



Electro-assisted filtration for biorefinery applications

The influence of ionic strength during electro-assisted filtration of microcrystalline cellulose

Master's thesis in Innovative and Sustainable Chemical Engineering

SANDRA JONSSON

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Department of Chemistry and Chemical Engineering Division of Chemical Engineering CHALMERS UNIVERSITY OF TECHNOLOGY Gothenburg, Sweden 2016 Electro-assisted filtration for biorefinery applications The influence of ionic strength during electro-assisted filtration of microcrystalline cellulose SANDRA JONSSON

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Abstract

One of the great challenges in biorefineries is the solid-liquid separation of the biomass. Many biomass particles form normally compressible filter cakes, which is very hard to dewater. A way to enhance filtration is to apply an electric field over the pressure filtration equipment and thus make use of electrokinetic forces to further drag out the liquid. This thesis studies the influence of the electric field on the filtration behaviour and also how an increase in ionic strength by adding a salt, Na₂CO₃, affects the system during electro-assisted filtration.

The material used was microcrystalline cellulose (MCC), which is known to form compressible filter cakes. The MCC was mechanically treated to increase the particle surface area and thus slow down the filtration rate. The filtration experiments were done with three levels of ionic strength: no extra addition, low and high addition of Na_2CO_3 . All cases were studied by regular pressure filtration and electro-assisted filtration.

The increasing ionic strength gave a higher filtration rate. The filter medium resistance and the filtration resistance decreased with increasing ionic strength, as can be correlated to lowering the surface charge of the MCC particles. The applied electric field enhanced the filtration behaviour, even for a reversed electric field. However, the negative electric field increased the power consumption, which increased the temperature. A significant heating effect was observed for electro-assisted filtration. The combination of applied voltage at higher ionic strength increased the filtration rate. The relative gain in filtration rate was much more significant for the lower ionic strength by electro-assisted filtration. The power consumption increased a lot with higher ionic strength, which can be a crucial parameter for biorefineries.

Keywords: electrofiltration, ionic strength, microcrystalline cellulose, particle surface charge, electroosmosis, ohmic heating.

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List of Symbols

Latin letters

A	flow area $[m^2]$			
с	mass of solids per filtrate volume $[\rm kg/m^3]$			
d_{γ}	average path length for γ -radiation [m]			
Ι	electric current [A]			
K	cake permeability per length unit $[m^2]$			
P	pressure [Pa]			
Q	filtrate flow rate $[m^3/s]$			
R	electric resistance $[\Omega]$			
R_m	filter medium resistance $[m^{-1}]$			
t	time [s]			
U	electric potential [V]			
V	volume [m ³]			
Greek letters				
α	local specific filtration resistance $[m/kg]$			
α_{avg}	average specific filtration resistance [m/kg]			
η_{γ}	number of observations $[-]$			

 $\eta_{\gamma,0}$ number of observations during background measurement [-]

 μ viscosity of the liquid phase [Pa · s]

- $\mu_{\gamma,l}$ attenuation coefficient for the liquid phase [m⁻¹]
- $\mu_{\gamma,s}$ attenuation coefficient for the solid phase [m⁻¹]
- ρ_s solid density [kg/m³]
- σ conductivity [μ S/cm]
- ϕ local solidosity $[m^3/m^3]$

1

Introduction

1.1 Background

A step in the direction for sustainability is using renewable products and processes. A biorefinery is a process that uses biomass as raw material for production of various new and renewable products and materials (Ragauskas *et al.*, 2006). One large part of the biorefinery process is the solid-liquid separation, which can be a great challenge due to the solid feedstock. Continuously during the process the biomass will be dissolved in and separated from the liquid. The choice of separation method is often pressure, or so called dead-end filtration, which is an energy-efficient way of performing the solid-liquid separation (Ramaswamy *et al.*, 2013).

During dead-end filtration a porous filter cake is formed over a filter medium, as the filter medium stops the solid particles and allows only the liquid to pass through. The bio-based material here gives the challenge and it may be crucial to improve the separation in order to make the process more efficient. Bio-based material tend to, during solid-liquid separation, form a very porous and compressible filter cake (Saveyn *et al.*, 2005a). The rate of filtration will depend on the formed cake and its properties. The difficulties in achieving a reasonable filtration rate depend mostly on the particle surface area as the flow resistance increases with decreasing particle size (Kozeny, 1927; Carman, 1937; Weber & Stahl, 2002). Thus, the particle surface structure also affects the filtration. A more uneven particle surface will result in a larger specific surface area and this will then further increase the filtration resistance (Wetterling *et al.*, 2014).

A way to enhance the separation is to combine the pressure filtration with an applied electric field over the filtration cell, a technique called electrofiltration (Weber & Stahl, 2002). The electric field will act on ions in the solution as well as on the charged solid particles to the electrode of opposite polarity and thus promote the separation. This can be describe by two simultaneously occurring effects: electroosmosis and electrophoresis. Two other effect can also occur during electrofiltration: electrolysis and ohmic heating. These four effects can affect the filtration, both beneficial and unfavourable, and have to be considered during the performance (Weber & Stahl, 2002; Mahmoud *et al.*, 2010).

The material used in this thesis will be microcrystalline cellulose (MCC), which is a wood-based product known to form a compressible filter cake (Mattsson *et al.*, 2012a). This thesis will study electrofiltration effects of MCC. The filtration behaviour of MCC has been studied previously, however not in a large extent for the influence of an electric field (Wetterling *et al.*, 2014; Mattsson *et al.*, 2012a,b).

1.2 Objective

This thesis aims to investigate how the electro-assisted filtration of microcrystalline cellulose is affected by the ionic strength of the suspension. The relation between electrokinetic effects and ohmic heating during the influence of ionic strength will be studied. Further on, both the ionic strength and the electric field strength will be varied and the influence of the two, respectively, will be investigated. The subsequent questions are formulated to help evaluate the aim of this thesis.

- 1. How will variation of ionic strength influence the filtration behaviour of microcrystalline cellulose?
- 2. How will the electric field strength influence the filtration behaviour of microcrystalline cellulose?
- 3. How will ionic strength influence the relation between electrokinetic effects and ohmic heating?

2

Theory

2.1 Cake filtration

Pressure, or dead-end, filtration consists mainly of two phases during the process: cake build-up and filter cake consolidation. During the cake build-up phase the pressure is applied over a slurry, achieving solid-liquid separation as the solid particles will be gathered on a filter medium whilst the liquid will slip through. The cake will be built on as the pressure filtration continues. When all free suspension above the formed cake is gone the cake consolidation phase takes place. A higher degree of dewatering is achieved by compression of the cake structure by the applied pressure.

2.1.1 Flow through porous bed

Filtration can be described as a fluid flow through a porous medium. The filter cake will be continuously formed on top of the filter medium and can be regarded as a porous bed. One of the governing laws for the flow through the filter cake is Darcy's equation, eq. 2.1 (Darcy, 1856). The driving force through the bed is the arisen pressure drop due to the flow and Darcy (1856) related the pressure drop to the filtrate flow rate Q, however the original equation did not contain a viscosity term.

$$Q = -\frac{KA}{\mu} \frac{dP}{dz} \tag{2.1}$$

K is the permeability of the formed cake, μ is the viscosity of the fluid, A is the flow area and $\frac{dP}{dz}$ is the differentiation of how the pressure drop develops with the thickness of the filter cake. The solid content of the filter cake will affect the rate of filtration by hindering the flow. How much solid material the filter cake consists of is given by the solidosity, ϕ , as described in eq. 2.2.

$$\phi = \frac{V_{solid}}{V_{total}} \tag{2.2}$$

 V_{solid} is the volume of the solid material and V_{total} is the total volume of the filter cake.

2.1.2 Filtration resistance

The specific filtration resistance in the filter cake, α , is a relation of the cake permeability and the solidosity, as described in eq. 2.3.

$$\alpha = \frac{1}{K\rho_s\phi} \tag{2.3}$$

where ρ_s is the density of the solid material.

Eq. 2.4 is usually known as the classical filtration equation, where the filtration rate is related to the average specific filtration resistance (α_{avg}) , the filter medium resistance (R_m) and the static pressure drop (ΔP) (Ruth, 1935).

$$\frac{dt}{dV} = \frac{\mu \left(\alpha_{avg} cV + R_m A\right)}{A^2 \Delta P} \tag{2.4}$$

c is the mass of solids per filtrate volume.

A general assumption is that most filter cakes are incompressible, which is far from true. Most systems show a compressible cake behaviour and thus the equations have to be modified to account for this compressibility. Eq. 2.1 and 2.3 are valid for incompressible filter cakes when using overall data; the solidosity and specific filtration resistance are assumed constant throughout the cake. To account for the compressibility the local properties in the filter cake have to be studied as well. The applied pressure will affect the cake differently in different locations in the cake (Tiller & Cooper, 1960) and the cake can no longer be regarded as uniform.

The expression for the local specific filtration resistance is given by eq. 2.5. This equation includes how the filtration rate is affected by the pressure drop, resulting in the local specific resistance. Eq. 2.5 is a combination of eq. 2.1 and 2.3 and can be regarded as Darcy's equation (eq. 2.1) with local properties.

$$\alpha = -\frac{1}{v\rho_s\phi\mu}\frac{dP_l}{dz} \tag{2.5}$$

Here, v is the superficial fluid velocity, μ is the viscosity of the fluid and the pressure drop over the filter cake is also included in accordance with Tiller and Cooper (1960).

2.2 Electric double layer

For a suspension of solid particles in a liquid, the solid particles will have a determined surface charge. If the liquid is an electrolytic solution there will be a lot of ions suspended in the fluid. The existing charge of the particle surface will attract the ions of opposite charge in the electrolytic solution and these ions will adhere to the surface forming a layer. Further out, more ions will be attracted and form a more diffuse and transient second layer, the electric double layer. The diffuse layer will have the same charge as the particle.

Helmholtz (1853) discovered that electrodes dipped in electrolytic solution attracted the counter-ions to the surface. This was then explained by the fact that two ionic layers of opposite polarity were formed around the electrode and the charges are stored electrostatically (Helmholtz, 1853). The double layer will work as an isolation, shown by a potential drop over the layers from the surface to the bulk liquid.

2.3 Electrofiltration

To enhance the filtration process an electric field can be applied, if the solid particles have a surface charge and an electric double layer is formed. During electrofiltration there are four main effects occurring: electroosmosis, electrophoresis, electrolysis and ohmic heating. These effects will occur in conjunction with the electric double layer.

2.3.1 Electrokinetic phenomena

Electroosmosis and electrophoresis are known as electrokinetic effects. These two effects combined can affect and improve the solid-liquid separation (Weber & Stahl, 2002; Mahmoud *et al.*, 2010; Loginov *et al.*, 2013). Electroosmosis will act on the charged liquid close to the particle surface and create a flow relative to the solid phase.

Simultaneously to electroosmosis electrophoresis is taking place. Electrophoresis will instead act on the charged solid particles, attracting them towards the electrode with opposite polarity. The solid particles will move relative to the electrolytic fluid.

2.3.1.1 Models

One of the first models to describe the electrokinetics in electrofiltration was formulated by Yukawa et al. (1976). This model was an extension of the general filtration equation seen in eq. 2.4 (Ruth, 1935). Here, electroosmosis was the driving force with an addition to the hydraulic pressure. This electroosmotic pressure is generated in the filter cake and the filter medium. For the electrophoretic force the filter cake build-up will decrease as the strength of the electric field increases. There will be a critical strength of the electric field (E_{cr}) and when this is reached the electrophoretic velocity will equal the filter cake formation rate and no filter cake can be formed at the filter medium. This was determined with a main equation for the pressure electrofiltration, eq. 2.6 (Yukawa *et al.*, 1976).

$$\frac{dt}{dV} = \frac{\mu \left(\alpha \cdot \nu_0 \cdot \left(\frac{E_{cr} - E}{E_{cr}}\right) \cdot \frac{V}{A} + R_m\right)}{A \cdot g_c \cdot (\Delta P_H + \Delta P_E)}$$
(2.6)

V is the volume of the filtrate, t is the time, μ is the viscosity of the filtrate, α is the specific resistance, ν_0 is the dry cake mass per unit volume of filtrate, E_{cr} and E are the critical and actual electric field strength, respectively, A is the filtration area, R_m is the filtration resistance for the filter medium, g_c is a conversion factor and ΔP_H and ΔP_E are the hydraulic and electroosmotic pressures, respectively.

Saveyn et al. (2005b) formulated other fundamental equations for the cake formation at each electrode, seen in eq. 2.7-2.9. These equations are derived from the filtrate flow rates both when only the pressure-driven filtration is taking place and when the electrokinetic processes affects the electrofiltration. Both the electroosmosis by attachment of the solid particles in the filter cake due to the surface charge and the electrophoresis by transport of the solid particles towards the cake are accounted for in this model (Saveyn *et al.*, 2005b).

$$Q_{p,an} = \frac{dV_{p,an}}{dt} = \frac{\Delta P_H A}{\eta \left(r_c L_{an} + R_m \right)} \tag{2.7}$$

The equation for pressure filtration at the anode side (eq. 2.7) is similar to the general filtration equation, eq. 2.4. Here, ΔP_H is the hydraulic filtration pressure, A is the filter area, η is the filtrate viscosity, r_c and R_m are the filter cake and filter medium resistances, respectively, and V is the volume of filtrate.

Eq. 2.8 and 2.9 are the equations for electroosmotic and electrophoretic driven filtrate flows at the cathode, respectively.

$$Q_{eo,ca} = \frac{dV_{eo,ca}}{dt} = -\frac{D\varepsilon_0\zeta}{\eta}E_c\varepsilon_cA$$
(2.8)

$$Q_{ef,ca} = +\frac{D\varepsilon_0 \zeta}{\eta} E_s \left(1 - \varepsilon_s\right) A \tag{2.9}$$

As seen, the electroosmosis is negative at the cathode whilst the electrophoresis is positive. At the anode, it will be the opposite case. D is the dielectric constant of the liquid phase, ε_0 is the permittivity of vacuum and ζ is the ζ -potential of the electric double layer. By further on study the thickness of the layer of slurry that is transformed into cake complete equations with both the pressure part and the electroosmotic part for determining filtrate flow rates at each electrode can be formulated, seen in eq. 2.10 and 2.11.

$$V_{ca} = \int Q_{p,ca} dt - \int Q_{eo,ca} dt \qquad (2.10)$$

$$V_{an} = \int Q_{p,an} dt + \int Q_{eo,an} dt \qquad (2.11)$$

2.3.2 Ohmic heating

During the influence of an electric field the applied current will result in a temperature rise in the filter cake. This mechanism is called ohmic heating (or Joule heating). The basic principle is that the conductor, in this case the liquid in filter cake, generates heat when the electric current is passed through. The amount of heat produced can be determined by Joule's law (Joule, 1841), seen in eq. 2.12.

$$\dot{Q} = I^2 \cdot R,\tag{2.12}$$

where \dot{Q} is the amount of heat produced per time unit, I is the current and R is the resistance of the conductor. In filtration theory this implies that temperature increase will decrease the filtrate viscosity and thus enhance the dewatering by increasing the filtration rate, according to Darcy's equation (eq. 2.1).

2.3.3 Electrolysis

Electrolysis is the process of an electrolytic solution that under the influence of a direct electric current (DC) will separate the solution into its building ions by rearrangement of the ions in the solution. This is also a process that occurs during water decomposition. Electrolysis occurs at the electrodes and the formed ions move towards the electrode of opposite polarity, creating an excess of the given polarity at each electrode.

Possible reactions to occur at the electrodes are given below (Lockhart, 1983). Reaction A1 and A2 are possible anode reactions.

$$M_A \to M_A^n + ne^- \tag{A1}$$

$$6H_2O + O_2 \rightarrow 4H_3O^+ + 4e^-$$
 (A2)

 M_A denotes the anode material. If M_A is a noble metal such as Ag, Pt, Au, Hg etc., reaction A2 will take place, but in general reaction A1 will take place at the anode. These reactions are oxidising reactions and will lead to a pH decrease at the anode. Reaction C1 and C2 are possible cathode reactions.

$$\mathbf{M}^{n+} + ne^- \to \mathbf{M} \tag{C1}$$

$$2\mathrm{H}_{2}\mathrm{O} + 2e^{-} \rightarrow \mathrm{H}_{2} + 2\mathrm{OH}^{-} \tag{C2}$$

Here M denotes the cation derived from the anode. Reaction C1 will be favoured over C2 for cations derived from the noble metals mentioned earlier. Though, reaction C2 will mostly occur due to the unlikeliness of a significantly large concentration

of the other cations. The reactions occurring at the cathode are reducing reactions and will lead to a pH increase locally at the cathode.

Methods

3.1 Filtration

The performed filtration was a dead-end filtration with an applied electric field, so called electrofiltration. The equipment used was remodelled from a previously custom-built equipment in order to perform these specific experiments with the applied electric field (Johansson & Theliander, 2003; Wetterling *et al.*, 2016).

3.1.1 Filtration equipment

The equipment consists of a scaffold holding a cylindrical piston with a diameter of 60 mm in the filter cell. The bottom sieve is a perforated plastic plate with four water-filled capillary tubes with openings of 0.6 mm diameter at the heights of 2, 4, 6, 8 mm into the filter cake. The purpose of the capillaries is to be able to measure the local hydrostatic pressure at different levels of the filter cake to get an accurate pressure profile. The electrodes are placed below the filter medium and inside the filter cell. The lower electrode is a fine platinum mesh (Unimesh 300), while the upper electrode is built of a network of 0.1 mm thin platinum thread with squared openings of 10 mm. The distance between the electrodes is kept constant at 25 mm. The filter cell is a plexiglas cylinder of 60 mm in diameter and 115 mm high, where the upper electrode is fixed in the cylinder. The filter cell spire down where the filter cake built up will take place and the diameter of the filter cake is thus 49 mm. The electrodes are attached to a DC generator (EA-PSI 5200-02 A, Elektro-Automatik) where the applied voltage and current can be regulated. The temperature inside the filter cake is measured by two PFA coated thermocouples connected to the filter cell at 5 mm (denoted T2) and 20 mm (T1) above the filter medium, respectively. The filtrate was collected below the filter cell and weighted continuously to determine the filtration rate. The filtration rate could also be determined from the piston position. Both piston position and filtrate weight as well as temperature, pressure, applied voltage, current and power consumption were measured and recorded in LABVIEW every 2 seconds. The design of the filtration equipment setup is described in figure 3.1.



Figure 3.1: Schematic description of the filter cell setup.

Adjacent to the filter cell is a ²⁴¹Am γ -radiation source. The purpose of the use of a radiation source is to be able to determine the local solidosity by measuring the radiation attenuation. The calibration of the attenuation coefficient was done by measuring the background radiation during 5 minutes to get the number of observations for the empty filter cell (denoted as $n_{\gamma,0}$ in eq. 3.1) as that solidosity will be known. The recorded observations were performed in the energy range of 33-83 keV.

The filter medium used was Supor®-450, polyethersulphone filter (Pall Corporation) with a nominal pore size of 0.45 μ m according to the product specifications. Also, a grade 5 Munktell filter was used as a supporting filter medium.

3.1.2 Solidosity measurements

The local solidosity can be calculated by the relation in eq. 3.1, which is known as Beer-Lamberts law for two phases.

$$-\ln\frac{n_{\gamma}}{n_{\gamma,0}} = \mu_{\gamma,l}d_{\gamma} + (\mu_{\gamma,s} - \mu_{\gamma,l})\,d_{\gamma}\phi \tag{3.1}$$

where $n_{\gamma,0}$ is the number of observations for the empty filter cell with background radiation and n_{γ} is the number of observations during the measurement. $\mu_{\gamma,l}$ and $\mu_{\gamma,s}$ are the attenuation coefficients for water and MCC, respectively, with values of 19.7 m⁻¹ for water and 29.1 m⁻¹ for MCC (Wetterling *et al.*, 2014). d_{γ} is the average path length in the filter cell, of which the radiation is passed through.

3.2 Material

The solid material used was microcrystalline cellulose (MCC), Avicel[®] PH-105 (FMC Biopolymers). The MCC can be commercially purchased and has according to the product specifications a nominal particle size of 20 μ m. The MCC was first mechanically treated before the filtration by using an IKA Ultra-Turrax T50 D. The treatment rugged the particle surface in order to increase the surface area and thus slow down the filtration. The mechanical treatment was performed on a 2 L slurry of 5 vol% solid material in deionised water and at 10 000 rpm for 5 min and then the slurry was diluted to 3.5 L of 3 vol%. The final slurry was left in a baffled mixing vessel for a minimum of 12 hours in order to let the MCC particles swell.

3.2.1 Characterisation

Different characterisation methods were used to closely study the material and verify the consistency of the mechanical treatment. Laser diffraction measurements were done to achieve a particle size distribution. The purpose was to observe the effect of the mechanical treatment on the particle size. The measurements were done by Malvern Mastersizer 2000. The particle size distribution was compared to the distribution for the slurry without prior mechanical treatment and no difference should be noticeable if the treatment only has increased the surface area.

BET adsorption measurements were done to analyse the specific surface area of the MCC particles before and after the mechanical treatment. Preparation was done by extracting a sample and drying out the particles by solvent exchange with acetone and cyclohexane by displacement washing, to try to retain as intact particles as possible (Stone & Scallan, 1965). Finally the particles were dried out totally with nitrogen as inert gas. Nitrogen was also used as adsorption gas when using a Micromeritics Tristar 3000 to measure the specific surface area.

3.3 Filtration experiments

The filtration experiments were done with three levels of ionic strength: no extra addition, low and high addition of salt. The chosen salt was sodium carbonate (Na_2CO_3) , to make use of the buffering effect to buffer some of the electrolytic reactions that occur. The added amounts of salt and the corresponding pH in the suspensions are given in table 3.1.

Table 3.1: The different levels of added Na_2CO_3 in the filtration experiments with the corresponding pH of the prepared slurry.

amount	[g/3.5~L]	рН
no addition	-	6.3
low addition Na_2CO_3	0.48	9.3
high addition Na_2CO_3	1.30	10.6

The filtration experiments were all performed with a constant filtration pressure of 2 bar. For the electro-assisted filtration three levels of electric field intensity were chosen: 0 V, 75 V and 150 V. For these voltages the experiments were done with the cathode beneath the filter medium, resulting in a positive electric field. Experiments with the high voltage (150 V) were also performed with a reversed electric field, by placing the anode beneath the filter medium, denoted -150 V.

4

Results and discussion

4.1 Characterisation

To verify that the mechanical treatment of the MCC particles was consistent and to know the properties of the material a number of characterisations were performed.

4.1.1 Particle surface charge

Figure 4.1 shows the surface charge for the MCC particles for different pH. By titration of linear pDADMAC the particle surface charge could be determined at different pH levels (Wetterling *et al.*, 2016). At acidic pH the surface charge is low. At neutral and alkaline pH the particle surface is strongly negatively charged. The difference between the surface charge for the neutral and alkaline pH is very small and indicates that the maximum charge is reached.



Figure 4.1: Surface charge of MCC particles at different pH, expressed in pDAD-MAC equivalents. Data from Wetterling (2016).

4.1.2 Particle size

The mechanical treatment was done as a preparation step for every new-made slurry. To verify that the mechanical treatment was consistent, a particle size distribution for every slurry was determined. A different distribution would indicate that the mechanical treatment would not have been repeatable. The particle size distributions for the mechanically untreated MCC slurry and the first mechanically treated MCC slurry used for experiments are shown in figure 4.2. The mechanical treatment gives a bit lower fraction of the larger particle sizes, but the effect on the particle size distribution as the first mechanically treated and can all be regarded as equivalent in preparation.



Figure 4.2: Particle size distribution for mechanically treated MCC particles.

4.1.3 Particle surface structure

The effect of a mechanical treatment similar to the one used in this study on the surface structure has been studied previously (Wetterling *et al.*, 2015). A Scanning Electron Microscope (SEM) was used to observe the surface. The comparison between the treated and untreated MCC particles are shown in figure 4.3, where the right figure is the untreated surface and the left figure the treated rugged surface. As seen, the particle surface now consists of smaller particle fragments after the mechanical treatment.

4.1.4 Particle surface area

To measure the change in surface area by the mechanical treatment a BET adsorption measurement was done. The particles dried by the solvent exchange procedure for both the mechanically treated and the untreated MCC were subjected to the BET adsorption. The measured surface areas are stated in table 4.1. The difference between the treated and untreated particles is large, as a result of the rugged surface structure and particle fragmentation. The results can be considered in line with earlier experiments with similar treatment (Wetterling, 2014).



Figure 4.3: SEM pictures for the untreated (left) and the mechanically treated (right) MCC particles used by Wetterling et al. (2015).

Mechanical treatment	A_{BET} , $[m^2/g]$
none	39.6 ± 0.1
$10\ 000\ \mathrm{rpm}$ for $5\ \mathrm{min}$	57.1 ± 5.5

 Table 4.1: Results from surface area characterisation by BET adsorption.

4.2 Filtration of microcrystalline cellulose

Figure 4.4 shows the inverse filtration rate for the three levels of ionic strength for MCC, as well as varying pH at the lowest level. pH for MCC in water is 6.3 and the other level is in the acidic region, pH 2.9, by addition of 0.1 M HCl. Here, it can be seen that with increasing ionic strength the filtration rate increases. The ionic strength influences the surface structure, making the filter cake resistance smaller. However, the lower pH level without addition of salt has the overall highest filtration rate in comparison. These results are in agreement with earlier studies that have shown that the pH influences the filtration behaviour of the MCC particles. The electrostatic forces in the low pH are more eager to agglomerate and fragments on the particle surface as a result of the mechanical treatment will tend to aggregate to the surface, resulting in reduction of the surface area that affects the filtration resistance (Wetterling *et al.*, 2015).

Table 4.2: Values of average specific filtration resistance, α_{avg} , at 2 bar filtration pressure.

	$\alpha_{avg} [{\rm m/kg}]$
no add, pH 2.9	$1.7 \cdot 10^{11}$
no add, pH 6.3	$120 \cdot 10^{11}$
low add Na_2CO_3	$13 \cdot 10^{11}$
high add Na_2CO_3	$6.2 \cdot 10^{11}$



Figure 4.4: Comparison of the inverse filtration rate at 0 V for the cases with addition of Na_2CO_3 and the cases without addition.

Table 4.2 states the α_{avg} for the low and high addition of Na₂CO₃. The higher addition of salt gives a lower α_{avg} values, which shows similar effects as lowering the pH. The higher ionic strength somewhat shields the surface charge and gives a similar behaviour as acidic pH.

Figure 4.6 shows inverse filtration rate for the two different pH levels of the MCC slurry without addition of salt. It can be seen that the lower pH gives a lot faster filtration rate. In figure 4.5a the pressure profile for the MCC slurry at pH 6.3 is shown, and no significant pressure drop is observed over the filter cake. This indicates that the pressure drop is only below the lowest pressure capillary (Mattsson *et al.*, 2012a). Figure 4.5b shows the pressure profile for the acidic MCC suspension and here a pressure drop can clearly be seen, indicating that the filter medium resistance is lowered and that the filtration resistance is distributed over the entire filter cake. This behaviour is in accordance with earlier results (Wetterling *et al.*, 2015), where MCC has low surface charge in acidic conditions.

The filtration equation (eq. 2.4) was fitted to the experimental data in figure 4.6. The fit was good and the slope of the line is proportional to the value of α_{avg} . The average specific filtration resistance for the neutral pH experiment will be regarded as the base line for resistance of this kind of 3 vol% MCC slurry. As the pH is lowered, so is α_{avq} . Further on, there is a change in filter medium resistance. At neutral pH there is a large electric resistance over the filter medium, but for acidic pH the filter medium resistance is drastically lowered.





(a) Pressure profile for 0 V experiment without any addition of salt, pH 6.3.

(b) Pressure profile for 0 V experiment without any addition of salt, pH 2.9.





(a) Inverse filtration rate with fitted line for 0 V experiment without any addition of salt, pH 6.3.

(b) Inverse filtration rate with fitted line for 0 V experiment without any addition of salt, pH 2.9.

Figure 4.6: Inverse filtration rate at 0 V and no addition of salt at pH 6.3 and 2.9, with fitted lines for calculation of the average specific filtration resistance, α_{avg} , according to eq. 2.4.

4.3 Electro-assisted filtration

To enhance the filtration an electric field was applied over the filter cell. Experiments with only MCC slurry was first done and further on experiments with addition of salt to study influence of the ionic strength.



Figure 4.7: Inverse filtration rate for applied electric field compared with regular filtration of MCC.

4.3.1 No addition of salt

Figure 4.7 shows the inverse filtration rate for three levels of applied voltage: one without applied voltage, one with the cathode placed beneath the filter medium (denoted positive electric field) and one with the anode place beneath the filter medium (negative electric field). There is a significant difference between the cases with voltage and the case without. As seen, when there is an applied electric field the filtration rate increased drastically. Here, both the positive and negative electric field enhance the filtration. The positive field filtration enhancement could be described as the electric field adding an electroosmotic driving force to the pressure filtration. The electroosmosis further drags the liquid from the solid particles and through the filter. Additionally, this direction of the electric field could decrease the filter cake

growth through electrophoretic action. This behaviour could thereby be described by eq. 2.6 (Yukawa *et al.*, 1976). However, reversing the electric field still resulted in an increased filtrate flow rate, indicating that the electroosmosis is not a dominating effect during electro-assisted filtration.

One effect that could affect the filtration rate is the ohmic heating. The heating effect would increase the temperature, leading to a decrease in viscosity.



Figure 4.8: Temperature profile for the cases with applied electric field for no addition of salt at 5 (T2) and 20 (T1) mm above the filter medium.

Figure 4.8 shows the temperature profiles for 150 V and -150 V for no addition of salt. A small increase in temperature can be noticed for the thermocouple at 5 mm above the filter medium (T2). Though, the total increase for T2 was only 23 - 29°C, which equals a decrease in viscosity by 13 % (Kestin *et al.*, 1978) and this has no significant effect on the viscosity of the filtrate. As seen in the figure the temperature effect has only a small impact and other factors instead affect the filtration rate for the negative electric field.

Figure 4.9 shows the two pressure profiles for the positive and negative electric field without any addition of salt in the slurry. What can be seen here is that for the positive field the pressure drop occurs close to the filter medium. For the negative electric field on the other hand a clear pressure drop is shown over the filter cake indicating that the resistance is now distributed. These differences may be due to



(a) Pressure profile for 150 V experiment without any addition of salt.

(b) Pressure profile for -150 V experiment without any addition of salt.

Figure 4.9: Pressure profile for 150 V and -150 V without any addition of salt.

a pH profile inside the filter cake as a result of the electrode reactions. The pH in the filtrate for figure 4.9a and 4.9b are at 9.7 and 3.9, respectively. At the surface of the filter medium the pH is in the alkaline region for the positive electric field. The pH was measured in the filtrate, which will directly flow from beneath the filter medium, where the cathode is located. At the top of the filter cake the pH is acidic, due to the reactions at the anode. Electrolytic reactions will hence give this pH profile from acidic to alkaline in the filter cake for the positive electric field. For the negative electric field the filtrate is acidic and thus the pH profile can be supposed to be alkaline at top and acidic close to the filter medium. This profile will probably affect the filtration resistance locally in the cake. As earlier seen in table 4.2 the α_{avg} at acidic pH is much lower than the neutral/alkaline pH, indicating that the filtration resistance probably is lower for the acidic part of the filter cake than for the alkaline and neutral part of the filter cake.

4.3.2 Addition of Na_2CO_3 to the MCC slurry

Figure 4.10 shows the difference in inverse filtration rate for the zero voltage case and the cases with applied voltage for the low addition of Na_2CO_3 . As for the cases without salt, there is a significant difference between the zero voltage case and the cases with applied electric field. Further on, there is also a difference between the lower (75 V) and the higher electric field intensity (150 V). The higher voltage gives a lower inverse rate, which again indicates that the applied electric field enhance the filtration rate. For the electric field cases the inverse filtration rates seems constant and the filtration resistance, α_{avg} , is lowered, as can be seen in table 4.4 compared to table 4.2. For the zero voltage case the α_{avg} is much higher; low resistance in the beginning gives a high filtration rate, and when the cake starts to form the resistance will increase. For all cases in figure 4.10 the filtration rates are faster than corresponding cases without addition of salt.



Figure 4.10: Inverse filtration rate for low addition of Na₂CO₃.

Table 4.3: pH measurement of the filtrate during the experiments with low amount of added Na_2CO_3 at three time stamps. There is also the measured pH of the slurry before the experiments started.

	1.	2.	3.
before start	9.3	-	-
75 V	11.3	10.8	10.5
150 V	11.7	10.4	10.2
-150 V	7.1	4.6	4.0

In table 4.3 the pH measured in the filtrate during ongoing experiments for low addition of Na_2CO_3 are stated, together with the pH of the slurry before the experiments started. Figure 4.11 shows the filtrate sampling points during the experiments together with the measured pH at each extraction point for the values in table 4.3. One measurement is taken in the beginning of the experiment, one after about half

way through the filtration and one in the second half of the experiment. For the cases with a positive electric field the pH are in the alkaline region with just a small decrease of the pH. For the experiment with a negative electric field the pH is in the neutral region and the acidity increases during the filtration. This indicates that electrolytic reactions are taking place and H^+ and OH^- ions as well as H_2 gas are formed. The same trends are valid for the higher addition of Na_2CO_3 , where the positive electric field cases have filtrate pH in the highly alkaline region that slowly lowers with ongoing filtration and for the negative electric field the pH in the filtrate is in the acidic region. This further supports the supposed pH profile in the filter cake, from acidic to alkaline for the positive electric field.



Figure 4.11: Marking of time stamps for sampling of filtrate for pH measurements for low addition of Na_2CO_3 . The measured pH are stated in table 4.3.

In figure 4.12 the pressure profiles for each case with applied voltage for low amount of added Na_2CO_3 are illustrated. By comparing the cases with positive electric field with each other it is clear that the higher the applied voltage is, the larger the pressure drop, and the resistance below the lowest pressure capillary has decreased. Both the filtration resistance and the filter medium resistance have decreased for the positive electric field cases. For the negative electric field the pressure drop is large, which indicates a large resistance distributed over the entire cake. The filter medium resistance and the filtration resistance have decreased but not as much as for the positive field, indicating other effects of the negative field.



(a) Pressure profile for 0 V experiment with low addition of Na_2CO_3 .



3.5 × 10° 3.5 × 10° 3.5 × 10° 3.5 × 10° 4.7 × 10° 5.5 × 10° 1.5 × 10°

(b) Pressure profile for 75 V experiment with low addition of Na_2CO_3 .



(c) Pressure profile for 150 V experiment with low addition of Na_2CO_3 .

(d) Pressure profile for -150 V experiment with low addition of Na₂CO₃.

Figure 4.12: Pressure profile for varying voltage with pressure as a function of volume of filtrate for low addition of Na_2CO_3 .

For the higher amount of added Na_2CO_3 the same general pressure profiles are given. The pressure drop is significant for all cases and each case also has a larger pressure drop than the corresponding case for the low salt addition. This indicates that the filtration is enhanced by the higher ionic strength and the filtration resistance is again more evenly distributed over the cake.



Figure 4.13: Inverse filtration rate for high addition of Na_2CO_3 .

Figure 4.13 shows the inverse filtration rate for the higher addition of Na₂CO₃. By comparing the slopes for the high addition of Na₂CO₃ with the lower addition in figure 4.10 the α_{avg} values increase with increasing ionic strength. This would then imply that the average filtration resistance increases, even though the filtration rate is increased for the electro-assisted filtration for high levels of ionic strength. For this system of MCC the average value is then probably not a good evaluation parameter, as other factors still indicate reduction of the filtration resistance at higher electric field intensity. The α_{avg} for the addition of Na₂CO₃ are determined by linear regression in figure 4.10 and 4.13 and the results are found in table 4.4. However, the curves in figure 4.13 are not entirely linear and the α_{avg} values were thus not accurately fitted. This also indicates that there are other effects that more dominate the filtration rate at high level of ionic strength.

Table 4.4: α_{avg} values for the two levels of ionic strength at applied electric field determined by linear regression for the curves in figure 4.10 and 4.13.

	low add, Na_2CO_3 [m/kg]	high add, Na_2CO_3 [m/kg]
$75 \mathrm{V}$	$1.38\cdot 10^{10}$	$21 \cdot 10^{10}$
$150 \mathrm{~V}$	$4.51 \cdot 10^{10}$	$16 \cdot 10^{10}$
- 150 V	$11 \cdot 10^{10}$	$22 \cdot 10^{10}$

Figure 4.14a shows the temperature profile for the electric field cases for low addition of Na_2CO_3 . No significant temperature increase can be noticed for 75 V. This can be verified in figure 4.14b, where the power consumption for the 75 V case is low and the temperature effect can be neglected for 75 V. For the 150 V and -150 V cases the temperature increases. The most significant increase is for the negative electric field case as a result of the increased conductivity giving a higher power.



(a) Temperature profile for the two thermocouples for low addition of Na_2CO_3 .

(b) Power development profile for low addition of Na_2CO_3 .

Figure 4.14: Temperature profile of the two thermocouples for low addition of Na_2CO_3 and corresponding power consumption.

Further on, a temperature profile is observed over the filter cake as seen in figure 4.14a, where there is a slight difference between the measured temperatures for each thermocouple. The lower thermocouple (T2) shows a bit higher temperature than the upper thermocouple (T2). The heating of the filtrate occurs in between the two electrodes, which leads to that at T2 the filtrate have had more time to be heated later in the filtration sequence and will thus measure a higher temperature than the upper thermocouple. The heating will affect the viscosity of the filtrate and a higher filtrate temperature will decrease the resistance close to the filter medium as the fluid viscosity is decreased.

In figure 4.15 the power profiles for the different cases with high addition of Na_2CO_3 are shown. For low voltage (75 V) the power is low and constant. For the higher voltage (150 V) the power in total is higher but for the first part of experiment the power decreases. This can be explain by the choice of salt, as sodium carbonate has a buffering effect. For the case with a negative electric field the power demand will increase drastically during experiments with a constant applied voltage. The current profile has the same general look as figure 4.15, since the power relationship directly depends on the current. As the current increases, this indicates that the electric resistance over the cake has decreased. This will also explain the increase in temperature for the -150 V case; increased current gives increased ohmic heating, as seen in figure 4.14a. The same reasoning is valid for both levels of ionic strength, as seen in figure 4.14b compared to 4.15.



Figure 4.15: Power development profile for high addition of Na_2CO_3 .

Some calculation were done considering buffering effect, pH and the current for 150 V cases (used model is found in appendix A). A cell-averaged pH was determined in two points of each curve, one in the start (I_0) of the experiment and one when the current had seemed to stabilised (I_1) . Values are stated in table 4.5, where the pH variations during each experiment are highlighted for comparison. The average pH in the filter cell does not change significantly as the current (and power) drops, from pH 10.5 to 10.0 for low addition of Na₂CO₃ and from pH 10.5 to 9.6 for high addition of Na₂CO₃. The decrease in pH can be considered minor as the current drop is, in this case, large. This indicates that the buffering effect counteracts the electrolytic reactions as the formation of H⁺ and OH⁻ ions does not affect the pH in a larger sense.

150 V,			150 V,		
low add Na ₂ CO ₃			high add Na ₂ CO ₃		
	I_0	0.15 A		I_0	0.40 A
	σ	$125 \ \mu S/cm$		σ	$330 \ \mu S/cm$
	IonS	$0.002 {\rm M}$		IonS	$0.0054~\mathrm{M}$
	pH	10.5		pH	10.5
	I_1	0.10 A		I_1	0.20 A
	σ	$83 \ \mu S/cm$		σ	$166 \ \mu S/cm$
	IonS	$0.0013 {\rm M}$		IonS	$0.0027~\mathrm{M}$
	\mathbf{pH}	10.0		\mathbf{pH}	9.6

Table 4.5: Example calculation of the buffering effect for addition of Na_2CO_3 . Formulas used are found in appendix A.2.

4.4 Summary of results

Both the ionic strength and the increasing electric field intensity affects the filtration of MCC. These effects combined are shown in figure 4.16. The graph shows filtration and electrofiltration of MCC in deionised water as well as for two levels of added Na_2CO_3 . What can here be seen is that the applied electric field increases the filtration rate. The increasing ionic strength also increases the filtration rate at each level. An interesting observation is that the gain in filtration rate is larger for lower ionic strength, i.e. the increase in filtration rate is very small for the high addition of Na_2CO_3 when applying an electric field over the filter cell. At high ionic strength the shielding of the MCC particles is large, which will result in only a small impact by the electric field.



Figure 4.16: The true filtration velocity for all cases studied.

Further on, the power consumption can be a crucial parameter in a possible scale-up for industrial use. Figure 4.17 show the power consumption for the different levels of ionic strength at an applied electric field of 150 V. The high addition of Na_2CO_3 gives a very high power in the beginning of the filtration and the power decreases with ongoing experiment as a result of the buffering action on the electrolytic reactions. However, the power consumption in the end of the filtration is still much higher than the power for the two lower ionic strengths.



Figure 4.17: Power consumption for three levels of ionic strength at 150 V.

Conclusion

Increasing ionic strength increases the filtration rate of microcrystalline cellulose suspensions. This phenomenon can be correlated to shielding of the particle surface charge. By increasing the ionic strength a significant temperature increase could be observed and the ohmic heating influenced the filtration at high electric field intensity during electrofiltration.

The electro-assisted filtration will be in favour compared to regular pressure filtration, as the electric field makes use of the electroosmotic force to enhance the separation of liquid from the solid particles. A higher electric field intensity increases the filtration rate, but the power consumption also increases, which can be a crucial cost in a possible scale-up. The filtration rate increased independently of the direction of the electric field, indicating that the electroosmosis and the pH effect from the electrolytic reactions were not the only dominating driving forces, as the negative electric field also enhanced the filtration rate.

The combination of these two effects gives the conclusion that adding an electric field to the filtration system gave the largest enhancement for lower ionic strengths. The relative gain in filtration rate was much more significant for the case of the lowest ionic strength, the case without added salt. However, by just slightly increase the ionic strength and also apply an electric field a major increase in filtration rate was achieved, to the cost of a slightly increased power demand.

Future work:

The next step in the research about electrofiltration of MCC can be to mathematically try to describe the system. The local data for the filter cake need to be applied and further studied to be able to fully consider all occurring processes. This can also include trying to more elaborately describe the pH profile in the filter cake as well as be able to identify what processes affect in electro-assisted filtration with reversed electric field.

5. Conclusion

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A

Appendix A

A.1 Deprotonation of sodium carbonate

$$Na_2CO_3(s) + H_2O \rightarrow 2Na^+ + OH^- + HCO_3^-$$
(A.1)

$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq)$$
(A.2)

$$HCO_3^{-}(aq) + H_2O(l) \rightleftharpoons H_3O^{+}(aq) + CO_3^{2-}(aq)$$
(A.3)

$$K_{a1} = \frac{\left[\mathrm{H}_{3}\mathrm{O}^{+}\right]\left[\mathrm{HCO}_{3}^{-}\right]}{\left[\mathrm{H}_{2}\mathrm{CO}_{3}\right]} = 4.3 \cdot 10^{-7} \tag{A.4}$$

$$K_{a2} = \frac{\left[\mathrm{H}_{3}\mathrm{O}^{+}\right]\left[\mathrm{CO}_{3}^{2-}\right]}{\left[\mathrm{HCO}_{3}^{-}\right]} = 5.6 \cdot 10^{-11}$$
(A.5)

A.2 Buffering calculations

Conductivity, σ :

$$\sigma = \frac{I \cdot L}{A_{\text{filter cell}} \cdot U} \tag{A.6}$$

I is the current, L is the length between the electrodes (25 mm), A is the cross-sectional area of the filter cell (0.00196 m²) and U is the voltage.

Given the ionic strength:

$$\sigma = 6.2 \cdot 10^4 \cdot \text{IonS} \tag{A.7}$$

The ionic strength can be calculated by the concentration of ions in the solution.

$$\text{IonS} = \frac{1}{2} \sum_{i} c_i z_i^2 \tag{A.8}$$

 c_i is the concentration of ion i and z_i is the charge number for ion i.