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FOULING CAUSED BY FATS AND OILS AT HIGH TEMPERATURES

–The Suitability of Falex 450 Thermal Fouler for
Fats and Oils



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The aim of this thesis was to examine if Falex 450 Thermal Fouler test equipment could be reliably used to evaluate fouling tendency of lipid based samples. The equipment was designed to evaluate coking propensity of process fluids and Neste Corporation had used it mainly for fossil oil refinery samples. There had been unexplained issues with measurements during test runs. Another goal was to investigate what causes the fluctuation in measurements and could it be eliminated.

The fouling experiments were conducted with different test parameters with 6 different lipid qualities. Repetitions were conducted in certain test points. The studied variables besides feed quality were temperature, flow-rate, rod condition and run mode (recycling and once-through). The composition of liquid feed samples and solid deposit samples were analysed in Neste Corporation's Research Analytics laboratory.

The unexplained and severe fluctuation in measurements was solved to be caused by a magnetic stirrer under the feed tank. The magnetic stirrer was not an original part of the equipment and after it was decommissioned the severe fluctuation did not occur anymore. After the fluctuation was eliminated the results were logic within a sample: the fouling increased with higher temperatures. The actual mechanisms of fluctuation remained unclear but it was assumed to be caused by electrical issues that interfered the delicate measurement instruments.

The fouling results of this thesis indicate that fouling tendencies of lipid samples could be reliably evaluated with the equipment but a stirring device that does not cause fluctuation should be introduced to the feed tank to prevent particle and dregs settling as dregs content seemed to have an enhancing effect on fouling. The results also indicate that fouling tendency of sample can not be estimated by the concentrations of elements that are considered as impurities, thus a more comprehensive analysis of feed sample composition is necessary to understand which components and compounds act as foulants.

KEYWORDS:

Fouling, Fat, Oil, Lipid, Triglyceride, Fouling resistance

Olli Byman

RASVOJEN AIHEUTTAMA LIKAANTUMINEN KORKEISSA LÄMPÖTILOISSA

- Falex 450 Thermal Fouler -likaantumistestauslaitteiston soveltuvuus rasva- ja öljynäytteille

Tämän opinnäytetyön tavoitteina oli selvittää Falex 450 Thermal Fouler -likaantumistestauslaitteiston soveltuvuus lipidipohjaisten raaka-aineiden likaantumisen tutkimiseen sekä selvittää mistä laitteistoa vaivanneet häiriöt mittauksissa johtuivat ja voitaisiinko ne korjata.

Likaantumiskokeet suoritettiin kuudella eri lipidilaadulla eri prosessiolosuhteissa. Kokeista tehtiin toistoja tietyissä koepisteissä. Tutkittuja muuttujia syötön laadun lisäksi olivat lämpötila, virtausnopeus, sauvan kunto sekä ajotapa (palautus ja kerran läpi -ajo). Nestemäisten syöttönäytteiden sekä kiinteiden likanäytteiden koostumusta analysoitiin Nesteen tutkimuskeskuksen Tutkimusanalytiikan laboratorioissa.

Työn aikana selvisi, että laitteistoa vaivanneet häiriöt mittauksissa johtuivat syöttösäiliön alla olevasta magneettisekoittajasta. Magneettisekoittaja ei ollut laitteiston alkuperäinen osa ja kun sen käyttö lopetettiin, myös häiriöt loppuivat. Häiriöiden loppumisen jälkeen tulokset olivat johdonmukaisia: likaantuminen oli selvästi runsaampaa korkeammassa lämpötiloissa. Mittausten häiriöiden todellista syytä ei selvitetty, mutta niiden uskottiin johtuvan magneettisekoittajan tai sekoituksen aiheuttamasta sähköilmiöstä, joka aiheutti häiriötä herkissä mittalaitteissa.

Tässä työssä saadut likaantumistulokset osoittavat, että rasvanäytteiden likaantumista voidaan luotettavasti arvioida tällä laitteistolla, mutta häiriötön sekoituslaite olisi syytä asentaa laitteistoon estämään kiintoaineiden ja sakan laskeutumista syöttösäiliön pohjalle, sillä niillä näytti olevan merkittävä vaikutus näytteen likaavuuteen. Tulokset myös osoittavat, että näytteen likaavuutta ei voi ennustaa pelkkien epäpuhtauksiksi luokiteltujen alkuaineiden pitoisuuksien perusteella, joten syöttöaineiden sisältämien yhdisteiden kattavampi analysointi ja tunnistaminen ovat tarpeen, jotta saadaan tietoa mitkä yhdisteet ja osatekijät vaikuttavat näytteen likaavuuteen.

ASIASANAT:

Likaantuminen, Rasva, Öljy, Lipidi, Triglyseridi, Likaantumisvastus

PUBLIC VERSION NOTE

This is the public version of this thesis. All the confidential information is censored or removed from this version.

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LIST OF ABBREVIATIONS (OR) SYMBOLS

C_p	Heat capacity
EOR	End of run
IR	Infrared
OT	Once-through
Re	Reynolds number
R_f	Fouling resistance
SOR	Start of run
U	Overall heat transfer coefficient
XRF	X-ray fluorescence
XRD	X-ray diffraction

1 INTRODUCTION

Fouling in heat exchangers is usually defined as accumulation and formation of unwanted deposits on surfaces and it occurs in most process and chemical industries. It is very complex phenomenon which has always been recognized as a problem but still is not completely understood. Despite the amount of accumulated operating experience of years and the amount of fouling literature, fouling is considered to be the single most unknown factor in heat exchanger designing. The wide range of operating conditions and process streams make most fouling situations unique thus making general conclusions challenging. (Awad 2011, 505)

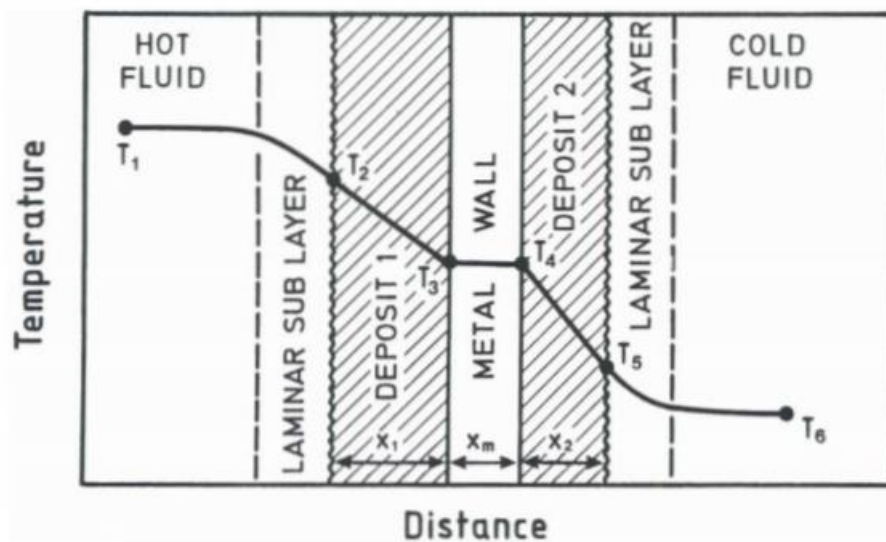
Fouling is one of the most important problems in heat transfer processes because it will decrease the heat transfer capacity of the equipment. Fouling can occur on any fluid-solid surface and it produces other unwanted effects than reduction of heat transfer. A deposit on a heat exchanger surface increases pressure drop and demands more pumping energy. (Awad 2011, 505) Very severe fouling may result in completely clogged heat exchangers which causes thermal stress and subsequent mechanical damage to the equipment and forces the process to be shut down for cleaning. (Theodore 2011, 447)

Fouling is usually taken into account in heat exchanger design by overscaling the heat exchanger or designing a standby heat exchangers to be used during maintenance. However, fouling may be caused by a contaminant in bulk fluid even in small quantities (Bott 1995, 1, 5). In most processes the quality of feedstock may vary which might result in undesirable surprises in heat exchangers that were designed for certain quality bulk material or even for completely different feedstock.

Problems caused by fouling cost money and spend extra energy and other utilities. As it was stated above fouling situations may be unique thus it would be important to be able to predict the fouling tendency of specific bulk materials in certain process conditions. An acknowledged research method for fouling tendency would establish a way to study which factors increase fouling and how it could be mitigated by suitable pre-treatment or additive chemicals. The aim of this thesis was to examine whether the fouling of lipid based renewable feedstock could be reliably studied with an equipment primarily designed for crude oil fouling research.

2 FOULING

The general definition of fouling is the accumulation and formation of unwanted materials on the surfaces of processing equipment (Awad 2011, 505). The thermal conductivity of deposits is usually low compared to metals which decreases heat transfer and reduces the efficiency of heat exchanger. In order to maintain the desired heat transfer capacity the fouled exchangers must be run with larger temperature difference than clean ones. (Bott 1995, 7) An illustrated example of temperature distribution in a fouled heat exchange system is shown in Picture 1.



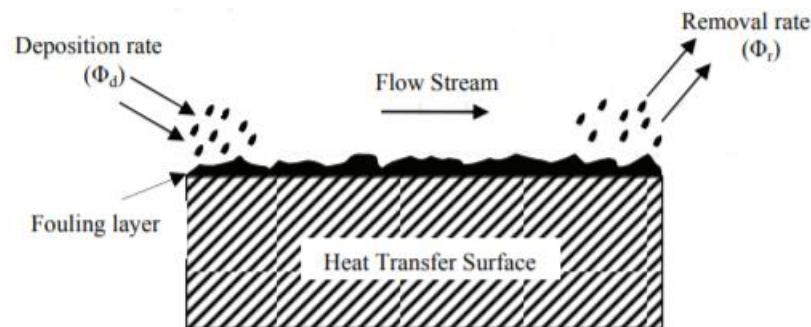
Picture 1. Temperature distribution in a fouled heat exchange system. (Bott 1995, 7)

T_1 and T_6 are the temperatures of the bulk hot and cold fluids under their turbulent flow conditions. The temperature in turbulent flow conditions is quite even due to mixing and physically happening heat distribution. The laminar flow layers between turbulent bulk fluid and deposit surface also resist heat transfer. (Bott 1995, 7)

The foulants may be crystalline compounds, biological matter, products of chemical reactions including corrosion or solid particles. The type of deposit is dependable on the fluid passing the hot surface. Most often the fouling problem is caused by some form of contaminant within the fluid. The contaminant may increase fouling in very low concentrations and it may consist e.g. from solid particles or micro-organisms. At high process temperatures bulk fluid itself may also start to decompose to components that have higher fouling tendency. Almost any solid or semi-solid materials can cause fouling

in heat exchangers. The most recognized and common inorganic foulants are airborne dust and grit, waterborne mud and silts, iron oxide and calcium and magnesium salts. The most common organic foulants are biological substances such as bacteria, fungi and algae oils, heavy organic deposits as polymers and tar waxes, greases and carbon. (Bott 1995, 1)

The fouling process is commonly considered to be a net result of two simultaneous happening sub-processes: deposition and detaching process. Picture 2 is a schematic illustration of ongoing fouling.



Picture 2. Schematic illustration of fouling in process. (Awad 2011, 508)

The sum of these two basic components represents the growth of the deposit on the surface. In a simple model deposit growth can be regarded as the remainder of deposition and removal rates. (Awad 2011, 509)

2.1 Fouling types

The fouling on heat exchanger surface usually consists of different types of fouling. The occasional fouling type is classified by the identified chemical and physical processes involved. The main fouling types are classified as particulate fouling, crystallization or precipitating fouling, chemical reaction fouling, corrosion fouling, biological fouling and solidification or freezing fouling. (Serth and Lestina 2014, 77 - 79; Awad 2011, 506) Although the main fouling types are identified it should be emphasized that in practice it usually occurs more than one fouling mechanism simultaneously having synergistic effects which makes it impossible to form an accurate common fouling theory (Awad 2011, 509). Even in fields such as crude oil and hydrocarbon refining where fouling has been intensively studied for decades the understanding of real process fouling phenomenon is more conjectural than exact. (Hewitt 2014, 26)

2.1.1 Chemical reaction fouling

Chemical reaction fouling is caused by one or more chemical reactions between components in the flowing fluid and it is usually associated with organic chemicals. The temperature in heat exchanger may cause the chemical reactions so that heat transfer surface material is not a participant in these reactions but it may act as a catalyst in some circumstances. The surface material can also inhibit and reduce the extent of unwanted chemical reactions. The reactions are usually complex and they include cracking, polymerization, coking and autoxidation. This fouling occurs in range of temperatures from ambient to over 1000 °C but it is more typical at higher temperature. Chemical reaction fouling is common phenomenon in many process industries such as petrochemical industry, oil refining, food processing, vapour-phase pyrolysis, polymerization processes and cooling of gas and oils. Thermally instable components such as asphaltenes and proteins are known to induce fouling precursors. Fouling caused by biological fluids may involve complex heterogeneous reactions and physicochemical processes. Deposits from chemical reactions fouling are may increase corrosion if they inhibit the formation of protective oxide layer on the heat exchanger surface. (Bott 1995, 185; Awad 2011, 507)

Besides carbon and hydrogen the deposits may contain significant amounts of inorganic components which may aid further chemical degradation by catalysing other reactions or participating in corrosion. The origin of inorganic components vary and here are some of the most common sources:

- 1) Dissolved salts in aqueous fraction within an organic fluid. For instance in crude oil processing there is a process step called "desalter" in which most these salts are removed but it does not remove the salts completely.
- 2) Organic molecules with inorganic heteroatom. For example sulphur occurs in a form of mercaptan or other organo-sulphur compound in crude oil.
- 3) Organic compounds with metals. Some complex organic compounds may contain metals in combination.
- 4) Corrosion products detached from upstream processes that are trapped in deposits produced by chemical reactions.

(Bott 1995, 186)

2.1.2 Particulate fouling

Particulate fouling is the deposition of suspended particles contained by process streams. Particulate fouling is called sedimentation fouling if it occurs due to gravitational settling. Therefore the complete definition would be the accumulation of particles from heat exchanger fluids on the heat transfer surface. Most often this kind of fouling is caused by corrosion products in fluids, clay and mineral particles, magnetic particles in economizers, suspended solids in cooling water, soot particles of incomplete combustion, dust particles in air coolers, salts in desalination systems, particulates present in fire-side fouling of boilers and so on. The particles may also form in the fluid while being processed or exposed to high temperatures. Factors that affect particulate fouling are amount of suspended particles, fluid flow velocity, temperature and heat flux at the fouling surface. (Awad 2011, 506; Bott 1995, 55 - 56)

2.1.3 Crystallization and precipitation fouling

Crystallization fouling is caused by crystallization of dissolved salts from saturated solutions due to solubility changes with respect to changes in temperature. Crystallization causes the salts to precipitate on heat exchanger surfaces. It is most common with aqueous solutions and other liquids that contain soluble salts and which are being heated or cooled. The phenomena of inverse solubility salts depositing on heated surface is called "scaling" and the generated layer is hard and tenacious. The deposit caused by normal solubility salts on cooled surface has usually porous and mushy layers and it called "sludge", "softscale" or "powdery deposit." Crystallization fouling is common with all salt containing solutions such as sea water, untreated water, geothermal water, aqueous caustic soda solutions and brine. The most dominant phenomena in crystallization fouling is crystal growth during and after precipitation which first requires the formation of primary nucleus. (Awad 2011, 506 - 507) Formation of nucleus may be spontaneous, induced by particles or induced by crystals (Bott 1995, 110).

2.1.4 Corrosion fouling

Corrosion is defined as deterioration and loss of material caused by chemical or electrochemical reaction between the heat transfer surface and the components in process stream. The corrosion may be caused by the process fluid itself or the presence of impurities in it even in small quantities. The corrosion products change the surface characteristics and foul it. Corrosion fouling happens in two ways:

- 1) Corrosion products accumulate and attach to the surface resisting heat transfer
- 2) Corrosion products are formed and transported as particulate material to another site of the system

Corrosion fouling often occurs in applications where chemical reaction fouling happens and prevents the formation of oxide layer on the heat exchange surface or where the oxide layer is removed by erosion. Corrosion fouling could be limited or eliminated by choosing right materials but the cost penalty may often become a prohibitive factor. (Bott 1995, 149; Awad 2011, 507)

2.1.5 Biological fouling

Biological fouling is the accumulation of living organisms on the heat exchanger surface. Micro-organisms include bacteria, algae and fungi. Macro-organisms are vegetation from seaweed, mussels and other macro-sized aquatic life forms. Biological fouling is most often an issue in processes where the temperature does not differ drastically from natural environments. For example cooling water systems are prone to biological fouling because there are nutrients in water and the temperature is often near to the biological activity optimal. Non-aqueous fluids may also cause biological activity. For instance, metal working fluids may contain emulsions which are formed with organic components that provide nutrients for micro-organisms. (Bott 1995, 149)

Bio-based deposit layer is usually mucous, uneven, filamentous and difficult to remove (Awad 2011, 507). Biological layers on heat exchanger surfaces may enhance other fouling phenomena. It is common to find particulate deposition, scale formation and corrosion under the biological layers. This is caused by metabolic activity of organisms which include chemical reactions that change conditions by releasing chemicals and altering pH under the biological mass. Micro-organisms also promote fouling by

producing and releasing components outside their cells that enable particulate matter to attach. (Bott 195, 223)

2.1.6 Freezing fouling or solidification

Freezing fouling is the solidification of a pure liquid or multicomponent solution on cooled surface. Solidification may occur so that only one or few components of the solution solidify. Examples of solidification fouling are solidification of paraffins when cooling hydrocarbon streams and formation of ice from air moisture on air-conditioners. The main factors affecting solidification fouling are mass flow rate, temperature, surface conditions, crystallization conditions and concentration of solidifying components in fluid. (Bott 195, 137; Awad 2011, 508)

2.2 Deposition and removal mechanisms

All the above mentioned fouling mechanisms are governed by a sequence of events. These events determine the overall fouling process and its total impact on heat exchanger performance. As shown in Picture 2, there are two main processes that govern fouling: deposition and removal process.

Deposition process:

- Formation of foulant or precursor in bulk fluid
- Transport to the deposit-fluid surface
- Attachment or formation reaction at the deposit-fluid interface

Removal process:

- Removal of the fouling deposit
- Transport from the deposit-fluid interface

In different fouling cases different events may dominate the fouling process and deposit formation. (Awad 2011, 509) An idealised deposit growth is illustrated in Figure 1.

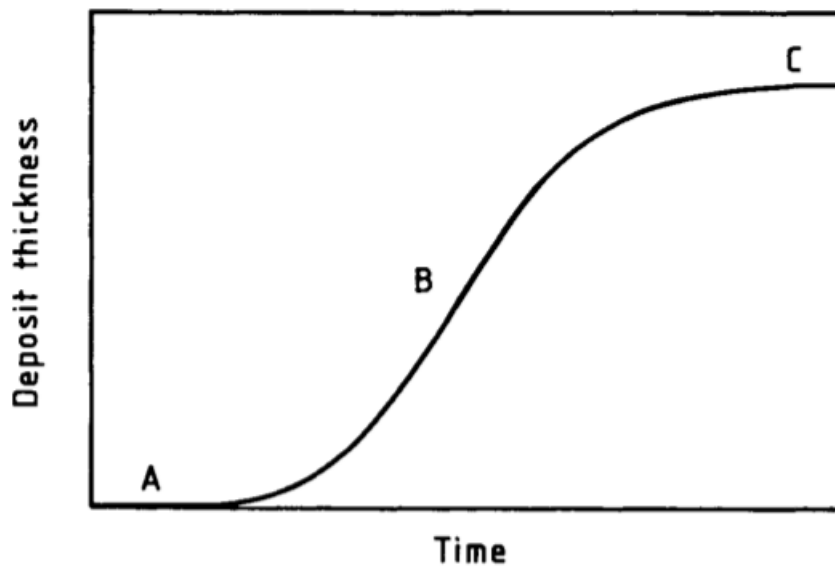


Figure 1. Idealised deposit thickness growth graph. (Bott 1995, 4)

In phase A the attaching is initiated. The duration of this phase varies from few seconds to several weeks depending on process variables. Phase B is the steady growth phase where happens both attaching and detaching of deposit. In phase C the deposit thickness remains virtually constant because the rate of detaching is equal to the rate of attaching. (Bott 1995, 4) The main deposition and removal mechanisms are summarized in following subchapters.

2.2.1 The formation of foulants in bulk or initiation of fouling

The formation of foulant materials or initiation of the fouling is the first event of fouling process. It is usually preceded by a varying delay period. Heterogeneous nucleation is the basic mechanism involved during in this phase and the delay time is longer with lower nucleation rate.

The factors affecting delay period are fluid velocity, temperature, bulk material and condition and nature of the surface. Surfaces that are in contact with liquid usually have shorter delay period. In chemical reaction fouling initiation time decreases with increasing surface temperature. In crystallization fouling initiation time decreases with increasing degree of supersaturation. In all fouling mechanisms rougher surface decreases delay time because it provides more available sites for nucleation, adhesion and adsorption. (Awad 2011, 510)

2.2.2 The transportation of depositing foulants

Transport of potentially depositing foulants from bulk fluid to surface means that the possible foulants must be brought to be in contact with the surface. Transport of foulants take usually place through one or more of these mechanisms:

- Diffusion: Diffusion drives foulants to be equally distributed in the solution thus keeping the foulant concentration steady at the surface.
- Electrophoresis: Fouling particles with electric charge may move towards or away from surface depending on the polarity of particles and surfaces. Surface forces such as double layer interaction and London-van der Waals forces are commonly responsible for electrophoretic effects.
- Sedimentation: Sedimentation means deposition of particulate matters such as clay, rust particles and dust to deposit on the surface by gravity. The sedimentation can only occur if gravitational force is greater than upward push caused by flow and it occurs more easily with low fluid velocities and large particles.
- Inertial impaction: Inertial impaction takes place when larger particles have sufficient inertia to resist fluid streamlines and they deposit on surface.
- Thermophoresis: Thermophoretic forces move fine particles from high temperature to colder temperature and with hot surfaces it prevents particles from deposition and promotes fouling with cooler wall. Thermophoretic effect is stronger with gases than liquids.
- Turbulent downsweeps: The stagnant laminar layer closest to the surface is not always truly steady thus the fluid may be transported towards the surface by random turbulent sweeps. (Awad 2011, 510)
- Brownian motion: Brownian motion is the random movement of molecules in a fluid or gas phase caused by collisions with the other molecules in the same phase. This is notable transportation mechanism in stationary fluids and with laminar flow conditions. (Bott 195, 37, 61)
- Diffusiophoresis: Diffusiophoresis is the net force on the particles caused by the flow of condensing vapour moving to a cooler surface (Bott 1995, 73).

2.2.3 The attachment of the foulants

Attachment of foulants involve chemical and physical processes and it is not completely understood. The attachment factors affect the attachment simultaneously and combined.

- Surface properties: The important surface conditions are surface free energy, heat of immersion and wettability. Wettable or high-energy surfaces have shorter delay period than low-energy and unwettable but they suffer more from deposition.
- Surface forces: The most crucial surface force is the London-van der Waals force. It is an intermolecular attraction between nonpolar molecules and it is always attractive. Even-though electrons are rather symmetrically distributed in nonpolar molecules, they are still constantly on the move causing slight fluctuation in the electron density, which causes electric moment on their neighbouring molecules (Hanahan 1997, 29). Another important surface force is the electric double layer interaction force which can be repulsive or attractive. Hydrodynamic forces have effect on how the particles move to the wall and it is highly affected by the surface, flow-rate and bulk fluid viscosity.
- Sticking probability describes the amount of particles that attach the wall after arriving there and stay there before any detaching occurs. It is a statistical concept used to explain and analyse this complicated event. (Awad 2011, 511)

2.2.4 The removal of the foulants

Removal of the deposits from wall may occur simultaneously with deposition. Removal occurs by action of one or more of the following mechanisms: shear forces, turbulent bursts, erosion and re-solution of deposit.

- Shear forces are the shear stresses caused by the fluid flowing past the deposit layer and sweeping the deposit away. As the fouling deposit builds up decreasing the cross-sectional area the flow is more restricted which causes increase in flow-rate which results in increase in shear stress and possibly in removal rate. New deposits are able to form only if the depositing factors are greater than the shear forces.

- Turbulent bursts that happen randomly lift deposited material from the surface. Besides turbulent bursts there may be gentler sweeps of turbulent fluid behaviour.
- Re-solution: The deposits are insoluble as they are attached but they may become soluble again if there is a change in temperature, pH or other process variable.
- Erosion is highly dependent on the shear strength of deposit. Erosion is associated with removal of particulate matter. For example, erosion removes effectively components that are formed of large variety of salts with different crystal properties but is very ineffective with pure materials with stronger crystals. (Awad 2011, 511-512)

2.3 Fouling curves

As it was shown in Picture 2, build up rate of deposit could be viewed as the difference of deposition and removal rate. The overall fouling process is usually perceived as increase of fouling resistance (R_f) with reference to time and these graphs are called fouling curves. (Bott 1995, 23; Awad 2011, 512) An idealised fouling curve was introduced in Figure 1, but the fouling does not always follow the same pattern due different fouling phenomena and events. Other possible and common shapes of fouling curves are represented in Figure 2.

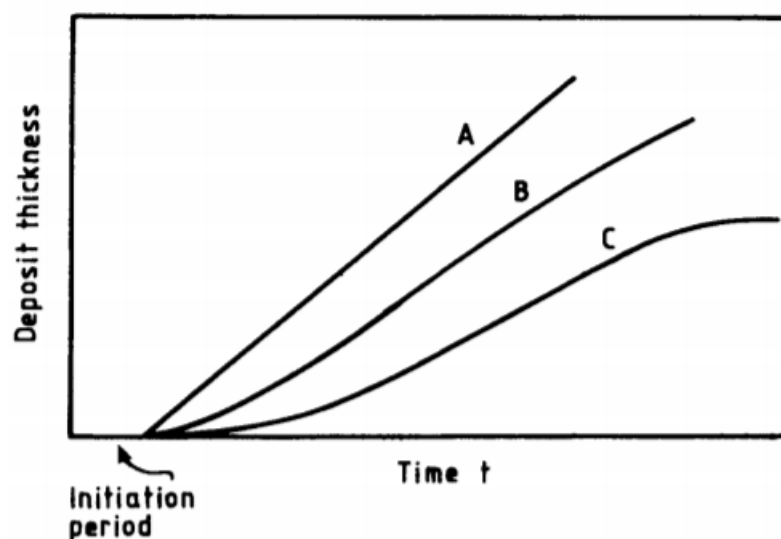


Figure 2. Ideal shapes of fouling curves. (Bott 195, 25)

The initiation period is the time that elapses before fouling begins. Curve A represents linear fouling curve. With this type of fouling the accumulation of deposit is steady after the initiation period. This is possible if there is no removal of the deposit, the removal rate is negligible or the rates of deposition and removal are constant. Curve C is similar asymptotic fouling curve as seen in Figure 1. With this type of fouling the fouling rate falls gradually with time and the system reaches a steady state when there is no increase or removal of deposits on the surface and the system can still continue operating. Curve B represents falling rate fouling curve which is caused by decreasing deposition rate while removal rate is being constant or increasing over time. Curve B is essentially the beginning part of curve C and the curve B would get a similar shape than curve C if the equipment would be let run for longer period of time. (Bott 1995, 24 - 25M; Awad 2011, 512 - 513)

Roughness of the deposit surface will differ from clean heat exchange surface. The deposit surface is usually rougher and after the initiation phase the deposit surface is the dominant surface feature. Besides of more available sites for nucleation, adhesion and adsorption rougher surface results in greater turbulence near the surface. Greater turbulence will enhance the heat transfer but also bring more particles available to the surface or remove them more efficiently from it. The initiation period of fouling is usually shorter with cleaned and reused surfaces than with untouched surfaces so it should be noted that when comparing fouling curves the initiation should not be taken into account. (Bott 195, 24, 200; Awad 2011, 512)

The curves represented in previous chapter were ideal situations but in industrial or experimental environment ideality may not always be achieved. A fouling curve might have so called "saw tooth" effect which is caused by partial removal of deposit. The partial removal of larger pieces of deposit might be observed as a sudden decrease of fouling rate followed by a fast build up of deposit on the more exposed hot spot on the surface. An example of asymptotic fouling curve with deposit sloughing is presented in Figure 3. The waving graph follows asymptotic shape curve (dashed line) but similar kind of curve can take place with any type of fouling curves as well. (Awad 2011, 513 - 514)

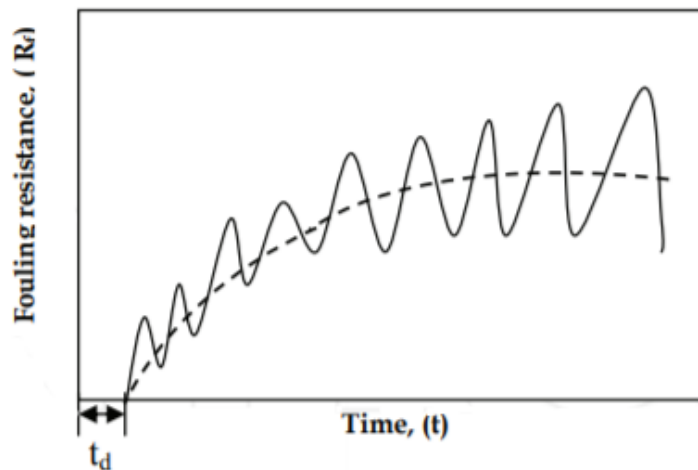


Figure 3. Example of asymptotic fouling curve with deposit sloughing. (Awad 2011, 514)

2.4 Flow velocity and Reynolds number

Thick deposit layer has adverse features. In addition to the increased pressure drop and increased heat transfer resistance the presence of thick foulant layer can have two further consequences: the reduced cross-sectional area of a severely fouled tube results in faster flow velocity of the fluid and increase in Reynolds number. The flow velocity must speed up to keep the volume flow constant and if the equipment is capable to keep the volume flow constant it will increase the Reynolds number. Faster flow velocity effects fouling rates by hydrodynamic effects as higher shear-stress and eddies which both affect deposition and removal rates. (Bott 1995, 23; Awad 2011, 517)

As flow characteristic plays important role on fouling process it is important to know the type of flow in addition to the velocity. The Reynolds number is dimensionless number that is used to evaluate whether flow is laminar or turbulent. Laminar flow can be imagined to like a deck of cards where the layers closer to the solid surface move more slowly. In turbulent flow there are eddies and small currents. The Reynolds number is dependent on the fluid density, velocity, viscosity and the cross-sectional area size.

The Reynolds number in a tube can be calculated with Equation 1:

$$Re = DV\rho/\mu$$

Equation 1. Reynold number.

Where Re = Reynolds number, D = inside diameter of the pipe (km), V = fluid velocity (m/s), ρ = fluid density (kg/m^3) and μ = fluid viscosity (kg/(m*s)). (Theodore 2011, 30)

2.5 The chemical characterization of deposit

Analytical characterization of deposits may provide useful information which helps to understand the mechanisms that lead to fouling, to find the potential fouling precursors and determine the root cause. The results of characterization can also be utilized to establish the most suitable fouling mitigation and foulant cleaning method. The samples are usually quite complex by their composition which means that there is no single method for their complete characterization thus their analysis must rely on several methods that are capable for providing partial information. (Hewitt 2014, 95)

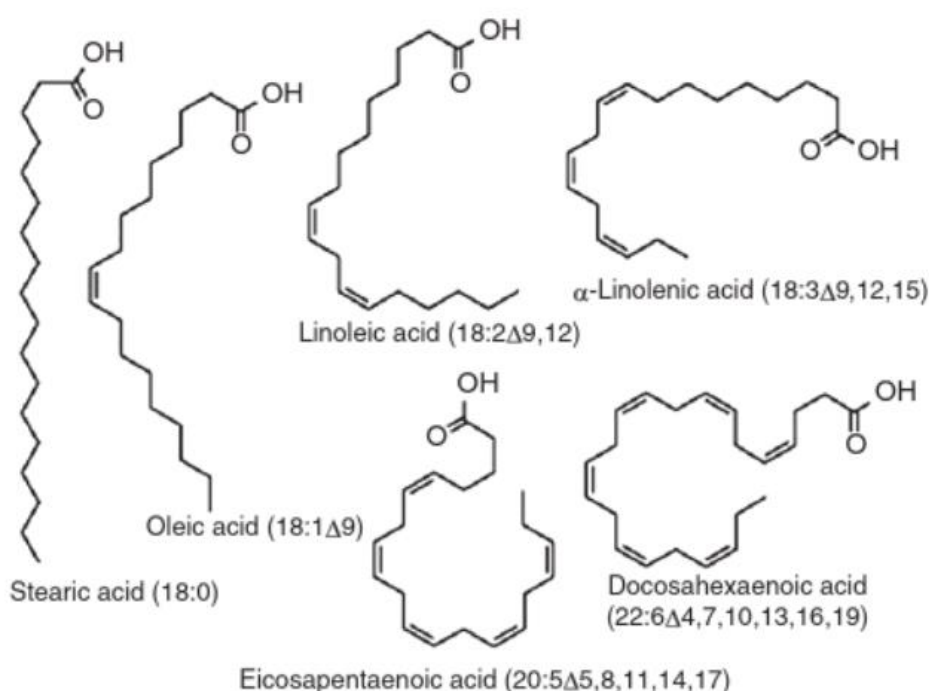
However it must be taken into account that very often the deposit analyses reveal only the products of several reactions and it may be difficult to define the underlying mechanism of fouling especially in cases where fouling is caused by combination of mechanisms. (Hewitt 2014, 26) It must also be noted that on the cold side of a heat exchanger the surface of the deposit is cooler than the inner part. The composition of the deposit depends on the conditions where it forms so the composition usually differs between the inner parts and surface of the deposit. Also chemical reactions may occur more effectively in the inner part of the cake in as the temperature is higher thus the time the deposit has been in place may affect the final chemical composition of the deposit. (Bott 1995, 187)

3 COMPOSITION OF FATS AND OILS

The main component of fats and oils are fatty acids that are esterified to glycerol. Fats and oils are also called triglycerides or triacylglycerols which both mean "triesters of glycerol". They are called fats if they are in solid form at room temperature and oils if in liquid form. Most animal derived triglycerides, such as lard or tallow, are fats. The body heat of living animal keeps them fluid allowing the body to move easier. Triglycerides from plants and cold-blooded animals are usually oils because they are exposed to lower temperatures and their solidifying would have adverse consequences on the organism. Examples of widely utilised oils are olive oil, fish oil and corn oil. (Singh 2010, 346; Kamal-Eldin 2013, 39)

3.1 Fatty acids

Fatty acids (or fatty acyls) are the main component of biological lipids including triglycerides. Fatty acids are consisted of hydrocarbon chain with a carboxylic head group. The carbon chain can be linear, branched, saturated, unsaturated, oxygenated, halogenated sulphated or nitrogenated. Fatty acids are vital constituents of tissues in living organisms. They are commonly called by their given trivial name which usually refers to their origin or source but there is also a systematic way to describe their composition. The systematic way of naming fatty acids works so that the number of carbon atoms and the double bond's position or another substituent is indicated in numbers. For example oleic acid (18:1 Δ 9) has 18 carbon atoms and one double bond after ninth carbon counted from carboxyl head group. There is also another system called "omega nomenclature" where the position last double bond is counted from methyl group and indicated as ω x or n-x where x is the position from methyl group. The omega nomenclature is more useful when studying the metabolism of fatty acids. Examples of different kinds of fatty acids are shown in Picture 3. (Kamal-Eldin 2013, 18-20)



Picture 3. Structures of saturated, unsaturated and polyunsaturated fatty acids (Kamal-Eldin 2013, 21).

Three main types of fatty acids classified by their saturation rate are explained below:

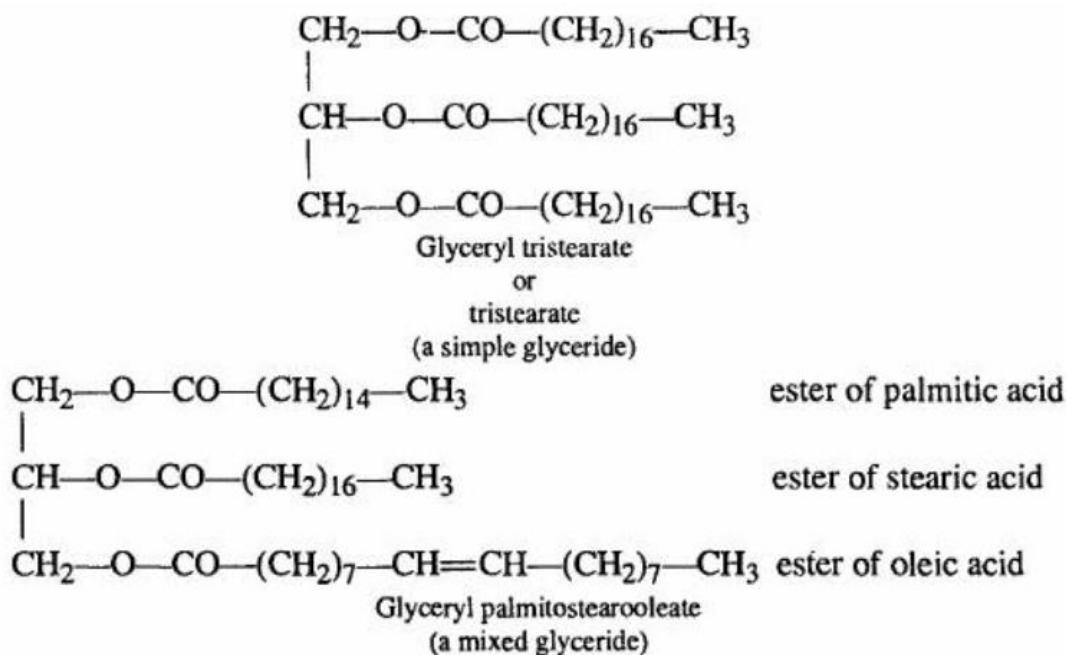
- 1) Saturated fatty acids: animals and plants can synthesize saturated fatty acids from their basic components via different biochemical pathways. Fatty acids with even carbon number from C4 to C24 are typical in animals and larger flora while odd carbon number fatty acids are more present in micro-organisms. Saturated fatty acids can be artificially generated by hydrogenating vegetable oils.
- 2) Monounsaturated fatty acids: these are fatty acids with one double bond. All natural monounsaturated fatty acids have a cis configuration but trans configured monounsaturated fatty acids can be produced as a side product in hydrogenation. The most common monounsaturated fatty acid in nature is oleic acid. Some monounsaturated fatty acids may contain hydroxyl groups.
- 3) Polyunsaturated fatty acids: this group includes a great number of fatty acids with different double bond amount, double bond position and carbon atom count. These fatty acids exist in plants, animals, micro-organisms and most highly unsaturated fatty acids are found in fish and other marine species. Usually the double bonds in these fatty acids occurs once in three carbons but there exceptions such as a group of fatty acids with conjugated double bonds. There is also a diverse group of fatty acids with special

functional groups as triple bonds, cyclic constructions, rings containing nitrogen and oxygen, long-chained fatty alcohols, fatty aldehydes and compounds containing a heteroatom. (Kamal-Eldin 2013, 21)

3.2 Glycerolipids, triglycerides and phospholipids

All compounds that include fatty acids esterified to trihydric alcohol glycerol are called glycerolipids except glycerophospholipids because of their abundance. Glycerol has three hydroxyl groups. It can be esterified one, two or three fatty acids forming respectively monoglyceride, diglyceride or triglyceride. Fatty acids can also be esterified to glycerol that has other molecules in the other one or two hydroxyl groups. Triglycerides are the major components of fats and oils. (Kamal Eldin 2013, 22)

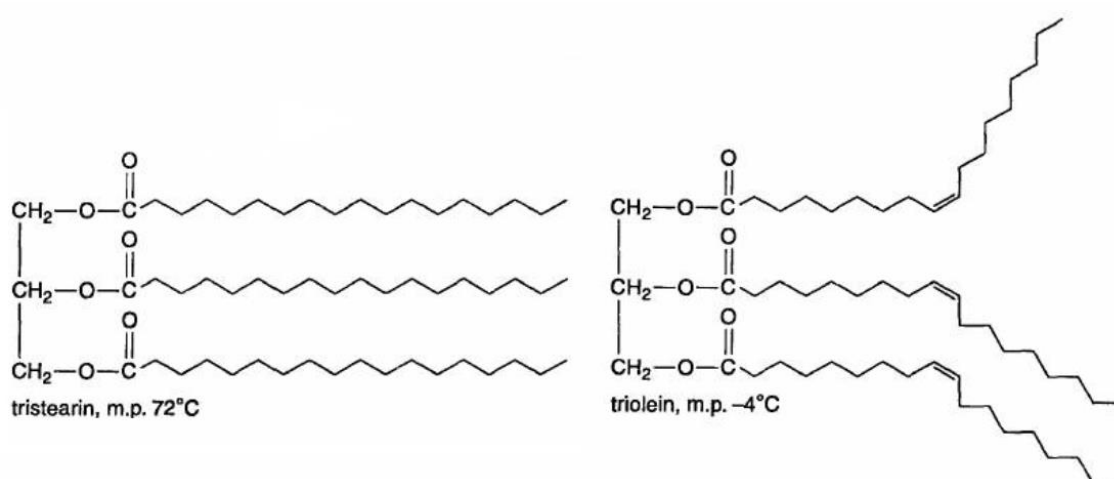
Usually the fatty acids of triglycerides are long, straight chain carboxylic acids with generally 12 to 20 carbon atoms. The number of carbon atoms is even when they are produced in biological system because they are formed from units which have two carbon atoms. Many naturally occurring fatty acids have two to three double bonds. Single triglycerides contains only identical fatty acids and mixed triglycerides contain different types of fatty acids. Single and mixed triglycerides are represented in Picture 4. (Singh 2010, 346)



Picture 4. Structures of a single and a mixed triglyceride. (Singh 2010, 347)

A fat or oil generally consists of a mixture of triglycerides instead of just one. For that reason the composition is often expressed as the percentage of different acids. The count of different fatty acids in different type of fat and oil sample vary greatly. Some have only one or two different acids with negligible amounts of other whereas for instance butter fat has at least 14 different acids. (Singh 2010, 347 - 348)

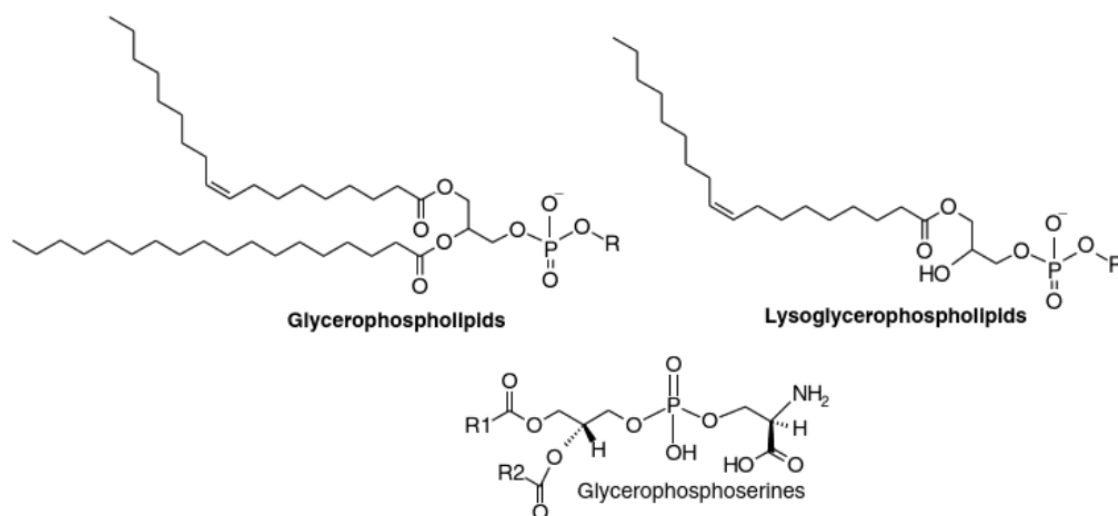
The melting point that divides triglycerides into fats and oils is defined by the saturation rate of their fatty acids. The melting points of unsaturated fatty acids are much lower than with saturated fatty acids and that applies to triglycerides as well: oil triglycerides contain more double bonds than fat triglycerides and thus have lower melting points. Saturated fatty acid carbon chains tend to stay extended because it decreases steric repulsions with the methylene groups next to them. They also pack more efficiently into crystals causing higher van der Waals forces which is the reason for higher melting points. The cis configuration caused by double bonds bend the molecules and causes them to pack more loosely which reduces their van der Waals forces which results in lower melting points. (Singh 2010, 348) Example of saturated and unsaturated triglycerides are illustrated in Picture 5. Saturated tristearin has a melting point of 72 °C whereas unsaturated triolein has melting point of -4 °C.



Picture 5. Examples of saturated and unsaturated triglycerides and their melting points. (Singh 2009, 348)

Glycerophospholipids (or phospholipids) are compounds where a phosphate compound is attached to the other end of the glycerol and an unsaturated and a saturated fatty acid to the other end and the centre hydroxyl group. If the middle hydroxyl group is free and

there is a fatty acid in the other and phosphate group in the other end of the glycerol the compound is called lysophospholipid. The phosphate group may include other components covalently bonded for example nitrogen based molecules. Phospholipids have polar head which is hydrophilic and a non-polar tail which is lipophilic. Due to their amphiphilic nature they are a major component in cell membranes where they form permeable, fluid and elastic bilayers. Due to their tendency to form layers they are used as emulsifying agents and surfactants in chemical industry. Examples of phospholipids and a lysophospholipid are presented in Picture 6. (Kamal-Eldin 2013, 23 - 25)



Picture 6. Phospholipids and a lysophospholipid. (Kamal-Eldin 2013, 24)

3.3 Heat induced chemical reactions of fats and oils

The effect of heat on fats and oils is a studied subject in food industry. The common food industry processes where fats and oils are exposed to elevated temperatures are bleaching and deodorizing. Shortly put the principle of bleaching is adding absorbent clay to the material and then filtrating it through a pre-coated filter. The temperature range in bleaching is usually 80 - 160 °C. Bleaching removes colouring agents, soaps, metals, environmental contaminants and phosphatide residues. Deodorizing is a vacuum distillation process and it is used to remove undesired odour and flavour components. The temperature range in deodorizing is usually 200 - 260 °C. (Hamm et al 2013, 56; Kamal-Eldin 2013, 95-97)

Some changes happen already in temperatures 80 °C - 160 °C at least with added bleaching clay but more significant alterations happen during deodorizing process at 200 - 260 °C. (Hamm et al 2013, 56) These alterations include hydrolysis, oxidation, interesterification, isomerization and polymerization. Hydrolysis is the breakdown of triglycerides into fatty acids, di- and monoglycerides. Hydrolysis occurs due to lipase activity and when triglycerides are exposed to heat and moisture. Oxidation is the incorporation of oxygen into the double bonds and it is induced by metals, air and heat. A peroxide is formed where the oxygen is attached and the peroxide decomposes into carboxylic compounds such as aldehydes and ketones. Interesterification is the reaction between esters of different molecules. It can be an exchange of an ester with other triglycerides, alcohols or fatty acids but it can also be a rearrangement of esters in the same triglyceride when it is also called randomization. Isomerization is the change from cis to trans form of fatty acids. The fatty acids can also change position under high temperatures or by activity of catalyst. Polymerization is the reaction where fatty acids bond together and form larger molecules. Polymerization needs double bonds to happen and it is usually coupled with oxidation reaction. (Kamal-Eldin 2013, 90 - 91)

There is not much published research or literature concerning fouling caused by untreated fats and oils, but according to R. W. Serth polymerization reactions causing fouling can occur when certain unsaturated organic compounds are heated or are exposed to a hot metal wall. The reaction products can form a very tough plastic-like deposit which can be extremely difficult to remove. (Serth 2007, 96)

4 FOULING TESTING

As it was stated in previous chapters, fouling situations are usually unique and it is risky to draw conclusions from common fouling knowledge. In literature there are few books completely addressed to heat exchanger fouling and the most reliable way to gain information about fouling tendencies of specific samples is to conduct experiments with suitable equipment in manufacturing plant scale, pilot scale or laboratory scale.

Fouling data from plants have challenges compared to more precisely controlled laboratory or pilot experiments. The drawbacks of using plant data is slower progression of work and the conditions and feed quality may vary more which complicates making scientific conclusions. However the data acquired from actual process has the actual time - temperature history of the sample and thus it represents the actual fouling in the precise situation most accurately. The good features of smaller scale equipment are that they provide results in more rapid fashion, offer more precise control over process and studied surfaces and deposits are often easily accessible for further studying. An ideal fouling equipment enables well controlled operating conditions that mimic the actual process conditions such as:

- Surface and bulk temperature
- pressure
- flow-velocity
- Reynolds number
- Shear stress
- once-through or recycled flow (Hewitt 2014, 51; Smith 2018, 4 - 6)

Fouling in testing equipment can be observed and assessed in various ways. The simplest method for measuring the extent of deposit is weighing it. This method requires detachable sample bed and an accurate balance, but small changes in deposit mass may be challenging to detect. The thickness of the deposit may also be measured if there is reasonable access to the deposit after experiment. The fouling resistance can be determined from the changes in heat transfer during fouling process. The requirements of this method are presented in more detail in chapter 5. The forming of deposit can also be assessed indirectly by monitoring developing pressure drop and then comparing the pressure drop curves. Accumulation of deposits can also be studied by using radioactive tracers and optical methods. (Awad 2011, 520 - 530) If the aim of the experiments is to

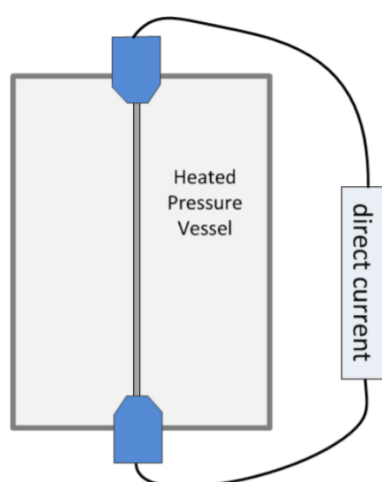
understand the particular process fouling mechanisms, the determination of chemistry, structure and physical characteristic of generated deposits is important (Hewitt 2014, 5).

4.1 Lab scale equipment

In crude oil research laboratory fouling testing has been recognized to be a valuable tool for studying the fouling tendencies of different crude oils and their blends. Even though the laboratory experiments do not completely correspond the real process conditions, they may provide useful information how the samples may react on heated surface. (Hewitt 2014, 66) For more real-process simulating test conditions there are pilot-scale fouling units available, but they are not included in this thesis. Principles and features of selected laboratory scale flow-monitor test equipment types are introduced in the following subchapters.

4.1.1 Hot-wire instruments

The working principle of hot-wire probe is that a rod or a loop is kept at the target temperature merged in studied substance. The hot rod acts as the fouling surface. A schematic illustration of hot-wire equipment is in Picture 7.



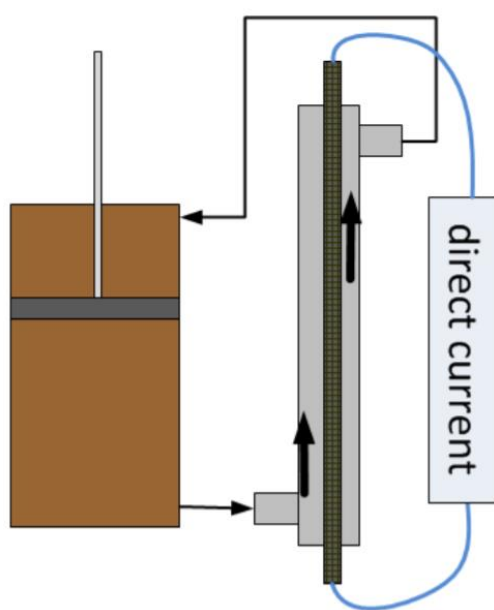
Picture 7. Hot-wire instrument (Smith 2018, 9)

Ideal features of this type of equipment is that run durations are usually short and the deposit is formed on external surface available for investigation after experiment. Non-

ideal features are that these are batch systems and if there is no flow or mixing it will cause particle settling and density variation due to natural convection. (Smith 2018, 9) A variety of these kind of equipment is widely used in laboratories (Sinčić, D. et al. 2015, 465). A modified version of a hot-wire instrument with a turbine stirrer is introduced in aforementioned reference. In crude oil fouling research some of the microbomb reactors working with similar principle require only 8 ml of sample (Hewitt 2014, 60).

4.1.2 Capillary instruments/Flow loops

Capillary instruments work so that a sample is pumped past a rod that is kept at a target temperature. The rod acts as a fouling surface. The fouling is observed as the change of overall heat transfer coefficient. (Alcor 2019, 3) schematic illustration of capillary fouling instrument is in Picture 8.

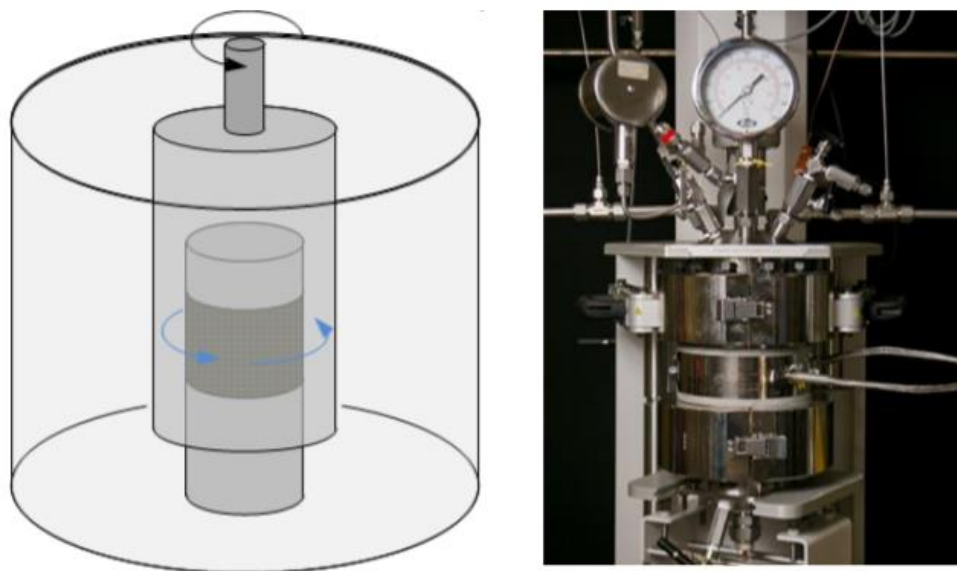


Picture 8. Capillary fouling instrument. (Smith 2018, 10)

Ideal feature of this kind of equipment is that they can provide in situ information how the fouling deposit forms and the rods are removable thus they can be comprehensively inspected after run. These kind of equipment also allow short run durations. Non-ideal features are deep laminar flow due to slow flow-rates and small flow path which may lead to clogging. (Smith 2018, 10) Examples of capillary fouling instruments are Alcor HLPS 400 and Falex 450 Thermal Fouler. (Alcor 2019; Falex Corporation B 2019)

4.1.3 Spinning cup instrument

A spinning cup instrument has a heated probe which is covered by a spinning cup which induces flow. A schematic image of spinning cup instrument is in Picture 9.



Picture 9. Spinning cup instrument. (Smith 2018, 11)

This type of instruments enables higher shear stresses than other laboratory scale instruments thus it may simulate actual process more precisely. The run durations can be kept short and the fouling surface is available for inspection after experiment. A non-ideal feature is that the equipment is batch system. (Smith 2018, 11; Hewitt 2014, 50)

5 EXPERIMENTAL PART

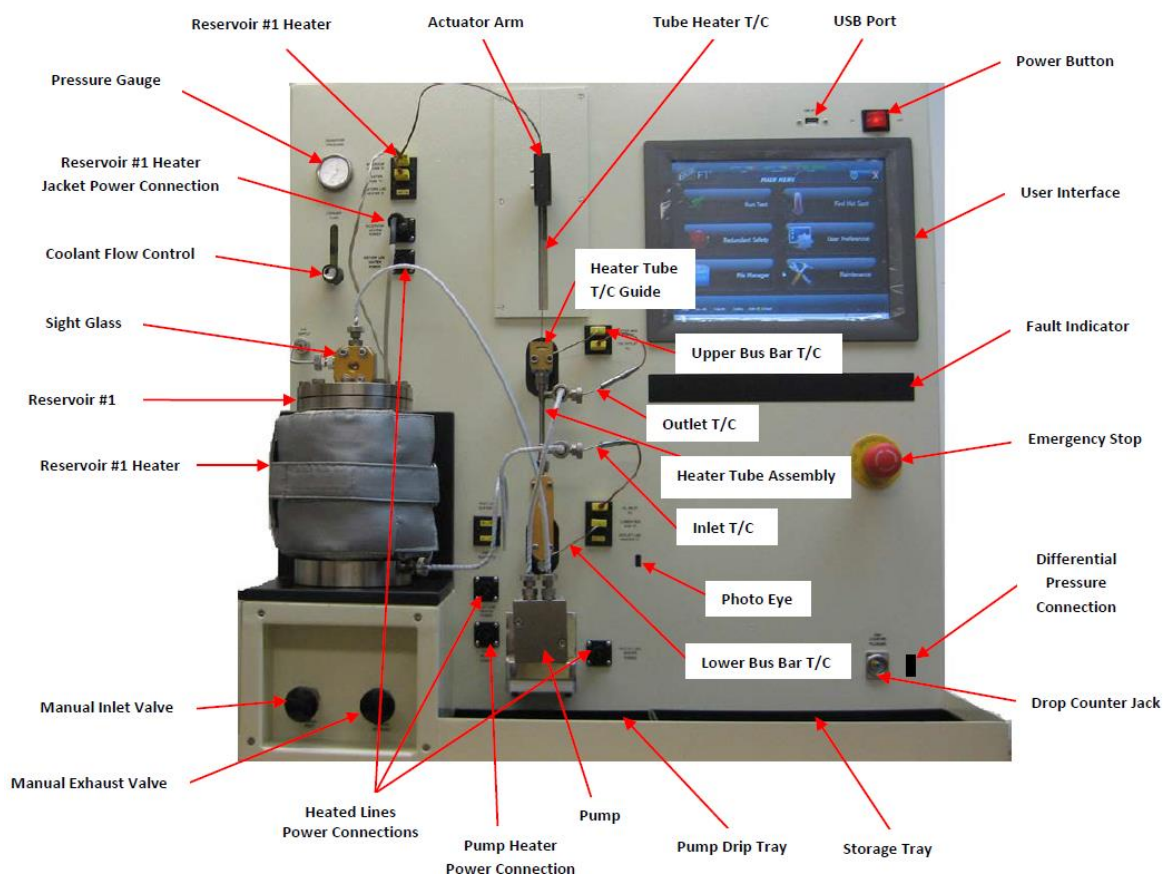
In the experimental part high temperature surface fouling caused by lipids was studied with a commercially available laboratory scale fouling equipment. The equipment was Falex 450 Thermal Fouling Test Machine (FT²) which is a capillary fouling instrument by Falex Corporation. The background of this study was that as new kind of feedstocks are processed in elevated temperatures it would be crucial to be able to predict their fouling tendencies. There had been unexplained fluctuation in measurements during previous test-runs with lipid samples. The fluctuation made results comparison difficult or impossible, thus a comprehensive insight was needed to find out whether the equipment could be reliably used to evaluate fouling tendency of lipid samples.

The fouling experiments included troubleshooting test-runs concerning the fluctuation, test-runs with different lipid qualities with different test parameters and modifications to the equipment and results calculations. The test runs were conducted in Neste Corporation's R&D center in Kilpilahti. The chemical analyses of liquid and deposit samples were carried out in Neste Corporation's R&D Research Analytics laboratory.

The emphasis of this thesis was on how to establish a reliable way to conduct fouling test-runs with lipid samples with the existing equipment. The fouling theory part of this thesis bears valuable information which phenomena affect fouling, how to interpret fouling graphs and what phenomena should be taken into account when planning fouling experiments. The chemical composition of fats and oils were presented on general level. In fouling experiments the amount of other compounds and impurities in samples might have a significant effect on fouling results which emphasises the importance of thorough knowledge of studied samples and comprehensive enough chemical analyses.

6 MATERIALS AND METHODS

The equipment used in the experiments was Falex 450 Thermal Fouling Test Machine (FT²) by Falex Corporation. The Falex 450 is designed to evaluate the coking tendency of process fluids in conditions where the flow is single phased (Falex Corporation, 8). The working principle of the equipment is following: The sample is pumped past a rod which is kept steadily at a target temperature. Temperature of the sample is measured before and after the rod. Possible foulants start to accumulate on the surface of the rod reducing heat transfer from the rod to the sample which is observed in decreasing outlet temperature as the run continues. An estimate of fouling tendency can be formed from decrease in outlet temperature, change in power requirement to keep the rod at target temperature and from physical deposit on the rod surface. (Falex Corporation 2019, 1) The Falex 450 and its functional parts are presented in Picture 10.



Picture 10. Falex 450 Thermal Fouling Test Machine (FT²) (Falex Corporation, p. 8)

The rods are kept at target temperature by electric current. The rods are available in different materials and stainless steel 316 was used in these tests because it corresponds most accurately to the materials used in industrial heat exchangers. A clean rod and a rod after run with fouling deposit are in Picture 11. The rods used in these experiments were mechanically cleaned with turning machine and abrasive paper before test runs.



Picture 11. A clean and a used rod.

The standard run mode was recycling mode where the sample is recycled back to the feed tank after it has passed the rod. The recycling mode allows longer run times with less sample and it is suitable for samples that foul less because of unlimited run time. The equipment can also be operated in once-through mode where the sample is collected to another container after it has passed the rod. This mode simulates real process conditions more precisely but the amount of sample and flow-rate set the limits for possible run times.

6.1 Data processing and calculations

The equipment collects time-stamped data during process from following subjects:

- Rod temperature (°C)
- Oil inlet temperature (°C)
- Oil outlet temperature (°C)
- Feed tank/reservoir temperature (°C)
- System pressure (psi)
- Rod temperature probe distance (mm)
- Rod current (A)
- Rod voltage (V)
- Rod power (W)
- Upper and Lower bus bar temperature (°C)

If fouling occurs the outlet temperature decreases during the run. The possible deposit layer insulates the rod from the bulk fluid so the rod current and power might also slightly decrease during a fouling test run but the rod temperature and other subjects stay stable during a successful test run.

The results of these experiments are reported in Fouling resistance (R_f , $\text{m}^2\text{K/kW}$), which indicates how much fouling resists heat transfer. The equation for R_f is

$$R_f = \frac{1}{U_{\text{dirty}}} - \frac{1}{U_{\text{clean}}}$$

Equation 2. Fouling resistance.

where U_{dirty} is overall heat transfer coefficient of fouled heat exchanger surface and U_{clean} overall heat transfer coefficient for clean surface. (Theodore, L. 2011. p. 271) The results could also be viewed in Fouling rate (dR_f/dt , $\text{m}^2\text{K/kW/h}$) which describes how fast fouling resistance increases. The advantage of using fouling rate is that comparison between results could be done by comparing a single output value but the drawback is that fouling rate applies only for linear type of fouling.

In order to calculate R_f , the overall heat transfer coefficient must be calculated which can be done by applying basic heat flux equations:

The basic equation for heat flux through a plane wall is

$$Q = UA\Delta T$$

Equation 3. Heat flux through a wall.

where Q = total heat flux, U = overall heat transfer coefficient, A = surface area and ΔT = mean temperature difference driving force, which was logarithmic mean temperature difference (LMTD) in the case of this thesis. (Theodore 2011, 262, 269) The heat flux can also be calculated from mass flow, heat capacity and temperature change

$$Q = m C_p (T_o - T_1)$$

Equation 4. Heat flux.

Where Q = Total heat flux, m = mass flow, C_p = heat capacity, T_o = temperature at start point, T_1 = temperature at end point. (Texas gateway, 2019)

With the equipment the overall heat transfer coefficient was calculated with the Equation 5 induced from Equations 3 and 4.

$$U = \frac{m C_p (T_0 - T_1)}{A \Delta T}$$

Equation 5. Overall heat transfer coefficient.

The cross-sectional area of the flow channel in used equipment was rather modest thus a deposit layer on the surface has an impact on the surface velocity on the rod. The increase in surface velocity on rod was not taken into account in the calculations. The increased surface velocity may cause the R_f values increase as the outlet temperature decreases because the sample has less contact time with the hot surface.

6.2 Flow properties

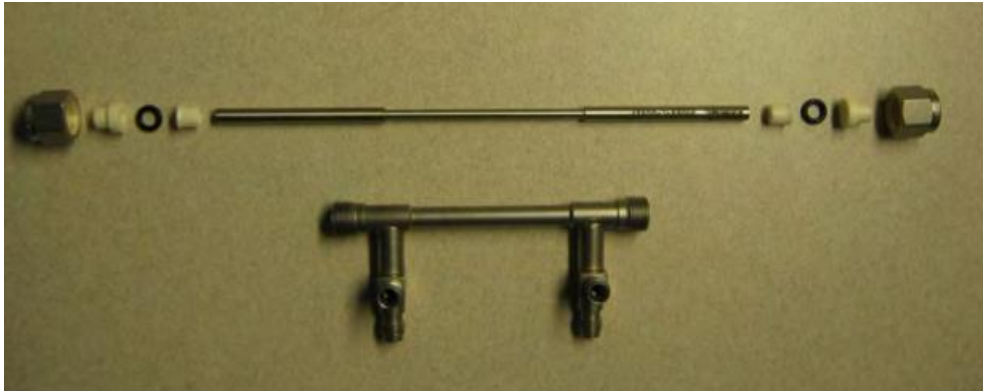
The outer diameter of the heat exchange rod was 3,175 mm and the inner diameter of the pipe was 5 mm. Therefore the distance from the rod surface to the pipe surface was 0,91 mm and the cross-sectional area was 11,7 mm². As the cross-sectional area of flow channel and velocity of fluid was remarkably small the Reynolds numbers remained very low which indicate that the flow was deeply laminar.

Here is an example of Reynolds number at 330 °C with standard flow-rate of 0,6 g/min. The Equation 1 is for Reynolds number in a pipe. In these calculations the cross-section area is considered to have a shape of a circle although in practice it had the shape of a ring due to the rod inside the pipe. The density value is from Lipico's palm oil properties chart (Lipico 2019) as it was known to have similar properties. The density value is taken from temperature of 215 °C because that is approximately the outlet temperature in the beginning of run at 330 °C. In practice the fluid temperature in pipe is higher because it has time to cool down in the uninsulated pipe until it meets the outlet temperature probe. Reynolds number with aforementioned assumptions for a lipid test run at 330 °C with flow-rate of 0,6 g/min is:

$$Re = DV\rho/\mu = 0,00193 \text{ m} * 0,001 \text{ m/s} * 870 \text{ kg/m}^3 / 0,0021 \text{ Pa*s} \approx \mathbf{0,8}.$$

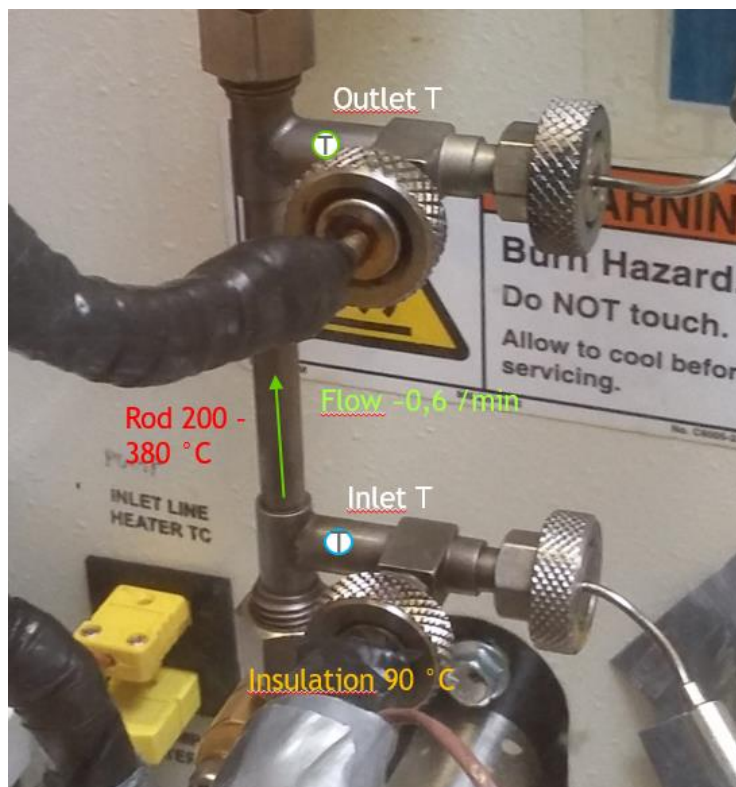
Reynolds number values over 2100 indicate turbulent flow in a pipe (Theodore 2011, 30). With the parameters used in this thesis it can be assumed that the flow was completely laminar. Actually the Reynolds number would have been even smaller

because the shape of the flow-channel is narrower in ring than circle shape. A rod, the pipe and assembly parts are presented in Picture 12.



Picture 12. A rod, the pipe and assembly parts. (Falex Corporation B 2019, 28)

The rod and piping are behind a plexiglass screen when the test-runs are conducted. It is a safety issue but the plexiglass screen also keeps the temperature more stable than regular room air. The temperature inside the plexiglass screen is higher than room temperature as the equipment heats it. Closeup of the assembled rod, piping and probes are presented in Picture 13.



Picture 13. Assembled rod, piping and probes.

The temperature of the surroundings affects the measurements to some extent and some of the heat is transferred to the air since the pipe where the probes are is not insulated. The head of the temperature probes are close to the rod but not attached to it. It was observed that if a test run clogged so severely that the total flow rate decreased, the inlet and outlet temperature decreased. This happened because the sample had more time to cool down before reaching the temperature probes. In test runs with higher flow-rate it was observed that inlet temperature and outlet temperature were both higher than with runs with slower flow-rate with the same temperatures.

6.3 The methods of chemical analyses

The chemical analyses of samples were performed in the Neste Corporation's research analytical laboratory. The analyses and the Neste Corporation's internal methods are in Table 1.

Table 1. Chemical analyses and methods.

Liquid samples	
Analysis	Method
Density (kg/m ³)	ENISO12185
Nitrogen (ppm)	ASTMD5762
Metals (ppm)	NM553-B
Phosphorus (ppm)	NM553-B
Sulphur (ppm)	NM-380
Glyceride distribution (%)	NM494
Solid samples	
Crystalline compounds, x-ray diffraction	NM411
Elements (wt%), x-ray fluorescence	NM411
Compounds, infrared spectroscopy	FT-IR ATR

Density analysis is based on the change of oscillation frequency caused by the change of mass in a tube. A sample is introduced into an oscillating sample tube and oscillation frequency change is compared to calibration data to determine the density of the sample. (Neste A 2019)

The used nitrogen method is based on chemiluminescence. The sample is combusted in high temperature and nitrogen is oxidized to nitric oxide in an oxygen atmosphere. The nitric oxide is converted to excited nitrogen dioxide by ozone. Excited nitrogen

dioxide emits light as it returns back to the lower state of excitement. A photomultiplier measures the emitted light and turns it into a signal which is converted to nitrogen content. (Neste B 2019)

Metals and phosphorus concentrations were analysed with ICP-MS technique (inductively coupled plasma mass spectrometry). The sample is ionized and atomized by inductively coupled plasma. The formed atomic and polyatomic ions are detected with MS detector. (Neste D 2019)

Sulphur was determined by a x-ray diffraction method. The measurement is based of wavelength dispersive x-ray fluorescence (Neste E 2019).

Glyceride distribution analysis tells the estimated portions of different type of glycerides in total amount of glycerides. The components are fractionated by their size (hydrodynamic volume) with a GPC-HPLC equipment. The fractionated compounds are monoglycerides, diglycerides, triglycerides, oligomers and free fatty acids. Oligomers are molecules with size bigger than three C22:0 fatty acid containing triglycerides. The results do not tell the absolute amount of glycerides but the distribution of compounds with similar size. (Neste F 2019)

X-ray diffraction is based on how x-ray photons scatter from different atoms. XRD is suitable for determining crystalline components and crystal size from solid samples. Amorphous samples, low quantities and wide peaks interfere identification. This method is not quantitative. (Neste G 2019)

Infrared spectroscopy is based on the vibrations of the atoms in a molecule. An infrared radiation is passed through a sample and the absorbed fractions of the particular energy are measured. The absorption peaks in spectrum corresponds to the frequency of sample molecules vibration and the compound is identified. (Stuart 2004, 2) Attenuated total reflection (ATR) spectroscopy is based on the phenomenon of total internal reflection. A special electromagnetic wave called the evanescent wave is formed on the other side of the reflecting surface during total internal reflection. An absorbing material in contact with totally reflecting interface absorbs some of the evanescent wave and the intensity of reflected light is attenuated compared to the incoming light. (Milosevic 2012, 5) This method was used to identify which compounds the fouling deposits were consisted of. This method is not quantitative.

7 EXPERIMENTAL DESIGN

There were two main goals for this study: first was to investigate the reason for measurement fluctuation and could it be eliminated and the second was to study how reliable the results are with lipid samples. Different qualities of a specific lipid type, run modes and process variables were tested. Changes in the chemical composition of samples after run were studied by analysing metals, phosphorus and glyceride distribution of selected samples before and after run. The deposits were studied with infrared spectroscopy and X-ray diffraction after detaching them from the rods. The rod condition after mechanical cleaning was studied with an electron microscope and two test runs were conducted with brand new rods to see if the rod condition affects fouling.

7.1 Feed samples

The samples used in these experiments were Neste Corporation's lipid samples. The lipid type and one pretreatment method are confidential information so the samples are referred as Lipids and the treatment as X-treatment. The feed samples and their metals and phosphorus concentrations are shown in Figure 4.

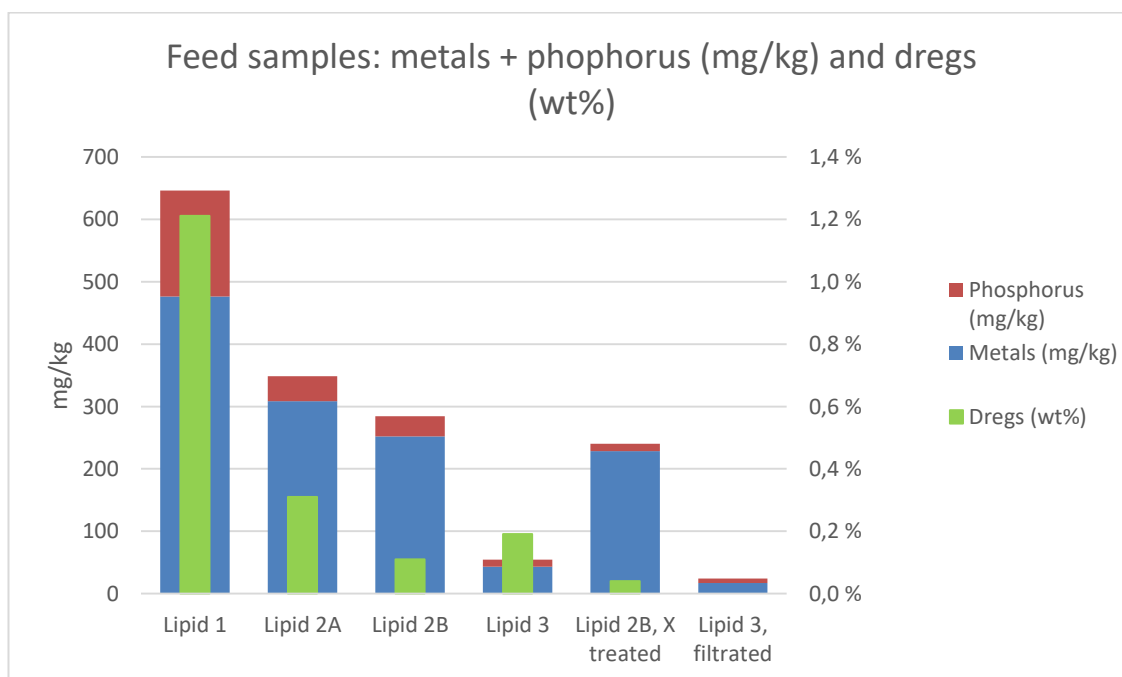


Figure 4. Feed samples and their metals and phosphorus concentrations.

The Lipid 1 sample was untreated. The Lipid 2A and Lipid 2B were collected from a larger scale process. There was supposed to be only one Lipid 2 sample but during test runs it turned out that the Lipid 2A contained isopropanol remains. The isopropanol interfered the test runs so another Lipid 2 sample was collected and named as Lipid 2B. The Lipid 3 sample was untreated. In addition to these untreated samples test runs with X-treated Lipid 2B and filtrated Lipid 3 were also conducted.

The Lipid 2A and Lipid 2B samples were supposed to be untreated but it was later discovered that some settling had happened with Lipid 2B. In addition to settling there were possibly some oxygen and VOC removal in Lipid 2B as some of the sample bottles were collected after process step where the sample was held in vacuum conditions. The oxygen or VOC concentrations were not analysed but studies indicate that dissolved oxygen can lead to gum formation and fouling at least with hydrocarbon fouling literature (Hewitt 2014, 25; Watkinson 2009, 1).

7.2 Test parameters

The test parameters can be saved in equipment memory. The parameters used in the experiments are presented in Table 2.

Table 2. The standardly used test parameters.

Test options	Overall parameters	Startup Sequence
Reservoir Heat: 90 °C	Tube Material: 316 Stainless	1. Pressure
Line Heat: 90 °C	Heat Ramp Up Time: 10 min	2. Reservoir heat
Singe Pass (Res.#2): OFF	Cool Down Time: 30 min	3. Purge
Conduct Profile #1: OFF	Pump Rate: 3.00 %	
Conduct Profile #2: OFF	Purge Time: 3 min	
Differential Pressure: OFF	System Pressure: 219 PSI	
Hot Spot Override: OFF	Test Duration 18 h	

Feed tank (reservoir) and lines were kept at 90 °C to keep the sample in liquid form. The flow-rate during test was determined by pump settings. The chosen pump output was 3,00 % which translated to a flow-rate of 0,6 g/min with the studied samples. The correlation between pump outputs and the actual flow-rates was also determined in this thesis and the results are represented in chapter 7.4.1. The system was pressurised to 219 PSI with nitrogen to keep the possibly evaporating components in liquid phase. The test duration was 18 hours with recycling and once-through mode with flow-rate of 0,6

g/min. With the faster flow-rates in the once-through experiments the test time was only 3,5 - 4 hours due to the feed tank size of 1000 ml.

7.3 Conducted experiments

The conducted experiments in recycling mode are presented in Table 3.

Table 3. The experiments conducted in recycling mode.

Sample	Run mode: recycling				
	200 °C	250 °C	290 °C	330 °C	380 °C
Lipid 1	1*		2*	1* + 1	
Lipid 2A	2*	3*	1*		
Lipid 2B		2	2	2* + 3	1
Lipid 3			1	2** + 3	1
Lipid 2B, X-treated			1		1
Lipid 3, filtrated				1	

*Magnetic stirrer in feed tank

**New rod

Five different temperatures were selected based on previous experience to produce different levels of fouling. There was a magnetic stirrer under the feed tank that was used to stir the samples and prevent settling during run but it was disabled after some test runs due to issues it caused. The test runs with stirring are marked with asterisk. The experiments were conducted with mechanically cleaned rod by default. The cleaning with turning machine and sand paper is quite rough so a new and mechanically cleaned rods were photographed with electron microscope to see if the surface was different. Two test runs were conducted with brand new rods to see if the difference in surface properties affect fouling. The runs with new rods are marked with two asterisks.

The equipment can be run in once-through mode where the sample goes to another container after the rod. The advantages of once-through mode is that it simulates real processes more precisely and in this equipment allows more accurate flow monitoring by placing a scale under the product tank and logging the weighing results. The flow monitoring in recycling mode was rather suggestive: flow was observed by counting drops that were seen through a small glass window. The experiments run in once-through mode are presented in Table 4.

Table 4. Once-through experiments

	Run mode: once through	
	290 °C	330 °C
Lipid 1	1*	1*
Lipid 3		1+1**

*faster flowrate

**Scale for flow monitor

In faster flow-rate experiments the flow was four times faster than in default runs. These fast flow experiments were conducted with the Lipid 1 sample. In one run with the Lipid 3 sample a scale was installed under the product tank to monitor pump consistency and actual flow-rates during run.

7.4 Preparations before experiments

Before experiments were started certain procedures were executed to ensure as precise measurements as possible. Grounding cables were installed to the equipment. Actual sample flow rate was determined with different pump settings. The spot where rod temperature should be measured was determined. The results calculation formula was adjusted to be more precise and suitable for lipid samples.

7.4.1 Actual flow rate determination for different pump output settings

The flow-monitoring with the equipment is based on frequency of drops that are observed through a glass in return line to the feed tank when the equipment is running. The method is quite robust and it does not provide totally precise values with different samples.

A more accurate flow rate determination with different pump outputs was conducted so that the temperature of feed tank, lines and pump was set to 90 °C as they were used in the experiments. The sample was pumped to a decanter glass for 2 minutes and weighed after that. The procedure was conducted with 5 different pump output values with 2 repetitions in each point. The results are shown in Figure 5.

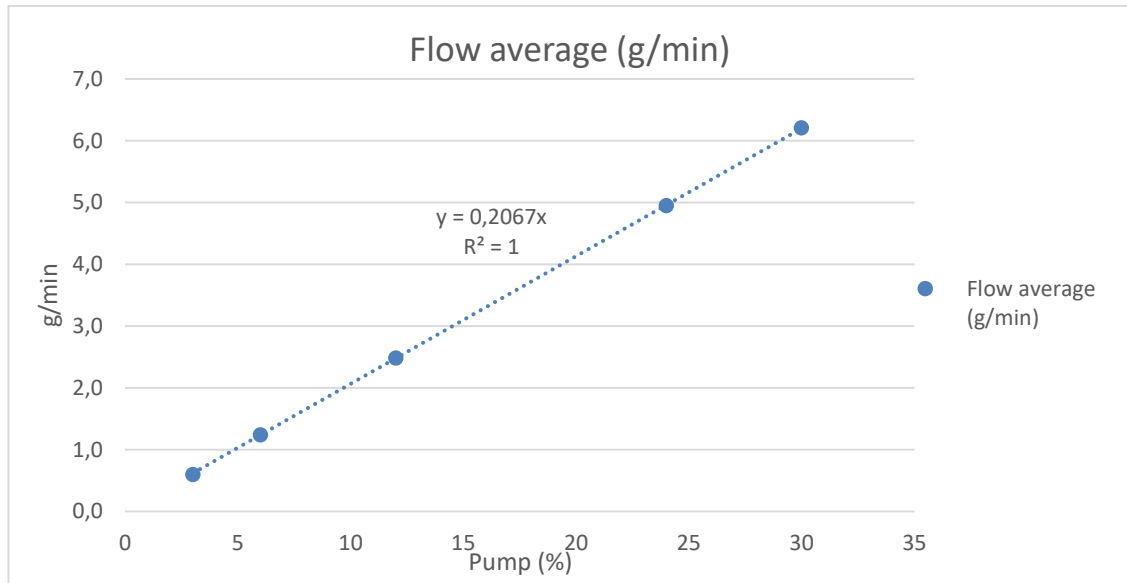


Figure 5. Pump output value and measured flow rate with lipid sample used in the experiments.

The repetitions were very similar and the flow rate is very linear with the pump output value. The pump output used in the experiments was normally 3 % and 12 % for two experiments with faster flow-rate. 3 % translated to a flow rate of 0,6 g/min and 12 % to 2,5 g/min. Surface velocity on rod was 1 mm/s with 3 % and 4 mm/s with 12 %.

7.4.2 Hot spot determination and validation

The equipment has a test program with fixed parameters for detecting the position where the rod temperature should be measured. The fixed parameter tests are hot spot determination and hot spot validation and they are approved by Society of Automotive Engineers International and their standard tag is SAE ARP5996. (Falex Corporation, 34) These run modes ensure that the test results are as reliable as possible. In the hot spot determination test the equipment determines the temperature measurement spot of the rod to the position where temperature is highest. The temperature profile of rod is created so that the actuator arm moves a thermocouple inside the rod during the test and measures the temperature at different heights. After the hot spot determination test the position with highest measured temperature will be used in further tests. (Falex Corporation, 95)

The hot spot validation test ensures that the hot spot determination test result is correct and it should be performed every time after hot spot determination test or any time when the hot spot location is questioned (Falex Corporation, 83 - 84). Hot spot determination and validation tests were conducted before the actual test runs were started and the results are shown in Figure 6.

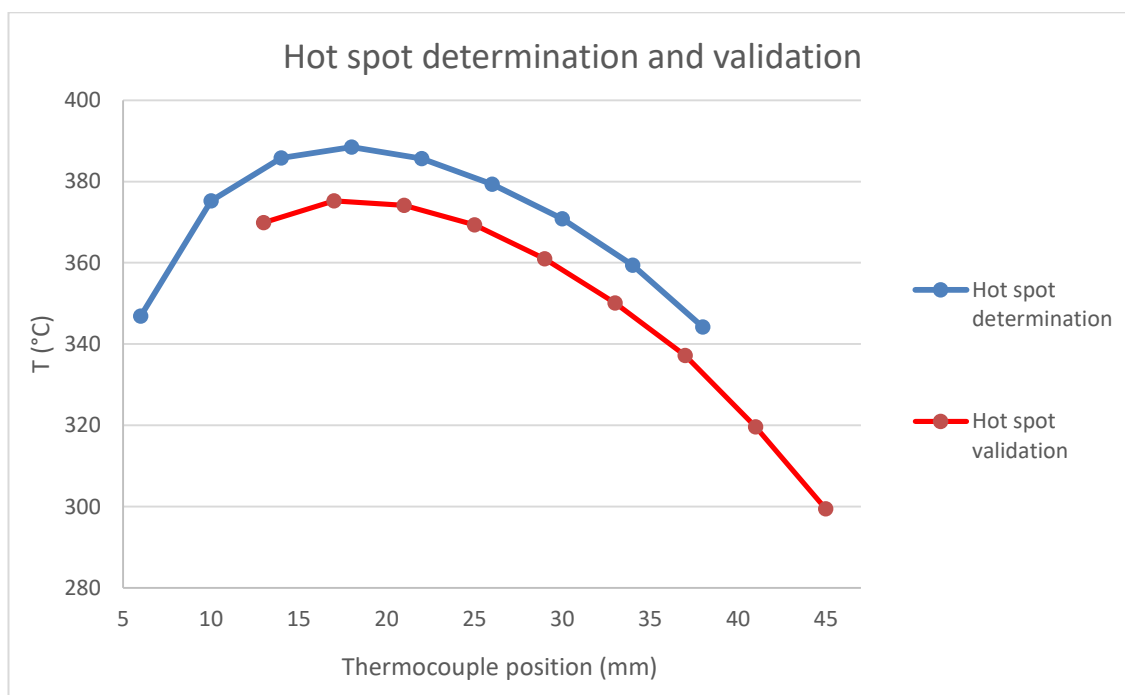


Figure 6. The hot spot determination and validation results.

The determination and validation for stainless steel (316) rods were conducted 23.5.2019. The used liquid was Conostan Base Oil 75 cST. The highest temperature was in thermocouple position 17 mm.

7.4.3 Adjustments to results calculation

As the equipment had been mostly used to study fouling of hydrocarbon samples the heat capacity C_p value before these test runs was set to suit hydrocarbon samples so it was needed to be changed to get more precise R_f values. The heat capacity values for the used lipid in different temperatures were unknown so Lipico Technologies' values for palm oil was used in the calculations because the chemical properties of palm oil are rather similar. (Lipico Technologies, 2019)

Temperature affects samples heat capacity value. The overall heat transfer coefficient equation was changed so that the heat capacity value was calculated with more precise values in every data point whereas in previous calculations the temperature affecting the heat capacity was taken from the first measurements. The densities of different feed samples were known and the mass flow value for every sample was calculated from the flow rate experiments with actual densities for every sample.

8 RESULTS

The results section is divided into different chapters. The fluctuation issue and the solution is introduced first. Additional feed characterization, fouling results and chemical analyses results are introduced in the following subchapters.

8.1 The measurement fluctuation issue

The fluctuation occurred as a sudden change in the temperature measurements and in the tube current and power. Before the thesis test runs were started a grounding cable was installed to the equipment. It seemed to have a reducing effect on the fluctuation but it did not eliminate it completely. The severe and sudden fluctuation was discovered to be caused by the magnetic mixer under the feed tank although the mechanism of the fluctuation remained unclear. The magnetic stirrer was not an original part of the equipment. After the stirrer was decommissioned the sudden and severe fluctuation did not occur any more. Due to this the earlier test runs of this thesis were conducted with stirrer and the latter test runs without it. Besides these sudden and notable fluctuations in measurements there was also some subtle swaying in temperature measurements in some runs without stirrer.

The ultimate reason for the notable fluctuation remained unclear. Possible explanations are interference caused by static electricity produced by moving sample or magnet, interference caused by electromagnetic induction (spinning magnet) or a defective stirrer. A prominent feature in the fluctuation was that it occurred only with higher temperatures. This could be caused by the higher currents in rod and the equipment. One possibility for sloughing to happen only with stirrer is that there would be some components that form softer deposit and they settle in the feed tank without stirring. Though there would happen that kind of sloughing it would not explain how the outlet temperature increased higher than it was in the beginning of the run in some cases. The results that proved the fluctuation caused by the mixer are presented in Figure 15 in chapter 8.6 where 5 repetitions were made with same sample and parameters so that the mixer was used in 2 of them and decommissioned in 3 of them.

In the test-runs the actual flow-rate was not monitored in runs where the severe fluctuation took place so there is no information available how the pump functioned

during the severe fluctuation. It was noticed that change in flow-rate causes change in outlet and inlet temperature measurements. However the flow monitor was enabled in a test-run where occurred prolonged swaying within 1-2 °C and the pump flow was constant. The reason for prolonged swaying also remained unclear and it could possibly be studied by measuring the surface temperature of the pipes with auxiliary thermometer to find out if the changes in temperature are real or also interference in measurements.

8.2 Feed sample analyses

It was known that even trace quantities of impurities or fouling compounds may have pronounced effect on fouling rates (Bott 1995, 188). Metals and phosphorus concentrations were analyzed for every feed sample and they were presented in Figure 4 in chapter 7.1. Sulphur and nitrogen contents were analyzed of every sample except filtrated Lipid 3 and sulphur from Lipid 2B and they are presented in Figure 7.

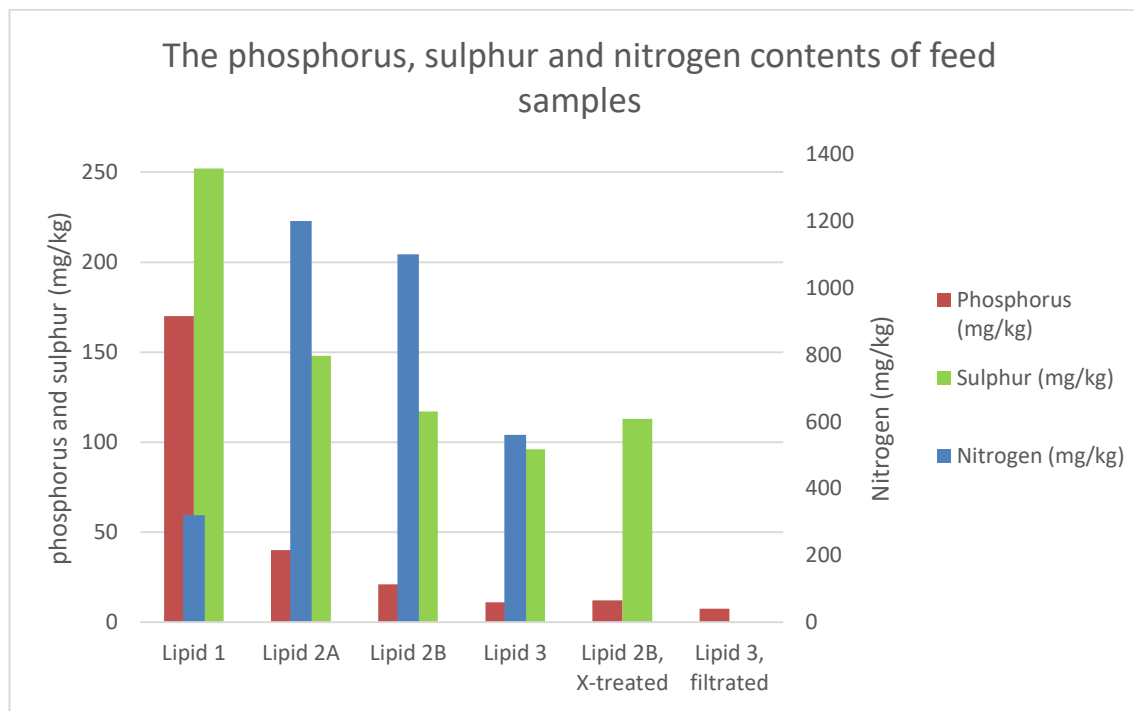


Figure 7. Phosphorus, sulphur and nitrogen content of feed samples.

8.2.1 Dregs content and composition (IR)

Common knowledge in fouling theory suggests that solid particles in bulk sample increase fouling (Awad 2011, 506). The dregs contents are presented in Figure 8.

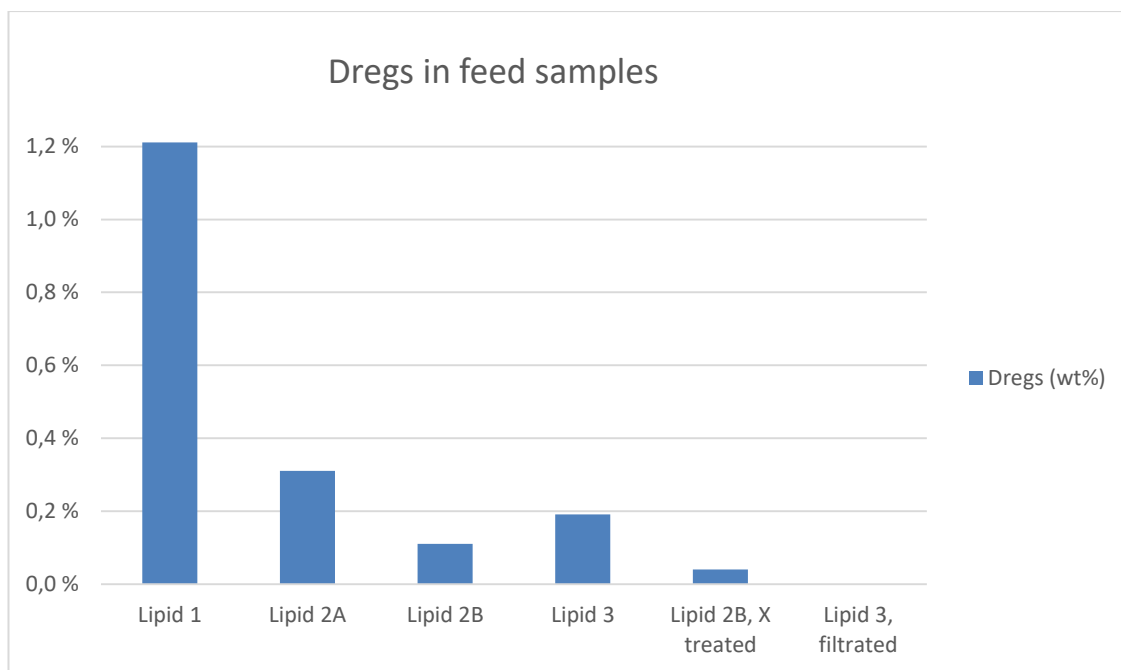


Figure 8. Dregs amount of feed samples.

Dregs contents were measured by centrifuging approximately 400 grams of samples with 4300 rpm for 30 minutes in 85 °C. After centrifuging the flasks were dried upside down for 30 minutes in 85 °C to let the remaining fat drain from the bottles. Then the bottles and dregs were weighed and the dregs amount were calculated from the mass of centrifuged sample.

The samples Lipid 2B and X-treated Lipid 2B had had a spontaneous settling which decreased the dregs content. The filtrated Lipid 3 sample did not have any dregs which indicates that the used filtration method was very effective in removing dregs. The dregs from sample Lipid 1, Lipid 2B and Lipid 3 were analysed with IR. The IR analysis was conducted so that fat-soluble components were removed with heptane and IR spectra were measured from both the fat-soluble and insoluble fractions.

- Lipid 1 dregs IR results:

Heptane-soluble material: (67 wt%) partly unsaturated high molecular weight carboxylic acid esters and phospholipids. Heptane-insoluble material (33 wt%) contained mostly proteins and small amounts of carboxylic acid salts.

- Lipid 2B dregs IR results:

Heptane-soluble material (72 wt%): partly unsaturated high molecular weight carboxylic acid esters, free carboxylic acids and phospholipids. Heptane-insoluble material (28 wt%): proteins.

- Lipid 3 dregs IR results:

Heptane-soluble material (96 wt%): partly unsaturated high molecular weight carboxylic acid esters and some free carboxylic acids. Heptane-insoluble material (4 wt%): proteins.

8.3 Lipid 1 fouling results in recycling mode

The results are not in chronological order because the experiment plan was modulated as some problems and surprising results occurred during the work. The results are reported in fouling resistance (R_f , $\text{m}^2\text{K/kW}$) which means higher the value the more fouling there was. The Lipid names are abbreviated to L# in figures. The single numbers in the legends of graphs are the numbers of the repetition experiment.

The Lipid 1 was run in recycled mode and in once-through mode with faster flow-rate. The Lipid 1 was selected to be run in faster flow-rate in once-through mode because it was known to cause abundant fouling and increase in flow-rate is generally known to decrease fouling. The fouling results of Lipid 1 in recycling mode are presented in Figure 9.

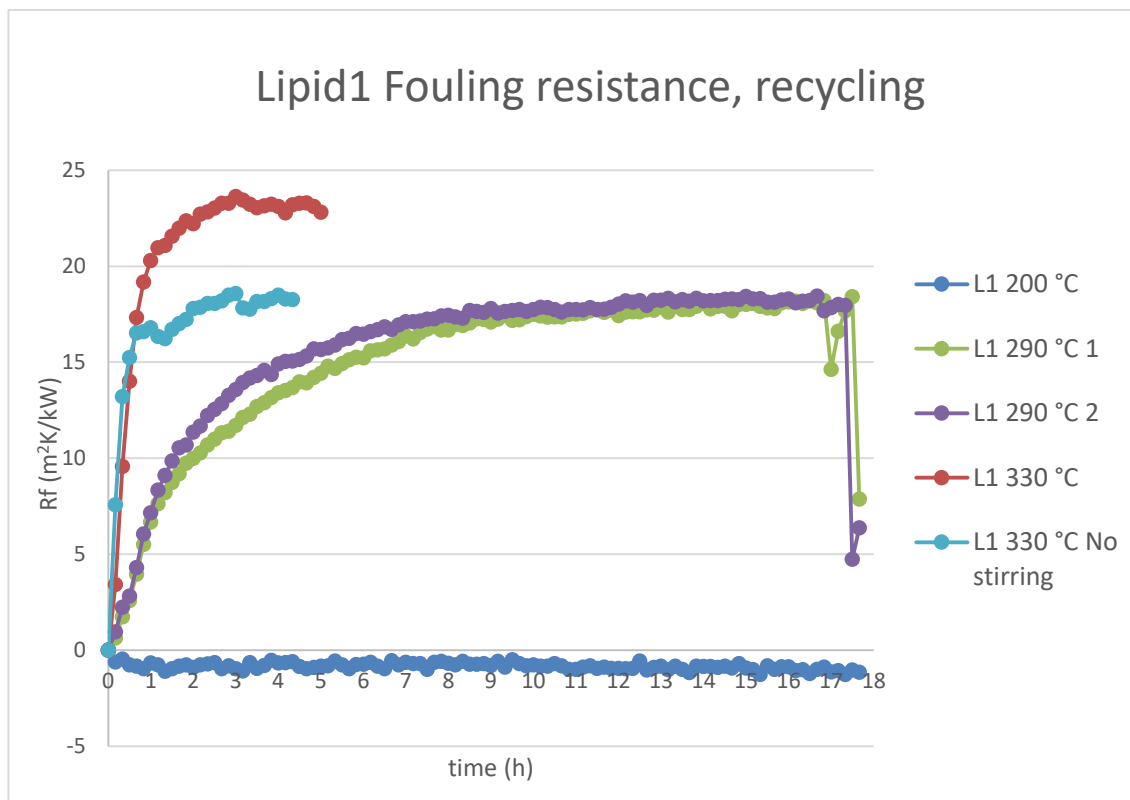


Figure 9. Lipid 1 fouling results in recycling mode.

At 200 °C there was practically no fouling. There was some colour on the rod but it did not affect heat transfer. The R_f (fouling resistance) gives negative values after start because the outlet temperature slightly increased after the first used data point and then stayed roughly at the same value. At 290 °C there was so abundant fouling that the foulants formed a thick deposit cake and the R_f graph took the asymptotic shape. The fouling rate started to decelerate after 60 minutes probably because the surface of the deposit cake was not as hot as the bare rod or then the deposit started to detach more. It seemed that the earthing cables reduced the fluctuation in temperature measurements but at the end of both runs conducted at 290 °C there were sudden unexplained increases in outlet temperature which is seen as drastic decrease in R_f .

There were two runs conducted at 330 °C with Lipid 1: one with stirrer and one conducted later without a stirrer. The sample seemed reach the state where the fouling had ceased faster than at 290 °C. At 330 °C the cake was so thick that the pipe got clogged in both runs after 4 - 5 hours. The pipe was not completely clogged but decrease in total flow-rate and changes in inlet temperature were observed. The values shown in Figure 9 are calculated from values before clogging was observed. These results indicate that stirring

increases fouling possibly because stirring prevents settling in feed tank and that phenomenon was also observed with other samples when comparing results with and without stirring. The Lipid 1 330 °C runs were only runs where clogging occurred so severely that decrease in total flow-rate was observed in the end of the run. In these runs the inlet temperature started to increase and outlet temperature started to decrease after the steady state. It is not exactly known when the flow-rate started to decrease but it could be interpreted that decrease in overall flow-rate in causes outlet temperature to decrease because the sample has more time to cool down before temperature probe and inlet temperature simultaneously increase probably because more heat is conducted from the rod to inlet temperature probe.

The Lipid 1 results in fouling rate (dR_f/dt) are presented in Figure 10.

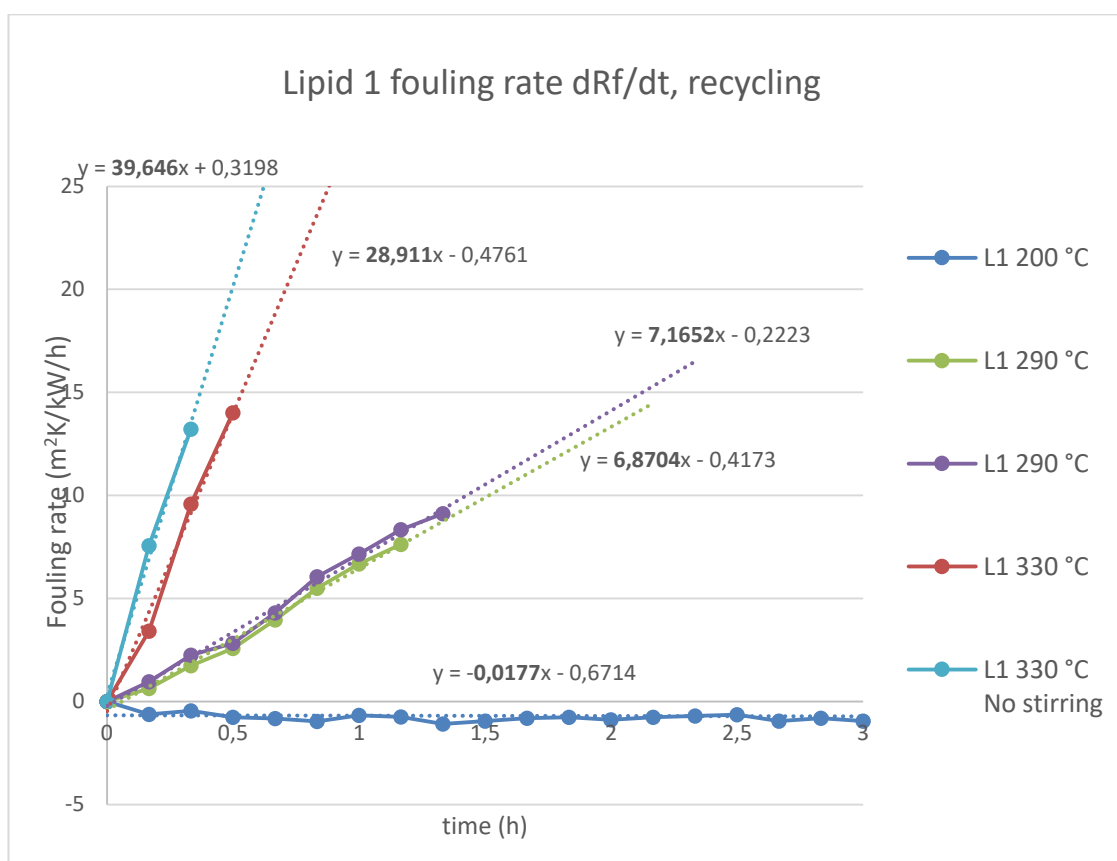


Figure 10. Fouling rates of Lipid 1 tests in recycling mode.

The fouling rate approach is safe to use if the fouling results are completely or mostly linear. With these values fouling rate is calculated only with the linear part of the graphs. It is suggested to review the whole graphs if the R_f graphs are not linear. At 330 °C the run with no stirring seems to foul faster than run with stirring although it reached lower

R_f values at the asymptotic state than the run at 330 °C with stirring. The faster initiation time could have been caused by difference in rod condition or then the settling components that enhance fouling concentrate on the bottom in the beginning of the run whereas they are more evenly distributed with stirring. However the pipe to the rod is not completely on the bottom of the feed tank thus the settling components settle under it when the settling is complete which explain why the runs with no stirring reach lower R_f values in the end run.

8.3.1 Lipid 1 fouling results in once-through mode with faster flowrate

In these tests the pump setting was 12,00 % which translates to a flow-rate of 2,49 g/min, which is approximately four times faster than in the other experiments in this thesis. The sample velocity on rod surface was 4,1 mm/s with this flow-rate whereas it was 1 mm/s with the flow-rate of 0,6 g/min. The amount of sample used was 800 grams and the run-times were 3,5 hours and 4 hours. The magnetic stirrer was disabled in these experiments as it was discovered to cause the interference in measurements in other experiments before these. The Lipid 1 fouling results in once-through mode with faster flow-rate are presented in Figure 11.

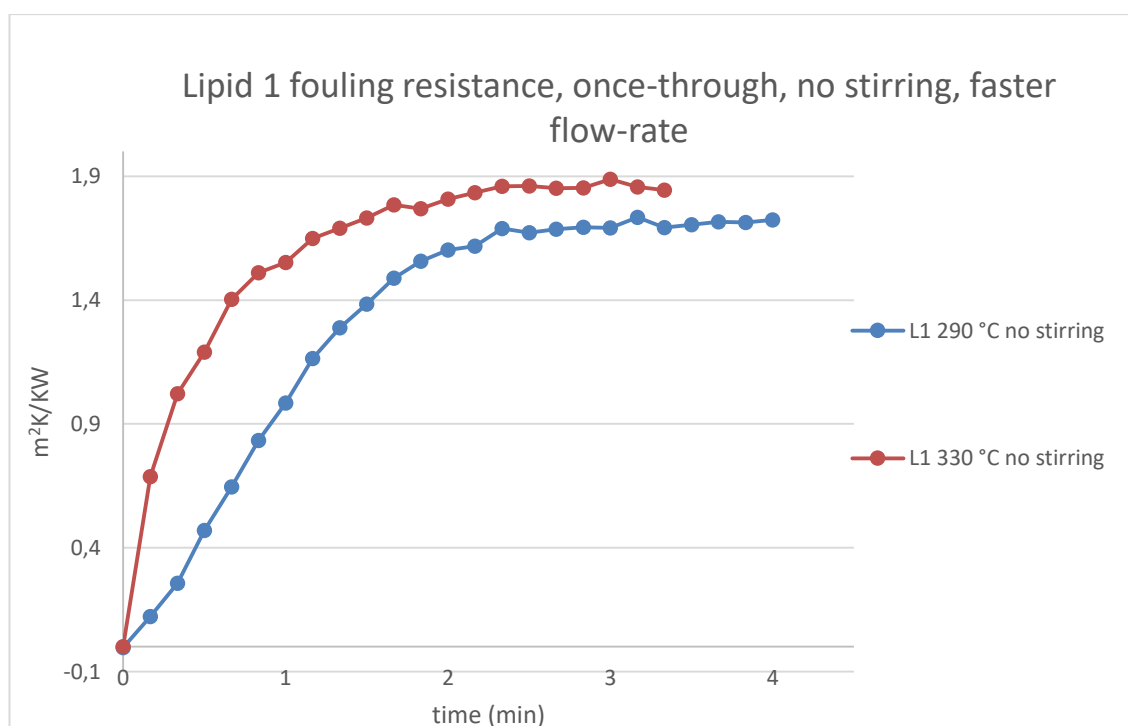


Figure 11. The Lipid 1 fouling results with once-through mode with faster flow-rate.

The 290 °C result is not totally comparable to the Lipid 1 290 °C recycling mode results as there was stirring in recycling mode experiment at 290 °C. At 330 °C the linear part of the R_f graph is shorter than in recycling mode with slower flow-rate. The shapes of R_f graphs are quite similar with these parameters and recycling-mode with slower flow-rate as they both reach the asymptotic state concerning fouling rate but the most significant difference is that the growth of fouling deposit ceases at much lower R_f value than in the slower flow-rate experiments. The deposit cakes were rather modest and their constitution was quite delicate comparing to experiments with slow flow. Pictures of rods and deposit cakes after slower flow in recycling mode and fast flow in once-through mode are shown in Picture 15.



Picture 14. Rods and deposit cakes after run at 290 °C with slow flow rate in recycling and faster flow-rate in once-through mode.

The slow flow rate Picture is quite dark but it can be seen that the cake is so thick that the flow channel is almost clogged whereas the deposit layer with faster flow-rate is very thin. This clearly indicates that the foulants are very flow-rate sensitive since higher flow-rate with increasing shear-stress prevent the foulants to attach the surface. The deposit structure was rather soft in both cases and most of it detached during gentle solvent rinse after weighing. Nevertheless, these results indicate that the equipment is suitable for samples with high fouling tendency if the parameters are right.

8.4 Lipid 2A fouling results in recycling mode

The Lipid 2A was contaminated by isopropanol which was not known when these test runs were started. Several test runs were conducted because some of them seemed to be valid and the occurred surprising results were thought to be caused by unsolved electrical issues. The stirrer was used in all of these experiments. The Lipid 2A fouling results in recycling mode are shown in Figure 12.

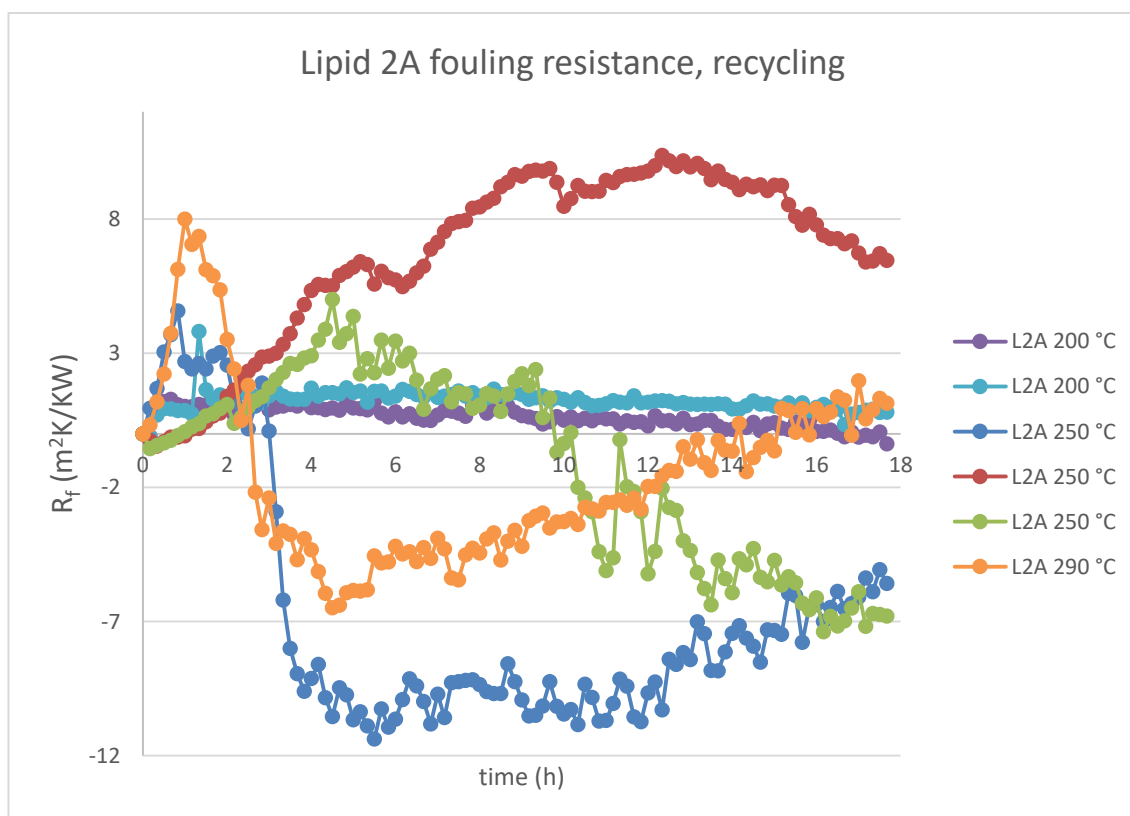


Figure 12. Lipid 2A fouling resistance results in recycling mode.

The runs at 250 °C were conducted first. The red graph run had no severe and sudden fluctuation in measurements but the temperature was swaying strangely. The R_f value should never decrease during a successful run. After that run earthing cable positions were changed to nearer the pump but the fluctuation seemed to have gotten worse in the next run. More earthing cables were installed to different parts of the equipment but the results were undesired. The runs at 200 °C seemed quite valid so it was thought that the fluctuation might be caused by some evaporating components that stay in liquid phase at temperatures lower than 200 °C but evaporate at 250 °C in spite of pressure of 219 PSI.

The results indicate that sample with evaporating components can be run with the equipment if the temperature and pressure are at levels where sample or components will not evaporate. The manufacturer states that the maximum operating pressure of the equipment is 1000 psi (68,9 bar). It was tried to pressurize the equipment up to 650 psi but the pressure leaked out thus the 219 psi was highest pressure used.

Nevertheless the equipment could be used to study evaporating samples but then the evaluation of fouling tendency could only be based on the amount and type of deposit on the rod because the outlet temperature measurement sways heavily. The amount of attached foulants can be measured by weighing the deposit after run. In this method a heavier deposit means higher fouling tendency. The type of deposit can be studied by chemical analysis of the deposit sample and by investigating how the deposits detach from the rod for example by scraping it with a spatula. Different fouling mechanisms cause different kind of deposits. For example particulate fouling cause softer deposits whereas crystallization fouling might produce very hard deposits (Awad 2011, 506).

There are two possible explanation for increase in outlet temperature when evaporation occurs: firstly the evaporated steam might go past the temperature probe faster after it has evaporated thus transferring the heat more efficiently versus the situation where the liquid slowly flows past the temperature probe. Because of the slow flow-rate the sample cools down after the rod before temperature measurement. Secondly, the evaporated sample might condensate back to liquid phase on surfaces giving heat energy where the condensation takes place.

8.5 Lipid 2B and X-treated Lipid 2B fouling results in recycling mode

This sample was partially settled which was concluded by the method it was collected and seen in the dregs results in Figure 8. Stirring was disabled in these experiments as it was discovered to cause interference in measurements. The Lipid 2B fouling resistance results are presented in Figure 13.

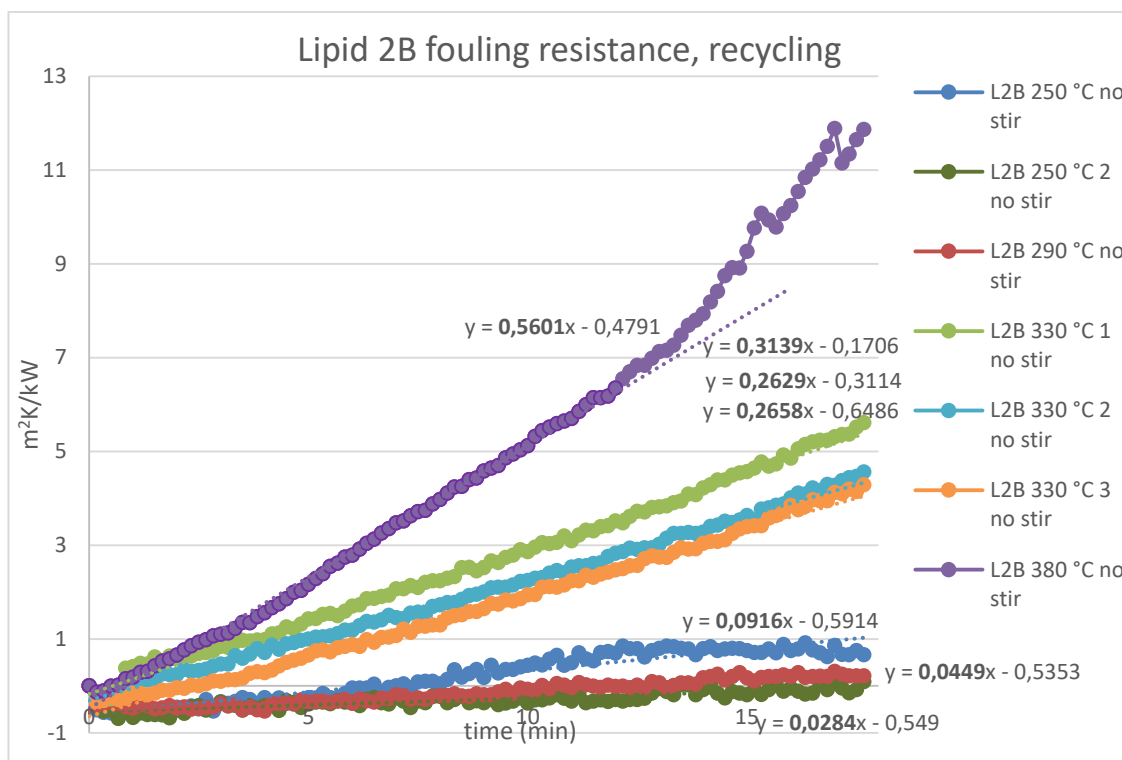


Figure 13. Lipid 2A fouling results in recycling mode.

Two test runs were conducted at 250 °C. Both runs did not foul in the beginning of the run but the fouling resistance started to increase for unknown reason in the other run but then it settled to a quite stable value instead of continuing to foul. The results indicate that this sample fouled very slightly if at all at the temperature of 290 °C.

Three repetitions were made at 330 °C. The slopes of the graphs are quite similar but there is variance in the R_f value the different runs reach after 18 hours. One of the runs at 330 °C seems to have a sudden increase in fouling in the beginning of the run. That could be caused by a rougher rod or another external variable. The difference in the R_f end value between runs 330 °C 1 and 330 °C 3 is $1,3 \text{ m}^2\text{K}/\text{kW}$. The difference in fouling rate dR_f/dt between was $0,051 \text{ m}^2\text{K}/\text{kW}/\text{h}$.

At 380 °C the fouling rate was linear for the first 13 hours but then it started to increase. A possible reason for this could be a chemical reaction taking place and forming fouling precursors in bulk fluid as it is exposed to high temperatures when moving past the rod. In recycling mode the sample goes past the rod and is returned to the feed tank so the possible fouling precursors will have a chance to get in contact with the rod again. Another explanation for increase in fouling rate is that the deposit layer could be rougher in higher temperature thus enhancing fouling. The outlet temperature had two

unexplained increases in the end part of the run. However they were not as rapid or severe as the fluctuation that occurred with stirrer. The increase in fouling rate during run at temperatures of 380 °C in recycling was observed also with sample X-treated Lipid 2B.

Comparison between Lipid 2B and X-treated Lipid 2B results are presented in Figure 14.

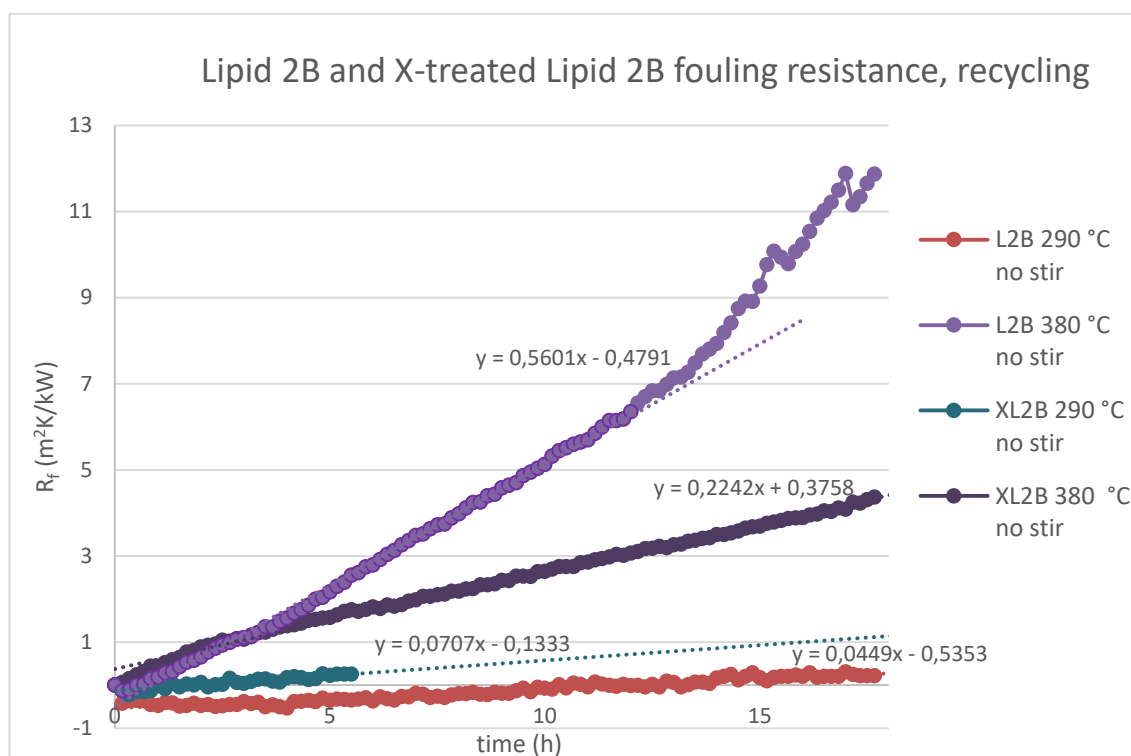


Figure 14. Comparison between Lipid 2B and X-treated Lipid 2B results.

At 290 °C the run with X-treated Lipid 2B was aborted after 5 hours because the pressure leaked from the equipment. That run seemed to have linear R_f graph so the trend line in Figure 14 was continued to 18 h. According to these results the X-treated Lipid 2B seemed to foul more at 290 °C than Lipid 2B which was against exceptions but it was seen that repetitions with same sample and parameters varied more than 1 m²K/kW in the end of the run value thus it is assumed that fouling tendency of these samples is quite equal at 290 °C.

At 380 °C the Lipid 2B fouled more than twice as much as X-treated Lipid 2B. That was excepted since the X-treated Lipid 2B was X-treated and more settled than Lipid 2B and it contained less metals, phosphorus and dregs.

8.6 Lipid 3 and filtrated Lipid 3 fouling results in recycling mode

The difference between using the stirrer and not using the stirrer was discovered with the Lipid 3 sample. Fouling resistance results with and without stirring at 330 °C are presented in Figure 15.

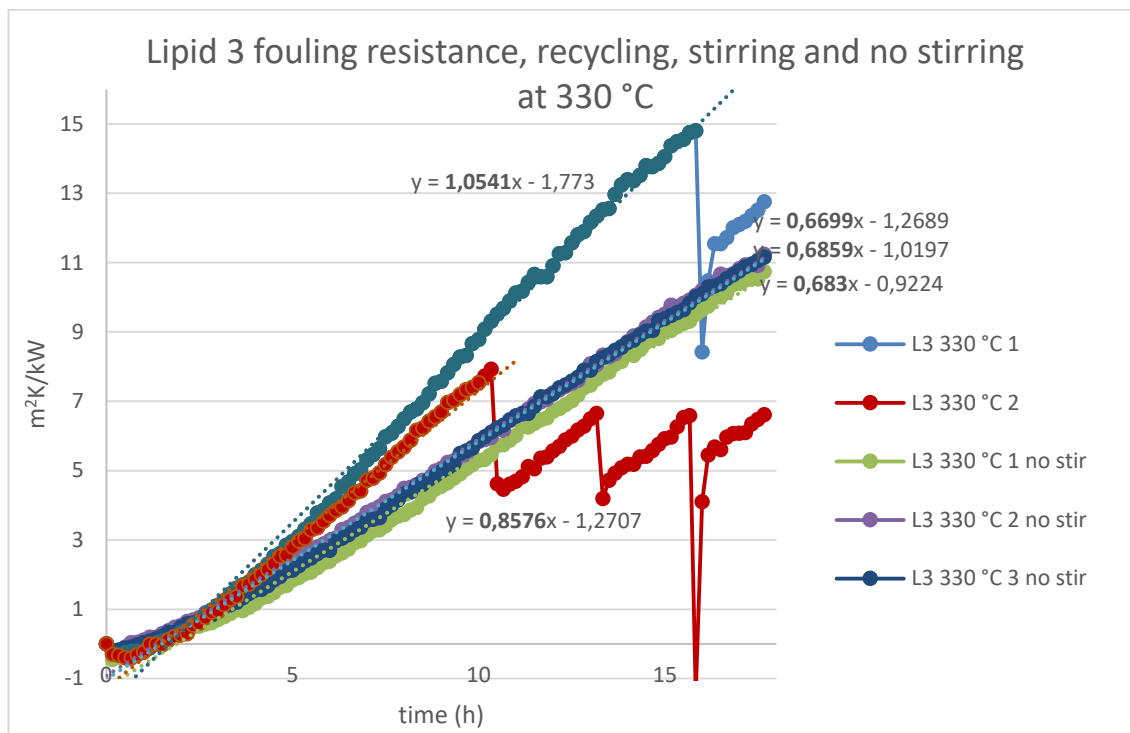


Figure 15. Lipid 3 sample fouling resistance results at 330 °C with and without stirring.

All five runs are conducted in the same temperature. The results clearly indicate that stirring increases fouling and causes sudden and significant increase in outlet temperature and interference in other temperature measurements. After these 5 test runs the mixer was disabled and the sudden significant increases in outlet temperature measurements did not occur. The results also show that stirring increases fouling probably because it prevents settling.

One theory about the fluctuation was that it was caused by deposit sloughing during test-runs. Nevertheless that seemed not to be the case, because in L3 330 °C 2 the outlet temperature increased to a higher level that it was in the beginning of the run which is seen in the R_f graph as well. That should not be possible because the rod should have had become suddenly cleaner or more heat conducting than it was in the beginning. In this particular case the tube current also increased, but it increased the rod temperature

only 1-2 °C for a short period of time which does not explain the notable increase in outlet temperature. The data screen of this run (L3 330 °C run 2) is in appendix 1. In this example it was seen that during the fluctuation peak the inlet temperature first slightly increased and then decreased and stayed lower than before the fluctuation. That is controversial because the inlet temperature is not affected by the deposit cake and it should only increase if tube temperature increases because the heat transfers to the inlet temperature probe by conduction. Also the deposit cake looked smooth and not cracked after the runs and there were no solid chunks seen in the liquid samples.

It was also discussed if the possible electric interference could have interfered the pump controller causing the pump to change its output. From data of faster flow-rate experiments it was concluded that faster flow-rate increases outlet temperature and inlet temperature values compared to slower flow rate because the piping is not insulated before temperature probes and the sample has less time to cool down before probes. Thus a sudden increase in flowrate would increase the outlet and inlet temperature but that seemed not to be the case in this example because the inlet temperature did not increase and stay higher as the outlet temperature. An increase in flow-rate would also probably decrease fouling rate whereas it remained quite similar after the fluctuation.

The rest of the Lipid 3 results in recycling mode and filtrated Lipid 3 results are presented in Figure 16.

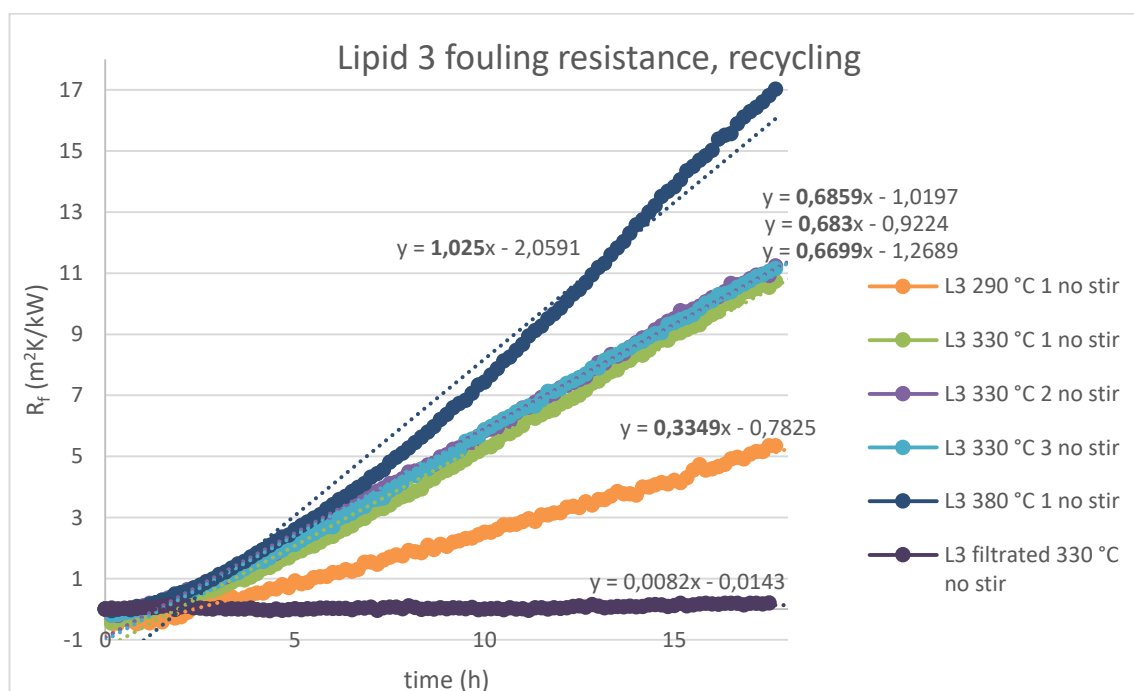


Figure 16. Lipid 3 and Filtrated Lipid 3 sample results in recycling mode.

At 330 °C three repetitions were run and repeatability was excellent. At 380 °C there was no noise in measurements and the sample reached higher R_f value than with lower temperatures. The fouling rate seemed to increase during run at 380 °C which may indicate that some fouling precursors fouled during recycling or then the composition of cake is different at higher temperatures because the graphs were more linear in lower temperatures. Filtrated Lipid 3 sample caused no fouling at all at 330 °C. All in all the Lipid 3 fouled more than Lipid 2B in every temperature which indicates that removing dregs by settling decrease samples fouling tendency. The result that filtrated Lipid 3 did not foul at all at 330 °C verifies that removing dregs and reducing other impurity levels in a sample decreases its fouling tendency.

8.6.1 Lipid 3 fouling results in once-through mode

In these experiments a scale was installed under the product container for more accurate flow monitor. The fouling resistance results are presented in Figure 17.

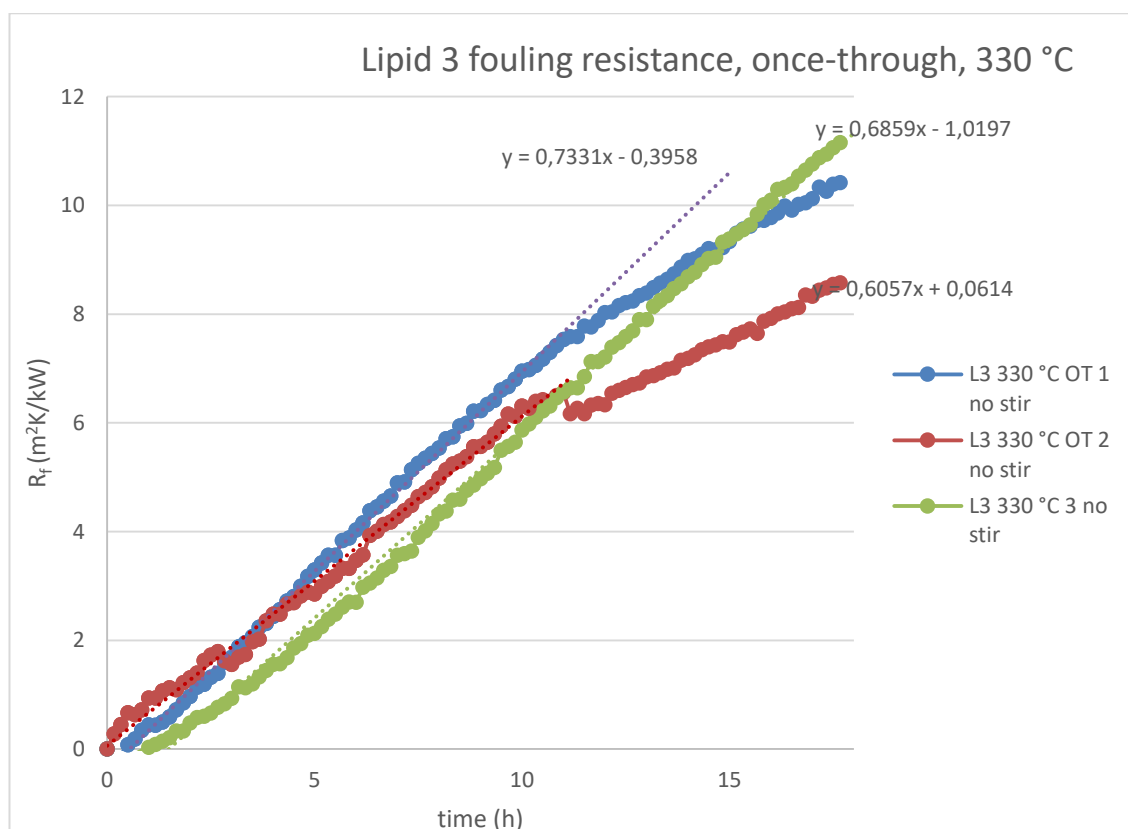


Figure 17. Lipid 3 fouling resistance results with once-through mode.

Two repetitions were made at 330 °C in once-through mode. The gray graph is for comparison between recycling and once-through mode. The results indicate that a sample fouls less in once-through mode at least without stirring. In recycling mode the fouling rate is linear but once-through mode the fouling rate started to decrease approximately after 10 hours. This might be caused by more effective settling in once-through mode. In recycling mode the sample is recycled back to the feed tank from the top which keeps the possibly easily fouling dregs, possibly formed fouling precursors and other fouling components on the move more than in once-through mode. The rods after run were also dirtier with recycling mode so the decreasing fouling rate in recycling-mode was not caused by rod insulating fouling cake. The fouling rate value comparison for the linear parts show that the fouling rate is quite equal before it starts to decrease with once-through mode.

The measurements were swaying in the once-through run 2 as seen in Figure 17. The data screen of all measurements from that run is in appendix 2. It was suspected that unstable flow-rate causes the subtle swaying in temperature measurements. However that was not true at least in this run. The flow-rate measured with scale under the container and inlet temperature are presented in Figure 18.

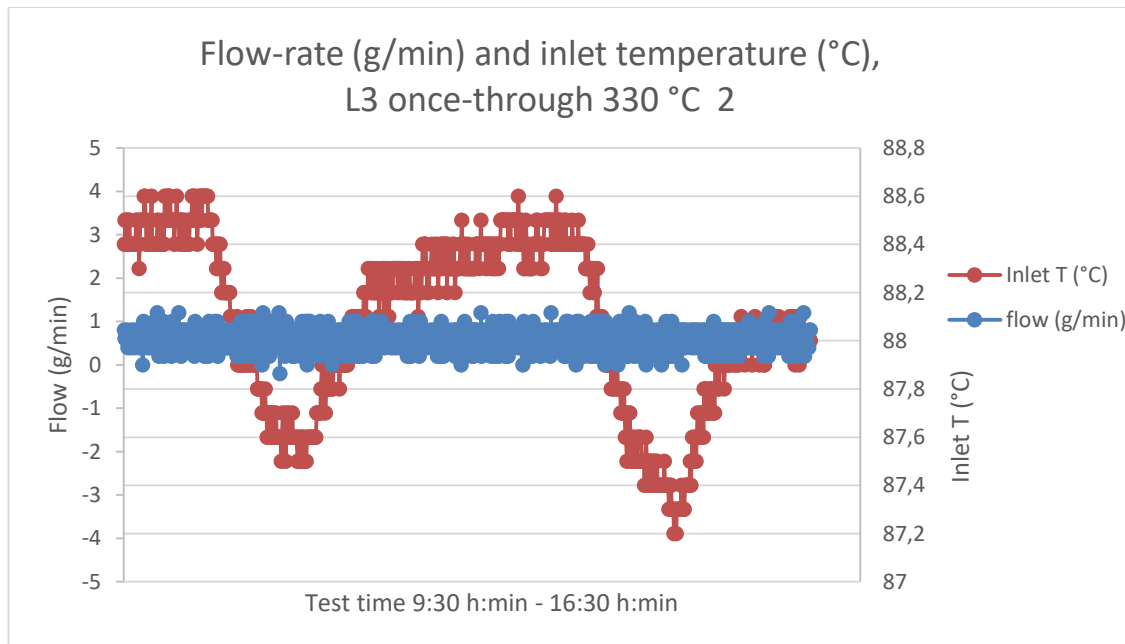


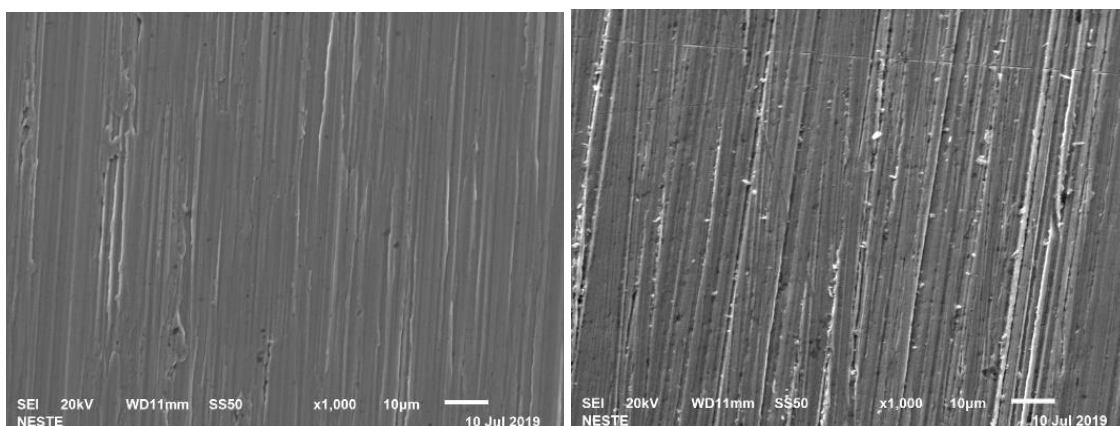
Figure 18. Flow-rate and inlet temperature during L3 once-through °C run 2.

The flow-rate was calculated from product mass once in every 30 sec. The graph indicates that there was no systematic change in flow-rate during the changes of inlet

temperature thus the swaying is caused by something else than change in flow-rate. The flow-rate average was 0,6 g/min for that run.

8.7 The effect of rod condition on fouling

The rods used in these experiments were cleaned in turning machine with sandpaper and solvent. Conditions of a new and a cleaned rod were photographed with an electron microscope. The 1000x magnification of a new and a cleaned rod is in Picture 16.



Picture 15. New and a cleaned rod in 1000x magnification. A new rod is on left side and a cleaned rod on right side.

The cleaned rod seemed clearly more rugged than the new one. The possible effect of rugged surface was tested with Lipid 2B sample so that two runs were conducted with a new rod and three runs with a cleaned rod in same temperature. The results are presented in Figure 19.

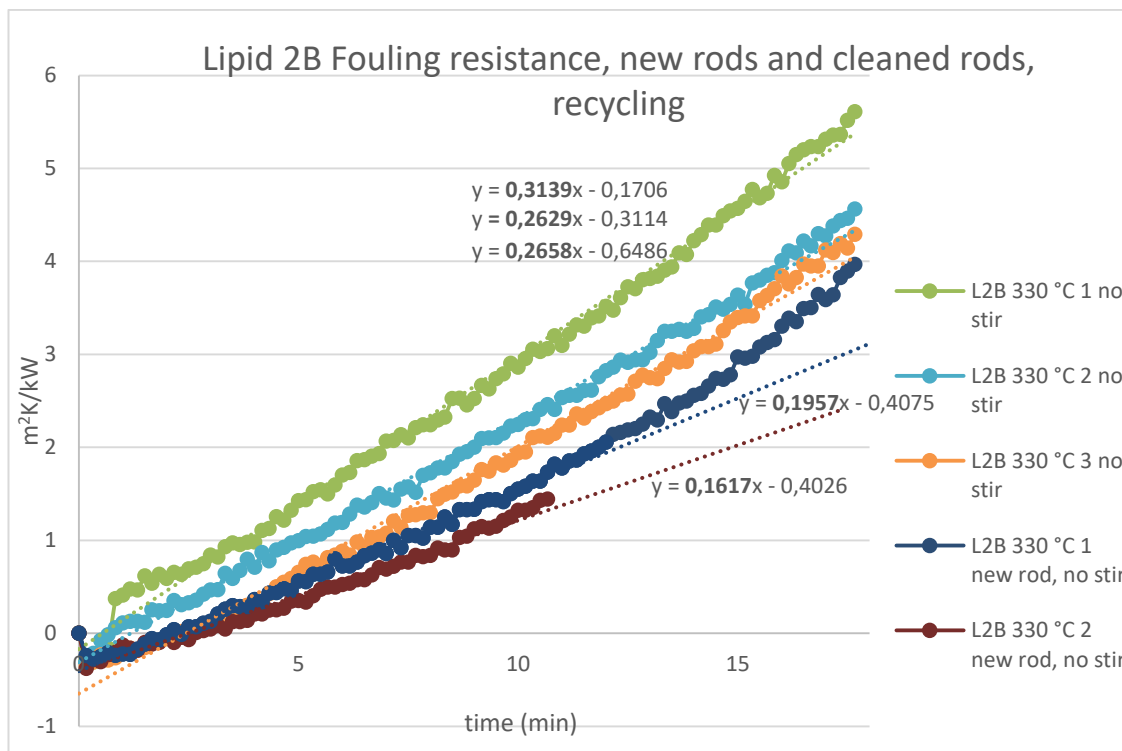


Figure 19. Comparison between new rods and cleaned rods with Lipid 2B at 330 °C.

As the rods were cleaned with semi rough abrasive paper without any subtle finishing treatment the ruggedness of rods might have varied a bit. In runs 1 and 2 with cleaned rods the fouling rate was faster in the beginning of the run whereas in run 3 it was on similar level with new rods. The faster fouling rate in the beginning could have been caused by difference in rod condition but then again that kind of variance was not recorded with other samples so it might also been caused by swaying in outlet temperature. In the beginning of run 1 the decrease in outlet temperature was 1,3 °C which caused 0,65 increase in R_f value. The fouling rates in the beginnings of runs with new rods were slower than with cleaned rods but the fouling rate seems to increase after halfway in run 1 with new rod. The pressure leaked during run 2 and this phenomenon was not confirmed with another repetition. The shapes of the graphs with new rods are slightly more curved than with the clean rods. These results indicate that cleaned rods might start to foul with faster fouling rate and foul slightly more.

In fouling literature it is stated that cleaned and reused surfaces have usually shorter initiation time in fouling. (Awad 2011, 512) In this case there was no difference in initiation time as the new rods started to foul immediately when the run was started but the fouling rate was slower than with cleaned rods with the exception of run L2B 330 °C 3. As the

rod conditions were not inspected in detail before runs it might be that the rod was smoother in that run than the with the other cleaned rod runs. However in the other experiments with cleaned rods there was no phase of fast fouling rate in the beginning of runs. After these slightly controversial results and with no successful repetitions with new rods more experiments are needed to find out in more detail how the rod condition affects fouling.

8.8 Metals and phosphorus concentrations and glyceride distribution before and after runs

The changes in metals and phosphorus contents and glyceride distributions of the liquid samples were studied by comparing the EOR (End of Run) analysis results to the SOR (Start of Run) sample analysis results. The comparison was carried out with four selected recycling mode test runs: Lipid 1 330 °C, Lipid 2A 290 °C and L3 330 °C 1 and 2.

8.8.1 Lipid 1

The metals and phosphorus analysis results for Lipid 1 are shown in Figure 20 and the glyceride distribution results are shown in Figure 21.

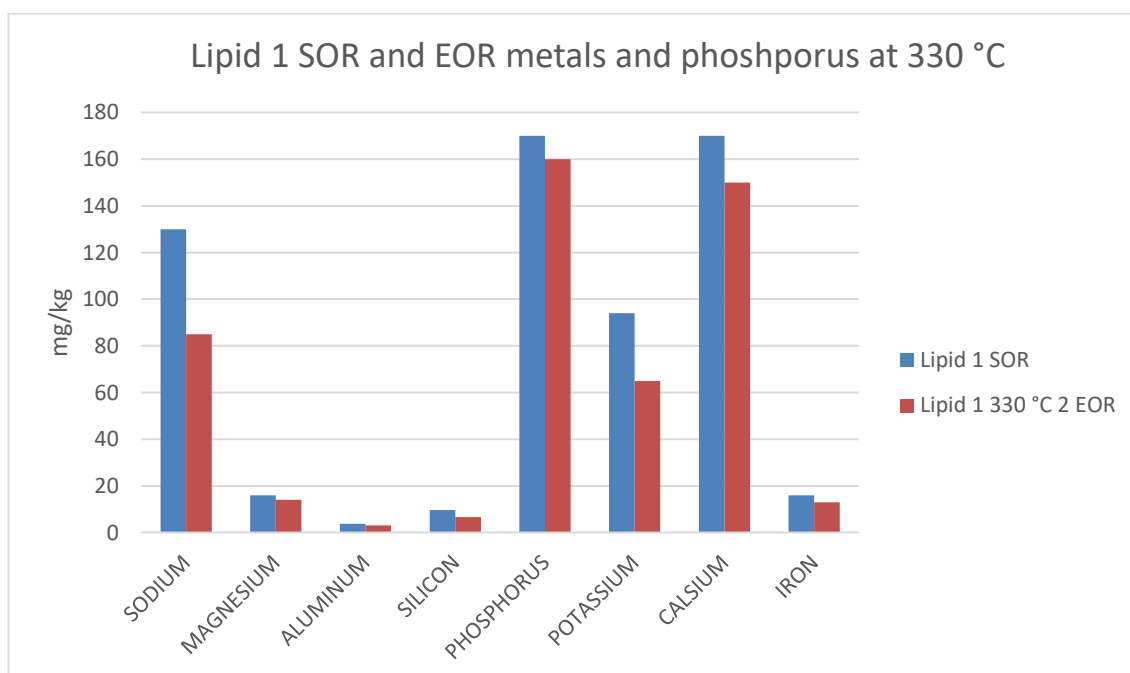


Figure 20. Lipid 1 metals and phosphorus results before (SOR) and after run (EOR).

Lipid 1 formed the heaviest fouling cakes so the decreases in metals and phosphorus concentrations after run were also higher than with other selected samples. Sodium, calcium and potassium concentrations decreased the most even though the calcium and phosphorus SOR concentrations were equally high.

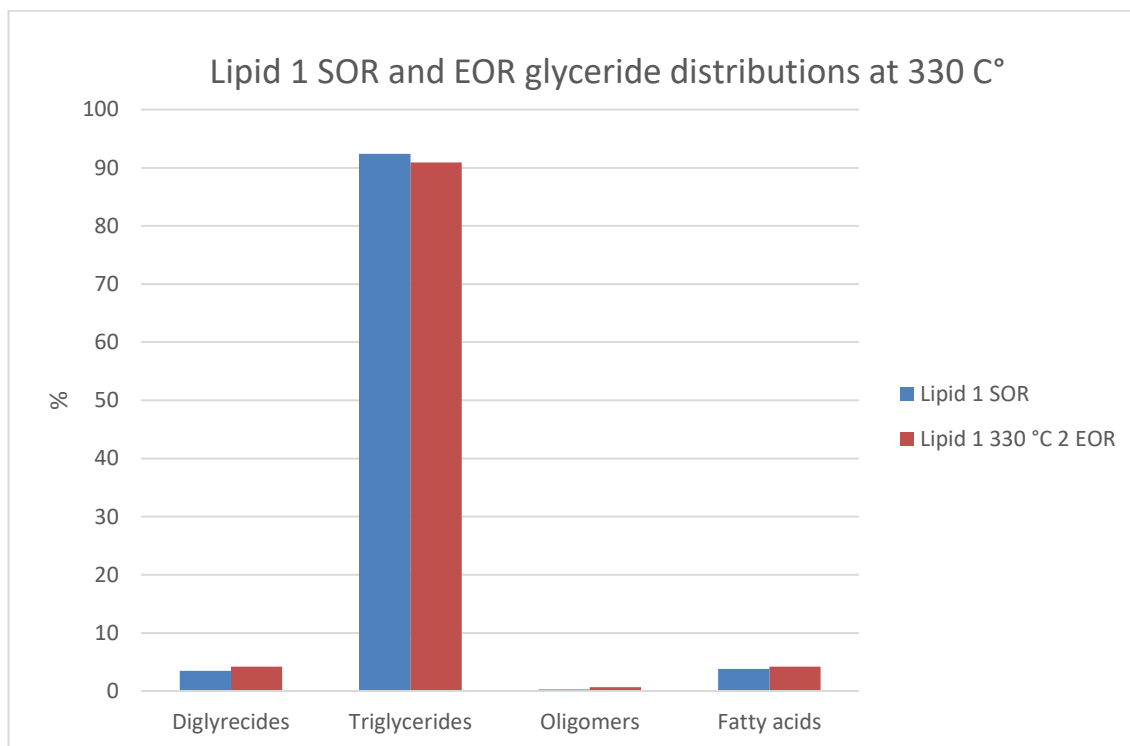


Figure 21. Lipid 1 SOR and EOR glyceride distribution at 330 °C.

The sample did not contain monoglycerides at all before and after test runs. There is a slight decrease in triglyceride share whereas the diglyceride, oligomer and fatty acid portions increase. This indicates that hydrolysis reactions and polymerization reactions happen in slight amounts.

8.8.2 Lipid 2A

The Lipid 2A metals and phosphorus results are presented in Figure 22 and glyceride distribution results in Figure 23.

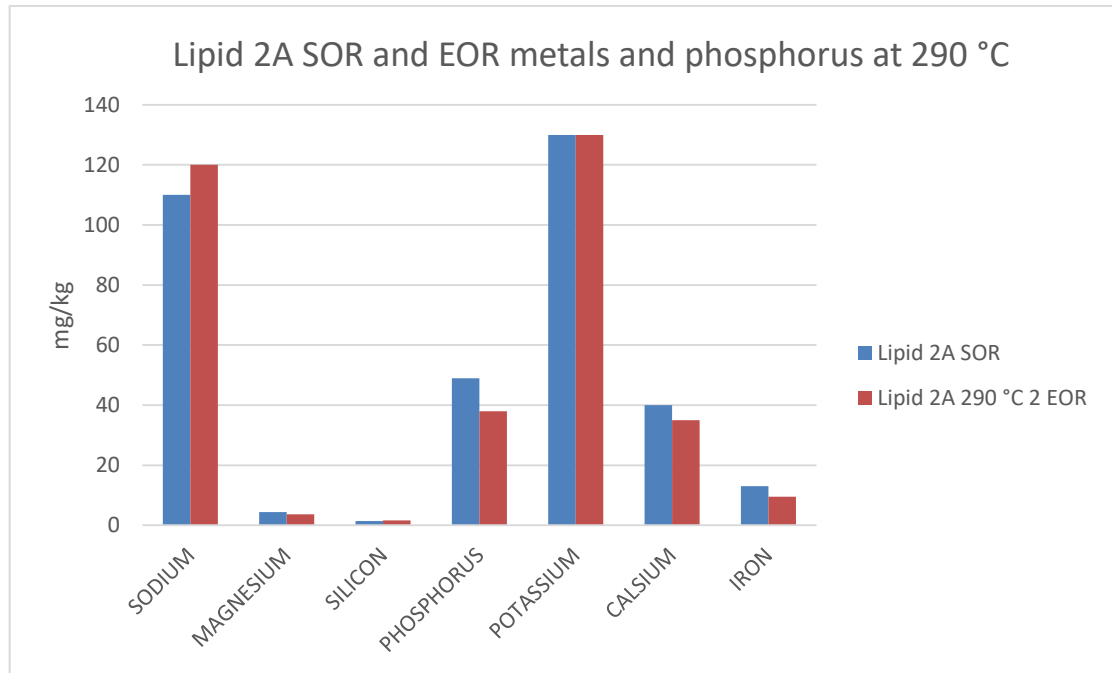


Figure 22. Lipid 2A metals and phosphorus results before and after run.

Sodium and potassium results are controversial as the EOR results are higher or equal to the SOR results, which must be caused by inaccuracy in analytics. The rest of the results indicate that phosphorus fouled proportionally more than metal impurities with this sample at a temperature of 290 °C.

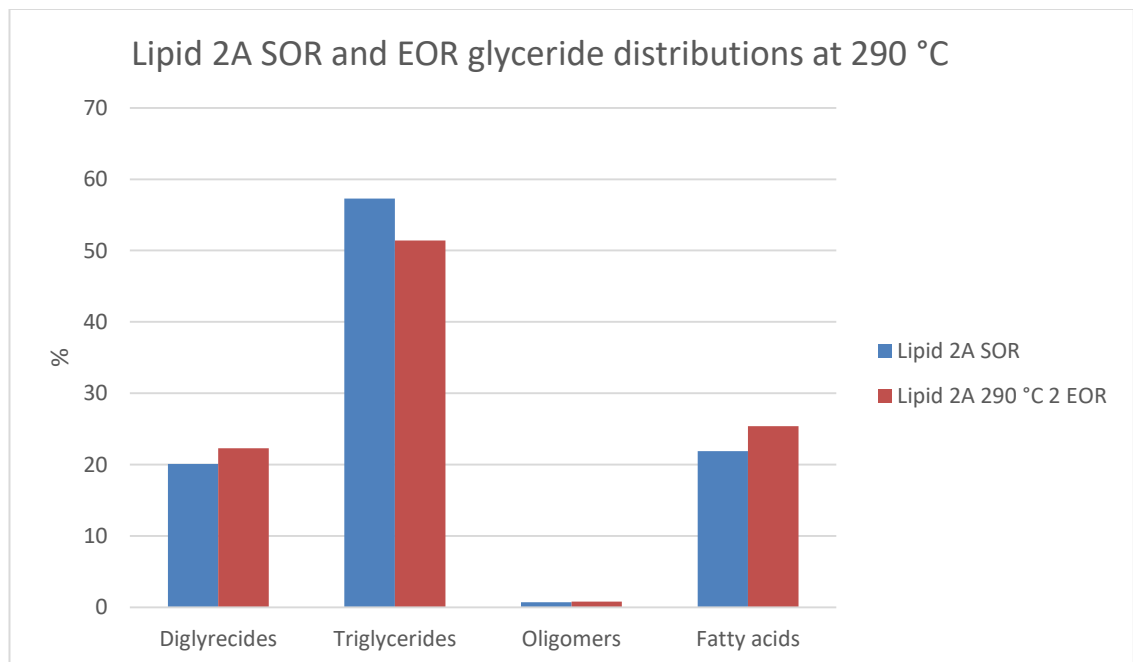


Figure 23. Lipid 2A SOR and EOR glyceride distribution 290 °C.

The changes are similar with Lipid 2A and Lipid 1: triglyceride portion decreases and other portions increase. Nevertheless the changes in portions were larger with Lipid 2A at 290 °C than with Lipid 1 at 330 °C apart from oligomer portion which increased only 0,1 % with Lipid 2A sample. The presence of water and solvents have probably increased the hydrolysis of triglycerides in this lower temperature and the slightly lower temperature had possibly hindered the polymerization. The water content of the samples were analysed with coulometric Karl-Fischer method and the Lipid 2A contained ~0,7 wt% of water whereas the other samples contained less than 0,06 wt%.

8.8.3 Lipid 3

With Lipid 3 EOR samples from two repetitions at same experiment point were analysed. Metals and phosphorus results are presented in Figure 24 and glyceride distributions results in Figure 25.

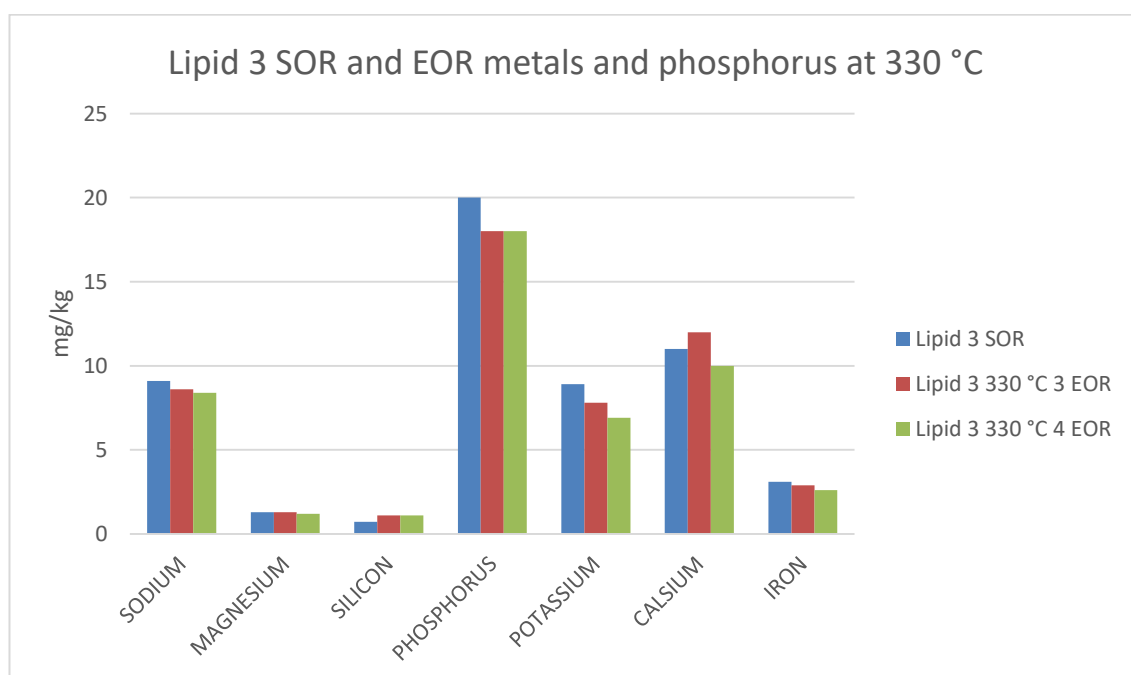


Figure 24. Lipid 3 SOR and EOR metals and phosphorus results

The repeatability of fouling results were good with this sample at 330 °C. There was slight variation in the metals and phosphorus EOR results and some controversial results but they are caused by inaccuracy of analysis. On average the phosphorus and

potassium concentration seemed to decrease proportionally more than other impurity concentrations.

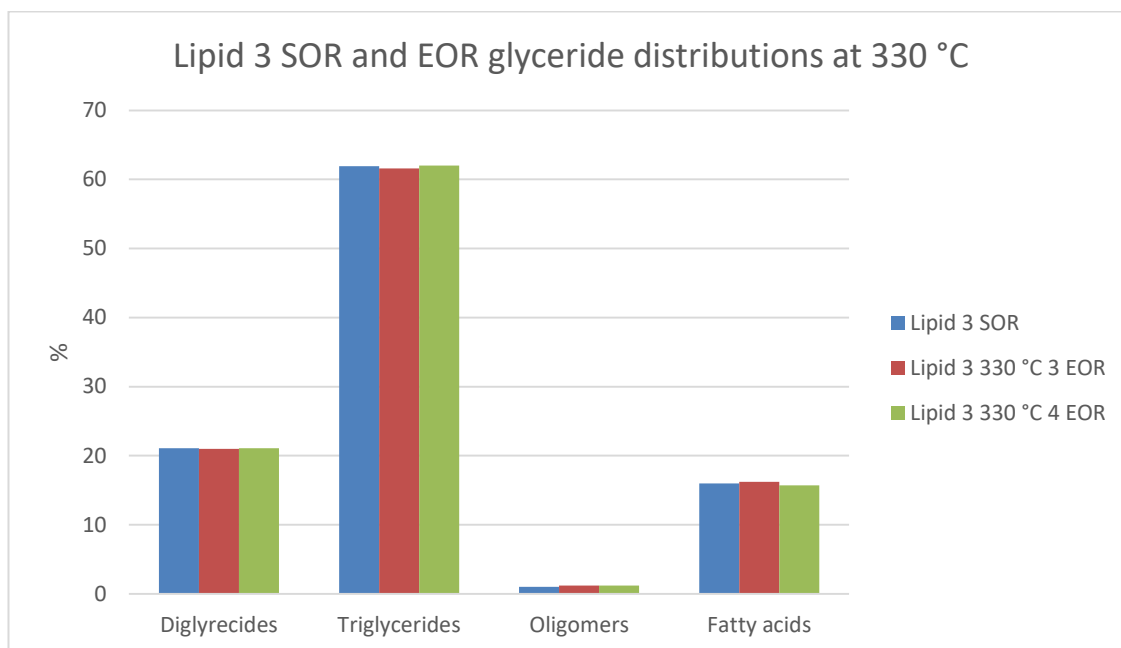


Figure 25. Lipid 3 SOR and EOR glyceride distribution results.

The changes of glyceride distribution was very negligible with this sample even at 330 °C. This sample contained water the least (0,045 wt%).

8.9 Deposit analyses

After test runs the rods were detached from equipment and kept in oven at 85 °C for 30 min to let the sample remains to drain from the rod surface. The rods and deposits were photographed and weighed after draining. After weighing the rods were rinsed with xylene and acetone for 5 seconds to remove the last fat remains from rod surface. After that the rods were weighed and photographed again. The deposits were detached from rods and analysed with infrared spectroscopy and x-ray diffraction and x-ray fluorescence.

8.10 Deposit masses

The rods and deposits were not weighed if the deposit cake was clearly cracked or the test run was interrupted due to clogging or pressure leakage. The average deposit masses of recycling runs are presented in Figure 26.

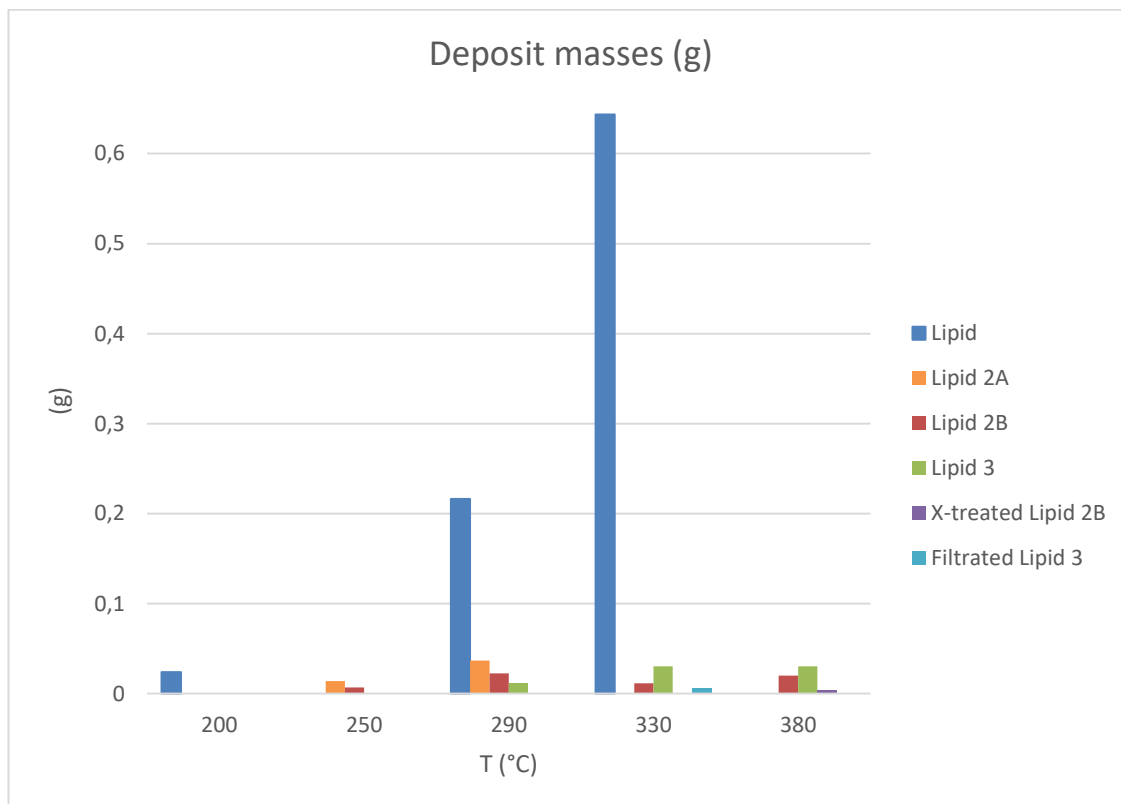


Figure 26. Average of weighed deposit masses of recycling mode runs.

The deposit mass results show that Lipid 1 had significantly more deposit on the rod. The Lipid 1 had some light coloured matter on the rod after run at 200 °C but it did not affect the R_f results. These results also show that Lipid 2A fouled secondly most although there was no reasonable outlet T measurement data available due to the evaporating solvents.

The amount of deposit should be proportional with temperature within a sample but for low fouling tendency samples the amount of deposit was so small that the fat remains on the rod had interfered the weighing results. The weighing results after solvent rinse were not studied because the solvents rinsed some of the cake off the rod in some cases. With some samples acetone formed a layer of light colored matter on the surface which could have interfered the weighing results.

8.11 Deposit infrared spectroscopy, X-ray diffraction and X-ray fluorescence

The selected deposit cakes were analysed with IR to investigate which compounds they consist of. The most thick deposit cakes were also analysed with XRD and XRF since there was enough sample for that analysis.

After test runs it was noticed that in some cases there were clearly two fouling zones on the rod: one deposit zone was on the lower part of the rod and other was on the upper part. The rod and the sample temperature is lower at the lower part of the rod thus this indicates that some compounds attach to the rod at lower temperatures whereas others need more heat to foul. An example of two fouling zones are shown in Picture 17. The rod and deposits are from recycling run L3 330 °C 2 (no stir).



Picture 16. Rod and deposits from run L3 330 °C 2, recycling, no stir.

The rod is in vertical position in equipment and in Picture 17 the flow direction is from left to right. At rod temperature 330 °C the inlet temperature measurement for bulk sample is 85 °C and outlet temperature starts at 215 °C. The actual temperature that sample reaches in contact with rod is unknown because the piping is not insulated and due to slow flow rate the sample has time to cool down before temperature measurement after it comes from the rod. From that run the lower and upper deposit cakes were analysed separately with IR whereas a combined sample was made with other samples. Deposit cakes were rinsed with xylene and acetone before analyses.

8.11.1 Infrared spectroscopy

There was a note within the Lipid 2B and the Lipid 3 upper and lower zone sample results that the amount of analysed sample was very low which may reduce reliability of the results. The IR analysed samples and identified components were:

- Lipid 1 330 °C 2 (no stir): mostly pyrophosphate salts, sulphate salts, carboxylic acid esters, proteins.
- Lipid 2A 290 °C: Phosphate salts, sulphate salts, pyrophosphates (debatable), carboxylic acid esters, proteins.
- Lipid 2B 330 °C 2 (no stir): mostly sulphates
- Lipid 3 330 °C 1 (no stir): Sulphate salts, phosphate salts, pyrophosphate salts
- Lipid 3 °C 2 no stir (lower fouling zone): Sulphate salts, phosphate salts, pyrophosphate salts (debatable)
- Lipid 3 330 °C 2 no stir (upper fouling zone): Sulphate salts, phosphate salts, pyrophosphate salts (debatable)

There were differences in identified components between different deposit samples although the feed samples had similar impurities according to chemical analyses in chapter 8.2. Albeit there were similar elemental impurities the concentrations of them were different in each sample and the heterogeneity of the components were unknown.

Sulphate and phosphate salts were found in every deposit. This indicates crystallization fouling since the solubility of at least some sulphate salts decrease with increasing temperature (Serth 2007, 94) The effect of sulphur on fouling is complex and it contribute on various fouling mechanisms at least in crude oil fouling (Hewitt 2014, 25). Nevertheless, the fouling results indicate that the total sulphur content of sample was not the key factor in these fouling experiments: the Lipid 3 that had significantly less sulphur but it fouled more than Lipid 2B and X-treated Lipid 2B. The sulphur and phosphorus concentrations were presented in Figure 7.

Phosphate and pyrophosphate salts were found in every sample except Lipid 2B 330 °C which is surprising since that feed had more phosphorus than Lipid 3 and X-treated Lipid 2B. This may indicate that the composition of phosphorus is essential in phosphorus related fouling or then the low quantity of sample affected the results. As with sulphur, the total amount of phosphorus was not the dominant factor affecting the overall fouling

tendency of sample. The Lipid 3 had less phosphorus than Lipid 2B and X-treated Lipid 2B but it fouled more.

The Lipid 3 feed sample had less impurities but the total amount of dregs was larger than with Lipid 2A and Lipid 2B. The Lipid 3 had significantly higher fouling tendency than Lipid 2B. This indicates that the dregs enhance fouling significantly.

With the thicker deposits of samples Lipid 1 and Lipid 2A there were organic compounds in form of protein remains and ester remains from carboxylic acids. Proteins are known to denaturize in high temperature (Ustunol 2014, 25) and fouling of proteins is a severe problem in dairy industries (Beuf 2003, 1) so it is assumed that feeds with proteins will cause fouling on hot surface. Certain unsaturated organic compounds are known to cause fouling in high temperatures (Serth 2007, 96) and the studied feedstock contains notable amount of partly unsaturated organic compounds. However, these kind of compounds were not found in Lipid 2B and Lipid 3 deposit samples even at 330 °C thus it can be concluded that the unsaturated organic compounds in these kind of samples do not foul without other impurities at 330 °C. This was verified by the R_f result of the filtrated Lipid 3 sample which did not foul at all 330 °C as shown in Figure 16. Ester remains from carboxylic acids were found in Lipid 1 330 °C and Lipid 2A 290 °C deposit samples. As they were attached to the surface even at 290 °C it seemed that proteins or other foulants enhance the fouling of lipids which would not foul in pure solution.

The lower and upper part samples of run Lipid 3 330 °C 2 had similar compositions. There are possible explanations for that: different phosphates have different temperatures when the solubility starts to decrease with increasing temperature, there were components that cause fouling which are not detected by this analysis method, the sample amount was insufficient, the composition of deposit cake has changed during the contact with hot surface or the other components were flushed or dissolved by solvent rinse after run. Otherwise it is not logical that there is a gap between these two fouling zones when the deposits have similar composition.

8.11.2 X-ray diffraction and fluorescence results

Lipid 1 330 °C and Lipid 2A 290 °C had enough sample to carry out XRD and XRF analysis. When interpreting the XRD results it must be noted that it identifies only crystalline compounds and that organic sample matrix causes noise in results so that components with abundant presence are identified. Following crystalline compounds were identified in the XRD analysis:

- Lipid 1 330 °C: Reliably phosphates (potassium, calcium and sodium). Debatable: nitrides (phosphorus and oxide) and silicates (calcium, magnesium and iron)
- Lipid 2A 290 °C: Reliably phosphates (calcium, magnesium, iron, hydrogen).

XRD results confirm that there were phosphate salts. The lack of identified sulphate components indicate that the presence of sulphate components was not as abundant as with phosphate compounds. This is supported by XRF analysis of which results are in Figure 27.

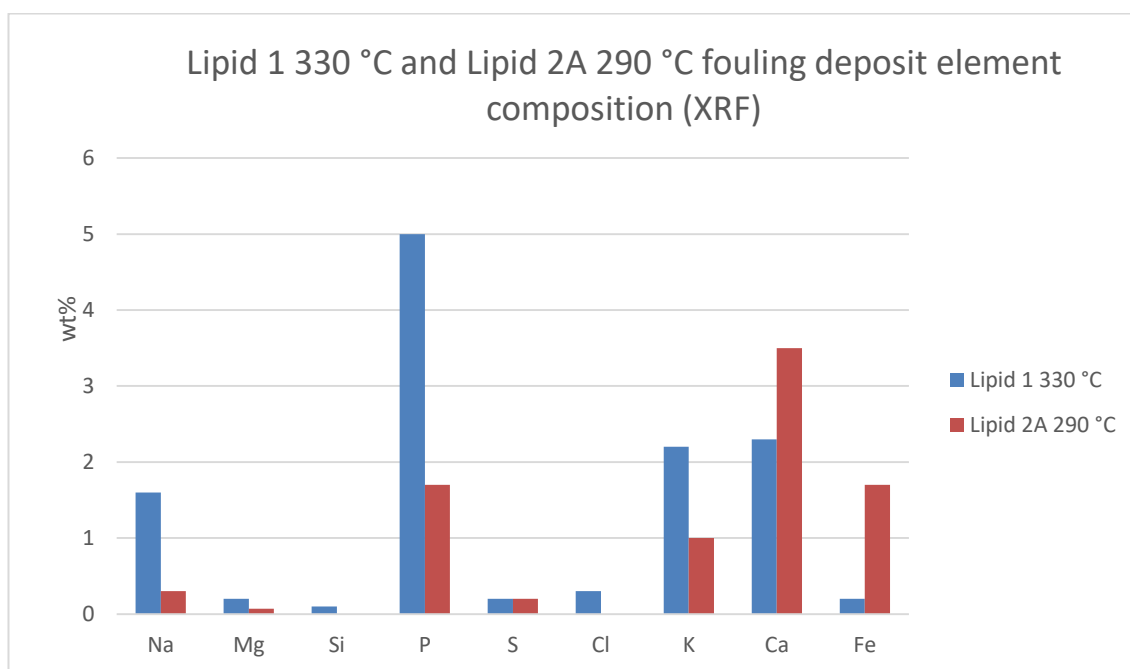


Figure 27. Lipid 1 330 °C and Lipid 2A 290 °C fouling deposit element composition by XRF.

Albeit the results are only referential the difference between phosphorus and sulphur content is significant with both temperatures and both samples. The phosphorus

concentrations in feed sample analyses were significantly smaller than sulphur concentrations within same sample thus phosphorus appears to have stronger tendency to be a fouling precursor than sulphur with these abundantly fouling samples Lipid 1 and Lipid 2A. However, the Lipid 2B with low fouling tendency had no phosphorus-based compounds identified in IR analysis. Unfortunately the sample amount of the low fouling samples were not sufficient enough to carry out a XRF or XRD analysis.

9 CONCLUSIONS

Even though the Falex 450 thermal fouler does not correspond industrial sized heat exchangers in operating conditions it could be used to study the fundamental features of fouling with lipid samples. After the severe fluctuation of measurements was eliminated the results were logical within a sample: a higher temperature caused more fouling and the R_f graphs were clear. More accuracy to the results could be obtained by paying more attention to the rod condition. A subtle mechanical finishing treatment could be applied to the cleaned rods to make them smoother and more identical regarding the surface roughness or only new rods should be used if the results are needed to be as accurate as possible.

According to fouling theory about solids in fluids (Bott 195, 1) and the results achieved, the importance of stirring must be emphasized. Settling particles and other heterogeneous features of the studied sample affect results significantly. If the severe and sudden fluctuation continues despite a new type of stirring device, the sloughing of deposit could be verified by auxiliary temperature measurement. An auxiliary temperature measurement device could also be used to verify that the small swaying of temperature measurement is actually happening in the process.

The samples from highest to lowest fouling tendency were Lipid 1, Lipid 2A, Lipid 3, Lipid 2B, X-treated Lipid 2B and filtrated Lipid 3. There were two prominent results: the Lipid 3 fouled more than Lipid 2B even though the Lipid 3 contained less phosphorus, metals, nitrogen and sulphur. The amount of dregs was higher in Lipid 3. An unclear factor concerning Lipid 2B was that some of that sample had been in vacuum which also could have removed some components that contribute to fouling. The other prominent result was that the filtrated Lipid 3 did not foul at all at 330 °C which indicates that lipid samples have very low fouling tendency at 330 °C if they are appropriately treated before heating. After all a single component that was dominantly responsible for fouling could not be pointed out by the results of this thesis but the amount of dregs seemed to correlate with fouling tendency more than the concentration of elements which were considered as impurities.

The fouling types in these tests were assumedly crystallization fouling, particulate fouling and chemical reaction fouling. Some salts have inverse solubility meaning they start to crystallize again in high temperatures and there were sulphate and phosphate salts in

almost every analyzed deposit. The enhancing effect of dregs amount on fouling suggests that there were some particulate fouling. Two other observations also contribute to particular fouling theory: some of the thicker cakes were quite soft and the faster flow-rate decreased the fouling significantly. The presence of proteins and unsaturated carboxylic acid esters in deposits indicate chemical reaction fouling as well. Denaturated proteins on rod establish a grainy surface which enhanced particulate fouling. The amount of visible solids and particles in liquid samples after test runs were not observed thoroughly in these experiments.

The results achieved with Falex 450 could be compared with actual plant or pilot plant data to find dependencies to examine how accurately the fouling in actual processes could be predicted from laboratory scale results. In comparison tests with larger scale equipment it must be taken carefully into account that the used feed samples are as corresponding as possible. In these comparison tests to obtain data that corresponds actual process more precisely the tests should be run in once-through mode with higher flow-rate. The actual processes are once-through type and faster flow-rate would probably hinder particulate fouling which is not occurring so abundantly with faster flow-rates. The volume of feed tank limits the duration of fast flow-rate and once-through mode runs, but the size of the feed and the product tank could be increased if the tests are regarded to give valuable information. The tests runs with higher flow-rate could also be run with recycling mode if the recycling is not considered to be an issue when comparing fouling tendencies.

The Falex 450 Fouler is a suitable tool for fundamental research of fouling and combined with the Neste Corporation's in-house chemical analysis know-how valuable information could be achieved. The most interesting topics are the ways to mitigate fouling by suitable pre-treatment or chemical addition and more comprehensive chemical composition analysis of feed sample impurities and deposits. The pre-treatment tests could include studying the effects of settling, centrifuging, filtration, chemical addition, degassing and drying. The chemical composition studies could include as detailed analysis of impurity composition as possible and modeling substance tests. Also the most suitable ways of determining particle and solid content in liquid samples should be discussed.

None of the laboratory scale fouling equipment correspond completely the industrial fouling conditions and the greatest draw-back of Falex 450 thermal fouler is that the flow velocity on surface is on completely different level in industrial heat exchangers. If the

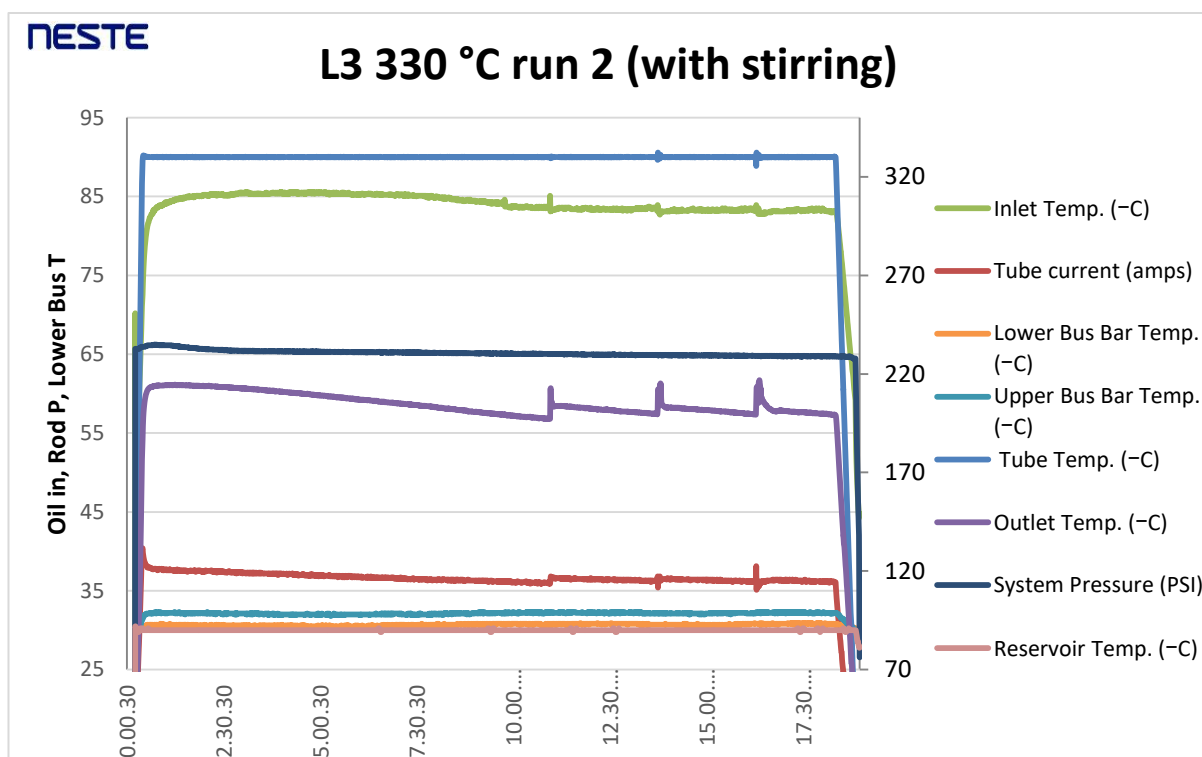
comparison between Falex 450 Fouler results and larger scale fouling data is carried out in future it would be interesting to add another fouling testing equipment in the experiment plan, for example a spinning cup type of equipment. The experiments would provide the information if more accurate prediction of industrial scale fouling could be achieved with an equipment with faster surface velocity and turbulent flow.

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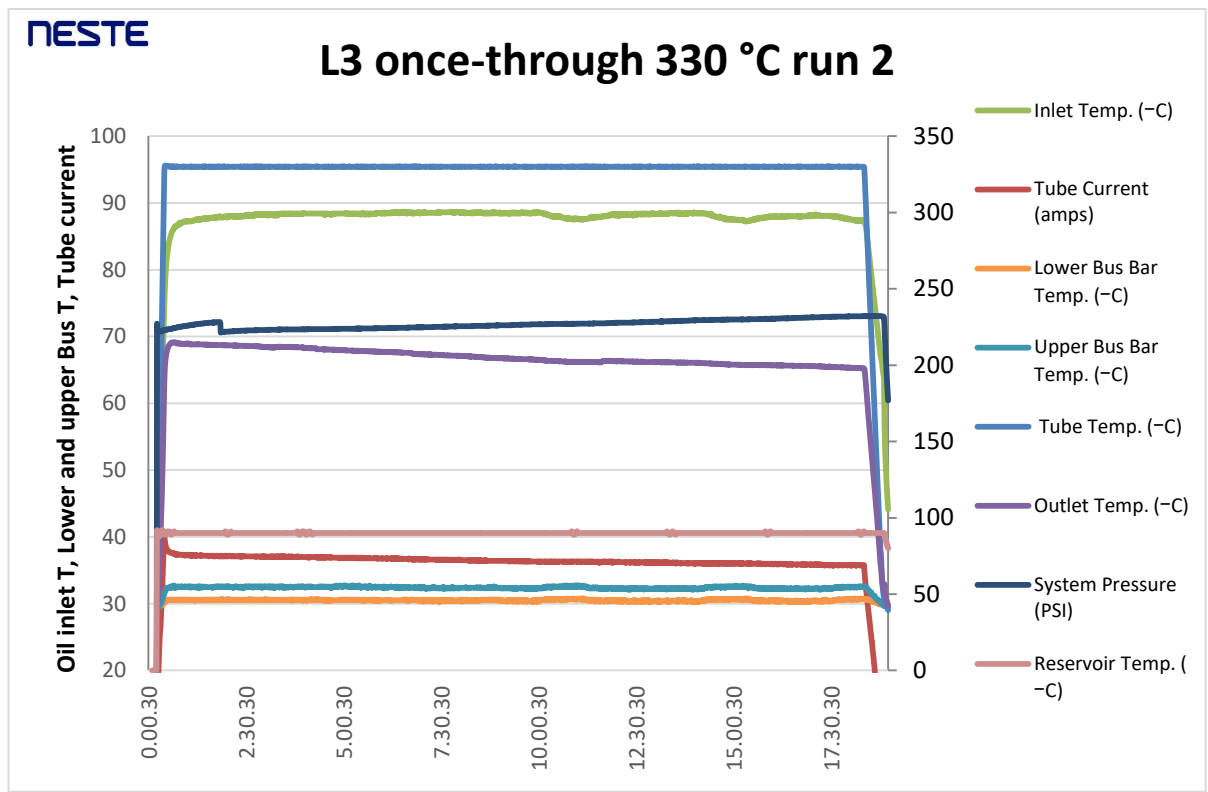
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The data screen of Lipid 3 330 °C 2 (R250)



Data screen of run L3 330 °C 2. During the fluctuation peaks the outlet temperature value increased to higher level than it was in the beginning of the run.

The data screen of Lipid 3 330 °C once-through run 2



There was swaying in inlet temperature, outlet temperature and upper bus bar and lower bus bar temperature. The drop in pressure in the beginning of run was operated intentionally.