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Modelling the Mass Transfer of N-Methylmorpholine N-Oxide during the Washing Process of a Cellulose Filament Bundle

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Affidavit

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Abstract

In this master thesis, the mass transfer of N-Methylmorpholine N-Oxide during the washing step of a filament production plant is investigated. The main point of interest is the identification and quantification of all influencing variables.

Experiments were conducted on a pilot plant of the industry partner one-A engineering Austria. The performance of the washing plant was measured at different wash water temperatures, wash water volume and filament titre. The results show the expected increase of the washing performance when increasing the wash water temperature as well as increasing the wash water volume or decreasing the filament titre.

However, inconsistencies in the upstream parts of the pilot plant caused a variation of the filament towing speed in the washing plant, which make comparison between the different sets of experiments invalid. Additionally, the sampling locations for the determination of the N-Methylmorpholine N-Oxide concentration in the washing water were flawed which caused a significant deviation of the measured extracted solvent in the washing water to the total introduced solvent at the start of the washing plant.

Some conclusions could still be drawn:

- On average about 90 percent of the solvent present in the filament at the start of the washing plant is removed in the first washing stage, and a further 90 percent of the remaining solvent is removed in the second. This leads to the conclusion that the washing stages in the pilot plant are dimensioned oversized.
- With a solvent concentration in the washing water of the final washing stage at about 200 ppm NMMO during most experiments, no solvent flux was recorded in that washing stage at all. However during the experiments the filament product showed an average solvent concentration of one percent, leading to the conclusion that there is a significant mass transfer resistance inside the filament.
- An increase of the wash water volume by 70% was able to increase the total solvent extracted in the first washing stage from 89.2% to 91.5% where an increase of the temperature from 20°C to 55°C was able to increase the solvent extracted from 89.2% to 93.0%. While the influence of the temperature is more significant, it is still possible to optimize the washing effect by optimizing the fluid current.

Contents

List of Symbols and Abbreviations

Symbols

A	m	Mass transfer surface
$\overline{\Delta c}$	mol/m^3	Logarithmic concentration difference
C		Dimensionless multiplier in Sherwood equation
D	m^2/s	Diffusion coefficient
d	m	Specific length, average filament fibre diameter
IA_{HPLC}	$mAU \cdot min$	Integration area of a HPLC measurement
L	m	Length of one washing stage
$\dot{m}_{Carryover}$	kg/s	Fluid carryover from the spinning bath to washing stage 2
$\dot{m}_{Dope}$	kg/s	Mass flow rate of dope conveyed by the spinning pump
$\dot{m}_{Filament}$	kg/s	Mass flow rate of washed filament produced
$\dot{m}_{Overflow}$	kg/s	Mass flow rate of solvent loaded water removed from the spinning bath
$\dot{m}_{SPB}$	kg/s	Mass transfer rate of solvent removed from the filament in the Spinning Bath
$\dot{m}_{Stage\,i}$	kg/s	Mass transfer rate of solvent removed from the filament in washing stage i
$\dot{m}^{*}_{Stage\,i}$	kg/s	$\dot{m}_{Stage\,i}$ normalized using the spinning pump throughput of NMMO
$\dot{m}^{**}_{Stage\,i}$	kg/s	$\dot{m}^{*}_{Stage\,i}$ normalized using the sum of the mass transfers in all four washing stages
$\dot{m}_{Water}$	kg/s	Mass flow rate of demineralized water introduced into the spinning bath
m,n		Exponents in Sherwood equation
N		Number of fibres in a filament bundle
$\dot{n}_{NMMO}$	mol/s	Mass transfer rate of NMMO
n_{SP}	rpm	Spinning pump speed
n_{Pull}	rpm	Pulling speed of the last pulley in the washing plant

Symbols

Re		Reynolds number
Sc		Schmidt number
Sh		Sherwood number
Td	tex	Titre Denier
t_{Start}	s	Time when an experiment starts
t_{End}	s	Time when an experiment ends
$U_{relative}$	m/s	Velocity difference between fibres and WW bulk
V_{Stage}	L	Volume of one washing stage
$V_{SP,rev}$	cm^3/rev	Volume of dope conveyed per revolution of the spinning pump
$w_{i,NMMO}$	wt.%	Solvent mass fraction in mass flow i
$w_{i,Cell}$	wt.%	Cellulose mass fraction in mass flow i
β	m/s	Mass transfer coefficient
ν	m^2/s	Kinematic viscosity of the washing water
ρ_{Dope}	g/cm^3	Density of the dope
ρ_{WW}	g/cm^3	Density of the washing water
$\varphi_{Filament}$	wt.%	Relative humidity of a filament

Abbreviations

BP	Balance point
LL	Lower level
NMM	N-Methylmorpholine
NMMO	N-Methylmorpholine N-Oxide
NMMO MH	N-Methylmorpholine N-Oxide Monohydrate
MM	Measurement
SP	Sample point
UL	Upper level
WW	Washing water

1. Introduction

1.1. The Aim of this Master Thesis

The aim of this master thesis is the modelling of mass transfer of the solvent in a filament during the washing step of the fibre production. All factors influencing the mass transfer should be determined and their respective influence investigated to derive an equation able to depict the mass transfer as a function of the relevant factors.

In the short term, this equation can be used to reach optimal dimensioning, in regards to energy and water consumption, as well as investment and running costs, of the washing step in the production line of a filament producing factory.

In the long term, the information gained can be used as a basis to investigate specific influencing factors in detail to further optimise the process.

1.2. Initial Research and Points of Interest

In order to first identify possible influencing factors, a comprehensive literature research was conducted. While several factors influencing the mass transfer coefficient were identified, very seldom is the washing step even mentioned in the research. It seems that the majority of the topical research is focused on the forming of the filament in the spinneret and the spinning bath.

Several conclusions, however, could still be drawn. The drawing speed, which is identical (with corrections for shrinkage of the fibre) in the entire process, influences the crystallisation of the cellulose and thereby the diffusion coefficient of the solvent. It is also clear that the speed at which the fibre moves through the fluid changes the Reynolds number of the System, however a correlation to the Sherwood number is still unknown. To what extend the process is limited by the diffusion coefficient of the solvent in the filament will be determined over the course of this work.

By the same token, the influence of the velocity of the washing fluid will be investigated. Another important factor for any diffusion controlled system is the temperature. While the spinning bath temperature is defining for the crystallisation of the cellulose, the influence of the washing temperature on the fibre after the majority of the crystallisation has already occurred does not seem to be a topic that has been investigated thoroughly. As part of this master thesis, the influence of the temperature in the washing stage on the mass transfer, independent from the temperature in the spinning bath, will be investigated. Attention will be paid if and to what extend this change in temperature also influences fibre qualities. The last known determining factor is the fibre thickness, or titre. To what extend the diffusion changes, when the fibre diameter is varied, will be investigated.

1.3. The General Approach

For the purpose of investigating the aforementioned points of interest, it is possible to take measurements in a pilot plant powered by the industrial partner one-A engineering Austria GmbH. Over the course of this work, several series of experiments will be conducted, with the purpose of isolating and quantifying the defining factors in the washing process. The final step is an attempt to optimise the process using all gathered data, and derive a system specific equation that can be used to convey all the data gathered.

2. Literature Research

This chapter serves as an introduction into the theoretical part behind this master thesis. Previously conducted research on the field was examined, and significant details are summarised here. Some details directly impact the execution of this master thesis, others merely serve as a foundation or background information.

2.1. The Cellulose - N-Methylmorpholine N-Oxide - Water System

2.1.1. N-Methylmorpholine N-Oxide Hydrates and their use as Solvents for Cellulose

N-methylmorpholine N-oxide, in future called NMMO, has three crystalline hydrates with water, a monohydrate, a hydrate with 5 H_2O to 2 NMMO and a hydrate composed of 8 water molecules per NMMO molecule [1]. In the Lyocell Process (further described in chapter 2.2), the monohydrate finds use as a solvent for cellulose.

The $1H_2O$-1NMMO hydrate (86.7 wt% NMMO, 13.3 wt% H_2O) is stable and has a melting temperature between 72 and 78°C, which requires the entire process to be tempered above this critical range. The differences in the sources stem from the measuring method (all were DSC), where very minor changes in water content have a strong effect on DSC peak position [1].

Cellulose is a polar molecule with several hydroxyl groups leading to a strong hydrogen bonding ability. As a result, a polar solvent like water would be expected to be able to dissolve Cellulose. This is not the case, however, and researchers are not certain on the exact reason as to why this is the case. In general, no overlaying reason has been found as to why some solvents work and some do not, and research into possible solvents is always done on an empirical case to case basis [2].

The current consensus is that cellulose has a strong network of intermolecular hydrogen bonds, which must be disrupted without further breaking down the molecule in order to properly dissolve it. One of the first commercially used solvents was NMMO, which has the ability to dissolve up to 30% of its mass of high molecular mass cellulose without further derivatization [3].

NMMO is to date the standard solvent used in the Lyocell process. Other upcoming solvents are groups of Ionic Liquids that have similar solvent abilities as NMMO, even though they have little in common otherwise [4].

2.1.2. Dissolution of Cellulose with NMMO

In general, the cellulose is pretreated with an alkaline prior to the dissolution process to disrupt the crystalline structures and allow for an easier access of the solvent later on. This is called the activation step [5].

The dissolution then proceeds in several steps. First the diffusion of the solvent into the fibre leads to a swelling and ballooning of the fibres, as the solvent induces changes into the molecular order by overcoming to an extent the intermolecular interactions among the macromolecules [5]. Then the fibre starts to fragment until it is completely dissolved [6].

2.1.3. From Slurry to Dope to Fibre

At the point where complete wetting and swelling of the fibres takes place, the cellulose-solvent mixture is called a slurry [7]. Following this, water is removed to move the slurry into the solubility range for cellulose, most commonly in vacuum to keep the temperature below 120°C and minimize a degradation of the solvent.

When the cellulose is completely dissolved and sufficient water has been removed, the solution is called the dope. Dope generally has a mass fraction of NMMO between 70 and 80 wt.%, a cellulose fraction of 8 to 15 wt.% and the rest water.

In the spinning bath, the dope is submerged in water, reducing the NMMO concentration and causing coagulation. In the following washing plant, the remaining solvent is extracted, and the remaining wet filament is dried to remove the majority of the water content. In figure 2.1, the path from slurry to the finished fibre is shown in a ternary phase diagram.

2.2. The Lyocell Process

2.2.1. General Information

'Lyocell' is a trade name registered with the US FTC as a subcategory of 'Rayon' for a fibre product made from cellulose, in which no substitution of the hydroxyl groups of the cellulose takes place and no chemical

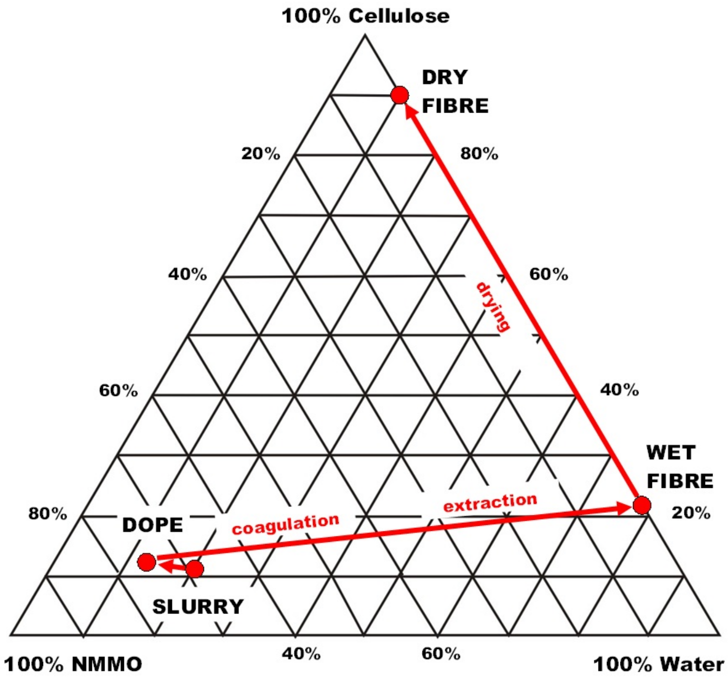

Figure 2.1.: This figure shows the path from slurry to dope to the finished cellulose fibre according to [7].

intermediates are formed. The basic process was developed in the 1970s by Akzo Nobel and first implemented by both Courtaulds and Lenzing AG [8]. Since then, the process has been innovated upon, and new derivatives of the original process are still being worked upon.

2.2.2. The Simplified Production Process

In the Lyocell process, cellulose is prepared for dissolution using various chemicals to improve the initial quality of the raw material. The cellulose is then mixed with a solvent. Generally NMMO monohydrate is used, however in recent years Ionic Liquids have also gained relevance as competitive solvents [4]. In this thesis, NMMO is used as the solvent, and when not otherwise mentioned, the word solvent refers to NMMO.

Water is usually introduced together with the cellulose and as a part of the solvent. The mixture is called the slurry. In order to dissolve the cellulose fibre, the water content has to be reduced. This is done by distillation under vacuum to protect the solvent from thermal destruction. The resulting dope produced in the Lyocell process is highly viscous and solidifies at room temperature, adding to the complexity of the process.

In the spinneret, the spinning mass is pressed through a perforated plate by the spinning pump, where it forms a fibre as it passes an air gap to fall into a spinning bath. Usually the fibre is pulled through the entire following process by a winder, from the spinning bath through the washing and drying station. Generally water is used to remove the NMMO from the fibre, because it does not damage the cellulose, and can easily be separated again from both fibre and solvent. A simplified flowsheet of the process can be found in figure 2.2.

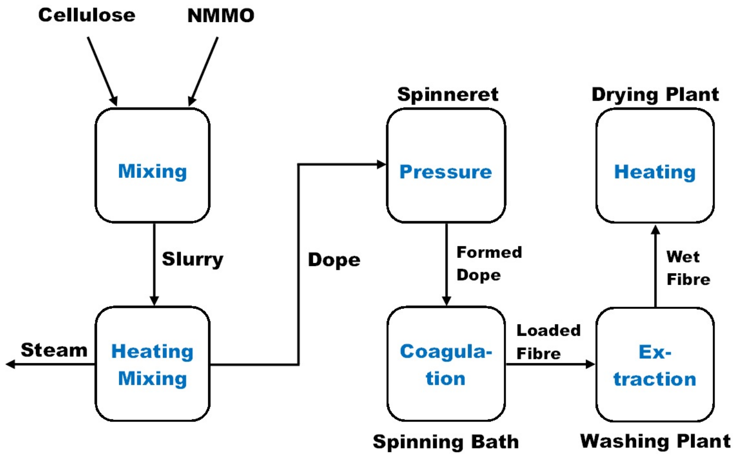

Figure 2.2.: In this flowsheet the simplified Lyocell Process is shown.

2.3. Cellulose Regeneration

The way cellulose is regenerated from the dope is a major factor in this work. As previously established, the forces acting upon the polymer solution determine the qualities of the final product. In order to investigate the process of cellulose precipitation and fibre forming, research into a multitude of effects has been done.

2.3.1. Cellulose Precipitation in Non-Spinning Conditions

One experimental setup used to map the properties of dope is a simple diffusion experiment. In this setup, an at room temperature solid sample of dope is immersed in distilled water and observed [9].

Alternatively the sample is molten at 90°C. The experiment shows that the diffusion of water into the sample is faster by a factor of ten than the diffusion of the NMMO outwards, leading to a swelling of the sample [10]. The precipitation functions according to spinodal decomposition at decreasing NMMO and increasing cellulose concentration in the dope.

The end result is a porous skin and a structure containing finger-like voids in the bulk of the sample [9].

2.3.2. Cellulose Precipitation in the Spinning Process

Another experimental setup has far more relevance for this work. In this setup, a fibre is spun at standard process parameters and the concentration of NMMO within the fibre in the spinning bath is observed at different washing times [11].

In order to determine the NMMO concentration in the fibre after specific times, the experiment is repeated several times. After it has travelled for a specific distance, the fibre is removed from the spinning bath, carefully dried, weighted and put into distilled water for a set period of time. Then the NMMO concentration in the water can be determined and the concentration in the fibre calculated.

This experiment shows that there are two separate diffusion regimes at play. First the diffusion takes place fairly rapidly, draining up to 60% of the NMMO in about one second. After that, the diffusion slows down abruptly by a factor of 10, reaching a diffusion coefficient in the region of $4 - 8 \cdot 10^{-7}$ cm^2/s [11]. This leads to the conclusion that, at a certain cellulose concentration in the dope, the filament walls solidify, vastly increasing the diffusion resistance towards the centre of the fibre.

3. Modelling and Determination of the Mass Transfer Coefficient

3.1. Suspected Influencing Factors and their Determination

The first step to the modelling of the mass transfer coefficient is the evaluation of possible influencing factors. The next step is to derive a method testing those assumed factors. Finally experiments on the pilot plant will allow the quantification of those factors and lead to a final model for the mass transfer coefficient.

The first factor known to influence any diffusion-controlled system is the temperature. As with any other similar system, the mass transfer is expected to increase with the temperature. Experiments with otherwise identical settings and a variable temperature will allow the determination of this increase.

Next is the motion of the system. While the majority of the mass transfer resistance is expected to be concentrated in the filament, the motion of the fluid around the filament fibres can significantly impact the mass transfer. Generally this is evaluated through variation of the velocity difference between the fluid bulk and the surface of the filament fibre.

Connected to the significance of the fluid velocity is the size of the filament bundle. In a bundle with a large number of fibres, the mass transfer from the centre of the bundle to the outside is expected to be impeded by the surrounding filament fibres. Depending on the fluid velocity it is also possible that the relative velocity between the fluid and the fibres varies depending on the location in the bundle. One way to test this theory is to vary the number of fibres in the bundle, however the execution of this is impractical in this pilot plant. Instead the titre will be varied, leading to a change in fibre diameter, which will have an impact on the internal mass transfer resistance. This influence is expected to lead to a correction factor for the mass transfer surface.

The crystalline structure of the filament fibre changes with the solvent concentration in the fibre [12]. This is also expected to have an impact on the mass transfer coefficient at different washing stages. In this setup, however, that impact is indistinguishable from the effect of a decreasing concentration difference Δc, and will not be further investigated.

It is known that the water transfer from the fluid into the fibres is faster than solvent transfer in reverse by a factor of ten [10]. This leads to a swelling of the filament as it is saturated with water. During the washing process, the fibre is pulled over rolls three times per washing stage as it changes directions. It is unknown whether or not the mechanical forces acting upon the fibre cause an extraction and subsequent renewal of the saturated water in the fibre. The pilot plant used in this thesis does not allow for a quantitative determination of this effect, however through measurement of the NMMO concentration found in the splashing water at the rerouting rolls it should be possible to determine if the effect is present at all.

3.2. The General Approach

In general the mass transfer by diffusion from a system in motion is modelled using the equation

$$\dot{n}_{NMMO} = \beta \cdot A \cdot \overline{\Delta c} \tag{3.1}$$

Here, $\dot{n}_{NMMO}$ is the rate of transferred solvent in moles per second, A is the transfer surface and $\overline{\Delta c}$ the logarithmic concentration difference. Using the experimental data, the mass transfer coefficient β remains the only unknown and can be determined separately for every experiment.

A Sherwood approach is useful to connect these separate findings in a dimensionless equation. The most simple equation is

$$Sh = \frac{\beta \cdot d}{D} = C \cdot Re^n \cdot Sc^m \tag{3.2}$$

with the Reynolds and Schmidt numbers defined as:

$$Re = \frac{U_{relative} \cdot d}{\nu} \tag{3.3}$$

$$Sc = \frac{\nu}{D} \tag{3.4}$$

A set of experiments with a constant Reynolds number (=constant drawing speed and fluid throughput), as well as a set with a constant Schmidt number (=constant temperature) is used to determine the exponents m and n respectively, with the constant C as the last unknown determined by the average of all experiments.

3.3. Definitions and Dependencies in this Approach

In this subsection, the parameters used in the modelling of the mass transfer coefficient are evaluated in further detail, and relevant dependencies are noted.

The transfer surface A used in equation (3.1) is defined as $A = N \cdot d\pi L$. N is the number of single filament fibres in the bundle, 900 for all experiments done in this thesis, and L is the length of the relevant washing stage.

The logarithmic concentration difference $\overline{\Delta c}$ is defined in equation (3.5).

$$\overline{\Delta c} = \frac{\Delta c_H - \Delta c_L}{ln\left(\frac{\Delta c_H}{\Delta c_L}\right)} \tag{3.5}$$

The components are shown in equation (3.6) and (3.7) and explained in figure 3.1.

$$\Delta c_H = c_{Fil,NMMO,In} - c_{WW,NMMO,In} \tag{3.6}$$

$$\Delta c_L = c_{Fil,NMMO,Out} - c_{WW,NMMO,Out} \tag{3.7}$$

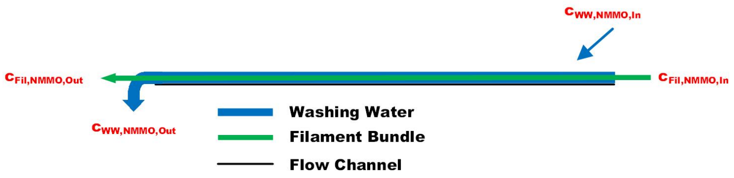

Figure 3.1.: Sketch of the contact between filament and washing water.

The logarithmic concentration difference is determined through measurements of the concentration of the washing water during the experiment. The concentration of NMMO in the washing water $c_{WW,NMMO,In}$ during the standard experiments is unsteady and rises at a close to constant rate. Because of this, the average solvent concentration in the washing water during the experiments is averaged from start to the end.

The concentration of the filament at the end of a washing stage is calculated from the measured starting concentration minus the measured transferred solvent. The calculated concentration is an average in the entire filament bundle. It is expected that the fibres on the outside of the filament bundle impede the mass transport to the centre of the bundle. Whether or not this has a significant effect on the mass transport overall has to be determined.

In order to use the logarithmic concentration difference as shown here, the system to be evaluated has to be at a steady state. Assumptions were made about the expected solvent concentrations in the washing plant at the end of the experiments, which allow for the application of this approach here. More can be found in chapter 5.1.1.

The diameter d in equations (3.2) and (3.3) is the mean diameter of a single filament fibre as calculated from the titre. It is well known that, in reality, the apparent diameter will be different, since the calculated dimension only accounts for the cellulose content. Especially at the beginning, the NMMO and water content will significantly increase the dimension of every single fibre, however it is not possible to measure the real dimensions during the washing process in this configuration.

The diffusion coefficient D is a function of temperature and can be determined through a series of experiments. However, in this thesis, values from literature were used [11].

The kinematic viscosity ν is a function of temperature and the solvent content in the washing water.

The velocity difference $U_{relative}$ between the filament bundle (=drawing speed) and the surrounding fluid cannot be measured easily because of the geometry of the washing plant. It is dependent on the drawing speed, geometry and the way washing water is circulated in the plant. As a result, the velocity difference varies and an average has to be calculated. In order to determine an approximation of the true velocity difference, a set of measurements was taken during the washing process. Further information can be found in chapter 7.7.

4. The Pilot Washing Plant

The hands on part of this thesis was done in a pilot plant of the sponsor company one-A engineering Austria GmbH. This chapter is an overview of the washing plant design and capability.

4.1. Design of the Washing Plant

The washing plant starts after the spinneret and spinning bath and is needed to recover as much solvent from the fibre as possible. The goal is a full recovery. Following the washing plant is the drying plant and the take off of the filament fibre.

The washing plant is built in 5 identical stages, and a sixth stage with half of the size on top, as shown in figure 4.1. Stages are numbered from bottom to top, meaning the pick up stage from the spinning bath is stage 1.

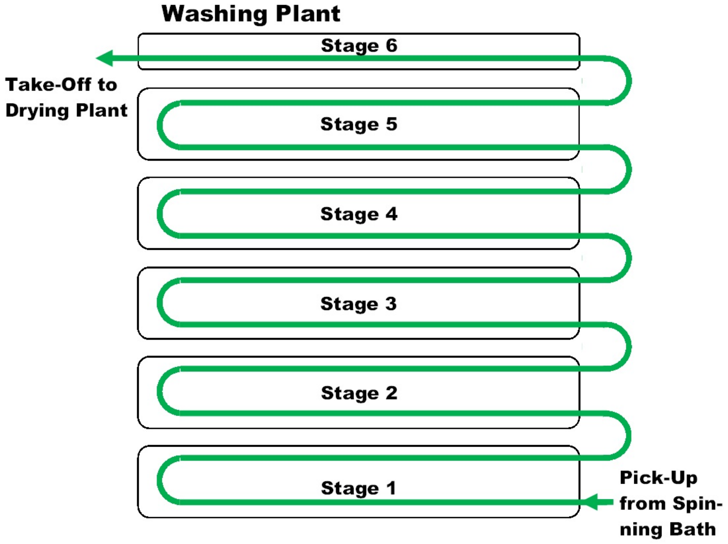

Figure 4.1.: Structure of the washing plant consisting of five identical stages, with a half-stage on top.

One stage consists of a buffer tank with a volume of about 20 litres and the stage itself, for a total of 55 litres water volume per stage during operation (see figure 4.2). Up to three separate identical 1.8 kW immersion heaters in the buffer tank control the temperature in the washing stage. One pump per stage, identical for stages one to five, circulates up to 35 L/min water through the nozzles in the washing side of the plant. The flow rate can be set using a flow regulation valve.

A powered pulley determines the speed at which the filament is towed through the plant. The pulleys of each stage are linked through the process control system with the master pulley, which is in stage six, to prevent a tear-off caused by different pulling speeds between the stages, with account for shrinkage as the solvent is removed.

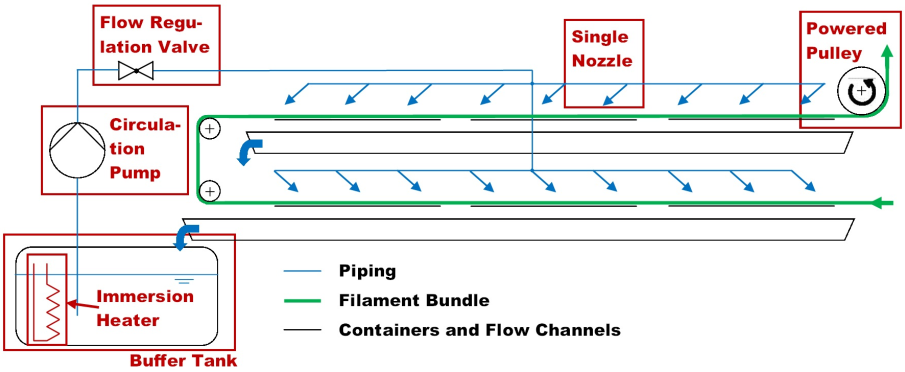

Figure 4.2.: One washing stage in detail. Marked are different components used to control the operation and performance of the washing plant.

Stage six is supplied with deionised water for a counter-current washing layout. The loaded washing water is drained through an overflow in each buffer tank down to the lower stages, resulting in an increase of the solvent concentration. Stage one is connected to the spinning bath with a circulation pump, where another overflow removes water from the washing plant.

Each stage is built in 2 levels (see figure 4.3) with a length of 6m for a total length of 12m per stage. Every level is separated in three identical parts: a 1.75m channel in which the filament bundle is guided, and three nozzles spraying water on the filament at a 45 degree angle opposed to the fibre movement direction. In total this makes 18 nozzles per stage.

The nozzles spray water on the filament which flows in the channels until the end of each part, where the water drains into a collection tray, from where it can flow back to the buffer tank.

During operation, the fibre bundle is towed through the washing plant by powered pulleys at the end of each washing stage. The last powered pulley of the washing plant is pressed against a spinning cylinder to dry squeeze the filament to relieve the following drying plant.

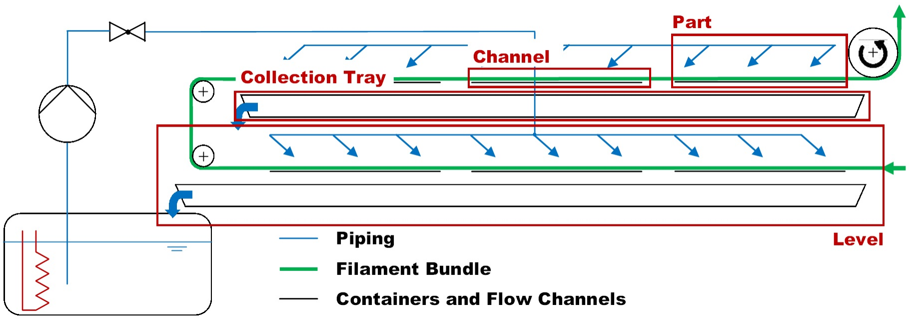

Figure 4.3.: Designations for different parts of the washing stage.

The start up for the operation of the washing plant has to be done by hand, guiding the filament through each washing stage while the powered rolls move at low speed.

4.2. The Washing Plant used in this Project

The goal as described in chapter 1.1 was to investigate the washing process in as controlled a fashion as possible. Toward this goal, the plant was modified slightly. Since the spinning bath is not the focus of this research, stage 1 of the washing plant was skipped entirely, and the pick up modified to lead into stage 2.

On the other end, the top stage 6 only consists of one level, not connected to a circulation pump, and has therefore characteristics different from the other remaining stages. As no clean water is introduced during the standard experiments (see chapter 5.1), it was held dry.

This leaves the identical stages 2 to 5 as the focus of this research. Any configurations and operating conditions were held identical in all four stages to allow for a valid and meaningful comparison.

4.3. Variable Process Configurations

It is possible to vary several process settings in the washing plant. Some will be intentionally varied over the course of the experiments to determine the dependencies of the diffusion coefficient. Others have to be controlled in order to ensure comparable results. A list of possible configurations, limits of the washing plant, intended variations and preferred standard values is shown here.

4.3.1. Drawing Speed

The drawing speed is determined at the end of the washing plant, however, since one roll in every stage is powered, the system must be calibrated in order to take account of the fibre shrinkage during the washing process and prevent tearing of the filament. The drawing speed can be varied between 0 and 240 m/min.

The process control system regulates the drawing speed to insure a constant titre and also to protect the spinning pump from overpressure or running dry. The goal is to remain at a constant speed of 120 m/min, however it will vary if the process control system requires it.

4.3.2. Temperature

The washing plant is fed by deionised water from the supply system of the pilot plant, limiting the lower temperature limit to the ambient temperature. Using immersion heaters in the buffer tanks, the temperature can be varied, however this does not allow for specific temperature control. Depending on the number of immersion heaters active in every washing stage, temperature will be brought to a specific value limited by heat loss through evaporation and convection to the surrounding air.

Experiments show that one active 1.8 kW immersion heater per stage is able to raise the washing water temperature from 18 to 37 °C (see chapter 7.2). A total of three active immersion heaters per stage will result in a final temperature of 52 to 55 °C, depending on the stage. When not otherwise specified, no immersion heater is active and the water is at 18 to 20 °C ambient temperature.

4.3.3. Nozzle Fluid Throughput

Every washing stage has its own identical pump to supply the nozzles in this stage. There are a total of 18 nozzles per stage, at two different elevations. While the pump only has an on and off setting, a valve can be used to regulate the total fluid throughput. Fully open, it allows for a throughput of about 32 to 35 L/min water. If regulated below 15 L/min the nozzles' flows start to drop and flow irregularly, especially at the higher elevation level of each washing stage.

A table with throughput measurements of every individual nozzle with a total pump performance of 20 L/min is shown in appendix C.1. This table shows that the elevation difference of the two height levels of the washing stage results in a 20 % lower throughput at the higher geodetic level. Each nozzle of an individual level however, has a very similar throughput with about 5 % variation. When not otherwise specified, the fluid throughput is set to 20 L/min.

4.3.4. Titre Denier and Fibre Count

The titre denier of the filament is a result of the settings in the spinneret and the drawing speed. For cellulose filament, it is defined as the mass of the filament per unit length, with a defined humidity of 11 wt% of the filament. In this thesis, if not otherwise mentioned, the word titre references to the single filament titre denier, and is calculated by the measurement of the total filament titre divided by the fibre count. It is measured as the mass in gram fibre of 10 000m fibre length with the unit dtex.

The process control system aims to ensure a constant titre and controls both the spinning pump speed and drawing speed to do so. It is also a measure of the amount of solvent that enters the washing plant, as there is a direct correlation of the amount of cellulose in the dope and in the filament. The titre can be varied between 1.3 and 3.0 dtex. When not otherwise specified, the fibre count is 900 at 2.1 dtex for a 1890 dtex total filament titre.

5. The Experimental Method

Over the course of this thesis, several different operating points of the washing plant (hereinafter called settings) will be studied. The results of every setting are given by samples of the washing water in each washing stage. They will be used to quantify the performance of the washing plant by measuring the NMMO content in them. From the resulting concentration profile, the diffusion coefficient of the solvent will be derived. Depending on the nature of the setting, a different method is necessary to gather the optimal samples. In the following sub chapters, the experimental method is explained in detail.

5.1. Setup Process for Standard Experiments - SE

In order to gather maximum information in the least amount of running time possible, and remove sources of errors caused by an unsteady system, a special initial condition for the washing plant will be prepared. First, the entire washing plant is cleaned and refilled with deionised water. The system is decoupled from the spinning bath, and incoming water is fed back. No clean water is introduced during the experiment in any stage.

The spinning process is started, and the filament threaded through the plant. This happens at a lower than production speed, generally at 20 m/min. When the filament arrives at the pickup roll, skipping the drying process, the washing plant can be brought up to a production speed of 120 m/min. Once the system is stationary at production speed, a timer is started and the first samples in the form of 500 ml washing water are taken from the buffer tanks.

For a fixed period of time, the process is kept running. The aim is at least 30 minutes of runtime in order to accumulate a sufficient solvent concentration in the system, and a maximum of 45 minutes to keep errors from water loss through splashing and evaporation low. Once the timer is stopped, another set of samples is taken. Using mass balance, the total accumulated solvent and average diffusion coefficient in the different stages can be determined. As a result of this method, it is not necessary to measure the NMMO concentration in the fibre in every stage, which would require the gathering of filament after every stage, interrupting the process and causing unsteadiness after the gathering of every sample. The final product, however, is still analysed for quality control.

Additionally, certain measurements are performed as required for different settings, such as the determination of the temperature for temperature variations. Details can be found in chapter 8.2.

5.1.1. Estimated Solvent Concentrations in the Washing Plant at the End of an Experiment

In order to verify the applicability of assumptions made in chapter 3.3 and check if this setup is viable, the solvent concentration in the washing plant at the end of a standard experiment is estimated here. Assumptions made in this estimation stem from practical knowledge of the industry partner.

First the produced filament fibre is evaluated: with a fibre count N of 900 fibres and a single fibre titre Td_{Single} of 2.1 dtex, the total filament mass per metre, $m_{Filament}$, can be calculated as:

$$m_{Filament} = N \cdot Td_{Single} = 0.189\,\frac{g\,Filament}{m\,Bundle} \tag{5.1}$$

The titre is defined with an 11 wt.% nominal humidity $\varphi_{Filament}$. With a cellulose mass fraction $w_{Dope,Cell}$ of 10 wt.% in the dope, the total amount of dope needed per metre fibre bundle can be calculated as:

$$\dot{m}_{Dope} = m_{Filament} \cdot \frac{(1-\varphi_{Filament})}{w_{Dope,Cell}} = 1.68\,\frac{g\,Dope}{m\,Filament\,Bundle} \tag{5.2}$$

$\dot{m}_{Dope,NMMO}$, the solvent introduced amounts to about 80 wt.% of the dope. With a pulling speed n_{Pull} of 120 m/min, this results in:

$$\dot{m}_{Dope,NMMO} = \dot{m}_{Dope} \cdot w_{Dope,NMMO} \cdot n_{Pull} = 2.69\,\frac{g}{s} \tag{5.3}$$

In a 45 minutes long experiment, 7.26 kg NMMO will be pumped by the spinning pump, extruded from the spinneret, and enter the spinning bath. From experience of the industrial partner, it is assumed that about one third of the solvent is removed at this stage and two thirds, or 4.84 kg NMMO, will enter the washing plant. Further, the industrial partner assumes that two thirds of the introduced solvent is removed in the first washing stage. With a wash water mass per stage of 56.5 kg (measured in chapter 7.1), this results in a rise in solvent mass fraction of 5.4 wt.% in the first stage from the start to the end of the experiment.

According to the same assumptions, the average mass fraction of solvent (based on the cellulose and solvent content only) in the filament at the start of the first washing stage is 84 wt.%, and 36 wt.% at the end. The difference in solvent content between the washing water and the filament is high compared to the rise of solvent content in the washing water during the experiment. This allows for the assumption that the mass balance system of each washing stage is stationary during the experiment.

The entire mass balance in detail can be found in chapter 9.1.

5.2. Setup Process for Verification Experiments - VE

The verification experiments are intended as a control, after the dependencies of the mass transfer have been determined. The process is set up as intended during normal operation, and kept running for several hours to ensure a steady process with a fixed concentration curve in the washing plant. Samples are taken from the buffer tanks and the finished filament product. Using the mass transfer equation resulting from the measurements of the standard experiments, the goal is to predict the mass fraction of solvent in every stage of the washing plant in a stationary process and verify with the results from the verification experiments.

5.3. Settings Chosen for Evaluation

First, a setting is chosen as the standard configuration for reference. All the other settings aim to be as similar as possible to the reference, with the exception of the variance parameter. The parameters chosen to be varied are the temperature for a change in the Schmidt number, the nozzle fluid throughput for a change in the Reynolds number, and the titre, to investigate whether or not a change in the single fibre diameter results in a significant change. Including the standard configuration, there are three variances for each varied parameter tested. The planned settings are shown in table 5.1.

Setting Number		1	2	3	4	5	6	7
Temperature	°C	20	37	55	20	20	20	20
Total Nozzle Throughput	L/min	20	20	20	25	30	20	20
Titre	dtex	2.1	2.1	2.1	2.1	2.1	1.7	2.5

Table 5.1.: Planned settings for investigation: Setting 1 is the reference for comparison, 2 and 3 aim to investigate the temperature dependence, 4 and 5 the total nozzle throughput dependence per stage and 6 and 7 the titre dependence.

6. The Analytical Methods

In order to evaluate later experiments for properly determining the diffusion coefficient of the solvent in the filament, it is necessary to find proper analytical methods. In a preliminary evaluation, the industrial partner conducted a series of experiments to determine the applicability of several methods. The results show that the most critical obstacle to a cheap and simple measuring method is the detection limit of the solvent in water.

While most methods are able to measure at a reasonable accuracy at higher concentrations, at lower concentration, as needed in this thesis, the methods fail to provide a reasonably accurate result. In the following chapters, the conducted evaluations will be discussed in detail.

6.1. Overview of the System to be Measured

Of interest for this thesis is the mass transfer of the solvent NMMO during the removal from a cellulose filament fibre into water. In order to determine the mass transfer rate, both the solvent mass fraction in the fibre and the solvent mass fraction in the water are of interest.

The solvent mass fraction in the fibre is expected to be as high as 60 wt.% NMMO at the entrance of the washing plant, and as low as 50 ppm in the final product. The solvent mass fraction in the water is expected to be below 10 wt.% at the highest, with no predetermined lower limit. A majority of the measuring samples are expected to be at solvent concentrations below 500 ppm, where the detection limit and absolute accuracy of the measuring method is of utmost importance.

6.2. Properties of NMMO and the Resulting Analytical Methods

As described in chapter 2.1, NMMO (N-Methylmorpholine N-oxide, $C_5H_{11}NO_2$) is an organic compound . It is solid at room temperature and dissolves fully in water. A water-NMMO mixture can be concentrated through simple evaporation up to the 1H2O-1NMMO monohydrate at approximately 86.7 wt%, since the solvent does not evaporate. However due to the boiling point elevation with rising concentration, it is necessary to distil under vacuum pressure of 100mbar, as the required temperature to reach this concentration at normal pressure leads to thermal decomposition of NMMO.

The NMMO concentration in water has direct influence on the refractive index, allowing for the measurement of the solvent mass fraction. NMMO shows multiple peaks in the IR/UV spectrum. Since the solvent is thermally destroyed before evaporation, analytical methods that require the sample to be gaseous cannot be used for NMMO. HPLC methods are applicable, and the nitrogen compound determination can be used to detect the nitrogen fraction of the solvent.

6.3. Evaluation of the Applicability of the Analytical Methods

In this chapter, several possible methods of measuring the NMMO content in liquids are investigated for applicability and practicality. While there are differences in quality for each method, depending on the quality of the measuring instrument, this evaluation is limited to methods within reasonable reach of the author, financial and otherwise. Criteria among others are

- the sensitivity of the method in the expected concentration range
- the lower detection limit
- the selectivity of the measurement
- the possibility to detect compounds other than NMMO that could influence the results
- the practical feasibility
- the costs per measurement

6.3.1. FTIR Analysis

FTIR spectroscopy is possible with NMMO in water, and accessible by the sponsor company in the form of a Bruker Alpha with a quicksnap platinum ATR module. The accuracy of measurement is competitive with other methods like HPLC for pure NMMO-water samples, however the measurement peaks overlap with the NMMO decomposition product N-Methylmorpholine (henceforth NMM). While it is technically possible to separate the components using a single peak that exists only in the NMMO spectrum, the peak has a very low adsorption coefficient and is close to other peaks, which decreases the accuracy by a large margin.

While it is not certain that NMM is present in the washing water, NMM is created by thermal decomposition of NMMO, which can be measured at 80°C and is noticeable at higher than 100°C, temperatures that are present in the Lyocell process.

6.3.2. Refractometry

The refractive index of water changes with the NMMO content. A calibration exists for measurements at 50°C with an accuracy of ± 0.5% absolute NMMO with the ABBE Refractometer AR4. This calibration starts at 1.5%, as lower concentrations cannot be detected.

Since the measurement result is only the refractive index, it is also impossible to detect contaminations from impurities. The measurement is quick, easily accessible and cheap, which makes this method useful for a quick overview when checking certain concentrations on the fly. However, it cannot be used to analyse the bulk of the experimental results.

6.3.3. HPLC-UV

In previous projects, the industry partner has developed an HPLC-UV method to detect NMMO and its decomposition products in a sample at the same time. This method is accurate at target concentrations (depending on the calibration) with a lower detection limit of 155 ppm NMMO. The nature of the measurement result allows for the detection of some impurities that show adsorption in the UV light range, including all thermal decomposition products of the solvent. Measurements are comparatively expensive and cannot be conducted locally at the pilot plant.

6.4. Methods Chosen for this Project

6.4.1. Determination of the NMMO Content of Liquid Samples

For this project, the analytical method chosen to determine the NMMO content of liquid samples is the aforementioned HPLC method. Both the column and eluents were replicated according to the given method, and measurements were conducted at the Technical University of Graz in the Institute of Process and Particle Engineering. All measurements were done in duplicate.

As the pilot plant is located at the industrial site of one-A engineering Austria GmbH, measurements can only be carried out after experiments have already concluded. To ensure constant operating conditions during experiments, some samples taken during the process were analysed using the refractive index method. The focus of these measurements was not a definite analysis of the NMMO content, only a qualitative analysis that the NMMO content remained similar during all the experiments. Further details are explained in chapter 8.

6.4.2. Determination of the NMMO Content in Solid Samples

Not yet addressed is the determination of the NMMO fraction in the fibre itself. This is planned for all the fibre products, and for spot checking at the entrance of the washing plant. The method was developed according to ÖNorm EN 647:1993. According to this, the fibre sample is cut, submerged in water, and heated and stirred for two hours at 80°C, extracting the remaining solvent. With the final fibre products, where a very low NMMO concentration is expected, this is done once. Using this method, it is not possible to fully extract one hundred percent of the solvent present in the solid sample, however the error decreases with the amount of water used compared to the solid sample mass. In order to reduce this measuring error, fibre samples taken from the entrance of the washing plant are washed twice.

The NMMO concentration in the resulting water-NMMO sample is determined as in any other liquid sample according to the chosen method, allowing for the calculation of the original NMMO mass fraction in the solid fibre sample.

6.4.3. Determination of the NMMO Content in Liquid Samples with very low Solvent Mass Fraction

In order to increase the measuring range of the chosen method and therefore include very low mass fractions, a rotavapor was used to concentrate liquid samples up to a satisfactory, measurable level. The process is described in chapter 7.6 with a proof of concept.

The refractive index of the samples was used to determine if it was necessary to increase the concentration. If a deviation in the refractive index of the sample from the value of water was not evident, meaning a lower than one percent mass fraction of NMMO, the sample mass fraction was increased using the rotavapor.

An analytical scale was used to determine the weigh in before and after concentration, to be able to calculate the original sample mass fraction.

6.4.4. Determination of Fibre Titre

The fibre titre was measured according to ASTM D885-03. 10 m of fibre bundle were measured, after discarding the first 200m of the sample roll, and put into a drying furnace at 120°C for at least 3 hours. Then the dry weight was measured using an analytical scale. This was repeated once more after another hour of drying, to ensure constant weight.

6.4.5. Determination of Nozzle Throughput

A selfmade device was used to convey the nozzle throughput of a single nozzle into a measuring beaker. During operation of the washing plant, measurements of the nozzle throughput were taken at defined times to determine the nozzle throughput. The process and results can be found in chapter 7.3.

6.4.6. Determination of the Flow Deflection caused by the Filament Bundle

Each stage consists of two levels, which consist of 3 part channels (more can be found in chapter 4.1). In every channel, three nozzles introduce water into the system, angled such that the flow direction is opposed to the fibre towing direction. This causes the water to flow in one direction when no filament is towed in the channel. Once the filament starts moving, however, it causes a reversal in flow direction in the middle of the channel caused by the viscous dragging effect.

As elaborated upon in chapter 3.3, the difference in fluid velocity and filament velocity determines the Reynolds number in the system. An indicator for this is the split in fluid moving in the direction of fibre flow, caused by the dragging action and fluid moving against the direction of fibre flow, caused by the initial momentum from the nozzles.

The geometry of the washing plant makes measuring this split difficult, as there is no space in the interior of the levels to measure the fluid volume flowing in one direction without interrupting it and causing a significant change. It is, however, possible to measure the flow direction at the leftmost channel, at the exit of every stage, using a selfmade device to convey the entire fluid flow into a measuring beaker without changing the flow in the system itself, as shown in figure 6.1. The measuring position names are identical as in appendix C.1.

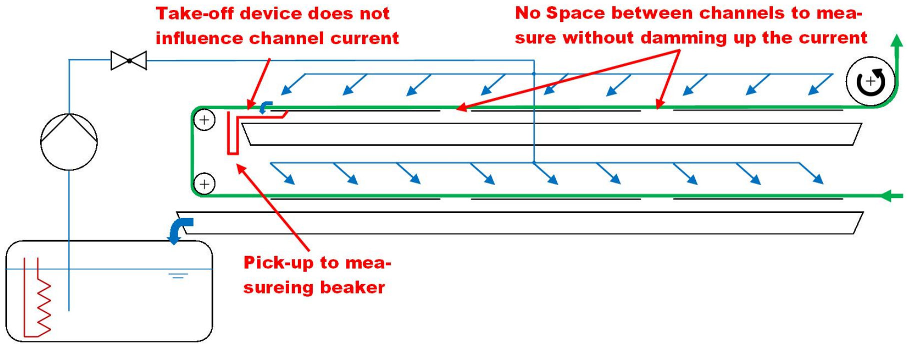

Figure 6.1.: Measuring position to determine the water volume exiting the channel to the left side.

7. Preliminary Experiments

In order to determine the feasibility of the analytical method and to get familiar with the pilot washing plant, several preliminary experiments were conducted. Each experiment either serves to confirm the function of an already known mechanism, or is necessary to eliminate possible sources of error in the standard experiments.

When not otherwise mentioned, the washing plant was put into operation using a clean filament product that was pulled off a spool, installed at the take-off from the spinning bath, instead of a filament product produced in the pilot plant.

7.1. Filling Volume and Water Loss

In this preliminary experiment, the pilot plant was started up and filled with water, until every stage was sufficiently full and the excess water drained through the overflows of the four stages.

A clean filament was threaded through the washing plant and the powered pulleys were started up and left running at different speeds for one hour for each speed. After the full hour, the buffer tanks were filled again, and the necessary amount to refill was recorded as water loss.

Since a significant percentage of the water volume is always in motion during operation, there is a certain delay until the circulation pump is able to distribute excess water from the buffer tank over the entire washing stage. It was noticed that, for minutes after refilling the buffer tanks, the water level in the tank would decrease again until a stable equilibrium was reached. The amount of water redistributed during that time usually was around one litre. As such, the accuracy of this measurement is limited, and the volume was rounded up to full litres.

Measurements were taken at ambient temperature with a nozzle fluid throughput of 20 L/min. The data can be found in table 7.1.

The main source of water loss was observed to be splash from the fibres at the pulleys between the levels and stages. Another main source, especially in the 2^{nd} stage, is believed to be the initial wetting of the dry fibre that is pulled of the spool at the take-off of the washing plant, a source not present in the general experiments. The water loss increased exponentially with the drawing speed, and tests at 240 m/min had to be

Filament Pulling Speed	m/min	60	120	180	240
Water Loss Stage 5	L/h	3	5	10	>20*
Water Loss Stage 4	L/h	3	5	9	>20*
Water Loss Stage 3	L/h	3	5	9	>20*
Water Loss Stage 2	L/h	4	7	12	>20*

Table 7.1.: Water loss of the different washing stages after one hour of operation with a nozzle fluid throughput of 20 L/min. *Measurements for 240 m/min had to be stopped early to preserve the pumps as the buffer tanks started to run dry.

stopped preemptively in order to preserve the pumps as the buffer tanks started to run dry.

While not the only reason, the increased water loss was one of the determining factors for the selection of 120 m/min pulling speed for the filament bundle. Furthermore it served to limit the testing time to less than one hour, in order to limit the error caused by water loss during the experiments.

After the conclusion of the testing, the filled-up washing plant was stopped and drained completely, stage per stage, into 50 L containers. Once full, those were weighed on a scale and emptied out, to determine the total filling volume of the washing plant for all four stages at 226kg water, or 56.5kg per stage on average. Not emptied out were the circulation pumps and piping for the nozzles, as the pumps cannot be allowed to run dry. Approximately 2 to 3 litres of water per stage are estimated to be contained there.

7.2. Testing different Temperature Levels

In order to vary the temperature in the washing plant, 12 identical 1.8 kW immersion heaters were bought for the testing. These immersion heaters were installed in the buffer tanks, three a piece.

During this set of preliminary experiments, the washing plant was started without a filament bundle, to minimise water loss. In three separate runs one, two and three immersion heaters per stage were activated and the system left to run until the temperature remained unchanged for 30 minutes. This took on average 2 hours. The temperature was measured using a mercury thermometer with one degree Celsius graduation marks. Measurement locations are the buffer tank where the immersion heaters are located, with considerations taken into account for distance from the heaters, and the return flow from the washing stages. The results are shown in table 7.2.

Immersion Heaters Active		1	2	3
Temperature in Buffer Tank Stage 5	°C	37	48	54
Temperature Drop Off in Return Flow	°C	0	1	1
Temperature in Buffer Tank Stage 4	°C	37	48	55
Temperature Drop Off in Return Flow	°C	0	1	1
Temperature in Buffer Tank Stage 3	°C	36	46	55
Temperature Drop Off in Return Flow	°C	1	1	1
Temperature in Buffer Tank Stage 2	°C	34	45	52
Temperature Drop Off in Return Flow	°C	1	2	2

Table 7.2.: The temperature in buffer tanks and drop off in the return flow, from the washing stage into the buffer tank, with one to three immersion heaters active.

The washing plant is located in a closed industrial hall. During the experiments, an influence of the ambient air condition was noticed. Initially the building gates were open. This caused the wash water temperature with one immersion heater to settle at 33°C, even though the outside and inside temperatures were comparable at 20°C and 22°C, respectively. After closing the gates and stopping the air flow through the hall, the temperature continued to rise to the values shown in table 7.2.

While some variation in temperature can be explained by different performance of the immersion heaters, a temperature rise from the bottom stage to the top stage is noticeable, likely caused by an increase in ambient temperature topwards through heat loss. The temperature drop off in the return flow from the washing stage into the buffer tank remained below 2°C, relative to the initial temperature in the buffer tank, even at the most intense conditions with three immersion heaters in stage two.

The water loss recorded during the experiments was different from the values recorded in chapter 7.1. Without splashing caused by a moving filament, and losses by the removal of the wet filament from the washing plant, an average of only 1 L/h was measured with one immersion heater active. The losses increased to 3 and 6 L/h with two and three immersion heaters respectively, likely caused by evaporation.

As a result of these measurements, one and three immersion heaters were chosen for the final settings, for average temperatures of 20, 36 and 54°C.

7.3. Investigating the Nozzle Throughput

In this set of preliminary experiments, the flow capacity of the nozzles and circulation pumps in the washing plant was investigated. As described in chapter 4.1, each washing stage has its own circulation pump, feeding 18 identical nozzles. The datasheet of the nozzles can be found in the appendix C.1.

In a first step, the blocking valve on the circulation pumps was opened completely, and first measurements were taken, using a self made device to redirect the water from individual nozzles into a measuring cup. Using a timer, the water flow in a certain time was measured and recorded. It quickly became apparent that the flow capacity varied widely, and it was necessary to clean the nozzles from fibre residues of former experiments.

In a second attempt, it became clear that the two height levels in every stage resulted in different throughputs for nozzles at a different height level relative to the circulation pump. Finally, the blocking valve in the circulating circuit was used to limit the total flow rate to about 20 L/min, and each individual nozzle throughput was recorded. The individual results can be found in appendix C.1, a summary in table 7.3.

		Stage 5	Stage 4	Stage 3	Stage 2
Total Pump Throughput	L/s	19.3	19.2	20.1	20.4
Av. Nozzle Throughput UL	ml/s	15.8	15.8	16.6	17.0
Std. Deviation UL	ml/s	0.9	0.8	0.7	0.6
Av. Nozzle Throughput LL	ml/s	19.9	19.8	20.5	20.8
Std. Deviation LL	ml/s	0.9	0.6	0.7	0.9
Throughput Ratio UL to LL	-	0.79	0.80	0.81	0.81

Table 7.3.: This table shows the average nozzle throughput calculated from individual data, as well as the average throughput of the upper height level compared to the lower.

The experiments found that the height difference between the upper and lower height levels of each stage resulted in throughput lowered by 20% in the upper level compared to the lower. Deviation between individual nozzles on one level was minimal.

Using this data, it was concluded that two measurements of nozzle throughputs per stage during the standard experiments, one on the upper and one on the lower level, will be enough to calculate the total throughput to a satisfactory degree of accuracy.

7.4. Calibration using the given HPLC Method

In order to prepare for future measurements, a test of the given HPLC method was conducted. Solutions with defined NMMO contents were prepared in a laboratory at the Technical University of Graz, using HPLC grade water and NMMO monohydrate as listed in appendix B.

The solutions were prepared by weighing in defined amounts of NMMO monohydrate using an analytical scale, and filling the volumetric flasks to the marked meniscus for 20 ml. Ultrasound was used to help dissolve the monohydrate crystals. A table of the solutions produced can be found in appendix C.2.

The solutions were measured by HPLC twice and fitted into a calibration diagram, found in figure 7.1.

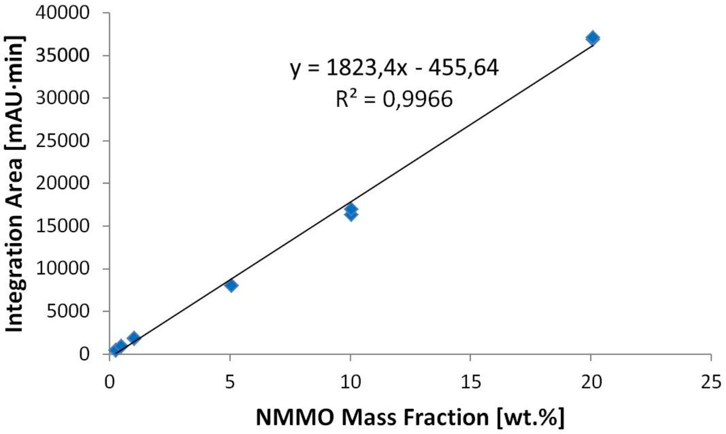

Figure 7.1.: The preliminary calibration results. More sample points in the area of interest between 2 and 10% NMMO are necessary.

While the results seemed satisfactory at a first overview, large errors at low concentrations are apparent, and more sample points in the area of interest between 2 and 10% NMMO are necessary for increased accuracy. An error discussion can be found in appendix C.2.

This calibration was used in further preliminary experiments, with more sample points added later. It was not used, however, for the analysis of the standard experiments, as those were conducted more than 6 months later. At this time the detector unit of the HPLC was replaced, and a new calibration became necessary, as a significant deviation during control measurements from this calibration was noticed (more in chapter 7.5). In the new calibration, the error decreased significantly, most likely because both NMMO and water were weighed in using an analytical scale, instead of relying on the graduation marks of a measurement flask.

7.5. Calibration for Measurement Analysis

As mentioned in chapter 7.4, the calibration had to be repeated, since control measurements showed a serious deviation of the previously recorded calibration. Reasons for that are most likely wear and tear of the HPLC pumps, as well as the replacement of the detector unit of the HPLC.

The new calibration solutions were weighed in using an analytical scale, not only for the NMMO weigh-in, but also for the water. As a result, the calibration shows much higher quality, with a lower deviation of the measuring points from the resulting calibration formula than in the first calibration of chapter 7.4.

The individual measurement results can be found in appendix C.3. Figure 7.2 shows the resulting graph. The measurements resulted in the calibration equation 7.1, which was used for the analysis of the standard experiments.

$$IA_{HPLC} = 2202.3 \cdot w_{Sample,NMMO} \tag{7.1}$$

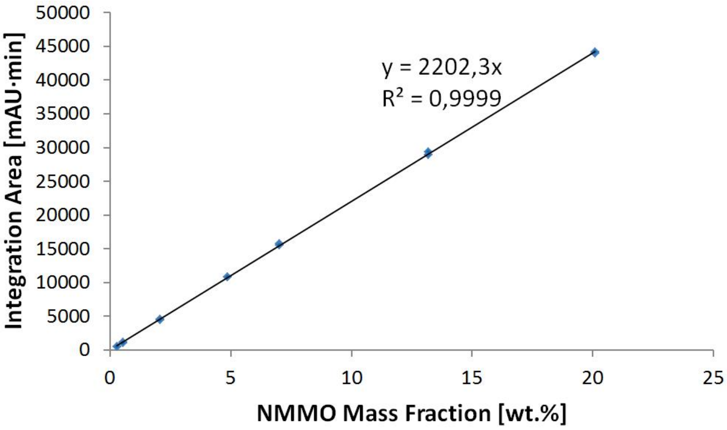

Figure 7.2.: Measurement integration surfaces at the calculated weigh-in mass fractions. The deviation of the weigh-in from the calculated result using the formula is below 2% at mass fractions higher than 1% NMMO.

7.6. Increasing the Measuring Range using a Rotavapor

As the chosen HPLC method was developed for measuring three separate components, there are drawbacks when using it for NMMO alone. The most significant is the timing of the measuring peak. It arrives just after the injection spike, leading to a distortion in the detection level at low concentrations. This limits the detection level of NMMO to 155 ppm, and 250ppm was chosen as the lower limit for calibration to still have a clearly detectable signal.

In this project, however, concentrations at this level and below are expected to occur frequently in stages 4 and 5 of the washing plant. In order to still be able to measure traces, a quality of NMMO was exploited. Since NMMO cannot evaporate and has no noticeable thermal decay below 80°C, a rotavapor can be used to concentrate the samples. In theory there should be no limit to the concentration coefficient, practically, however, we are limited by impurities that are concentrated as well, which can result in measurement peaks in the vicinity of the NMMO measurement peak causing a measurement error.

In order to test this procedure, samples at low concentrations were weighed in using an analytical scale, and concentrated by a factor between 5 and 10. Using the previously established calibration, the original concentrations were calculated and compared to the weigh-in. The results can be found in figure 7.3, the individual measuring data in appendix C.4.

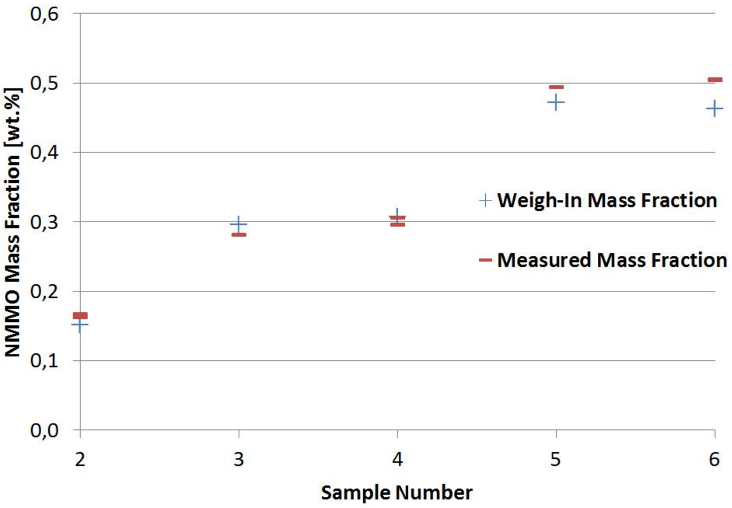

Figure 7.3.: Comparison between calculated weigh-in and measured mass fraction.

The results show an error below 10%, similar to the error of the preliminary calibration itself. This means that the method of extending the measurement range works as intended.

7.7. Investigating Split of Fluid Flow Caused by the Dragging Action from the Filament Bundle

During the preliminary experiments, while investigating the nozzle throughput, measurements according to the method described in chapter 6.4.6 were taken.

Position	WW Throughput without Filament	WW Throughput with Filament	Flow reduced to
	ml/s	ml/s	%
5-1-1	75.0	21.3	28.4
4-1-1	87.5	24.8	28.3
3-1-1	79.2	23.1	29.1
2-1-1	86.7	28.9	33.3

Table 7.4.: Washing water throughput on the left end of single channel with and without a moving filament.

The goal was to investigate the influence of the towed filament on the fluid velocity. The results in table 7.4 show that 70% of the water reverses direction and is dragged out with the filament bundle by the viscous action, with a dragging speed of the filament of 120 m/min.

While these results were obtained using a clean finished filament bundle and not the fibre produced by the pilot plant, the result was interesting nonetheless. The implication is that a majority of the water moves along with the filament bundle, causing a very low velocity difference between fluid and fibre, which results in a low Reynolds number.

8. Performing the Standard Experiments

The standard experiments were conducted according to the experimental method presented in chapter 5. In the present chapter, the final settings are listed and any anomalies that came up during the experiments are covered.

8.1. The Plan of Experiments

Caused by the batch nature of the pilot plant, the time available for one experiment is limited by the batch quantity of the spinning mass prepared. As the pilot plant requires significant preparation and cleanup before and after operation, the time for each experiment was limited, and an attempt was made to fit as many settings as possible in one operation day.

Initially four experiments were planned per operation day, however it was only possible to complete three settings each time. The settings conducted on the first day were one temperature, the reference case and one nozzle throughput. On the second day the second temperature and two titres were conducted. Each day started with the temperature setting, as it takes two hours of preparation time in order to heat the washing water in the washing plant. The draining and renewal of the washing plant water takes 45 minutes on average.

The final list of conducted settings can be found in table 8.1. While some measurements are taken in every setting, some are only relevant for specific ones. A detailed list of every measurement taken can be found in chapter 8.2.

8.2. Conducting the Standard Experiments

As described in chapter 5.1, samples of the washing waters for the evaluation of the NMMO concentration are taken from the buffer tanks at the start and at the end of every experiment. Samples of the final product are used to check the titre and the concentration of NMMO remaining in the product.

Setting Name	Varied Parameter
V01	Temperature approx. 37°C
V02	Reference
V03	Nozzle Throughput 34 L/min
V06	Temperature 54°C
V07	-20% Titre
V08	+20% Titre

Table 8.1.: List of conducted experiment settings. Missing is the second nozzle throughput variation from the intended settings found in table 5.1.

The temperature was measured in the settings where it was varied, and the nozzle thoughput was controlled at the start of every measuring day, and in the setting where it was varied. Also measured for the reference setting and the nozzle throughput variation was the split in fluid volume in the channel, explained in detail in chapter 7.7. The records of the spinning pump speed in the process control system are used to determine the totality of solvent that entered the system during the experiment time.

The experiments had different durations. While the goal was to have at least 30 minutes of constant production per experiment, with 45 minutes as the optimum, the pilot nature of the plant caused several interruptions. Sometimes this caused the experiment to be ended prematurely, other times the experiment was allowed additional time in order for the system to recover.

A detailed timeline for each experiment can be found in appendix D. The records show that there were significant problems during the operation of the washing plant, both instrumental (a pressure drop off caused by a clogging filter) and during controlling (late notice of pressure drop off's and unideal inputs for the feeding pump performance). A more detailed analysis is given in chapter 10.

8.3. Processing of Samples taken in Experiments

In a first step, liquid samples taken were stored in 800 ml capped measuring beakers. The filament roll was stored as well, as were any additional samples taken from the filament at the entry of the washing plant.

In the days following the experiments, liquid samples were analysed according to the method in chapter 6.4. Samples where the NMMO content was detectable using a refractometer were refilled immediately into 2 ml HPLC vials and sealed using Parafilm. Samples with an indistinguishable refractive index from water were concentrated using a Rotavapor at 200 mbar pressure with a water bath temperature of 70°C. A table with all the samples taken can be found in appendix C.5. Also included in this table are the measurements of the NMMO content in the fibre samples taken. Details can be found in the following chapters.

8.3.1. Determination of NMMO Concentration in Filament Products

In order to determine the remaining NMMO content of the filament product, the fibre sample was prepared according to the method described in chapter 6.4. Generally, the first 200 metres of fibre product were discarded, after which 10 to 30 g filament product were weighed in and submerged in 800 ml water, heated and stirred for two hours, and analysed. The liquid was prepared as any other liquid samples, the solid fibres were filtered an dried to determine the dry weight. From the resulting NMMO concentration in the liquid sample, the concentration in the solid sample can be calculated. A detailed table with the weigh-ins can be found in appendix C.6.

8.3.2. Determination of the Filament Titre

The filament titre was prepared according to the method described in chapter 6.4.

9. Results of Measurements

In this chapter, the results of the measurements made in the standard experiments are listed, and a preliminary analysis is made. The mass balance used to calculate the results is explained in the following section.

9.1. Overview of the Mass Balance of the Washing Plant

This section shows an overview of the mass balance borders. Included in the balance borders are the spinning bath, four washing stages, and the wind-up downstream.

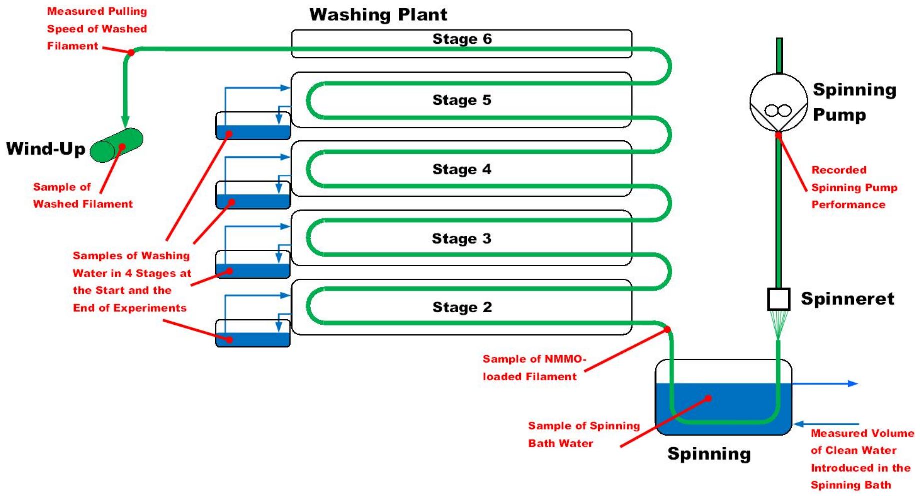

Figure 9.1.: The mass balance system with the sources of measurements used in the balance.

The balance system is shown in figure 9.1. Also shown are the locations for different measurements used in the mass balance.

The resulting abstracted balance system for the solvent can be found in figure 9.2. The mass flow rate $\dot{m}_{Dope}$ describes the total amount of dope conveyed by the spinning pump. The mass flow rate $\dot{m}_{Filament}$ describes the production volume of washed filament leaving the washing stages.

The mass flow rates $\dot{m}_{Stage\,i}$ result from change in the solvent mass fraction of the filament in each washing stage. These mass flow rates do not truly leave the balance area, but result in an accumulation of solvent in the washing water. They are calculated using the result of the washing water samples in each washing stage. $\dot{m}_{Water}$ and $\dot{m}_{Overflow}$ are the mass flow rates of demineralized water entering, as well as NMMO loaded water leaving the spinning bath, resulting in a solvent mass flow rate $\dot{m}_{SPB}$ leaving the filament.

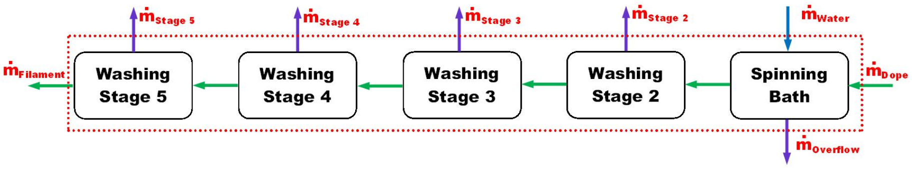

Figure 9.2.: The balance sheet variables used in the solvent mass balance system.

The resulting total balance for the solvent within the balance borders is shown in equation (9.1).

$$\dot{m}_{Dope,NMMO} = \dot{m}_{SPB} + \sum_{i=2}^{5} \dot{m}_{Stage\,i} + \dot{m}_{Filament,NMMO} \tag{9.1}$$

In the following chapters, all the quantities required to solve this total mass balance are calculated.

9.1.1. Definitions for the Solvent Mass Fraction in Solid and Liquid Samples Taken

It is not feasible to determine the mass fraction of water in the filament in this experimental setup. This is caused by the fact that there is no differentiation between water diffused within the solid sample, and water being carried along on the surface of the sample.

When a filament sample is taken at any location, the excess water on the surface is removed by the pressing forces caused by the wind-up of the filament. Additionally, it is suspected that these forces also remove part of the water stored within the filament, which makes the differentiation between surface water and stored water difficult.

For this reason, the water component is omitted in the calculated mass flow rates for the filament in the mass balance. The water content is only relevant for the spinning pump performance, to calculate the correct amount of solvent and cellulose introduced into the balance system.

This applies for solid filament samples. The total mass of solvent and cellulose of the sample are used to calculate the mass fraction, as shown in equation (9.2) for the washed filament sample.

$$w_{Filament,NMMO} = \frac{m_{Filament,NMMO}}{m_{Filament,NMMO} + m_{Filament,Cell}} \tag{9.2}$$

In any liquid sampled, only solvent and water are present, and solvent mass fraction is calculated as shown in equation (9.3) as example for washing stage 3.

$$w_{Stage\,3,NMMO} = \frac{m_{Stage\,3,NMMO}}{m_{Stage\,3,NMMO} + m_{Stage\,3,Water}} \tag{9.3}$$

9.2. Determination of the Amount of Dope Introduced

In order to calculate the sum of both NMMO, and cellulose introduced into the washing plant during the experiments, the records of the process control system were reviewed. The figures can be found in appendix D. The relevant value here is the spinning pump speed n_{SP}. It operates at high pressure and low speed, with a defined conveyed volume $V_{SP,rev}$ of 12.56 cm^3/rev. The density of the dope ρ_{Dope} is known to be about 1.12 g/cm^3. The mass flow rate of dope $\dot{m}_{Dope}$ can therefore be calculated as shown in equation (9.4).

$$\dot{m}_{Dope} = n_{SP(t)} \cdot V_{SP,rev} \cdot \rho_{Dope} \tag{9.4}$$

The current spinning pump speed is recorded once per second ($\Delta t_{step} = 1s$), resulting in a mass flow rate dependent on the time. In order to use the data to evaluate an entire experiment, an average mass flow rate is necessary. This calculation is shown in equation (9.5).

$$\overline{\dot{m}}_{Dope} = \frac{1}{t_{End} - t_{Start}} \sum_{t=t_{Start}}^{t_{End}} (\dot{m}_{Dope(t)} \cdot \Delta t_{step}) \tag{9.5}$$

The mass flow rate of introduced solvent $\overline{\dot{m}}_{Dope,NMMO}$, as well as the introduced cellulose $\overline{\dot{m}}_{Dope,Cell}$, can be derived from their mass fractions in the dope. The resulting starting point for the mass balance can be found in table 9.1.

Immediately visible is a significant deviation of the measurements of V06 from V02. According to the planned setting, V06 should be comparable to V01, V02 and V03. Setting V07 should be 20% lower than V02 and

Experiment Number		V01	V02	V03	V06	V07	V08
Experiment Duration	min	45	38	27	49	30	37
$\overline{n}_{SP}$	rpm	12.96	12.50	12.23	10.56	9.16	19.84
$\overline{\dot{m}}_{Dope,Cell}$	g/s	0.30	0.29	0.29	0.25	0.21	0.47
$\overline{\dot{m}}_{Dope,NMMO}$	g/s	2.43	2.34	2.29	1.98	1.72	3.72

Table 9.1.: Mass flow rates of NMMO and cellulose introduced on average according to the process control system.

V08 20% higher. In fact, technical difficulties in the production of the dope led to an inconsistent dope production which majorly impacted the performance of the entire process. This also significantly impacted the quality of the results of the different settings. A more detailed analysis can be found in chapter 10.

9.3. Solvent Mass Transfer in the Spinning Bath

The spinning bath is not a focus of this investigation, however in order to provide equal operating conditions, it has to be regulated. In that regard, the spinning bath was supplied with a fixed flow rate $\dot{m}_{Water}$ of 1 L/min demineralized water during the experiments, in order to offset the introduced solvent and keep the solvent mass fraction stable.

This introduced water results in an overflow $\dot{m}_{Overflow}$ of solvent loaded water in the spinning bath. Samples of the washing water in the spinning bath were taken at the start and at the end of every experiment, however only two were analysed using HPLC, the rest were checked for outliers using the refractive index. HPLC measurements were taken at the start of setting V06 and V08, showing 8.01 and 8.96% NMMO, respectively.

The resulting NMMO fluxes are calculated by setting up a mass balance of the spinning bath, as shown in figure 9.3.

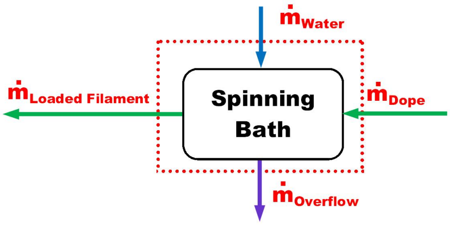

Figure 9.3.: The sub-system of the spinning bath.

The average accumulation of solvent in the spinning bath is zero. There is a small error in this assumption. This is caused by the fact that, while the introduced water into the spinning bath is constant at all times, the solvent introduced into the spinning bath was not constant in between the settings.

During the cleaning of the washing plant, in between settings, the spinneret continued to extrude dope at a reduced rate, which was removed periodically from the bath during the cleaning process. At the start and end of every setting, the NMMO mass fraction in spinning bath water was measured using a refractometer, to ensure no significant deviation from the target 8% solvent mass fraction. A variation in mass fraction by one percent from one measurement to another, remaining within one percent of the target mass fraction, was considered acceptable, and never exceeded.

The solvent removed by in the spinning bath is calculated in equation (9.6). In reality, the mass flow rate $\overline{\dot{m}}_{SPB}$ is split into the mass flow rate $\overline{\dot{m}}_{Overflow,NMMO}$ caused by the overflow in the spinning bath, and a carryover $\overline{\dot{m}}_{Carryover}$ into the washing plant.

This carryover is calculated in equation (9.7), and explained in chapter 9.3.1. However, concerning the balance of the washing plant, this detail is unnecessary, and the carryover is considered to be removed in the spinning bath.

$$\overline{\dot{m}}_{SPB} = \overline{\dot{m}}_{Overflow} \cdot w_{SPB,NMMO} \tag{9.6}$$

$$\overline{\dot{m}}_{Carryover,NMMO} = \overline{\dot{m}}_{Carryover} \cdot w_{SPB,NMMO} \tag{9.7}$$

The removed solvent in the spinning bath is normalized for comparison, using the total amount of introduced solvent, as shown in equation (9.8). This results in the NMMO fluxes shown in table 9.2.

$$\overline{\dot{m}}^{*}_{SPB,NMMO} = \frac{\overline{\dot{m}}_{SPB,NMMO}}{\overline{\dot{m}}_{BP_0,NMMO}} \tag{9.8}$$

Further shown is the calculated expected solvent mass fraction in a mass flow rate of solvent loaded filament $\dot{m}_{Loaded\,Filament}$, emerging from the spinning bath.

This calculated mass fraction can be compared with samples taken during setting 6, which show a mass fraction of 66 and 69%, reported in appendix C.6. Compared to the calculated 72% in setting 6 this is reasonably accurate.

Setting	$\overline{\dot{m}}^*_{SPB}$ %	$w_{Loaded\,Filament,NMMO}$ wt.%
V01	54.8	78.3
V02	56.9	77.5
V03	58.1	77.0
V06	67.4	72.3
V07	77.6	64.1
V08	38.0	83.2

Table 9.2.: Calculated normalized NMMO flux in the spinning bath. On average, more than half of the total solvent is recovered in the spinning bath.

9.3.1. Influence of the Carryover of Washing Water between Stages

The dragging forces of the filament cause a carryover of fluid adhering to the filament surface. Between stages, the filament is dragged over several rolls as it is changing direction. This causes a significant pressing force on the filament. Combined with the upward movement toward the next washing stage, this causes the majority of the fluid to be removed from the filament surface.

This could be observed in the preliminary experiments investigating the water loss in each stage, shown in chapter 7.1. There, the filament entered stage 2 in a dry state, which caused an increased water loss of 2 kg/h with 120 m/min pulling speed in that stage. That increase is partially caused by the initial wetting of the filament. Consequently, the water loss through carryover between stages cannot be greater than this increase of water loss observed in stage 2 compared to the other stages, and is therefore negligible.

During the standard experiments, an overflow of the buffer tank in washing stage 2 was observed. It was found that there was a significant carryover from the spinning bath into washing stage 2. The reason for that is that the spinning bath is located at a higher height level than the pickup in stage 2. The filament moves downwards over two rolls, without a major change in movement direction.

The buffer tank overflow $\overline{\dot{m}}_{Carryover}$ was measured to be 0.125 L/min washing water on average. Consequently, this means that at least the same amount of NMMO loaded water enters the washing stage from the spinning bath. As the solvent mass fraction in the spinning bath $w_{SPB,NMMO}$ is regulated to be between 8% and 9% at all times (assumed 8.5% for this calculation, more in chapter 9.3), the carry-over of solvent into washing stage 2 can be calculated.

The solvent carryover into washing stage 2 was deducted from the apparent mass transfer, as shown in equation (9.9).

$$\overline{\dot{m}}_{Stage\,2} = \overline{\dot{m}}_{Stage\,2,measurement} - \overline{\dot{m}}_{SPB,Carryover} \cdot w_{SPB,NMMO} \tag{9.9}$$

9.4. Calculation of the Solvent Mass Flow Rates in the Washing Plant

In this chapter, the measured NMMO contents of the samples during the experiments are used to calculate the solvent mass transfer from the filament to the washing water in each stage.

The balance for the washing stages 5 through 2 is calculated identically. Representative for all stages, the mass transfer in stage 3 is calculated using the solvent mass fraction in the washing water at the start of the experiment $w_{Stage\,3,NMMO,t_{Start}}$ as well as the final mass fraction $w_{Stage\,3,NMMO,t_{End}}$. The measurement results for these mass fractions can be found in appendix C.5.

The washing water volume V_{Stage} is 56.5 litres in each stage. The density of the washing water ρ_{WW} is assumed to be 1 g/cm^3 across the entire process. This results in an error in stage 2 as the density of the washing water is expected to be at 1.03 at 10% mass fraction, however that error is negligibly.

The average rate of accumulation of solvent in the washing stage represents the mass transfer of NMMO from the filament to the washing water. It is defined for Stages 5, 4 and 3 in equation (9.10). In stage 2 there is an additional component that is explained in chapter 9.3.1.

$$\overline{\dot{m}}_{Stage\,3} = V_{Stage} \cdot \rho_{WW} \cdot \frac{w_{Stage\,3,NMMO,t_{End}} - w_{Stage\,3,NMMO,t_{Start}}}{t_{End} - t_{Start}} \tag{9.10}$$

In order to compare the rate of mass transfer of solvent in the washing stages for different experiments, it was normalized using the total solvent mass flow rate introduced through the spinning pump. This is shown in equation (9.11).

$$\overline{\dot{m}}^{*}_{Stage\,3} = \frac{\overline{\dot{m}}_{Stage\,3}}{\overline{\dot{m}}_{Dope,NMMO}} \tag{9.11}$$

9.4.1. Results for the Mass Transfer in the Washing Plant

The relevant measurement results used for calculations in this chapter are reported in appendix C.5, and are condensed in tables 9.3 through 9.6, to show the performance of the washing stages during the experiments.

Setting	$w_{Stage\,2,NMMO,t_{Start}}$ %	$w_{Stage\,2,NMMO,t_{End}}$ %	$\overline{\dot{m}}_{Stage\,2}$ mg/s	$\overline{\dot{m}}^*_{Stage\,2}$ %
V01	7.38	18.69	2088.4	85.89
V02	0.99	9.35	1793.8	76.51
V03	0.99	5.39	1257.0	54.78
V06	1.60	10.73	1475.4	74.52
V07	1.28	5.35	1014.8	59.08
V08	5.09	16.00	2496.8	67.10

Table 9.3.: Calculated results of the solvent mass fraction and transport rate in stage 2 of the washing plant.

Table 9.3 shows the performance in washing stage 2. When comparing the normalized mass transfer $\overline{\dot{m}}^*_{Stage\,i}$ of the different stages, it is immediately apparent, that the majority of the solvent is removed in the second washing stage.

Setting	$w_{Stage\,3,NMMO,t_{Start}}$ ppm	$w_{Stage\,3,NMMO,t_{End}}$ ppm	$\overline{\dot{m}}_{Stage\,3}$ mg/s	$\overline{\dot{m}}^*_{Stage\,3}$ %
V01	4931	18020	273.9	11.26
V02	756	9062	205.8	8.78
V03	756	4021	113.9	4.96
V06	1288	6715	104.3	5.27
V07	202	2442	70.3	4.09
V08	3068	35306	820.5	22.05

Table 9.4.: Calculated results of the solvent mass fraction and transport rate in stage 3 of the washing plant.

In table 9.4 the performance in washing stage 3 is shown.

Table 9.5 shows a measurable performance in stage 4 for most experiments. Only setting V07, the decreased titre setting, does not show any mass transfer in this stage.

The measurements in washing stage 5 show, that almost all the reported values were below the detection limit. Overall, only in setting V06 a solvent flux could be detected at all, with only 0.03% of the total solvent removed from the filament (in regard to the total amount according to the spinning pump).

Setting	$w_{Stage\,4,NMMO,t_{Start}}$ ppm	$w_{Stage\,4,NMMO,t_{End}}$ ppm	$\bar{\dot{m}}_{Stage\,4}$ mg/s	$\bar{\dot{m}}^*_{Stage\,4}$ %
V01	1180*	2575*	29.2*	1.20*
V02	76*	521	11.0	0.47
V03	76*	142	2.3	0.10
V06	1198	1499	5.8	0.29
V07	<610*	<185*	0*	0*
V08	167	3613	87.7	2.36

Table 9.5.: Calculated results of the solvent mass fraction and transport rate in stage 4 of the washing plant.

Setting	$w_{Stage\,5,NMMO,t_{Start}}$ ppm	$w_{Stage\,5,NMMO,t_{End}}$ ppm	$\bar{\dot{m}}_{Stage\,5}$ mg/s	$\bar{\dot{m}}^*_{Stage\,5}$ %
V01	1477**	1460**	0**	0**
V02	<178*	<205*	0*	0*
V03	<178*	<184*	0*	0*
V06	1221	1251	0.58	0.03
V07	<207*	<306*	0*	0*
V08	<240*	<73*	0*	0*

Table 9.6.: Calculated results of the solvent mass fraction and transport rate in stage 5 of the washing plant.

Given that the filament exiting washing stage 5 shows about 1% mass fraction of solvent remains in the fibre (see chapter 9.5), it seems that the solvent mass fraction $w_{Stage\,5,NMMO,t_{Start}}$, introduced during the start up of the washing process, is enough to prevent the removal of the remaining solvent in the fibre in this manner.

9.5. Evaluation of the Filament leaving the Washing Plant

The filament samples taken in each experiment were prepared and analysed according to the method detailed in chapter 6.4. The weigh-ins can be found in appendix C.6, a summary in table 9.7.

The results for the solvent mass fraction of the final product samples $w_{Filament,NMMO}$ are shown in table 9.7. The measurements show a concentration below 1.4% in all cases, with some going below 1%, and in case of V07 entirely undetectable (lower detection range in this case being 40ppm). In case of V01 (marked **), the quality of the HPLC measurement precludes a definitive statement, and this concentration is an approximation only as shown in the appendix C.5. V06 also suffers from quality concerns, to a far lesser extent however.

Setting	$w_{Filament,NMMO}$ wt.%	$\overline{\dot{m}}_{Filament,NMMO}$ mg/s
V01	1.14**	3.5
V02	1.36	4.0
V03	1.06	3.1
V06	1.02*	2.6*
V07	<40ppm*	0.0*
V08	0.96	4.5

Table 9.7.: Measured results of the solvent mass fraction remaining in the filament fibres after the washing plant, and the resulting calculated solvent loss.

There are no sources of cellulose in the balance system, except for the dope extruding from the spinneret, and no cellulose losses in any stage. Consequently, the cellulose mass flow rate in the dope, listed for every setting in table 9.1, is also present in the washed filament. This is shown in equation (9.12).

$$\overline{\dot{m}}_{Filament,Cell} = \overline{\dot{m}}_{Dope,Cell} \tag{9.12}$$

Using the solvent concentration in the filament product shown in table 9.7 the solvent loss in the filament is calculated in equation (9.13).

$$\overline{\dot{m}}_{Filament,NMMO} = \overline{\dot{m}}_{Filament,Cell} \cdot \left(\frac{1}{1 - w_{Filament,NMMO}} - 1 \right) \tag{9.13}$$

The normalized solvent mass flow rate leaving the washing plant in the filament is negligible for the results of this thesis, at less than 0.1% of the total solvent introduced. On an industrial scale, however, this amount of solvent loss is a major factor, which has to be reduced further.

This factor is mitigated by the fact, that, as shown in chapter 9.4, the performance in the final washing stage was not detectable, and there was no clean water introduced during the course of the experiments. As such, the results for the solvent mass fraction in the finished product are not relevant for the reachable purity of the filament product in this pilot washing plant.

9.6. Comparing the Calculated Solvent Mass Transfer

In the previous chapters, all NMMO introduced into the balance system was accounted for by the spinning pump speed, and all NMMO leaving the balance system was accounted for by the mass transfers in the spinning bath, the four washing stages, and the filament product.

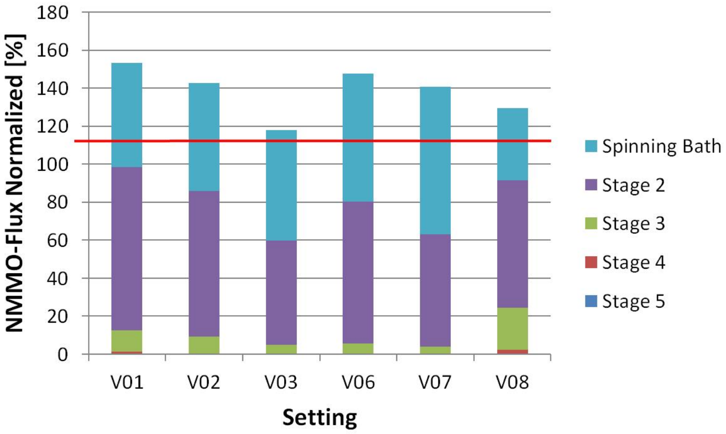

Figure 9.4.: The sum of normalized NMMO fluxes according to equation (9.16).

In reference to equation (9.1), equations (9.14) and (9.15) should be true.

$$\overline{\dot{m}}_{Dope,NMMO} = \overline{\dot{m}}_{SPB} + \sum_{i=2}^{5} \overline{\dot{m}}_{Stage\,i} + \overline{\dot{m}}_{Filament,NMMO} \tag{9.14}$$

$$\overline{\dot{m}}^{*}_{SPB} + \sum_{i=2}^{5} \overline{\dot{m}}^{*}_{Stage\,i} + \overline{\dot{m}}^{*}_{Filament,NMMO} = 100\% \tag{9.15}$$

Equation (9.15) can be simplified, as $\overline{\dot{m}}^{*}_{Filament,NMMO}$ is negligible, to result in equation (9.16).

$$\overline{\dot{m}}^{*}_{SPB} + \sum_{i=2}^{5} \overline{\dot{m}}^{*}_{Stage\,i} = 100\% \tag{9.16}$$

As shown in figure 9.4, the sum of solvent introduced is bigger by as much as 53% than the solvent introduced in most settings. An analysis for the likely causes of this difference can be found in chapter 10.

10. Interpretation and Discussion

In this chapter the results shown in chapter 9 are discussed in order to find satisfactory answers to the questions asked at the beginning of this thesis.

Even though it was shown in chapter 8.2 that there were significant problems during the operation of the washing plant, which give some comparisons a speculative nature, all results were discussed equally, with a remark when the quality of a measurement or the experiment itself are uncertain.

10.1. Investigating the Difference in Measured NMMO Input and Output

As shown in chapter 9, the measured NMMO output is greater than the input by up to 50% with different test parameters. This cannot be correct. Since the accuracy of the calibration has already been established, the most likely source of this discrepancy is an error in an underlying assumption. During the sampling of the NMMO-loaded water in each stage, it was assumed that the circulation pump has a throughput high enough to produce an uniform solvent concentration in the entire stage. As the total volume of each stage is about 55 litres, and the pump circulated generally 20 L/min out of a 20 litre buffer tank, this seemed a reasonable assumption to take.

After reviewing the results of the standard experiments, it seems that an accumulation of solvent takes place in the buffer tank, caused by insufficient mixing or a dead volume in the collection trays of the washing stages. This hypothesis is further reinforced by the results of settings 3 and 8 where the balance comes out reasonably. In setting 3, the pump throughput was increased by 70%, leading to higher turbulence and mixing in the washing stage. In setting 8, an error in the process control system settings caused an average drawing speed of 174 m/min, which also vastly increased the turbulence and subsequently the mixing in the washing plant. In both of those settings, the measured solvent input and output match very closely.

If this hypothesis is correct, it would allow for a normalization of the solvent flux, as each stage is structurally equal and may therefore have similar mixing errors and accumulation in the buffer tank. The normalization would cut the error in the water volume per stage caused by the dead volume, and would allow for a meaningful comparison between the settings, regardless of the error made in the sampling for the measurements.

In order to test this hypothesis, another experiment is required. Details can be found in the following section.

10.1.1. Testing a Hypothesis to Confirm an Error in the Solvent Sampling

In order to confirm the hypothesis made in chapter 10.1, another experiment was required, now called setting V10.

This chapter describes the theoretical method used to verify the stated hypothesis that there are areas in the washing stages that have dead volumes with less fluid circulation, causing a solvent concentration drop away from the buffer tanks. The experiment, however, could not be concluded in time before the thesis submission deadline, so results are pending.

The main feature of this experiment are additional solvent samples to be taken at the end of the experiment at four separate locations in stages 2 and 3, as shown in figure 10.1.

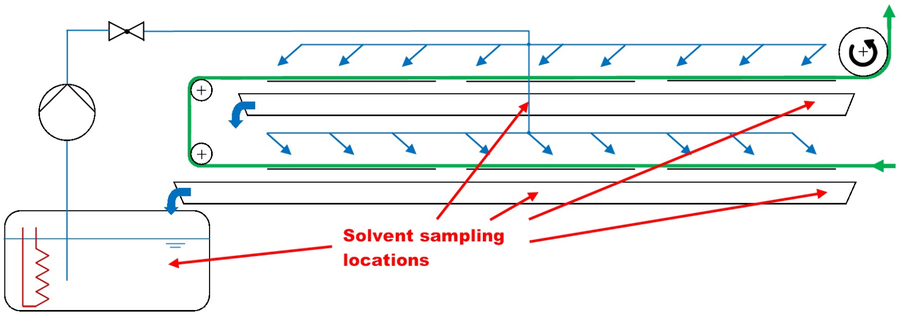

Figure 10.1.: The 5 sampling locations for setting V10 in stages 2 and 3 at the end of the experiment: one sample from the buffer tank, and two from each level, on the other end of the washing water drain.

If the results of setting V10 show different and lower mass fractions of solvent in the washing stages than in the buffer tank, it is possible to normalize the NMMO flux calculated from the concentrations in the buffer tanks and somewhat correct this error.

10.2. Normalizing the NMMO Flux in the Washing Plant

Since the experiment described in chapter 10.1.1 has not been concluded yet, the calculations done in this chapter are unverified. They are, however, necessary to try to derive some information from the currently existing experimental results.

For a comparison between the different settings, the performance of the washing stages was normalized, as shown in equation (10.1). The results are shown in figure 10.2.

$$\overline{\dot{m}}^{**}_{Stage\,j} = \frac{\overline{\dot{m}}^{*}_{Stage\,j}}{\sum\limits_{i=2}^{5} \overline{\dot{m}}^{*}_{Stage\,i}} \tag{10.1}$$

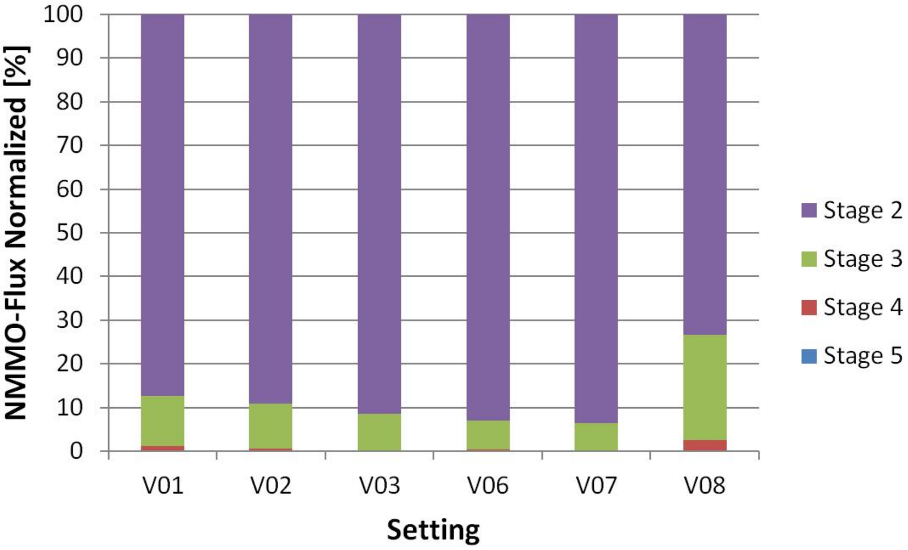

Figure 10.2.: The normalized solvent flux of the four washing stages in figure 9.4, normalized again for the washing plant only.

It is immediately apparent that the vast majority of the solvent removal from the fibre takes place in the first washing stage (stage 2), while almost no NMMO flux is found in stages 4 and 5. The washing performance is different, but of the same magnitude in most settings, with setting V08 as an outlier, most likely caused by the increased drawing speed.

10.3. Comparing Relevant Settings

In this chapter, the different experiments are compared according to the varied parameters of washing fluid volume, temperature and titre.

Figure 10.3 shows the performance of setting V03 compared to the reference V02. The increase of the nozzle throughput from 20 L/min to 34 L/min resulted in an increased washing effect, from 89.2% to 91.5% of the contained NMMO in the filament in stage 2.

This can be explained by the increased relative velocity between wash water and filament, and therefore increased turbulence in the wash water. As a representative value, the change in fluid direction of the wash water caused by the movement of the filament was recorded, according to the method described in chapter 6.4.6.

When the filament is not moving, 100% of the wash water leaves the washing channel in the direction of the angled nozzles. When the filament moves through the washing plant counter current to the original direction, the dragging action from the filament causes the majority of the fluid to change direction. In setting V03 with increased nozzle throughput, 30.6% of the washing water continues moving in the original direction, compared to a 24.1% average in the reference Setting V02. This is a relative increase of 27% on average.

The increase of the amount of wash water moving counter current to the filament movement direction is directly caused by the increased washing water impulse from the nozzles. This results in a lower effect of the dragging force of the filament, increasing the relative velocity between the two and resulting in an increased Reynolds number, effectively increasing the mass transfer of the solvent out of the filament fibre. Details for individual washing stages are shown in table 10.1.

	WW in V02	WW in V03	V03 to V02
	% remaining	% remaining	% increased
Stage 5	26.4	33.3	26.2
Stage 4	27.2	34.0	25.2
Stage 3	21.2	26.8	26.0
Stage 2	21.4	28.2	31.9
Average	24.1	30.6	27

Table 10.1.: The remaining wash water (WW) flow, after a reversal in direction of the bulk caused by the moving filament. When the filament is not moving, 100% of the wash water left the washing channel in the direction of the angled nozzles.

Figure 10.4 shows shows the performances at different temperatures of the washing water. Immediately apparent is that the performance of V01 with a temperature between that of the other two settings has the

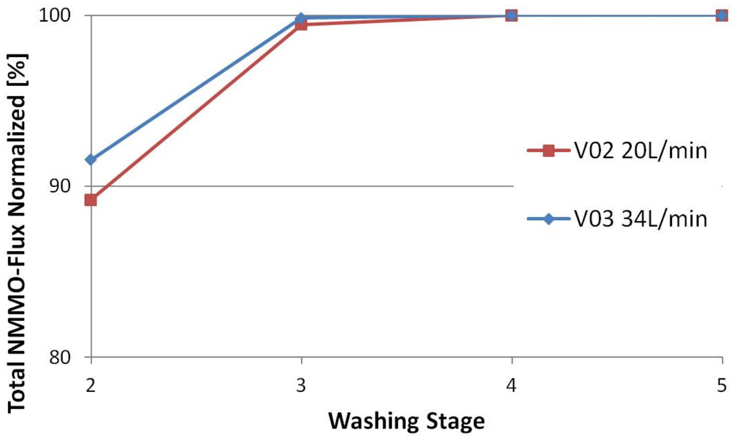

Figure 10.3.: The washing plant performance of setting V03 compared to the reference V02.

lowest washing performance, which points to an error in the execution of this experiment.

The most likely explanation is that, since V01 was the first setting conducted, it took some time until the filament was successfully threaded into the washing plant. The mass fraction measured during the experiment was 7.4% at the start and ended with 18.7%. It is, with the exception of the ending mass fraction of V08 at 16%, the only mass fraction that exceeds 10% during the experiments. As the mass fraction in the washing stage rises, the concentration difference between washing water and fibre decreases, which causes a decrease in NMMO transfer.

When comparing setting V06 to the reference V02, the increase of the temperature from 20°C to 55 °C increased the NMMO flux in stage 2 from 89.1% to 93.0%. It has to be mentioned that the spinning pump performance during V06 was not acceptable and varied widely, as shown in the timeline in appendix D.

As a result, the evaluation of the temperature influence on the washing plant performance cannot be conducted with just those data points. Ideally, settings V01 and V06 would have to be repeated to gain the information necessary.

Figure 10.5 shows the washing plant performance at different titres. As previously shown, setting V08 is an outlier caused by an error in the feeding pump performance, which resulted in an increased drawing speed. This precludes a meaningful comparison with the other settings.

The comparison of setting V07 with the reference, however, is fitting, and results in an increased washing performance in the early stages for the setting with a decreased titre.

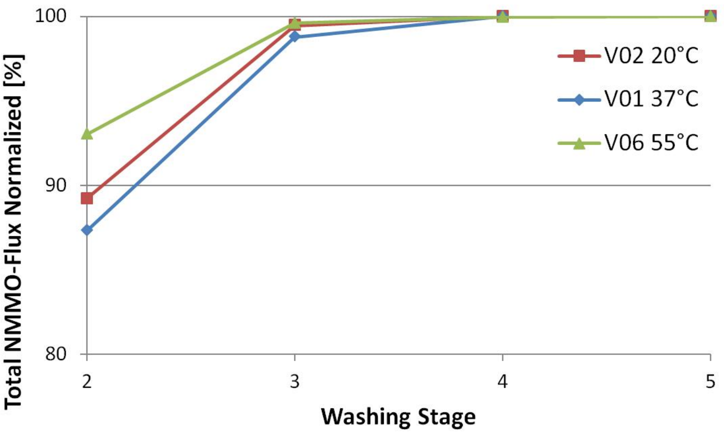

Figure 10.4.: The washing plant performance at different washing water temperatures.

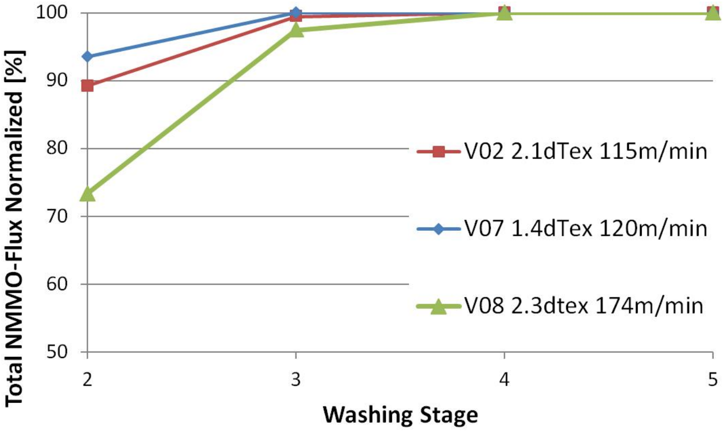

Figure 10.5.: This figure shows the washing plant performance of different titre variations.

10.4. Discussion of the Experimental Results

In this chapter, the results of the different experimental settings are analysed, and their NMMO fluxes are compared to see if the washing plant performed as expected when varying the different parameters. For the most parts, with a notable exception of V01, this was the case. Usually, the next step would be to follow the established method in chapter 3 and calculate the mass transfer coefficient in every stage for every setting to fit a Sherwood equation, followed by a verification experiment. In praxis, however, this method is not appropriate.

The biggest reason is the inadequate performance of the pilot plant during the experiments. As stated in chapter 5, in order to compare the different settings, all parameters but the one varied have to remain constant, or at least within an acceptable range. During the experiments performed, several incidents happened that caused other process parameters to change and prevent a meaningful comparison.

Complications arose, starting from beginners difficulties at the start of setting V01, where it took five tries to thread the filament through the washing plant. This caused a high solvent concentration in stage 2. Then there were problems caused by a clogging filter, which resulted in a pressure fall off and reduction of the drawing speed. In hindsight, these difficulties could have been prevented, had there been more preliminary experiments using the entire pilot plant instead of concentrating only on the washing plant. In praxis, however, costs limited the number of available experiments for this master thesis.

The sampling for the measurements in the washing stages was flawed, as shown in this chapter. While a control experiment is being worked on to explain the high deviation of introduced solvent though the spinning pump and outgoing NMMO flux into the washing water, no preliminary experiment was conducted to prevent errors like this in the first place. As a result, the normalization of the measured solvent flux to be able to compare the results is possibly correct. However, there is a large error potential that was not factored in. Care has to be taken in future experiments to prevent this sampling error from occurring again.

Another difficulty in the analysis of the results stems from the dimensioning of the washing plant. On average, about 90% of the washing performance took place in the first stage (stage 2), with a further 9 % in the following stage. This only gives two usable data points instead of four, with a high weighting on the first. This was only discovered during the analysis of the concentration in the washing stages, after the experiments had already been concluded, and could not have been changed as this was caused by the geometry of the plant itself. While no real dimensioning equation can be derived from the results of this thesis, that fact alone gives notice that the current dimensioning of the washing plant stages is fundamentally flawed, and can be improved through resizing of the washing stages.

11. Summary and Conclusions

The aim of this master thesis was to investigate the mass transfer of the solvent NMMO contained in filament fibres into the washing water during the washing step of the Lyocell process. Of interest was to determine all variables defining the rate of mass transfer and to investigate their respective influence. For this purpose, experiments were conducted at a pilot plant of the industry partner one-A engineering Austria GmbH.

The experiments focused on investigating the relative influence of wash water temperature, nozzle fluid throughput and filament titre. The results show the expected behaviour, however the outcomes are contentious as there were significant problems with the stability of the upstream processes during the experiments. This caused significant variations in filament drawing speed in the washing plant, which preclude a definitive comparison of the results.

In addition to that, errors were made in the sampling of the washing water for measuring the solvent concentration. Further experiments are required to be able to confirm assumptions made in the analysis of the experimental results. The resulting findings are therefore compromised, however some conclusions can still be drawn.

First, on average about 90 percent of the solvent, present in the filament at the start of the washing plant, are removed in the first washing stage, and a further 90 percent of the remaining solvent are removed in the second. This leads to the conclusion that the washing stages in the pilot plant are oversized.

Secondly, even though the solvent concentration in the washing water in the final washing stage was only around 200 ppm during most experiments, the solvent flux in that washing stage was negligible. The solvent concentration remaining in the filament product exceeded one percent in all cases except one, leading to the conclusion that there is a significant mass transfer resistance inside the filament. Further research is needed here to improve the purity of the filament product, and to reduce the loss of solvent.

Finally, increasing the nozzle throughput by 70% increased the total solvent extracted in the first washing stage from 89.2% to 91.5%, where an increase of the temperature from 20°C to 55°C was able to increase the concentration from 89.2% to 93.0%. Both the influence from fluid motion as well as wash water temperature seem equally influential to the mass transfer in this application. More detailed research will be necessary to find an optimum operation point, where the mass transfer is maximised without harming the filament fibre thermally or physically.

In summary, even though the goals stated at the beginning of this thesis could not be reached, a wealth of useful information was gained that can serve as a basis for further research in this area.

Bibliography

[1] O. Biganska, P. Navard, *Phase diagam of a cellulose solvent: N-methylmorpholine-N-oxide-water mixtures*, Polymer 44, 2003, p. 1035-1039.

[2] B. Medronho, A. Romano, M.G. Miguel, L. Stigsson, B. Lindman, *Rationalizing cellulose (in)solubility: reviewing basic physicochemical aspects and role of hydrophobic interactions*, Cellulose 19, 2012, p. 581-587.

[3] H. Zhao, J.H. Kwak, Y. Wang, J.A. Franz, J.M. White, J.E. Holladay, *Interactions between cellulose and N-methylmopholine-N-oxide*, Carbohydrate Polymers 67, 2007, p. 97-103.

[4] B. Kosan, C. Michels, F. Meister, *Dissolution and forming of cellulose with ionic liquids*, Cellulose 15, 2008, p. 59-66.

[5] B. Medronho, B. Lindman, *Competing forces during cellulose dissolution: From solvents to mechanisms*, Current Opinion in Colloid & Interface Science 19, 2014, p. 32-40.

[6] C. Chaudemanche, P. Navard, *Swelling and dissolution mechanisms of regenerated Lyocell cellulose fibers*, Cellulose 18, 2012, p. 1-15.

[7] H.-P. Fink, P. Weigel, H.J. Purz, J. Ganster, *Structure formation of regenerated cellulose materials from NMMO-solutions*, Prog. Polymer Science 26, 2001, p. 1473-1524.

[8] R.R. Mather, R.H. Wardman, *The Chemistry of Textile Fibres*, 2nd Edition, Royal Society of Chemistry, 2015, ISBN: 978-1-78262-023-5.

[9] O. Biganska, P. Navard, *Morphology of cellulose objects regenerated from cellulose-N-methylmorpholine N-oxide-water solutions*, Cellulose 16, 2009, p. 179-188.

[10] O. Biganska, P. Navard, *Kinetics of Precipitation of Cellulose from Cellulose-NMMO-Water Solutions*, Biomacromolecules 6, 2005, p. 1948-1953.

[11] R. Liu and X. Hu, *Precipitation Kinetics of Cellulose in the Lyocell Spinning Process*, Ind. Eng. Chem. Res. 45, 2006, p. 2840-2844.

[12] D.B. Kim, Y.M. Lee, W.S. Lee, S.M. Jo, B.C. Kim, *Double crystallization behavior in dry-jet wet spinning of cellulose/N-methylmorpholine-N-oxide hydrate solutions*, European Polymer Journal 38, 2002, p. 109-119.

Appendix

Appendix A.

Measurement Instruments

A.1. Analytical Scales

An analytical scale was used for the weigh-in of NMMO and water in the HPLC-UV calibration measurements. The device used was a Sartorius Entris. A different analytical balance, the VWR SE622, was used for the weigh-in and weigh-out of the concentration process using the rotavapor.

A.2. HPLC-UV

The HPLC-UV device used for measurements in this thesis was the HPLC 1100 of the company Agilent Technologies with a UV detection unit.

A.3. Refractive Index Measurement

The refractive index of the washing water was measured to determine if a sample needed to be concentrated using a Rotavapor. The device used was an ABBE Refractometer AR4.

Appendix B.

Chemicals Used for the HPLC-UV Method

The HPLC-UV method used requires two eluents. The first is water spiked with 0.05 moles of sodium metaborate tetrahydrate. The water used is ultra pure HPLC grade water. Sodium metaborate tetrahydrate was acquired with 98% purity. The second eluent is methanol, which was acquired as ultra pure HPLC grade with 99.8+% purity. NMMO was acquired for calibration purposes as 4-methylmorpholine N-oxide monohydrate with 98+% purity.

All chemicals were bought at the VWR online shop https://at.vwr.com.

Appendix C.

Tables of Measurement Results

C.1. Measurement of Nozzle Throughput

In this appendix, the results of the preliminary nozzle throughput measurements are shown. The numbering of nozzles is shown in figure C.1. The results of the measurements are shown in table C.1.

Pos.	Nozzle 1 ml in 45s	Nozzle 2 ml in 45s	Nozzle 3 ml in 45s	Nozzle 1 ml/s	Nozzle 2 ml/s	Nozzle 3 ml/s
5-1-1	700	750	750	15.6	16.7	16.7
5-1-2	700	710	760	15.6	15.8	16.9
5-1-3	650	650	720	14.4	14.4	16.0
5-2-1	880	920	850	19.6	20.4	18.9
5-2-2	950	950	910	21.1	21.1	20.2
5-2-3	880	840	880	19.6	18.7	19.6
4-1-1	740	740	740	16.4	16.4	16.4
4-1-2	700	760	720	15.6	16.9	16.0
4-1-3	680	670	650	15.1	14.9	14.4
4-2-1	840	900	900	18.7	20.0	20.0
4-2-2	920	870	900	20.4	19.3	20.0
4-2-3	900	860	910	20.0	19.1	20.2
3-1-1	750	760	810	16.7	16.9	18.0
3-1-2	760	700	740	16.9	15.6	16.4
3-1-3	740	740	730	16.4	16.4	16.2
3-2-1	920	940	960	20.4	20.9	21.3
3-2-2	960	900	860	21.3	20.0	19.1
3-2-3	930	940	900	20.7	20.9	20.0
2-1-1	800	760	750	17.8	16.9	16.7
2-1-2	700	760	780	15.6	16.9	17.3
2-1-3	780	780	760	17.3	17.3	16.9
2-2-1	880	960	960	19.6	21.3	21.3
2-2-2	940	1010	920	20.9	22.4	20.4
2-2-3	930	880	960	20.7	19.6	21.3

Table C.1.: Individual nozzle flow rates at approximately 20L/min total throughput per stage. Positions are explained in figure C.1

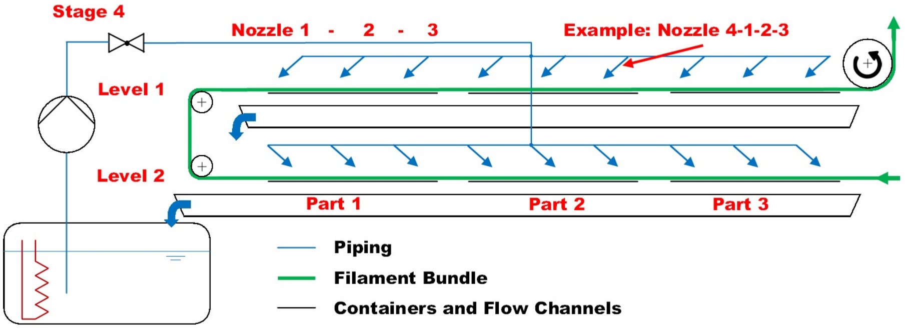

Figure C.1.: Naming convention for individual nozzles in the washing plant. The number is made up from [Stage] - [Stage Level] - [Stage Part] - [Nozzle Number], the example shown is nozzle 4-1-2-3, which is the 3^{rd} nozzle in stage 4, level 1, part 2.

C.2. Calibration during Preliminary Experiments

Table C.2 shows the initial weigh-in of NMMO monohydrate, as well as the resulting NMMO mass fraction for the preliminary HPLC calibration. The water fraction was always added to a 20 ml visual marking in the 20 ml flasks.

Weigh-In of NMMO MH	Resulting NMMO Mass Fraction	Integration Area MM 1	Integration Area MM 2
g	wt.%	mAu · min	mAu · min
0.0599	0.260	411.5	431.5
0.1149	0.498	877.6	872.9
0.2346	1.016	1816.7	1836.3
1.1879	5.085	7987.3	9034.2
2.3827	10.059	16349.0	16952.2
4.8901	20.089	36855.2	37062.6

Table C.2.: Weigh-in of NMMO in 20ml calibration solutions for preliminary experiments. Each solution was measured twice using the given HPLC method.

Ultrasound was used to help dissolve the NMMO crystals. A 2 ml sample was taken in an HPLC vial and measured twice. The resulting calibration was linearised in equation (C.1).

$$IA_{HPLC} = 1823.4 \cdot w_{Sample,NMMO} - 455.6 \tag{C.1}$$

In a second batch, more measurements were conducted in the mass fraction range of one to five percent, since this was the range where the washing water solvent content was expected. The weigh-in and resulting measurements are shown in table C.3. The results of the additional

Weigh-In of NMMO MH	Resulting NMMO Mass Fraction	Integration Area MM 1	Integration Area MM 2
g	wt.%	mAu · min	mAu · min
0.2980	1.29	2345.7	2315.9
0.7816	3.39	6688.6	6398.4
1.0816	4.70	9659.7	9515.8

Table C.3.: Further weigh-in of NMMO in 20ml calibration solutions for preliminary experiments between 1 and 5% NMMO to refine the calibration curve. Each solution was measured twice using the given HPLC method.

Weigh In of NMMO MH	Resulting NMMO Mass Fraction	Relative MM Error
g	wt.%	%
0.26	0.21	18.4
0.45	0.46	7.0
1.02	0.99	2.5
5.09	4.42	13.2
1.29	1.27	1.9
3.39	3.60	6.2
4.70	5.29	12.6

Table C.4.: Deviation between weigh-in mass fraction and the calculated mass fraction using the preliminary calibration between 0.25 and 5 wt%.

measurements were used to fit a preliminary calibration curve for measurements between 0.25 and 5% with equation (C.2).

$$IA_{HPLC} = 1805.7 \cdot w_{Sample,NMMO} + 38.4 \tag{C.2}$$

The new preliminary calibration shows a similar gradient between the integration area and the concentration, however the zero point deviation is decreased significantly. The deviation of the measurement values from the weighed-in values (shown in table C.4) is significant, even using the extended calibration function of table C.3. As this error is not present in the calibration function used for the standard experiments (see chapter 8), the most likely reason is the reliance of the optical marking when preparing the 20ml solutions.

C.3. Final Calibration Results

The samples for the standard experiments were collected five months after the initial preliminary calibration took place. For this reason, a

Weigh-In of NMMO MH	Weigh-In of Water	NMMO Mass Fraction	Integration Area 1	Integration Area 2
g	g	wt.%	mAu · min	mAu · min
1.0656	17.9617	4.85	10794.3	10842.3
1.6490	18.7292	7.01	15795.6	15550.5
0.5568	22.8046	2.07	4517.1	4490.8
0.1135	18.5301	0.53	1119.0	1060.7
3.1311	17.4543	13.18	28909.3	29329.6
5.2108	17.2697	20.09	43994.6	44185.5
0.0667	20.6859	0.28	539.6	483.0

Table C.5.: Weigh-in and resulting measurements for the final calibration.

Weigh-In NMMO Mass Fraction	NMMO Mass Fraction MM 1	NMMO Mass Fraction MM 2	Relative Error MM 1	Relative Error MM 2
wt.%	wt.%	wt.%	%	%
4.85	4.90	4.92	0.97	0.44
7.01	7.17	7.06	2.26	1.55
2.07	2.05	2.04	0.72	0.58
0.53	0.51	0.48	3.71	5.21
13.18	13.13	13.32	0.44	1.45
20.09	19.98	20.06	0.57	0.43
0.28	0.25	0.22	12.05	10.49

Table C.6.: Weigh-in and resulting measurements for the final calibration. Continuation of table C.5.

new calibration for the NMMO mass fraction in water was conducted. In order to neutralize the measurement error caused by relying on visual indicators for the water volume at the weigh-in, both water and NMMO were weighed-in using the analytical scale. The measuring data is shown in table C.5.

The measurements were fitted into equation (C.3).

$$IA_{HPLC} = 2202.3 \cdot w_{Sample,NMMO} \tag{C.3}$$

Compared to the preliminary calibration, the gradient between integration area and NMMO mass fraction differs significantly, and the zero-point deviation was eliminated.

The deviation of weigh-in from the calculated result is shown in table C.6 and shows a significantly lower error, below 2% at concentrations higher 1% NMMO, and only rising to 10% at the detection limit of 0.28%.

C.4. Concentration Evaluation in Preliminary Experiments

Sample Number		2	3	4	5	6
Weigh-In of NMMO MH	g	0.0886	0.1737	0.1785	0.2764	0.2736
NMMO Mass Fraction	wt.%	0.1512	0.2956	0.3076	0.4719	0.4628
Weigh-In before Conc.	g	49.85	49.94	49.33	49.74	50.14
Weigh-In after Conc.	g	8.81	5.12	5.35	6.24	7.16
Integration Area MM 1	-	1212.8	4537.6	4497.0	6702.2	5962.5
Integration Area MM 2	-	1255.7		4669.7		5981.6
Rel. Error in MM 1	%	6.96	5.04	4.24	4.36	8.61
Rel. Error in MM 2	%	9.71		0.90		8.93

Table C.7.: Weigh-in of NMMO in 50ml calibration solutions for preliminary experiments, as well as the results of the concentration experiment with a Rotavapor.

In this appendix, the measurements for the preliminary concentration experiments with a Rotavapor are shown. Table C.7 shows the weigh-in of NMMO in 50 ml calibration solutions for preliminary experiments. Sample number 1 was excluded because of an error in the procedure that was discovered too late to correct. The deviation of measured and calculated concentration remained in the same range as the error in the preliminary calibration, showing that no significant error occurred when using concentration to measure NMMO content.

C.5. Preparation of Liquid Samples for HPLC Measurement and Measurement Results

In tables C.8 through C.11, the sample preparation and measurement results are shown. Results are discussed further in chapter 9.4.

The quality of the HPLC measurements varies greatly. Some measurements only show the expected NMMO peak, and others only a small secondary peak ahead of the measurement peak, with little to no interference into the measurement result. These are unmarked in the table.

Some measurements have an increased secondary peak intruding into the measurement peak, but still separable from the target peak, however with an increased measurement error. These results are marked with a *, and used normally in the calculations, however the increased error of results using these measurements should be kept in mind.

Finally there are measurements where either the secondary peak surpasses the measurement peak, so they are inseparable for measurement, or measurements are below the detection limit. These results are marked

Sample Number	Weigh-In	Weigh-Out	Conc. Factor	Integration Area 1	Integration Area 2
	g	g	-	$mAu \cdot min$	$mAu \cdot min$
01-02	-	-	-	16807	15703
01-09	-	-	-	43236	39079
01-03	659.90	291.60	2.26	2461.0*	2454.5
01-08	-	-	-	3958.8*	3978.5
01-04	106.64	5.07	21.03	5146.1*	5781.7*
01-10	80.74	10.01	8.07	4467.1*	4681.9*
01-05	241.07	7.90	30.52	10245.0**	9612.4**
01-11	173.99	13.39	12.99	3870.4**	4483.8**
02-02	-	-	-	2178.7	2189.6
02-03	-	-	-	20816.8	20371.7
02-09	209.22	8.39	24.94	3901.8*	4403.8
02-05	-	-	-	1940.8	2050.5
02-10	232.2	6.19	37.51	683.3*	579.0*
02-06	198.72	3.38	58.79	6669.1*	6831.1
02-11	450.80	15.62	28.86	101.7**	-
02-08	202.51	16.62	14.87	118.8**	-
03-02	-	-	-	11835.8	11915.8
03-08	98.81	9.60	10.29	9171.7	9056.3
03-04	211.56	6.62	31.96	995.7	1008.8
03-05	327.97	15.18	21.61	50.5**	-

Table C.8.: Weigh-in for sample concentration as well as the concentration factor and the measurement results for settings V01 through V03.

with a **. The measured areas reported for these measurements are attempts at interpreting the result, however they should not be taken with any certainty. They are used in the mass balance and clearly marked.

Similarly marked with ** are measurements that fall below the detection limit of the HPLC method. These are corrected to the lowest possible mass fraction that could still be clearly detected. The corrected values (for concentration factor and quality) used for the mass balance are reported in column 'NMMO Conc. adjusted' in this table.

The sample number is used for internal identification only. The starting number accounts for the source experiment, for example 01-01 was conducted in experiment V01.

Sample Number	Weigh-In	Weigh-Out	Conc. Factor	Integration Area 1	Integration Area 2
	g	g	-	$mAu \cdot min$	$mAu \cdot min$
06-01	-	-	-	17687.1	17640.6
06-03	-	-	-	3632.9	3427.1
06-02	-	-	-	23788.6	23452.6
06-10	138.52	25.07	5.53	1646.6	1488.8
06-05	-	-	-	1524.1	1433.5
06-08	233.16	17.83	13.08	3391.8	3508.4
06-09	130.58	16.87	7.74	2543.9	2566.0
06-06	348.56	11.29	30.87	8248.2	8353.5
06-07	203.43	10.05	20.24	5555.4	5599.7
07-02	-	-	-	2898.9	2740.6
07-03	-	-	-	12003.7	11773.7
07-05	220.19	17.12	12.86	580.1	562.0
07-10	240.98	34.41	7.00	3753.3	3778.7
07-08	233.42	4.57	51.08	442.5**	-
07-09	195.87	15.07	13.00	322.2*	-
07-06	304.04	13.49	22.54	149.8**	-
07-07	348.30	9.10	38.27	221.9**	-
08-01	-	-	-	19836.9	19729.7
08-03	-	-	-	11434.3	10999.6
08-04	-	-	-	34552.5	35900.7
08-10	261.36	22.82	11.45	7739.4	7739.4
08-05	-	-	-	8101.7	7449.4
08-06	182.34	7.03	28.94	967.6	942.7
08-07	180.38	34.92	5.17	4108.1	4111.8
08-08	279.51	11.59	24.12	200.5**	-
08-09	27.66	37.93	7.37	399.4**	-

Table C.9.: Weigh-in for sample concentration as well as the concentration factor and the measurement results for settings V06 through V08.

Sample Number	NMMO Mass Frac. MM 1	NMMO Mass Frac. MM 2	NMMO Conc. adjusted	Sampling Time and Location
	wt.%	wt.%	wt.%	
01-02	7.63	7.13	7.38	Stage 2 at Start
01-09	19.63	17.74	18.69	Stage 2 at End
01-03	1.12*	1.11	0.49	Stage 3 at Start
01-08	1.80*	1.81	1.80	Stage 3 at End
01-04	2.34*	2.63*	0.118*	Stage 4 at Start
01-10	2.03*	2.13*	0.258*	Stage 4 at End
01-05	4.65**	4.36**	0.148**	Stage 5 at Start
01-11	1.76**	2.04**	0.146**	Stage 5 at End
02-02	0.99	0.99	0.99	Stage 2 at Start
02-03	9.45	9.25	9.35	Stage 2 at End
02-09	1.77*	2.00	0.076	Stage 3 at Start
02-05	0.88	0.93	0.90	Stage 3 at End
02-10	0.31*	0.26*	0.0076*	Stage 4 at Start
02-06	3.03*	3.10	0.052	Stage 4 at End
02-11	0.00**	-	<97ppm	Stage 5 at Start
02-08	0.00**	-	<187ppm	Stage 5 at End
03-02	5.37	5.41	4.39	Stage 2 at End
03-08	4.16	4.11	0.40	Stage 3 at End
03-04	0.45	0.46	0.014	Stage 4 at End
03-05	0.00**	-	<129ppm	Stage 5 at End

Table C.10.: NMMO mass fraction in the measurement samples according to the HPLC calibration, as well as the sampling time and location for settings V01 through V03.

Sample Number	NMMO Mass Frac. MM 1	NMMO Mass Frac. MM 2	NMMO Conc. adjusted	Sampling Time and Location
	wt.%	wt.%	wt.%	
06-01	8.03	8.01	8.02	SPB at Start
06-03	1.65	1.56	1.60	Stage 2 at Start
06-02	10.80	10.65	10.73	Stage 2 at End
06-10	0.75	0.68	0.129	Stage 3 at Start
06-05	0.69	0.65	0.67	Stage 3 at End
06-08	1.54	1.59	0.119	Stage 4 at Start
06-09	1.16	1.17	0.150	Stage 4 at End
06-06	3.75	3.79	0.122	Stage 5 at Start
06-07	2.52	2.54	0.125	Stage 5 at End
07-02	1.32	1.24	1.28	Stage 2 at Start
07-03	5.45	5.35	5.40	Stage 2 at End
07-05	0.26	0.26	0.020	Stage 3 at Start
07-10	1.70	1.72	0.244	Stage 3 at End
07-08	0.00**	-	<55ppm	Stage 4 at Start
07-09	0.00**	-	<214ppm	Stage 4 at End
07-06	0.00**	-	<124ppm	Stage 5 at Start
07-07	0.00**	-	<73ppm	Stage 5 at End
08-01	9.01	8.96	8.98	SPB at Start
08-03	5.19	4.99	5.09	Stage 2 at Start
08-04	15.69	16.30	16.00	Stage 2 at End
08-10	3.51	3.51	0.307	Stage 3 at Start
08-05	3.68	3.38	3.53	Stage 3 at End
08-06	0.44	0.43	0.017	Stage 4 at Start
08-07	1.87	1.87	0.36	Stage 4 at End
08-08	0.00**	-	<116ppm	Stage 5 at Start
08-09	0.00**	-	<378ppm	Stage 5 at End

Table C.11.: NMMO mass fraction in the measurement samples according to the HPLC calibration, as well as the sampling time and location for settings V06 through V08.

C.6. Preparation of Solid Fibre Samples to Determine the Remaining NMMO Content

In this appendix, the measurement tables for the analysis of the solvent concentration in solid samples are reported. Tables C.12 and C.13 list the measurements taken of the resulting filament products of every experiment, table C.14 lists measurements for the samples taken between spinning bath and washing plant.

Markings for the quality of the HPLC measurements apply as stated in appendix C.5.

Setting		V01	V02	V03
Fibre Sample Weigh-In	g	25.92	25.45	31.03
Washed Fibre Wet Weight	g	79.99	84.52	98.16
Remaining Washing Water	g	396.23	550.97	459.27
Fibre Dry Weight	g	16.71	15.57	18.46
NMMO in Washing Water	ppm	419**	346	367
Resulting NMMO per Sample	mg	193**	214	198
Original NMMO in Sample	wt.%	1.14**	1.36	1.06

Table C.12.: Measurements and resulting calculation of the solvent concentration remaining in the filament fibres after the washing plant for settings V01 through V03. Measurements marked with ** are approximations only. Overall the concentration remains below 1.4% solvent.

Setting		V06	V07	V08
Fibre Sample Weigh-In	g	13.91	11.49	32.59
Washed Fibre Wet Weight	g	61.18	48.64	121.27
Remaining Washing Water	g	345.33	433.17	587.93
Fibre Dry Weight	g	10.15	9.06	15.45
NMMO in Washing Water	ppm	263*	<78*	217
Resulting NMMO per Sample	mg	104*	<40ppm*	150
Original NMMO in Sample	wt.%	1.02*	0*	0.96

Table C.13.: Measurements and resulting calculation of the solvent concentration remaining in the filament fibres after the washing plant for settings V06 through V08. Measurements of setting V06 marked with * have an increased error potential. Overall the concentration remains below 1% solvent.

Setting		V05-1	V05-2
Fibre Sample Weigh-In	g	39.94	61.01
Remaining Washing Water 1^{st} Washing	g	723.23	634.17
Remaining Washing Water 2^{nd} Washing	g	505.83	559.07
Washed Fibre Wet Weight 2^{nd} Washing	g	70.00	93.90
Fibre Dry Weight	g	6.94	9.63
NMMO in Washing Water 1^{st} Washing	wt.%	1.702	0.223
NMMO in Washing Water 2^{nd} Washing	wt.%	2.877	0.545
Resulting NMMO per Sample	g	13.57	21.76
Original NMMO in Sample	wt.%	66.17	69.32

Table C.14.: These filament samples were taken after V06 between the washing plant and the spinning bath at normal operation. Samples were extracted twice in succession, and result in an initial solvent concentration of 66 to 69 % at the start of the washing plant.

Appendix D.

Timeline Recordings taken from the Process Control System

In this chapter, the records for the spinning pump in the process control system during the standard experiments (see chapter 8) are shown. The spinning pump is controlled by the pressure in the system, which is further controlled by an upstream feed pump. The drawing speed is calculated by the process control system to keep the titre constant by a fast acting controller, and is almost proportional to the spinning pump performance. The reason the spinning pump performance is an important variable is that it has a volumetrically defined flow rate with 12.56 cm^3/rev, which was used in chapter 9.4 to calculate the introduced solvent.

The following figures show the recorded spinning pump speed in rpm between the start and end of every experiment. The description contains a short interpretation and quality evaluation of the experiment in general, as well as the measured average drawing speed of the washing plant during the experiment.

The figures show that there were significant problems during the operation of the washing plant, both instrumental (a pressure drop off caused by a clogging filter) and during controlling (late notice of pressure drop offs and wrong inputs for feeding pump performance).

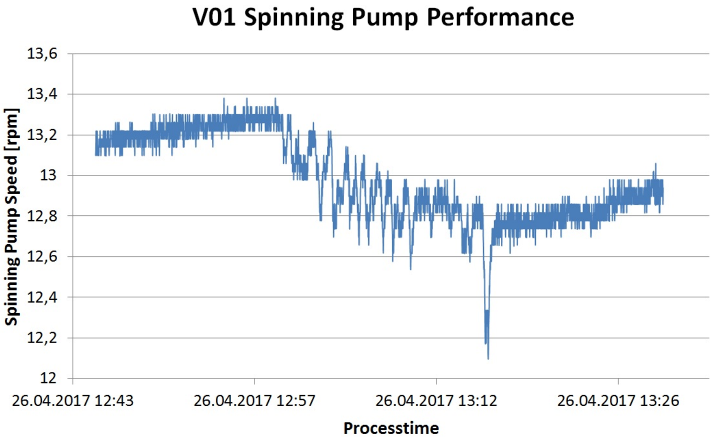

Figure D.1.: Spinning pump speed during the setting V01. It remains relatively constant between 12.5 and 13.5 rpm, which results in an average drawing speed of 129 m/min. Overall, this timeline is acceptable, even if the target drawing speed of 120 m/min was exceeded.

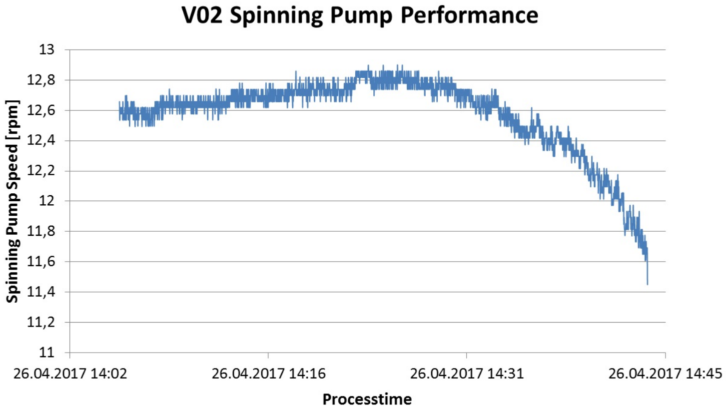

Figure D.2.: Spinning pump speed during the setting V02. It starts constant between 12.5 and 12.9 rpm, however there was a pressure drop off caused by a clogging filter, which resulted in a drop off of the spinning pump speed. As a result, the setting was stopped after 38 min, and the average drawing speed was 115 m/min, below the target of 120 m/min. Overall this timeline is barely acceptable.

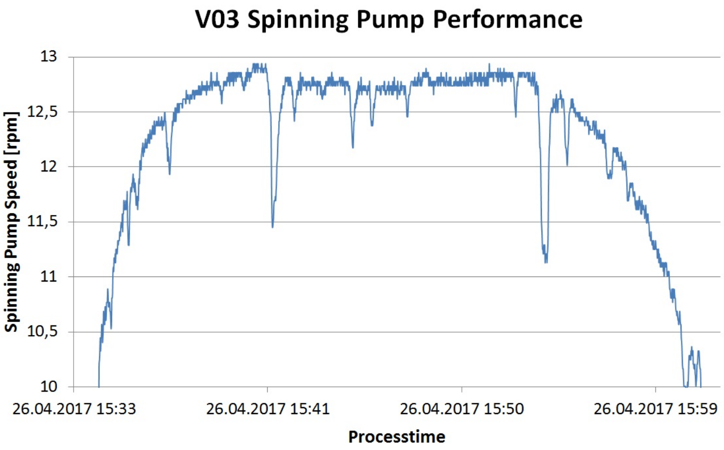

Figure D.3.: Spinning pump speed during the setting V03. Immediately apparent is the premature starting time of the experiment: the washing plant was not yet at full speed when the first measurements were taken. During the experiment, the spinning pump speed remained between 12.5 and 13 rpm, however as in setting V02 the clogging of a filter caused a pressure drop off which ended the experiment prematurely at 27 min. The average drawing speed was 118 m/min, close to the target of 120 m/min. Overall this timeline is barely acceptable.

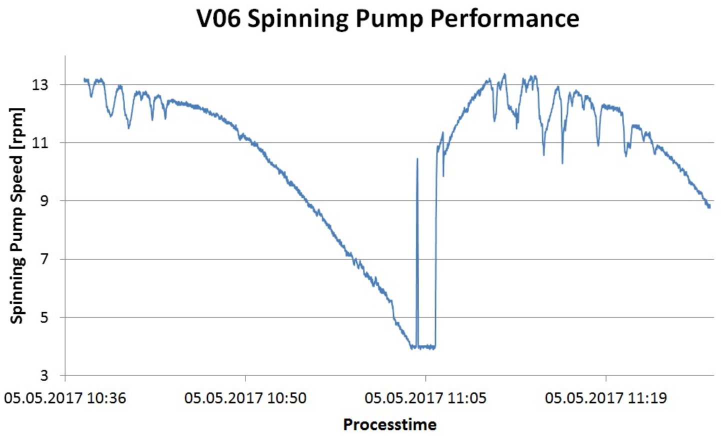

Figure D.4.: Spinning pump speed during the setting V06. During this setting there was another clogging of the filter, which was detected too late by the plant operator. As a result, the spinning pump speed dropped to an unacceptable level. The extent of the error was not immediately apparent during the execution of the experiment, so an attempt was made to minimize the error time by extending the experiment to 49 min. As this figure shows, however, this did not succeed. The average drawing speed during the entire setting was 111 m/min, however the variance is too high to allow for a serious comparison with the other settings.

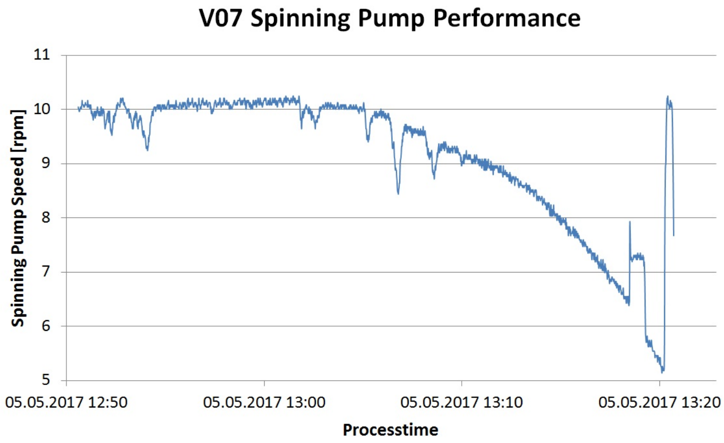

Figure D.5.: Spinning pump speed during the setting V07. While the spinning pump performance starts constant at 10 rpm, it drops off towards the end, causing a premature end of the experiment at 30 min. While the drop off is significant and impacts the quality of the experiment, it was not as serious as in setting V06. The average drawing speed was 120 m/min, right on target.

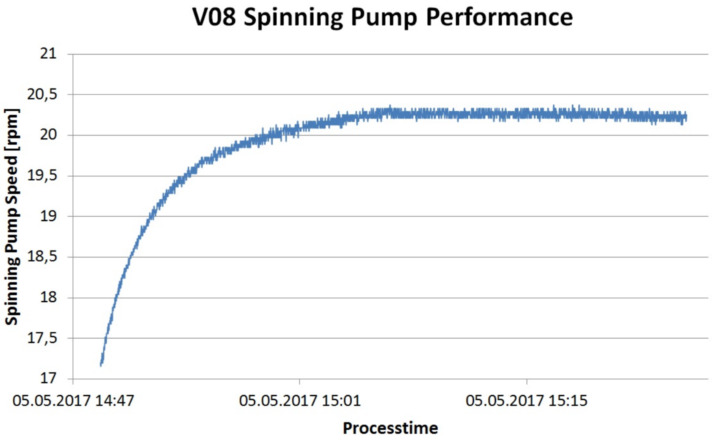

Figure D.6.: Spinning pump speed during the setting V08. As shown in the figure, the timeline starts at around 17 rpm, which was the target speed for the spinning pump. However, the upstream feeding pump was set to a too high speed, which caused the spinning pump to speed up to alleviate the pressure. This resulted in an average drawing speed of 174 m/min during the 37 minutes time, far above the target of 120 m/min. While the performance was relatively constant during this setting, it cannot be reasonably compared with the reference since both titre and the drawing speed were varied significantly.