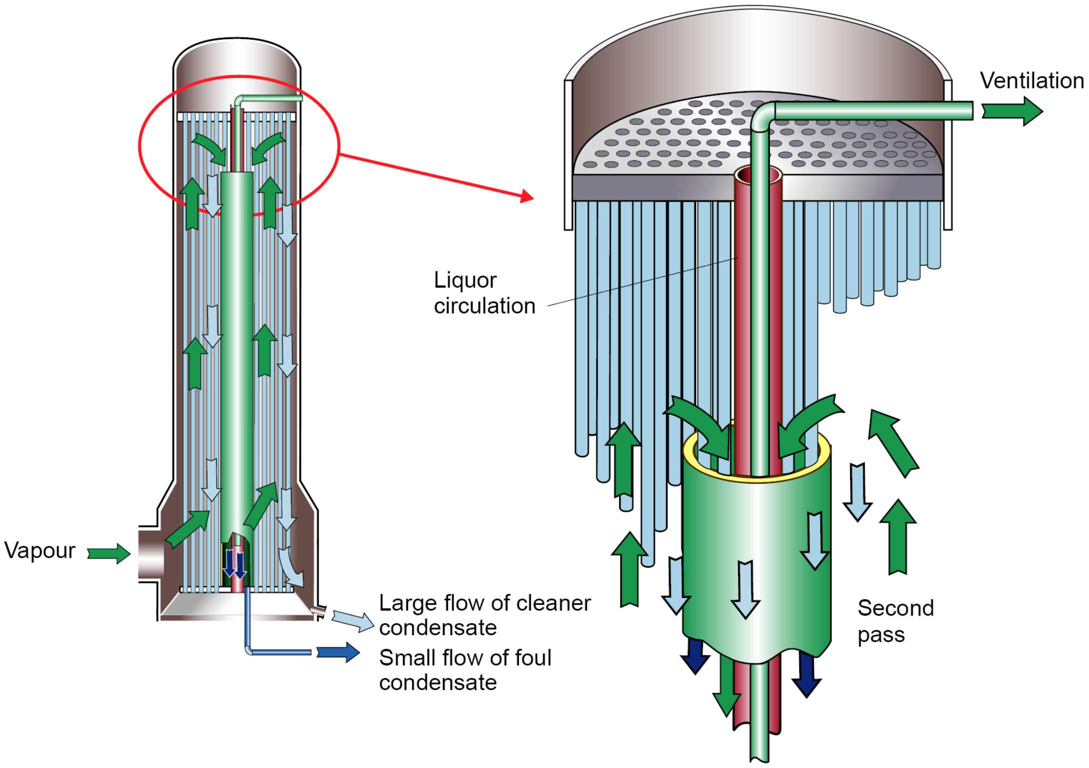

Figure 3-4. Segregation of condensate in a falling film evaporator.

3.2 Heat Transfer

In all separation operations there are different driving forces that make the separation possible, usually these forces is either thermally or mass driven. An evaporation stage or effect can be regarded as one big heat exchanger. The evaporation is driven by the temperature difference between the heating medium and the fluid which is to be concentrated. Depending on the initial concentration it will require more or less thermal energy hence the concentration time will vary accordingly.

For all thermal separation operations the heat transfer will be affected by the temperature difference between the heating medium and the fluid, ΔT_{lm} (logarithmic mean temperature), the surface area, A, and the overall heat transfer coefficient, U, according to Equation (3-2):

$$Q = U \cdot A \cdot \Delta T_{lm} \tag{3-2}$$

The surface area for a tubular falling film evaporator is calculated according to Equation (3-3):

$$A_o = (\pi \cdot d \cdot l) \cdot N_t \tag{3-3}$$

Where d is the outside diameter of the tube, l is the length of the tube and N_t is the number of tubes.

In the evaporation process in this thesis the heating media is condensing steam and the fluid, vinasse, is evaporated. Hence, both fluids undergo phase changes, thus the temperatures of both the solution and the heating medium can be considered constant across the tube. Thus, the average heat transfer coefficient can be simplified and expressed as:

$$U = \frac{Q}{A_o(T_{steam} - T_{vinasse})} \tag{3-4}$$

The overall heat transfer coefficient, U, can be estimated as the sum of the individual heat transfer resistances on the inside and outside of the tube and also the convective resistance in the material:

$$\frac{1}{UA_o} = \frac{1}{h_i A_i} + \frac{\delta_w}{k_w A_m} + \frac{1}{h_o A_o} \tag{3-5}$$

In Equation (3-5) fouling is neglected.

Where $A_m$is the mean surface area and is expressed as:

$$A_m = \frac{A_o - A_i}{\ln(\frac{A_o}{A_i})} \tag{3-6}$$

(Ekroth & Granlund, 1999)

Heat transfer in a fluid next to a surface is commonly represented by the dimensionless Nusselt number. For falling film free surface evaporation the standard definition of the Nusselt number is (Schnabel & Palen, 1998):

$$\mathrm{Nu} \equiv \frac{\mathrm{h}}{\mathrm{k}}\left(\frac{\nu^2}{\mathrm{g}}\right)^{\frac{1}{3}} = \frac{\mathrm{h}}{\mathrm{k}}\left(\frac{\mu^2}{\mathrm{g}\rho^2}\right)^{\frac{1}{3}} \tag{3-7}$$

Schnabel and Schlünder (1980) have proposed a correlation for determining the Nusselt number during falling film evaporation from the Reynolds and Prandtl numbers. This model has been showed to be fairly accurate for black liquor (Karlsson, et al., 2013) and is thus of interest to test with vinasse. The correlation is only valid for Prandtl numbers between 1.75 and 7, however in the work by Karlsson (2013) it was extrapolated up to significantly higher Pr-numbers. The model consists of two correlations; one for laminar flow and one for turbulent flow as follows:

$$\mathrm{Nu_{lam}} = 1.43\mathrm{Re}^{-1/3} \tag{3-8}$$

$$\mathrm{Nu_{turb}} = 0.0036\mathrm{Re}^{0.4}\mathrm{Pr}^{0.65} \tag{3-9}$$

Where the Prantl number is defined as:

$$Pr \equiv \frac{c_p\mu}{k} \tag{3-10}$$

and Re is defined as:

$$Re \equiv \frac{4 \cdot \Gamma}{\mu} \tag{3-11}$$

The Reynolds number (Re) represents the ratio between inertial forces and viscous forces. The laminar and turbulent parts are combined:

$$\mathrm{Nu} = \left(\mathrm{Nu_{lam}^2} + \mathrm{Nu_{turb}^2}\right)^{1/2} \tag{3-12}$$

Far from the transition point either laminar or turbulent flow is more dominant, hence Equation (3-12) can be used, independent of the flow regime.

3.3 Physical Parameters

The physical parameters, boiling point elevation and viscosity are of major importance in evaporation processes. Both parameters are dependent on the operating conditions, thus temperature and dry solid content and can vastly influence the temperature drop over the effects, thus the heat economy.

3.3.1 Boiling Point Elevation (BPE)

Boiling point elevation is one of the most important parameters in evaporation processes, since it determines to what temperature the solution has to be heated for the evaporation to occur. In a multistage evaporation process, fresh steam is fed to the first effect and evaporated solution is reused in the subsequent effects, resulting in a loss in temperature in each effect, due to the BPE.

The definition of boiling point elevation is the difference in boiling point temperature for a solution, containing a solute and the pure solution, measured at the same pressure. It is a colligative property which increases proportionally with increasing solute or molal concentration and is calculated according to Equation (3-13).

$$\Delta T_{BPE} = \frac{b M_{water} R T_{bw}^{2}}{\Delta \mathrm{H}_{v}} \tag{3-13}$$

(Adams, et al., 1997)

3.3.2 Viscosity

Viscosity is another important physical property which has a vast influence on evaporation. When the dry solid content increases, so does the viscosity. The detrimental effect of this is that the residence time of the solvent increases, thus inducing the risk of fouling and dry outs, hence lowering the heat transfer and efficiency of the evaporators.

Viscosity is the internal frictional force of a flowing fluid, which is affected by the magnitude of the shear stress exposed on the fluid. When viscosity increases the inertial force increases within the fluid, thus the generated flow decreases. Hence, the fluid film size increases. Hence, more energy is required for the outmost layer of the film to evaporate, thus the heat transfer decreases.

It is defined as the ratio of the shear stress to the shear rate for a fluid exposed to a shearing force, expressed in the Equation (3-14) below:

$$\tau = \mu \frac{\partial V}{\partial z} \tag{3-14}$$

Where τ is the shear stress, μ is the viscosity, V is the velocity and z is the distance from the surface normal to the direction of flow. Some of the most important properties for determining the viscosity of a liquid are temperature, concentration, molecular weight and colloidal state. Viscosity increases with dry solid content however it generally decreases with increasing temperature, although temperature is not necessarily increased simultaneously with the dry solid content.

Some liquids can be categorized as Newtonian. This means that the shear stress is directly proportional to the shear rate, which implies that the viscosity, μ, is independent of the flow conditions.

4 Experimental Setup

4.1 The Pilot Evaporator

The research evaporator plant used in this thesis is located at Chalmers University of Technology and was built in cooperation with Valmet Power AB. It was built to resemble real industrial conditions for black liquor evaporation. The evaporator has one single stage, constituting of one vertical tube with the evaporating fluid flowing on the outside. The tube is 4.5 m long and has an outside diameter of 60 mm, giving a heat transferring area of 0.848 m^2. The material of the tube is duplex stainless steel and the wall thickness is 5 mm, which is thicker than in industrial applications (1.0 or 1.2 mm in industry). The thicker tube wall was chosen to enable local heat flux measurements (Johansson, 2008).

In Figure 4-1 a process overview of the pilot evaporator and some of its auxiliary equipment is shown. The circulation pump feeds the liquid from the flash tank to the top of the evaporator. The liquid flows down on the outside of the tube were it is partially evaporated, remaining liquid is fed back to the flash tank, while the vapor goes to the condenser. To prevent too much of the fluid to spatter off the tube and drip beside it, a tube redistribution system was mounted on the tube. The condensate can either be recirculated to the flash tank to keep a constant dry solid content or drained from the system. With the latter option it is possible to collect the condensate for dilution of the concentrated product for further processing. The amount of liquid in the system is measured as the level in the flash tank. To fill up the flash tank, the feed pump is used. To regulate the level in the flash tank some of the circulation flow can be fed to either of the two feed/product tanks by a control valve. The feed pump can be set to control the density of the liquid in the system so that more fresh liquid (with lower dry solid content, hence lower density) is fed to the system, if the density increases.

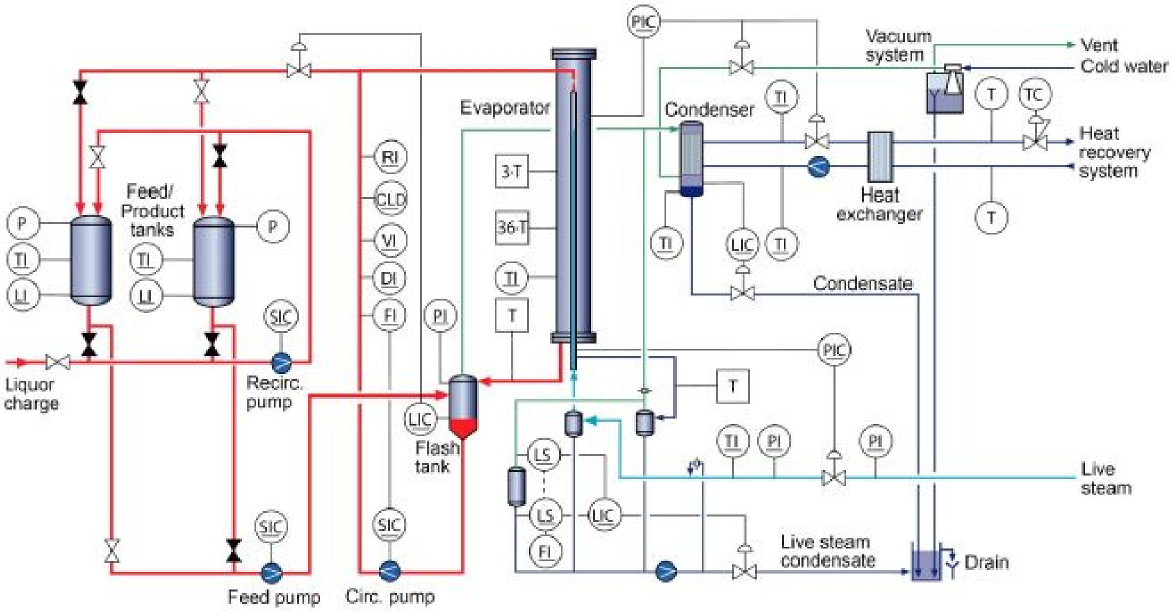

Figure 4-1. Process overview of the pilot evaporator and peripheral equipment.

The shell of the evaporator has sight glasses at three different locations, two at the top, two at the middle and two at bottom of the evaporator, making it possible to visually observe the flow and physical behavior on the tube. The heat needed for the evaporation is supplied by saturated steam condensing on the inside of the tube. To measure the rate of steam condensing a system with two liquid surface indicators at different height, is used. The measurement is based on the time it takes to fill up the volume, which is known, between the two liquid surface indicators. The evaporator plant is equipped with sensors for pressure and temperature at different locations. It also has measuring devices for density, viscosity and refractive index of the evaporated liquid in the flow before entering the evaporator. The viscometer measure the viscosity at a constant shear rate of 3450 s-1, if the fluid is non Newtonian this will be misleading since it not same shear rate as on the tube in the evaporator. A particle counter makes it possible to look at the amount of and cord length of particles present in the flow. The data is sampled once every minute. For more specifications on the measuring devices see Gourdon, 2009.

Some of the more important parameters that can be controlled are the temperature of the evaporated liquid, the pressure hence the temperature of the condensing steam and the volumetric circulation flow rate of the evaporated substance.

4.2 Evaluation procedure

To evaluate all the data collected from the research evaporator a MATLAB ® program was used. This program is based on fundamental heat and mass transfer correlations, using measurable parameters i.e. temperature, pressure and flow rates to calculate local and global heat transfer. The output from this program was then further analysed in Excel ®.

The present configuration of the evaporator is six different pairs of thermocouples, which used to calculate local heat fluxes. The local heat flux of the tube is obtained as:

$$q_{loc} = \frac{k_w}{\delta_w}(T_{i,loc} - T_{o,loc}) \tag{4-1}$$

From the local heat flux the local heat transfer coefficient, on both the inside and outside of the tube can be calculated as:

$$h_{o,loc} = \frac{q_{loc}}{(T_{o,loc} - T_{vinasse})} \tag{4-2}$$

$$h_{i,loc} = \frac{q_{loc}}{(T_{steam} - T_{i,loc})} \tag{4-3}$$

(Gourdon, 2009)

The global heat transfer in the evaporator, Q_{evap}, is calculated from the flow of heating steam condensate. The heat losses, Q_{loss}, in the system compensate for all the steam that is not used for evaporation. These losses have previously been determined by a set of experiments measuring the steam consumption without vaporisation.

$$Q_{evap} = \dot{m}_{cond}\Delta H_v - Q_{loss} \tag{4-4}$$

Using this heat transfer in Equation (3-4) gives the total heat transfer coefficient, U, for the evaporator. To get the fluid film heat transfer coefficient the Equation (3-5) can be rearranged to:

$$h_o = \frac{1}{A_o\left(\frac{1}{UA_o} - \frac{\delta_w}{k_w A_m} - \frac{1}{h_i A_i}\right)} \tag{4-5}$$

In this equation the tube material and dimensions are known which means that only the heat transfer for the condensate film on the inside is unknown. For this a correlation by Schnabel and Palen (1998) for condensation on vertical surface is used.

Since the tube walls is thinner in commercial evaporators than in the research evaporator a corrected total heat transfer coefficient is recalculated to be able to compare to other evaporators with existing data. The recalculated value for U is presented in the results from Equation (3-5) and using the earlier described values for h_o and h_i, for a wall thickness, δ_w, of 1 mm that is a standard dimension used at Valmet.

To retrieve a correlation between the boiling point elevation and dry solid content Equation (3-13) was used. Were the molality, b, is defined as:

$$b = \frac{n_{solid}}{m_{water}} \tag{4-6}$$

If it is assumed that:

$$n_{solid} \propto S$$

$$m_{water} \propto (100 - S)$$

where, S is the dry solid content, in percent.

Also, assuming that the heat of vaporisation is constant, which corresponds to an error up to 20 % in temperature interval 50-150 °C, and since M and R is constant, the equation can be simplified to:

$$\Delta T_{BPE} \approx C \frac{S}{100 - S} T_{bw}^2 \tag{4-7}$$

where C is a constant.

To be able to calculate the Nusselt and Prandtl numbers the heat capacity, c_p, and the thermal conductivity, k, is needed. Since these properties were unknown for sugarcane vinasse, they were taken for sugar beet vinasse (Hajinezhad & Senge, 2007). In the Hajinezad and Senge article, values for k and c_p were measured at 20 °C. In the article, vinasse from different crops was studied, however only the values from ethanol production were considered. For the thermal conductivity, k = 0.64 W/(m K) was used and assumed constant for all temperatures and dry solid content levels. This was considered reasonable since the conductivity for water has very small changes in the temperature interval of interest and 0.64 W/(m K) was close to the value of pure water. For the heat capacity the variation in temperature was still assumed to be small and was neglected. However, the variation with dry solid content was approximated as a linear relation:

$$c_{p,vinasse} = \left(\frac{100 - S}{100}\right) \cdot c_{p,water} + \left(\frac{S}{100}\right) \cdot c_{p,solid} \qquad (4\text{-}8)$$

where S is the dry solids in percent.

From the given data on $c_{p,\text{vinasse}}$ and dry solid content, the $c_{p,\text{solid}}$ was calculated as a mean value for two different vinasses to 1270 J/(kg K), giving a relation between dry solid content and heat capacity.

4.3 Experimental Procedure

The purpose of the experiments was to collect data of the heat transfer over the tube, boiling point elevation, viscosity, density and fouling rate of the vinasse at different operating conditions. Also samples of the concentrated vinasse and vinasse condensate were collected for chemical analyses. During the experiment possible problems that might appear such as foaming, were monitored and assessed.

In the experiments the aim was to simulate conditions that could be expected in a real, full scale evaporation plant as accurate as possible, regarding pressures, temperatures and the wetting degree. The wetting degree is controlled indirectly through the volumetric circulation flow rate. Since the relation between wetting degree and circulation flow is depending on the density, the wetting degree can change during the course of an experiment with constant circulation flow, if the temperature or concentration changes. This was the starting point for selecting the operating parameters and designing the experiments.

The vinasse was sent from sugar and ethanol producers in South America for this thesis work. Two different batches of about 500 l each, from different productions sites were used. The dry solids content of batch 1was measured to 9.0 %. Batch 2 had a dry solids content of 6.5 %. For the dry substance measurement the Tappi standard T 650 om-89 method for black liquor was used and assumed to be valid for vinasse.

It was decided to keep the two batches separated to be able to analyze any differences in their physical behavior. However, for experiments on higher dry solids content, above 50 %, the vinasse from both batches were needed to have enough volume to operate the plant safely and to reach 70 % ds.

Since there was only a limited amount of vinasse available care were needed in the planning of experiments, to utilize the vinasse to get as much relevant measurements and data as possible. The vinasse condensate was stored in a tank to be able to remix it with the vinasse to retrieve a lower concentration. However, reusing the same vinasse again has the drawback that the chemical composition might be different from the original vinasse. This can possibly be due to thermal decomposition of some compounds or depletion of fouling compounds that is washed away during cleaning of the evaporator. To minimize the later effect condensate was used and saved during most part of the cleaning. After most of the experiments the tube was cleaned to get as equal measurements as possible and to reduce the error margins when running with a partly dirty tube.

In the following subchapters all the experiments, there conditions and some problems with their implementation will be explained in detail. In Table 4-1 the conditions in the different experiments is listed. The dry solids content in the feed is dependent on if fresh vinasse is used or vinasse already concentrated in an earlier experiment. The reached dry solids content is controlled by choosing a target density. All the temperatures and the circulation flow rate are all directly set in the control system.

Table 4-1. Experimental setup with the different operating conditions

Experiment		Batch	Feed ds [%]	ds [%]	T_vinasse [°C]	Circ. flow [l/h]	ΔT [°C]
Increacing ds	1	1	9	51*	100	700	12
Constant low ds	2	1	9	13	80	400	12
		1	9	13	80	700	12
		1	9	13	55	700	12
		1	9	13	55	400	12
	3	1	13	20	100	400	12
		1	13	20	80	400	12
	4	1	19	32	100	400	12
Constant low ds	5	2	6.5	34	100	400	12
		2	6.5	34	100	800	12
Constant high ds	6	Mixed	25	53	100	800	10
		Mixed	25	64	100	800	10
		Mixed	25	72	100	800	10

* in the end of the experiment

4.3.1 Continuous Increase of Dry Solids Content

The first test of evaporating vinasse was an experiment where the dry solids content was continually increased. This type of experiment was chosen to get a first sense of how the vinasse would behave in the pilot evaporator, if any fouling would appear and how the control system should be operated. The vinasse from the batch 1 was used for this experiment.

4.3.1.1 Experiment 1, Batch 1 from 9% to 51 % ds

The temperature of vinasse was set to 100 °C and the steam was set to 112 °C, giving a $\Delta T = 12$ °C. According to earlier experience this corresponds to a $\Delta T \approx 7\text{-}10$ °C in an industrial evaporation plant were the tube wall is thinner. A maximum allowed temperature difference of 10 °C is standard in evaporation of black liquor, due to material restrictions. Also, above that temperature the probability of burn out on the tube increases substantially. In addition, these temperatures were chosen to be values in the midrange of what can be suitable in a full scale evaporation plant for vinasse. The circulation flow was set to 700 l/h. This value was based on the standard values used for high dry solids content in real evaporators.

The procedure was to start the evaporation from a system filled up to 100 % with vinasse. The dry solids content of the vinasse increase as water was evaporated, hence lowering the volume in the system. When the level in the flash tank reached 50 % the feed pump started feeding fresh vinasse to hold a constant level. The fresh feed was run in this mode for as long as possible with a time restriction of one day for the whole experiment. Vinasse samples were taken out periodically during the course of the experiment. When the experiment was finished, the concentrated vinasse was sent to one of the storage tanks and stored for later use. At the end a dry solid content of 51 % was reached.

During this experiment the viscometer started to show some strange measurements after a couple of hours, possibly originating from buildup of fouling.

4.3.2 Experiments on lower dry solid content

In the set of experiments on lower dry solid content the aim was to investigate the behavior of vinasse at different low dry solids contents at constant conditions. The purpose was also to evaporate water to get vinasse of higher dry solid content for later experiments.

The first experiments started with batch 1, with an initial dry solid content of 9.0 %. This batch was evaporated in steps to three different target concentrations: 12 %, 20 % and 30 %. This was based on expected industrial operating conditions in a multistage evaporator plant. Here, one dry solid concentration simulates more than one effect in a real process plant. These dry solid concentrations were also chosen to get suitable length of each experiment.

4.3.2.1 Experiment 2, Batch 1 from 9 % to 12 % ds

The procedure started with an amount of vinasse that filled up the evaporating system. The evaporation started when the preset temperature was reached. When the wanted dry matter content of 12 % (according to the control system) was reached the feeding with fresh vinasse started and concentrated vinasse was pumped into one of the feed/product tanks, keeping both the level in the system and the density (corresponding to the amount of dry solid content) constant. The plan was to start with a temperature of 80 °C for the vinasse, running for two hours and then lowering the temperature to 55 °C both with $\Delta T = 12$ °C. On both these temperature levels two different circulation flows were planned to be investigated, 400 l/h and 700 l/h, to test different operating conditions. The lower circulation flow was estimated based on wetting degrees in industrial conditions. The higher corresponds to the circulation flow used in the first experiment. This gives measurements of four different operating conditions. Due to some problems with the equipment and the handling of it, the experimental time on 55 °C became a bit shorter than planned but measurements at all conditions were carried out. The experiment was run until all the vinasse in the batch was concentrated to 12 % ds (according to the control system) which took about 10 hours. The real dry solids content measured from the samples taken showed that actual values were around 13 % ds. After finishing the experiment, the tube was considered clean enough that cleaning was not necessary.

It was noticed that the heat transfer values had a strange projection, with big fluctuations and even negative values on the lower temperature. After some investigation it was concluded that it originated from the measurements of the live steam condensate, which is used for heat transfer calculations.

A scale with a container was setup and the steam condensate was redirected to it to measure the amount condensed steam. The weight was logged on a computer to be able to calculate the actual condensate flow. The measurements showed that the actual flow of condensate was different from the logged by the system. Hence, correction factors were calculated for conditions as close to those in the experiment as possible.

Some work was put in on finding out were the spikes in condensate flow originated from but could not be determined. A setting that was thought to minimize these spikes was used for later experiments.

4.3.2.2 Experiment 3, Batch 1 from 12 to 20 % ds

The same experimental procedure was repeated with the concentrated 13 % ds vinasse which was planned to be evaporated to 20 % ds. The actual measurements on the samples showed that the real dry solid content was 20 % ds. The temperature levels were increased to 100 °C and 80 °C respectively, with the same ΔT and circulation flows as the previous experiment. In this experiment there were a lot of problems with the equipment or mostly the handling of it, with pumps that did not start properly and valves not in the correct position. Therefore it was difficult to get stable conditions. The available time for the experiment was shorter than calculated, so it was decided that only the lower circulation flow of 400 l/h was to be evaluated.

Because of the problems involved in this run, the data from this experiment was fluctuating more than in the other experiments. Also the log of the scale for steam condensate did not work properly so no data from that is available, hence no comparison of the condensate flow measurements could be done.

4.3.2.3 Experiment 4, Batch 1 from 20 to 30 % ds

In the third step the now 19 % ds vinasse was concentrated to around 32 % ds. For this level the estimated time for evaporating the remainder vinasse was limited (approximately 4 hours at an evaporation rate of 20 kg/h) so only one temperature level, 100 °C, and one circulation flow, 400 l/h, was chosen for the whole experiment. Again with the same temperature difference $\Delta T = 12$ °C.

This experiment ran without any major difficulties. The measurements of steam condensate from the two different ways of measuring; with the control system and with the scale showed similar results, still with some fluctuations. Although the viscosity measurements had some problem, were the viscosity increased during the experiment while the dry solid content and temperature were constant. Fouling of the viscosity meter was the probable cause for this.

4.3.2.4 Experiment 5, Batch 2 from 6.5 % to 30 % ds

The initial experiment with vinasse from batch 2 was evaporated to the target concentration 30 % straight away, during a three days experiment, from an initial dry solid content of 6.5 %, in a similar way as for batch 1. This setup was chosen to get a longer experiment which last over three days to see possible buildup of fouling and long term trends. The temperature of the vinasse was set to 100 °C for the whole experiment with $\Delta T = 12$ °C. The plan was to test two different circulation flows, starting with 400 l/h and then testing 800 l/h to see any effects of the circulation flow, hence the wetting degree.

The time required to reach the target dry solids content was so long that it was decided to increase ΔT to 15 °C until the right level was reached to speed it up. During this time it was noticed that the heat transfer was decreased substantially. After running at stable conditions on 400 l/h circulation flow for two hours it was decided to run the rest on the higher circulation flow. Afterwards it could be concluded that the tube had a thick fouling layer on it.

Once again, the viscosity indicator had problems in this experiment and showed very high values. If the viscosities actually were correct the samples would have been really thick, when cooled down. This was not the case and the samples were not that different from samples from earlier experiments. Due to this it was suspected that the viscometer might be contaminated. To investigate this, the viscometer was removed afterwards and it could be concluded that it was heavily fouled, Figure 4-2. It was cleaned and put back again. Thus the measured viscosity in this and the previous experiment could not be trusted.

Figure 4-2. Fouling of the viscometer after experiment 5

4.3.3 Experiment 6, Experiment at higher dry solids contents

In this experiment the behavior of evaporating vinasse at higher dry substance content, corresponding to the last effects in a real plant. The concentration levels to be tested were 50 %, 60 % and 70 % dry solids content. First the concentrated vinasse from both batches was mixed together to one batch to get enough volume for the experiments. This mix was expected to have a solid content of approximately 30 % dry solids content but in reality it was 25 % since some condensate used for the cleaning of the evaporator had been added. It was chosen to start with the system filled up with vinasse and letting the water evaporate to 50 % ds. When this level was reached the feed pump was started to feed more fresh vinasse to keep the dry solids content constant. No product was fed out, so the level in the system constantly increased. After one hour of steady state conditions and the in-feed was increased again to fill up the volume in the system. When this was completed the feed pump was stopped and the evaporation continued until the dry substance content reached 60 % ds. The same procedure was repeated to achieve 70 % ds.

The initial temperature was set to 100 °C but was planned to be increased to counteract the vast increase in viscosity at high dry solid content. As opposed to most of the other experiments the temperature difference was set to 10 °C to decrease the risk of vinasse dry outs on the tube surface but also to get a longer experiment and measurements. A relatively high circulating flow of 800 l/h was also chosen to increase the wetting degree of the tube, hence also to minimize the risk of dry outs.

In reality the dry solid content at de three different levels achieved were around 53 % ds, 64 % ds and 72 % ds respectively. On the measurement of the steam condensate, big spikes with high flow were present. However, the measured volume flow was similar for the two different ways of measuring.

5 Results and Discussion

The results from the experiments will be presented according to subcategories for the different important properties. The most important parameters; dry solid content, density, viscosity and boiling point elevation will be assessed in the physical properties section. Heat transfer, fouling and condensate quality will have their own subcategory and is analyzed there. Some figures will be presented to illustrate the behavior of vinasse but also to give a better picture of how different parameters changed over the course of the experiments.

5.1 Physical Properties

5.1.1 Density and Refractive Index

Generally density decreases with increasing temperature, due to thermal expansion. In an evaporation process the evaporation of volatile components increases the dry solid material and thus increases the density of the solution. In Figure 5-1, the compiled density increase from the experiments is displayed. The density increased with increasing concentration and decreased with temperature as expected.

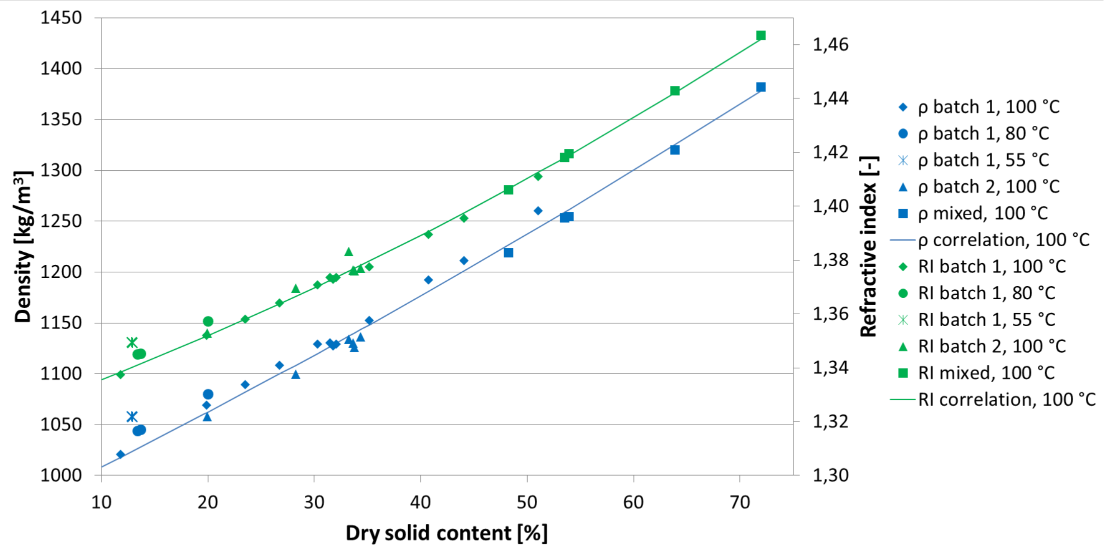

Figure 5-1. Density (blue) and refractive index (green) plotted versus dry solid content at different temperatures.

In addition to density measurements, a common industrial method is to measure the refractive index. This makes it possible to use a refractometer, which can be more favorable in some applications. The refractive index is also plotted in Figure 5-1. Refractive index shows a similar behavior as density when the ds and temperature changes.

From the data at 100 °C a quadratic correlation for density as a function of the dry solid content, S, was calculated:

$$\rho_{100} = 957 + 5.06S + 1.11 \cdot 10^{-2}S^2 \tag{5-1}$$

In the same way a correlation for refractive index was established:

$$RI_{100} = 1.32 + 1.40 \cdot 10^{-3}S + 7.83 \cdot 10^{-6}S^2 \tag{5-2}$$

5.1.2 Viscosity

Due to the fouling problems on the viscometer during two experiments, experiment 4 and 5 are regarded as corrupted and has been excluded. Also, the data from the first experiment is only believed to be valid for the first half of the experiment up to about 30 % ds. The rest of the viscosity data is believed to be reasonable.

The viscosity change with dry solid content is illustrated in Figure 5-2 including a comparison to calculated values for black liquor according to Valmet's calculation tool for black liquor.

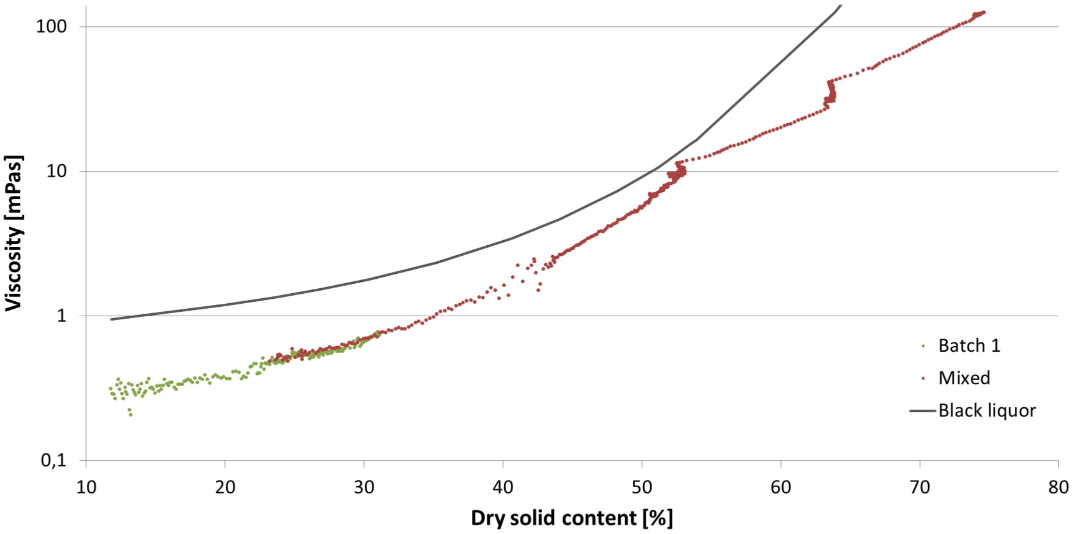

Figure 5-2. The viscosity measured on batch 1 and the mixed vinasse, as a function of dry solid content at 100 °C, compared with a correlation for black liquor.

At dry solid content below 45 % the viscosity is low, below 5 mPas. However, above 45 % ds the viscosity increases exponentially. This behavior is very important to establish when designing a multistage evaporator effect, especially in the latter effects. The exponential increase of viscosity occurs at higher dry solid content than for black liquor, thus the heat transfer area of the evaporators can be smaller, and hence the investment cost can be reduced.

The measured viscosity at high dry solid content is compared to the viscosity measured by (Välimäki, Erkki;, 2012) in Figure 5-3. The temperatures used by Välimäki were 140 °C and 160 °C, compared to the pilot plant which was at 100 °C. It was expected that the viscosity in the pilot plant, at lower temperature, would be higher than for the data from Välimäki. This was, however, not the case and the viscosity at 100 °C and 140 °C were rather similar. The reason for this could have been due to differences in the chemical composition of the vinasse used in the different measurements and also, because the measurement techniques differed. While the viscometer in the pilot plant used a shear rate of 3450 s^{-1}, Välimäki used 288s^{-1}. If the vinasse has a non-Newtonian behavior these two measurements would give different results. To get reliable measurements it is suggested to use a rheometer to establish the rheological behavior of the different vinasses.

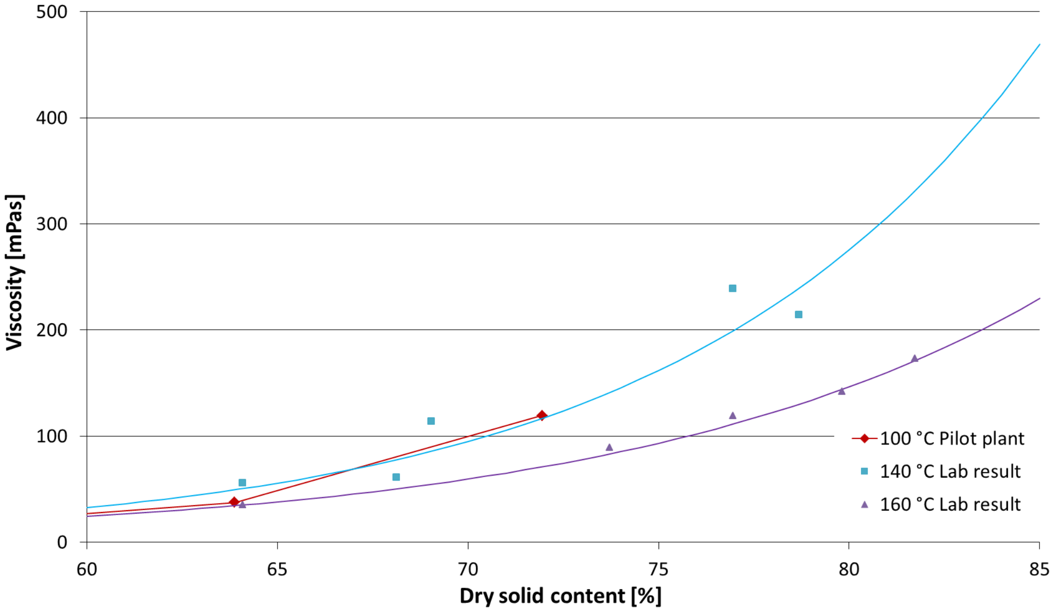

Figure 5-3. Comparison of viscosity measured in the pilot plant at 100 °C and viscosity measured by Välimäki at 140 °C and 160 °C.

5.1.3 BPE – Boiling Point Elevation

The measurement of boiling point elevation had some problems that were not noticed until after the experiments. The temperature of the evaporated steam was measured by a pressure indicator and converted to the corresponding saturation temperature. It was realized after the experiments that this pressure indicator did not show the correct pressure when exposed to the atmosphere. Also, strange BPE values were noticed at low pressures. Attempts were made to correct this by correction factors but that turned out to be difficult since it was unknown during the experiments and the error was inconsistent over time and pressure. Another way to attain the evaporation temperature was by a measuring of the temperature directly inside the shell of the evaporator. However, that measurement did not have the same precision since the cooling from the evaporator wall was unknown. Nevertheless, it was considered to be the best approximation and used in most of the experiments. Unfortunately, in some experiment it was fouled by vinasse and the corrected values from the pressure indicator were used. Due to these problems there is a large uncertainty in the results for BPE. The obtained values can be seen in Figure 5-4.

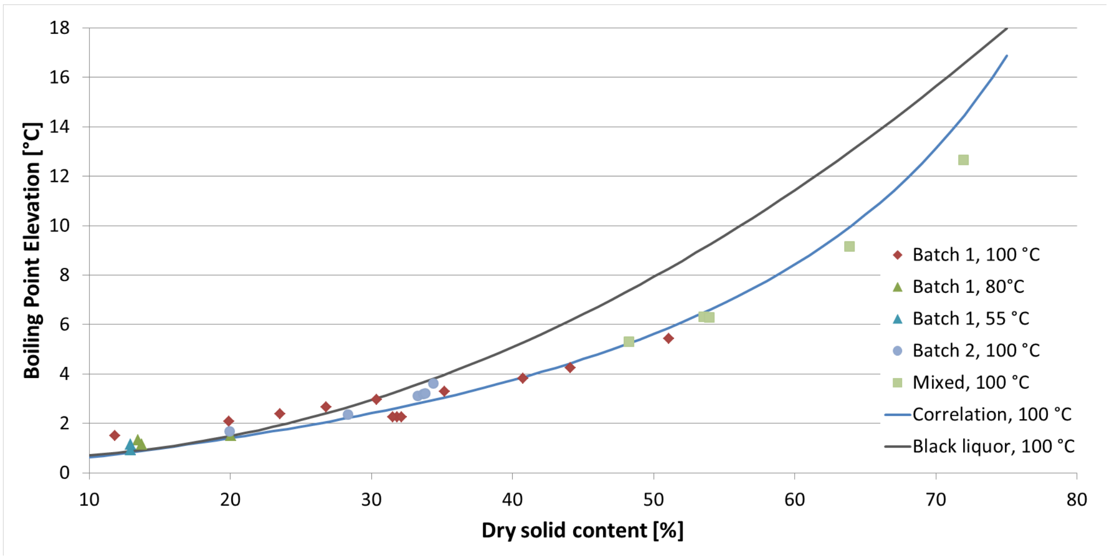

Figure 5-4. Measured BPE for vinasse from different experiments and calculated values from model and also calculated BPE values for black liquor.

As can be seen in Figure 5-4 the BPE increased with higher dry solids content. This was in accordance with Equation (4-7). With the measured data the constant, C, in that equation can be estimated and the equation written as:

$$\Delta T_{BPE} \approx 4.04 \cdot 10^{-5} \frac{S}{100 - S} T_{bw}^2 \tag{5-3}$$

Equation (5-3) is valid for $6\ \% < S < 75\ \%$

The validity for dry solid content over 75 % is uncertain and when S approaches 100 % the equation approaches infinity, which is unrealistic. Values for the BPE using this correlation at 100 °C, are plotted in Figure 5-4, as well as the estimated BPE for black liquor taken from Valmet's calculation tools. The theoretical correlation for BPE had a good fit to the experimental data. The BPE for the vinasse appears to be lower than for black liquor.

Comparing the BPE of vinasse to black liquor, it can be seen in Figure 5-4 that it was lower at higher dry solid content which is good when it comes to heat economy.

In Figure 5-5 the corrected BPE from the last experiment, 6, at 100 °C is plotted together with BPE measured by Välimäki. The temperature or more accurately the pressure at which Välimäki's measurements were conducted is unfortunately unknown. However, since it was not stated it was most likely at atmospheric pressure because this is the simplest experiment setup. The BPE from the experiments in the pilot plant is higher than from the laboratory analysis although they do not differ extensively. This might be explained by the use of different Vinasse used in the two studies. This, however, is an indication that the BPE measured is fairly reasonable.

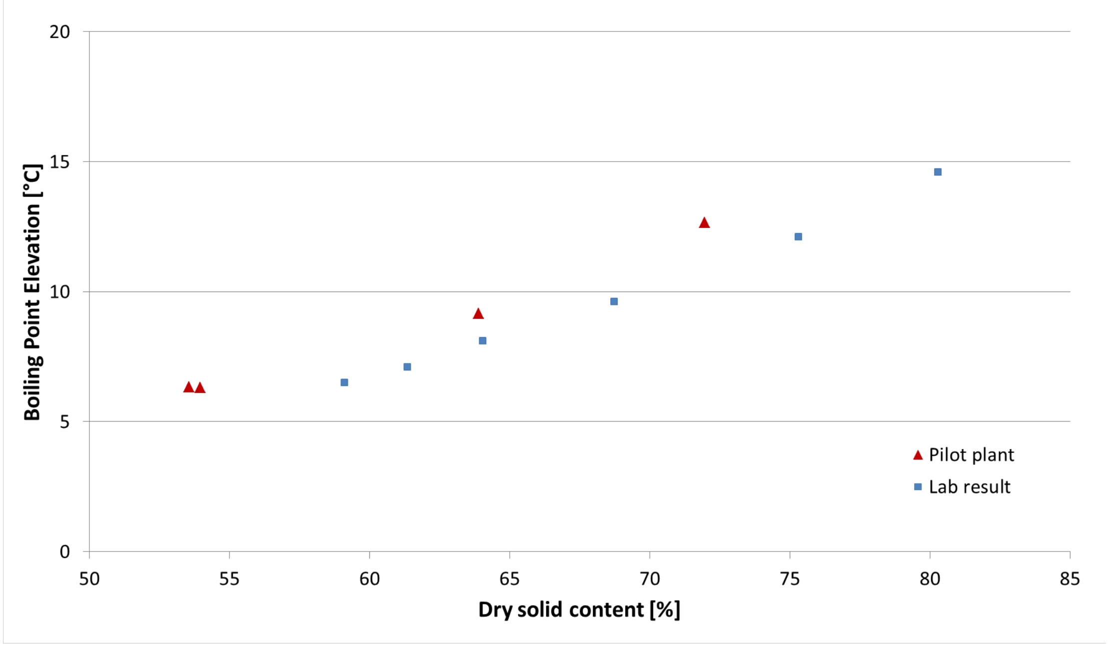

Figure 5-5. BPE from pilot plant experiment compared to values from Välimäki. Pilot plant experiments at 100 °C. Välimäkis at unknown temperature.

5.2 Heat Transfer

5.2.1 Experiment 1

As described earlier the tube wall in the pilot evaporator is 5 mm, much thicker than in commercial applications. The values for the total heat transfer coefficient, U, was recalculated for a wall thickness of 1 mm to get values that corresponds to an industrial application. Figure 5-6 shows how heat transfer decreased in experiment 1, from 9 % to 51 % ds.

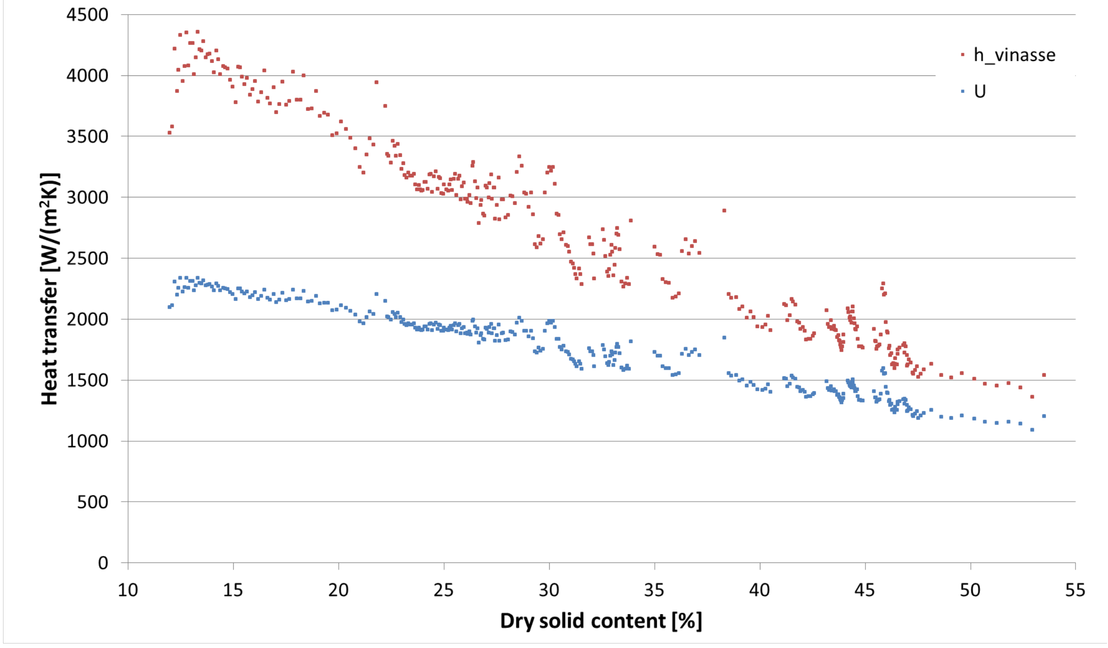

Figure 5-6. The overall heat transfer (U, red points) and the vinasse heat transfer coefficient (h_vinasse) as a function of dry solid content, indicating how viscosity affects the heat transfer.

As seen in Figure 5-6 the heat transfer decreased, which is naturally since the viscosity increases with higher dry solid content. It could also indicate that a layer of incrusts starts to form to the tube, thus affecting the heat transfer. The measured values are very fluctuating, this was mainly because of the fluctuating condensate flow mentioned in chapter 4.3.

The figure indicates that in the beginning of the experiment the heat transfer resistance in the vinasse film on the outside of the tube is small but when viscosity increases the resistance in the film increases, thus the heat transfer, h, decreases. It can also be seen that at higher dry solid contents the vinasse heat transfer resistance becomes more dominating for the overall heat transfer, U, according to (3-5).

5.2.2 Experiment 2-4

An obvious indication of the impact of fouling was when the dry solid content and the other physical parameters were kept constant. Figure 5-7 shows experiment 4 where the dry solid content was increased from approximately 20 % to 30 % and was kept constant on that level until all the vinasse in that batch was consumed.

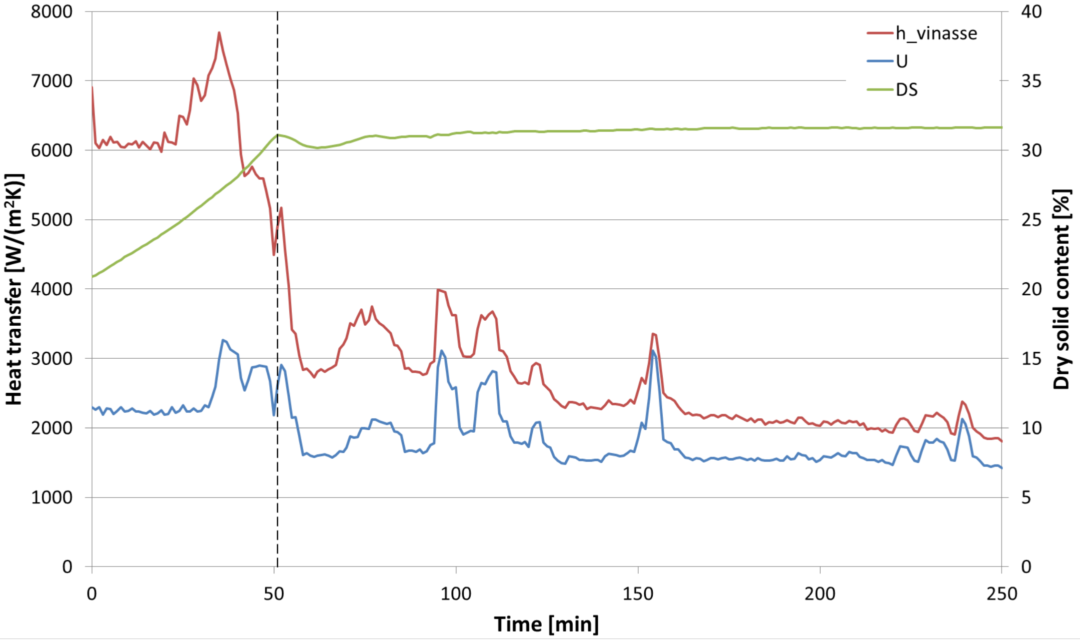

Figure 5-7. The overall and vinasse heat transfer decrease at constant conditions. The green line represents the dry solid content, the red line is the vinasse heat transfer coefficient and the blue line is the overall heat transfer coefficient. The dotted vertical line is when the dry solid content was reached and the operating conditions were kept constant.

In the beginning of the experiment, until the stable conditions were reached, the heat transfer fluctuated substantially, again because of the same reason as in the previous figure. Note should also be taken that the experiment displayed in Figure 5-7 was conducted at fairly low dry solid content so the decrease in heat transfer might not be that significant but it is still present and cannot be neglected and is an indication of the particles crystallizing and adhering to the tube. Similar decreases were noticed in the other experiments at lower dry solid content (experiment 2 and 3) when the dry solid content was kept constant. Despite the relatively low decrease in heat transfer, all the experiments were conducted during only 8-10 hours. In an industrial application the operating time will be substantially longer, so the fouling should be monitored closely.

5.2.3 Experiment 5

Experiment 5 was conducted on batch 2 where the aim was to investigate the long term build-up of fouling. Figure 5-8 shows how the overall heat transfer vastly decreased during the first hours of the experiment. At that time, the temperature difference where kept high to save time, to reach the target 30 % ds.

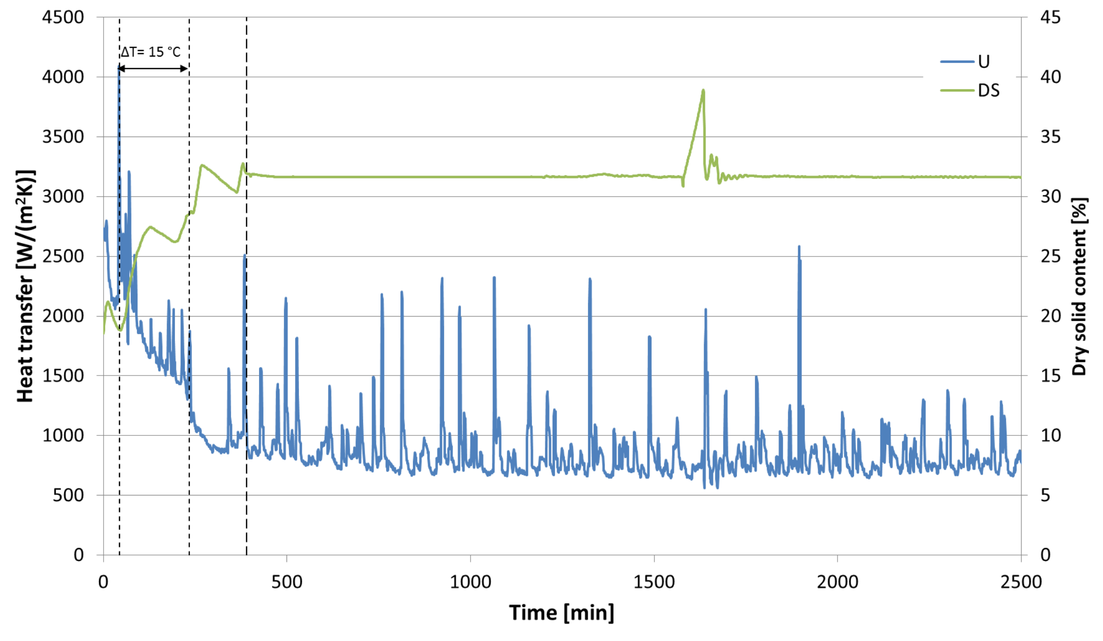

Figure 5-8. The decrease of the overall heat transfer (blue line) for batch 2 evaporated from 6.5 % to 30 % ds. The decrease in heat transfer is exclusively in the early stage of the experiment The green line represents the dry solid content

Here, the influence of the condensate flow measurements can be seen as big fluctuations in the heat transfer. Also, the spike in the dry solid measurement was due to malfunction of the feed pump. The two first vertical lines represents the time when the temperature difference was kept at 15 °C. The last vertical line represents when the target dry solid content was reached and the conditions were kept constant. At that point the heat transfer had decreased to 700-800 kW/m^{2}K and remained constant throughout the whole experiment. A thick fouling layer was built up during the early stage of the experiment, thus the heat transfer decrease and hindered the evaporation during the rest of the experiment. Despite the low heat transfer the vinasse still evaporated but at a much slower rate than expected. The fouling in this experiment will be further discussed in chapter 5.3.

5.2.4 Experiment 6

The last experiment was performed to reach at least 70 % ds and as previously mentioned the two batches were mixed to have enough volume to fill the system. The initial dry solid content was 25 %, due to the re-dilution of condensate when cleaning the tube in previous experiments. The setup of the experiment was to reach three different levels of dry solid content, 50 %, 60 % and 70 % and keep the operating conditions stable at those levels for some time. Due to the restricted volume of the experiment, stable conditions were only withheld for about an hour. The results can be seen in Figure 5-9.

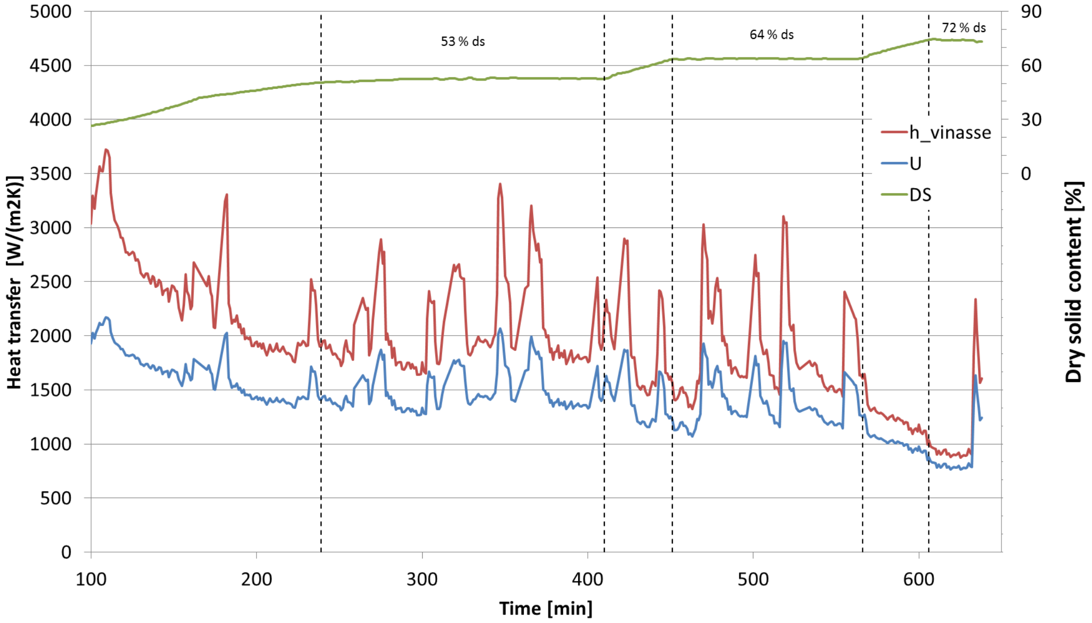

Figure 5-9. Heat transfer from experiment 6. The blue line represents the overall heat transfer coefficient, the red line represents the vinasse film heat transfer coefficient and the green line is the dry solid content.

The results displayed a decrease in heat transfer, mostly due to the vast, exponential increase of viscosity. The most fluctuating values were removed from the results, since it was determined that those measurements were unrealistic and incorrect. When 70 % ds was reached the heat transfer was just below 1000 W/m^2K, and here the heat transfer resistance in the vinasse film was dominating and all the other resistances could be neglected. Despite the high dry solid content, the heat transfer was still higher than for experiment 5. Also, during stable operating conditions at constant dry solid content the heat transfer was somewhat constant, which indicated that there was no or negligible fouling buildup. The decrease in heat transfer occurred when the dry solid content was increased, the viscosity were 10, 35 and 125 mPas for the dry solid content of 52, 64 and 72 % respectively. When 72 % ds were reached, about 97 % of the water content had been removed.

5.2.5 Heat transfer correlations

The dependence of the heat transfer on different parameters was investigated. There was no change in heat transfer observed when changing the wetting degree and keeping other physical parameters constant. There is, however, a limited amount of available data for this observation. In Figure 5-10 the congregated heat transfer coefficients, both the overall, U, and for the vinasse film, h, is plotted as a function of the dry solid content at different temperatures. The heat transfer goes down as the dry solid content increase. This is believed to depend on the increasing viscosity as discussed earlier. No clear temperature dependence is visible in these data, although at higher dry solid content an increase in temperature would decrease the viscosity and a better heat transfer would be expected. At lower dry solid contents the viscosity is low and has less impact on the heat transfer.

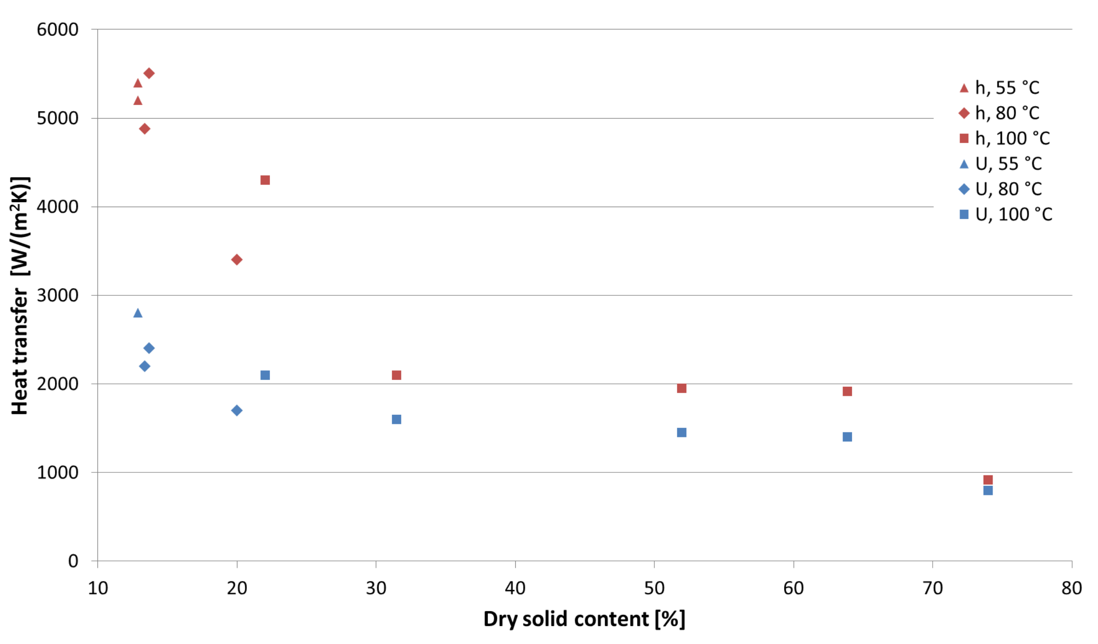

Figure 5-10. Vinasse film, h and overall, U, heat transfer coefficients as a function of dry solid content and temperature.

From the measured values of heat transfer the Nusselt number was calculated according to Equation (3-7). This was then compared with the correlation by Schnabel and Schlünder, Equation (3-12). The results can be seen in Table 5-1 and in Figure 5-11.

Table 5-1. Flow and heat transfer properties comparison. Pr over 7 is marked in grey since the correlation is only valid for lower Pr.

ds [%]	T [°C]	Γ [kg/(s·m)]	Re [-]	Pr [-]	Nu [-]	Nu_calc [-]	Nu_calc/Nu [-]
12.9	55	1.09	8180	3.2	0.24	0.29	1.21
12.9	55	0.62	5140	2.9	0.23	0.23	1.00
13.0	100	1.05	14741	1.7	0.13	0.24	1.83
13.4	80	1.08	10118	2.6	0.20	0.27	1.39
13.7	80	0.62	6333	2.3	0.21	0.22	1.06
19.5	100	1.09	11527	2.2	0.14	0.26	1.90
20.0	80	0.64	3846	3.8	0.18	0.25	1.39
22.0	100	0.63	8065	1.7	0.14	0.20	1.46
22.9	100	1.11	9481	2.6	0.14	0.27	1.92
30.6	100	1.16	6520	3.7	0.14	0.29	2.05
32.5	100	1.34	6482	4.2	0.15	0.32	2.09
37.7	100	1.37	4309	6.2	0.19	0.35	1.85
45.5	100	1.25	1075	20.9	0.33	0.45	1.37
48.6	100	1.27	693	31.9	0.37	0.49	1.34
52.0	100	1.47	616	40.2	0.55	0.55	0.98
60.7	100	1.54	289	80.7	0.73	0.64	0.87
63.9	100	1.56	185	122.7	1.21	0.71	0.59
66.0	100	1.57	127	176.6	1.08	0.77	0.72
70.9	100	1.61	78	274.7	1.37	0.86	0.63
74.0	100	1.63	54	386.3	1.32	0.93	0.71

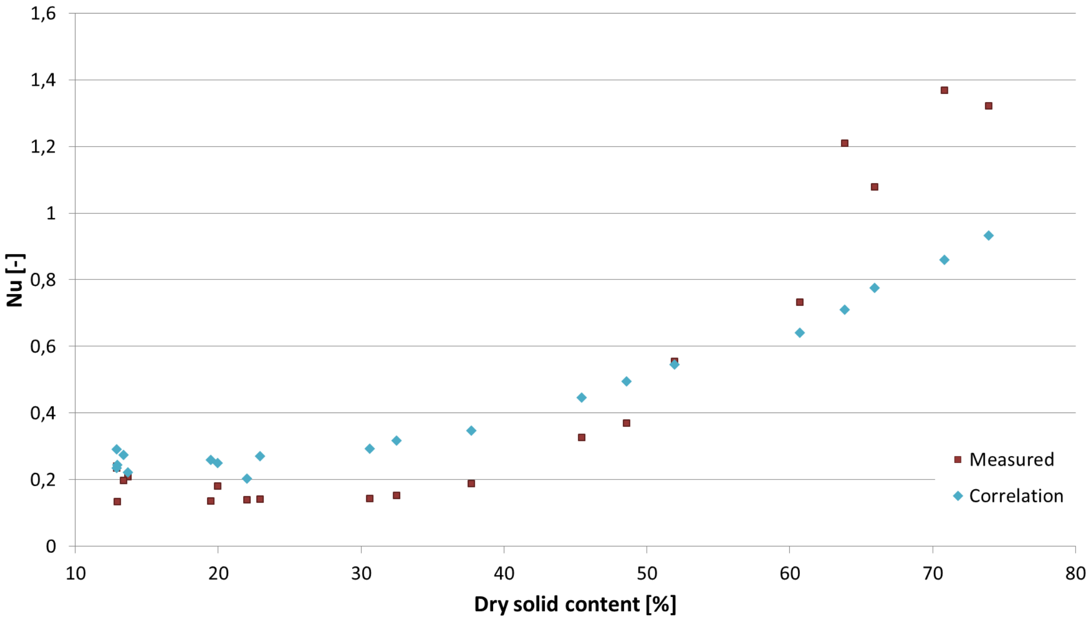

Figure 5-11. Comparison of Nusselt number from measurement and from correlation by Schnabel and Schlünder at different dry solid content.

Since the input data for these calculations are uncertain it also affects the results. The correlation does not fit the experimental data extracted for vinasse. For lower concentrations the correlation gives higher Nusselt number than the measured. At higher dry solid content the Prandtl numbers are greater than the allowed range for the correlation. Also, the measured Nusselt numbers are higher than the calculated given by the correlation.

Since the correlation by Schnabel and Schlünder had poor fit, a correlation for the heat transfer coefficient, h, at 100 °C was developed from the measured data:

$$h_{100} = 44100\, S^{-0.836} \tag{5-4}$$

Equation (5-4) is valid for $12\ \% < S < 75\ \%$

The measured data and the correlation can be seen in Figure 5-12. Here, most data was taken from the first and last experiment were the dry solid content was constantly increased, in contrast to the data in Figure 5-10 that were taken at steady state conditions. This was done to get enough data points to make a correlation. As can be seen in Figure 5-12 the correlation has a relatively good fit to the data in the investigated range of dry solid contents. It should be noted that this correlation should not be extrapolated down to lower values since it goes to infinity close to 0 % ds.

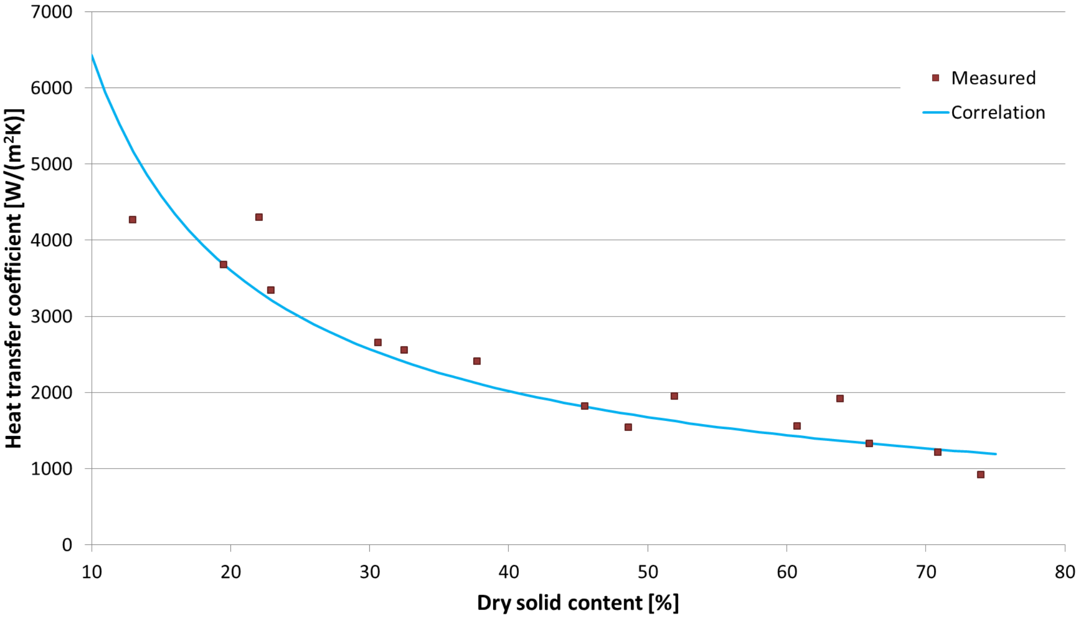

Figure 5-12. Comparison of measured and correlation values for the heat transfer coefficient, h, and as function of dry solid content at 100 °C.

5.3 Fouling

After each experiment the tube was visually investigated for fouling. During the experiments the tube is mostly covered with flowing vinasse and it was hard to see any fouling on the tube, especially at higher dry solid content when the viscosity was higher. However, during the experiments the particle counter indicated how much particles that was formed and how much were present in the vinasse. When crystals appear in the liquid phase it is an indication that a solubility limit has been exceeded and crystals start to form which can cause different magnitude of fouling.

A picture of the tube after experiment 1, where the dry solid content were constantly increased to 51 % ds, can be seen in Figure 5-13.

Figure 5-13. Tube appearance after experiment 1.

There was not much contamination after this experiment. As seen in the figure the tube was still wet and was not considered to be fouled. It was important to separate real fouling and residual vinasse. Still, there was a small sand-like layer that could possibly have been some sort of crystals. The particle counter showed a vast increase in particles when the vinasse reached around 32 % ds, see Figure 5-14.

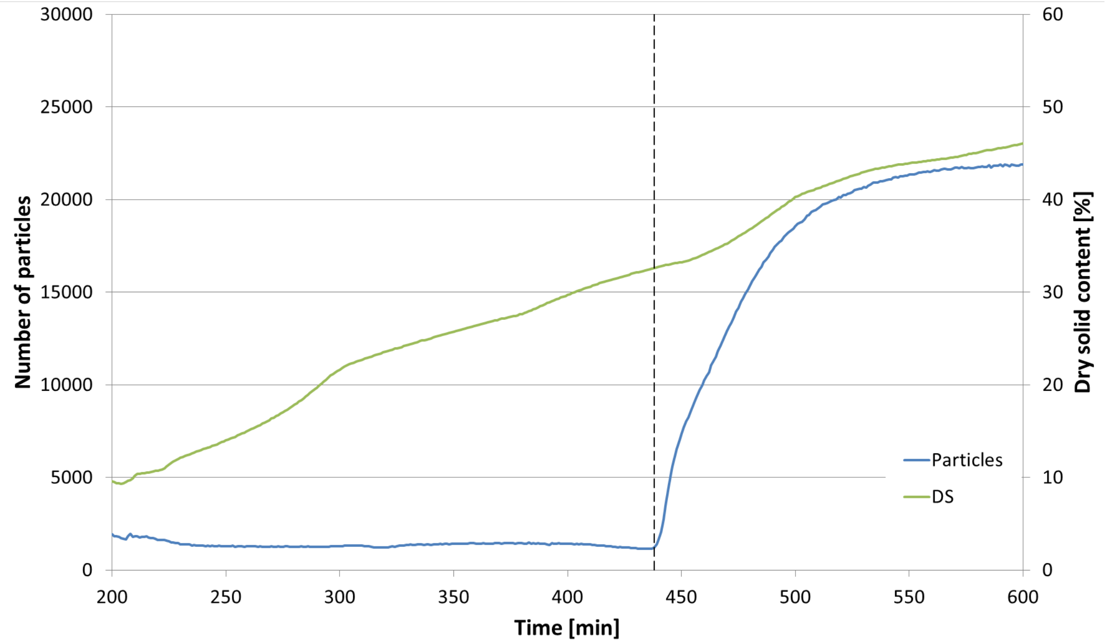

Figure 5-14. Number of particles and dry solid content in experiment 1. The vertical line indicates where the particles starts to form.

In experiment 2 there was no visible fouling and the particle levels were low throughout the whole experiment.

In experiment 3, a thin layer was formed on the tube, as can be seen in Figure 5-15. This appeared to be a crust that started to crack and fall off by itself. Also, the remaining crust, most likely consisting of crystals, was not difficult to dissolve in water. However, the number of particles was at a low level during the whole experiment.

Figure 5-15. Fouling on the tube after experiment 3.

The tube appearance after experiment 4, where the dry solid content was increased from 20 % to 30 % can be seen in Figure 5-16. In this experiment there was more fouling on the tube even thou it was shorter in time. But similar to the earlier experiment it was still easy to dissolve with water. Here an increase of the number of particles started at around 24 % ds as shown in Figure 5-16.

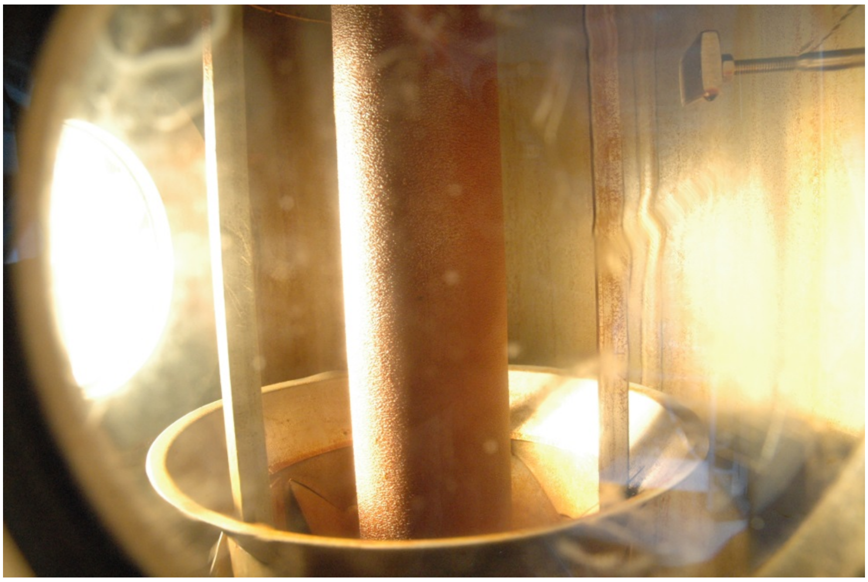

Figure 5-16. Fouling on the tube after experiment 4.

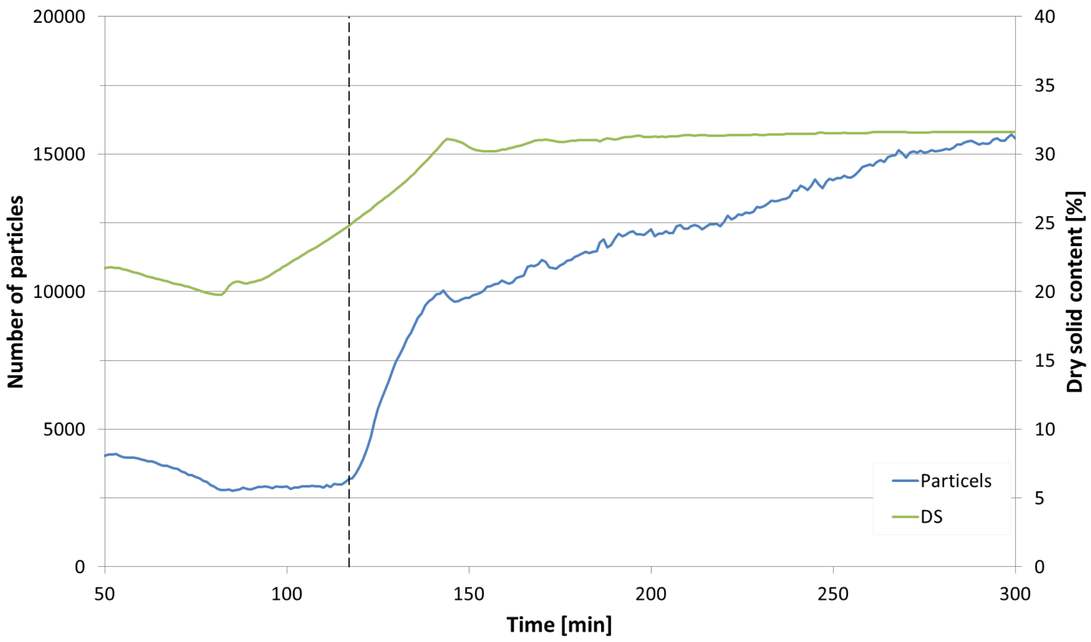

Figure 5-17. Number of particles (blue line) and ds (red line) in experiment 4, where particles starts to form at 24 % ds (vertical black line).

The first experiment with batch 2, experiment 5, was conducted during approximately 60 hours, to investigate fouling building up over a longer period of time. Already in the early stage of the experiment before stable conditions were established, the heat transfer started to drop substantially, as shown in Figure 5-8. When stable conditions where reached the heat transfer kept constant, indicating that most fouling build-up was during the start-up period. This was also the time when the temperature difference was 15 °C. However, not all the heat transfer drop occurred at the elevated temperature difference. It seemed like the heat transfer decreased when the dry solid content rapidly increased, which corresponds to when the feed pump fed less or no fresh vinasse. This implies that it could be something that is concentration dependent and is counteracted by the feeding of fresh vinasse.

Afterwards it could be seen that the tube was covered in a 2-3 mm thick red-brown soft material that, a short time after the experiment ended, turned in to dark brown with some sparkling dots, as can be seen in Figure 5-18. Samples of the coating and of the vinasse, before and after the time when it was believed the fouling started to form, were sent for analysis. The results of the chemical analysis can be seen in Appendix I.

Figure 5-18. Thick fouling layer after the long experiment 6, from 6.5 % to 30 % ds

The analysis showed that there was an enrichment of silicon, calcium and aluminum although the latter in small amounts. The organic part was not analyzed in detail but the ash content was 55.6 %, so a big part of the remainder was probably some sort of organic matter. It was believed that the substance was held together by the organic part with some crystals blended in.

The fouling layer on the tube was also hard to dissolve with water, when the equipment was cleaned, although it came off very easily with mechanical brushing. Some samples of it were put into small cups with different chemicals to observe the dissolving rates. The result after 24 hours at about 30 °C can be seen in Figure 5-19.

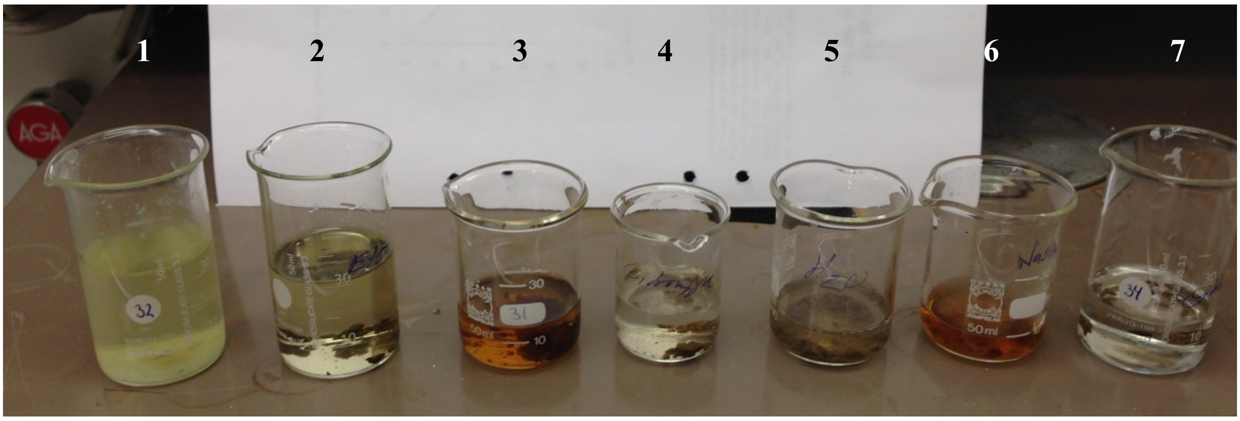

Figure 5-19. Different dissolution of the fouling layer on the tube. The different chemicals were: 1. Dishwasher detergent 2. Ethanol 3. Labwash 4. Citric acid 5. Water 6. Soduim hydroxide 7. Cyclohexane.

In Figure 5-19 it can be seen that none of the solutions had a very effective dissolution rate, although both labwash (number 3), which is an alkali detergent and sodium hydroxide (number 6) dissolved the fouling layer best. In an industrial process plant sodium hydroxide is more likely to be available, so in that it was determined that sodium hydroxide was most suitable for cleaning purpose in industrial use. In addition to the seven chemicals in Figure 5-19, potassium carbonate, was also tested. Unfortunately, the experiment failed and no obvious conclusion could be drawn about its dissolution rate of the tube fouling layer. However, since it is believed that potassium carbonate will be highly available at the evaporation plant it is strongly recommended that further experiments are done.

Since it was not chemically determined what the fouling substance consisted of, it was difficult to tell how and why the tube was heavily fouled in this experiment. One possible contributing factor could have been that the thermal load was higher during the startup, compared to the other experiments. A higher ΔT of 15 °C was used to save time to reach the target 30 % ds.

In the experiment 6, at the highest dry solid levels, the risk of highly viscous vinasse drying on the tube was too big, so water was used to wash it off quickly after the experiment was finished, thus removing the possibility for visual observation of fouling. During the experiment, the heavy vinasse made it hard to visually determine if there was any fouling on the tube. Hence, there was no observation of fouling layers from this experiment but the heat transfer in Figure 5-9 confirmed that there was no or negligible fouling. The particle counter still recorded an accumulation at around 34 % ds, see Figure 5-20.

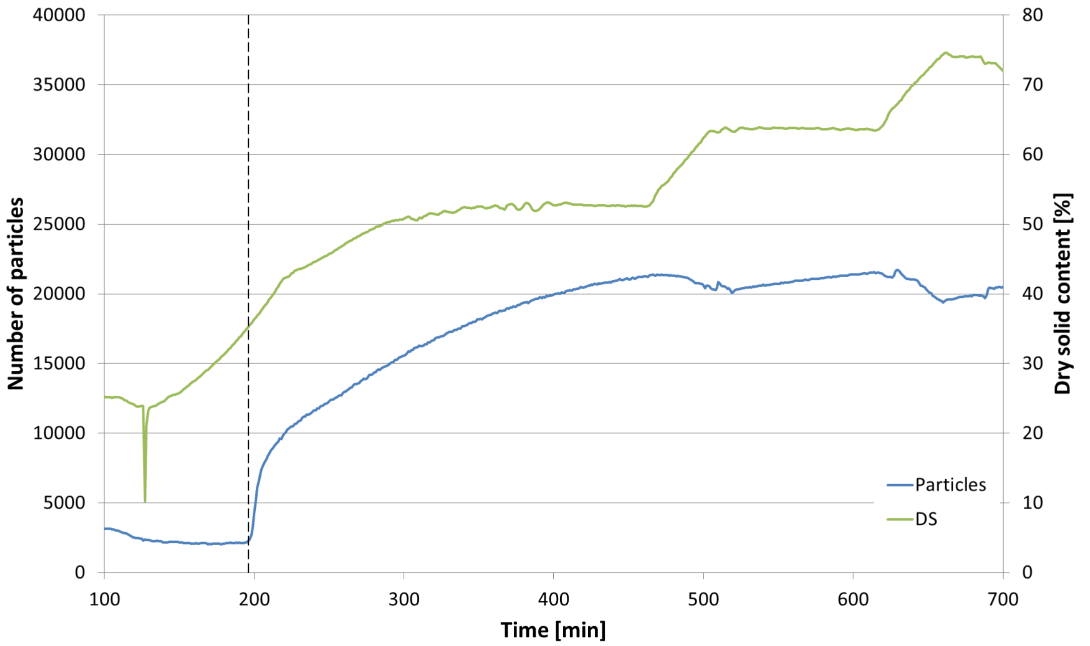

Figure 5-20. Number of particles and dry solid content versus time in the last experiment 6. Accumulation of particles at 34 % ds.

The conclusions of fouling in the experiments are that; no fouling was detected at the lowest concentrations up to 13 % ds. For higher dry solid contents most experiments showed a tendency to foul. The fouling layers were mostly quite thin but the experimental times were just a few hours and industrial evaporation plants will be built to run continuously. Most of the fouling layers were probably some sort of crystals that were easily dissolved in water. However, one case was a thick coating was formed and was difficult to dissolve and it was unclear exactly why. It was believed that the high temperature difference between the vinasse and the steam was one of the reasons for this fouling. If this happens in a real plant it could cause major problems.

It has been detected that a big increase in the number of particles present occurs somewhere in the range of 20-35 % ds. This implicates that this range can be extra critical for fouling. Why the increase in particles appears at 32-34 % ds in two experiments and at 24 % in another has not been determined. The temperature of the vinasse was 100 °C and had been stable for a longer period of time in all these experiments when the accumulation occurs.

No real tendency for foaming was detected during any of the experiments. In some experiments there was quiet a lot of bubbles but it did not form stable foam.

5.4 Condensate quality

During the experiments, a number of samples were taken of the vinasse condensate. Two of the samples were sent for chemical analysis and the results are presented in Table 5-2.

Table 5-2. Chemical analysis of vinasse condensate from experiment 1 and 5.

		Samples	
Compound	**Unit**	**K2**	**K502**
Hexanoic Acid	mg/L	<10	<10
Heptanoic acid	mg/L	<10	<10
COD	mg/L	1880	4930
Butyric acid	mg/L	<10	<10
Propionic Acid	mg/L	114	65
Furfural	mg/L	<20	<20
Etanol	mg/L	553	461
Formic Acid	mg/L	<100	<100
Acetic Acid	mg/L	<100	2500
Tot-S	mgS/L	<20	<20

The samples were taken from an early stage of the two experiments, minimizing the risk that the volatile components were evaporated before extraction. K2 was extracted during experiment 1 and K502 was extracted during experiment 5, thus one from each batch. The big differences between the two samples are the acetic acid and the COD. In K502 acetic acid constitutes a large share of the sample, thus increasing the COD substantially. One possible reason for the differences in chemical composition is that the samples were taken from two different batches. Depending on the COD restriction it is suggested that this is closely monitored to withhold the environmental criteria. Another constituent that contributes to the COD is ethanol. Ethanol is however the main product in the original sugar-cane process. Hence, there is a great value of extracting it with a stripper column in the evaporation process, thus increasing the ethanol yield and decreasing the environmental impact by reducing the COD.

6 Process design

Process Design

Based on the experimental results, a preliminary process design has been performed using an in-house calculation tool at Valmet Power. The results from the experiments indicated that the viscosity of vinasse increased exponentially at higher dry solid content than for black liquor and that the boiling point elevation was lower at higher dry solid content (above 30% ds). From the experimental data it was also decided to use the calculated correlations for the physical parameters in the design.

Based on the initial dry solid content of 10.2 % ds and a target of 70 % ds, the calculated evaporation capacity was 500 t/h, which corresponds to a vinasse flow rate of about 585 t/h, and the steam consumption 91 t/h at 3 bar absolute pressure. This flow is approximate and has also been estimated based on the previous volumes produced at ethanol plants involved in the Valmet project in South America. Also, this is to secure a yearly operation of the evaporation plant. Figure 6-1 illustrates the evaporation design.

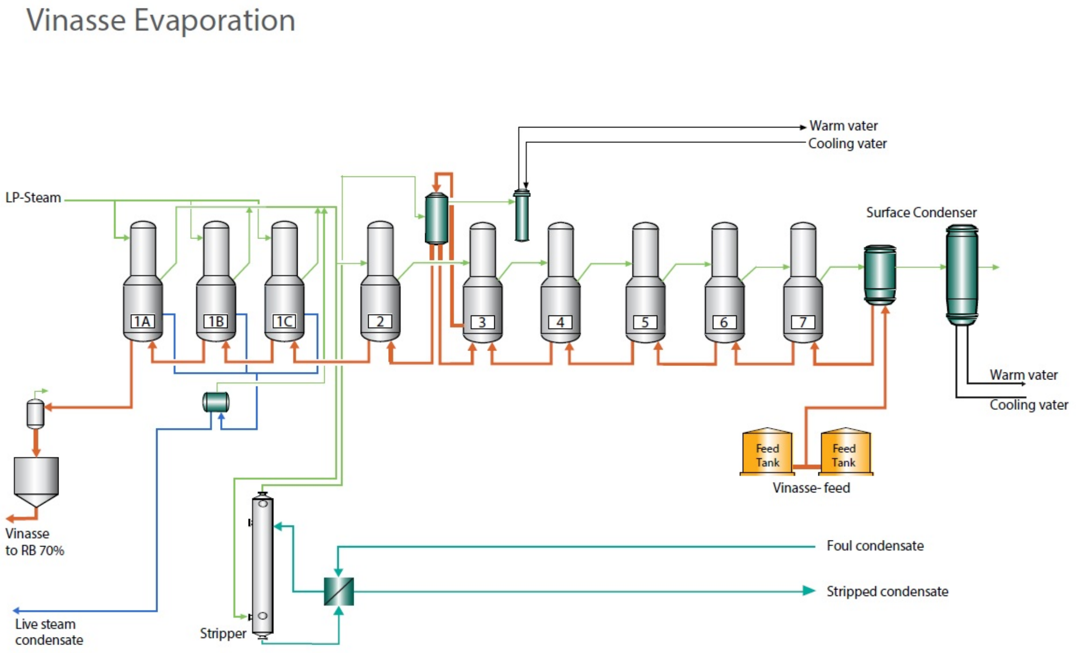

Figure 6-1. The preliminary process design. A seven effect evaporation plant with counter current flow. A stripper is included in the design to purify the condensate and retrieve part of the ethanol.

The design is based on previous experience on black liquor evaporation, the accessibility of steam and the fact that vinasse indicated lower viscosity and boiling point elevation. The lower values of the physical parameters also contributes to a possibility to decrease the heat transfer surface in each effect, thus the same number of effects can be used to a lower cost. On these bases and the probable level of initial dry solid content, the optimal number of effects was estimated to be seven (Wennberg & Wimby, 2013). The foundation for this is also a cost and capacity optimization and has its origin in efficient heat economy. The flow of the evaporation plant is counter-current, thus the steam is fed to the first effect and the vinasse is fed to the condenser where it is preheated, to decrease steam usage, before it is fed to the last (seventh) effect. This configuration is due to the low temperature of the feed-vinasse entering the evaporation plant, thus the temperature of the vinasse is increased in every subsequent effect and an efficient heat (steam) economy is established rendering in lower operation costs. Another important aspect taken to account in a counter-current design is the purity and temperature of the condensate, which has a significant role in an integrated evaporation plant. The purity of the condensate often determines if and where it can be reused in the process, which has been assessed in chapter 5.4. The stripper is used to purify the foul condensate, to be able to reuse it in some parts of the process and to meet certain environmental criteria of allowed carbon- or biological oxygen demand (COD or BOD) for effluent disposal.

In this particular process, originating from ethanol production, there is also a great value in extracting residual ethanol, thus the stripper has multiple functions and plays an important role in the evaporation plant. Based on the condensate quality found in Table 5-2, the amount of ethanol extracted from the vinasse was calculated to approximately 0.5 kg/t vinasse.

The total heat transfer area will be approximately 31 700 m^2 divided over the seven effects, excluding the reflux condenser, stripper and surface condenser.

Based on the experiments which showed fouling tendencies in an interval of 25-35 % ds, it is suggested to mix the feed vinasse with concentrated vinasse in order to bypass that region.

7 Conclusions

In this thesis it was shown that it is possible to evaporate vinasse up to a high dry solid content of 72 % ds. This corresponds to removing 97 % of the water in the original vinasse. This was done without any major difficulty and it therefore reasonable to believe that the dry solids content can be increased even further. The critical region where particles started to form was between 20-35 % ds. Most of the experiments showed no or minor fouling and had minimal effect on the heat transfer. The minor fouling layers were also proven to be easily soluble in water. No foaming was noticed during any of the experiments. However, one experiment showed heavy fouling in the critical region. It was believed that this was influenced by the high temperature difference between the vinasse and the steam in the first stage of the experiment. The heavy fouling was insoluble in water and a series of experiments with different chemicals were conducted and the fouling was best soluble in alkaline conditions. It is suggested that, in the designing of an evaporation plant, the critical region must either be very closely monitored or built around, i.e. mixing heavy vinasse with light vinasse to increase the feed concentration to the evaporator.

Correlations for density, refractive index and the heat transfer coefficient have been established as a function of dry solid content at 100 °C. A correlation for boiling point elevation as a function of dry solid content and temperature has also been developed. The density and refractive index correlations were concluded to be equally good as a measurement tool in measurement of dry solid content. The correlations could be used as a basis in the design and construction of an industrial evaporation plant.

The change in physical parameters during different conditions was measured. The boiling point elevation and viscosity were determined to be slightly lower than for black liquor at the same dry solids content. The heat transfer was compared to a general falling film heat transfer model and it was seen that the correlation did not show a high agreement with the measured heat transfer for vinasse. Finally, the boiling point elevation and the viscosity contribute to a better heat economy than for black liquor. Thus, there is a possibility, in the process design, to decrease the heat transfer area compared to black liquor.

8 Further Research

Based on the experiments conducted and the results in this thesis, the following further research is suggested:

- Determine viscosity and BPE in laboratory scale at different temperatures to minimize any error in the measurements presented here.
- Additional experiments with increasing dry solid content at different temperatures to retrieve more data points for different dry solid contents.
- Mapping of fouling tendencies in the critical region 20-35 % ds. Test additional vinasse from different process plants to investigate possible differences in particle accumulation at different dry solid content.
- Evaluate cost versus efficiency of evaporating the vinasse to dry solid content above 70 %. It might be economically beneficial to reduce the water content further to improve combustion but also transportation costs.
- Investigate fouling tendencies at temperatures above 100 °C. Since the first effects in an industrial evaporation process will have higher temperatures and temperatures higher than 100 °C has not been investigated in this thesis.
- Investigate the influence of wetting degree to check if it possibly can affect the heat transfer.

9 References

Adams, T. N. o.a., 1997. *Kraft Recovery Boilers.* Atlanta: TAPPI PRESS.

Billet, R., 1989. *Evaporation technology : principles, applications, economics.* Cambridge: VCH Verlagsgesellschaft.

Braunbeck, O. A. & Cortez, L. A., 2000. SUGAR-CANE CULTURE AND USE OF RESIDUE. i: F. Rosillo-Calle, S. V.Bajay & H. Rothman, red. *Industrial Uses of Biomass Energy.* London: CRC Press, pp. 119- 139.

Christofoletti, C. A. et al., 2013. Sugarcane vinasse: Environmental implication of its use. *Waste Management.*

Coulson, J. & Richardson, J., 2005. *Chemical Engineering.* Oxford: Butterworth-Heinemann.

Ekroth, I. & Granlund, E., 1999. *Tillämpad Termodynamik.* u.o.:u.n.

Gourdon, M., 2009. *Sodium Salt Scaling in Black Liquor Evaporators.* Gothenburg: Chalmers University of Technology.

Hajinezhad, A. & Senge, B., 2007. Fliesseigenschaften und wärmephysikalische Kennwerte von Rübenvinasse. *Zuckerindustrie,* 132(9), pp. 704-709.

Johansson, M., 2008. *Heat Transfer and Hydrodynamics in Falling Film Evaporation of Black Liquor.* Gothenburg: Chalmers University of Technology.

Karlsson, E., Gourdon, M., Olausson, L. & Vamling, L., 2013. Heat transfer for falling film evaporation of black liquor up to very high. *International Journal of Heat and Mass Transfer,* Issue 65, pp. 907-918.

Kassberg, M., 1994. *Lutindunstning och biprodukter.* Markaryd: Skogsindustrins Utbildning i Markaryd AB.

Metso Power AB, 2013. *Paper and Pulp: Chemical Recovery: Evaporators: Evaporators brochure (pdf).* [Online]
Available at:
http://www.metso.com/pulpandpaper/recovery_boiler_prod.nsf/WebWID/WTB-090513-22575-07DFC?OpenDocument&mid=F3BCF67AB00D524EC22575B00047C0E3
[Använd 9 December 2013].

Minton, P. E., 1986. *Handbook of Evaporation Technology.* Park Ridge(New Jearsey): Noyes Publications.

Renewable Fuel Association, 2013. *RFA - Renewable Fuel Association.* [Online]
Available at: http://www.ethanolrfa.org/
[Accessed 28 October 2013].

Schnabel, G. & Palen, J., 1998. *Wärmeübergang an senkrechten berieselten Flächen.* 8th red. u.o.:VDI Wärmeatlas.

Schnabel, G. & Schünder, E. U., 1980. Wärmeübergang von senkrechten Wänden an nichtsiedende und siedende Rieselfilme. *Heat Transfer from Vertical Walls to Falling Liquid Films with or Without Evaporation,* Volym 14, pp. 79-83.

Theliander, H., 2008. The recovery and burning of black liquor. i: *The Ljungberg Textbook, Cellulose Technology.* u.o.:u.n.

Wennberg, O. & Wimby, M., 2013. *Personal Conversation.* Metso Power AB, Gothenburg: s.n.

Välimäki, Erkki;, 2012. *Chemical Analysis of Sugar Cane Vinasse.* u.o.:Metso Power.

Appendix I: Analytical results from MoRe Research Örnsköldsvik AB.

TEST RESULTS

Assignment: **KA20132573**

		V501	*V503*	*Tube fouling from exp 5*	*K2*	*K502*
Ash 525°C	%	40,0	38,8	55,6	-	-
Sulfate	g/L	10,9	15,6	-	-	-
Silicon	mg/kg	4750,0	4500,0	18900,0	-	-
Hexanoic Acid	mg/L	-	-	-	<10	<10
Heptanoic Acid	mg/L	-	-	-	<10	<10
Sulfite	g/L	1,41	2,5	-	-	-
Carbonate	g/kg	-	-	47	-	-
Carbonate	mg/kg	<15	<15	-	-	-
COD	mg/L	-	-	-	1880	4930
Butyric acid	mg/L	-	-	-	<10	<10
Propionic Acid	mg/L	-	-	-	114	65
Iron	mg/kg	97	173	296	-	-
Aluminium	mg/kg	6,6	9,4	131	-	-
Potassium	mg/kg	22000	38300	102000	-	-
Magnesium	mg/kg	1439	2567	3659	-	-
Calcium	mg/kg	4320	5870	50060	-	-
Arabinose	g/kg TS	-	-	4,58	-	-
Arabinose Tot	g/L	1,82	3,23	-	-	-
Xylose	g/kg TS	-	-	2,49	-	-
Xylos Tot	g/L	0,997	1,70	-	-	-
Glucose	g/kg TS	-	-	31,0	-	-
Glucose Tot	g/L	10,9	18,2	-	-	-
Mannose	g/kg TS	-	-	4,46	-	-
Mannose Tot	g/L	1,55	2,70	-	-	-
Furfural	g/L	-	-	-	<0.02	<0.02
Etanol	mg/L	-	-	-	553	461
HMF	g/L	-	-	-	<0.02	<0.02
Formic Acid	g/L	-	-	-	<0.1	<0.1
Acetic Acid	g/L	-	-	-	<0.1	2,5
Zinc	mg/L	1,21	1,74	3,68	-	-
Dry Substance	%	18,5	32,1	71,0	-	-
Galactose Tot	g/L	2,27	4,03	-	-	-
Galactose	g/kg TS	-	-	6,64	-	-
FTIR		-	-	>>	-	-
Scanning Electron Microscopy		-	-	>>	-	-
Sodium	mg/kg	861	1322	3572	-	-
Phosphor	mg/kg	210	380	900	-	-
Tot-S	gS/kg	3,4	3,8	25,6	-	-
Tot-S	gS/L	-	-	-	<0.02	<0.02

Appendix II: Full chemical analysis of vinasse and kraft pulp

(Välimäki, Erkki;, 2012)

				Vinasse					Kraft
Dry substance		%	SCAN-N 22:77	8,4	**Dry substance**		%	SCAN-N 22:77	19,7
pH				4,5					
In dry matter					**In dry matter**				
ash		%	KCL 59:83	32,9	**ash**		%	KCL 59:83	47,6
carbon	C	%	ASTM D 5373	31,8	**carbon**	C	%	ASTM D 5373	34,9
hydrogen	H	%	ASTM D 5373	4,9	**hydrogen**	H	%	ASTM D 5373	3,4
nitrogen (Kjeldahl)	N	%	SFS 5505 modif.	1,25	**nitrogen**	N	%	ASTM D 5373	0,1
sodium	Na	%	SCAN-N 37:98	0,1	**sodium**	Na	%	SCAN-N 37:98	20
potassium	K	%	SCAN-N 37:98	13,5	**potassium**	K	g/kg	SCAN-N 37:98	1,1
zinc	Zn	mg/kg	SCAN-N 38:10	260	**zinc**	Zn	mg/kg	SCAN-N 38:10	2,3
iron	Fe	mg/kg	SCAN-N 38:10	670	**iron**	Fe	mg/kg	SCAN-N 38:10	7,8
manganese	Mn	mg/kg	SCAN-N 38:10	130	**manganese**	Mn	mg/kg	SCAN-N 38:10	2,7
vanadium	V	mg/kg	SCAN-N 38:10	5,0	**vanadium**	V	mg/kg	SCAN-N 38:10	< 5
copper	Cu	mg/kg	SCAN-N 38:10	48	**copper**	Cu	mg/kg	SCAN-N 38:10	1,1
aluminum	Al	mg/kg	SCAN-N 38:10	150	**aluminum**	Al	mg/kg	SCAN-N 38:10	13
magnesium	Mg	g/kg	SCAN-N 38:10	6,1	**magnesium**	Mg	mg/kg	SCAN-N 38:10	110
silicon	Si	g/kg	SCAN-N 38:10	3,8	**silicon**	Si	mg/kg	SCAN-N 38:10	13
phosphorus	P	g/kg	SCAN-N 38:10	1,6	**phosphorus**	P	mg/kg	SCAN-N 38:10	51
calsium , tot	Ca	g/kg	SCAN-N 38:10	26	**calsium, tot**	Ca	mg/kg	SCAN-N 38:10	480
calsium , soluble	Ca	g/kg	SCAN-N 38:10	25	**calsium, soluble**	Ca	mg/kg	SCAN-N 38:10	430
sulfur	S	%	SCAN-N 38:10	3,1	**sulfur**	S	g/kg	SCAN-N 38:10	52
clorine	Cl	%	AOX-instrument	1,6	**clorine**	Cl	mg/kg	AOX-instrument	440
oxygen	O	%	calculated value	43,8					
chloride	Cl^-	%	titrimetric method	1,4					
carbonate	$CO_3^=$	%	SCAN-N 32:98	1,0	**carbonate**	$CO_3^=$	%	SCAN-N 32:98	5,6
sulfate	$SO_4^=$	%	KCL 71:81	n.d.	**sulfate**	$SO_4^=$	%	KCL 71:81	<0,5
residual alkali	NaOH	%	SCAN-N 33:94	n.d.	**residual alkali**	NaOH	%	SCAN-N 33:94	5,2
lignin		%	UV-spektrofotometer	22,8	**lignin**		%	UV-spektrofotometer	38,2
fibre content		mg/kg	SCAN-N 22:96	30,8	**fibre content**		mg/kg	SCAN-N 22:96	72,1
methanol	CH_3OH	mg/kg	Gas chromatograph	n.d.	**methanol**	CH_3OH	mg/kg	Gas chromatograph	1200
ethanol	C_2H_5OH	g/kg	Gas chromatograph	54	**ethanol**	C_2H_5OH	mg/kg	Gas chromatograph	220
COD		g/kg	SFS 5504:1988 modif.	220	**COD**		g/kg	SFS 5504 modif.	
inorg./org.-ratio			KCL 61:83	0,38	**inorg./org.-ratio**			KCL 61:83	0,5
gross calorific value		MJ/kg	Automatic calorimeter	14,18	**gross calorific value**		MJ/kg	Automatic calorimeter	13,98
net calorific value		MJ/kg		12,14	**net calorific value**		MJ/kg		11,60
Net calorific value as sample received		MJ/kg		-1,21	**Net calorific value as sample received**		MJ/kg		0,30
Dynamic viscosity		mPa*s	DS 55....80 %, T 117 °	ok	**Dynamic viscosity**		mPa*s		
BPR			DS 55....85 %	ok	**BPR**				ok
n.d = Not detetected									