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LUT School of Engineering Science  
Degree Programme of Chemical Engineering



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**MEANS FOR IMPROVING THE LIQUID-LIQUID PHASE SEPARATION  
PROCESS AND REDUCING THE ORGANIC SOLVENT LOSSES OF  
HYDROGEN PEROXIDE PRODUCTION**

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This master's thesis work was conducted for Solvay Chemicals Finland Oy in 2018. The goal of the work was to investigate the current organic solvent losses and improve both the environmental and economic aspects of hydrogen peroxide production. Right from the start, I was convinced and hopeful that there was potential to reduce losses and make the process more profitable. The challenge presented to me was part of the new guidelines and operational targets set by Solvay. I would like to thank Site Manager Juha Pipponen for trusting in my knowledge and giving me the opportunity to work on this interesting subject. I am glad that I was able to complete the work on schedule without any significant delays during the thesis work as that was necessary because the topic was quite extensive.

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Henri Heikura



Kouvola, 17 May 2018

## **ABSTRACT**

Lappeenranta University of Technology  
School of Engineering Science  
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### **Means for improving the liquid-liquid phase separation process and reducing the organic solvent losses of hydrogen peroxide production**

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73 pages, 27 figures, 8 tables, 3 appendices

Examiners: Professor, DSc (Tech) Mika Sillanpää  
DSc (Tech) Nina Salmela-Mäkelä

Keywords: liquid-liquid phase separation, emulsion, gravitational, coalescence

The chemical process industry uses a wide range of various liquid-liquid phase separation processes to ensure a good quality of products, correct content of process streams for ensuring stable operations and to reduce the environmental impact by removing wastes. Slight changes in the phase separation performance can lead to significant benefits in both process profitability and the environmental aspects. Growing interest in the carbon footprint of manufactured products and other key figures set by customers force companies to focus more on sustainable manufacturing methods and responsible materials. In this study, phase separation processes and some other manual labour operations were investigated and improvements were suggested to reduce organic solvent losses, thereby resulting in a longer lifetime of valuable raw materials used in hydrogen peroxide manufacturing.

The literature part presents the basic principle of hydrogen peroxide production and background for thesis work. The theory of emulsion formation, stability and measures to affect emulsion deformation is presented for understanding the phenomena behind phase separation. The designing of gravitationally operated decanters and settlers are also presented and other possible measures to improve phase separation are described in the literature part. The experimental part can be divided into 3 different phases starting from baseline laboratory experiments to investigate the effect of temperature, pH and phase fraction on the settling tendency of emulsions present in hydrogen peroxide plant and also TOC levels of aqueous phases in contact with organic solvent and working solution. The second phase was gathering and analysing wastewater streams from several assumed solvent loss sources. Finally, the received data was processed and analysed to have more detailed information about the reasons why phase separation is not complete.

The laboratory test results indicate that the emulsion temperature and pH are good parameters for adjusting the terminal settling velocity, but changes tend to have a minor overall impact. Based on the received results, at least half of the current losses were located and most of the loss sources can be improved with minor changes to piping and equipment construction.

## TIIVISTELMÄ

Lappeenrannan Teknillinen Yliopisto  
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Henri Heikura

### **Menetelmät neste-neste faasierotuksen parantamiseen ja orgaanisten liuotin häviöiden vähentäminen vetyperoksidin tuotannossa**

Diplomityö  
2018

73 sivua, 27 kuvaa, 8 taulukkoa, 3 liitettä

Tarkastaja: Professori, TkT Mika Sillanpää  
TkT Nina Salmela-Mäkelä

Avainsanat: neste-neste faasierotus, painovoimainen, emulsio, pisaranerotus

Neste-neste faasierotus prosessit ovat yleisiä ja hyvin tärkeitä menetelmiä hyvän tuote laadun ylläpitämisessä, prosessivirtojen laadunhallinnassa, joka takaa tasaiset tuotanto-olosuhteet, sekä jäteveden käsittelyssä. Pienilläkin faasinerotustehokkuuden muutoksilla voidaan saavuttaa merkittäviä parannuksia niin tuotannon kannattavuudessa kuin ympäristön kannalta. Nykyinen ympäristöystävällisempi ajattelumaailma niin asiakkaiden kuin viranomaistahojen puolesta on asettanut paineen teollisuudelle panostaa enemmän kestäväan kehitykseen ja vastuulliseen tuotteiden valmistukseen. Tässä työssä tutkittiin prosessin eri faasinerotusvaiheiden sekä huoltotöiden suorituksiin liittyviä työvaiheita liuotinhäviöiden paikallistamiseen. Kun syy liuotinhäviölle on selvitetty jokaiselle kohteelle valmisteltiin parannusehdotukset työn tuloksien mukaan. Parannuksilla voidaan saavuttaa nykyistä pidempi raaka-aineiden elinkaari prosessissa.

Työn kirjallisuusosa käsittelee yksinkertaistetusti vetyperoksidin valmistuksen, emulsion muodostuksen teorian sekä emulsion hajoamiseen vaikuttavia tekijöitä. Näiden lisäksi käsitellään painovoimaisen faasierotuksen teoriaa ja yleisimmin käytettävissä olevien faasierottimien toimintaa, suunnittelua sekä rakenteellisia muutoksia erotuksen parantamiseen. Kokeellinen osa koostuu laboratoriossa suoritetuista nollataso kokeista, joilla selvitettiin lämpötilan, pH:n ja faasisuhteen vaikutusta emulsion selkeytymisnopeuteen. Selkeytymiskokeiden lisäksi raskaan vesifaasin hiilipitoisuutta analysoitiin orgaanisen liuotineseoksen sekä työliuoksen kanssa. Laboratoriokokeiden tuloksia verrattiin prosessinäytteistä saatuihin tuloksiin ja laskennan tuloksia käytettiin hyödyksi faasierotuksen ongelmakohtien selvitykseen.

Laboratoriotulosten pohjalta voidaan todeta, että lämpötilaa sekä pH:ta säätämällä voidaan saavuttaa hyötyjä faasierotuksessa, mutta tässä tapauksessa saavutettavat hyödyt jäävät pieniksi. Laskujen tulosten pohjalta vähintään puolet syntyvistä häviöistä paikannettiin ja suurin osa häviöistä voidaan välttää tekemällä muutoksia olemassa oleviin prosessilaitteisiin tai putkistoihin.

## NOMENCLATURE

### Roman symbols

$A$	Area, $m^2$
$A_I$	Cross sectional area of interphase, $m^2$
$D$	Diameter, m
$D_p$	Droplet diameter, m
$D_H$	Hydraulic diameter, m
$f$	Relation factor, -
$G$	Gibbs free energy of formation, J
$g$	Gravitational acceleration, $m\ s^{-2}$
$H_D$	Height of the emulsion band, m
$h$	Height of interface, m
$h_l$	Height of lower interface, mm
$h_u$	Height of upper interface, mm
$L$	Length, m
$m$	Mass, kg
$\dot{m}$	Mass flow rate, $kg\ s^{-1}$
$N_{Re}$	Degree of turbulence, -
$n_k$	Number of components,-
$P_h$	Heywood settling factor, $m^{-1}$
$p$	Pressure, Pa
$Q_H$	Heywood settling factor, $m\ s^{-1}$
$Re'$	Reynolds number, -
$r$	Economical vessel ratio (L/D), -
$S$	Entropy, $J\ K^{-1}$
$T$	Temperature, K
$t_{avg}$	Average volumetric residence time, s
$t_{cross}$	Time available to cross emulsion band, s
$t_{media}$	Average residence time in fibre media, s
$t_{min}$	Minimum residence time, s
$u$	Settling velocity, $m\ s^{-1}$
$u_T$	Terminal settling velocity, $m\ s^{-1}$

$u_{min}$	Minimum settling velocity of dispersed phase to outlet, $m\ s^{-1}$
$V$	Volume, $m^3$
$V_{loss}$	Volume of lost solvent, L
$\dot{V}$	Volumetric flow rate, $m^3\ s^{-1}$

### **Greek symbols**

$\gamma$	Interfacial tension, $mN\ m^{-1}$
$\eta$	Viscosity, $Pa\ s^{-1}$
$\Theta$	Factor predicting which phase is dispersed phase,-
$\mu$	Chemical potential, $J\ mol^{-1}$
$\rho$	Density, $kg\ m^{-3}$

### **Subscripts**

$c$	Continuous fluid phase
$f$	Feed stream
$free$	Free solvent
$h$	Heavy phase
$i$	Individual phase
$k$	Individual component
$l$	Light phase
$o$	Overflow
$p$	Settling particle (or dispersed phase)
$u$	Underflow
$ww$	Wastewater

## **Abbreviations**

AO	Autoxidation
AQ	Anthraquinone
DMW	Demineralised water
L/D	Length to diameter
LQR	Linear Quadratic Regulator
O/W	Oil in water
PBT	Polybutylene terephthalate
PET	Polyethylene terephthalate
PI	Proportional integral
PP	Polypropylene
PU	Polyurethane
W/O	Water in oil
WS	Working solution

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# 1 INTRODUCTION

Liquid-Liquid phase separation processes are mostly used by the petro- and chemical industry to treat disperse systems. Phase separation units are often operated in water treatment plants and after mass transfer units, where phases are mixed to increase the interfacial area to promote mass flux. Disperse systems consist of at least two immiscible or partly miscible phases. Disperse systems have a continuous phase and finely distributed dispersed phase wherein liquids are called emulsions. Nevertheless, the goal is to separate the product from the process stream or treat wastes. Traditional gravitational separation methods are commonly used for their simplicity, low investment and operating costs (Heusch & Reizlein, 2012).

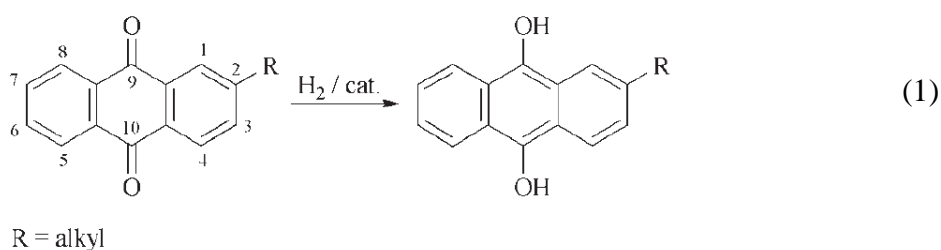
Rising concern about pollution and the CO<sub>2</sub> footprint is forcing chemical industries to improve their processes and waste disposal methodology. Separation equipment should be sized sufficiently to ensure excessive entailment of water in the hydrocarbon phase and vice versa the entailment of hydrocarbons to wastewaters (Müller, et al., 2012). Green Chemistry and Engineering is an approximately 20 year old mindset altering phenomena that changed our ways of designing processes. The groundbreaking purpose was to remove risk by mitigating hazardous chemicals or operations. The main principle of green chemistry is to accomplish sustainable product manufacturing, safer processing and a healthy working environment for personnel. Reducing the amount of waste generated by processes has an economic and environmental impact. Savings are generated by lower waste treatment costs and also reduced chemical consumption in continuous processes (Bourne & Poliakoff, 2011).

## 1.1 Background

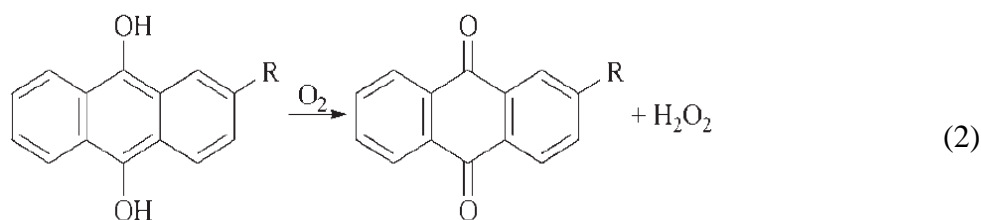
Solvay Chemical Finland Oy (SCF Oy) produces hydrogen peroxide by organic autoxidation (AO). The autoxidation process has enabled large-scale hydrogen peroxide production facilities. The anthraquinone (AQ) process (aka Riedel-Pfleiderer process) produces hydrogen peroxide by reducing and oxidising the so-called working solution (WS) circulated in the process. WS consists of AQ and a mixture of polar and non-polar

solvents (Goor, et al., 2007). Due to the different solubility specifications of quinones and hydroquinones, the usage of a combination of solvents are required (Eul, et al., 2001).

With the presence of catalyst, 2-alkyl-9,10-anthraquinones are reduced with hydrogen to produce equivalent hydroquinones. Reaction equation for 2-alkyl-9,10-anthraquinone reduction is shown in Eq. 1.



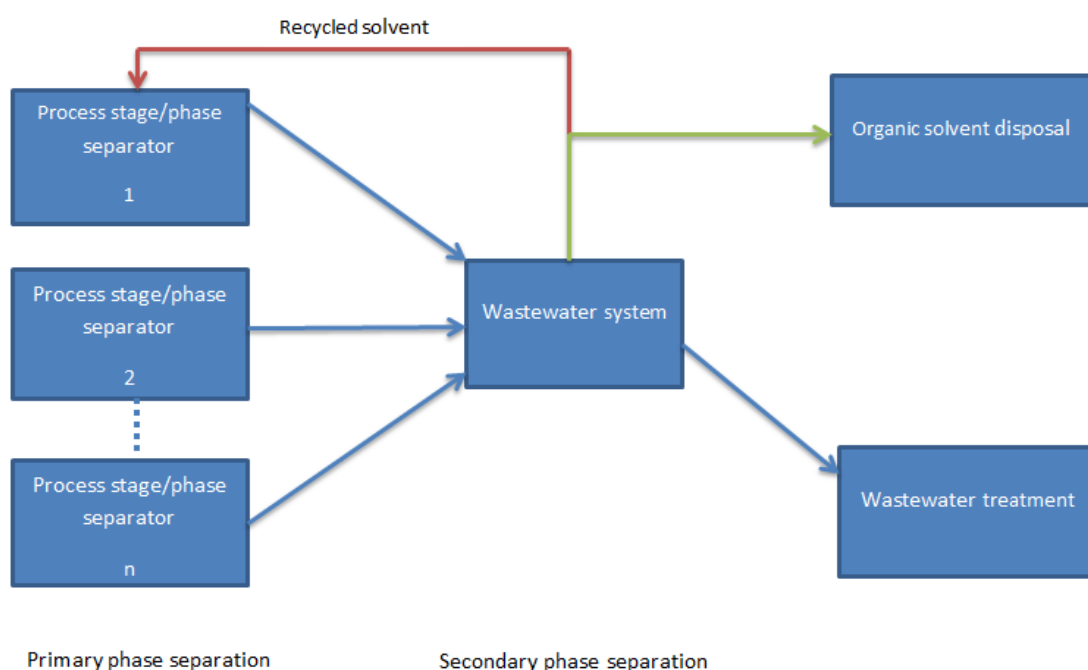
Hydroquinones are then processed further by oxidising the WS mixture to produce hydrogen peroxide and 2-alkyl-9,10-anthraquinones.



Hydrogen peroxide is extracted from WS to water and stored in different concentrations. As seen in the reaction in Eq. 2, AQ containing WS can be circulated in the process almost completely. A small amount of AQ is degraded to non-active quinones which do not take part in hydrogen peroxide production. Depending on the quality of the formed degradation products, a part of these products can be converted back into active quinone and the rest is removed from the WS circulation loop (Goor, et al., 2007).

In addition to the degradation of AQ and the need to add new AQ in the process, WS can be lost from different process stages in hydrogenation, oxidation, extraction and working solution regeneration processes (Eul, et al., 2001). Conventional gravitational separators and centrifuges are used to separate the emulsions of WS and aqueous phase. Previous instructions and guidelines made solvent and WS recycling possible from the wastewater system and, therefore, the loss amounts were lower. A new mindset includes that only

losses from controlled and uncontaminated sources are acceptable. This means that solvent and WS in the wastewater system is in contact with contaminated wastewater streams from concrete floors and outside sewer systems. Due to the new guidelines, a secondary phase separation stage is not in use and all the valuable materials accumulating in the secondary phase separation stage are considered as waste. The basic principle of the past and current configuration is shown in the flow diagram in Figure 1.



**Figure 1.** Basic principle of hydrogen peroxide plants wastewater flow diagram. Stream marked red is the previous WS recycle stream from the wastewater system and the green marked stream is the current instructed operation.

## 1.2 Target and scope of work

Solvay has launched a programme to drastically reduce the annual WS losses by the end of 2020. The aim of the programme is to improve process efficiency and personnel safety by leak control. Therefore, the goal for this study is to find and quantify the current WS loss points (1), analyse the reasons for WS loss from the found locations (2), optimise the process conditions to reduce losses (3) and propose updates on the bottlenecks on phase separation equipment (4).

The literature part of this thesis will be covered in Chapters 2–5. Gravitational phase separation theory and factor affecting clean separation of phases will be presented in Chapter 2 of this thesis. Chapter 3 contains factors leading to the formation of emulsions in

chemical processes, emulsion properties, and methods to accelerate emulsion destabilisation and separation. Chapter 4 will cover the general performance equation and procedure to evaluate phase separators performance, gravitational separation equipment are presented with design equations for determining vessel capacity and dimension, and also structural methods for improving the phase separation efficiency of emulsions are introduced in Chapter 5.

The experimental part of this thesis is presented in Chapters 6-8. It contains lab results from solvent/water and WS/water emulsion batch settling experiments and also the TOC level analysis of the aqueous phase in contact with both of the light organic phases. The analysis data from different process wastewater streams is compared to the results from the laboratory experiments for accurate estimates of individual loss amounts. Information about the test runs done is also discussed and analysed to investigate the possible measures to improve the operations of current phase separation units. Estimated solvent/WS losses are presented, and different improvement options are proposed. Due to the confidential nature of this thesis, any specific information about equipment configuration or sample point locations will not be discussed in the public version of this master's thesis.

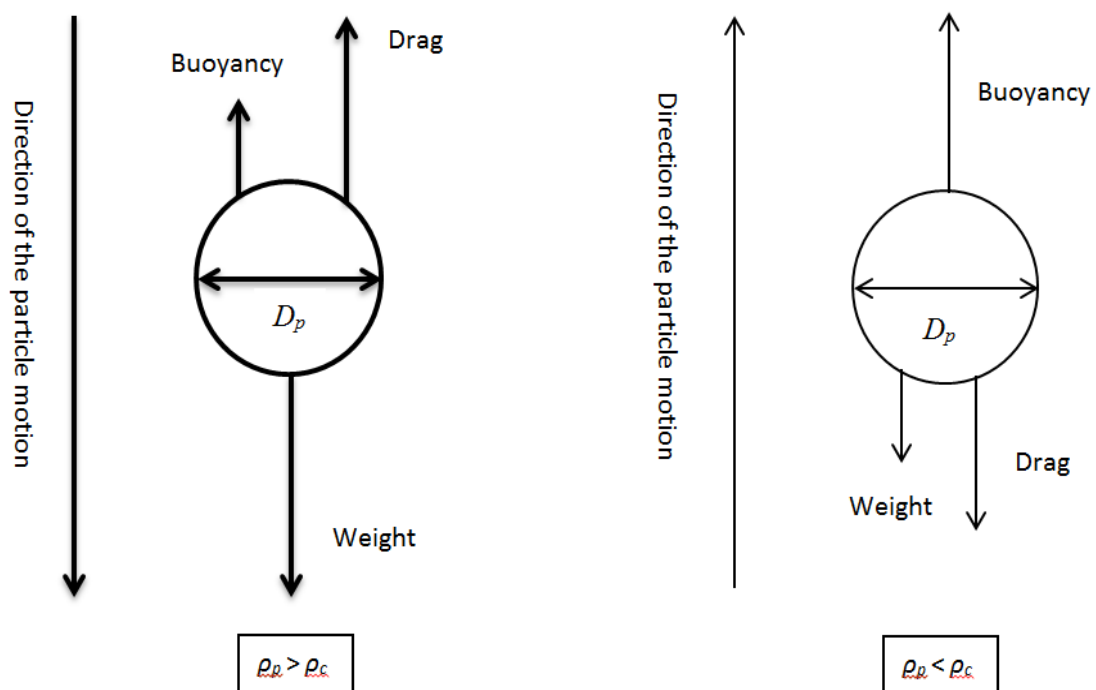
## **LITERATURE PART**

### **2 LIQUID-LIQUID PHASE SEPARATION**

As stated by Svarovsky (2000), phase separation technology includes almost half of the investments made by chemical industries nowadays. The separation of phases between the process stages or treatment of end products and wastes require distribution to multiple material streams. This chapter will introduce the phenomena present in particle settling and the relevant equations. The discussed theorems are generated by solid particle motion in fluid, but from the particle technology point of view, the term particle is in fact a solid particle, liquid droplet or gas bubble merged in a continuous fluid. The same laws and boundaries are present in both gas and liquid separation processes, although some of the forces affecting droplet or bubble settling have a more significant role (Holdich, 2002).

## 2.1 Spherical particle motion in fluid

The reason for two phases having been separated from each other is their motion in gravitational fields due to the density difference. The phase with a higher density is separating nearest to the centre of gravitation. Forces affecting particles during motion in fluid are particle weight generated by mass and gravitational acceleration, buoyancy and motion resistance generated by particle motion in fluid, which is called drag force. Figure 2 shows the forces on settling particle depending on the direction of the particle motion in fluid. The particle will achieve its terminal velocity when the gravitational and resisting forces are equal. Particle settling in dilute systems where adjacent particles do not interact with each other is called free settling. In more concentrated systems, adjacent settling particles interact with each other and reducing terminal settling velocity leading to hindered settling (Holdich, 2002).



**Figure 2.** Forces affecting the spherical particle with diameter  $D_p$  in continuous fluid. The direction of the particle motion is dependent on the density difference between the settling particle and the fluid. Drag force always runs parallel to the fluid motion (Tilton, 1997; Svarovsky, 2000).

Dimensionless Reynolds number is used to determine flow behaviour around the particle. Stream conditions around the particle can be laminar, turbulent or a combination of both regimes. When the stream conditions near the particle shifts from laminar to turbulent, the

acting drag force on the particle is greater and leads to a decrease in the settling velocity. The particle's Reynolds number is defined as

$$Re' = \frac{uD_p\rho_c}{\eta_c} \quad (3)$$

where

$u$	Settling velocity, m s <sup>-1</sup>
$D_p$	Diameter of the settling particle, m
$\rho_c$	Fluid phase density, kg m <sup>-3</sup>
$\eta_c$	Fluid phase viscosity, Pa s

Stokes law is applied on a dilute system, where the particle settles under the laminar flow regime ( $Re' < 0.2$ ) (Holdich, 2002). An equation derived from the Stokes law for terminal settling velocity in dilute system is described as (Richardson & Harker, 2002)

$$u_T = \frac{D_p^2(\rho_p - \rho_c)g}{18\eta_c} \quad (4)$$

where

$\rho_p$	Density of the settling particle, kg m <sup>-3</sup>
$g$	Gravitational acceleration, m s <sup>-2</sup>

Equation shows that the particle size has a notable effect on the terminal settling velocity. The settling particle is assumed to be spherical, but mostly settling particles have irregular shapes and roughness, which affects particle motion. In the turbulent regime, the Reynolds number is over 500, where the conditions around the particle settle and the resistances on the particle are constant (Holdich, 2002). This regime is called Newton's regime, and the equation for terminal velocity under turbulent conditions is formed as follows (Richardson & Harker, 2002)

$$u_T = \sqrt{\frac{3gD_p(\rho_p - \rho_c)}{\rho_c}} \quad (5)$$

The region between the laminar and turbulent region is called an intermediate region, where both laminar and turbulent conditions manifest. Motion resisting forces at the intermediate region can be determined graphically from the diagram or with empirical equations (Svarovsky, 2000). At the intermediate region ( $0.2 < Re' < 500$ ), eddies are starting to form around the particle. The size of eddies is the function of the particle's Reynolds

number, thus the terminal settling velocity is reduced when  $Re'$  is increasing (Richardson & Harker, 2002).

From Equations 4 and 5 presented hereinabove, it can be seen that the diameter of the settling particle has a crucial role on the terminal settling velocity. This fact can be utilised for the purposes of phase separation processes and the most common means to enhance liquid-liquid separation is discussed in more detail later on. On the other hand, increasing the diameter of the settling particle will have an increasing impact on the particle's Reynolds number, thus having a reduced influence on the settling time.

Holdich (2002) presents Heywood's method to determine the terminal velocity of the settling particle. Heywood's tables show the correlation of  $\log_{10}(P_H d_p)$  against  $\log_{10}(u_t/Q_h)$ . Heywood's tables can be used for a wide range of different particle sizes and most notably Heywood's tables are applicable for all flow regimes. Heywood settling factor  $P_h$  is formed as

$$P_h = \left[ \frac{4(\rho_p - \rho_c)\rho_c g}{3\eta_c^2} \right]^{\frac{1}{3}} \quad (6)$$

And the second Heywood settling factor  $Q_h$  calculated with

$$Q_H = \left[ \frac{4(\rho_p - \rho_c)\eta_c g}{3\rho_c^2} \right]^{\frac{1}{3}} \quad (7)$$

For certain sized settling particle Heywood's tables are used starting with calculating value of  $\log_{10}(P_H d_p)$ , where Eq. 6 is used to determine value of the Heywood settling factor  $P_h$ . Then, the determined value is used to determine  $\log_{10}(u_t/Q_h)$ . The terminal settling velocity for the given particle size is then calculated with the use of Eq. 7. Although the Heywood's method can be useful, in most cases Eq. 4 produces the appropriate results with less calculating effort. Heywood tables are presented in Appendix I.

## 2.2 Settling phenomena applied on liquid-liquid systems

As mentioned before, the settling of gas or liquid in fluid is very similar with the solid particle motion in fluid, but typically the drag force acting on the bubble or droplet deviates from the particle's drag force of similar shape and diameter. The reason for the



deviation with the drag force is circular currents that take place inside the bubble or droplet. Coulson & Richardson (2002) states that the velocity gradient at the surface is reduced and that leads to reduced drag force on the particle.

According to Coulson & Richardson (2002), the surface tension does not affect very small droplets because the surface tension nullifies the tendency for circulating current in the droplets and, therefore, falling droplets tend to have a terminal velocity close to the falling particle. Droplets and bubbles also have a tendency to deform because pressure will be different across the surface area. Falling/rising tends to flatten the drops because both the hydrostatic and impact pressure are greater on the face of the droplet towards the direction of movement. This phenomenon is applied on larger drops, while the surface tension keeps smaller droplets spherical.

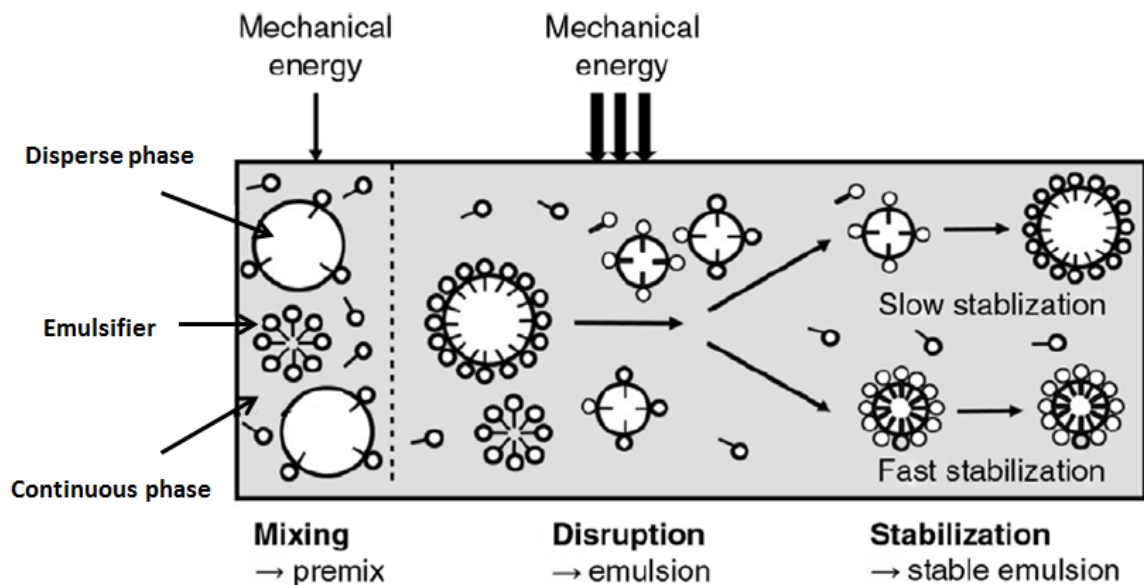
### **3 EMULSIONS**

Emulsions are a combination of two mixed immiscible or slightly miscible liquid phases; continuous and dispersed phase and usually some kind of surface active emulsifier or surfactant agent is present. Emulsions have been used by the process industry in a wide range of applications and products. With optimal process conditions, a mixture of at least two phases can form droplets in the other phase. Without emulsifiers, these emulsions are unstable and tend to separate. Unwanted stable emulsions can be formed during chemical production, which might be a consequence of process instability or problems with reagents (Leal-Calderon, et al., 2007). This chapter contains a discussion on emulsion formation, the causes affecting emulsion stability and the means to enhance emulsion deformation when considering efficient phase separation.

#### **3.1 Emulsion formation**

Emulsion formation requires an increase on the interface surface area between the aqueous and oil phase. The literature describes emulsions systems as a mixture of an oil and water phase, which might be misleading, but generally the oil phase can be any type of phase that is immiscible to the aqueous phase. The interface is created by introducing shear into the system and one of the phases forms droplets in the continuous phase. Emulsions containing

a continuous oil phase and aqueous phase as droplets are called water-in-oil emulsions (W/O), and systems where oil is droplets in the continuous water phase are called oil-in-water emulsions (O/W). Emulsion orientation is dependent on the phase ratio and emulsifier properties. More complicated dispersed systems are also possible, where droplets can act as a continuous phase for the third phase (W/O/W or O/W/O). Mean droplet diameters in emulsions vary between 0.05 and 100  $\mu\text{m}$ . Emulsions with a droplet size under 1  $\mu\text{m}$  are called microemulsions or submicroemulsions and with less than 100 nm drop size and are referred to as nanoemulsions (van der Schaaf, 2017). In figure 3, a general schematic of emulsion formation with a mechanical emulsification environment is shown.



**Figure 3.** Formation mechanisms of emulsions with the presence of slow and fast surface active emulsifiers (Karbstein, 1994).

The droplet size is determined by the amount of energy introduced into the system and forces keeping the droplets spherical. The Gibbs free energy of formation is dependent on the work done and the increase in entropy. The equation for the Gibbs free energy of formation is formed as follows (van der Schaaf, 2017)

$$dG = Vdp - SdT + \sum_k \mu_k dn_k + \gamma dA \quad (8)$$

where  $V$  Volume,  $\text{m}^3$   
 $p$  Pressure, Pa

$S$	Entropy, J K <sup>-1</sup>
$T$	Temperature, K
$\mu_k$	Chemical potential of individual component, J mol <sup>-1</sup>
$n_k$	Number of individual components,-
$\gamma$	Interfacial tension, mN m <sup>-1</sup>
$A$	Interfacial surface area, m <sup>3</sup>

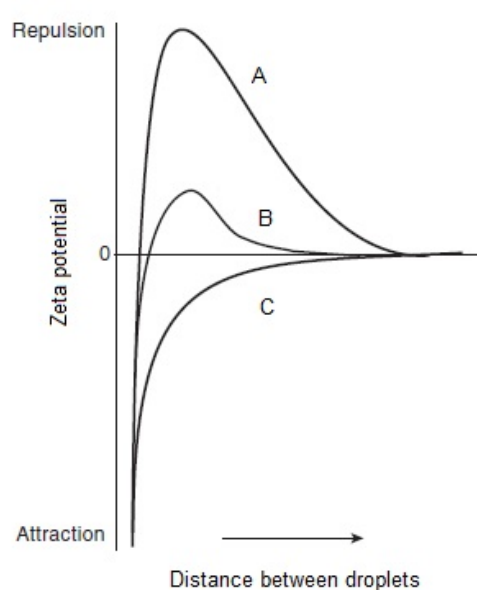
According to Kostansek (2012), the work term in the equation is larger than the entropy term, which leads to positive Gibbs free energy of formation. After formation, the created system immediately shifts to the minimum energy state, which might lead to a partial or complete deformation of emulsion. For this reason, emulsifier is added to stabilise the formed emulsion by reducing the interfacial tension between the two phases. On the other hand, emulsifiers reduce the energy needed to form emulsions.

### 3.2 Emulsion stability

The deformation of emulsions will happen by two mechanisms. The first deformation mechanism is called Ostwald ripening, which means that, over time, the dispersed phase will be diffusing into the continuous phase. Emulsions with non-uniform droplet size distribution tend to deform. The driving force exists between smaller and larger droplets where matter will migrate over the continuous phase from small droplets to the larger ones. When time passes, the count of droplets will be reduced and the mean droplet diameter increases. The second mechanism of emulsion deformation is coalescence, where thin film will rupture between two adjacent droplets, which lead to fusion between the two droplets. The film rupture is only possible when a hole is formatted within thin film which then gets larger (Leal-Calderon, et al., 2007). According to Robbins & Cusack (1997), unstable dispersion contains droplets of 1 mm or above and settling is very fast. Very stable emulsions contain droplets under 100  $\mu\text{m}$  in diameter.

The collision of two droplets will lead to coalescence due motion and van der Waals attraction energy, unless there is a strong enough repulsion barrier to keep the droplets apart. All natural systems tend to seek the energy minimum stage which in this case means that the potential energy of two adjacent droplets is at the lowest possible value. The

potential energy between droplets also known as zeta potential is a combination of both attractive and repulsive energy and it is a useful tool to illustrate the interaction between adjacent emulsion droplets (Kostansek, 2012). Electrostatic stabilisation results from an ionic surfactant agent in the emulsion. Electrostatic surfactant molecule is adsorbed at the surface on the droplet enhancing the electrostatic repulsion between the droplets (Heusch & Reizlein, 2012). Figure 4 shows zeta potential energy curves for the two droplets approaching each other in three different conditions. Zeta potential is plotted on the y-axis and the distance between the droplets is plotted on the x-axis.



**Figure 4.** The zeta potential as a function of distance between the two adjacent droplets in three different cases. Case A curve shows the barrier formed by low electrostatic surfactant concentration. The formed barrier is adequately high to prevent coalescence. In Case B, the surfactant concentration increases resulting in unwanted reduction on repulsion force. Case C is emulsion without any surfactant (Kostansek, 2012).

Another path to stabilised emulsion is steric stabilisation. The emulsion droplets are stabilised with non-ionic oligomeric surfactants or polymers, which form a physical barrier between the droplets. The droplets are not able to get close enough for van der Waals attraction forces to carry out the film rupture. Although steric stabilisers prevent coalescence, the continuous phase can influence emulsion stability and attractive forces can manifest because of poor solvent properties (Kostansek, 2012).

### 3.3 Emulsion destabilisation

The presence of emulsions can be harmful and unwanted phenomenon in some petro- and chemical industries. According to Kostansek (2012), the reasons for emulsion destabilisation might be the recovery of tertiary oils and solvent, where the W/O emulsion needs to be broken to recover the valuable chemicals. Some practical methods to promote emulsion destruction have been presented by Kostansek (2012) and Heusch & Reizlein (2012). Table I shows the possible method of the successful emulsion destruction.

**Table I** Methods used to enhance emulsion destabilisation and resulting mechanism leading to coalescence.

Method	Result	Source
Increasing thermal energy	Elevated temperature might affect surfactant adsorption conditions, which promotes changes in the zeta potential.	(Heusch & Reizlein, 2012) (Kostansek, 2012)
Electrolyte addition	Reduced electrical double layer and the electrostatic repulsion force.	(Heusch & Reizlein, 2012) (Kostansek, 2012)
Desorption of emulsifier	Adding a salt or altering the pH of system, might affect emulsifier solubility.	(Heusch & Reizlein, 2012)
Mechanical shear	Destabilisation by centrifugation, filtration and mixing might lead to emulsion deformation.	(Kostansek, 2012)
Surfactant addition	Disturbance in the system balance.	(Kostansek, 2012)
Freezing	Can lead to disturbance of emulsion.	(Heusch & Reizlein, 2012) (Kostansek, 2012)

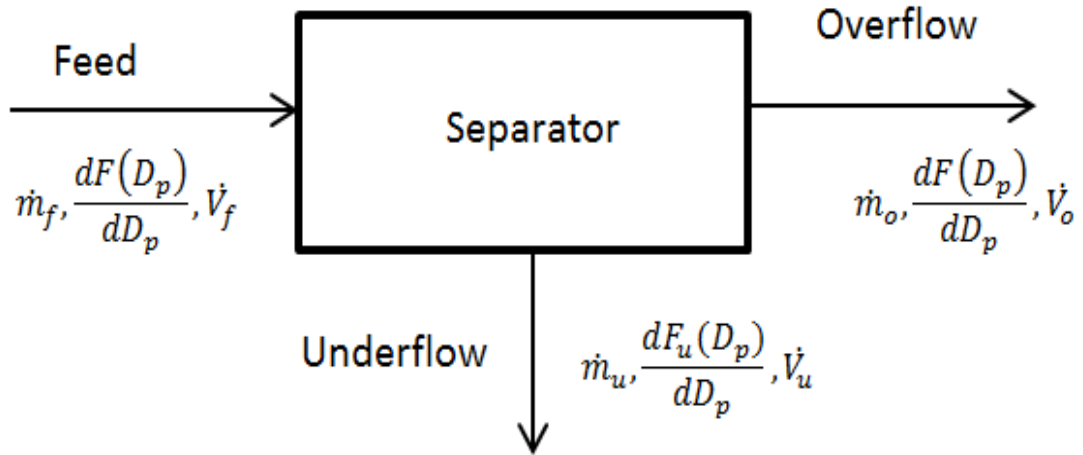
As mentioned before in some unit operations, the emulsion formation might be desired, but for further processing, the sufficient phase separation of dispersed system is necessary. Stable emulsions might be the reason for difficulties in further unit operations, impurities in the products, losing valuable raw materials and even loss in productivity. Depending on the process and its configuration some of the destabilisation methods are ruled out. From Table I above manipulating stream pH and the changing temperature of the process are easier to conduct and should be applied first on emulsion destabilisation treatment.

## **4 GRAVITATIONAL PHASE SEPARATORS**

This chapter will introduce the gravitational phase separators commonly used in chemical processes. Different separator designs are discussed and the methodology of the equipment sizing is introduced mostly for understanding the later processing of the laboratory data received from the process.

### **4.1 Determination of phase separation performance**

Phase separation performance can be determined by deriving the mass balance of a given separation application. Let us assume that there is no accumulation of material in the system and, therefore, the mass of the outlets are equal to the total mass flow of feed (Svarovsky, 2000). A basic schematic of a single-stage separation unit is presented below in Figure 5.



**Figure 5.** Schematic of a single-stage separator. The feed flow to separator is divided into two or more streams. Parameters present are  $\dot{m}$  mass flow of a specific stream,  $F(D_p)$  droplet diameter distribution, and  $\dot{V}$  volumetric flow of a specific stream (Svarovsky, 2000).

An overall separation efficiency  $E_T$  can be determined for a single separation unit with the use of the equation

$$E_T = \frac{\dot{m}_u}{\dot{m}_f} = 1 - \frac{\dot{m}_o}{\dot{m}_f} \quad (9)$$

where

$\dot{m}_f$	Mass flow rate of the feed, $\text{kg s}^{-1}$
$\dot{m}_u$	Mass flow rate of the underflow, $\text{kg s}^{-1}$
$\dot{m}_o$	Mass flow rate of the overflow, $\text{kg s}^{-1}$

## 4.2 Decanter

Gravity settlers or decanters are the simplest phase separation equipment by design. The decanter tanks are continuously operated liquid-liquid separators, which are operated similarly as clarifiers and thickeners in gravitational solid-liquid phase separation applications. As mentioned previously, a droplet surrounded by continuous phase in a gravitational field will separate over time. The direction of the droplet can be upwards or downwards depending on the densities of dispersed and continuous phase. The separation

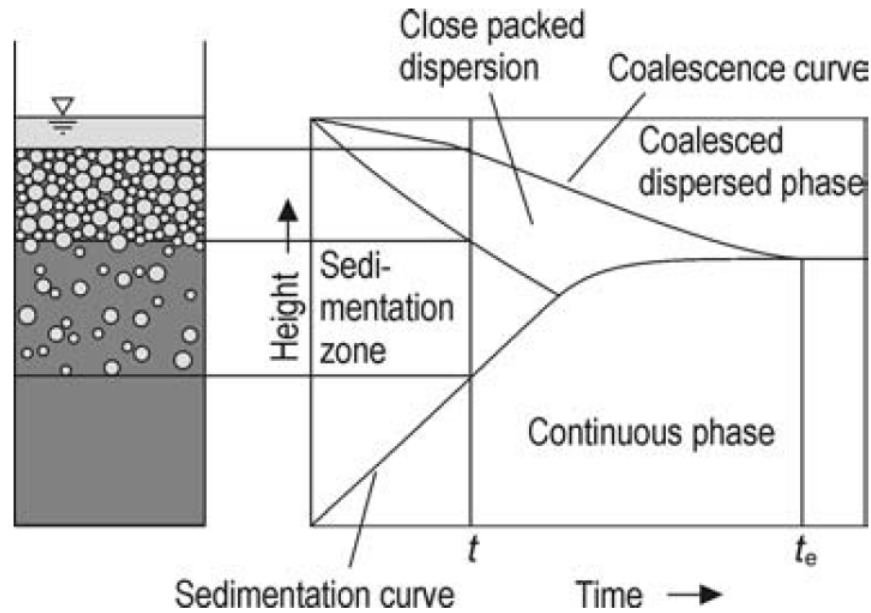
of droplets will generally happen faster than solid spheres with the same diameter (Müller, et al., 2012).

#### **4.2.1 Settling in decanters and decanter structure**

Decanters can be operated with a horizontal or vertical configuration. According to Coker, (2007) the best separation is achieved with the horizontal gravity settling units. The clear light phase is gathered continuously from the top and the heavy phase from the bottom. Decanters can operate with or without automation. Without instrumentation, the decanter is controlled with different structural modifications, where the height of the heavy phase leg above the surface is controlled by balancing the height of the lighter liquid phase surface. In automated systems, the interface level is measured and the removal of the bottom phase is operated based on the information received from the level measurement unit with an automatic valve. Light phase will overflow automatically from the vessel as height of the light phase reaches outlet (Robbins & Cusack, 1997).

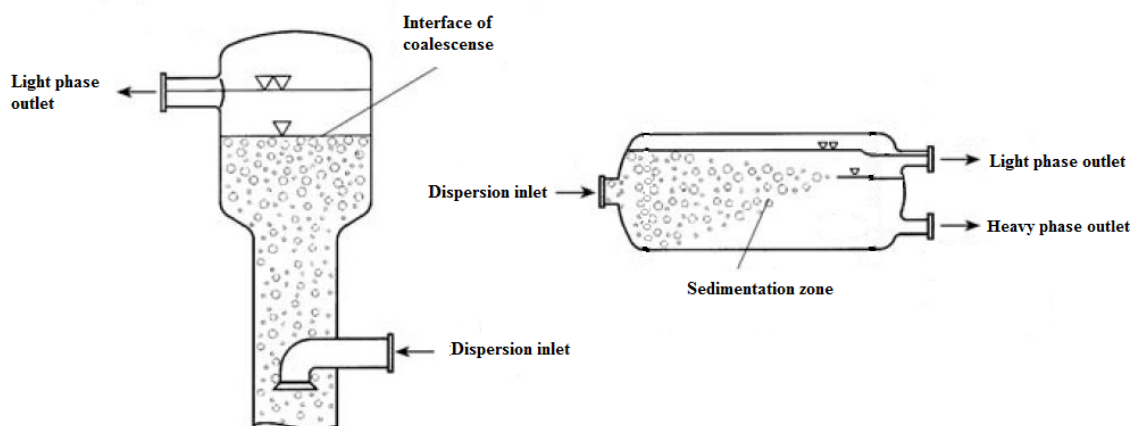
Especially in horizontal decanters different settling regimes are clearly present in the decanter. The thicknesses of vertical regimes are changing when moving from the dispersion inlet towards phase outlets. Settling zones can be divided into the continuous phase, sedimentation zone, coalescing zone and coalesced disperse phase (Svarovsky, 2000). When designing a sufficient decanter for the liquid-liquid phase, separation dimensions are calculated with the use of empirical equations and with batch settling experiments done in the laboratory. Most commonly, the laboratory test is performed in a glass cylinder and the heights of interfaces are recorded over time (Müller, et al., 2012). The data gathered by laboratory experiments are then plotted where the height of interfaces are at vertical axis and time is on horizontal axis. The basic schematic illustration of the batch settling test is shown in Figure 6.





**Figure 6.** Batch settling experiment and interface height evolution plotted against time during experiment (Müller, et al., 2012).

In Figure 6, it can be seen that the four different regimes are present in settling applications. The sedimentation and coalescence curve is generated by recording the height of both the clear continuous and dispersed phase over time. The interface height between close packed dispersion and the almost clear continuous phase is recorded in a separate sedimentation zone from the coalescence zone. In the horizontal separation vessels, phase regimes are almost similar to the batch settling experiments, but with the exception that the height of the regimes are a function of vessel length. The fluid flow in the decanter is also assumed to be in the laminar regime and no mixing of phases is present. The basic construction of vertical and horizontal gravity decanter and the formed interfaces present in decanter is shown in Figure 7.



**Figure 7.** The structure of a vertical and horizontal gravity decanter. The vertical gravity decanter is on the left and the top half of the decanter unit is shown (Müller, et al., 2012).

The separation efficiency is dependent on the structure of the decanter unit (1), adequate density difference between phases (2), emulsion feed flow (3) and feed composition (4). Fluctuation in parameters 2–4 might lead to disturbances in the interface level of phases in the decanter unit, leading to the entrainment of light phase in heavy phase or vice versa. A study conducted by Rostami et al. (2011) states that inlet aperture on settling basin has a noteworthy role on settling performance. The position of the inlet should minimise the kinetic energy of feed flow (1), prevent short-circuiting (2), diminish the effect of density currents (3) and reduce disturbances to the clear phase interface (4). According to Rostami et al. (2011) dividing the inlet flow across the cross sectional area of the horizontal settling basin reduces turbidity at the decanter feed. Modifications on the inlet positioning and dividing feed inlet positions to couple nozzles enhanced separation performance at the withdraw location.

#### 4.2.2 Decanter sizing

Many different styles for designing gravity decanters and settlers are available in various journals and rule-of-thumb methods. The most common geometry for a decanter is cuboid, but other shapes are also used (McKetta, 1993). The required residence time for satisfactory phase separation in a vessel is a function of the terminal settling velocity  $u_T$  of the dispersed phase through the continuous phase. In most cases, the residence time is

between 30 minute and 1 hour. Some kind of separator capacity or separation performance problems might manifest, if the mean diameter of the droplets are mistakenly assumed to be higher than in the normal operations. The sufficient minimum droplet diameter in dispersion is 100–150  $\mu\text{m}$  for designing purposes (Coker, 2007). General practice shows that typical droplet diameters are in the range of 500–5,000  $\mu\text{m}$  within agitated systems. Smaller than 500  $\mu\text{m}$  droplets are rarely present in the turbulent pipeline flow (Couper, et al., 2012).

Depending on the feed composition of the gravity settler feed the dispersed system can be either W/O or O/W. Determination of which phase is the dispersed phase can be predicted with the equation presented by Schweitzer (1979).

$$\Theta = \frac{\dot{V}_l}{\dot{V}_h} \left( \frac{\rho_l \eta_h}{\rho_h \eta_l} \right)^{0.3} \quad (10)$$

where	$\dot{V}_l$	Volumetric flow rate of light phase, $\text{m}^3 \text{s}^{-1}$
	$\dot{V}_h$	Volumetric flow rate of heavy phase, $\text{m}^3 \text{s}^{-1}$
	$\rho_l$	Density of light phase, $\text{kg m}^{-3}$
	$\rho_h$	Density of heavy phase, $\text{kg m}^{-3}$
	$\eta_l$	Dynamic viscosity of light phase, $\text{kg m}^{-1} \text{s}^{-1}$
	$\eta_h$	Dynamic viscosity of heavy phase, $\text{kg m}^{-1} \text{s}^{-1}$

The value from Eq. 10 can then be used to determine which phase is the dispersed phase in Table II.

**Table II.** Values of  $\Theta$  used to determine orientation of the treated dispersed system Schweitzer (1979).

Value of $\Theta$ (Eq. 10)	Result
< 0.3	Light phase always dispersed
0.3–0.5	Light phase probably dispersed
0.5–2.0	Phase inversion is possible
2.0–3.3	Heavy phase probably dispersed
> 3.3	Heavy phase always dispersed

Eq. 4 is used to determine the terminal settling velocity for the smallest dispersed phase body. Typical length-to-diameter ratio  $L/D$  is between 3.5 and 5, for the most cost-effective separator (Seader, et al., 2011).

For the successful separation of the phases, the terminal settling velocity must be higher than the flow rate of continuous phase divided with phase-interface area  $A_I$ .

$$\frac{\dot{V}_c}{A_I} < u_T \quad (11)$$

where  $A_I$  Phase-interface area,  $\text{m}^2$

As a rule of thumb, the height of the emulsion coalescence zone is 10% of the vessel diameter and time available to cross the coalescence zone is used to analyse the separation process. The time available should be higher than between 2 min to 5 min (Coker, 2007). The time available to cross the emulsion band is evaluated with

$$t_{cross} = \frac{1}{2} H_D \frac{A_I}{\dot{V}_p} \quad (12)$$

where  $H_D$  Height of the emulsion band, m

To keep both phases separated, the velocities of light and heavy phase should be equal across the separation unit. The nozzle to the vessel should be sized to adjust the feed flow velocity to approximately 0.15 –0.45 m/s. The degree of turbulence  $N_{Re}$  is used to inspect the flow conditions at the clear heavy and light phase layer (Schweitzer, 1979).

$$N_{Re} = \frac{u_c D_H \rho_c}{\eta_c} \quad (13)$$

where  $u_c$  Velocity of continuous phase through flow channel,  $\text{m s}^{-1}$

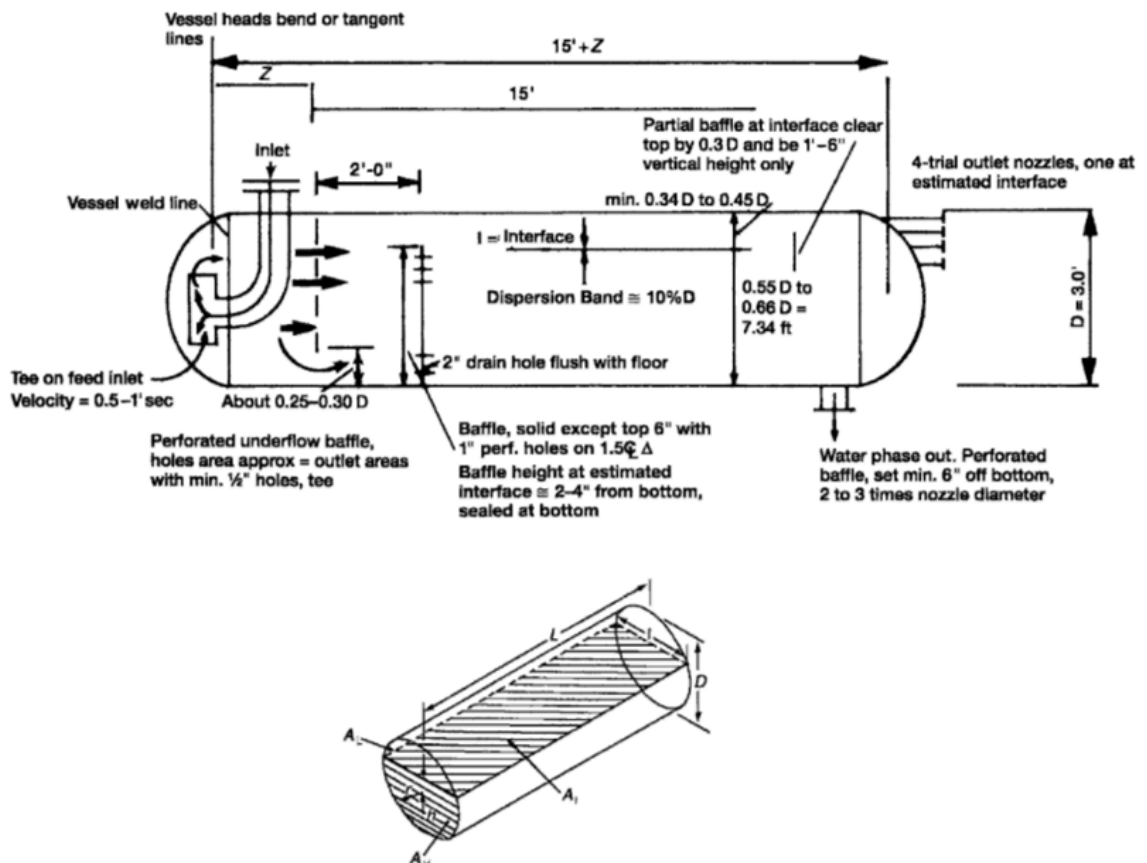
$D_H$  Hydraulic diameter of flow channel, m

The degree of turbulence demonstrates the flow conditions of the phases and high flow rates might lead to problems, when the motion of settling droplet is interfered by the lateral flow of the continuous phase. In Table III, the possible scenario on the phase separation with the different value of the degree of turbulence is shown.

**Table III.** The rules on determining interference effect on phase separator performance. (Couper, et al., 2012)

$N_{Re}$	Result
< 5000	Minor issues with separation
5,000-20,000	Restrictions on separation
20,000-50,000	Major problems
>50,000	No separation

One possible layout of the horizontal gravity decanter is proposed by Coker (2007) and shown in Figure 8 with common important structural modification to the decanter structure.

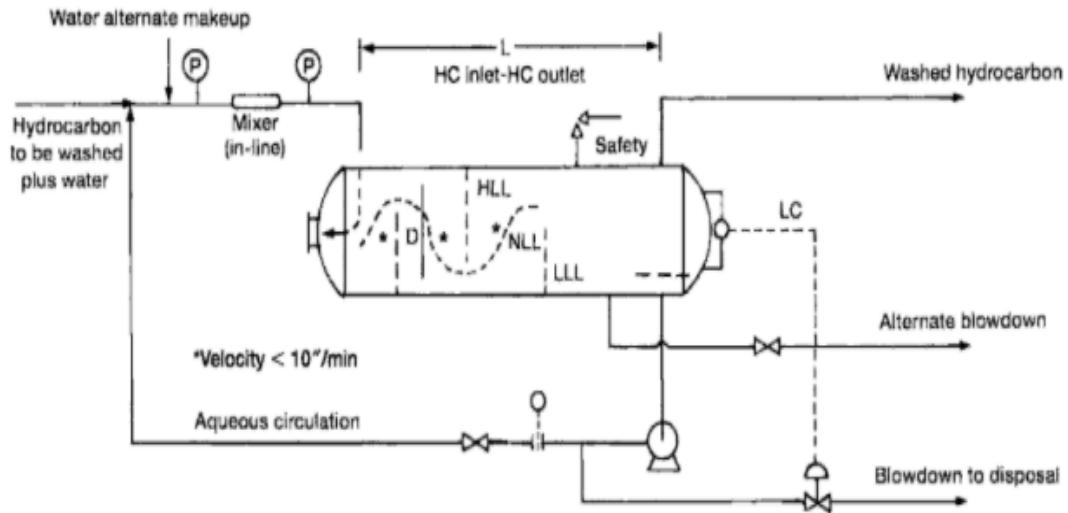


**Figure 8.** Gravitational decanter for liquid-liquid separation processes with the basic characteristic dimensions indicated (modified from Coker, 2007)

### 4.3 Gravity settler

The main difference between a decanter and gravity settler is that the decanter is a vessel that does not use the complete volume of the vessel. With a gravity separator, the whole volume of vessel is occupied with liquid (McKetta, 1993). Most commonly, cylindrical gravity settlers are used and, according to Coker (2007), horizontal units with cylindrical geometry are more appropriate up to 2.5 m compared to other shapes. This is mostly due to the increased interfacial area between the two phases and much shorter vertical distance required for dispersed phase to reach coalescing zone (Couper, et al., 2012).

The phase interface levels in a gravity settler are controlled with the regulating outflow of the heavy phase and in some cases part of the heavy phase is circulated back to settler feed. Circulation can be useful when low concentration emulsions are fed into the separator. Circulation of the dispersed phase back to the separator feed increases the droplet count in the coalescing zone, and more interaction between the coalescing droplets occurs (Warnier, 2017). In some petroleum industry applications, hydrocarbons are also washed with water, and water phase circulation can be part of the wash sequence. The basic design of a horizontal gravity settler used in a hydrocarbon wash in the petroleum industry is presented in Figure 9.



**Figure 9.** A gravity settler used by the petroleum industry to wash hydrocarbons. In the dirty hydrocarbon phase, water is fed to the settler trough mixer and the washed hydrocarbons are gathered from the overflow channel. A part of the wash water is circulated back before the mixer. The remaining amount of water is removed from the underflow (McKetta, 1993).

Draining of the heavy phase can cause some disturbances between interfaces and especially on the settlers the interface level can oscillate remarkably. These disturbances can be reduced by adding a draining pot under vessel, where the blowdown of the vessel is performed. These pots are very commonly used in coalescers, where the concentration of dispersed phase is very low (Couper, et al., 2012). Coalescers are discussed in more detail later on.

A study was conducted by Chonwattana et al. (2017) on the interface level estimation and control in a two-phase vertical decanter with a palm-oil/water system. The conventional instruments used in single-phase systems do not apply straight on two-phase systems because density is variable across settling equipment. The interface level does not reach steady-state conditions, since the decanter is operated by regulating outflows. Oscillation on the interface levels has an effect on phase separation efficiency. Chonwattana, et al. (2017) made an estimation of the interface level with the model using information from pressure sensor and ultrasonic sensor. This arrangement led to better performance in comparison with the common PI and LQR (Linear Quadratic Regulator) controllers.

### 4.3.1 Sizing of a gravity settler

Maintaining the steady and sharp phase interface level is crucial to prevent residues of separated phases to end up in the wrong stream. A steady phase interface can be achieved with the correct fixing of the separation unit and ensuring steady removal flow rates of both separated phases. Identifying and removing any possible disturbances when designing the separator is important. The boundary for the maximum value of the droplet settling velocity is set to 0.26 m/min (Happel, 1958). The height of an interface in a cylinder can be approximated to be (McKetta, 1993)

$$h = \frac{38.4A}{\pi D} + 1.2D \quad (14)$$

where  $A$  Area of segment of a circle,  $m^2$   
 $D$  Diameter of vessel,  $m$

Eq. 14 is valid when the segment formed by the interface is between 25% and 75% of the area of the circle. With these assumptions the height of interface is between 30% and 70% of vessel diameter. Average volumetric residence time in a settling vessel can be determined with (McKetta, 1993)

$$t_{avg} = \frac{7.48V_i}{\dot{V}_i} \quad (15)$$

where  $V_i$  Active volume occupied by specific phase,  $m^3$   
 $\dot{V}_i$  Flow rate of specific phase,  $m^3 s^{-1}$

The minimum residence time can be determined by dividing the interface height with the terminal settling velocity from Stokes' law. The relation between the average residence time and the minimum residence time can be expressed as (McKetta, 1993)

$$t_{avg} = f_i t_{min} \quad (16)$$

where  $f$  Relation factor for specific phase, -

The height of the individual phase interface in the settler can be approximated with (McKetta, 1993)



$$h_i = \frac{7.48A_{I,i}Lu_{T,i}}{f_i\dot{V}_i} \quad (17)$$

where  $A_{I,i}$  cross sectional area of specific phase  
 $L$  Length of the vessel  
 $u_{T,i}$  Terminal settling velocity of a specific phase

The phases present in settling applications are clear phases of continuous, dispersed phases and layer of coalescing dispersion between the two clear phases. Equations 14 and 17 are rearranged to give the cross-sectional area of the individual interface (McKetta, 1993)

$$A_{I,i} = 1.2D \left[ \frac{7.48Lu_{T,i}}{f_iV_i} - \frac{38.4}{\pi D} \right]^{-1} \quad (18)$$

When determining the optimal settler diameter, 20% of the cross-sectional area is occupied by a treated emulsion. Actually, this area is a range where the interface level will oscillate during steady operations and it is referred to as the death zone. This means that (McKetta, 1993)

$$A_{I,l} + A_{I,h} = \frac{0.8\pi D^2}{4} \quad (19)$$

Eq. 18 is substituted to Eq. 19 for both heavy and light phase yielding (McKetta, 1993)

$$D^4 - aD^2 + b = 0 \quad (20)$$

where parameters  $a$  and  $b$  are defined as (McKetta, 1993)

$$a = 1.889 \frac{u_{T,l}f_h\dot{V}_h + u_{T,h}f_l\dot{V}_l}{ru_{T,l}u_{T,h}} \quad (21)$$

and

$$b = 3.505 \frac{f_h\dot{V}_hf_l\dot{V}_l}{r^2u_{T,l}u_{T,h}} \quad (22)$$

where  $r$  Economical vessel ration ( $L/D$ ),-

The optimal vessel diameter can then be solved with the equation (McKetta, 1993)

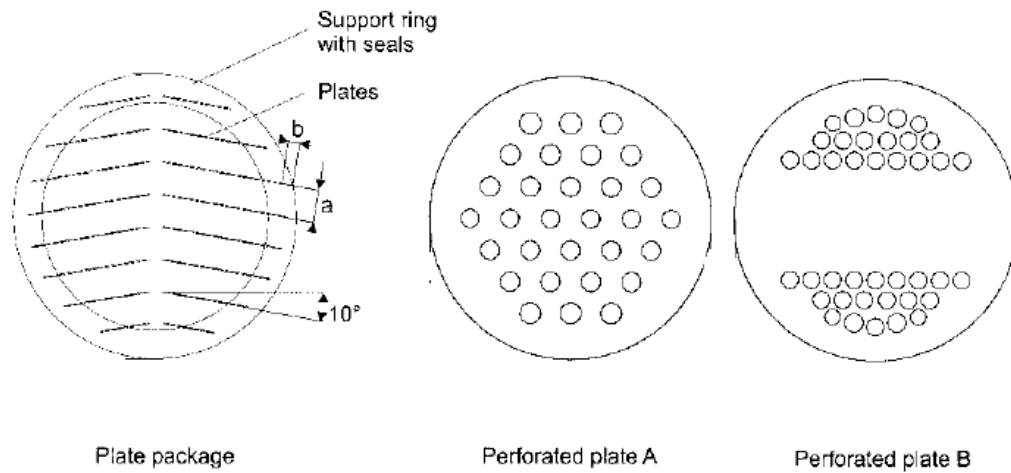
$$D = \pm \left[ \frac{a}{2} \pm \frac{(a^2 - 4b)^{\frac{1}{2}}}{2} \right]^{-\frac{1}{2}} \quad (23)$$

## 5 COALESCING AIDS

Two kinds of chemical processing vessels are used by the chemical industry. Process vessels can be constructed without internals or with internals. The later presented category is discussed in this chapter. A couple possible methods exist to make phase separation faster. Coalescing aids reduce residence time required for separation and thus reducing vessel length. Emulsion properties will determine the significance of coalescing aid effect on phase separation. According to Müller et al. (2012), the vessel length can be reduced by a factor of 2–5. The most commonly used coalescing aids are inclined **(1)** or corrugated baffles **(2)**, and fibre bed filters **(3)**. Other possible configurations are fixed beds of packings **(4)**, porous sinters **(5)**, and membranes **(6)**. In this chapter, the most common stacked internal baffles and fibre beds are described.

### 5.1 Internal plates

Internal plates can be used in both the horizontal and vertical settler, but it is necessary that the feed is distributed evenly at the settler entry over the cross-sectional area. Uniform feed flow to plate package is essential for each plate stacks to operate well and perforated plates with different distributions of perforation and sizes are used. Plates are typically stacked and are slightly inclined. Optimal inclination varies in the range of 10° to 15°. One example of the cross-section of inclined plates with a 10° inclination and two different perforated plates is shown in Figure 10.



**Figure 10.** Inclined plate package with an inclination of  $10^\circ$ , distance between plates  $a$ , and distance of plate tip from vessel wall  $b$ . Perforated plate A has uniform perforation and distance between adjacent holes is equal, whereas perforated plate B has tight perforations at the top and bottom section (Schlieper, et al., 2004).

The main benefit of the plates is that the settling distance of a single droplet is reduced and the coalescing interface area is larger. It can be said that adding the plate package to the vessel creates several separated parallel settling stages to the system. Internals will increase retention time of the emulsion compared to the clear phases, due to higher flow resistance on the plate surface. With higher retention, the time phases have more time to separate and thus lead to better separation performance. This phenomenon is present in most of the cases in chemical industries. Growing process flows caused by increased production capacity leads to the larger settler dimensions, thereby increasing the turbulence in the system due to the larger characteristic dimensions. Stacked plates reduce the characteristic dimension of the flow and ensure laminar flow conditions (Müller, et al., 2012).

Trickling film of coalescing droplets is formed on the plate surface due to a hydrostatic pressure difference of droplets. The complete wettability of a plate is preferred by the dispersed phase. Müller et al. (2012) has gathered the guidelines to consider on plate package configuration. These guidelines are shown in Table IV.

**Table IV** Guidelines for the most commonly used criteria on inclined plate configurations. The guidelines are gathered from several scientific experiments and combined by Müller et al. (2012)

Number	Guideline
1	Laminar trickling film should be formed on the plate surface. Shear stress on film is increased to promote the coalescence.
2	Plate material should be wettable by dispersed phase.
3	Dispersed phase should be evenly distributed over the width of plate.
4	Structural modifications to reduce film thickness increase performance of the settler.
5	Sufficient length for the plate package is 400 mm.
6	Surfactant has a minor impact on coalescence because the film is continuously carrying surfactant to the plate outflow and thus preventing accumulation.
7	Some conditions might lead to situations where coalescence leaves secondary droplets, due incomplete coalescence. The diameters of secondary droplets are very small and thus entrainment to the continuous phase is possible.

A study has been conducted by Schlieper et al. (2004) on the liquid-liquid phase separation in gravity settlers with inclined plates. Laboratory experiments were conducted with three different water-oil emulsions of *n*-butanol, tridecanol and cyclohexanone. The phase fraction of the phases and the distances between plates were variables. As a result of the study according to Schlieper et al. (2004), there is a direct relationship between a settling test with or without inclined plate internals. This relationship on settler length with internals is presented with equation

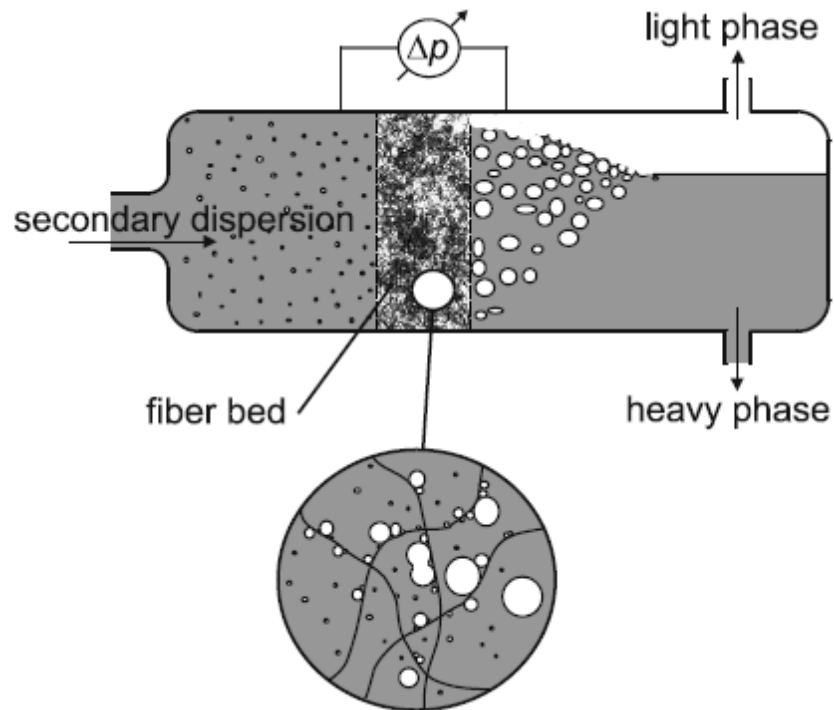
$$L_{with\ internals} = \frac{t_{internals} L_{without\ internals}}{t_{without\ internals}} \quad (24)$$

where  $t_{internals}$  Residence time with internals, s  
 $t_{without\ internals}$  Residence time without internals, s  
 $L_{without\ internals}$  Vessel length without internals, m

Eq. 24 can be directly used for calculations on separator length with internals from design models presented before on separator without internals.

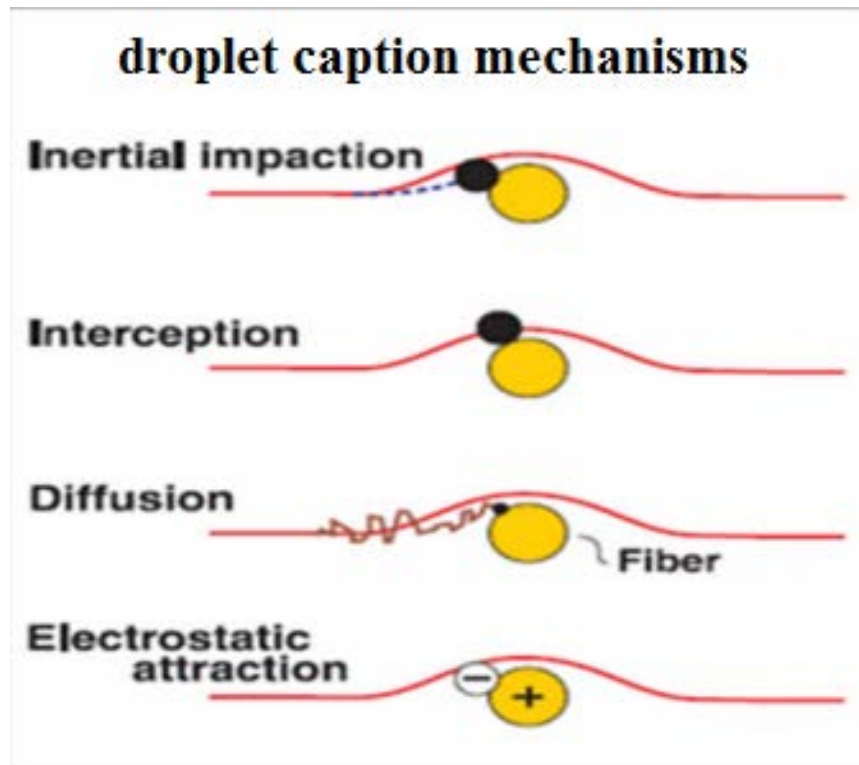
## **5.2 Fibre bed filters aka Coalescers**

Fibre beds and pads are used on the separation of secondary dispersions, which have an excessively long requirement for residence time (typically, droplets below 100  $\mu\text{m}$ ) in settlers (Coker, 2007). A very high portion of the entrained phase can be recovered from the dispersion, closely up to the solubility limit. Gravitational separators operating with fibre beds and pads are named in some instances as coalescers. These vessels are actually more like droplet agglomeration vessels than conventional gravity settlers because the actual separation of the phase is happening after coalescing aid. Many small droplets are merged to produce a lower number of droplets with a larger diameter. Within the chemical industries, coalescers are a remarkably attractive method due to good performance and simple construction. According to Speth et al. (2002), fibre bed coalescer design is based on experimental data and heuristic, but currently development on a physically founded design models are under investigation. Important criteria on coalescers are the pressure drop across coalescing aid and separation efficiency. Basic fundamentals of a coalescer unit are shown in Figure 11.



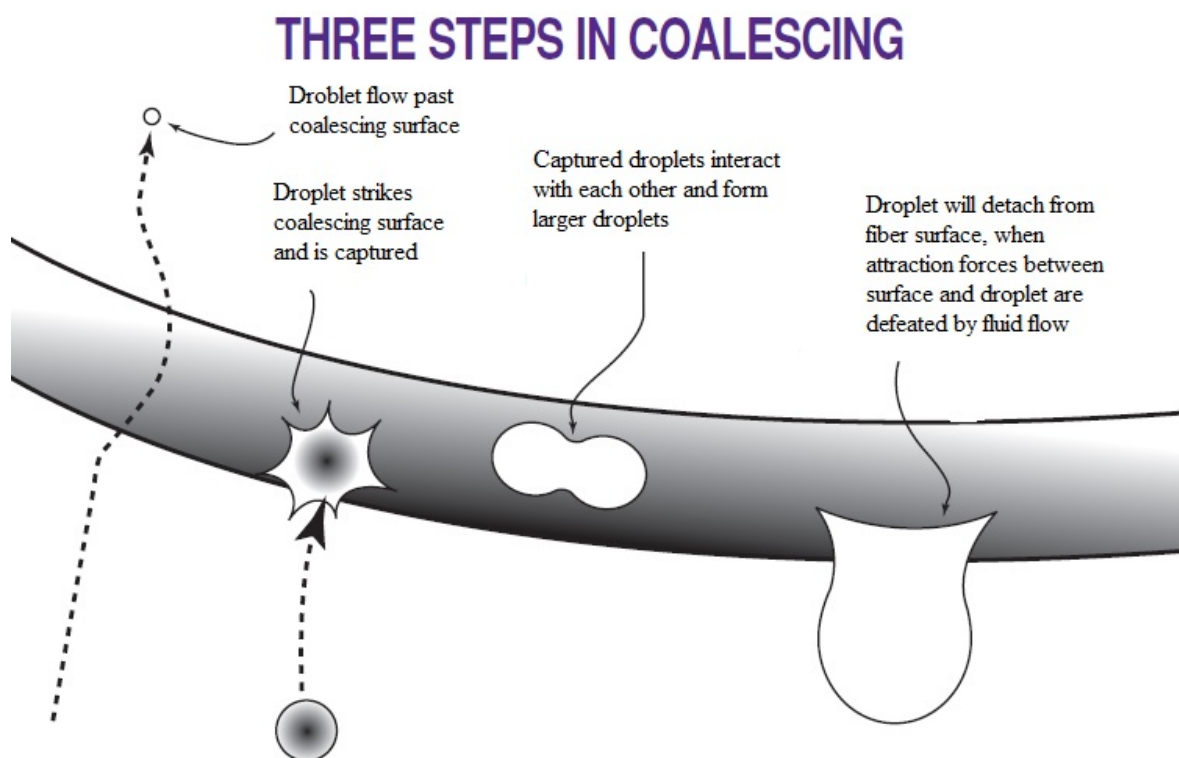
**Figure 11.** Operation principle of secondary dispersion treatment with a fibre bed coalescer and magnification of droplet interaction with individual fibre surface. Where  $\Delta p$  is pressure drop cross fibre bed (Speth, et al., 2002).

Fibre coalescers can be constructed with fibre packing between wire mesh keeping packings in place, also woven fibre cartridges can be installed on a perforated plate. When emulsion is flowing through the fibre bed droplets stick to the fibre surface. The entrainment of dispersed phase can happen by direct interception (1), inertial impaction (2), electrostatic attraction (3), and diffusion by Brownian capture (4). Different droplet entrainment mechanisms are presented in Figure 12.



**Figure 12.** Different mechanism of droplet interaction with fibre surface (Vengadasalam, 2016).

During the time on fibre surface, adjacent droplets will interact with each other and coalescing is started. When coalescing droplets acquire specific size, droplet will detach from the fibre surface due to drag force created by fluid flow around droplet (Coker, 2007). The three steps of coalescence are shown in Figure 13.



**Figure 13.** Steps in coalescing process on fibre material surface (Modified from AMACS Process Tower Internals, 2006).

Parameters affecting the performance of the coalescing aid are the properties of separated phases, flow conditions and fibre characteristics. Such factors are mean droplet size (1), density difference (2), interfacial tension (3), and existence of any surfactants (4). Coalescing aid properties affecting separation are pore size (5), fibre roughness (6), permeability (7), surface energy (8) and thickness (9). (Speth, et al., 2002)

Coalescers are one form of deep-bed filtration application and are mostly utilised in the field of water treatment. During the flow of emulsion through a filter media dispersed phase is bounded onto the filter media. The entire volume of the filter media is utilised for dispersed phase bonding. The most significant advantage of coalescers is their performance with low phase ratio dispersions and even droplets with a diameter of approximately 0.1  $\mu\text{m}$  can be captured (Svarovsky, 2000). Typical forces affecting droplets with a diameter above 10  $\mu\text{m}$  are hydrostatic and gravitational forces. While dominant forces on particles under 10  $\mu\text{m}$  are double-layer forces, van der Waals forces and Brownian diffusion. The nature of these forces are electrochemical, thus some electrochemical properties might be required on filter media (Ghidaglia, et al., 1995).



A major drawback on the deep-bed filtration process is its tendency to be an unsteady process. Solid resins carried by emulsion flow are continuously attached on the filter media and thus altering the void structure of the pores during the operations. Decrease in bed porosity leads to changes in the filter efficiency and permeability. The permeability of filter media is monitored by measuring the pressure drop between filter entrance and exit (Ghidaglia, et al., 1995).

### **5.2.1 Fibre bed media materials and properties**

In this section, coalescing aid media materials, properties and structures are discussed in more detail. Same fibre media is used in some solid-liquid separation filtration processes and mostly characteristics of fibre media is based on permeability and retention. Although, in coalescers, fibre media is used mainly to increase droplet diameter, solid impurities are captured by the fibre media. The overall performance of coalescing is directly dependent on the filter media properties.

The fibrous filter materials used can be made from natural, synthetic or glass fibres, woven or non-woven cloth, paper and cellulosic or synthetic membrane from paper. Decision on the chosen material of fibre media is balanced between the unit costs and process requirements. Glass fibre, polypropylene (PP), polyurethane (PU), and polyethylene terephthalate (PET) from synthetic fibres are most commonly used. Also some more alternative materials are used, but the materials mentioned before are the commercially most utilised and studied fibre materials (Coker, 2007).

Coalescences fineness and operational performance are dependent on the structure of fibre media, the predominant mechanism of the droplets interact with the media, which is mostly dependent on the media and emulsion properties, and on the used measurement methods. For example, pressure difference across coalescing aid can be used as an indicator for the need of maintenance. Fibre media characteristics are affected by the size and shape of the holes. Regarding the pathing of the hole through the fibre media, the hole can be either straight or twisting. The number of holes per unit area and their uniformity has also impact on media performance. Although the characteristics mentioned before are important to understand, the fact is that the nature of the holes is complicated and thus these properties are really difficult to determine. This is especially an issue with woven fabrics with

flexible materials and media with random structures. Fibrous materials are typically in this category (Dickenson, 1997).

Cartridge fibre filters are one of the most commonly used types of coalescing aids. The fibre medium is constructed from wound wires that can be supported on a perforated cylindrical support. The fibre can be either round or wedge shaped. For wire wound cartridges the retention range starts from 5  $\mu\text{m}$ . Each layer of the wounded fibres can be brushed to raise the nap of filter media. This is used to achieve the desired thickness and within each layer the nap varies the closeness of the winding through the coalescing media. The porosity of cartridges fibre media can be controlled with pitch of the winding, tension, fibre length and thickness (Svarovsky, 2000).

The materials used to produce bonded cartridges can be fine wool fibres, cotton, cellulose, glass and synthetic materials. The production of bonded cartridge is a process where specific filtration technique is used to form fibre tube in wet conditions. After tubes are dried out, the tube is cured and impregnated with resin. Bonded cartridges have strong structure and additional support is not needed. Bonded cartridges are light and very porous (Svarovsky, 2000).

Bonded and wound cartridge media are described as depth filters, which means that primary entrainment occurs within the interstices of medium. The achieved benefits are easy disposal, high dirt-holding capacity with capability to remove solids down to 1  $\mu\text{m}$  from liquid phase. Down side with cartridge is quite small surface area, but it can be increased by cutting wedges on the outer surface. Also fibre cartridges cannot be reused by washing the fibre element (Svarovsky, 2000). Different types of fibre cartridges are shown in Figure 14.



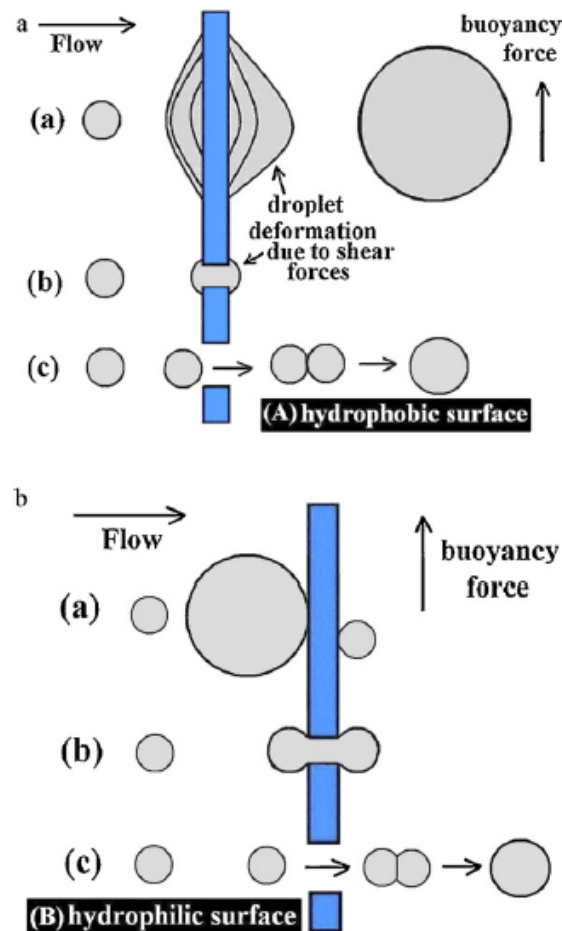
**Figure 14.** Different types of cartridges used in chemical processes. Cartridges number 1,2 and 4 are made from glass fibre and numbers 3, 5 and 6 from PP. The cartridges from 1–4 are wound type filters and last two are bonded type. Thick fabric sock is added around cartridge 1 to prohibit fibre materials detaching to process stream. Cartridge 6 has grooves cut to increase the surface area and reduce clogging. Cartridges have 25  $\mu\text{m}$  retention diameters, except number 4 has 5  $\mu\text{m}$  retention diameters.

When comparing fibre cartridges 2 (25  $\mu\text{m}$ ) and 4 (5  $\mu\text{m}$ ) in Figure 13, fibres are wound more firmly on cartridge 4 than cartridge 2. Selection of the proper coalescing aid is almost the most important part of the phase separation process. Correct coalescing aid media is decided based on the requirements set from the process and operating costs. These main factors are balanced to produce best possible results. There is no guaranteed rules-of-thumb method to determine the correct media, which requires tests in a laboratory, pilot or full-scale, including the product supplier might be able to give recommendations based on experience (Svarovsky, 2000).

### 5.2.2 Studies on coalescing aid properties

According to the study results obtained by Bansal et al. (2011), separation efficiency is increasing when the mean pore size of fibre material is smaller, which is due to the better entrainment of secondary droplets. In this study, five different fibre materials were used.

The materials used were non-woven cellulose, PET-woven, needled non-woven PET, spunbond PET and meltblown PBT with spunbond PET. Wettability of material by dispersed phase is referred to be high because dispersed phase will displace continuous phase from filter media. After the displacement of the continuous phase concentration of dispersed phase increases and favourable coalescence occurs. Wettability is a measure of contact between liquid and solid surface, which is dependent on both liquid surface tension and surface energy of the filter media. Filter material with low surface energy are wettable with non-polar substances, thus meaning that material has hydrophobic surface. In this case, adhesive forces between filter material and oil phase are high. The behaviour of oil droplet in contact with hydrophobic and hydrophilic surface is shown in Figure 15.



**Figure 15.** Behaviour of oil droplet in contact with hydrophobic and hydrophilic surface in continuous water phase. Case (a) illustrates droplet capture and coalescence on the fibre surface. In case (b) droplet flows through fibre pore and is deformed due to shear forces. Case (c) illustrates droplet flows past fibre and coalescence spontaneously in the flow stream (Bansal, et al., 2011).

Wettability can be simply determined by measuring the contact angle of droplet at the surface of material. If the angle is greater than 90 degrees, the system is defined as non-wettable by liquid phase. With contact angles under 90 degrees, the system is defined as wettable (Bansal, et al., 2011).

Agarwal et al. (2013) studied oil in water emulsion separation performance of three different nano-coated coalescing filter mats and their combinations. Changing parameters in study were superficial velocity and the direction of the flow (radial and horizontal). Six different combinations of coalescing aid elements were fabricated from the three nano-coated mats. Fibre diameter, porosity, thickness and pore size is varying across distance in the filter media. From the research result combination of uncoated material with a small pore size on the feed side of filter and coated hydrophobic filter media with larger pores on outlet side had highest separation performance and wettability had lesser importance on separation. More desired factors were the total surface area of the capture layer and fibre size. Undesired redispersion and the deformation of emulsion occurred when both filter mats were coated and permeability of filter media was reduced. Deformation is a result from higher shear forces from reduced permeability.

Although there are many studies that recommend coalescing aids to have good wettability, some studies have been performed with results neglecting materials' wettability on separation efficiency. In these studies, the material properties like surface roughness and superficial flow velocity had a more significant role. The electrokinetic properties of the fibre materials have also been evaluated with a highly different result on separation. Magiera & Blass (1997) presents that it would be recommended that the surface charge between selected material and dispersed phase should be opposite in nature. This could have positive results when the zeta potential is shifting towards the desired attractive forces in the dominant system. Based on literature reviews and studies, it is difficult to predict the behaviour of coalescing aid material with treated dispersion. This is the reason why it is recommended to do a pilot test before installation in the process system.

## **EXPERIMENTAL PART**

### **6 MATERIALS AND METHODS**

The objective of the experimental part was to locate and quantify solvent/WS losses of hydrogen peroxide production plant. To begin with the determination of loss points, some background information was received from laboratory scale experiments to ensure accurate and reliable results. The effects of temperature, pH and phase fraction on the terminal settling velocity of formed emulsions and emulsion TOC levels of aqueous phase were analysed and monitored. Received results from laboratory experiments were exploited to recognise current loss points and used as baseline for quantifying solvent and WS amounts.

#### **6.1 Used chemicals and sample preparation**

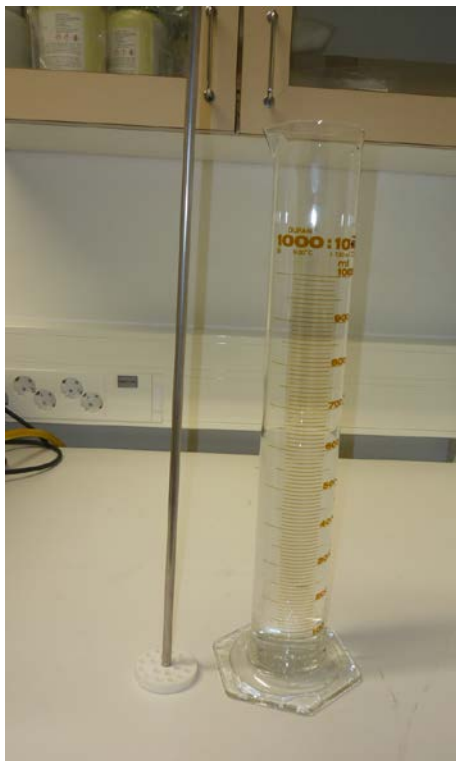
The light phases used in both the batch settling experiments and TOC level analysis were WS and prepared solvent mixture. Solvent mixture used in batch settling experiments was prepared from non-polar and polar solvent both used in hydrogen peroxide manufacturing process. Pure solvents were gathered straight from storage units. The WS samples were gathered directly from process at the start of the working day to prevent sample contamination and reduce the effect of crystallisation of AQ. WS used in settling experiments was gathered from the same location for each batch settling test and the source was decided in a way that samples are the most representative.

Heavy aqueous phase was prepared from Demineralised water (DMW) from onsite reverse osmosis equipment. DMW required pH adjustment before experiments and the pH adjustment was done with diluted 10% nitric acid ( $\text{HNO}_3$ ; CAS: 7697-37-2).

#### **6.2 Batch settling experiments**

The batch settling behaviour experiments were conducted for both WS and solvent mixture as light phase. Densities of light phases were approximately 940 and 850  $\text{kg/m}^3$ , respectively. Batch settling experiments were conducted in a 1 L measuring glass with installed height measurement scale. Before actual settling experiments light and heavy phase was heated on a hotplate to target temperature and transferred into the measuring glass. At the start of experiments light and heavy phase were mixed with specially made

mixer to create emulsion. The mixer was a perforated PTFE plate which fits inside the measuring glass. The used measurement equipment and mixer are shown in Figure 16.



**Figure 16.** Equipment used in the batch settling experiments. Perforated PTFE plate mixer on the left and measuring glass on the right.

The development of the height of the phase interfaces was monitored over time for both light and heavy phase. All of the conducted settling experiments were recorded with video camera and the results were gathered from the video materials. Recording was stopped when both phases were separated completely. Every measurement was replicated two times to avoid and identify any errors during the experiments. The parameters that varied were the temperature of the emulsion, pH of the aqueous phase and the volume fraction of the organic phase. The value range for each variable was chosen to cover each different phase separation process condition in the experimental part of the thesis work. The ranges of the parameters are presented in Table V.

**Table V.** The value range of each parameter used to investigate the phase separation process of solvent/water and WS/water emulsions.

Variable	Value
Temperature [°C]	20–50
pH [-]	2–4
Phase fraction [-]	0.25–0.75

### 6.3 TOC level analysis

In addition to batch settling experiments, the baseline TOC levels of the aqueous phases in different conditions were studied. Both a light phase and a heavy phase were prepared similar to batch settling experiments. A fixed volume of light and heavy phases were transferred to 100 ml glass bottle and then shaken to form emulsion and enhance mass transfer between the two phases. Glass bottles were submerged into thermostatic bath and the bottles were shaken roughly 1 h and after shaking the bottles were let to settle for another hour before TOC analysis. The aqueous phase pH value was between 2 and 4 and the emulsion temperature was varied between 20 and 50°C. WS and water emulsions with pH 2, 3 and 4 after shaking and left to settle for 30 min are shown in Figure 17.



**Figure 17.** Room temperature (20°C) WS and water emulsions shaken for 1 hour and left for settle 1h. Picture is taken when half of the desired settling time has passed. Aqueous phase pH values were 2, 3 and 4, respectively from left to right.



After settling part of the aqueous phase was removed from the bottle and diluted with pH adjusted water. The reason for dilution is to prevent solvent droplets or high carbon concentrations to disturb analyser. Pure water was injected in to the analyser regularly to wash any remaining residues of carbon from the previous samples. Used TOC analyser was Shimadzu TOC-V CSN with regular 5/64" aluminium supported platinum catalyst. Furnace temperature was set to 680°C for standard TOC analysis. Carrier gas supply pressure was set between 300 and 600 kPa and flow rate of the carrier gas was set to 90 mL/min.

The TOC analysis sequence starts with 2 syringe washes with the sample. 16 mL of the sample is injected in to the catalyst filled furnace where carbon is completely combusted and oxidised. Combustion products are fed to detector and results are calculated based on detection peak area. Analyser was calibrated once a week. The number of sample injections were set to 2 and maximum number of injections to 5. Two injections are sufficient, if standard deviation and coefficient of variation is below given values 0.1 and 2, respectively. When either of the values is higher than the set value, injections are continued to a point when the required standard deviation and coefficient of variation is achieved or 5 injections are done.

### **6.3 Sample and data gathering from process**

To locate and quantify solvent/WS loss locations at hydrogen peroxide plant samples were taken from several process stages. Mainly gathered samples were wastewater streams leaving the phase separation unit. Samples were taken either directly from the wastewater side of phase separator unit, inline sample point or complete volume of the wastewater stream was captured, depending on the construction of the piping and vessels.

Amount of free solvent was measured from the gathered samples by separating phases with separation funnel and then the volume of free solvent was measured. TOC analysis was conducted for each wastewater sample and the results are compared to laboratory test runs with similar conditions. Process conditions were monitored with both information gathered from process data handling tool AspenTech Aspen Process Explorer and with thermometer and pH meter.

## **7 RESULTS & DISCUSSION**

In this Chapter, the results from the baseline laboratory experiments and process samples are presented and discussed. To ensure the confidential nature of this master thesis, each different sample location is numbered and named as SP. No specific information about the location of the process stage or process equipment configurations is presented in the public version of this thesis.

### **7.1 Batch settling**

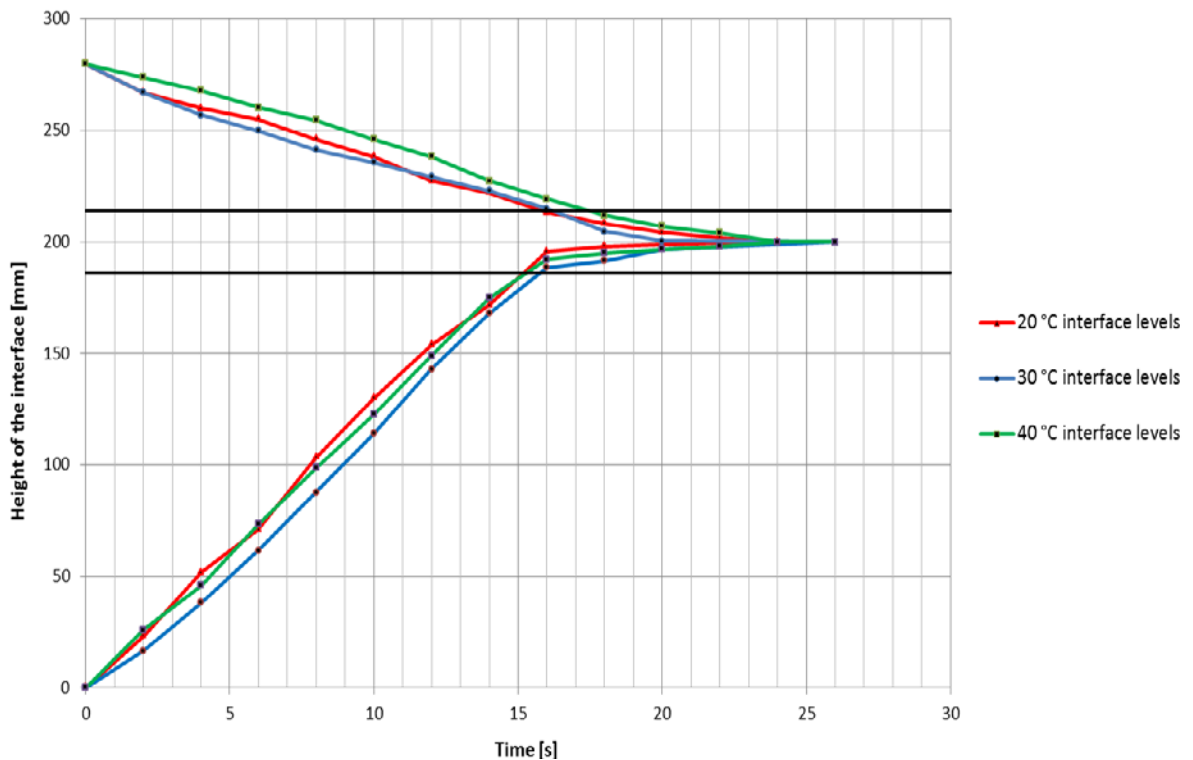
The settling behaviour of solvent/water and WS/water emulsions were studied in different conditions which are typical for phase separation stages in hydrogen peroxide manufacturing. The main goal for the experiment was to understand which parameter has the most impact on the phase separation process performance. Chosen parameters were temperature, pH and phase fraction of the solvent. Both upper and lower interface levels were monitored, but the phase interface between emulsion band and heavy phase is more important for wastewater purposes. The tracking interface level between the light phase and emulsion band was impossible visually with WS/water emulsions.

Settling experiments were done 3 times for each condition and average of the interface height was determined from the results. One of the three replicate results can be ignored if the difference between the results is notable. In the case where the comparability of the results would not be possible more batch settling test were done. Measurement data from the batch settling experiments are presented in more detail in Appendix 2

To compare the settling results with each other the height of the emulsion interface has been assumed to be 10% of the complete liquid height and the time for interface height to reach this point was interpolated from the batch settling data. The minimum settling velocity of the dispersed phase was also determined from a maximum distance for dispersed phase to reach the phase interface and the time required to reach this point. Now the determined settling velocity can be then used to calculate the minimum droplet diameter of the dispersed phase from Eq.4.

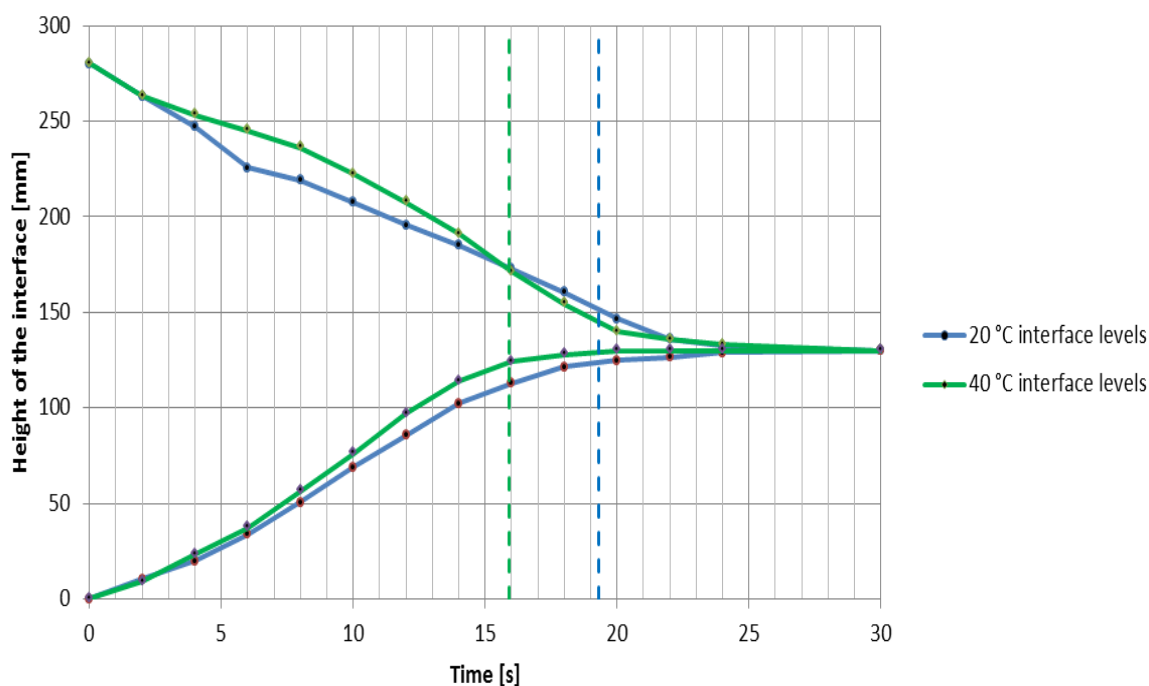
### 7.1.1 Effect of temperature on settling

During the experiments, the pH of the aqueous phase and phase fraction were kept constant. Solvent/water emulsion with aqueous phase pH 3.3 and phase fraction of solvent 0.25 is presented in three different temperatures in Figure 18.



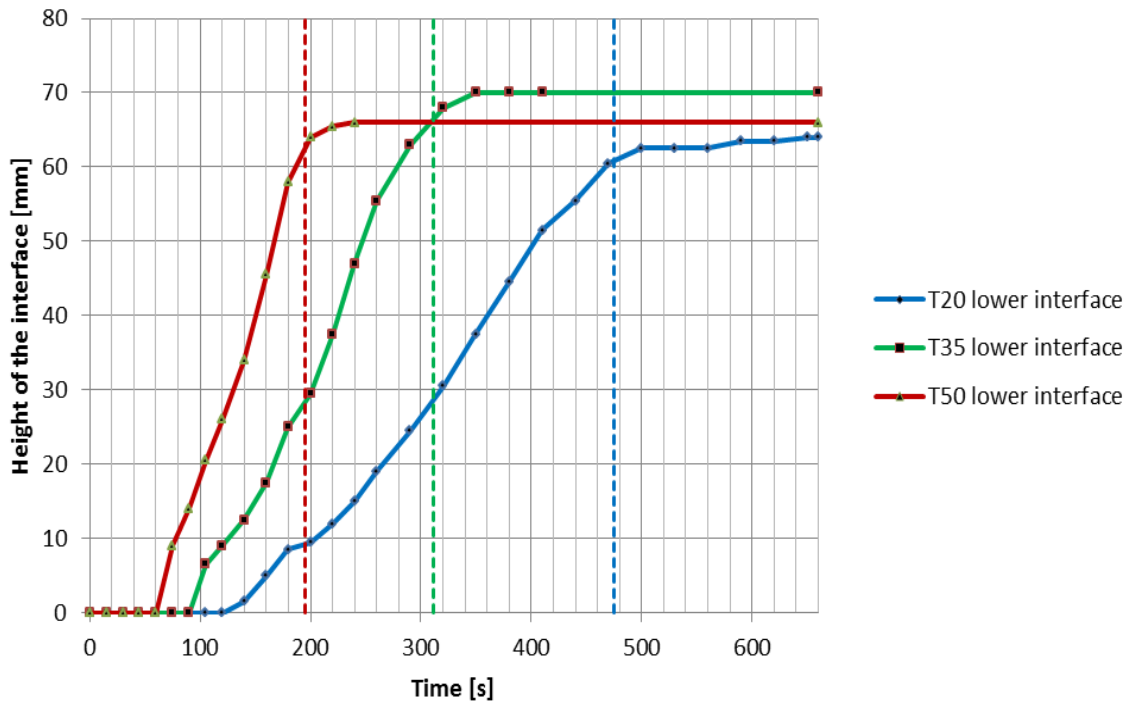
**Figure 18.** Evolution of the phase interface level over time in temperatures 20, 30 and 40°C. Phase fraction of solvent was set to 0.25 and pH of the aqueous phase was 3.3. Calculated minimum droplet sizes were 553, 530 and 550  $\mu\text{m}$  from lower temperature to a higher temperature.

As figure 18 shows, the temperature does not have an effect on the settling when emulsion contains more water than solvent. The two black vertical lines drawn in Figure 18 shows the 10% emulsion band height and later on the results are presented with horizontal lines that will show the time when interface height intercepts the emulsion band. Theoretically increasing temperature should reduce time required for separation as viscosity of the continuous phase decreases. This effect can be seen in Figure 19, where the amount of solvent is same as water (phase fraction 0.5) and pH of aqueous phase is kept at 3.3.



**Figure 19.** Evolution of the phase interface level over time in temperatures 20 and 40°C. Phase fraction of solvent was set to 0.5 and pH of the aqueous phase was 3.3. Calculated minimum droplet diameters were 400 and 441  $\mu\text{m}$ .

When increasing the temperature 20 degrees Celsius the time required for the lower interface to intercept the emulsion band is reduced from 19.2 seconds to 15.9 seconds. Although reduction on the separation time is approximately 17%, overall benefit acquired with heating might be low due to increased heating costs. The same temperature dependency experiments were conducted for WS/water emulsions. WS composition of non-polar and polar solvent were different compared to the used solvent mixture, but most likely it was not the reason for differences between the results from solvent mixture and WS emulsion experiments. It is likely that AQ affects the emulsion formation tendency by reducing the interfacial tension and more stable emulsions are formed. WS/water emulsion with aqueous phase pH 2.0 and phase fraction of WS 0.75 is presented in three different temperatures in Figure 20.

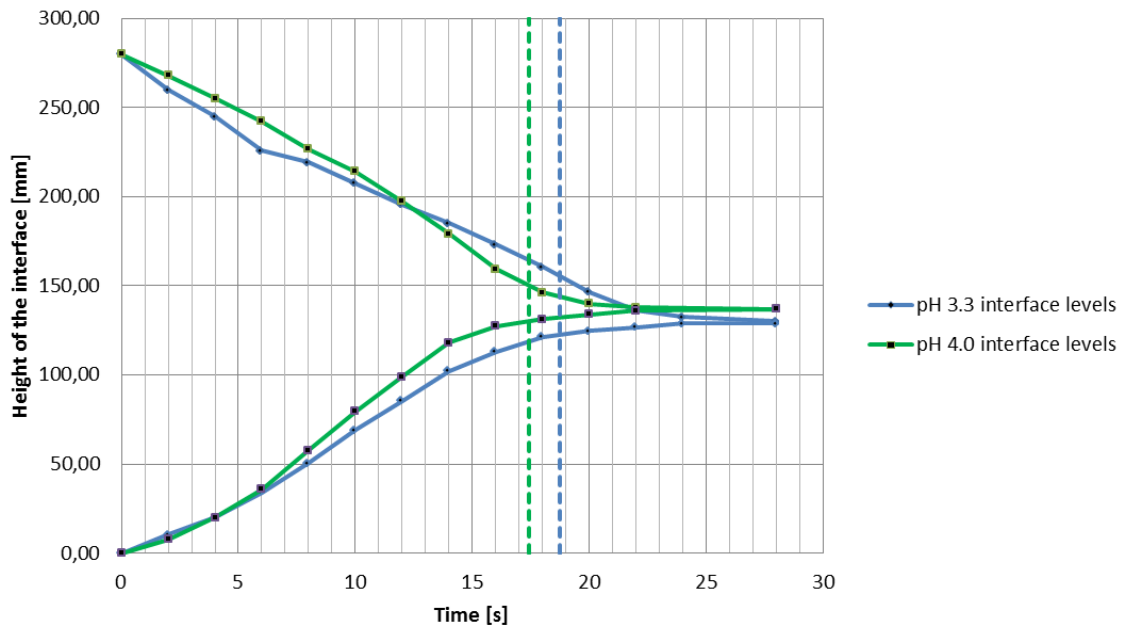


**Figure 20.** Height of the lower interface level as a function of time, where emulsion temperatures were 20, 35 and 50°C. With a phase fraction of WS 0.75 and aqueous phase pH 2.0. Calculated Minimum droplet diameters of dispersed phases were 57, 73 and 90  $\mu\text{m}$  from lower temperature to higher.

As seen in Figure 20, temperature has a more significant effect on the settling of WS/water emulsions. In addition, the time required to reach 10% emulsion band thickness is much higher. Required separation time is reduced by 115 seconds (approx. 37% reduction) when temperature is increased from 35 to 50°C. It also seems that with higher temperatures the rate of coalescing is higher. This can be seen from 20°C curve where the increase of interface height slows right before the phases are completely separated. When considering options to improve the phase separation process, it is beneficial to keep the operating temperature high.

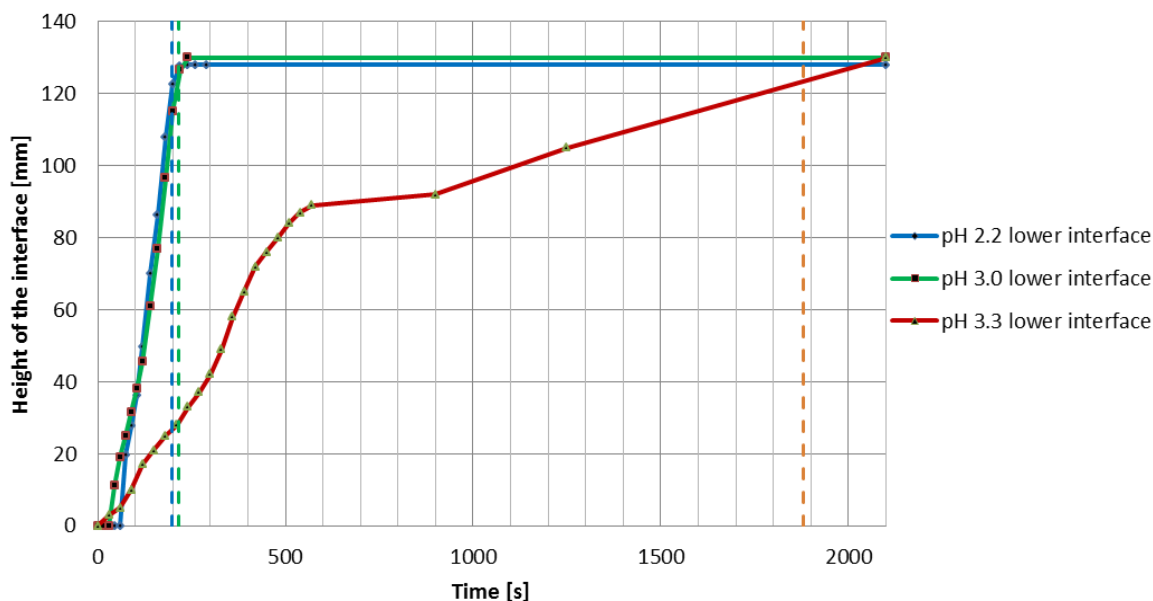
### 7.1.2 Effect of pH on settling

The effect of pH on the settling rates was also studied, while the temperature and phase fraction were kept constant. Adjusting the pH level of the settling process might have an effect on the solubility of surface active substance or reduce electrical charge on the droplet surface as mentioned in Chapter 2.3. Solvent/water emulsion with phase fraction 0.25 at a temperature of 20°C with two different aqueous phases of pH 3.3 and 4.0 as shown in Figure 21.



**Figure 21.** Evolution of the phase interface level over time at a temperature of 20°C. The phase fraction of solvent was 0.25 and pH of the aqueous phase were 3.3 and 4.0. Where calculated minimum droplet diameters were 405 and 433  $\mu\text{m}$ , respectively.

In addition to temperatures the effect on the phase separation performance of solvent/water emulsions pH also had no considerable change on the separation rates. This would indicate that water/solvent emulsions are very unstable and the formation of stable emulsion is not probable. The results from the experiments would suggest that adjusting pH and temperature high would improve separation of pure solvent based emulsions, but the achieved benefits can be slight compared to the increased operational costs. Rather different results were obtained from the settling experiment with WS. This difference is shown in Figure 22. Where WS/water emulsion with a phase fraction of 0.25 at 50°C was studied with the pH levels 2.2, 3.0 and 3.3.

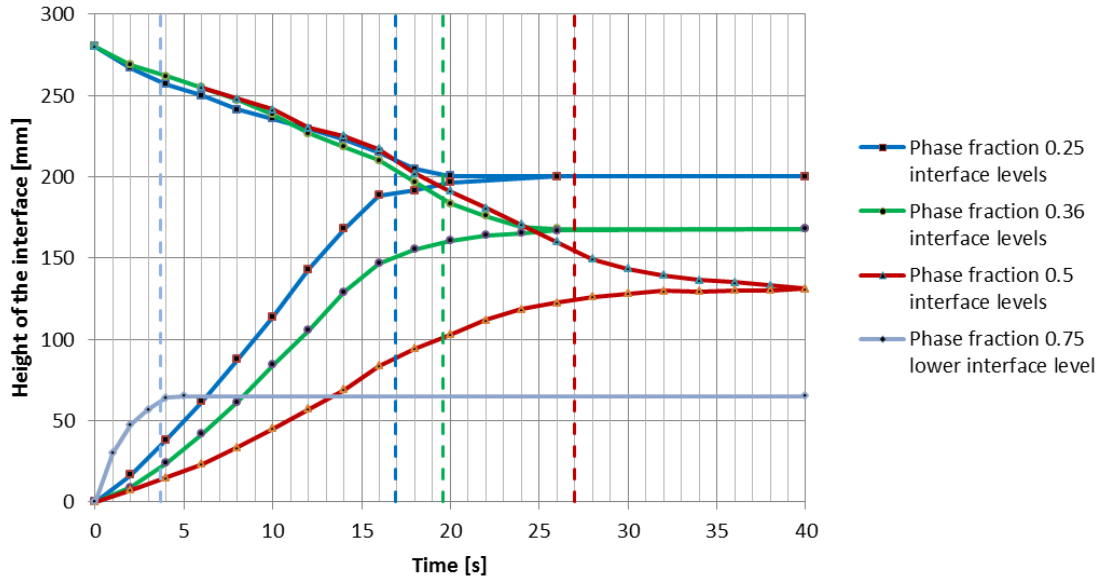


**Figure 22.** Evolution of the phase interface level over time at 50 °C. Phase fraction of WS was set to 0.25 and pH of the aqueous phase used was 2.2, 3.0 and 3.3. The minimum droplet diameters were 124, 120 and 41  $\mu\text{m}$ , respectively.

Based on the gathered result from the settling experiments when working in acidic conditions phase separation is not improved when operating between pH 2.2 to 3.0. More notable change occurs between pH 3.0 to 3.3, where formed emulsion is substantially more stable. Required separation time goes from 3.5 min to 31.5 min and the minimum droplet diameter decreases from 120 to 40  $\mu\text{m}$ , which will cause problems in phase separation. As mentioned previously droplets with less than 100  $\mu\text{m}$  diameter typically form very stable emulsion. Higher pH levels are managed with installed fibre media and internal plating to improve dispersed phase droplet to coalesce.

### 7.1.3 Effect of phase fraction on settling

Dependency of phase fraction on settling behaviour was studied while the system temperature and pH were kept constant. Previous process heuristics would indicate that solvent recycle, meaning a higher phase fraction of solvent, could have an improving effect on separation. Theoretically, this is the result of change on emulsions phase orientation where added solvent would force heavy aqueous phase to disperse. Shift of the phase orientation would then lead to increased terminal settling velocity because the viscosity of solvent mixture is much lower compared to aqueous phase viscosity. Solvent/water emulsion at a temperature of 30°C and with the aqueous phase pH 3.0 where the phase fraction of solvent mixture is varied from 0.25 to 0.75 are shown in Figure 23.

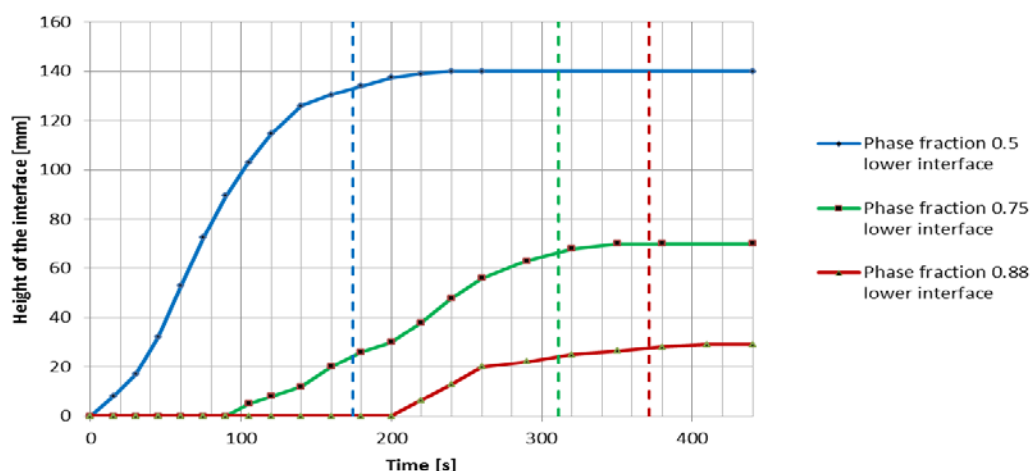


**Figure 23.** Height of the phase interface levels as a function of time. Temperature and pH of the aqueous phase were kept constant at 30°C and 3.0. Where calculated minimum droplet diameters from phase fraction 0.25 to 0.5 are 531, 452 and 340  $\mu\text{m}$ . Phase orientation has changed with 0.75 phase fraction of solvent and calculated minimum droplet diameter for water droplet is 61  $\mu\text{m}$ .

The gathered result would indicate that increasing the amount of solvent is going to increase the time required for phase separation to a point when phase orientation changes. With the phase fraction 0.75 phase separation was so fast that tracking upper interface level was not possible. When phase orientation changes required separation time decreases significantly due to the lower viscosity of the light phase. This would be useful in locations where the recycle of separated solvent back to phase separator feed is possible.

Similar phenomena did not occur in the WS experiments. Based on the phase orientation calculation results from Eq. 10, heavy aqueous phase is most probably dispersed with phase fraction 0.75 and above. The required phase separation time increases when the phase fraction increases which can be seen in Figure 24.



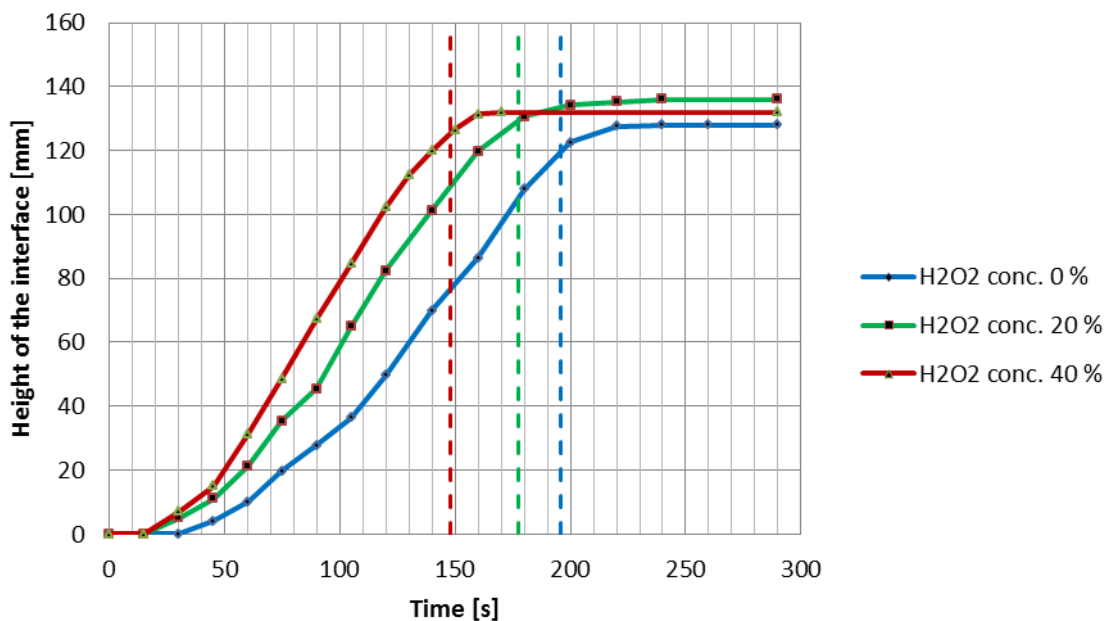


**Figure 24.** Height of the phase interface levels as a function of time. Temperature and pH of the aqueous phase were kept constant at 35°C and 2.2. Where calculated minimum droplet diameters from phase fraction 0.5 to 0.88 are 138, 207 and 206  $\mu\text{m}$ .

Increase on the required separation time is due to increased distance for droplet to reach the coalescing zone which can be seen from droplet diameter staying constant with phase fractions 0.75 and 0.88. When the droplet diameter remains constant there is no change in the settling velocity of the dispersed phase.

#### 7.1.4 Effect of $\text{H}_2\text{O}_2$ concentration on WS/water emulsion settling

The final batch settling experiments were conducted by increasing  $\text{H}_2\text{O}_2$  concentration of the aqueous phase. Heavy aqueous phase was prepared by diluting 60% product with pH 3.3 adjusted DMW. Used aqueous phase concentrations were 20 and 40%  $\text{H}_2\text{O}_2$ . None of the investigated phase separation stages has high  $\text{H}_2\text{O}_2$  concentrations, but some of the phase separation units are secondary phase separation stage. Therefore improved primary phase separation can assist secondary phase separation units by reducing load of later phase separation stages. The density difference of the heavy and light phase increases as the  $\text{H}_2\text{O}_2$  concentration is higher, but also other benefits might be acquired by deviation in the interfacial tension. Settling experiment results of WS/water emulsion with 0, 20 and 40% aqueous phase  $\text{H}_2\text{O}_2$  concentration are shown in Figure 25. The temperature of the system was set to 50°C and final pH of the aqueous phase was 2.2.



**Figure 25.** Height of the phase interface levels as a function of time. The temperature and pH of the aqueous phase were kept constant at 50°C and 2.2. Where calculated minimum droplet diameters starting from lower concentration to higher are 153, 165 and 178  $\mu\text{m}$ .

As assumed previously, the density difference increase improves the separation process. In addition, to the density difference higher H<sub>2</sub>O<sub>2</sub> concentration seems to make emulsions more unstable because the time required for separation is not decreasing in a linear fashion, but the terminal settling velocity increases with higher fashion.

## 7.2 TOC analysis results

In addition to traditional batch settling experiments, TOC analyses were done to enable calculating the possible solvent losses due to incomplete phase separation at the primary phase separation stages. Because solvent mixtures and WS used in process contain polar solvent, part of the carbon species will always be soluble to aqueous phase along with polar organic compounds. Laboratory experiments were conducted to determine baseline concentrations of carbon substances in aqueous phase in contact with both solvent mixtures with or without AQ. This chapter presents both baseline results and also results from process sample points.

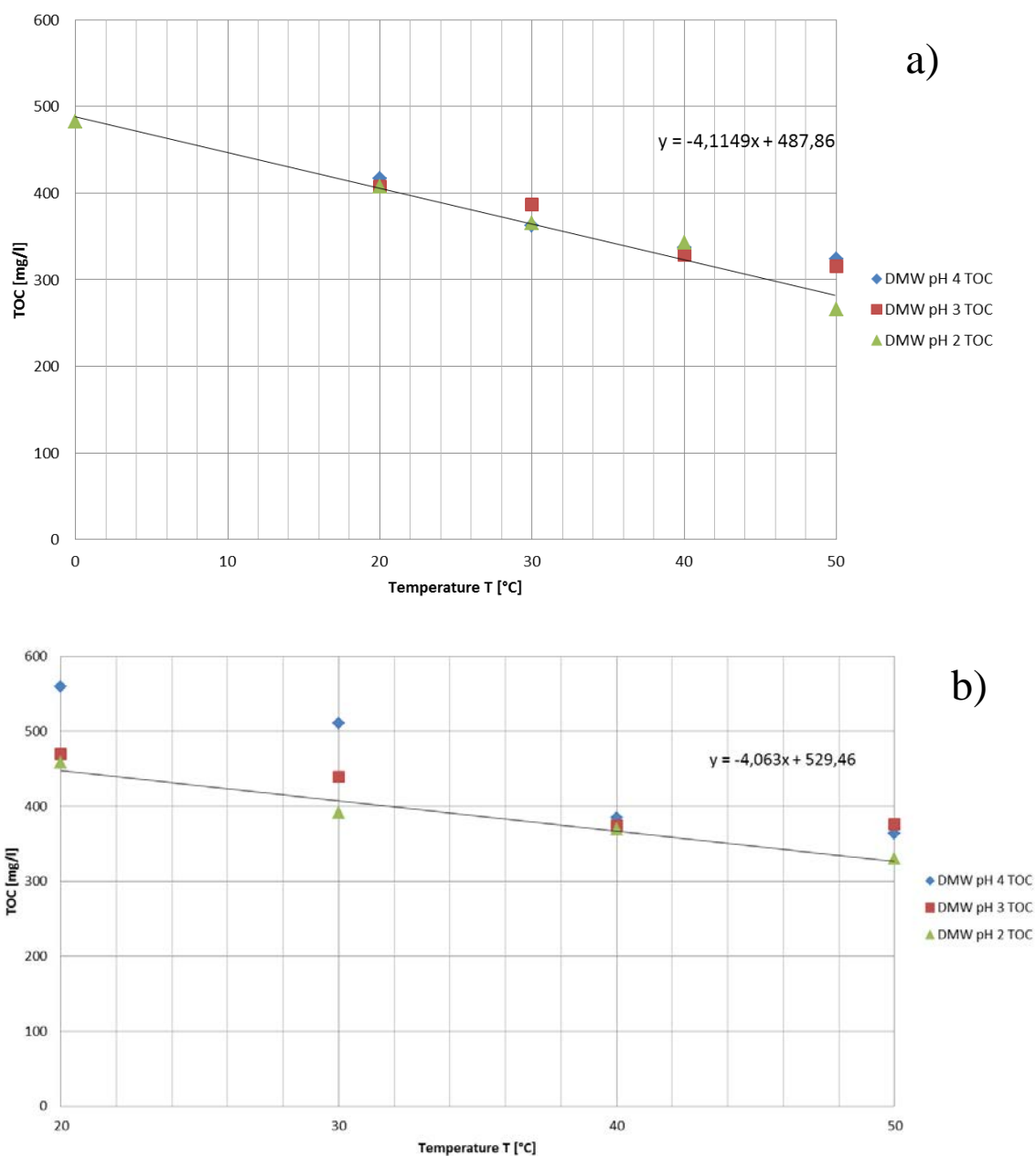
To determine equilibrium TOC level of aqueous phase in contact with solvent or WS laboratory experiment were conducted in different conditions. Aqueous phase pH and the temperature of the emulsion were varied. Used pH levels were 2, 3 and 4 and for the temperature 20, 30, 40 and 50°C. Also for solvent/water emulsion, an additional check of

the TOC level was done at the freezing point of water. To ensure accurate results, the same experiment sets were done twice and the average of the TOC levels were calculated for each condition. The results for the baseline TOC level determination are shown in Table VI.

**Table VI.** The result of aqueous phase TOC levels from both solvent and WS solubility experiments. pH and temperature were set as changing variables, and the phase fraction was kept constant.

pH	Temperature [°C]	TOC level of aqueous phase in contact with solvent [mg/L]	TOC level of aqueous phase in contact with WS [mg/L]
2	20	408	458
	30	365	392
	40	342	370
	50	266	330
3	20	407	470
	30	387	439
	40	329	374
	50	315	376
4	20	416	560
	30	362	510
	40	337	385
	50	324	364

The equilibrium TOC levels were reached in all experiments except the experiments with a pH 4 WS test showed higher carbon concentrations due to reduced settling. The pH did not have an effect on equilibrium, but only the sharp separation of phases is not possible in the given time. This can also be seen in Figure 16 where the cloudiness of the aqueous phase changes with pH. The TOC analysis results are plotted as a function of time in Figures 26 a-b.



**Figure 26ab.** TOC level as a function of emulsion temperature with pH values 2, 3 and 4 for solvent/water (a) and WS/water (b) emulsions. Linear equations were determined for both pH 2 aqueous phase emulsions.

The equilibrium concentration of carbon species in the aqueous phase is a function of temperature and the concentration decreases when temperature increases. The TOC level changes linearly and for further analysis linear equations from the pH 2 experiment data were fitted for both solvent and WS emulsions. The fitted linear equation for solvent and WS emulsions were formed as follows

$$TOC_{solvent(aq)} = -4.12T + 487.87 \quad (25)$$

$$TOC_{WS(aq)} = -4.06T + 529.46 \quad (26)$$

The equations presented hereinabove are used later on for detecting the possible incomplete phase separation by comparing wastewater stream TOC to equilibrium TOC in similar process conditions and also in wastewater system conditions. The TOC analysis results from wastewater streams are shown in Table VII.

**Table VII.** TOC analysis results from wastewater stream leaving phase separation process with comments on sampling procedure.

SP	Average TOC of wastewater stream [mg/L]	Comment
1	473.5	Complete wastewater stream collected in 2 min time periods.
2	438.0	Same sampling location as SP.1, but with different operating conditions.
3	431.2	Collected directly from equipment.
4	303.5	Collected directly from equipment.
5	504.7	Part of the wastewater stream collected.
6	340.4	Part of the wastewater stream collected.
7	306.8	Part of the wastewater stream collected.
8	384.7	Part of the wastewater stream collected.
9	-	No collectable wastewater stream.
10	355.2	Collected directly from equipment.
11	-	No collectable wastewater stream.
12	-	Representative sample not collectable.
13	175.3	Complete wastewater stream collected.

Most of the wastewater streams seem to have TOC levels between 300 and 500 mg/L. SP.13 has TOC level under 200 mg/L and it was not included in later data processing because solvent is not lost from this location. The most interesting locations are sample points with above 400 mg/L concentrations. High TOC level itself does not indicate the significance on losses but when combined with the volume flow rate of free solvent and the total volume flow rate of wastewater stream losses can be estimated. Sample points without TOC analysis do not have collectable or prominent wastewater stream and the

losses are mostly from maintenance operations or malfunction in phase separation equipment occurring due to clogged pipelines. Detailed wastewater stream data is presented in Appendix 3.

### **7.3 Solvent and WS losses**

In this part of the thesis work, an overview of the estimated solvent/WS losses is presented and the results of losses with more detailed information on phase separation parameters and calculations are presented for individual loss point in Appendix 3. The presented results are based on the data gathered from process data handling toolkit Aspen Process Explorer and samples gathered from phase separation processes mainly from February to April 2018. The sampling time is important to note because the annual variation of the cooling water temperature supply might affect temperatures of wastewater streams in some individual locations. During the sampling time, the temperature of the cooling water was its lowest, which might affect monthly solvent/WS loss depending on the current season. An overview of the estimated monthly losses during sampling time is presented on the next page in Table VIII.

During the sampling period, the production facility operated with stable high production rate and no significant complications occurred, but couple minor disturbances which had impact on total solvent/WS loss during the sampling period. Nevertheless, of the monthly disturbances, solvent losses were in scope with past experiences on the loss amount and the saving potential is noticeable. The tracking of solvent/WS losses online is challenging due to long distances between source and wastewater system. A delay between a loss incident and detection from the wastewater system can be delayed several hours due to construction and the way the wastewater system operates.

**Table VIII.** Calculated estimates of solvent/WS loss for each individual process stage. Experiments included 15 sampling locations, but two of the locations were noticed to operate without solvent losses. Nine of the sample points were received after phase separation stage and remaining five were directly from vessel or wastewater stream without phase separation.

Source of solvent/WS loss	Quantity [L/month]	Comment
SP.1&2	250	Based on free solvent volume from wastewater stream samples completely gathered over 2 month.
SP.3	85-165	Estimate based on assumed phase separation performance of 99.95–99.90%. Identical Vessels.
SP.4	250-500	
SP.5	100	Same type of equipment. Calculated from volume flow rate of wastewater and TOC level difference of baseline and sample.
SP.6	residues	
SP.7	residues	Low TOC level
SP.8	50	Calculated from volume flow rate of wastewater stream and TOC level difference of baseline and sample.
SP.9	285	Event occurs approximately 3 times per month and calculated approximate amount lost from each maintenance operation was 95 L.
SP.10	780	Based on the solvent layer increase in the process equipment.
SP.11	580	Works properly when decanters heavy phase removal is not clogged. Tank volume is typically transferred to waste.
SP.12	<100	Operations at this location are conducted manually. Manual operating differences between working shifts is a possibility or losses due to human error.
SP.13	No loss	Low TOC level
SP.14&15	50-75	Two identical vessels. When maintenance is required, vessel emptying leads to losses.

Losses from sample points 1 and 2 are from same location and operation conditions before wastewater stream is changing between the sampling points. Volume fraction of the solvent remained constant during the sampling time, but volume flow rate of the wastewater stream did decrease. Losses from SP.1&2 are dependent on current operating capacity of the process and also lower carbon composition of the feed stream can have reducing influence on the losses.

Combined solvent losses from SP.3 and 4 are one of the most substantial and these locations are discussed combined due to identical construction, similar flow rate of the feed stream and vessels are located at same process location. One slight difference between the loss points are that one is operated continuously and one is operated approximately 7 hours per day. Online time varies during the year mostly based on the cooling water temperature and air humidity. Samples are gathered directly from the equipment because no actual sampling points are installed on the wastewater pipeline. Due to the sampling method, the free solvent amount of the sample varies a lot and, therefore, loss amounts are calculated based on estimated phase separator performance. A combined estimation of the solvent loss 665 L/month is based on optimistic evaluation on good separation performance and the actual loss amounts can, therefore, be higher.

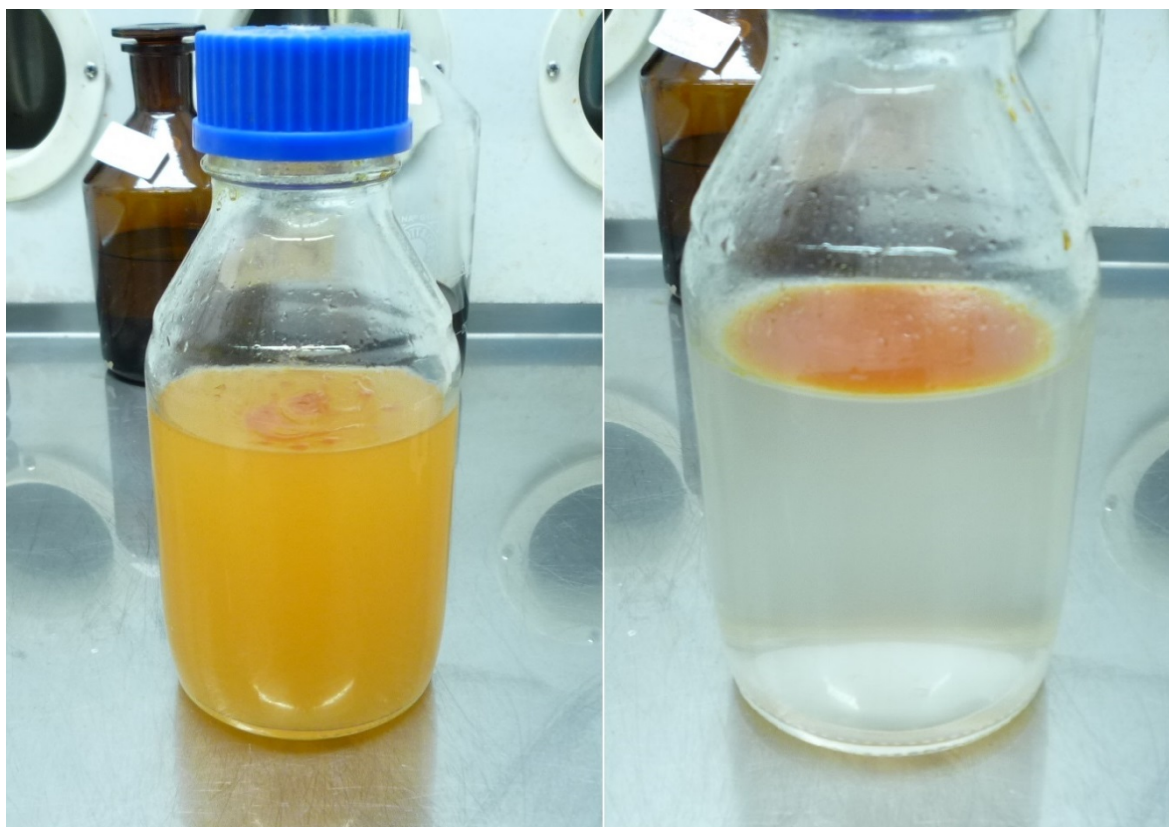
In addition with no sampling points process stage has none instrumentation to measure the volume flow rates of feed or exiting streams from the vessels. The flow rates are calculated from the surface level increase over time when characteristic dimensions of the equipment are known. During the sampling time feed flow rates to SP.3 and 4 remained constant, but after the sampling period the feed flow rate seems to have been increasing over time and also visually the amount of free solvent on the wastewater stream has increased. The feed flow to the SP.4 was observed to have pulsating flow profile which, furthermore, disturbs the clean phase interfaces and also short-circuiting is probably occurring with both SP.3 and 4.

Likewise, SP.3 and 4 the next two sample points have similar design of construction at the same process location. When compared to the previous two phase separation processes SP. 5 and 6 have phase separation enhancing coalescing aids and inclined plates installed. Aqueous phase stream has quite high pH level of 3.5–4.1 and, therefore, stable emulsions are formed which require more effective separation. A minor amount of WS is lost from SP.5 where WS is dispersed in the aqueous phase and is most likely to separate later on in



the wastewater system. The wastewater system operates in lower pH level approximately at 2.0 and the deformation of emulsion is enhanced. SP.6 has low TOC levels and aqueous phase samples were clear meaning that there were no WS lost from this location during normal operations. Most likely the reasons for the hindered separation performance are lower residence times in both the separator vessel and fibre media. Residence times for SP. 5 and 6 are 186 and 315 s, respectively. Although issues with phase separation are observed based on calculations, the degree of turbulence and the time available to cross the emulsion band are sufficient for both phase separation units. In the case with SP. 5 previously mentioned values are lower when compared to SP.6.

SP.7 phase separation unit also utilising phase separation enhancing fibre media and inclined plates. The calculation results show that SP.7 has even more time to separate phases and it is working properly. There is no WS lost from this location during normal operations. Some separation problems were manifesting after sampling period due to increased heavy phase feed to the separation unit. During that time, WS was lost to the wastewater stream. The formed emulsion is shown in Figure 27 before and after settling.



**Figure 27.** Before and after settling of sample taken from SP.7 wastewater stream. Separation performance was influenced by increased heavy phase fraction and feed flow rate.

Sample taken straight from SP.7 wastewater stream is remarkably cloudy and coloured in addition with free WS on surface. The sample color or cloudiness increases progressively when TOC level increases and it can be used as visual indicator to evaluate separation process. SP.8 has slightly elevated TOC levels which could result in 50 L/month WS loss.

Based on the results, the highest individual solvent loss comes from SP.10. Approximately 780 L of solvent flows to the vessel monthly and it is going to the organic solvent disposal. SP.10 is not a separation unit, but the storage tank between loss source and wastewater system. Residence time in vessel is sufficient for phases to separate clearly and no visible emulsion band is formed. SP.1, 2 and 10 are connected with each other and, therefore, both are affected by feed composition and operating capacity.

The rest of the sample points are related to maintenance operations performed in different process stages to ensure steady and reliable production of hydrogen peroxide. Except SP.13 is appropriately operating phase separator. The occurring frequency of these maintenance operations can vary depending on the current state of the process and,

therefore, these solvent loss amounts are estimated from maintenance operations in 2017. Previously, the solvent and WS quality collected from the wastewater system were treated as recyclable solvents and, therefore, the current piping and equipment are built based on this assumption. Most of the maintenance operations waste streams are fed to wastewater system and separating solvents are collected from wastewater.

#### **7.4 Recommended improvements**

According to the results received from calculations all of the phase separation processes are operating in acceptable design conditions, but some slight improvements on the construction design are recommended to improve phase separation. If recommended improvements do not lead to the desired result, increasing the current phase separation capacity or adding additional phase separation stage is necessary. Some wastewater stream can be redirected to a new location to prevent the contamination of solvent/WS in the wastewater system.

In case of SP.3 and 4, the feed flow to the vessels should be modified to reduce the disturbances on the phase interfaces. The direction of the inline pipeline could be changed away from the heavy phase collection, internal walls to prevent short-circuiting of emulsion or splitting the feed flow for entire width of the separator. The current inlet location is most likely the reason for incomplete phase separation. This can be seen from the vessel where free solvent enters the aqueous phase separation section directly from the inlet side of the vessel.

Improving the current operating performance of SP.5 phase separator is not possible. Removal of wastewater is automated, but replacing current level switch system with continuous phase interface level measurement could reduce disturbances to phase interface. The retention time of the vessel is the shortest from the investigated units and due to this reason phase separation might be incomplete. Fixing this issue would require structural modifications to increase the vessel volume. Another option would be to increase the volume of internal fibre media to, furthermore, enhance the coalescing of the dispersed phase.

Maintenance operations for SP.9 and 11 are connected by partly using same equipment to do the required maintenance. The storage capacity of the system is limited and during the maintenance work from SP.9, WS can overflow to the wastewater system. It is

recommended to separate the current maintenance operations from each other because experience shows that the quality of WS from SP.9 is not in an acceptable boundary. WS coming to the system from maintenance work SP.9 most likely contaminates the solvent used in SP.11 and an increasing monthly loss amount by 580L.

Wastewater stream from SP.1 and 2 can be redirected to vessel SP.10 and current vessel construction enables the possibility to install temporary connection or more permanent pipeline connection to remove solvent from the vessel. The combined monthly loss reduction would be approximately 1 m<sup>3</sup> which would be highly profitable modification with small investment cost and short payback time due to high amount of solvent recovered.

For the remaining investigated solvent or WS loss points some structural modifications are suggested to redirect the streams to more suitable locations to prevent solvent losses to the wastewater system before maintenance operations are conducted. Manually operated phase separations should be investigated to ensure knowledge of the personnel and update guides related to these operations.

The operating conditions of the process were changed to improve the separation performance of SP.4, 7 and 8. During the sampling time period the operating temperature of the SP.4 was approximately 10°C. Cooling water feed amount to the previous process stage was altered and the performance of phase separation process was monitored during the time period. Increasing the operating temperature of phase separation process should have an improving effect on separation, but in this case no benefits have been observed. Due to the increased temperature later, the process stages consumed more energy to reach the instructed process values and, therefore, it is recommended to operate SP.4 with the lowest achievable temperature with current construction.

The pH of both SP.7 and 8 were increased to determine how investigated phase separation processes manage higher pH levels. Higher pH levels would be more beneficial for the overall profitability of hydrogen peroxide production and therefore these test runs were conducted. With the increase of the process pH levels, the amount of wastewater from phase separation processes slightly increased and also minor elevation of TOC levels were observed. There was no free WS formation on the sample surface during the test runs. According to the test run results of the pH level, an increase would indicate that an

increase from 1.9 to 2.4 did result in double the monthly losses of WS. Although the aim of the thesis was to locate and prevent losses in this process, the location usage of higher pH conditions might be more beneficial for the whole process. The loss amount from the SP.7 and 8 was not as noticeable compared to the other process stages.

## **8 CONCLUSIONS**

The main goal of this thesis work was to quantify and locate Solvay Chemicals Finland Oy hydrogen peroxide plants organic solvent losses. Improvement suggestions and operational conditions were changed to try to optimise the process. To support decision making and have more accurate estimates for solvent losses, laboratory experiments were conducted. Batch settling experiments were conducted to investigate the settling tendency of emulsions in different operating conditions. In the batch settling experiments, the emulsion temperature, pH of the aqueous phase and phase fraction were variables. In addition to the batch settling experiment baseline, TOC analysis was conducted to investigate the phase separation performance of each phase separation process by comparing the baseline TOC levels with wastewater stream TOC leaving the phase separator unit.

Batch settling experiments show that phase separation operations are quite dependent on the operational conditions and changing operation conditions can lead to reduced losses. Increasing the temperature of the emulsion system enhances emulsion deformation and settling is faster. With the aqueous phase pH, no significant benefits were observed on settling velocity, but WS/water emulsions to deform the pH level is recommended to be under 3.0–3.3. Due to the complexity of the hydrogen peroxide manufacturing process and current process equipment configuration altering phase separator conditions is affecting the actual process conditions and in most cases benefits achieved in phase separation can lead to problems or reduced productivity of hydrogen peroxide, thereby resulting in increased production costs per hydrogen peroxide tonne.

During the sampling period, approximately 10 m<sup>3</sup> of organic materials were classified as waste. The results of the thesis work indicate that approximately half of the losses during the sampling time are from the investigated process locations. The solvent losses from both SP.4 and 5 were not possible to accurately quantify. Actual solvent losses from these locations are most likely higher and the located amount is higher than half of current losses

during normal operation. Seasonal alterations have an effect on some investigated phase separators by increasing feed flow to the separator and disturbing the separation.

By implementing the suggested improvements, the solvent/WS loss amount can be considerably reduced. The required improvements are minor modifications on the current piping and vessel construction with a low investment cost and can lead to significant savings on operational costs and thereby make it rather compelling. Another possibility would be to invest in a completely new phase separator with a higher investment cost and longer payback time.

To obtain comprehensive data, the sampling time should be much longer and also the effect of the changing production capacity on the losses would be beneficial to investigate. In addition, different types of unplanned events on the process did not occur during the sampling period which might have an effect on the loss amounts. When the most remarkable solvent loss sources are fixed, a possible further investigation of the remaining phase separation processes is recommended. One possible option would be to use CFD simulations to investigate the phase separator for more detailed information.

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**Heywood's table (1/2) for determining the terminal settling velocity from Equations 6 and 7 for settling particle.**

$\log P_{Hx}$	0.00	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09
-0.2	-1.780									
-0.1	-1.580	-1.600	-1.620	-1.640	-1.660	-1.680	-1.700	-1.720	-1.740	-1.760
-0.0	-1.382	-1.402	-1.422	-1.442	-1.461	-1.481	-1.501	-1.521	-1.541	-1.560
0.0	-1.382	-1.362	-1.343	-1.323	-1.303	-1.283	-1.264	-1.244	-1.225	-1.205
0.1	-1.185	-1.166	-1.146	-1.126	-1.106	-1.087	-1.068	-1.048	-1.029	-1.010
0.2	-0.990	-0.971	-0.952	-0.932	-0.912	-0.893	-0.874	-0.855	-0.836	-0.817
0.3	-0.799	-0.780	-0.762	-0.743	-0.725	-0.707	-0.688	-0.670	-0.652	-0.634
0.4	-0.616	-0.598	-0.580	-0.562	-0.544	-0.527	-0.510	-0.492	-0.475	-0.457
0.5	-0.440	-0.423	-0.406	-0.389	-0.373	-0.357	-0.341	-0.325	-0.308	-0.292
0.6	-0.276	-0.260	-0.245	-0.229	-0.213	-0.198	-0.183	-0.168	-0.153	-0.138
0.7	-0.123	-0.109	-0.095	-0.080	-0.066	-0.052	-0.038	-0.024	-0.011	0.003
0.8	0.017	0.030	0.043	0.057	0.070	0.083	0.096	0.109	0.122	0.135
0.9	0.148	0.161	0.173	0.186	0.199	0.211	0.224	0.236	0.248	0.261
1.0	0.273	0.285	0.297	0.309	0.321	0.333	0.345	0.356	0.368	0.380
1.1	0.391	0.402	0.414	0.425	0.436	0.447	0.458	0.469	0.480	0.491
1.2	0.502	0.513	0.523	0.534	0.545	0.555	0.565	0.576	0.586	0.596
1.3	0.607	0.617	0.627	0.637	0.647	0.657	0.667	0.677	0.686	0.696
1.4	0.706	0.715	0.725	0.734	0.744	0.753	0.762	0.772	0.781	0.790
1.5	0.800	0.809	0.818	0.827	0.836	0.844	0.853	0.862	0.870	0.879
1.6	0.887	0.895	0.904	0.912	0.920	0.928	0.936	0.944	0.951	0.959
1.7	0.967	0.974	0.981	0.989	0.996	1.004	1.011	1.018	1.026	1.031
1.8	1.040	1.048	1.055	1.062	1.069	1.076	1.083	1.090	1.097	1.104
1.9	1.111	1.118	1.125	1.132	1.139	1.146	1.153	1.160	1.167	1.174
2.0	1.180	1.187	1.194	1.200	1.207	1.214	1.220	1.227	1.233	1.240
2.1	1.246	1.253	1.259	1.265	1.272	1.278	1.284	1.290	1.296	1.302
2.2	1.307	1.313	1.319	1.324	1.329	1.335	1.340	1.345	1.350	1.355
2.3	1.360	1.364	1.369	1.374	1.378	1.383	1.388	1.392	1.397	1.401
2.4	1.406	1.411	1.415	1.420	1.424	1.428	1.433	1.437	1.441	1.445
2.5	1.450	1.454	1.458	1.462	1.466	1.470	1.474	1.478	1.482	1.486
2.6	1.490	1.494	1.498	1.502	1.506	1.510	1.514	1.518	1.521	1.525
2.7	1.529	1.533	1.537	1.541	1.545	1.549	1.553	1.557	1.561	1.565
2.8	1.569	1.573	1.578	1.582	1.586	1.590	1.594	1.598	1.603	1.607
2.9	1.611	1.616	1.620	1.624	1.629	1.633	1.637	1.642	1.646	1.651
3.0	1.655	1.660	1.665	1.669	1.674	1.679	1.684	1.689	1.694	1.698
3.1	1.703	1.708	1.713	1.718	1.724	1.729	1.734	1.740	1.746	1.751
3.2	1.757	1.763	1.770	1.776	1.782	1.788	1.795	1.801	1.808	1.814
3.3	1.821	1.828	1.834	1.841	1.848	1.854	1.861	1.868	1.875	1.881

Heywood's table (2/2) for determining terminal settling velocity from Equations 6 and 7 for settling particle.

$\log U_t/Q_H$	0.00	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09
-1.7	-0.160									
-1.6	-0.110	-0.115	-0.120	-0.125	-0.130	-0.135	-0.140	-0.145	-0.150	-0.155
-1.5	-0.060	-0.065	-0.070	-0.075	-0.080	-0.085	-0.900	-0.095	-0.100	-0.105
-1.4	-0.009	-0.014	-0.019	-0.024	-0.029	-0.034	-0.040	-0.045	-0.050	-0.055
-1.3	0.041	0.036	0.031	0.026	0.021	0.016	0.011	0.006	0.001	-0.004
-1.2	0.093	0.087	0.082	0.077	0.072	0.067	0.062	0.057	0.052	0.046
-1.1	0.143	0.138	0.133	0.128	0.123	0.118	0.113	0.108	0.103	0.098
-1.0	0.195	0.190	0.185	0.179	0.174	0.169	0.164	0.159	0.154	0.148
-0.9	0.246	0.241	0.236	0.231	0.226	0.221	0.216	0.211	0.206	0.200
-0.8	0.299	0.293	0.288	0.283	0.278	0.272	0.267	0.262	0.257	0.252
-0.7	0.354	0.348	0.343	0.337	0.332	0.326	0.321	0.316	0.310	0.305
-0.6	0.409	0.404	0.398	0.392	0.387	0.382	0.376	0.370	0.364	0.359
-0.5	0.465	0.460	0.454	0.448	0.442	0.437	0.432	0.426	0.420	0.414
-0.4	0.524	0.518	0.512	0.506	0.500	0.494	0.488	0.483	0.477	0.471
-0.3	0.585	0.579	0.573	0.567	0.561	0.555	0.548	0.542	0.536	0.530
-0.2	0.649	0.642	0.636	0.629	0.623	0.616	0.610	0.604	0.597	0.591
-0.1	0.716	0.709	0.702	0.695	0.688	0.682	0.675	0.668	0.662	0.656
-0.0	0.781	0.773	0.766	0.759	0.752	0.745	0.738	0.730	0.723	
0.0	0.788	0.795	0.802	0.810	0.818	0.825	0.832	0.840	0.848	0.856
0.1	0.863	0.871	0.879	0.886	0.894	0.902	0.910	0.917	0.925	0.933
0.2	0.941	0.949	0.957	0.965	0.973	0.981	0.989	0.997	1.006	1.014
0.3	1.022	1.031	1.039	1.048	1.056	1.064	1.073	1.082	1.090	1.099
0.4	1.108	1.117	1.126	1.135	1.144	1.153	1.162	1.171	1.180	1.189
0.5	1.198	1.208	1.217	1.227	1.236	1.245	1.255	1.265	1.274	1.284
0.6	1.294	1.303	1.313	1.323	1.333	1.343	1.353	1.363	1.373	1.384
0.7	1.394	1.404	1.415	1.425	1.436	1.446	1.457	1.468	1.479	1.490
0.8	1.500	1.511	1.522	1.533	1.545	1.557	1.568	1.580	1.592	1.604
0.9	1.616	1.628	1.640	1.652	1.665	1.678	1.691	1.704	1.718	1.731
1.0	1.745	1.759	1.773	1.786	1.800	1.813	1.827	1.841	1.855	1.870
1.1	1.884	1.899	1.913	1.927	1.941	1.956	1.970	1.985	2.000	2.015
1.2	2.030	2.045	2.060	2.075	2.090	2.106	2.122	2.138	2.154	2.170
1.3	2.187	2.204	2.222	2.241	2.260	2.280	2.300	2.321	2.343	2.365
1.4	2.387	2.409	2.431	2.454	2.477	2.500	2.524	2.549	2.574	2.600
1.5	2.626	2.651	2.677	2.703	2.728	2.753	2.778	2.803	2.827	2.851
1.6	2.874	2.897	2.920	2.943	2.966	2.988	3.010	3.032	3.053	3.073
1.7	3.093	3.113	3.133	3.152	3.170	3.188	3.204	3.220	3.236	3.252
1.8	3.268	3.283	3.298	3.313	3.328	3.343	3.358	3.373	3.388	3.402

**Measurement data from solvent/water batch settling experiments.**

pH 3.3	Solvent/water (Solvent 25 vol-%) emulsion settling data.					
Temperature $T$ [°C]	20		30		40	
Time $t$ [s]	Upper interface height $h_u$ [mm]	Lower interface height $h_l$ [mm]	Upper interface height $h_u$ [mm]	Lower interface height $h_l$ [mm]	Upper interface height $h_u$ [mm]	Lower interface height $h_l$ [mm]
0	280	0	280	0	280	0
2	-	23	-	17	-	26
4	-	52	-	38	268	46
6	260	71	250	62	260	73
8	246	103	241	88	255	99
10	238	130	236	114	246	123
12	228	154	229	143	238	149
14	222	172	223	168	227	175
16	213	196	215	189	219	192
18	208	198	205	192	212	195
20	204	199	200	197	207	197
22	202	200	-	-	204	198

Temperature $T$ 20 °C	Solvent/water (Solvent 25 vol-%) emulsion settling data.					
pH [-]	2.6		3.3		4.0	
Time $t$ [s]	Upper interface height $h_u$ [mm]	Lower interface height $h_l$ [mm]	Upper interface height $h_u$ [mm]	Lower interface height $h_l$ [mm]	Upper interface height $h_u$ [mm]	Lower interface height $h_l$ [mm]
0	278	0	280	0	280	0
2	-	8	-	23	-	12
4	-	20	-	52	--	36
6	259	28	260	71	255	67
8	255	41	246	103	250	94
10	241	54	238	130	241	127
12	237	62	228	154	232	163
14	234	69	222	172	223	193
16	231	77	213	196	210	197
18	229	84	208	198	200	200
20	225	90	204	199	-	-
22	224	103	202	200	-	-
24	221	123	200	200	-	-
48	196	196	-	-	-	-

pH 3.3		Solvent/water (Solvent 50 vol-%) emulsion settling data.				
Temperature $T$ [°C]	20		30		40	
	Upper interface height $h_u$ [mm]	Lower interface height $h_l$ [mm]	Upper interface height $h_u$ [mm]	Lower interface height $h_l$ [mm]	Upper interface height $h_u$ [mm]	Lower interface height $h_l$ [mm]
0	280	0	280	0	280	0
2	-	10	280	7	258	9
4	-	20	280	15	253	23
6	226	34	255	23	245	37
8	219	51	248	34	236	56
10	208	69	241	45	222	76
12	196	86	235	57	208	97
14	185	102	226	69	191	114
16	173	113	217	84	171	124
18	161	121	202	94	154	128
20	147	125	191	103	140	130
22	136	127	181	112	136	130
24	132	129	171	119	133	130
26	-	-	160	123	-	-
28	-	-	149	126	-	-
30	-	-	143	128	-	-
32	-	-	139	130	-	-
34	-	-	136,5	129,5	-	-
36	-	-	135	130	-	-

Temperature $T$ 20 °C	Solvent/water (Solvent 50 vol-%) emulsion settling data.					
pH [-]	2.6		3.3		4.0	
Time $t$ [s]	Upper interface height $h_u$ [mm]	Lower interface height $h_l$ [mm]	Upper interface height $h_u$ [mm]	Lower interface height $h_l$ [mm]	Upper interface height $h_u$ [mm]	Lower interface height $h_l$ [mm]
0	280	0	280	0	280	0
2	-	10	-	10	-	8
4	-	16	-	20	-	20
6	245	22	226	34	242	36
8	232	29	219	51	227	58
10	230	37	208	69	214	80
12	223	44	196	86	197	99
14	221	53	185	102	179	118
16	215	60	173	113	159	127
18	211	70	161	121	146	131
20	207	77	147	125	140	134
22	202	85	136	127	138	136
48	138	132	133	133	137	137

pH 3.3	Solvent/water (Solvent 75 vol-%) emulsion settling data.		
Temperature $T$ [°C]	20	30	40
Time $t$ [s]	Lower interface height $h_l$ [mm]	Lower interface height $h_l$ [mm]	Lower interface height $h_l$ [mm]
0	-	0	-
1	-	30	-
2	-	48	-
3	-	57	-
4	65	64	65
5	-	65	-

**Measurement data from WS/water batch settling experiments.**

pH 2.1	WS/water (WS 50 %-vol) emulsion settling data		
Temperature $T$ [°C]	20	35	50
Time $t$ [s]	Lower interface height $h_l$ [mm]	Lower interface height $h_l$ [mm]	Lower interface height $h_l$ [mm]
0	0	0	0
15	5	8	0
30	13	17	0
45	30	32	0
60	54	53	0
75	83	73	20
90	102	90	28
105	116	103	36
120	126	115	50
140	131	126	70
160	133	131	86
180	133	134	108
200	-	138	123
220	-	139	128
240	-	140	128
260	-	140	128

Temperature $T$ 20 °C	WS/water (WS 50 %-vol) emulsion settling data		
pH [-]	2.1	2.7	3.0
Time $t$ [s]	Lower interface height $h_l$ [mm]	Lower interface height $h_l$ [mm]	Lower interface height $h_l$ [mm]
0	0	0	0
15	5	0	0
30	13	5	10
45	30	14	17
60	54	24	23
75	83	36	33
90	102	48	43
105	116	60	48
120	126	70	53
140	131	79	53
160	133	87	53
180	133	93	78
200	-	100	78
220	-	106	78
240	-	110	94
260	-	114	94
290	-	118	94
320	-	121	119
350	-	124	125
380	-	126	129
410	-	127	130
440	-	127	-



Temperature $T$ 50 °C	WS/water (WS 50 %-vol) emulsion settling data			
pH [-]	2.2	3.0	3.3	
Time $t$ [s]	Lower interface height $h_l$ [mm]	Lower interface height $h_l$ [mm]	Time [s]	Lower interface height $h_l$ [mm]
0	0	0	0	0
15	0	0	30	0
30	0	0	60	5
45	0	11	90	10
60	0	19	120	17
75	20	25	150	21
90	28	32	180	25
105	36	38	210	28
120	50	46	240	33
140	70	61	270	37
160	86	77	300	42
180	108	97	330	49
200	123	115	360	58
220	128	127	390	65
240	128	130	1250	105
260	128	130	2100	130

pH 2.1	WS/water (WS 75 %-vol) emulsion settling data		
Temperature $T$ [°C]	20	35	50
Time $t$ [s]	Lower interface height $h_l$ [mm]	Lower interface height $h_l$ [mm]	Lower interface height $h_l$ [mm]
0	0		0
15	0	0	0
30	0	0	0
45	0	0	0
60	0	0	0
75	0	0	9
90	0	0	14
105	0	0	21
120	0	7	26
140	2	9	34
160	5	13	46
180	9	18	58
200	10	25	64
220	12	30	66
240	15	38	66
260	19	47	-
290	25	56	-
320	31	63	-
350	38	68	-
380	45	70	-
410	52	70	-
440	56	-	-
470	61	-	-
500	63	-	-
530	63	-	-
560	63	-	-
590	64	-	-
620	64	-	-
650	64	-	-

Temperature $T$ 20 °C	WS/water (WS 75 %-vol) emulsion settling data	
pH [-]	2.2	2.7
Time $t$ [s]	Lower interface height $h_l$ [mm]	Lower interface height $h_l$ [mm]
0	0	0
15	0	0
30	0	0
45	0	0
60	0	0
75	0	0
90	0	0
105	0	0
120	0	0
140	2	0
160	5	0
180	9	0
200	10	0
220	12	0
240	15	1
260	19	4
290	25	6
320	31	9
350	38	13
380	45	15
410	52	19
440	56	24
470	61	28
500	63	33
530	63	39
560	63	44
590	64	48
620	64	50
650	64	54
660	-	55
700	-	60

Constants	
Temperature of wastewater system $T$ [°C]	30
pH of wastewater system [-]	2.2
Solvent density $\rho_l$ [kg/m <sup>3</sup> ]	850 or 940 (based on composition)

SP.1	Sampling data from sample point 1. Sampling time is 2 min and the complete process stream is collected.				
Sampling date	Volume of a sample $V_{sample}$ [ml]	Volume flow rate of wastewater stream $\dot{V}_{ww}$ [L/h]	Volume of free solvent $V_{free}$ [ml]	Volume flow rate of free solvent $\dot{V}_{free}$ [L/h]	Volume fraction of solvent [-]
31.1.2018	430	12.9	15	0.450	0.035
1.2.2018	460	13.8	20	0.600	0.043
5.2.2018	445	13.4	20	0.600	0.045
5.2.2018	430	12.9	15	0.450	0.035
1.3.2018	350	10.5	12	0.144	0.034
1.3.2018	380	11.4	17	0.204	0.045
5.3.2018	240	7.2	7.5	0.225	0.031
12.3.2018	240	7.2	8.5	0.255	0.035
13.3.2018	260	7.8	8	0.240	0.031
Average	359	10.8	13.7	0.352	0.037

SP.2	Sampling data from sample point 2. Sampling time is 2 min and the complete process stream is collected.				
Sampling date	Volume of a sample $V_{sample}$ [ml]	Volume flow rate of wastewater stream $\dot{V}_{ww}$ [L/h]	Volume of free solvent $V_{free}$ [ml]	Volume flow rate of free solvent $\dot{V}_{free}$ [L/h]	Volume fraction of solvent [-]
1.2.2018	470	14.1	15	0.450	0.032
6.2.2018	450	13.5	15	0.450	0.033
6.2.2018	440	13.2	15	0.450	0.034
6.2.2018	460	13.8	13	0.390	0.028
2.3.2018	520	15.6	16	0.192	0.031
7.3.2018	240	7.2	6.5	0.195	0.027
9.3.2018	230	6.9	6.5	0.195	0.028
19.3.2018	250	7.5	6.5	0.195	0.026
Average	383	11.5	11.7	0.315	0.030

SP.3	Sampling data from sample point 3.				
Sampling date	TOC level of aqueous phase [mg/L]	Volume flow rate of the feed $\dot{V}_f$ [m <sup>3</sup> /h] <sup>(1)</sup>	Volume flow rate of wastewater stream $\dot{V}_{ww}$ [m <sup>3</sup> /h] <sup>(1)</sup>	Volume of a sample $V_{sample}$ [ml] <sup>(2)</sup>	Volume of free solvent $V_{free}$ [ml] <sup>(2)</sup>
14.3.2018	437	0.78	0.67	-	-
17.3.2018	427	0.78	0.67	260	6
19.3.2018	426	0.78	0.67	-	-
21.3.2018	419	0.78	0.67	-	-
21.3.2018 (aged sample)	338	0.78	0.67	-	-
23.3.2018	473	0.78	0.67	-	-
26.3.2018	483	0.78	0.67	380	2
6.4.2018	447	0.78	0.67	320	10
Average	445	0.78	0.67		

(1) Volume flow rate is calculated based on characteristic equipment dimensions and surface level increase over time. When equipment is online.

(2) Samples are collected directly from process equipment because there are no proper sampling points to evaluate the process stream. Due to the used sampling method, the data gathered from process is unreliable for quantifying the amount of free solvent.

Variables	
Temperature of wastewater stream $T$ [°C]	10
pH of wastewater stream [-]	4.1
Estimated volume fraction of solvent in wastewater stream	0.0005-0.001
Calculations	
Phase orientation $\theta$ [-]	0.13
Feed flow rate to phase-interface area $\dot{V}_f/A_I$ [cm/s]	0.02
minimum droplet diameter $D_p$ [μm]	68.11
Height of the emulsion band $H_D$ [m]	0.04
Available time to cross the emulsion band $t_{cross}$ [min]	10.35
Degree of turbulence $N_{Re}$ [-]	260.09
Average volumetric residence time $t_{avg}$ [min]	63
Volume of wastewater per month $V_{ww}$ [m <sup>3</sup> ]	142.6
Estimated volume of free solvent to wastewater system $V_{free}$ [L]	70-150
Average TOC of the samples [mg/L]	445
Equilibrium TOC in operation conditions [mg/L]	446.7
Equilibrium TOC in wastewater system conditions [mg/L]	364.353
$\Delta$ TOC [mg/L]	82.3
Amount of additional separation potential in wastewater system [L]	13.8
Monthly loss $V_{loss}$ [L]	85-165

SP.4	Sampling data from sample point 4.		
Sampling date	TOC level of aqueous phase [mg/L]	Volume flow rate of the feed $\dot{V}_f$ [m <sup>3</sup> /h] <sup>(1)</sup>	Volume flow rate of wastewater $\dot{V}_{ww}$ [m <sup>3</sup> /h] <sup>(1)</sup>
12.3.2018	315	0.88	0.62
13.3.2018	288	0.88	0.62
14.3.2018	277	0.88	0.62
15.3.2018	290	0.88	0.62
16.3.2018	294	0.88	0.62
19.3.2018	309	0.88	0.62
21.3.2018	310	0.88	0.62
21.3.2018	270	0.88	0.62
22.3.2018	311	0.88	0.62
26.3.2018	332	0.88	0.62
4.4.2018	323	0.88	0.62
5.4.2018	324	0.88	0.62
Average	301	0.88	0.62

(1) Volume flow rate is calculated based on characteristic equipment dimensions and surface level increase over time.

Variables	
Temperature of wastewater stream $T$ [°C]	10
pH of wastewater stream [-]	4.1
Estimated volume fraction of solvent in wastewater stream	0.0005-0.001
Calculations	
Phase orientation $\Theta$ [-]	0.31
Feed flow rate to phase-interface area $\dot{V}_f/A_I$ [cm/s]	0.02
Minimum droplet diameter $D_p$ [μm]	65.72
Height of the emulsion band $H_D$ [m]	0.04
Available time to cross the emulsion band $t_{cross}$ [min]	4.64
Degree of turbulence $N_{Re}$ [-]	242.15
Average volumetric residence time $t_{avg}$ [min]	56
Volume of wastewater per month $V_{ww}$ [m <sup>3</sup> ]	446.9
Amount of additional separation potential in wastewater system [L]	Stream TOC under equilibrium value. No increased solvent losses.
Monthly loss $V_{loss}$ [L]	225-450

SP.5		Sampling data from sample point 5.			
Sampling date <sup>(1)</sup>	TOC level of aqueous phase [mg/L]	Volume flow rate of the feed $\dot{V}_f$ [m <sup>3</sup> /h]	Volume flow rate of wastewater stream $\dot{V}_{ww}$ [m <sup>3</sup> /h]	Mass flow of the carbon in wastewater stream $\dot{m}_l$ [g/h]	Mass of separating organic residues $\dot{m}_p$ [g/h]
6.3.2018	442	176	1.12	493.3	
8.3.2018	508	176	0.84	423.9	
12.3.2018	369	176	1.27	468.0	
12.3.2018	470	176	1.32	619.3	
13.3.2018	448	176	1.33	596.7	
A&A	357	176	1.33	475.1	121.6
16.3.2018	595	176	0.65	389.3	
A&A	434	176	0.65	283.5	105.8
19.3.2018	498	176	1.30	646.2	
A&A	413	176	1.30	535.3	110.9
21.3.2018	546	181	1.12	609.8	
A&A	385	181	1.12	429.7	180.1
22.3.2018	482	181	1.21	581.2	
A&A	393	181	1.21	474.0	107.1
23.4.2018	553	181	1.21	586.7	
A&A	419	181	1.21	444.6	142.2
Average (A&A not included)	491	177	1.13	504.7 (Sample) 403.6 (A&A)	127.9

(1) A&A: pH of the sample is adjusted to wastewater system pH and the emulsion is left to deform.

Variables	
Temperature of wastewater stream $T$ [°C]	45
pH of wastewater stream [-]	4
Calculations	
Average volumetric residence time $t_{avg}$ [s]	186.1
Residence time in fibre media $t_{media}$ [s]	3.9
Available time for separation $t_{min}$ [s]	138.6
Minimum settling velocity required $u_{min}$ [cm/s]	1.1
Minimum droplet diameter $D_p$ [µm]	821.9
Phase orientation $\theta$ [-]	116.5
Available time to cross the emulsion band $t_{cross}$ [min]	15.5
The degree of turbulence $N_{Re}$ [-]	705.2
Equilibrium TOC in operation conditions [mg/L]	346.6
Average TOC of the samples [mg/L]	504.7
Equilibrium TOC in wastewater system conditions [mg/L]	407.6
$\Delta$ TOC [mg/L]	97.2
Monthly loss $V_{loss}$ [L]	85.0

SP.6	Sampling data from sample point 6.			
Sampling date <sup>(1)</sup>	TOC level of aqueous phase [mg/L]	Volume flow rate of the feed $\dot{V}_f$ [m <sup>3</sup> /h]	Volume flow rate of wastewater stream $\dot{V}_{ww}$ [m <sup>3</sup> /h]	Mass flow of the carbon in wastewater stream $\dot{m}_l$ [g/h]
6.3.2018 14.00	390.0	488	0.98	383.5
8.3.2018 7.40	372.4	488	0.95	355.3
9.3.2018 7.30	355.1	488	0.97	345.5
12.2.2018 7.30	334.1	488	0.97	322.4
13.3.2018 7.30	301.7	488	1.00	300.2
16.3.2018 7.30	322.9	488	1.00	323.5
19.3.2018 7.30	331.7	488	0.99	326.7
21.3.2018 8.30	333.9	488	0.97	325.2
A&A	321.5	488	0.97	313.1
Average (A&A not included)	343	488	0.98	335.3

(1) A&A: pH of the sample is adjusted to wastewater system pH and the emulsion is left to deform.

Variables	
Temperature of wastewater stream $T$ [°C]	45
pH of wastewater stream [-]	3
Temperature of wastewater system $T$ [°C]	30
pH of wastewater system [-]	2.2
Solvent density $\rho_l$ [kg/m <sup>3</sup> ]	941
Calculations	
Average volumetric residence time $t_{avg}$ [s]	315
Residence time in fibre media $t_{media}$ [s]	5
Available time for separation $t_{min}$ [s]	224
Minimum settling velocity required $u_{min}$ [cm/s]	1
Minimum droplet diameter $D_p$ [µm]	902
Phase orientation $\theta$ [-]	371
Available time to cross the emulsion band $t_{cross}$ [min]	78
The degree of turbulence $N_{Re}$ [-]	320
Equilibrium TOC in operation conditions [mg/L]	347
Average TOC of the samples [mg/L]	340
Equilibrium TOC in wastewater system conditions [mg/L]	408
$\Delta$ TOC [mg/L]	-61
Monthly loss $V_{loss}$ [L]	no loss



SP.7	Sampling data from sample point 7.				
Sampling date	pH of the wastewater stream <sup>(1)</sup> [-]	TOC level of aqueous phase [mg/L]	Volume flow rate of the feed $\dot{V}_f$ [m <sup>3</sup> /h]	Volume flow rate of wastewater stream $\dot{V}_{ww}$ [m <sup>3</sup> /h]	Mass flow of the carbon in wastewater stream $\dot{m}_l$ [g/h]
6.3.2018	1.96	363.8	40	0.82	296.8
8.3.2018	2.01	349.0	40	0.98	341.3
8.3.2018	2.15	339.6	40	1.03	350.8
8.3.2018	2.31	334.8	40	1.10	368.9
8.3.2018	2.42	335.1	40	1.05	352.8
9.3.2018	2.14	317.1	41	0.98	311.0
12.3.2018	2.25	315.1	40	0.93	291.4
13.3.2018	2.05	289.0	40	0.98	282.6
14.3.2018	2.08	294.4	40	0.93	273.4
16.3.2018	2.15	315.5	40	1.03	323.4
19.3.2018	2.06	311.6	40	1.01	315.3
21.3.2018	2.11	311.6	41	1.05	328.4
21.3.2018	2.11	300.3	41	1.05	316.5
Average (test run not included)	2.09	307	40	0.99	305.3

(1) Test run on the 8.3.

Variables	
Temperature of wastewater stream [°C]	55
pH of wastewater stream [-]	2.3
Calculations	
Average volumetric residence time $t_{avg}$ [s]	366.2
Residence time in fibre media $t_{media}$ [s]	8.4
Available time for separation $t_{min}$ [s]	254.7
Minimum settling velocity required $u_{min}$ [cm/s]	0.4
Minimum droplet diameter $D_p$ [µm]	496
Phase orientation $\Theta$ [-]	31.1
Available time to cross the emulsion band $t_{cross}$ [min]	8.2
The degree of turbulence $N_{Re}$ [-]	826.6
Equilibrium TOC in operation conditions [mg/L]	306.0
Average TOC of the samples [mg/L]	305.3
Equilibrium TOC in wastewater system conditions [mg/L]	407.6
$\Delta$ TOC [mg/L]	-101.6
Monthly loss $V_{loss}$ [L]	no loss

SP.8	Sampling data from sample point 8.			
Sampling date <sup>(1)</sup>	pH of the wastewater stream <sup>(2)</sup> [-]	TOC level of aqueous phase [mg/L]	Volume flow rate of wastewater stream $\dot{V}_f$ [m <sup>3</sup> /h]	Mass flow of the carbon in wastewater stream $m_l$ [g/h]
8.3.2018	1.71	404.9	1.28	518
8.3.2018	1.91	421.5	1.25	528
8.3.2018	1.97	423.8	1.34	566
9.3.2018	1.96	374.8	1.37	513
13.3.2018	1.98	339.3	1.38	468
14.3.2018	1.98	332.7	1.41	468
16.3.2018	2.02	383.6	1.33	509
19.3.2018	1.98	384	1.34	513
21.3.2018	2.11	404.8	1.36	550
A&A	2.11	332.1	1.36	451
22.3.2018	2.11	377.1	1.36	512
Average (test run and A&A not included)	2.02	370.9	1.36	505

(1) A&A: pH of the sample is adjusted to wastewater system pH and the emulsion is left to deform.

(2) Test run on the 8.3.

Variables	
Temperature of wastewater stream [°C]	55
pH of wastewater stream [-]	2
Calculations	
Phase orientation $\theta$ [-]	22.5
Feed flow rate to phase-interface area $\dot{V}_f/A_I$ [cm/s]	0.01
Minimum droplet diameter $D_p$ [ $\mu$ m]	917.6
Height of the emulsion band $H_D$ [m]	0.05
Available time to cross the emulsion band $t_{cross}$ [min]	2.6
Degree of turbulence $N_{Re}$ [-]	328.0
Average volumetric residence time $t_{avg}$ [min]	33.5
Volume of wastewater per month $V_{ww}$ [m <sup>3</sup> ]	961.6
Equilibrium TOC in operation conditions [mg/L]	306.0
Average TOC of the samples [mg/L]	370.9
TOC level after settling [mg/L]	332.1
$\Delta$ TOC [mg/L]	38.8
Monthly loss $V_{loss}$ [L]	39.6

SP.9	Sampling data from sample point 9.			
Sampling date	Weight before treatment $m_{wet}$ [kg]	Weight after treatment $m_{dry}$ [kg]	Volume of removed solvent $V_l$ [L]	Volume per dry weight $V_l/m$ [L/kg]
23.2.2018	491	359	140	0.39
3.3.2018	334	223	118	0.53
13.3.2018 (1)	259	210	52	0.25
2.4.2018	245	166	84	0.51

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**Calculations**

Average volume per dry weight $V_l/m_{dry}$ [L/kg]	0,47
Monthly occurrence of operations	3
Desired dry weight after treatment $m_{dry}$ [kg]	200
Monthly loss $V_{loss}$ [L]	285

SP.10	Sampling data from sample point 10.			
Sampling date	TOC level of aqueous phase [mg/L]	Volume flow rate of the feed $V_f$ [m <sup>3</sup> /h] <sup>(1)</sup>	Volume of a sample $V_{sample}$ [ml] <sup>(2)</sup>	Free solvent in sample $V_{free}$ [ml]
14.3.2018	328,3	0,3159	420	13
15.3.2018	345,6	0,3159	500	54
16.3.2018	391,7	0,3159	460	146
29.3.2018	-	0,3159	Solvent layer thickness 15 cm	
average	355,2	0,3159	-	-

(1) Volume flow rate is calculated based on characteristic equipment dimensions and surface level increase over time.

(2) Samples are collected directly from process equipment because there are no proper sampling points to evaluate process stream. Due to the used sampling method, the data gathered from the process is unreliable for quantifying the amount of free solvent. No solvent on the surface at 14.3.

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**Calculations**

Average volumetric residence time $t_{avg}$ [min]	519
Volume of wastewater per month $V_{ww}$ [m <sup>3</sup> ]	227,4
Equilibrium TOC in wastewater system conditions [mg/L]	364,4
Average TOC of the samples [mg/L]	355,2
$\Delta$ TOC [mg/L]	9,2
Volume of accumulated solvent in process equipment $V_{free}$ [m <sup>3</sup> ]	0,4
Time span of solvent accumulation $t$ [d]	15
Monthly loss $V_{loss}$ [L]	780

SP	Volume of solvent loss per month $V_{loss}$ [L]	Comment
11	583	Maintenance work
12	<100	Make-up solvent operations
13	0	Low TOC and no free solvent
14&15	50-75	Maintenance work