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PURIFICATION OF HYDROCARBON WASTE STREAMS

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ABSTRACT

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Purification of Hydrocarbon Waste Streams

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Purification of hydrocarbon waste streams is needed to recycle valuable hydrocarbon products, reduce hazardous impacts on environment, and save energy. To obtain these goals, research must be focused on the search of effective and feasible purification and re-refining technologies.

Hydrocarbon waste streams can contain both deliberately added additives to original product and during operation cycle accumulated undesired contaminants. Compounds may have degenerated or cross-reacted. Thus, the presence of unknown species cause additional challenges for the purification process.

Adsorption process is most suitable to reduce impurities to very low concentrations. Main advantages are availability of selective commercial adsorbents and the regeneration option to recycle used separation material.

Used hydrocarbon fraction was purified with various separation materials in the experimental part. First screening of suitable materials was done. In the second stage, temperature dependence and adsorption kinetics were studied. Finally, one fixed bed experiment was done with the most suitable material. Additionally, FTIR-measurements of hydrocarbon samples were carried out to develop a model to monitor the concentrations of three target impurities based on spectral data.

Adsorption capacities of the tested separation materials were observed to be low to achieve high enough removal efficiencies for target impurities. Based on the obtained data, batch process would be more suitable than a fixed bed process and operation at high temperatures is favorable. Additional pretreatment step is recommended to improve removal efficiency. The FTIR-measurement was proven to be a reliable and fast analysis method for challenging hydrocarbon samples.

TIIVISTELMÄ

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Hiilivetyjätevirtojen puhdistaminen

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76 sivua, 26 kuvaa, 26 taulukkoa ja 6 liitettä

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Hakusanat: hiilivety, jätevirrat, puhdistus, kierrätys, adsorptio

Hiilivetyjätevirtojen puhdistaminen mahdollistaa arvokkaiden hiilivetytuotteiden kierrättämisen, ympäristöhaittojen vähentämisen ja energian säästämisen. Jotta nämä puhdistustavoitteet saavutetaan, tutkimusta tarvitaan toimivien ja kustannustehokkaiden puhdistus- ja uudelleenjalostusteknologioiden löytämiseksi.

Hiilivetyjätevirrat voivat sisältää useita eri epäpuhtauksia vaihtelevin pitoisuuksin. Nämä sisältävät tarkoituksella alkuperäiseen tuotteeseen lisätyt lisäaineet sekä käytön aikana kertyneet ei-toivotut yhdisteet. Yhdisteet ovat voineet hajota tai reagoida keskenään. Siten tuntemattomien yhdisteiden mukanaolo aiheuttaa lisähaasteita puhdistusprosessille.

Adsorptioprosessi on sopivin vaihtoehto epäpuhtauksien vähentämiseen mataliin pitoisuuksiin. Pääedut liittyvät kaupallisten ja selektiivisten adsorbenttien saatavuuteen ja mahdollisuuteen regeneroida käytetty erotusmateriaali.

Kokeellisessa osassa puhdistettiin käytettyä hiilivetyjaetta erilaisilla erotusmateriaaleilla. Ensimmäisessä vaiheessa selvitettiin sopivimmat materiaalit. Toisessa vaiheessa tutkittiin lämpötilan vaikutusta ja adsorptiokinetiikkaa. Lopuksi tehtiin kiintopetiko sopivimmaksi osoittautuneella materiaalilla. Lisäksi näytteille tehtiin FTIR-mittauksia mahdollistamaan spektridataan perustuvan pitoisuusmallin kehittäminen kolmen valitun epäpuhtauskomponentin pitoisuuksien tarkkailuun.

Testattujen erotusmateriaalien adsorptiokapasiteetit osoittautuivat mataliksi, joten tehokasta poistumaa ei saavutettu. Tulosten perusteella panosprosessi sopisi paremmin kiintopetiprosessin sijaan. Ylimääräinen esikäsittelyvaihe on suosituksena poistuman parantamiseksi. FTIR-mittauksen todistettiin olevan melko luotettava ja nopea analyysimenetelmä haastaville hiilivetynäytteille.

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NOMENCLATURE

Abbreviations

API	American Petroleum Institute
ATR	attenuated total reflection
CEP	Chemical Engineering Partners
EU	European Union
FTIR	Fourier transform infrared spectroscopy
GC/MS	gas chromatography and mass spectrometry
ICP-MS	inductively coupled plasma mass spectrometry
LOD	limit of detection, ppm
MEK	methylethyl ketone
MIBK	methyl-iso-butyl ketone
NMP	N-methyl-2-pyrrolidone
NMR	nuclear magnetic resonance
OEM	original equipment manufacturer
PAO	polyalphaolefins
PCDD/F	polychlorinated dibenzodioxins or dibenzofurans
SM	separation material
ULO	used lubricating oil
U.S. EPA	United States Environmental Protection Agency
XRF	X-ray fluorescence spectrometer
ZDDP	zinc dialkyldithiophosphate

Symbols

A	absorbance, -
BV	bed volume, -
c	sample concentration, ppm
c_0	feed concentration, ppm
c_{CAL}	calibration concentration, ppm
c_{EST}	estimated concentration, ppm
c_{eq}	equilibrium concentration, ppm
d	diameter, mm
d_i	inner diameter, mm
d_p	particle diameter, μm
D_e	effective diffusion coefficient, $\text{m}^2 \text{s}^{-1}$
f	flow rate, mL min^{-1}
F	fractional uptake, -
ΔH	adsorption enthalpy, J mol^{-1}
K	equilibrium constant in Henry's law isotherm, -
m_{OIL}	mass of oil in the batch, g
m_{SM}	mass of added separation material, mg
q	adsorbed amount, g/kg
r	radius of the particle, m
R	reduction, %
R_g	gas constant, $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$
t	time, min
T	temperature, $^{\circ}\text{C}$
TAN	acid number, $\text{mg}_{\text{KOH}} \text{g}^{-1}$

w mass fraction, %

Greek letters

ρ density, kg m^{-3}

ν viscosity, $\text{mm}^2 \text{s}^{-1}$

1. INTRODUCTION

Global development within industrialization and motorization is heavily dependent on crude oil derivatives. These hydrocarbon streams also include lubricants which are used to prevent frictional contact between two metal surfaces. Due to necessity of lubrication, these products are needed in various applications, ranging from conventional combustion engines and gearboxes to industrial machinery like hydraulics and turbines. Lubricant should withstand high temperature, pressure, and also maintain sufficient viscosity in a wide temperature range [1, p. 15].

Large volumes of lubricants are produced globally, e.g. total annual lubricant demand in EU is about 5.7 million tons [2]. Crude oil derived lubricants are most common. Also hydrocarbon-based synthetic lubricants are available. The main component of any lubricant, the base oil is mixed with a wide array of additives to improve oil characteristics [3, p. 44]. Automotive industry consumes more than half of the annually produced lubricant stock and different industrial end users form the second largest market group [4]. This can be seen in Fig. 1 where the percentage distribution of lubricating oil global consumption is presented in a pie chart.

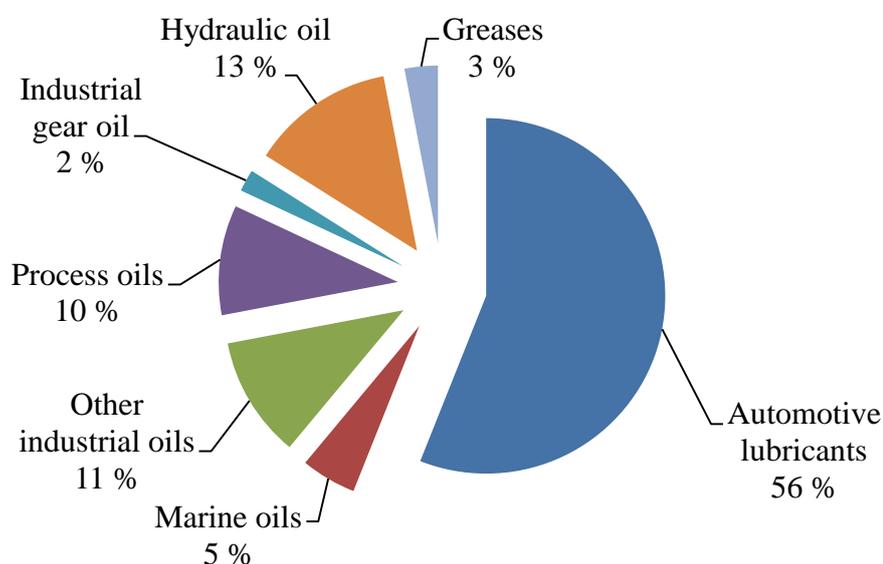


Figure 1. Estimated percentage contribution of lubricating oil global consumption, modified from [4].

Although lubricant manufacturers are constantly improving their products and inventing new additives, lubricating oil must be changed before oil reaches the limits of its service life. Especially oxidation threatens to weaken the usability of lubricating oil due to increased viscosity and sludge deposits [5].

Lubricating oil that has lost lubricating properties and cannot be used anymore is treated as used oil [6]. Approximately half of the introduced lubricating oil can be collected as used oil [2]. Some amount of used oil is always lost in containers during handling and transportation. Moreover, even 30 % of used lubricant is illegally burnt or dumped to environment in EU countries [7]. Notably the share of incorrectly disposed oil can be even higher in other countries. Thus, serious environmental damages will occur if the hydrocarbon compounds are leaked to soil or water bodies. Several studies have indicated that petroleum hydrocarbons cause serious harm to marine species. For example crude oil spill in aquatic environment can severely poison early life-stages of marine life forms [8]. Correspondingly, environmental authorities estimate that only one volume unit of waste lubricating oil can contaminate even million volume units of fresh water [9, 10] so improper used oil treatment generates huge risks. Studies have also indicated that lubricating oil base stocks are not easily biodegraded [11] so spillage can cause serious long-term environmental problems.

Surprisingly, the basic composition of used oil is still pretty similar as in the fresh oil. [12] The loss of lubricating characteristics is due to the degradation of additives and presence of other impurities like dust and metal particles in addition to oxidation products. These contaminants can be removed with regeneration procedure. There are various commercialized industrial technologies available for this recycling task [13]. Other option besides regeneration is to incinerate used oil to energy but combustion of possible heavy metal contaminated waste oil can cause dangerous emissions [14]. Also U.S. Environmental Protection Agency has stated that re-refining base oil from used oil requires only one-third of the energy when base oil is produced from crude oil [15]. On this basis, purification of used oil has clear advantages.

The main purpose of this thesis is to gather the most recent information from literature about purification of waste lubricating oils. Primary focus was on the removal of phosphorus, silicon, and chlorine. The removal process of these components was experimentally studied using different separation materials.

2. RECYCLING OF WASTE LUBRICATING OILS

Hydrocarbon waste streams can be purified with several technologies depending on the level and type of contamination. For example, processes involving settling and filtration are useful if only the presence of solids cause problems. However, usually only reprocessing is not sufficient and some re-refining is also needed, especially when producing base oils. In the worst case scenario, the oil is so heavily contaminated e.g. with polychlorinated biphenyls (PCBs) or terphenyls (PCTs) that incineration may be the only feasible process. [16] Still, EU has introduced a directive which gives a concentration limit of 50 ppm for PCB or PCT content even if waste oil is to be burned [17]. Burning of oil should be implemented at very high temperatures (> 2000 °C) to ensure complete destruction of contaminants. Usually rotating cement kilns are most suitable due to extremely high temperatures reaching even 2400 °C. Kanokkantapong *et al.* (2009) have compared different incineration methods with other oil management techniques. Authors stated that without high-temperature cement kilns the process creates also quite severe heavy metal emissions. [18]

2.1. Background

Lin *et al.* (2007) have investigated methods to increase waste lubricating oil recycling rate. They focused on the waste oil generated by Taiwanese fishing vessels. Authors estimated the annual volume of waste lubricating oil from fishing vessels alone to be 386.2 m³ in 2005. The amount of waste oil recovered during maintenance depends on whether the engine maintenance is done at the shipyard or at sea. Most of the shipyards are able to collect most of the oil and thus gathered waste oil can be recycled. However, in the case of maintenance at sea, the waste oil is drained into the bilge-water tank and mixed with water. This water-rich mixture has very limited recycling value and so it is very common among Taiwanese fleets to dump oily bilge water into the ocean during voyage. [19]

Leong and Laortanakul (2003) have taken environmental perspective for used oil management. Their focus was on potential waste lubricating oil sources in the area of Bangkok, Thailand. Authors also estimated the feasibility of the collection system. Firstly, households were mentioned in the review as despite small scale but still noteworthy source of waste oil. This oil from home garages etc. was compared

as almost equally uniform as waste oil from automotive service centres. Biggest differences between these two are related to challenges to maintain economically feasible waste supply from the households. That is why commercial oil collecting companies are strongly linked to automotive service centres. Waste oil has been given away for free but nowadays some service centres are even selling the oil to collectors. Similarly to previous example, also commercial engine fleet have already established high recycling rate for waste lubricating oil. Last two significant sources are industrial sector and marine fleets. Authors remind that industrial waste oils are collected from various units like turbines, gas engines, and hydraulic systems. Therefore, the waste oil may contain contaminants such as solvents and synthetic additives. In addition, both industrial and marine waste oils may contain indefinite amount of water. [20]

2.2. Specifications

Maxwell *et al.* (1996) compared virgin lube oil and re-refined lube oil from various types of vehicles. Researchers used gas chromatography equipped with mass spectrophotometry to analyze chemical differences. All analyses were performed with hexane as the solvent. Based on the results, the higher level of poly-nuclear aromatics was the only detectable difference in the composition of re-refined base oil compared to virgin oil. These compounds are formed due to high temperature and pressure inside the combustion engine. Nonetheless, the concentrations are usually very low and re-refined lube oil does not significantly differ from virgin lube oil. [21]

American Petroleum Institute (API) has determined grouping system for different base oil groups based on the viscosity index, percentage of saturates *i.e.* paraffinic hydrocarbons, and sulphur. This classification is widely used among industry. [22] Groups are explained in Table I.

Table I API groups for various base oil stocks. [22]

Group :	Viscosity index, -	Saturates (paraffinic hydrocarbons), %	Sulphur, %	Description:
I	80 - 120	< 90	> 0.03	conventional solvent refined base stocks
II	80 - 120	≥ 90	≤ 0.03	moderately hydrocracked and dewaxed base stocks
III	> 120	≥ 90	≤ 0.03	cracked or isomerised wax products
IV	-	-	-	polyalphaolefin synthetic hydrocarbon base stocks
V	-	-	-	all other base stocks and synthetics

Anwar *et al.* (2002) have categorized all four base oil groups in their overview article. Group I manufacturers have moved towards Groups II and III during the 21th century. However, production of heavy duty and single-grade motor oils is still dependent on Group I base oils. [23]

Most of Group II base oil manufacturers utilize Chevron based license. One of the biggest benefits of the licensed technology is the ability to produce both Group II and III base oils. [23] More recently, ExxonMobil has pushed forward the production of Group II oils with the patented technology. Patented two-step, single-stage process includes first hydroconversion and then the cold hydrofinishing step. Obtained effluent goes through catalytic or solvent dewaxing. [24] The process leaves an option to produce also Group I oils [23, 24].

Main advantages of Group III base oils are related to its high viscosity index. This gives the oil desirable characteristics such as low volatility and good performance on wide temperature range. The low volatility increases fuel economy and decreases oil consumption and the oil change frequency. Therefore, most original equipment manufacturers (OEMs) e.g. Ford, DaimlerCrysler, and General Motors favor Group III base oils. [23]

Fourth base oil group is limited to only polyalphaolefins (PAOs). PAOs are free of sulphur, phosphorus, metals, and waxes. As a wax-free, Group IV oils are used in low temperature applications. Viscosity index is quite high, between 170 and 300 but products with lower viscosity index range are also available. PAOs are also well miscible with mineral oils. However, disadvantageously additive-free PAOs have

poor oxidation stability and there is also a risk that PAOs may shrink gaskets. These deficiencies can be reduced by additives like antioxidants and esters. In addition, PAOs face tough competition from cheaper base oils from Group III. [23]

Group V, as described in Table I, is a collection of various, mainly synthetic base oil stocks. Usually this group contains oils designed for very special applications which require extreme durability. For example non-flammability, radiation resistance and chemical stability are properties that definitely raise the price of Group IV oils. [23]

2.3. Current Situation

There are great differences in waste lubricating oil recovery rates among countries. Hsu *et al.* (2009) give a very clear example about this by comparing Taiwan with EU in their article. Recovery rate of waste lubricating oil was as low as 4 % in Taiwan 2005. By comparison, an average EU country recovered 50 % of waste lubricating oil in 2000. The difference is even clearer if the time scale is noted, because Taiwanese statistics are five years more recent than EU recycle rate value. [25] It should also be noted that the engine oil change interval may greatly differ depending on the driving conditions, oil quality, and also the engine type and age [26]. In Europe, engine oil needs to be changed usually after 15,000–30,000 km interval [Machinery lubrication - oil change filter sensors] but in developing countries like Bangladesh, oil change is necessary already after three months of use or after 3,000 km [27]. Therefore the volume of total generated waste oil may be significantly higher in developing countries.

Leavens (2012) has analyzed present and future global base oil demands on the economical basis. In 2010, global demand of base oils from Groups I to IV was about 35 million tons. Group I base oils have the predominant share, clearly over 50 % of the total demand. Due to steady growth, global base oil demand is predicted to rise to nearly 44 million tons by 2030. During the next decades, demand of Group I oils is estimated to decrease while demand of Group II and especially the demand of Group III oils is going to increase. [28]

Although the global base oil demand is rising, demand in Europe and North America is decreasing. Demand of Group I base oils will decline sharply by the

year 2030 in these two regions but these base oils still retain strong position in industrial and marine lubricants. Reformation of automotive fleets in Europe and North America is shifting the demand towards mid- and top-tier engine oils *i.e.* Group II and Group III. European mid-tier classification covers also the blends of Group I and Group II or Group III. [28]

The growth in global base oil demand arises from the Asia following the rapid industrialization and expansion of vehicle fleet. Group I base oils will hold its largest share, because the quality requirements and legislation follow development of the Western world with a delay. South Korea is already providing a large supply of Group III oils so the orientation is moving towards mid- and top-tier lubricants at the same time with eventual modernization of automotive fleets. [28]

2.4. Legislation

U.S. Department of Energy has considered ways to increase the recycling of waste oils. In 1995, one major drawback was considered to be the capital costs of re-refineries. Department of Energy strongly points out that if legislative measures and limitations concerning usage of waste oils are strengthened, interest to re-refine may increase rapidly. Especially landfill bans and composition regulations for burnable waste oil are seen as most important drivers towards recycling of oil. [29]

EU directive on waste highlights the importance of waste hierarchy. Waste hierarchy lists different techniques to prevent and treat wastes. These are prevention, re-use, recycling, energy recovery, and the least favorable option *i.e.* disposal. [30] Thus, re-refining of used lubricating oil is located clearly on the more favorable steps.

The European Re-refining Industry Section of Independent Union of the European Lubricants industry presents Greece as a case example how implementation of pro-recycling legislation had a diverse effect on the whole disposal route. After new legislation concerning waste oil management and increased re-refining activity was implemented at 2004, waste oil collection rate increased from 8,000 to 42,000 MT per year by 2007. Of course, start-up of the new re-refinery at the same time also increased the overall waste oil demand but start-up must have been backed by the

new legislation. [31] Therefore, the legislation was one of the root causes for the more efficient recycling activity.

Despite of positive case examples, some sources disagree on the positive effects of the directives viewed on recycling side. European Petroleum Industry Association (2003) has considered legal and technical aspects of oil recycling. They regarded that EU directive [30] on waste oils directs the disposal towards combustion in cement kilns instead of recycling if availability of good quality grade used oil is too limited. [32] Obviously, legislation cannot be the only contributor to improve the recycling interest.

Besides legislation, also standardized and practical used oil classification system will improve recycling and eventually ease the evaluation task of different used oil feedstocks. Stan'kovski *et al.* (2010) describe how used lubricant collectors need better classification tools to determine the quality of used oil in the Russian Federation. Authors suggested additional analysis to determine saponification number. This value can be used as an indirect index of the residual content of additives and decomposition products. If collectors have oil which does not fulfil standardized quality requirements for example due to the excessive water content, there should be classification which tells what type of pretreatment method e.g. vacuum distillation must be used before feedstock can be processed. [33]

Furthermore, public awareness of proper waste oil disposal ways and environmental hazards must be increased to intensify the amount of collectable oil. Particularly, USA has been very active as information distributor. Most of the states offer an own localized version [34, 35]. Compared to USA, EU seems to be lacking widely distributed guidebooks on a local level.

2.5. Lubricant Oil Recycling Methods

Several scientific studies have focused on the purification of waste lubricating oils. Studied purification technologies vary from well-known and conventional processes to more novel and experimental methods. Some of these studies are presented in this chapter so different alternatives are easier to understand.

Acid-clay method is perhaps the earliest waste oil treatment technology. Rahman *et al.* (2008) used pilot-scale equipment to purify waste oil that was collected from

Bangladeshi vehicles, variable workshop machineries and industries. After pretreatment with gravity settling, oil was directed to catalytic cracking, washing, and dehydration. Cooled oil was treated with 92 % sulphuric acid. After 24 h acid treatment Fuller's earth was added to oil. Oil was then vacuum-distilled. Bottom product from distillation unit was filtered to remove clay. This fraction was considered as re-refined base-oil. Authors point out that acid-clay process does not generate enough profits even in a developing country which is a clear indication that there is a requirement for more advanced re-refining technologies. [27]

Isah *et al.* (2013) purified used engine oil with sulphuric acid treatment, sedimentation, and bleaching with 6 wt% industrial bleaching earth or activated carbon at 110 °C. Treated oil was then neutralized with 4 wt% hydrated lime, sedimented and filtrated. Analyses regarding viscosity, specific gravity, total acid number and color were carried out. Researchers proposed that industrial bleaching earth was most suitable adsorbent material based on this laboratory-scale experiment. [36] Although purification was somewhat successful, still the fact that experiments were carried out in a bench scale at controlled conditions must be taken into account. Increased waste volumes will be linked to higher costs and reduced feasibility.

Solvent extraction is another example of basic technology besides acid-clay method. Kamal and Khan (2009) combined solvent extraction and adsorption to enhance the purification efficiency. They listed typical solvents to be n-heptane, n-hexane, methyl-iso-butyl ketone (MIBK), methylethyl ketone (MEK), 1-butanol, 2-butanol, benzene, and 1-hexanol. Commercial alumina, silica gel and also Pakistani magnesite rock were used as adsorbents. Commercial adsorbents had particle size of 70–230 mesh and the particle sizes of magnesite varied between 16–50, 50–100, 70–230, 100–230 mesh. Solvent to oil ratio was 3:1 (V:V). Adsorbent was used to decolorize the oil. Authors pointed out that magnesite has a smaller surface area, $100\text{--}150\text{ m}^2\text{ g}^{-1}$, compared to alumina ($300\text{--}350\text{ m}^2\text{ g}^{-1}$) or silica gel ($750\text{--}800\text{ m}^2\text{ g}^{-1}$). However due to bigger pore sizes of magnesite, it removed colorizing material most efficiently. Based on the results, it was concluded that oil to sorbent ratio should not exceed 75 g per 100 g of adsorbent. Additionally, 100–230 mesh size was found to be optimal for magnesite based adsorption. Researchers therefore chose to use magnesite in the further experiments. MEK was chosen as primary

solvent for the extraction step. Also n-hexane was noted to be inexpensive and suitable eluent solvent for the process. Disadvantage of the proposed purification method is that it requires two solvent recovery steps thus increasing the investment costs. [37]

Mohammed *et al.* (2013) also studied the combination of solvent extraction and adsorption on solids. Researchers gathered waste lubricating oil from collecting stations in the city of Mosul, Iraq. They run experiments with n-hexane, 1-butanol, petroleum ether, 1-hexanol, carbon tetrachloride, and acetone. Adsorbents were chosen based on local availability. Therefore, almond shell, walnut shell, eggshell, each having particle size 30 to 60 mesh and acid activated clay with particle size 100 to 230 mesh were used as adsorbents. Solvent to oil ratio was varied between 1:1 and 3:1. Also 1.0–3.0 g of KOH was added to enhance extraction-flocculation. 15 wt% of adsorbent was added to extracted oil, vigorously mixed for 10 min and then left to room temperature for 1 h. Purified oil was obtained by filtration. [38]

Purification effect of solvent extraction was measured by monitoring the percentage of sludge removal. Thus, optimal conditions were 1-butanol as the solvent, 3:1 solvent to oil ratio, and 2 g of KOH addition. Effect of adsorption treatment was estimating typical oil quality factors like viscosity, ash and water content and total base and total acid number. Results indicate clearly the superior performance of acid activated clay compared to other adsorbents. Even though less effective, these shell adsorbents are inexpensive so they could be implemented to process depending on the purification requirements. [38]

Both of these studies concerning solvent extraction–adsorption method lack more detailed information about elemental analysis of used or purified lube oil. Thus, it is difficult to state how efficient the purification method actually was. These data would definitely be needed if purified oil is going to be sold. Also the large amount of used solvent will be undesirable for large-scale process.

Ion-exchange and adsorption are key technologies enabling transition to more effective processes generating less waste. Ion-exchange has already acquired a stable position as *in-situ* solution to industrial oil purifying task. Patented applications include *in-situ* treatment of hydraulic fluids and lubricants. Purification is carried out in a resin-filled cartridge. Acidic hydrolysis products cause corrosion

and deteriorate fluid properties. Therefore, ion-exchange resin, e.g. Hilite E, is used to remove these degradation products. Patented structure is designed to withstand swelling of the resin. Swelling is caused primarily by water adsorption to resin material. [39] The Hilliard Corporation provides filter cartridges filled with ion-exchange media. These Hilite cartridges remove only acids and oxidation products. Thus, no active additives are removed so then the lifetime of lubricating oil can be maximized. [40]

Duchowski *et al.* (2001) reviewed ion-exchange process added to vacuum dehydration treatment. The article focused on phosphate ester hydraulic fluids. Therefore, reviewed purification treatment was targeted on against oxidized or hydrolyzed phosphate ester degradation products. Experimental data used in comparisons were obtained from various power plant hydraulic systems. In one case, the required amount of ion-exchange resin was only 0.1 % of total fluid weight. Plant tests were also made using Fuller's earth but then same acidity removal efficiency was obtained with significantly higher amount of adsorbent, *i.e.* 0.6 % of total fluid weight. Ion-exchange resin was kept wet to achieve best removal efficiency. Thus, vacuum dehydration was necessary to remove water originated from the resin. [41]

Jones *et al.* (2001) used non-aqueous ion-exchange column cartridges to isolate aliphatic and naphthenic acids from crude oil. With the help of these cartridges authors were able to analyze these acid fractions by gas chromatography and mass spectrometry. The solid-phase extraction (SPE) column was packed with a strong anion exchanger material containing quaternary ammonium groups. [42]

Adsorptive methods are related to previously discussed ion-exchange technologies. Abdel-Jabbar *et al.* (2010) performed adsorbent based purification experiments to re-refine waste lubricating oil. Authors used an unspecified oil adsorbent material, bentonite, dried date palm kernel powder, and dried egg shale powder. Also acid activated bentonite and acid activated date palm kernel powder was used. Waste oil was diluted by 3:1 solvent to oil ratio with petroleum hydrocarbon stabilized condensate from BP Amoco plant, United Arab Emirates. Stabilized condensate included oil demulsifier. 15 wt-% of adsorbent was added to oil and mixed at room temperature. Adsorption time was varied between 1 to 6 hours. After the treatment,

mixture was filtered and distillation was used for solvent removal. Waste oil contained 632 mg kg⁻¹ of phosphorus, 11 mg kg⁻¹ of silicon, and various trace metals. Results clearly show that acid activated bentonite removed impurities most efficiently. Purified oil had 381 mg kg⁻¹ of phosphorus and lower than 1 mg kg⁻¹ of silicon. [43]

2.6. Process Example

Due to strict regulations concerning used oil disposal practices in Western Europe and North America, these regions have the highest collection rates of used oil. Europe stands out even more clearly than North America when the rate of re-refining is compared. At 2009 about 50 % of collected used oil was re-refined in Europe but in North America re-refiners obtained only 12 % of collected used oil. Main difference between these two continents is that in North America about 80 % of collected oil is burned. [44] Of course, the situation has changed since 2009 and the re-refining gap has probably been narrowed.

Therefore various re-refining plants are located in Europe utilizing many different patented technologies. Kupareva *et al.* (2013) have reviewed these technologies in their article. The scope of the review included European re-refineries having capacity greater than 40 000 tons per year. Historically the first re-refining plants used acid-clay process to produce base oils from used lubricating oils. However, due to the need of both large amounts of sulphuric acid and porcelain or aluminum silicate clays, this technology has almost totally been replaced by more modern technologies. Acid-clay method also generates significant amounts of hard-to-treat waste. Thus, even some developing countries like India in 2003 [45] have banned the use of this technology. Also the quality of re-refined base oil product is below Group I specification. Additionally, produced base oil contains 4 or even 17 times more polycyclic aromatic hydrocarbons than unused base oils. [13]

Fluid Solutions GmbH has designed more sophisticated process for waste oil re-refining which surprisingly still utilizes acid-clay method to some extent. The difference is that the process has a special plasma tubular reactor in the pretreatment stage which improves the contaminant removal efficiency. In Europe, there is one plant which has been in operation for almost two decades in Germany. Feed oil is first dehydrated to remove water and light hydrocarbons. Next the diesel fraction is

separated with pre-vaporization. Then dried oil feed is directed to plasma tube reactor with simultaneous addition of alkali. Plasma tube reactor is operated at high (380 °C) temperature and under vacuum (10–20 mbar). Heated oil compounds reach high molecular velocity, which in addition to catalytical participation of sodium or potassium ions, removes contaminants very efficiently. If for example sodium hydroxide is added, plasma zone will contain catalytic metallic sodium which desulphurizes and dechlorinates oil feed. These impurities are removed as a residual bottom product. Acid-clay method is introduced after the plasma stage for decolorization of plasma treated oil. Concentrated sulphuric acid is added and acid tar is removed after settling. Then bleaching clay is mixed with oil. Vaporisator removes spindle oil by-product streams from the base oil stock-clay mixture which is then finally filtered twice with second clay addition to achieve final base stock product. [46] Even though plasma tube reactor definitely will enhance re-refining process, still there is no clear answer to the post-processing of hazardous and acidic waste streams. Process will also certainly produce significant amounts of spent clay in addition to acid tar fraction. Furthermore, the company does not explicitly reveal in which of API base oil group specifications the purified oil will be located. This may indicate that the re-refined oil could contain sulphur more than 0.03 wt-%.

Another process based on older technology uses propane or solvent extraction to remove impurities from used oil. Propane is used to extract base oil components from the de-asphalting unit. Process operates with high propane–oil ratio which is at the same time the biggest disadvantage. To cope with high operating costs, propane is replaced with special solvent, N-methyl-2-pyrrolidone (NMP) in patented solvent extraction technology. NMP has high selectivity towards oil impurities, especially aromatics and thus less solvent is required. NMP is not particularly toxic or volatile [47] so it quite ideal to be used in the extraction process. Both propane and NMP can be recycled within the process. The obtained base oil is otherwise good quality but usually high sulphur content prevents reaching the Group II specifications. However, notable advantage is quite high oil yield, even 91 %. [13]

Adding a hydroprocessing unit to the plant is one way to respond the challenge related to base oil quality requirements. It has to be noted that like previously mentioned processes, also these hydrotreating technologies are combinations of

various pretreatment stages and distillation units. Therefore, vacuum distillation, thin film evaporation, thermal de-asphalting or even solvent extraction could be used with hydrofinishing. [13] Chemical Engineering Partners (CEP) has patented improved process for the production of base stock oils from used oil [48, 49]. First and still the only CEP process in Europe has been in operation since 2009 in Hamina, Finland with an annual capacity of 60 000 tons of which Group II base oils comprise 42 000 tons. [13, 50] Block flow diagram of the CEP process is presented in Fig. 2.

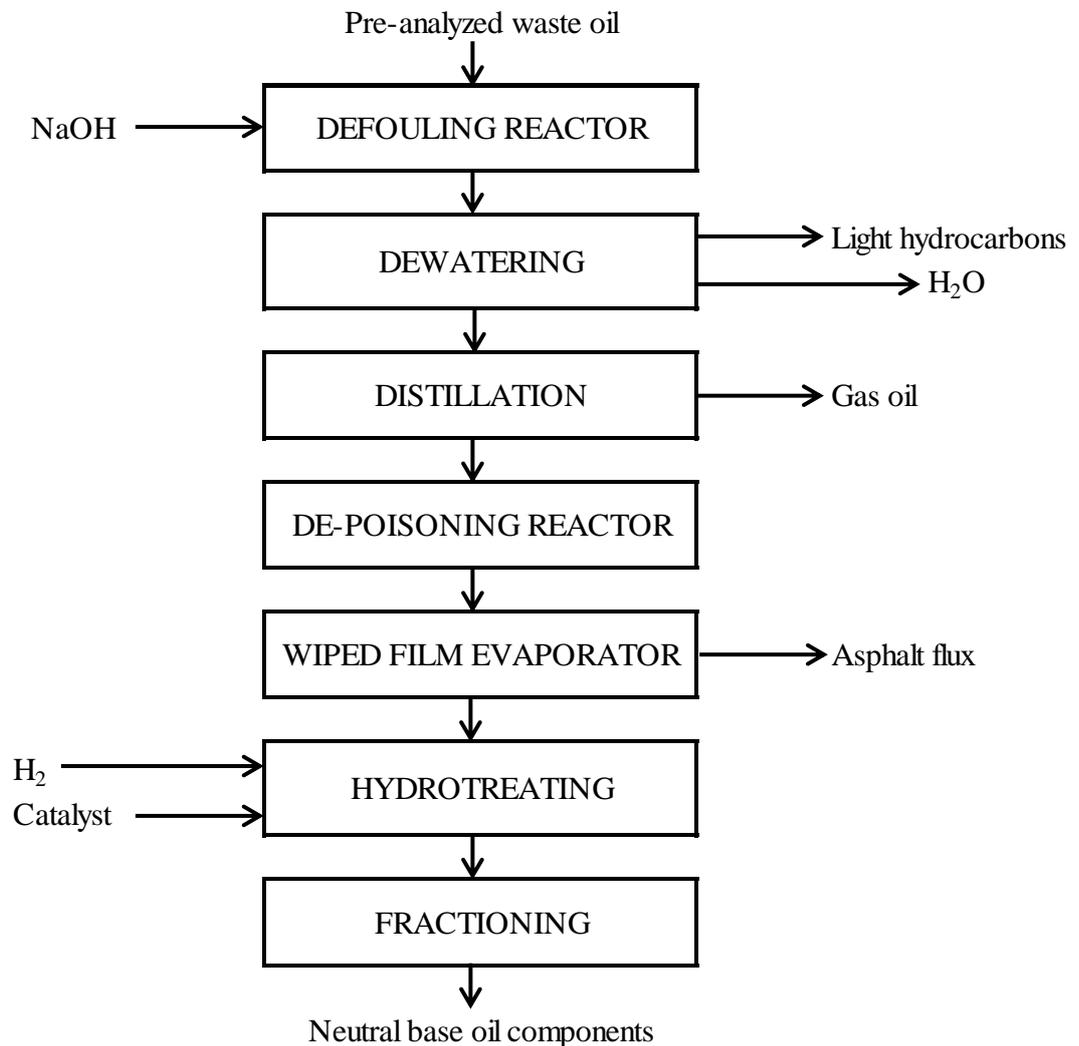


Figure 2. Block flow diagram of CEP process, modified from [13, 49].

Crankcase motor oil is the most preferred feedstock but also gear oil and both transmission and hydraulic fluids are accepted with certain limitations. Feedstock must be pre-analyzed to ensure its suitability. Used oil should have water content lower than 10 % and feed should not contain vegetable oils, some types of synthetic

oils, or PCB's [49]. Vegetable oils and synthetic compounds cause problems during pretreatment with sodium hydroxide. This is due to the saponification of vegetable oils and destabilization phenomenon with synthetic oils [13]. Sodium hydroxide is required to reduce the concentration of phosphorus compounds, which otherwise shorten the catalyst lifetime. Insoluble metal phosphates are produced in the reaction with NaOH. This alkaline treatment also neutralizes acidic groups and therefore reduces the corrosion risks. However, if the dosage of NaOH is-excessive, by-product asphalt occurs in gel-like form which greatly reduces the yield of base oil. [48] After the alkaline treatment, water and fuel originated light hydrocarbons are removed with distillation. These light hydrocarbons are used as fuel on site or are sold forward [13, 49]. Then the oil is distilled to remove gas oil *i.e.* diesel which can be treated similarly as light hydrocarbons. Despite the pretreatment procedures, a de-poisoning reactor is needed due to the possible presence of catalyst poisons. Exact operating principles and used separation materials are guarded with patents and so information is not available [49]. After the de-poisoning reactor, feed is directed to wiped film evaporator. Asphalt flux is obtained as a by-product containing metals and additive degradation products. After this stage, oil is fed to three hydrotreating reactors operating in high temperature and high pressure [49] where nitrogen, sulphur, chlorine and oxygenated organic compounds are removed. [13] Reactors use CEP-HRX hydrotreating catalyst which is designed to have maximal catalyst life-time [49]. Finally, vacuum distillation is used to enable fractionation of different viscosity cuts. [13, 49]. Final product is transparent and fulfills API Group II requirements [49].

3. PROPERTIES OF IMPURITIES IN WASTE LUBRICATING OILS

Impurities are gradually emerging through degradation of lubricant additives and through oil contamination by dirt and wear. Especially oxidation dramatically changes the additive properties and thus originally intentionally added useful additives will degrade over time and start to deteriorate the properties of the lubricating oil. Impurity buildup is problem not only during lubricant usage but particularly challenging when the used oil is subjected to re-refining procedures. That is why the properties of different contaminants should be known in advance.

3.1. Impurities Containing Phosphorus, Silicon, and Chlorine

Phosphorus, silicon, and chlorine were chosen to be examined in this thesis because of significant additional challenges caused against re-refining efforts by these three elements. All of them are found at quite high concentrations in most of waste oil streams.

Phosphorus is especially hazardous for catalysts. When producing lube oils from waste oils, hydrotreating catalysts are deactivated after 2–4 weeks. This is significantly shorter than the catalyst life-time of several years found in hydrotreating lube oils produced from the virgin base stocks. [48]

Adverse effects of silicon are not so well studied concerning the waste oil re-refining industry. Nonetheless, silica poisoning is a well-known phenomenon in petroleum refineries during thermal cracking and coking of hydrocarbons [51]. Pérez-Romo *et al.* (2012) describe how the silica deactivates activated alumina hydrotreating catalyst. Silica is adsorbed into the adsorbent surface which gradually decreases the catalyst activity. Authors explain that silicon species form Al–O–Si Brønsted acid sites and therefore hydrotreating reactions cannot occur [51]. Catalyst manufacturer Haldor Topsøe has extensively studied the silica poisoning in hydrotreating units. Similarly to lubricating oils, silica is originally introduced to the process as an antifoam agent to prevent light hydrocarbons to form foam. Silica is adsorbed to catalytically active sites located on the adsorbent surface. Moreover, more silica is adsorbed when temperature is increased. Silica deactivates catalyst so severely that the catalyst even becomes unregenerable. Especially denitrogenation activity of the catalyst is almost entirely lost if one fifth of the catalyst surface is covered with SiO₂. Desulphurization activity is not so strongly affected but still reduced below 80 % when compared to fresh catalyst. [52]

Chlorine present in the waste oil is always problematic even if the waste oil is incinerated. Almost all of the chlorine is in organic form and these compounds start to decompose to hydrochloric acid already at moderate temperatures. [53] Thus, e.g. distillation procedure is not usually suitable because of increased corrosion risks throughout the re-refining process [53, 54]. Acceptable total chlorine level in used oil is between 0.2 and in some cases even 0.5 wt-% if oil will be re-refined [54].

3.1.1. Sources

Phosphorus in used lubricating oil is in almost all cases originating from additives.

Synthetic oils containing mostly polysiloxanes should not be mixed with hydrocarbon-based waste lubricating oil streams. Some research has been done to depolymerize polysiloxanes to cyclic siloxanes. These can be used for the production of silicone polymers [55]. However, authors used pure siloxane in experimental section so actually the treatment of even silicone oils could be too challenging due to various impurities interfering the depolymerization process.

In some cases some silicon may be transferred from engine coolants to lubricating oil due to coolant leakage. Silicon compounds are used in diesel engine cooling systems as an antifoam and an anti-corrosion agents [56]. Increased silicon concentration in lubricating oil may also indicate contamination with dirt or fly ash but particularly with new engines, the reason for risen levels may be the residual engine component casting sand and silicon sealants [57].

Chlorine-containing additives are added as dispersants to retain dirt in suspension. Usually chlorine is bound in long-chain organic molecules. Normal chlorine levels are around 100–150 mg L⁻¹. Amount of chlorine has been reduced since 80's but low chlorine (<100 mg L⁻¹) dispersants weaken engine performance due to increased friction. Analyses revealed that polychlorinated dibenzodioxins or dibenzofurans (PCDD/F) were found in the emissions at only picogram level. Also researchers made a significant observation that varying chloride level in lubricating oil between 12–259 ppm did not have effect on PCDD/F emission levels. Case was similar even if the diesel oxidation catalyst was removed, although then the emission concentrations were higher. [58]

Additives

Additives are chemical compounds which are needed to enhance performance of the lubricating base oil [3, p. 44]. Petroleum base mineral oils have much poorer oxidation stability compared to synthetic base oils. That is why more additives are required with conventional base oils [59]. There are numerous additives but the most important would be antioxidants, metal deactivators, detergents, anti-wear additives, extreme pressure compounds, antifoam agents, and viscosity index

improvers. Additives degrade during the use. The degradation effect may even generate toxic substances. [3, pp. 45–51, 16]

Oil oxidation is a result of free radical chain reaction. Unstable oil molecules undergo transformation to peroxy radicals in the presence of oxygen. These radicals then react with other oil molecules forming new initiators and peroxy radicals. Antioxidant is a chemical which either react with the initiators and form stable compounds or break down initiators to less reactive compounds. Oxidation is not a significant problem at temperatures below 93 °C and first-mentioned antioxidants are most suitable. These cases include e.g. turbine and hydraulic oils. However, at higher temperatures metals begin to act as catalysts to increase oil oxidation. Therefore, for example dithiophosphates are used as antioxidant additives to coat metal surfaces. Additionally, dithiophosphates decompose hydroperoxides and this effect intensifies the antioxidative properties. [3, pp. 47–49]

Detergents are additives which are used to chemically neutralize deposit precursors. Deposit precursors are by-products from the burning of fuels. Most common detergents are organic soaps and salts of e. g. barium, calcium, or magnesium. [3, p. 49]

Anti-wear additives shield metal surfaces when the lubricating oil film is thinning. Anti-wear effect of lubricating oil film decreases when surface encounters increasing temperatures and loads. Additive compounds include long chain molecules like fatty oils, acids, and esters. Polar end of the molecule attaches to metal surface and chains form protective layer upwards the planar surface. [3, p. 50]

In relation to anti-wear additives, extreme pressure additives are needed in the case of very high temperatures or heavy loads. These compounds chemically react with the surface and form oil insoluble surface film. Film is constantly reinforced by the film formation reaction. Additive compounds incorporate elements like sulphur, chlorine, and/or phosphorus but the type of metal surface determines the suitable chemical. [3, pp. 50–51]

Antifoam agents are needed when stirring causes lubricating oil to foam. Foam can cause serious problems with oil flow. Oil-insoluble silicone polymers are used as

defoamers. Main problem with this additive group is linked to settling of silicone polymers during prolonged storage. Therefore, antifoam agent dosage should be in ppm scale and polymer size must be chosen carefully. Obviously the mixing should be conducted accurately. Anyhow, organic polymers can be used as substitutes to evade these challenges. However, organic polymers are needed in much higher concentrations than traditional silicone polymers. Antifoam agent sticks to air bubble in lubricating oil phase and cause smaller bubbles to unite. United bigger bubbles are more likely to travel on the surface of foam layer and burst. [3, p. 46]

Viscosity index improvers are long chain polymers with high molecular weight. The main purpose with these additives is to increase viscosity at high temperatures. However, viscosity index improver should not enhance relative viscosity at low temperatures which could lead to weakened flow characteristics. Thus, at low temperatures molecules are in tight entangled form while at high temperatures molecules straighten out. Although polymer chains may momentarily line up improperly due to mild shear stress, this phenomenon is exploited during cold engine starts. Then the decreased viscosity of oil helps the start-up procedure. Suitable compounds are for example methacrylate, acrylate, and olefin polymers. [3, p. 45]

Additive blending can be quite uncontrolled sector in some countries. For example in Asia, there is an information gap between oil refiners and automakers. [60] The excessive use of additives without regulative measures will most likely cause problems for the used oil re-refineries. Quality of the used oil feed may therefore greatly vary depending which region the oil was collected.

Contaminants

Lubrication properties of lubricating oil deteriorate during the usage. Diphare *et al.* (2013) have listed the main contaminants in addition to base oil and degraded additives. Authors presented these to be metallic debris, oxidation products, and carbon soot. Also water, chlorinated solvents, unburned fuel, and dust are accumulated in the used lubricating oil. [16]

Lubricant base oil may also contain small quantities of aromatics. As mentioned earlier, the primary operating principle of extreme-pressure and anti-wear additives

and friction modifiers is to generate connection between surface and the additive molecule. Aromatics can cause competing adsorption towards these additives thus decreasing their effect. [61]

3.2. Chemical Properties

Dominguez-Rosado and Pichtel (2003) have characterized fresh, used and weathered motor oil. They used combined gas chromatography and mass spectrometry (GC/MS), nuclear magnetic resonance (NMR), and Fourier transform infrared spectroscopy (FTIR) techniques for these analyses. Used motor oil contained more benzene compounds and compounds that are similar to naphthalene compounds than fresh oil based on the results from GC/MS analysis. FTIR analysis did not reveal any major differences between fresh and used motor oil. Nonetheless, indications of esters, ketones or acids were present in used oil. Also organic acid groups and aromatics may be present in used motor oil. NMR revealed new aromatic compounds from the used oil. Researchers also measured heavy metal concentrations but did not focus on phosphorus, silicon, or chlorine concentrations. [62]

Kupareva *et al.* (2013) used similar analytical techniques in their study to compare fresh, spent, and used oil. Used oil was mainly motor oil with the presence of 5–15 % industrial oil. Spent oil was gathered after 7000 km of engine run. GC analysis showed smaller hydrocarbon chains in used oil. Also antioxidant additives were not present anymore in spent oil. Many unidentified compounds could be seen in the results. FTIR analysis proved that zinc dialkyl dithiophosphates were no longer in detectable levels in both spent and used oil. Fresh oil also contained alcohols and phenols. Authors found out that only used oil resulted FTIR peaks related to Si-H bonds. They suggested that the presence of industrial oil may be the cause to this result. NMR indicated oxidation and also loss of antioxidant phenols in used oil. In contrast to article of Dominguez-Rosado and Pichtel, Kupareva *et al.* also used elemental analysis (CHNS/O) to compare elemental concentrations of fresh and used oil. Amount of carbon was almost the same in both samples. Slightly more hydrogen was present in the fresh oil. Previously observed oxidation of used oil was confirmed by higher oxygen levels in the used oil. Similarly, also nitrogen and sulphur were present in higher concentrations in used oil. In fact, no sulphur was

found in the fresh oil. However, authors pointed out the possible inaccuracy of the used analytical method. Therefore, the elemental analysis results should be verified with multiple analytical techniques. [63]

3.2.1. Chemical Properties in the Fresh Oil

U.S. Environmental Protection Agency has published a comprehensive report about zinc dialkyldithiophosphate (ZDDP) compounds used in lubricants. Different ZDDP's share a common structure of phosphorodithioic acid ester with alkyl or alkaryl substituent groups. [64] Generalized structural formula is presented in Fig. 3.

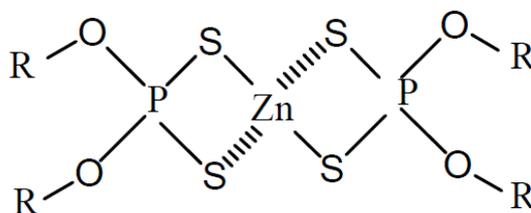


Figure 3. Structural formula of zinc dialkyldithiophosphate additive. [64]

The letter R in the structure refers to the alkyl or alkaryl groups. Alkyl group can be linear and/or branched hydrocarbon chains with three to ten carbon atoms. Alkaryl group is branched hydrocarbon chain with 12 carbon atoms or tetrapropenylphenol with 10 to 15 carbon atoms. Variability in the structure can be seen in range of molecular mass which varies between 580 to 1300 g mol⁻¹. [64]

EPA also reviewed the environmental fate of ZDDPs and found out that these additives are very stable in normal conditions. After 28-day biodegradability test, highest biodegradation was 5.9 % based on amount of generated carbon dioxide. Also no hydrolysis or photodegradation was possible under environmentally relevant conditions. [64]

Silicon in fresh oil originates from organosilicate, in the engine oils most commonly from polydimethylpolysiloxane. Chemical structure of the repeating unit in polydimethylpolysiloxane is presented in Fig. 4.

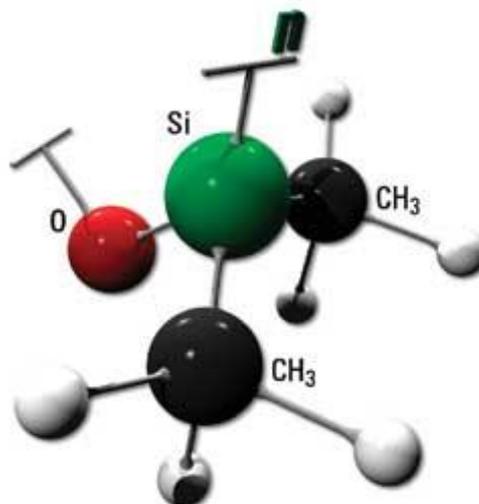


Figure 4. Chemical structure of polydimethylpolysiloxane. [65]

Other silicone based anti-foam additive examples with similar structure are listed as octamethylcyclotetrasiloxane and decamethylpentasiloxane [66]. Some commercial lubricant antifoams like TP367 also contain hazardous 2-ethylhexanol and 4-allyl-2-methoxyphenol besides siloxanes [67]. Thus, siloxanes may not be easily replaced without using harmful alternatives.

When different chlorine compounds which may be added to fresh oil are considered, chlorinated paraffins are maybe the most potential group. These chlorinated hydrocarbons are used in high pressure lubricating oils, most commonly used within metal industry for example in cutting oils. Chlorinated paraffins are straight-chain molecules with general formula (1): [68]



where x number of carbon atoms in the chain
 y number of chlorine atoms in the chain.

Usually the length of the chain is between 10 and 30 carbon atoms with 40–70 % chlorination [68]. Bridjanian and Sattarin (2006) have measured chlorine content of different lubricating oil samples. Based on these data, chlorine content in additive-free base lube oil was 2.1, in additive blended lube oil 38, in used oil 14, and in lab scale hydrotreated re-refined oil 2.9 ppm. [69] The authors did not give any comments what type of chlorine compounds were present or how geographically specific the detected chlorine levels were.

Technical bulletin concerning the current state of chlorine added engine oils published by U.S.A All American company addresses that common statement about highly reactive chlorine compounds is linked to chlorinated solvents and short-chain chlorinated hydrocarbons. However, nowadays more popular long-chain chlorinated hydrocarbons are very stable and thus non-corrosive. [70] These claims are from non peer-reviewed source published by lubricant marketer which should be considered when making any further conclusions. Aforementioned source does not comment on possible recycling of chlorine containing used oil. If chlorinated hydrocarbon is indeed in unreacted form, it may be removed during purification process without corrosion problems. Anyhow, this is highly debatable.

3.2.2. Chemical Properties in the Waste Oil

Lubricants are used in so many different applications with various additives so there are only a few studies available where for example chemical forms of additives in waste oil have been investigated. This may even be irrelevant due to inconsistent operating conditions in which different lubricants are exposed to. Thus, some case studies should be familiarized with but not taken as an only possible outcome.

Elo (2013) has given some typical concentration values present in used lubricating oil. Based on his presentation, silicon content is around 100 ppm and phosphorus content about 800 ppm. Maximum levels are said to be 200 and 1200 ppm respectively. [71] Again, these values are just one case example and not universally applicable.

Somayaji (2008) has studied oxidation stability of zinc dialkyl dithiophosphates. Author describes the decomposition reactions of ZDDP to be very complex, because compound may be exposed to thermal [72], chemisorption affected catalytic [73], hydrolytic [74] or oxidative [75] degradation [76]. Thermal decomposition becomes evident at temperatures above 150 °C and in hydrocarbon solution with ZDDP, mercaptides, alkyl sulphides, H₂S, and olefins are produced as decomposition products. Also insoluble glassy products are formed containing phosphorus, oxygen zinc, and sulphur. If acids are present, the thermal degradation of ZDDP is catalyzed. [72]. In the presence of water, ZDDP chain length is shorter due to depolymerization [74]. Properties of ZDDP as an anti-oxidant are disturbed with high iron or basic additive concentrations [75] It is suggested that ZDDP or

the decomposition products react with hydroperoxides which replaces phosphorus bonded sulphur to oxygen [75, 76].

Rahimi *et al.* (2012) have studied physicochemical properties of a mineral based engine oil by taking oils samples with usage intervals between operation from 0 to 11,500 km. Among other parameters, authors also followed changes phosphorus and silicon content. They found out that concentrations of both elements decreased. Phosphorus was reduced from 811.2 to 411.9 ppm and silicon from 61.4 to 50.1 ppm. Zinc was also depleting in a similar way. [77] Unfortunately, authors do not make any further suggestions where removed components end up. It could be possible that additives react and form such compound that not detected anymore with ICP. In that case, P and Si compounds could still be present in the used oil.

Chlorine in waste lubricating oil may be present as chlorinated hydrocarbons *i.e.* trichloroethanes, trichloroethylenes, perchloroethylenes [78]. Risen chlorine content in used oil can also be caused by contamination with chlorinated solvents or transformer oils, oil additives, and lead scavengers. Chlorinated lead scavengers are added to leaded gasoline. Furthermore, additional source can be chlorinated industrial cleaning solutions. [54]

4. PURIFICATION METHODS

There are various methods to purify used lubricating oils. However, only a few technologies can successfully produce high quality base oils. Al-Ghouti and Al-Atoum (2009) compared virgin and recycled engine oils collected from Jordanian markets. Visually all of the oil samples may seem to be identical but authors noticed significant differences when samples were analyzed by FTIR and ICP. Therefore, simple recycling and purification processes were not efficient enough to remove silicon, metals, and oxidation products. For example, one recycled oil sample contained 20 ppm of silicon. [79] Generally, only the modern and sophisticated re-refining processes are able to remove impurities to low levels. As seen in the above mentioned studies and process examples, adsorption technologies have been proved as efficient solutions to this challenge.

4.1. Principles of Adsorption and Ion-Exchange

Adsorption is a process where components are separated from surrounding phase into the solid particle. Components can be either in gas or liquid phase. [80, pp. 1–2] The reaction between the adsorbent surface and the adsorbed component can be reversible or irreversible [80, p. 29]. The opposite phenomenon of adsorption is called desorption [80, p. 305].

Adsorption phenomena are roughly divided in physical adsorption or physisorption and chemisorption. The reason behind physisorption is the van der Waals forces between the component and the surface. In comparison, chemisorption includes electron transfer which forms the bond. Physisorption involves low adsorption enthalpy while chemisorption has high heat of adsorption. Heat of adsorption is used to determine the interaction strength between surface and adsorbate. Thus, physisorption is usually reversible but chemisorption can be more commonly irreversible. Chemisorption is also highly specific and can take place both low and high temperatures. Chemisorbed compounds only form monolayers and may dissociate. Physisorption also includes multilayer adsorption. Unlike chemisorption, physisorption is effective only at low temperatures. However, physisorption is rapid as chemisorption can be slow. [80, pp. 29–30]

Adsorption separation process is highly dependent on the type of selected adsorbent. Adsorbents can be grouped based on the pore width. Microporous materials have pore widths smaller than 2 nm, mesoporous materials have pore widths between 2 and 50 nm, and macroporous materials have pore widths larger than 50 nm [81]. Material should withstand the operating conditions and preferably have maximal separation factor in those conditions [80, p. 4]. Good capacity with slow kinetics is as unfavorable as fast kinetics with low capacity. High surface area or pore volume enables sufficient capacity and large pore network is needed for fast transport of compounds into the particle [82, p.2]. Selectivity towards target compounds is essential to achieve high feasibility [80, p. 3]

However, some adsorbent materials may not adsorb the desired element but actually can even increase the concentration of that contaminant. This undesirable phenomenon was observed in the article of Al Zubaidy *et al.* (2013). Authors used commercial activated carbon, trade name NORIT, as the adsorbent material for

sulphur removal from diesel oil. Although the use of activated carbon reduced sulphur concentration from 410 ppm to 251 ppm, simultaneously concentrations of phosphorus, silicon and chlorine increased. Biggest addition was in silicon content which rose more than 154 % from 16.2 ppm to 41.1 ppm. Similarly, treated diesel oil contained 19 % more phosphorus and over 9 % more chlorine. [83] One of the biggest activated carbon producers, Cabot Norit Activated Carbon has stated that the material may contain crystalline silica but most of it is very strongly bounded into the carbon structure [84].

Commonly used set-up for adsorption process is the fixed bed column. Schematic picture of fixed bed column is presented in Fig. 5.

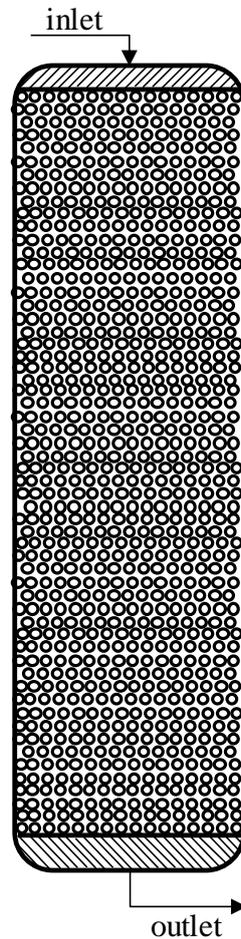


Figure 5. Schematic picture of fixed bed column.

Design of this type packed bed system must consider mass transfer resistance, amount of void space, and steady flow through the bed among other things. Adsorption equilibria and mass transfer can be studied theoretically and/or

experimentally. Most simplified set-up is an isothermal system with one component in inert gas or solution. Then there is only a single mass transfer zone and the analysis is quite straightforward. Adding more components or changing the carrier to non-inert gas or solvent complicates the modeling of the dynamic behavior due to the coupling of equilibrium isotherms and rate equations for multiple species. [80, pp. 220–221]

To some extent, ion-exchange is a similar process than adsorption. Ion-exchangers are generally defined as insoluble solid materials carrying exchangeable cations or anions. Also amphoteric ion-exchangers for both cation and anion exchange do exist. Ion-exchange occurs in contact between the ion-exchange material and the electrolyte solution. Number of ions exchanged between the electrolyte solution and material cannot exceed the number of the exchangeable ions in the material. Thus, stoichiometry sets limit to purification efficiency. [85, p. 5] Also liquid ion-exchangers consisting of two immiscible fluids are available [85, p. 19] but these are ignored in this study due to the incompatibility with the topic.

A solid ion-exchanger is structured of framework, co-ions and counter-ions. Chemical bonds (cross-links) or lattice energy keeps the structure together. Counter ions can move freely in the framework enabling the ion-exchange between the material and electrolyte solution. Electroneutrality must be maintained so counter ion cannot leave the framework unless an equivalent amount of new counter ion enters from the electrolyte solution to framework. Also solvent may flow into pores causing swelling of the ion-exchanger. If co-ions are invaded in the resin together with the solvent, then the swelling simultaneously increases counter ion capacity of the material. [85, pp. 6–7]

Resin is a general term for organic ion-exchanger. Zeolites are most common example of inorganic ion-exchangers. Degree of cross-linking of hydrocarbon chain matrix of the resin determines the chemical, thermal, and mechanical durability. Therefore, ion-exchanger should not be exposed to such a strong solvent which can break the intra-particle bonds. When compared with zeolites, somewhat more fragile organic resins still possess significant advantage due to flexible and elastic framework. This allows significant swelling of the resins which is beneficial in terms of counter ion capacity. [85, pp. 14–15]

Ion-exchange is usually reversible process. Ion-exchanger which has exchanged all its ions is called exhausted. Regeneration process can be used to restore exchanger to original composition. The regeneration solution must contain the ions which will be returned to material. [85, pp. 5–6]

Strongly acidic ion-exchange resins can be used instead of strong acids to purify the used oil. Then the corrosion risks of the equipment are greatly reduced. For example Girolamo and Marchionna (2001) experimented the use of strongly acidic resin in dimerization of isobutene. From the corrosion point of view, macroporous resin was found safer to use than the utilization of homogenous. [86]

4.2. Phosphorus Removal

Murray *et al.* (2003) patented a process utilizing separation material to remove phosphorus-containing impurities from olefin *i.e.* C14–C18 stream. Impurities include organophosphines and corresponding oxides. These are difficult to remove by distillation due to the co-distillation with olefin feed. Most preferable materials are said to be acidic ion-exchange resin, acidic zeolite, and acidic alumina. Also neutral activated carbon and particularly metal impregnated activated carbons. Removal efficiency of acidic ion-exchange resin, Amberlyst 15, was used as an example. Phosphorus concentration decreased from 24 to less than 0.6 ppm when olefin to sorbent weight ratio was 100. Using higher olefin to sorbent weight ratio, 500, resulted equilibrium phosphorus concentration of 11.9 ppm. Suitable system was described to be up-flow fixed bed reactor. Up-flow was used to ensure better wetting of the bed. Temperature was between 10 to 50 °C. [87] If the feed stream contained more impurities than only phosphorus, the presented removal efficiency would probably be much lower. This scenario will most likely become concrete when re-refining used lubricating oils.

Ali *et al.* (2010) studied how effectively zeolite adsorbs heavy metals from used lubricating oil. Due to the observed selectivity towards zinc, zeolite may also simultaneously remove phosphorus if the phosphorus is part of ZDDP in the oil. The used oil was pretreated with 2-propanol and MEK mixture. KOH was used as a flocculating agent to improve settling. After settling and evaporation, recovered base oil fraction was subjected to zeolite treatment. As a conclusion, optimum conditions were treatment time of 10 min, temperature of 30–50 °C, and zeolite

addition of 5 g. Zinc removal was determined to be 62 %, although oil-adsorbent mass ratio was not specified. [88]

4.3. Silicon Removal

Catalyst manufacturer Haldor Topsøe suggests the use of guard adsorbent beds to prevent silicon reaching the hydrotreating catalysts. In their coker naphtha catalyst bed, the first layer is formed with guarding catalyst TK-439, then the next layer, TK-437, is mainly designed to saturate diolefins but this catalyst also adsorbs silicon compounds although not as efficiently as TK-439. Bottom layer, TK-431 works as the actual main bed. TK-439 has additional 30 % capability to adsorb silicon compounds compared to the main bed and similarly TK-437 adsorbs silicon 10 % more than the main bed. The main difference between TK-439 and TK-437 is the total absence of metals in the TK-439 catalyst. TK-439 is also inactive to denitrogenation or –sulphurization reactions so the sole purpose of this catalyst is to remove silicon compounds. [52]

Matjie *et al.* (2009) removed dissolved inorganics from gas condensate with Selexsorb alumina adsorbent. The authors treated 20 L of gas condensate in fixed bed system packed with 200 g of alumina at 40 °C temperature for 60 min. Initial silicon concentrate was 18.8 ppm and after treating 250 mL of the condensate, 87.7 % of silicon was removed. Anyhow, removal efficiency was reducing during operation and finally stabilized to removal value of 66.4 %. This resulted silicon content of 6.3 ppm in purified condensate. Alumina was noticed to leach aluminium to condensate reaching aluminium content of 16 ppm. Despite the challenges, the breakthrough volume was not reached. [89] It should be noted that no regeneration study was included. SEM analysis suggested that silicon has reacted with the adsorbent surface [89]. Therefore, regeneration may be quite challenging.

Zink *et al.* (2012) have patented process for improving a re-refined lube oil stream. Process should remove both organic phosphorus and organic silicon impurities at least if maximum operating temperature, 450 °C, is used. Described process utilizes noble metal catalyst including <2 wt-% of platinum and/or palladium. Catalyst should have strong hydrogenation characteristics. [90] Unfortunately, patent does not give any information of acceptable impurity levels or removal rates, so further evaluation of the described process cannot be provided.

4.4. Chlorine Removal

Petroleum industry has removed chlorine with special chlorine scavengers. These separation materials can be made of different metal oxides or hydroxides. A few examples include alumina, CaO, Ca(OH)₂, Na₂O, NaOH, K₂O, KOH, MgO, and Mg(OH)₂. Especially calcium oxide and hydroxide are most active for the chlorine removal task. Chlorine removal is based on adsorption at temperatures below 100 °C and atmospheric pressure. However, this treatment can usually only remove 15 % of chlorine. Therefore Laborde and Dolbecq have patented dechlorination process for re-refining of spent oil which is able to achieve even 80 % dechlorination at 350 °C with initial chlorine concentration of 325 ppm. They used commercial chlorine adsorbent which is composed of active CaO and ZnO carrier. [53]

Bridjanian and Sattarin (2006) re-refined used lubricating oil in a small, lab scale hydro-treating reactor. Temperature was between 250–370 °C and pressure between 60–73 bar. Interestingly, a spent middle-distillate hydro-cracking catalyst (HC-102) was used in the process achieving chlorine removal from initial 14 ppm to 2.9 ppm. At first, the spent catalyst was washed with naphta to remove hydrocarbons and with acetic acid to remove precipitated metals. Coke was removed in electrical furnace at 425 °C for 5 h. Lastly, catalyst was pre-sulfided with dimethylsulfide gas scrubbing at 340 °C for 12 h. Although authors did not evaluate the processing cost related to this catalyst pretreatment stage, they pointed out that some re-refineries may want to use fresh lube oil hydro-finishing catalysts, for example DN-190 or C-411. [69]

Puralube GmbH has marketed their catalyst used in HyLube re-refining process to be able to remove also chlorine compounds among other impurities. Published technical paper suggests that chlorine is present in antiwear additives. Therefore, it is not clear is the marketed catalyst selective to chlorine or is chlorine conveniently removed along the antiwear compound. All in all, company states that process accepts feed with chlorine concentration of 0.216 wt-%. [91]

4.5. Regeneration

Various regeneration techniques have been presented in the literature regarding the material type. Xie *et al.* (2010) used pentane and methanol washing to regenerate used anion exchange resin which was used to remove neutral nitrogen compounds from fuel. Used resin was first vacuum-filtered and washed with four resin volumes of pentane to remove residual fuel. The actual regeneration was done twice with four volumes of methanol. Solvent was removed under vacuum. Also other polar organic solvents were evaluated to be suitable for the regeneration task. [92]

Yan and Shu (1987) describe a method to regenerate used cation exchange resin, Amberlyst 15. Resin was used to remove model nitrogen compound, pyridine, from xylene. Anhydrous HCl was used to accomplish non-aqueous regeneration. HCl reacted with the sorbed pyridine forming oil-insoluble pyridinium salt. Then methylene chloride was used to dissolve and remove the pyridinium salt. Authors suggested that also small amount of hydrocarbon feed could eliminate the need to use solvent washing at final part of regeneration. Pyridinium salt is then removed from feed by extraction with water. [93] Even though the study took a quite narrow perspective on general regeneration issue, still it presented pretty simple and effective nonaqueous regeneration method. Again, main disadvantage of this method would be the presence of reactive chloride if the method was implemented to used lubricating oil re-refinery.

Other option for nonaqueous regeneration is flowing nitrogen gas through the separation material bed at high temperature [87]

4.6. Disposal of Used Separation Material

Even if used separation material can be regenerated and re-used several times, the material will eventually lose its separation properties. The spent material can be highly contaminated and thus categorized as hazardous waste. Therefore, proper disposal methods are should be considered beforehand.

Dubois *et al.* (1995) have separately used pyrolysis and incineration to treat acid-form cation exchange (Duolite C 20-H⁺) and base-form anion exchange (Duolite A 101-OH⁻) resins. Authors describe that under oxygen atmosphere both resins thermally degrade in following stages; first water is evaporated, then resin is

depolymerized and side groups are split, and finally polystyrenic structure is destroyed. Main difference between both resins was that degradation of anionic resin generated higher amount of volatiles. Obviously the emitted gases were also different based on sulfonated styrene-divinylbenzene copolymer structure of cation exchanger and trimethylaminated styrene-divinylbenzene structure of anion exchanger. Cationic resin generated sulphur dioxide while anionic resin emitted trimethylamine during thermal degradation at 300 °C. Additionally, both pyrolysis and incineration generated polycyclic aromatic compounds and carbon monoxide. Only option to prevent the formation of these hazardous volatile organics was incineration at 800 °C. [94]

In contrast to the previous study with separated resin batches, Chun *et al.* (1998) tested pyrolysis 50-50 (by weight) mixture of cationic resin (Amberlite IRN77) with sulfonic acid functional group and anionic resin (Amberlite INR78) with trimethylammonium functional group with styrene-divinyl benzene copolymer. During pyrolysis of the resin mixture H₂S, SO₂, CO, NO, NO₂, and O₂ were detected in the off-gas. When pyrolysis temperature was higher than 500 °C, carbon monoxide was only major component in the off-gas stream. [95] Both articles show the need for degradation temperature if the emission of most hazardous gases is desired to be eliminated. Otherwise, off-gas collection system could be required which would further increase the costs. One method to optimize thermal degradation would be to combine disposal of used separation material and highly polluted waste oil to for example same cement kiln. Even more efficiently the nearby kiln could create beneficial synergy with the re-refinery plant with alternative energy source.

Combined recovering and disposal process can be considered if the used separation material contains high-value metals. Dufresne (2007) has listed regeneration and recycling methods for petrochemical catalysts. The author describes how precious metals are recovered with hydro- or pyrometallurgical reclamation process. Coke is removed in the first step of hydrometallurgical process, then catalyst is leached with H₂SO₄ or NaOH to remove the substrate, and finally metals are recovered from the solution. Other option *i.e.* pyrometallurgical process involves melting of the dry catalyst at 1200–1500 °C. Metal alloys are recovered from the formed slag. Both

methods have the same problem with feasibility, because the prices of recovered metals may not compensate the recycling costs. [96]

5. EXPERIMENTAL

5.1. Materials

Used and distilled lubricating oil was obtained from Neste Oil. Commercially available products were used as separation materials.

5.1.1. The Oil Feed

Two used lubricating oil batches were used as feeds in experiments. Both oils were dark brown colored fluids at room temperature with a strong odor reminding burnt carbon. First one was pretreated first with atmospheric distillation to remove water and light hydrocarbons. Then the bottom product from the distillation column was filtered with an 18-micron filter. Filtered oil was vacuum distilled with thin film evaporator. Oil fraction from distillation range of 100 to 500 °C was collected for experiments.

The second and larger used lubricating oil batch was pretreated with atmospheric distillation in a range of 135.6 to 744 °C (5–95 % within the range of 182.0–476.2 °C). Mid-distillate was gathered for experiments. Tables II to IV present the different properties of the feeds.

Table II Concentration of nitrogen, organic chlorine, total chlorine, silicon, phosphorus, and total sulphur.

name:	c(N), ppm	c(Cl _{org}), ppm	c(Cl _{tot}), ppm	c(Si), ppm	c(P), ppm	c(S _{tot}), ppm
FEED 1	560	20	16	4.8	342	2150
FEED 2	360	-	260	297	52.6	2780

Table III Concentration of copper, iron, sodium, nickel, lead, tin, calcium, magnesium, and zinc.

name:	c(Cu), ppm	c(Fe), ppm	c(Na), ppm	c(Ni), ppm	c(Pb), ppm	c(Sn), ppm	c(Ca), ppm	c(Mg), ppm	c(Zn), ppm
FEED 1	34.3	9.9	4.1	LOD	1.3	LOD	205	49.8	106
FEED 2	0.4	LOD	4.3	LOD	LOD	LOD	LOD	LOD	0.7

LOD – limit of detection

Table IV Density (ρ), viscosity (ν) at 40 °C, amount of water $w(\text{H}_2\text{O})$ and ash $w(\text{ash})$, and the total acid number (TAN).

name:	ρ , kg m^{-3}	ν (40 °C), $\text{mm}^2 \text{s}^{-1}$	$w(\text{H}_2\text{O})$, wt-%	$w(\text{ash})$, wt-%	TAN, $\text{mg}_{\text{KOH}} \text{g}^{-1}$
FEED 1	828.4	24.33	0.01	0.139	0.9
FEED 2	860.5	4.933	0.07	0.004	8.5

Feed oils were stored in two metal containers at room temperature. The oil container was heated for 12 h at 60 °C in a hot air oven and mixed thoroughly before oil batch was taken and used in experiments.

5.1.2. Separation Materials

Several separation materials were tested for purification of the used lubricating oils. Both commercial adsorbents, ion-exchange resins and also experimental materials *i.e.* aluminium oxide powder and spent unregenerated oil refining catalyst were used and all materials are listed in Table V.

Table V. Separation materials which were used in experiments. [97, 98, 99]

type:	material:	application:
commercial adsorbent 1	unknown	removal of gaseous chlorine
commercial adsorbent 2	aluminium oxide with inorganic surface modifier	removal of HCl from vapor or liquid phase
commercial adsorbent 3	activated alumina	removal of organochlorides from vapor or liquid phase
commercial adsorbent 4	non-fibrous aluminium oxide	removal of organosilicates from hydrotreater naphta feed streams
Purolite A170/4675, weak base anion exchange resin	crosslinked polyacrylate-divinylbenzene copolymer	removal of anionic forms of heavy metals from acidic processing solutions
Amberlyst 15, strongly acidic polymeric resin	crosslinked polystyrene-divinylbenzene copolymer	catalyst in various organic reactions or removal of multiple components for column chromatography
Merck, aluminium oxide powder commercial bleaching earth	aluminium oxide acid-activated sepiolite	purification, decolorization, and deodorization of edible oils
Merck, activated carbon	carbon	removal of multiple impurities
spent TCC catalyst from Naantali refinery	noble metals (Pt, PtO, PtO ₂ , PdO), V ₂ O ₅ , on alumina	waste, fresh catalyst is used in oil refining

Commercial adsorbents 1–4 and spent TCC catalyst were obtained in large pellets or spherical particles with an estimated diameter of 5 mm. Therefore, these materials were manually grinded in mortar and sieved. Two sieves were chosen to collect particles in a size range from 500 to 710 μm . Also the generated dust was

collected for further use. Ion-exchange resins were washed thoroughly with distilled water.

All separation materials were dried for 12 h before experiments. The drying of all materials except two resins was carried out at 100 °C in a hot air oven. Ion-exchange resins were dried at 40 °C in a vacuum oven to prevent any structural damages caused by too intense drying temperature. Commercial bleaching earth was also used without drying in one experiment.

5.2. Methods

At first, suitability and efficiency of separation materials were tested with screening tests. Target impurities were chosen to be silicon, chlorine, and phosphorus. After the selection of potential materials, the temperature dependence of purification and adsorption kinetics were determined. Lastly, one fixed bed experiment was carried out with the most efficient separation material. Additionally, FTIR spectra measurements were conducted alongside with previously mentioned experiments.

5.2.1. Screening Tests

Screening tests were done in four series where type and adsorbent/oil weight ratio were varied. First feed (FEED 1) was used in series 1 and 2. Respectively, the second feed (FEED 2) was used in series 3 and 4.

20 g of heated and mixed feed oil was measured to a 50 mL Schott bottle. Then 100, 500, 1000, or 2000 mg of dried separation material was added into the bottle. Exact weighed amounts are presented in the Table II of Appendix II. Manual shaking was used to ensure a uniform mixture. Also one blank sample without added separation material was included in every series. The purpose of blank was to monitor what happens to the impurity concentrations during the screening treatment without the effect of separation material.

Closed bottles were then placed in an incubator (Heidolph Unimax 1010) at 65 °C for 24 h. Shaker mixed contents of bottles at speed of 200 rpm throughout the experiment run. After the incubator stage, solids and oil were separated centrifugally (Heraeus Megafuge 1.0). Rotation speed of 2500 rpm was used for

7 min. Also the blank sample was centrifuged. Separated oil was poured to sample bottle which was sent to analyses.

Sample concentrations are presented in Tables III–VII of Appendix II.

Concentration data were converted to reductions and capacities defined in Eqs 2 and 3.

$$R = \left(1 - \frac{c_{eq}}{c_0}\right) 100 \% \quad (2)$$

where R reduction
 c_{eq} equilibrium concentration
 c_0 feed concentration.

$$q = \frac{(c_0 - c_{eq})m_{OIL}}{m_{SM}} \quad (3)$$

where q adsorbed amount
 m_{OIL} mass of oil in the batch
 m_{SM} mass of added separation material.

When determining the R and q values for each series, concentration of the blank sample was taken as feed concentration. Thus, any possible impurity decrement caused by heating, centrifuging, etc. can be separated from the adsorption results.

5.2.2. Temperature Dependence Tests

Two separation materials were chosen for the study of temperature dependence of purification efficiency. Three different temperatures, 25, 65, and 130 °C were used for each material. Also one blank sample without added material was included. The second feed (FEED 2) was used in all temperature dependence experiments.

150 g of heated and mixed feed oil was measured to a 500 mL three-necked glass flask. The flask was placed in an oil bath equipped with a magnetic stirrer and hot plate heater (Heidolph MR Hei-Standard). Additionally egg-shaped magnetic bar was inserted to each flask. Stirring speed was set to 500 rpm. Two temperature sensors were used, one in the oil bath and the other in the oil flask. 15 g of separation material powder ($d_p < 500 \mu\text{m}$) was added to the flask after the target temperature was reached. Exact weighed amounts are presented in the Table X of Appendix III. Flask necks were sealed using one cap equipped with the temperature sensor and

two standard caps. After the material dosage, timer was started and the experiment lasted for 4 h.

After the heating, oil was separated by filtration through 0.45 μm membrane filter (Millipore, mixture of cellulose acetate and cellulose nitrate) in a Büchner funnel by vacuum suction. Filtrate oil was collected and sent to analyses.

Temperature dependency of adsorption can be analyzed using the the integrated van't Hoff Eq. 4 [100, p. 40]. The equilibrium constant was estimated assuming a linear isotherm given in Eq. 5.

$$\frac{d \ln K}{d \left(\frac{1}{T} \right)} = - \frac{\Delta H}{R_g} \quad (4)$$

$$q = Kc \quad (5)$$

where K equilibrium constant in Henry's law isotherm
 ΔH adsorption enthalpy
 R_g gas constant.

5.2.3. Adsorption Kinetics Test

One separation material was used to determine the kinetics of the adsorption at 130 °C. 700 g of the second feed (FEED 2) was measured in the 2 L cylindrical round bottom reaction vessel made of glass. Also one analysis sample was taken from the feed oil container. The vessel was placed in an oil bath. Nitrogen flow was directed above the oil to prevent hot oil reacting with oxygen. Oil was heated to target temperature. Motor with a four bladed steel mixer (d = 55.55 mm) unit was used to stir the studied oil. Mixing speed was set to 400 rpm. Three baffles (103.70 x 16.80 mm) were inserted into a reaction vessel to prevent vortex formation caused by the mixing.

After the target temperature of 130 °C was reached, 70 g of separation material was added to the oil. Exact weighed amounts are presented in the Table XV of Appendix IV. Timer was started and 15 mL samples were taken at 2, 5, 10, 15, 30, 60, 120, 180, 240, and 300 min. Sampling was done with a 5 mL graduated pipette. Pipetted oil was filtered with a 0.45 μm syringe filter (Pall Gelman Acrodisc) and the sample was sent to analyses.

Kinetics of adsorption in batch systems can be analyzed using the fractional uptake value defined in Eq. 6 [80, pp. 168–170, 82, pp. 537–539].

$$F = \frac{c - c_0}{c_{eq} - c_0} \quad (6)$$

where F fractional uptake.

Effective diffusion coefficient was estimated with simplified method presented by Terzyk and Gauden (2001). Eq. 7 is based on Fick's law of diffusion and applies to the initial, linear part of the adsorption curve. [101]

$$F = \frac{6}{r} D_e^{0.5} \pi^{-0.5} t^{0.5} \quad (7)$$

where D_e effective diffusion coefficient.
 r radius of the adsorbent particle.

The authors approximated particles to be nonporous spherical objects, adsorption process to take place in the linear Henry's region of the isotherm, and diffusion to be radial.

5.2.4. Fixed Bed Experiment

Same separation material as in the previously mentioned kinetics test was used in the fixed bed experiment. Similarly, the second feed oil (FEED 2) was used. Temperature was set to 65 °C.

1.5 L of the oil was poured to a 2 L Schott bottle. Bottle with the oil and magnetic bar was placed on a hot plate with a magnetic stirrer. Stirring speed was set to 250 rpm and the oil was let to temper to 65 °C.

90 g of separation material was measured to the decanter. Exact weight is presented in the Table XVIII of Appendix V. Analysis grade n-octane (Fluka) was mixed with the material. Generated slurry was poured into the n-octane filled column ($d_i = 30$ mm). Height of the bed was 198 mm and therefore bed volume, BV was 140 mL. N-octane was used to remove any air bubbles which could get trapped in the fixed bed matrix. Also the tubing was filled with n-octane. The column was equipped with a water circulation jacket so it could be heated to target temperature.

Schott bottle was connected to a peristaltic pump (Cole-Parmer Instrument Company MasterFlex L/S) which was connected to the bottom of the column. Special tube (MasterFlex PharMed, $d_i = 8.0$ mm) was used in the pump section. Additional tube was directed from the top of the column to a sampling site.

When target temperature was reached both in bottle and column, pump and timer were switched on. Flow rate was set to 10 mL min^{-1} (4.3 BV h^{-1}). First sample was collected from the outlet when no more octane was flowing out based on visual inspection. Experiment lasted 120 min and total of 46 samples were taken. Out of these samples, 12 were chosen and sent to analyses. Possibility of sample dilution by n-octane in the first samples was checked by sending two samples to GC/MS analysis.

5.2.5. Analysis of Samples

Samples were sent to Neste Oil laboratory for analysis. These analyses included the determination of metal, total silicon, and total phosphorus concentrations by inductively coupled plasma mass spectrometry (ICP-MS), organic chlorine content by micro-coulometry, and total chlorine concentration by X-ray fluorescence spectrometer (XRF). Micro-coulometry was used if chlorine concentration was below 100 ppm and if concentration was over 100 ppm, XRF was used. Detection limits are presented in the Table I of Appendix I.

5.2.6. FTIR Measurements

FTIR spectra were measured by using two devices, PerkinElmer Frontier FT-IR spectrometer and Thermo Scientific Nicolet iS10 ATR-FTIR. Based on the article of Kupareva *et al.* (2013), wavenumber region between 4000 and 400 cm^{-1} was used with interval of 1 cm^{-1} [63]. Resolution was 4 and the number of scans 64. Due to the limitations of ATR-FTIR, wavenumber region from 4000 to 650 cm^{-1} was used with that spectrometer. Resolution was 4 and the number of scans 32.

PerkinElmer spectrometer required more sample preparation than the ATR-FTIR. 100 mg of dried KBr was grinded and pressed to a disc in a SPECAC press under 8000 kg pressure for 2 min. Two identical discs were prepared. Both discs were placed in the sample holder and the background spectrum was measured. Then one disc was removed and $10 \mu\text{L}$ of oil sample was pipetted on top of the KBr disc.

Removed KBr disc was replaced and sample spectrum was determined. New discs and background spectra were prepared for each sample. Acquired spectra were adjusted to same level based on the position of the baseline.

Mixing of the sample and pipetting the oil on top of the ATR diamond were only sample preparation steps needed in ATR-FTIR measurements. One background spectrum was measured in the beginning of experiments.

6. RESULTS AND DISCUSSION

Results are divided in separate chapters based on the experiment type. Discussion of results is positioned after results in each chapter.

6.1. Screening Tests

Calculated reduction values for screening tests are presented in the Table VIII of Appendix II. Silicon, phosphorus, and chlorine concentrations from screening tests are presented in Figs 6–8. These figures include initial feed and blank sample concentrations and also the equilibrium concentrations from samples treated with different separation materials.

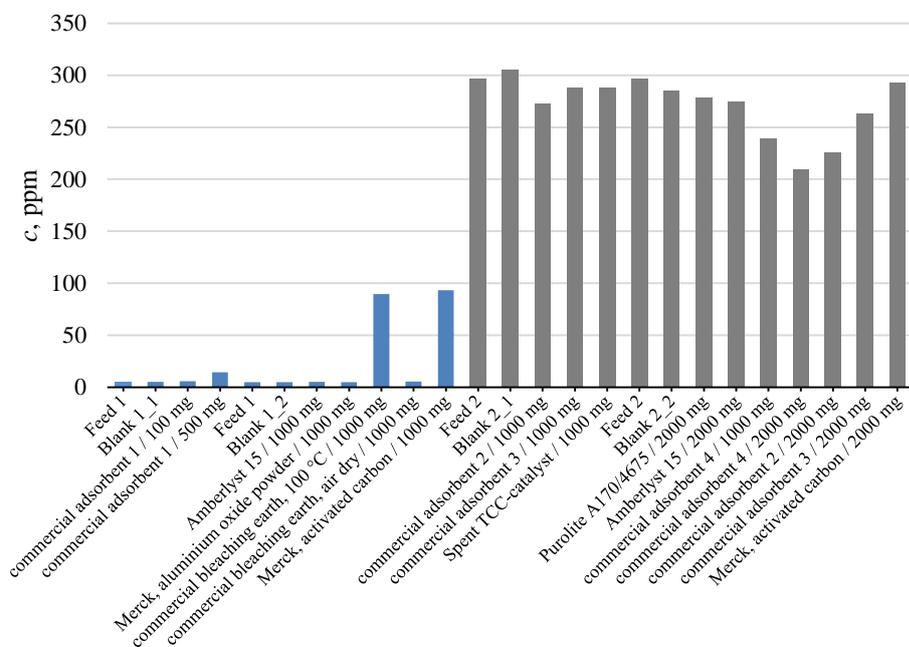


Figure 6. Silicon concentrations measured in the screening tests.

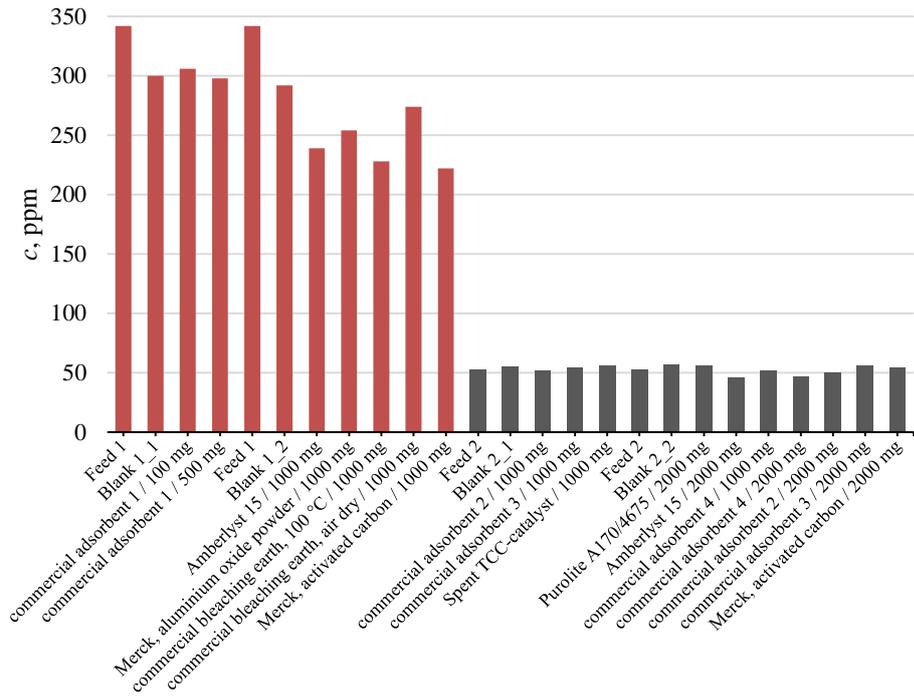


Figure 7. Phosphorus concentrations measured in the screening tests.

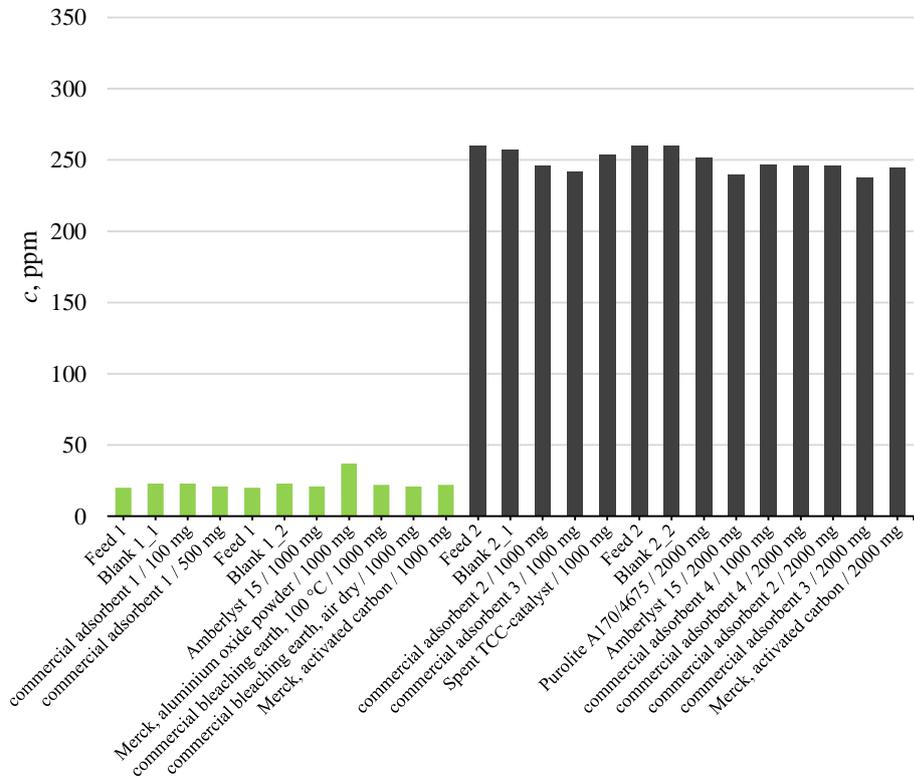


Figure 8. Chlorine concentrations measured in the screening tests.

Fig. 9 includes reduction values presented as bars and adsorbed amounts drawn as lines from screening tests.

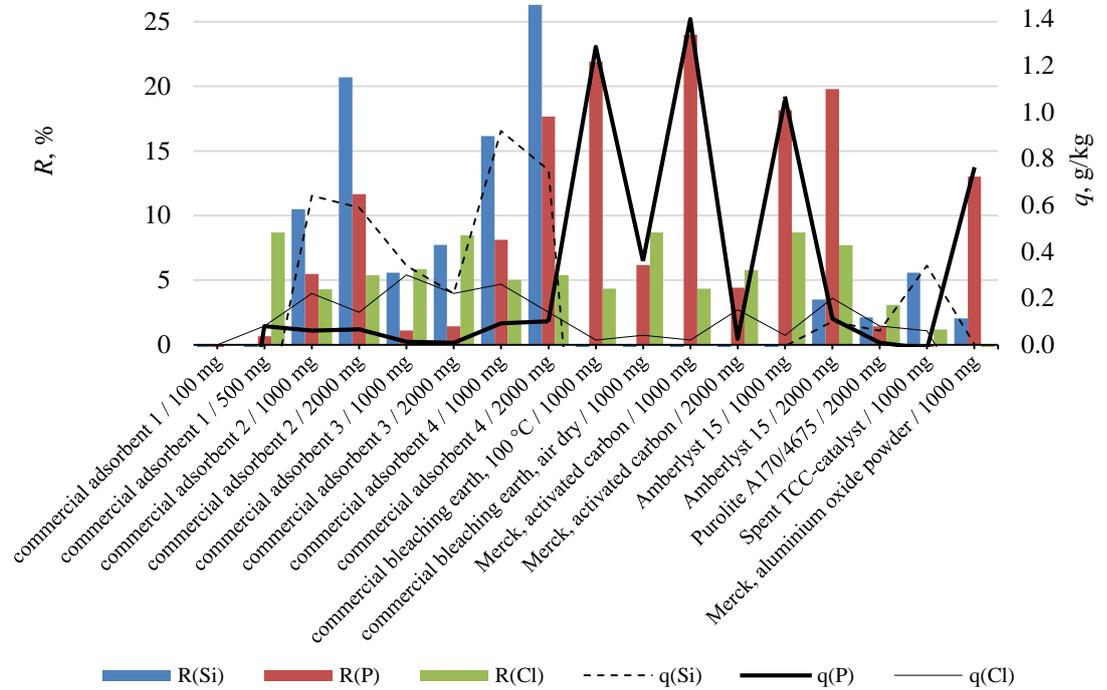


Figure 9. Reduction values and adsorbed amounts of silicon, phosphorus, and chlorine measured in the screening tests.

The major difference in the feed concentrations of Si, Cl, and P between the first feed (FEED 1, series 1–2) and the second feed (FEED 2, series 3–4) should be noted. Lower concentrations in the first feed increase reduction values even if the removed impurity quantity is minimal. Glassware used in experiments or centrifuging did not seem to affect silicon concentrations based on the results from blank samples.

When looking reduction values as a whole, they seem to differ quite much. There are also many negative values which were removed from Fig. 8. These results indicate that the impurity concentration has increased due to ions leached from the separation materials. It is also possible that centrifuging may not have completely separated the oil from the material. In that case, some fine solid particles pass through to analyses with the sample oil. Consequently, centrifuged oil sample was collected via pipetting instead of pouring from series 3 onwards to cope with this issue. For example $c(\text{Fe})$, $c(\text{Na})$, and $c(\text{Si})$ increased during the screening treatment.

Reduction of silicon is negative with both 1000 and 2000 mg activated carbon dosages. This implies that silicon is released from the activated carbon material to oil as was happened in the study of Al Zubaidy *et al.* (2013) [83]. Unexpectedly, oven drying at 100 °C caused commercial bleaching earth to leak more silicon to oil than the air drying treatment with the same material. However, the drawing of any major conclusions out of this observation, without repeating the tests, should be avoided.

Focusing on three target impurities in Fig. 8, it is seen that even achieving 30 % reduction is a challenge even at an adsorbent dosage of 10 wt-%. Commercial adsorbent 4 removed silicon most efficiently with a 26.3 % reduction. Respectively, commercial adsorbent 3 removed highest amount chlorine with an 8.5 % reduction. Amberlyst 15 was observed to remove most phosphorus with a reduction of 19.8 %. Especially commercial adsorbent 4 showed potentiality because with 5.4 % chlorine and 17.7 % phosphorus reduction it can compete with these two previously mentioned materials. Especially high reduction values and adsorbed amounts of phosphorus with 1000 mg of both commercial bleaching earth dried at 100 °C and activated carbon could be affected by the fact that FEED 1 contained significantly higher amount of phosphorus and very low silicon and chlorine content. Therefore, it seems that phosphorus was adsorbed more efficiently under these conditions.

Similarly with the reduction values, also capacity values remain at a low level, generally under 1 g of impurity component per kg of separation material. Calculated capacities for chosen impurities from screening tests are presented in Table IX of Appendix II and shown in Fig. 8. Besides capacities of organic chlorine, silicon, phosphorus and total chlorine, also capacities for copper and zinc were listed. These two impurities were chosen based on the distinctive capacity variations and the fact that zinc is included in the lubricant additive ZDDP [64]. Thus, phosphorus removal should be accompanied by adsorption of zinc. The P/Zn ratio is of course dependent on the degradation of ZDDP but the zinc–phosphorus relationship seems plausible.

Highest capacity for silicon, 0.9 or 0.8 g kg⁻¹, was achieved with 1000–2000 mg addition of commercial adsorbent 4. Maximum capacity for chlorine was 0.2 g kg⁻¹ with 2000 mg of commercial adsorbent 3 or activated carbon and 0.3 g kg⁻¹ with 1000 mg of commercial adsorbent 4. Phosphorus was removed most efficiently

with activated carbon when capacity 1.4 g kg^{-1} was achieved but again, the effect of FEED 1 should be noted. Commercial adsorbent 4 was designed to remove organosilicates so the achievement of the highest capacity is logical. However, when comparing chlorine concentrations and removal capacities, there seems to be great variation in analytical results. Thus, significant uncertainty should be noted in evaluation of chlorine results. In the phosphorus case, the effect of first feed is clear, because in that feed the phosphorus concentration was over six times higher than in the second feed. Higher initial phosphorus concentration and low silicon and chlorine content must have been the key factors when best capacity with activated carbon was achieved. When the addition of this material was doubled and the second feed was used, very low capacity of 0.03 g kg^{-1} was witnessed for phosphorus.

Unlike in other series, significant color change during the treatment in one sample was observed in series 4. When 2000 mg of Amberlyst was added to 20 g of the second feed, the dark color of the oil changed totally to transparent yellow. Similar color changes were seen with the 2000 mg addition of activated carbon or commercial adsorbent 3 but in these cases the color changed only slightly still remaining brown. Comparison of these three samples with the blank sample is presented in Fig. 10.

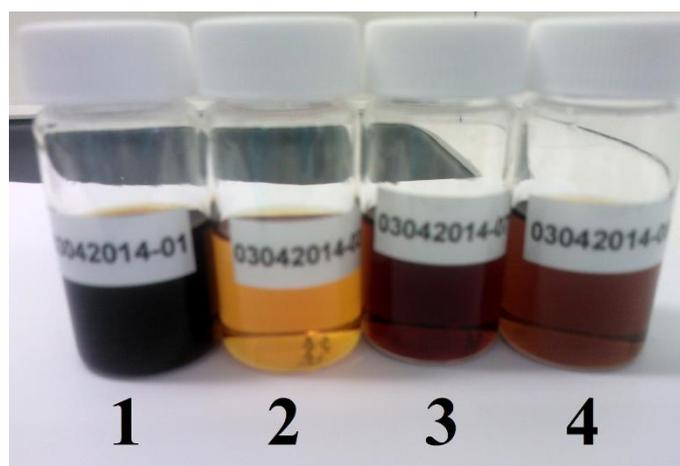


Figure 10. Color comparison of samples from series 4. No: 1 = blank sample, 2 = Amberlyst 15 / 2000 mg, 3 = commercial adsorbent 3 / 2000 mg, and 4 = Merck, activated carbon / 2000 mg. Amount of oil per batch = 20 g, $T = 65 \text{ }^{\circ}\text{C}$, $t = 24 \text{ h}$.

No color change was noticed in series 2 or 3, where the same materials were used with a lower dosage of 1000 mg. However, rather surprisingly the yellow-colored sample purified with Amberlyst 15 still contained significant amounts of silicon, phosphorus and chlorine. Only phosphorus reduction, 19.8 %, was clearly higher than in other samples of the same series. Therefore, the reason for the de-colorization could be associated with the decreased content of nitrogen. Nitrogen concentration in the purified sample was not determined but the feed contained 360 ppm nitrogen. All in all, the possible usage of Amberlyst 15 as oil de-colorant should be studied. Dosage was quite high, about 10 wt-% of oil, which affects the feasibility of the purification step in larger scale.

6.2. Temperature Dependence of Adsorption

Sample concentrations are presented in Tables XI and XII and the calculated reduction and capacity values are presented in Tables XIII and XIV of Appendix III. Commercial adsorbent 3 and 4 were used in these tests. Concentrations of Si, P, and Cl are presented as columns in Fig. 11 with temperature drawn as a line. Similarly, reduction values of Si, P, and Cl are presented in Fig. 12.

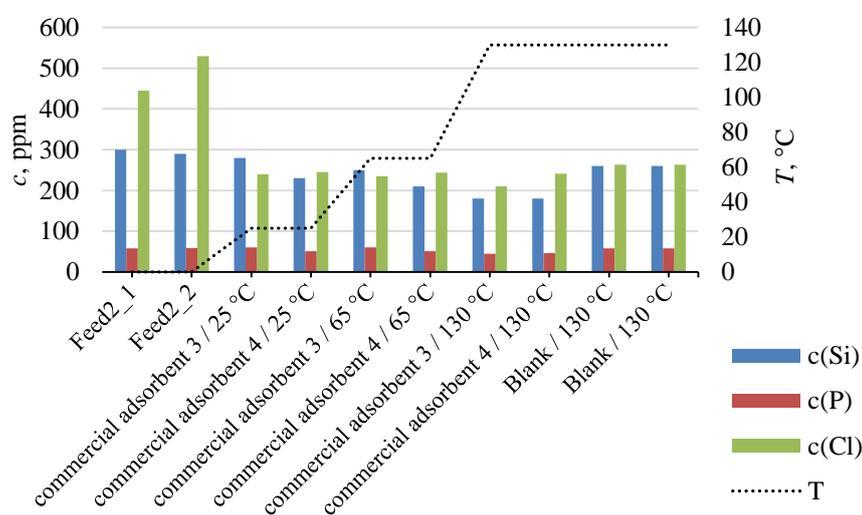


Figure 11. Concentrations of silicon, phosphorus, and chlorine at different temperatures.

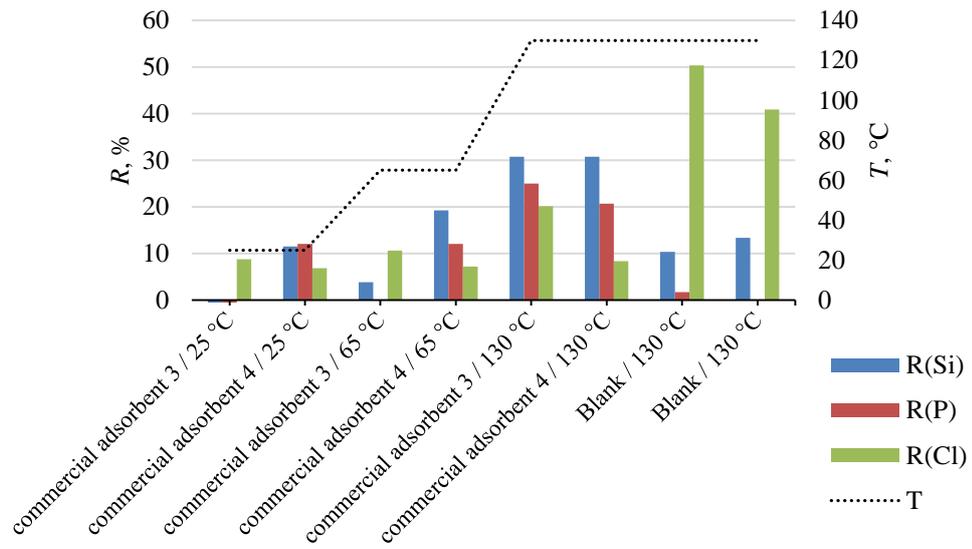


Figure 12. Reduction values of silicon, phosphorus, and chlorine at different temperatures.

Fig. 13 shows van't Hoff plots for silicon, phosphorus, and chlorine when adsorbed on the commercial adsorbent 3.

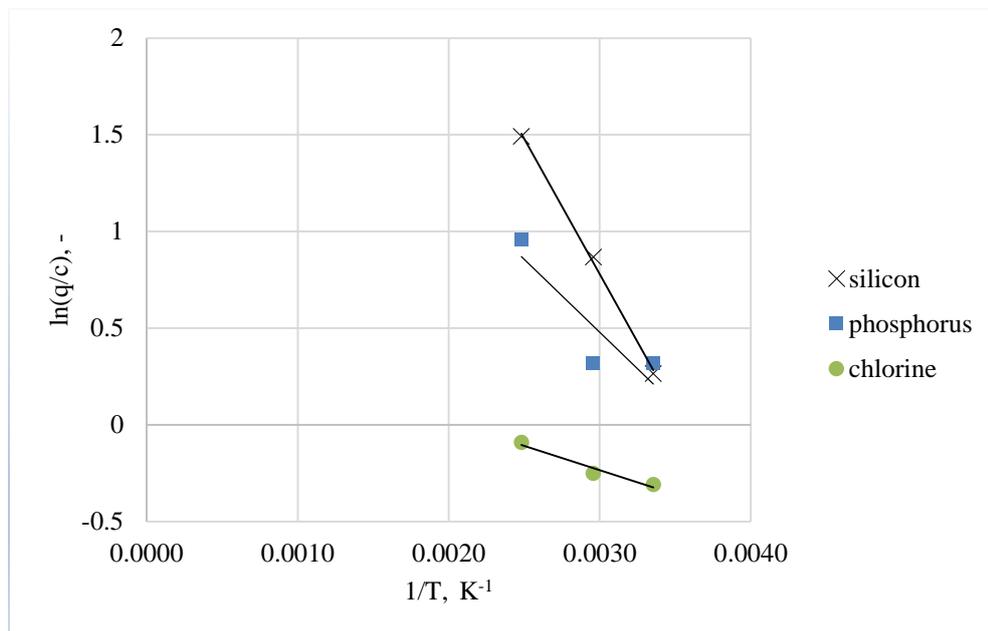


Figure 13. van't Hoff plots for commercial adsorbent 3.

The slopes estimated from Fig. 13 are -1400, -755, and -250 K for Si, P and Cl, respectively. According to Eq. 4, the corresponding adsorption enthalpies are 11.6, 6.2, and 2.1 kJ mol⁻¹. Margielewski *et al.* (2006) studied adsorption of ZDDP on

zirconia powder. The authors synthesized ZDDP compounds with different alkyl chain lengths and blended those to n-decane. Blend and zirconia powder were continuously stirred in 1:1 ratio at 25 and 35 °C. Remaining ZDDP content in blend was measured with FTIR. With initial ZDDP concentration of 1 wt-%, the equilibrium was reached after 15 and 20 min, at 25 and 35 °C respectively. The authors stated that the adsorbed ZDDP amount is logically strongly dependent on the alkyl chain length. Longer and therefore larger ZDDP molecules require larger area on the zirconia surface. Interestingly, when the ZDDP is structured from mono-n-alkyl derivatives instead of di-n-alkylphenyl derivatives, the adsorbed amount can be two-fold higher at 25 °C. The authors also suggested physisorption being the main interaction between ZDDP and zirconia due to lower adsorption quantities of all n-alkyl ZDDPs at higher temperature. Nonetheless, chemisorption could not totally be ruled out, because mono-n-alkylphenyl structured ZDDP adsorbed more efficiently at higher temperature. The study included ΔH values measured at different surface coverages. The authors were able to determine that at 25 °C adsorption of n-alkyl derivatives was exothermic, down to -30 kJ mol^{-1} . In the case of di-n-alkyl phenyl derivatives, adsorption was endothermic (10 kJ mol^{-1}) at low surface coverages but exothermic (-10 kJ mol^{-1}) after reaching a surface coverage of 0.6. At 35 °C n-alkyl ZDDPs are endothermic ($0\text{--}5 \text{ kJ mol}^{-1}$) and alkyl aryl ZDDPs are exothermic (-10 to -30 kJ mol^{-1}). [102] In view of these data, the adsorption enthalpy, 6.2 kJ mol^{-1} , measured in the present study for adsorption of phosphorus compounds seems reasonable.

Major difference in iron and tin concentrations was seen by comparing the feed samples to the original sample from the second feed (FEED 2). Indeed, the iron content had increased from limit of detection to over 600 ppm and the tin content increased from limit of detection to over 20 ppm. Also more dark-colored solid particles were visible in the oil. Therefore, the surface of the metal container must have been worn out. Sharply increased metal concentrations could lead to some kind of catalytic reactions within the oil.

Both adsorbents removed silicon, phosphorus, and chlorine more efficiently when temperature was raised. Reduction of silicon increased from 11.5 to 30.8, reduction of phosphorus from 12.1 to 20.7, and reduction of chlorine increased from 6.8 to 8.4 % with commercial adsorbent 4. Respectively with commercial adsorbent 3,

reduction of silicon increased from -7.7 to 30.8, reduction of phosphorus from -3.4 to 25.0, reduction of chlorine from 8.7 to 20.2 %. Negative reduction of silicon at 25 °C with commercial adsorbent 3 could indicate the presence of silica in the adsorbent.

Due to the possible benefits from the use of high temperature, also the blank test was done at 130 °C. Depending on the feed sample for which the blank is compared, 10.3 to 13.3 reduction of silicon and 40.9 to 50.4 % reduction of chlorine was achieved without the separation material. There may again be high uncertainty in the chlorine results. Still the reduction of silicon with the blank sample cannot be ignored. Decreased silicon content may be connected to the earlier mentioned increased concentrations of iron and tin. Notably both iron and tin content in oil rose during the blank treatment. Concentration of iron was 350 ppm in sample “commercial adsorbent 4 / 130 °C”, 400 ppm in “commercial adsorbent 3 / 130 °C”, and 670 ppm in the blank sample. There were no differences in the amount of treated oil, treatment time, temperature, or sample filtration procedure. However, one explanation to the increased metal concentration could be that the observed metal particles reacted more easily with the oil during heat treatment than in the presence of separation material. Also adsorbent may have acted as an additional filter layer above the filter membrane. In that case metal ions could be adsorbed to this layer. Indeed, a visible cake formed from very fine adsorbent particles was noticed on the used filter with both series.

6.3. Adsorption Kinetics

Tests were made with the commercial adsorbent 4. Sample concentrations for adsorption kinetics experiments are presented in the Table of Appendix IV. Fig. 14 represents concentrations results as a function of time. If the removed oil is taken into an account, mass of removed oil can be calculated and impurity concentrations can be changed to masses of impurities left in oil. Calculated data are presented in the Table XVI of Appendix IV. Fig. 15 includes these data.

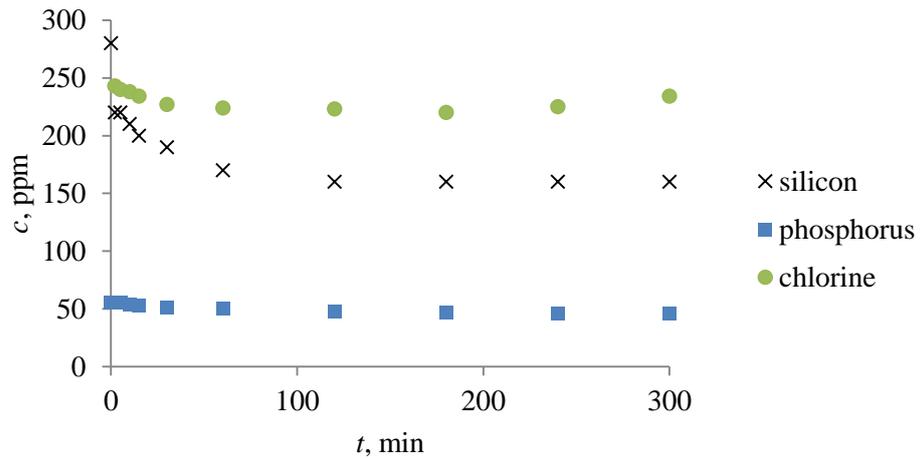


Figure 14. Concentration of silicon, phosphorus, and chlorine as a function of time. $T = 130\text{ }^{\circ}\text{C}$, $t = 5\text{ h}$, $n = 400\text{ rpm}$.

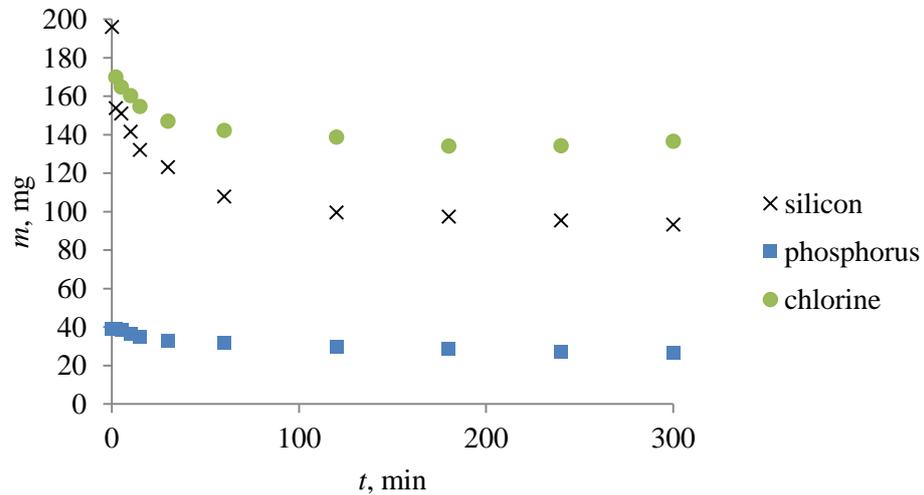


Figure 15. Masses of silicon, phosphorus, and chlorine left in the oil after sampling as a function of time. $T = 130\text{ }^{\circ}\text{C}$, $t = 5\text{ h}$, $n = 400\text{ rpm}$.

All curves in both Figs 14 and 15 are similar and all three impurities are removed from oil batch until 60 min is reached.

Fractional uptake curves of silicon, phosphorus, and chlorine are presented in Fig. 16. Feed concentration values were adjusted so coherent graphs could be achieved. Thus, the feed concentration for silicon was set to 250, for phosphorus 60, and for chlorine 250 ppm. The feed concentration of chlorine was reduced by half due to the suspected inaccuracy and challenges during sampling and analysis.

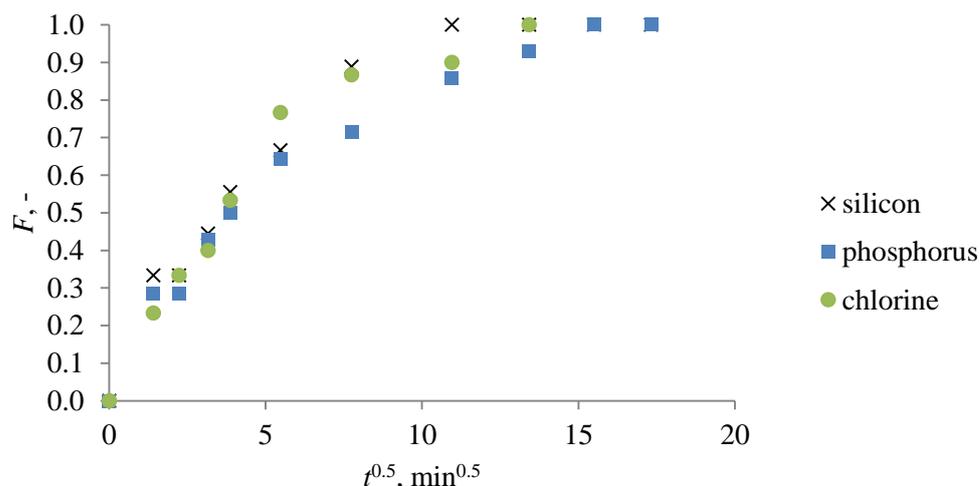


Figure 16. Fractional uptake values of silicon, phosphorus, and chlorine as a function of normalized time. $T = 130\text{ }^{\circ}\text{C}$, $t = 5\text{ h}$, $n = 400\text{ rpm}$.

Removal of all three target impurities is surprisingly similar and 50 % uptake is obtained in about 15 min. The linear section is seen to extend to about $F = 0.5$ and consisted of the first six data points. The obtained averaged slope for all three graphs is approximately $0.12\text{ min}^{-0.5}$. Using Eq. 7, rough estimate of $1.2 \cdot 10^{-10}\text{ m}^2\text{ s}^{-1}$ for the effective diffusion coefficient was obtained. Yamaguchi *et al.* (1997) experimentally determined the diffusion coefficient of neutral diisobutyl zinc dithiophosphate in hexane to be approximately $1.0 \cdot 10^{-9}\text{ m}^2\text{ s}^{-1}$. [103] As compared with this value, the calculated effective diffusion coefficient is only about one order of magnitude lower. This is understandable, because diffusion in the adsorbent takes place in the pore fluid rather than in the solid matrix.

Most significant concentration change is observed with silicon, which is consistent with the high equilibrium uptake capacity of the organosilicate selective adsorbent.

6.4. Fixed Bed Experiment

Tests were performed with the commercial adsorbent 4. Sample concentrations from fixed bed tests are presented in the Table XIX of Appendix V. Mass of oil flown through the bed was measured and therefore also the bed volume (BV) *i.e.* the volume of effluent equal to the volume of packed bed can be calculated [104]. Feed concentration values were adjusted for silicon to 230, for phosphorus to 57, and for chlorine to 250 ppm. These modifications enabled the break-through curves to end up at $c/c_0 = 1.000$ when bed capacity is fully exhausted. Calculated bed

volumes are presented in Table XX of Appendix V. With these data, a breakthrough curve can be drawn. The curve is presented in Fig. 17.

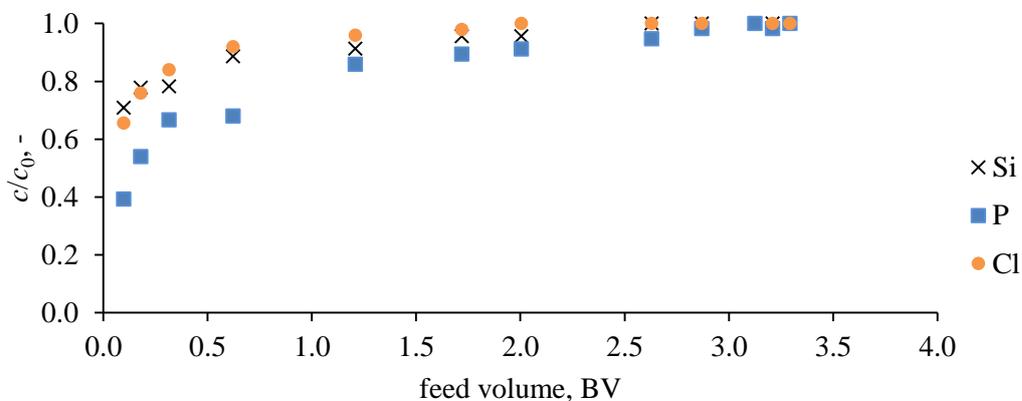


Figure 17. Ratio of effluent and feed concentration as a function of bed volume. $T = 65\text{ }^{\circ}\text{C}$, $f = 10\text{--}13\text{ mL min}^{-1}$.

One of the most important sources of error with the fixed bed experiment was the possible presence of n-octane in oil samples. Even though the density of n-octane, 0.70 g mL^{-1} (Fluka) is lower than the density of used lubricating oil, 0.86 g mL^{-1} , blending of these two fluids can happen when the oil is flowing through the bed and displacing the solvent. GC-analysis was done for the first sample taken from the outlet after 6 min and it was compared to the GC-sample from the feed oil. GC-results obviously did not indicate significant amount of n-octane in the feed. However, evident n-octane peak was noticed in the 6 min sample. No other samples were analyzed with GC. Based on these results, n-octane related dilution effect must be noted. Therefore, impurity concentrations are decreased partly by dilution and not only by adsorption. To measure the total effect of n-octane, actual n-octane concentrations should be determined in all samples.

Anyhow, the low capacity levels observed on previous tests and the behavior of adsorption kinetics already indicated that the breakthrough curve may first sharply rise, then stabilize and slowly continue to rise towards the feed concentration. If the findings from earlier experiments are taken into account, it can be concluded that actual adsorption is very fast but low capacity affects to the behavior of breakthrough curve. Curves of Fig. 17 indicate that even one bed volume of oil is too much for the system. This is totally different situation when test is compared to case where water based solution is purified with the fixed bed. Medvidovic *et al.*

(2006) studied lead removal from aqueous solutions. Fixed bed was packed with natural zeolite-clinoptilolite. When initial lead concentration of synthetic solution was 212.5 ppm with the flow of 1.0 mL min^{-1} , breakthrough point was reached after 336 bed volumes of solution had passed through the bed. Obtained breakthrough curves tend to be more of an S-shaped type compared to curves presented in Fig. 17. Authors were also able to regenerate the used bed with sodium nitrate solution at least three times without significant loss of removal efficiency. [104]

This one fixed bed experiment clearly gave poor results. Nonetheless, the use of higher temperature, more intensively executed observation of the n-octane content and by decreasing the oil flow through the bed could enhance the mass transfer from oil to bed. All in all, the used lubricating oil will most likely need some pretreatment stage before adsorption step is utilized.

6.5. FTIR Spectra

All the measured FTIR spectra were sent to Neste Oil for chemometric modeling tests. Partial least squares (PLS) regression model was developed [105] for all three target impurities. This model was used for prediction of sample concentrations from absorbance data of the spectrum. Most representative peaks were found for silicon at 800–690, for phosphorus at 1750–1700 and for chlorine at 3000–2800 and also 1780–1300 cm^{-1} regions. Degree of explained variance for silicon values was 95, for phosphorus 93, and for chlorine 84 %. [105] Obviously the difficulties related to chlorine analysis are also seen in the spectra and in model estimates.

FTIR analyses usually resulted in reproducible spectra. Typical group of spectra is presented in Fig. 18. Spectral data from adsorption kinetics test were chosen due to the largest impurity concentration differences among samples. Thus, there should also be visible absorbance differences between spectra.

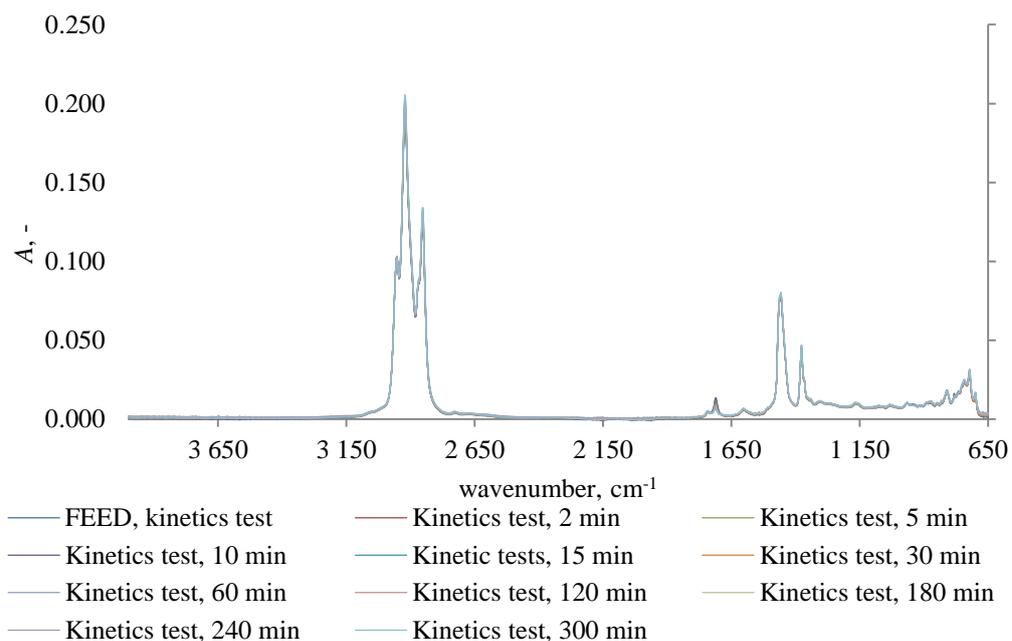


Figure 18. Experimental spectra of the samples measured in the kinetics test. Thermo Scientific Nicolet iS10 ATR-FTIR, wavenumber region 4000–650 cm^{-1} .

The large peaks at 3000–2650 cm^{-1} are caused by hydrocarbons [106]. Distinctive fingerprint region is located at range between 1700 cm^{-1} and the end of the spectrum [63]. Differences in spectra are rather difficult to locate in Fig. 18 due to the scaling issues. Thus, the representative peaks are individually presented for each three target impurities in Figs 19–22.

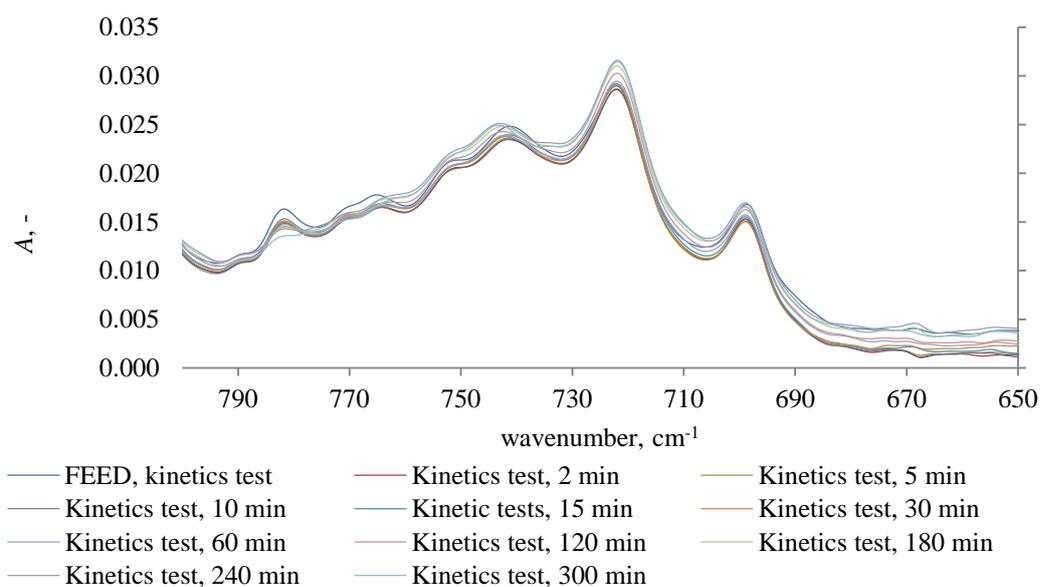


Figure 19. Experimental spectra of the samples measured in the kinetics tests focused on representative peaks of silicon. Thermo Scientific Nicolet iS10 ATR-FTIR, wavenumber region 900–650 cm^{-1} .

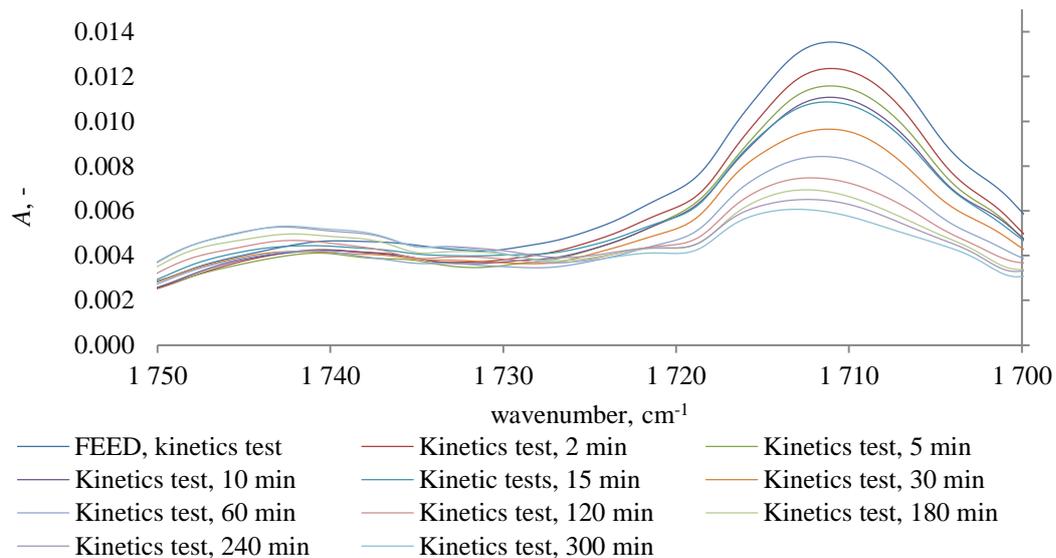


Figure 20. Experimental spectra of the samples measured in the kinetics tests focused on representative peaks of phosphorus. Thermo Scientific Nicolet iS10 ATR-FTIR, wavenumber region 1750–1700 cm^{-1} .

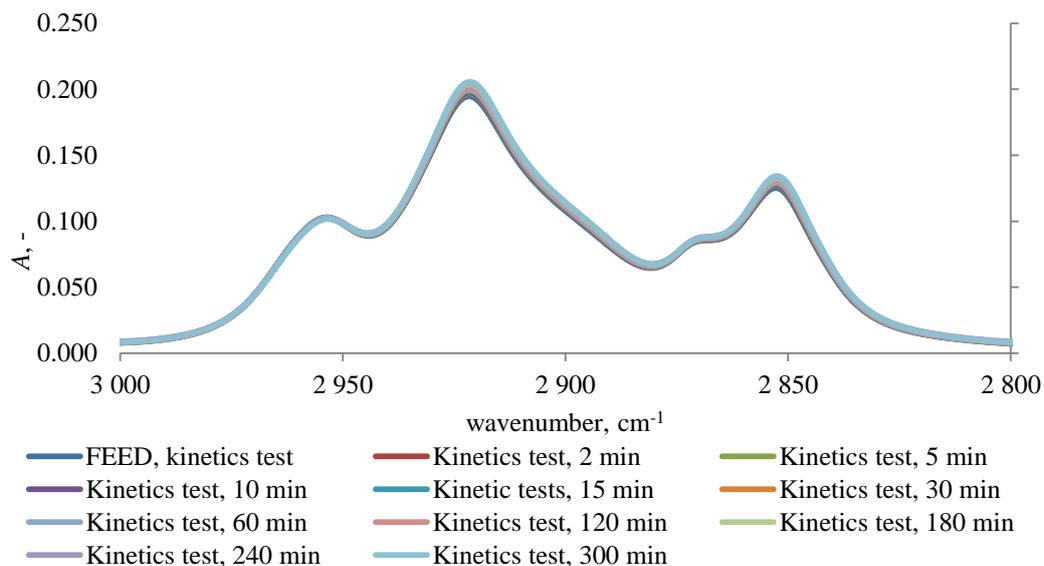


Figure 21. Experimental spectra of the samples measured in the kinetics tests focused on representative peaks of chlorine. Thermo Scientific Nicolet iS10 ATR-FTIR, wavenumber region 3000–2800 cm^{-1} .

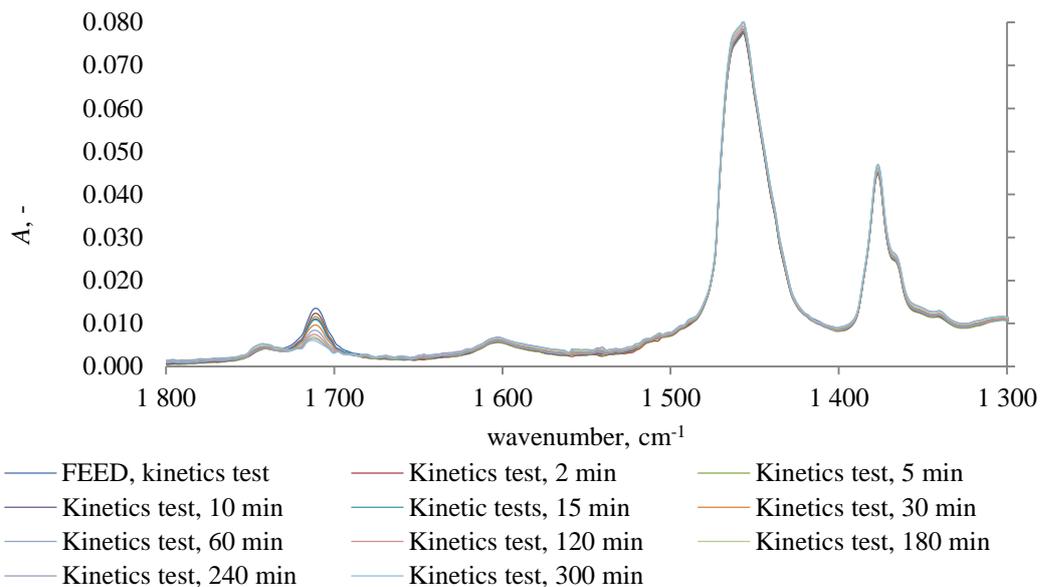


Figure 22. Experimental spectra of the samples measured in the kinetics tests focused on representative peaks of chlorine. Thermo Scientific Nicolet iS10 ATR-FTIR, background correction done, wavenumber region 1800–1300 cm^{-1} .

Comparing the spectra of Fig. 19 for silicon to literature data, some attention can be focused on certain areas. Socrates (1994) has listed spectral regions for organic silicon compounds. Si-C bonds have strong absorbance in the range between 870 and 765 cm^{-1} . Typical bonds and compounds include Si-CH₃, phenylsilanes, and siloxanes. [106]. Visual observation of spectra does not give any precise conclusions so modeling is needed for further analysis.

More distinctive spectral features can be seen in Fig. 20, where absorption with weak or medium intensity by phosphorus compounds can be found [106]. All spectra are settled in order of sampling time at the region between 1720 and 1700 cm^{-1} . In that region, the sample with lowest phosphorus concentration *i.e.* the sample taken at 300 min gave lowest absorbance and highest absorbance was measured with the feed sample with the highest phosphorus content. Hence, all other sample spectra are located between these two from 240 to 2 min with constantly increasing absorbance values. Of course the possible influence of other impurities to this observation should also be taken into account.

As mentioned earlier, PLS modeling revealed two specific spectral ranges for chlorine. In Fig. 21 there are two peaks present, one at 2920 and the other at 2850 cm^{-1} . Closer examination of tops of these peaks interestingly revealed that the

highest absorbance was caused by the 300 min sample and the lowest absorbance by the feed sample. Other spectra from highest absorbance to lowest are from 240 to 2 min with minor exceptions. Although the absorbance differences are small, still there could be some connection between this phenomenon and impurity concentration. Similar observations can be done with the two peaks at 1460 and 1380 cm^{-1} in Fig. 22. Also there highest absorbance is witnessed with the 300 min sample. Previously covered phosphorus specific wavenumber region is included in this figure so the possible link between chlorine and phosphorus impurity compounds should be determined. Chlorine can be present as organic or inorganic forms so this could explain also the analytical difficulties that arose during both XRF- and FTIR-measurements.

The three target impurity concentrations were measured from 31 samples with ATR-FTIR to adjust and test the PLS regression model for used lubricating oil. The regression model was created based on the spectra data from earlier measurements including measurements done with PerkinElmer Frontier FT-IR spectrometer. Model usability is demonstrated with Figs 23–25. Sample information and measured calibration concentrations are presented with the modeled [105] concentrations in the Table XXI of Appendix VI. Samples 1 and 21–31 were not used to adjust the model.

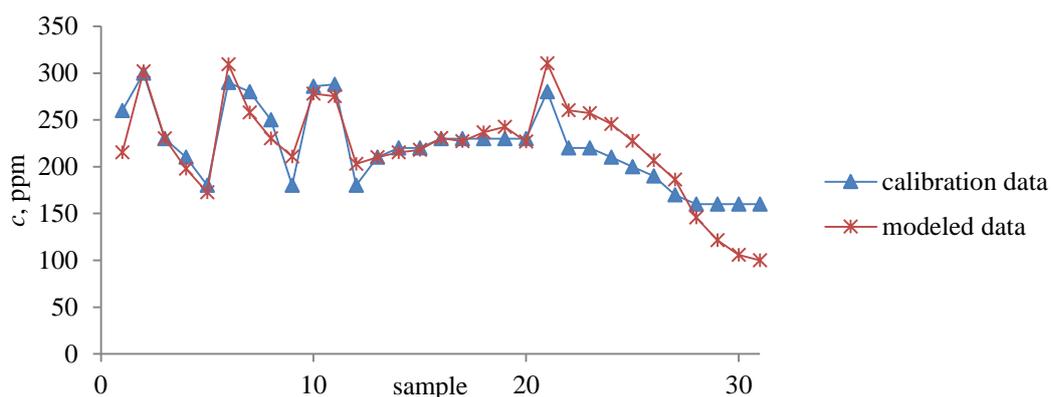


Figure 23. Analyzed and modeled [105] silicon concentrations for 31 samples. Thermo Scientific Nicolet iS10 ATR-FTIR, background correction done, wavenumber region 4000–650 cm^{-1} .

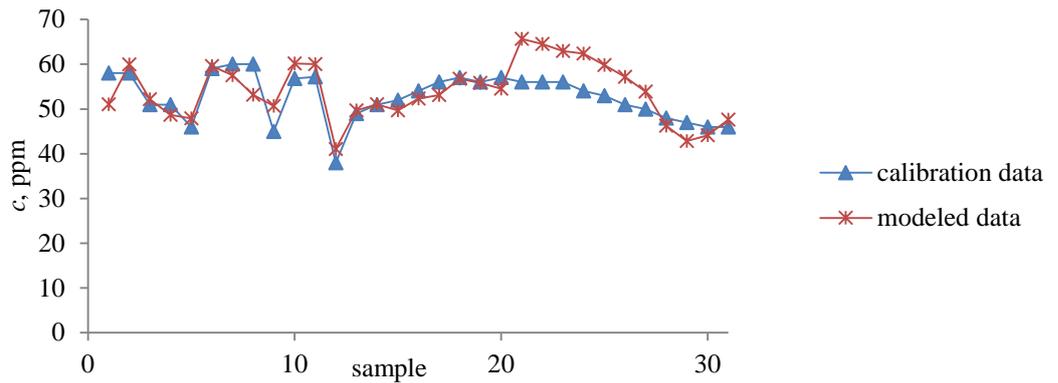


Figure 24. Analyzed and modeled [105] phosphorus concentrations for 31 samples. Thermo Scientific Nicolet iS10 ATR-FTIR, background correction done, wavenumber region $4000\text{--}650\text{ cm}^{-1}$.

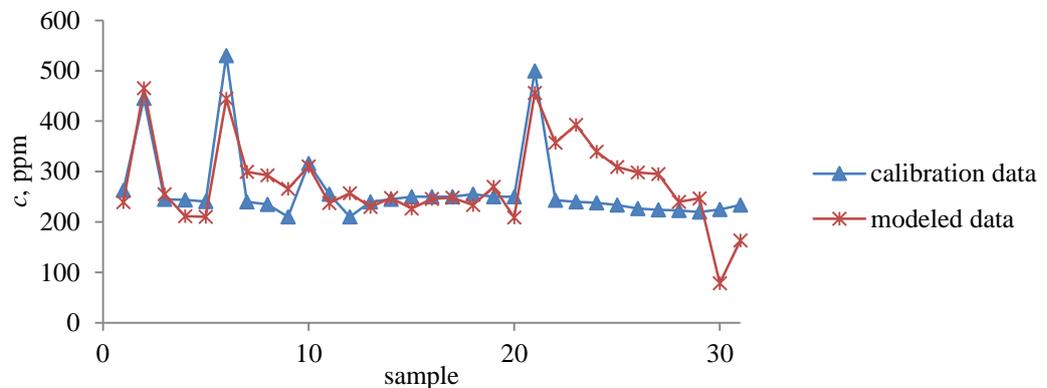


Figure 25. Analyzed and modeled [105] chlorine concentrations for 31 samples. Thermo Scientific Nicolet iS10 ATR-FTIR, background correction done, wavenumber region $4000\text{--}650\text{ cm}^{-1}$.

Both graphs based on measured calibration and estimated concentrations of silicon and phosphorus are quite uniform until the sample 21. After that the model gives higher concentrations than the measurements till the sample 28. The following estimates for samples 28–31 result too low concentrations for silicon and phosphorus. Only exception is the last sample when the model predicts higher phosphorus concentration than the actual measurement gave. Modeled estimates and measured calibration data are presented in a diagonal graph in Fig. 26 to summarize these observations.

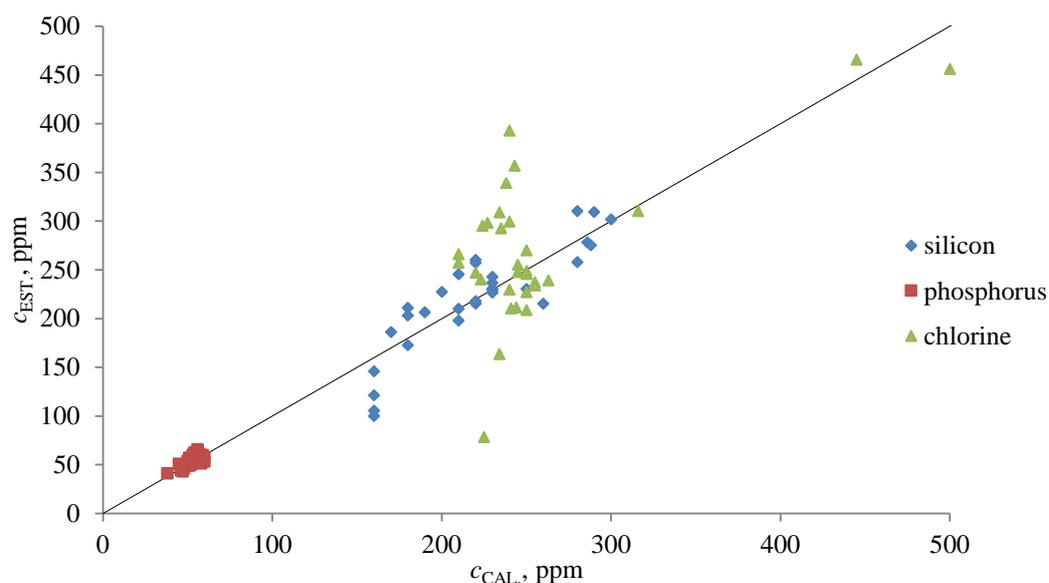


Figure 26. Calibration and estimated concentrations of silicon, phosphorus, and chlorine [105] with a diagonal line for 31 samples. Thermo Scientific Nicolet iS10 ATR-FTIR, background correction done, wavenumber region $4000\text{--}650\text{ cm}^{-1}$.

In summary, the predicted values deviated quite similarly from measured values of both silicon and phosphorus when the concentration range is taken into account. The most substantial variation was found for the chlorine concentration estimates seen in Figs 25 and 26. This uncertainty of the model is either caused by the analytical difficulties or the incapability of FTIR spectrometry to detect chlorine compounds.

Adams *et al.* (2007) have reviewed the use FTIR to monitor antioxidant content and the total acid number of synthetic turbine oils. The authors created a model based estimation tool to validate the oil quality. They stated that due to the matrix variations, developed model may not be suitable for different engines even if the type of studied oil is not changed. Thus, FTIR based quality control method can be used as a versatile and fast analysis aid if the limitations are taken into account. [107]

Additionally, FTIR based determination can be successfully used to check various quality parameters among already tested or mentioned subjects. Al-Ghouti *et al.* (2010) combined chemometrics to FTIR analysis to determine viscosity index and base number of 30 different engine oil samples. [108] FTIR as a user-friendly and rapid analysis device could be used to classify collected used oil batches at the

collection stations. Then the undesired mixing of lowest grade waste oil to better quality used oil could be avoided.

7. CONCLUSIONS

Purification tests were performed in laboratory scale to remove impurities from used lubricating oil. The focus was on three target impurities *i.e.* silicon, phosphorus, and chlorine. As expected on the basis of the literature study, used lubricating oil is a very complex mixture of multiple compounds. Additives originally added in the tested feed oils are not all known and similarly the degradation products are not identified.

Especially the analysis of chlorine concentrations proved to be difficult. This could be due to the high concentration of sulphur in feeds (> 2000 ppm) which affects the chlorine analysis. Also other important factor is the number and concentration of organic and inorganic chlorine compounds which could be present in the used oil. Additionally, the sampling procedure must be carried out carefully and consistently.

Equilibrium capacities of different separation materials were evaluated in screening tests at 65 °C. Highest silicon capacity was 0.8 – 0.9 g kg⁻¹ for commercial adsorbent 4, phosphorus capacity was 1.4 g kg⁻¹ for activated carbon, and the chlorine capacity was 0.2 – 0.3 g kg⁻¹ for most of the tested separation materials. Added amount of the separation material was between 5.0 and 10 wt-%. Thus, equilibrium capacities remained quite low even though the separation materials was added rather large quantities.

In order to investigate influence of temperature on equilibrium uptake of the impurities, commercial adsorbents 3 and 4 were tested at temperatures 25 , 65 , and 130 °C. Results clearly indicated that adsorption of Si, P and Cl compounds is endothermic and utilization of higher temperature is beneficial for the purification process. More testing should be done to find the optimal temperature range for different separation materials.

Batch adsorption kinetics measured with commercial adsorbent 4 at 130 °C indicated that equilibrium is attained in about 100 min. When the relatively slow adsorption rate is put together with low equilibrium capacities determined in screening tests, it is really challenging to purify waste oils containing high

concentrations of Si, P and Cl with chosen separation materials. The results suggest that batch adsorption process is more suitable rather than the fixed bed process. Fixed bed experiment made with the commercial adsorbents 4 corroborated this conclusion. At 65 °C, break-through of all three target impurities Si, P, and Cl took place almost immediately, probably because of both low adsorption capacity and low adsorption rate.

In the other part of the study, FTIR spectrometry was utilized to analyse used and purified lubricating oil samples. Chemometric modeling of the data gave promising results and showed potential for the further use. Concentrations of silicon and phosphorus could be estimated quite well. Estimation of chlorine content included more variation in the results when modeled values were compared to measured calibration values. There is no need for time consuming sample preparation when the ATR-FTIR is used. This is a major advantage and thus FTIR should be used in further studies if faster analysis is needed.

Even though large dosages of separation material were added and higher temperatures were tested, still concentrations of three target impurities remained at high level in all samples. Therefore, the utilization of pretreatment step before adsorption with the separation material, is strongly advised. Particularly high impurity content should be decreased with a simple and cost-effective pretreatment step utilizing for example alkali, solvent, or propane treatment as is done in some commercial processes. This would reduce the separation material costs by lowering material dosages and also extend lifetime of the material. It was noticed, for example, that Amberlyst 15 effectively decolorizes the used lubricating oil. Therefore, further studies with prepurified feed are recommended to achieve higher capacities.

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APPENDICES

Appendix I	Detection limits
Appendix II	Screening tests
Appendix III	Temperature dependence tests
Appendix IV	Adsorption kinetics test
Appendix V	Fixed bed experiment
Appendix VI	FTIR spectra

Detection limitsTable I Limit of detection values for determined components.

<u>component:</u>	<u>LOD, ppm</u>
Si	<0.3
P	<0.6
organic Cl	<1
Ba	<0.3
Ca	<0.3
Cu	<0.1
Fe	<0.1
Mg	<0.3
Na	<0.1
Ni	<0.5
Pb	<0.6
Sn	<1
V	<0.3
Zn	<0.5

Screening tests

Table II Used feeds, serie numbers, separation materials, separation material and oil weighings from the screening tests.

feed:	serie:	separation material, SM:	m(SM), mg	m(oil), mg
1	1	commercial adsorbent 1	100.5	20.0104
1	1	commercial adsorbent 1	500.2	20.0097
1	2	Amberlyst 15	1000.0	20.0076
1	2	Merck, aluminium oxide powder	1000.0	20.0089
1	2	commercial bleaching earth, 100 °C	1000.1	20.0092
1	2	commercial bleaching earth, air dry	1000.2	20.0075
1	2	Merck, activated carbon	1000.3	20.0041
2	3	commercial adsorbent 2	1000.1	20.0013
2	3	commercial adsorbent 3	1000.2	20.0002
2	3	spent TCC-catalyst	1000.8	20.0053
2	4	Purolite A170/4675	2000.3	20.0096
2	4	Amberlyst 15	2001.0	20.0080
2	4	commercial adsorbent 4	1000.6	20.0091
2	4	commercial adsorbent 4	2000.8	20.0090
2	4	commercial adsorbent 2	2000.4	20.0086
2	4	commercial adsorbent 3	2000.1	20.0052
2	4	Merck, activated carbon	2000.6	20.0078

Table III Concentrations of organic chlorine, Cu, Fe, Na, Pb, Si, Sn, Ca, Mg, P, Zn, Cl, and S for feed and blank samples measured in the screening tests.

sample name:	c(Cl _{org}), ppm	c(Cu), ppm	c(Fe), ppm	c(Na), ppm	c(Pb), ppm	c(Si), ppm	c(Sn), ppm	c(Ca), ppm	c(Mg), ppm	c(P), ppm	c(Zn), ppm	c(Cl _{tot}), ppm	c(S _{tot}), ppm
Feed 1	20.0	34.3	9.9	4.1	1.3	4.8	LOD	205.0	49.8	342.0	106.0	16.0	2150.0
Blank 1_1	23.0	32.9	9.5	5.8	1.3	5.1	LOD	192.0	47.4	300.0	87.7	-	-
Blank 1_2	23.0	32.5	9.3	5.7	1.5	4.9	LOD	172.0	47.2	292.0	87.5	-	-
Feed 2	-	0.4	LOD	4.3	LOD	297.0	LOD	LOD	LOD	52.6	0.7	260	2780.0
Blank 2_1	-	LOD	5.7	1.8	LOD	305.0	LOD	LOD	LOD	54.9	LOD	257.0	-
Blank 2_2	-	LOD	19.2	1.1	LOD	285.0	7.8	LOD	LOD	56.6	LOD	260.0	-

Table IV Concentrations of organic chlorine, Cu, Fe, Na, Pb, Si, Sn, Ca, Mg, P, Zn, and Cl for serie 1 measured in the screening tests.

sample name:	c(Cl _{org.}), ppm	c(Cu), ppm	c(Fe), ppm	c(Na), ppm	c(Pb), ppm	c(Si), ppm	c(Sn), ppm	c(Ca), ppm	c(Mg), ppm	c(P), ppm	c(Zn), ppm	c(Cl _{tot}), ppm
Feed 1	20.0	34.3	9.9	4.1	1.3	4.8	LOD	205.0	49.8	342.0	106.0	16.0
Blank 1_1	23.0	32.9	9.5	5.8	1.3	5.1	LOD	192.0	47.4	300.0	87.7	-
commercial adsorbent 1 / 100 mg	23.0	33.1	9.7	6.3	1.4	5.7	LOD	191.0	47.8	306.0	237	-
commercial adsorbent 1 / 500 mg	21.0	4.3	10.4	9.8	1.4	14.3	LOD	189.0	43.3	298.0	379	-

Table V Concentrations of organic chlorine, Cu, Fe, Na, Pb, Si, Sn, Ca, Mg, P, Zn, and Cl for serie 2 measured in the screening tests.

sample name:	c(Cl _{org}), ppm	c(Cu), ppm	c(Fe), ppm	c(Na), ppm	c(Pb), ppm	c(Si), ppm	c(Sn), ppm	c(Ca), ppm	c(Mg), ppm	c(P), ppm	c(Zn), ppm	c(Cl _{tot}), ppm
Feed 1	20.0	34.3	9.9	4.1	1.3	4.8	LOD	205.0	49.8	342.0	106.0	16.0
Blank 1_2	23.0	32.5	9.3	5.7	1.5	4.9	LOD	172.0	47.2	292.0	87.5	-
Amberlyst 15 / 1000 mg	21.0	17.9	8.3	4.0	1.4	5.2	LOD	174.0	35.1	239.0	54.8	-
Merck, aluminium oxide powder / 1000 mg	37.0	30.1	9.1	5.4	1.3	4.8	LOD	177.0	44.7	254.0	69.5	-
commercial bleaching earth, 100 °C / 1000 mg	22.0	18.0	16.1	3.6	1.4	89.6	LOD	158.0	31.4	228.0	52.9	-
commercial bleaching earth, air dry / 1000 mg	21.0	31.5	9.3	5.8	1.5	5.4	LOD	175.0	44	274.0	81.3	-
Merck, activated carbon / 1000 mg	22.0	23.3	22.7	5.7	1.2	93.4	LOD	132.0	17.7	222.0	25.6	-

Table VI Concentrations of organic chlorine, Cu, Fe, Na, Pb, Si, Sn, Ca, Mg, P, Zn, and Cl for serie 3 measured in the screening tests.

sample name:	c(Cl _{org}), ppm	c(Cu), ppm	c(Fe), ppm	c(Na), ppm	c(Pb), ppm	c(Si), ppm	c(Sn), ppm	c(Ca), ppm	c(Mg), ppm	c(P), ppm	c(Zn), ppm	c(Cl _{tot}), ppm
Feed 2	-	0.4	LOD	4.3	LOD	297.0	LOD	LOD	LOD	52.6	0.7	260
Blank 2_1	-	LOD	5.7	1.8	LOD	305.0	LOD	LOD	LOD	54.9	LOD	257.0
commercial adsorbent 2 / 1000 mg	-	0.2	6.2	364	LOD	273.0	LOD	0.4	LOD	51.9	0.6	246.0
commercial adsorbent 3 / 1000 mg	-	LOD	8.8	5.3	LOD	288.0	LOD	0.4	5.1	54.3	LOD	242.0
Spent TCC-catalyst / 1000 mg	-	LOD	7.0	1.4	LOD	288.0	LOD	LOD	LOD	55.7	LOD	254.0

Table VII Concentrations of organic chlorine, Cu, Fe, Na, Pb, Si, Sn, Ca, Mg, P, Zn, and Cl for serie 4 measured in the screening tests.

sample name:	c(Cl _{org}), ppm	c(Cu), ppm	c(Fe), ppm	c(Na), ppm	c(Pb), ppm	c(Si), ppm	c(Sn), ppm	c(Ca), ppm	c(Mg), ppm	c(P), ppm	c(Zn), ppm	c(Cl _{tot}), ppm
Feed 2	-	0.4	LOD	4.3	LOD	297.0	LOD	LOD	LOD	52.6	0.7	260
Blank 2_2	-	LOD	19.2	1.1	LOD	285.0	7.8	LOD	LOD	56.6	LOD	260.0
Purolite A170/4675 / 2000 mg	-	LOD	17.3	LOD	LOD	279.0	3.2	LOD	LOD	55.8	LOD	252.0
Amberlyst 15 / 2000 mg	-	LOD	LOD	LOD	LOD	275.0	LOD	LOD	LOD	45.4	LOD	240.0
commercial adsorbent 4 / 1000 mg	-	LOD	18.3	3.5	LOD	239.0	6.4	LOD	LOD	52	LOD	247.0
commercial adsorbent 4 / 2000 mg	-	LOD	18.7	3.2	LOD	210.0	5.4	LOD	LOD	46.6	LOD	246.0
commercial adsorbent 2 / 2000 mg	-	0.2	19.4	134	LOD	226.0	7.7	LOD	LOD	50	LOD	246.0
commercial adsorbent 3 / 2000 mg	-	LOD	26.2	9.3	LOD	263.0	4.6	LOD	10.9	55.8	LOD	238.0
Merck, activated carbon / 2000 mg	-	LOD	15.9	LOD	LOD	293.0	3.1	7.7	0.8	54.1	LOD	245.0

Table VIII Calculated organic chlorine, Cu, Fe, Na, Pb, Si, Sn, Ca, Mg, P, Zn, and Cl reduction values from the screening series.

sample name:	R(Cl _{org}), %	R(Cu), %	R(Fe), %	R(Na), %	R(Pb), %	R(Si), %	R(Sn), %	R(Ca), %	R(Mg), %	R(P), %	R(Zn), %	R(Cl _{tot}), %
commercial adsorbent 1 / 100 mg	0.0	-0.6	-2.1	-8.6	-7.7	-11.8	-	0.5	-0.8	-2.0	-170.2	-
commercial adsorbent 1 / 500 mg	8.7	86.9	-9.5	-69.0	-7.7	-180.4	-	1.6	8.6	0.7	-332.2	-
Amberlyst 15 / 1000 mg	8.7	44.9	10.8	29.8	6.7	-6.1	-	-1.2	25.6	18.2	37.4	-
Merck, aluminium oxide powder / 1000 mg	-60.9	7.4	2.2	5.3	13.3	2.0	-	-2.9	5.3	13.0	20.6	-
commercial bleaching earth, 100 °C / 1000 mg	4.3	44.6	-73.1	36.8	6.7	-1728.6	-	8.1	33.5	21.9	39.5	-
commercial bleaching earth, air dry / 1000 mg	8.7	3.1	0.0	-1.8	0.0	-10.2	-	-1.7	6.8	6.2	7.1	-
Merck, activated carbon / 1000 mg	4.3	28.3	-144.1	0.0	20.0	-1806.1	-	23.3	62.5	24.0	70.7	-
commercial adsorbent 2 / 1000 mg	-	-	-8.8	-20122.2	-	10.5	-	0.4	-	5.5	-	4.3
commercial adsorbent 3 / 1000 mg	-	-	-54.4	-194.4	-	5.6	-	0.4	-	1.1	-	5.8
Spent TCC-catalyst / 1000 mg	-	-	-22.8	22.2	-	5.6	-	-	-	-1.5	-	1.2
Purolite A170/4675 / 2000 mg	-	-	9.9	-	-	2.1	59.0	-	-	1.4	-	3.1
Amberlyst 15 / 2000 mg	-	-	-	-	-	3.5	-	-	-	19.8	-	7.7
commercial adsorbent 4 / 1000 mg	-	-	4.7	-218.2	-	16.1	17.9	-	-	8.1	-	5.0
commercial adsorbent 4 / 2000 mg	-	-	2.6	-190.9	-	26.3	30.8	-	-	17.7	-	5.4
commercial adsorbent 2 / 2000 mg	-	-	-1.0	-12081.8	-	20.7	1.3	-	-	11.7	-	5.4
commercial adsorbent 3 / 2000 mg	-	-	-36.5	-745.5	-	7.7	41.0	-	-	1.4	-	8.5
Merck, activated carbon / 2000 mg	-	-	17.2	-	-	-2.8	60.3	-	-	4.4	-	5.8

Table IX Calculated capacities of organic chlorine, Cu, Si, P, Zn, and Cl from the screening series.

sample name:	$q(\text{Cl}_{\text{org}})$, g/kg	$q(\text{Cu})$, g/kg	$q(\text{Si})$, g/kg	$q(\text{P})$, g/kg	$q(\text{Zn})$, g/kg	$q(\text{Cl}_{\text{tot}})$, g/kg
commercial adsorbent 1 / 100 mg	0.0	0.0	-0.1	-1.2	-29.7	-
commercial adsorbent 1 / 500 mg	0.1	1.1	-0.4	0.1	-11.7	-
Amberlyst 15 / 1000 mg	0.0	0.3	0.0	1.1	0.7	-
Merck, aluminium oxide powder / 1000 mg	-0.3	0.0	0.0	0.8	0.4	-
commercial bleaching earth, 100 °C / 1000 mg	0.0	0.3	-1.7	1.3	0.7	-
commercial bleaching earth, air dry / 1000 mg	0.0	0.0	0.0	0.4	0.1	-
Merck, activated carbon / 1000 mg	0.0	0.2	-1.8	1.4	1.2	-
commercial adsorbent 2 / 1000 mg	-	-	0.6	0.1	-	0.2
commercial adsorbent 3 / 1000 mg	-	-	0.3	0.0	-	0.3
Spent TCC-catalyst / 1000 mg	-	-	0.3	0.0	-	0.1
Purolite A170/4675 / 2000 mg	-	-	0.1	0.0	-	0.1
Amberlyst 15 / 2000 mg	-	-	0.1	0.1	-	0.2
commercial adsorbent 4 / 1000 mg	-	-	0.9	0.1	-	0.3
commercial adsorbent 4 / 2000 mg	-	-	0.8	0.1	-	0.1
commercial adsorbent 2 / 2000 mg	-	-	0.6	0.1	-	0.1
commercial adsorbent 3 / 2000 mg	-	-	0.2	0.0	-	0.2
Merck, activated carbon / 2000 mg	-	-	-0.1	0.0	-	0.2

Temperature dependence tests

Table X Used feeds, serie numbers, separation materials, separation material and oil weighings from the temperature dependence tests.

feed:	serie:	SM:	m(SM), g	m(oil), g
2	1	commercial adsorbent 4 / 25 °C	15.00	150
2	1	commercial adsorbent 4 / 65 °C	15.00	150
2	1	commercial adsorbent 4 / 130 °C	15.00	150
2	2	commercial adsorbent 3 / 25 °C	15.00	150
2	2	commercial adsorbent 3 / 65 °C	15.00	150
2	2	commercial adsorbent 3 / 130 °C	15.00	150

Table XI Concentrations of Cu, Fe, Na, Pb, Si, Sn, Ca, Mg, P, Zn, and Cl for serie 1 measured in the temperature dependence tests.

sample name:	c(Cu), ppm	c(Fe), ppm	c(Na), ppm	c(Pb), ppm	c(Si), ppm	c(Sn), ppm	c(Ca), ppm	c(Mg), ppm	c(P), ppm	c(Zn), ppm	c(Cl _{tot}), ppm
Feed 2_1	LOD	620	LOD	LOD	300	25	LOD	LOD	58	LOD	445
Blank / 130 °C	LOD	670	LOD	LOD	260	36	LOD	LOD	58	LOD	263
commercial adsorbent 4 / 25 °C	LOD	620	3	LOD	230	24	LOD	LOD	51	LOD	245
commercial adsorbent 4 / 65 °C	LOD	590	5.7	LOD	210	23	LOD	LOD	51	LOD	244
commercial adsorbent 4 / 130 °C	LOD	350	5	LOD	180	17	LOD	LOD	46	LOD	241

Table XII Concentrations of Cu, Fe, Na, Pb, Si, Sn, Ca, Mg, P, Zn, and Cl for serie 2 measured in the temperature dependence tests.

sample name:	c(Cu), ppm	c(Fe), ppm	c(Na), ppm	c(Pb), ppm	c(Si), ppm	c(Sn), ppm	c(Ca), ppm	c(Mg), ppm	c(P), ppm	c(Zn), ppm	c(Cl _{tot}), ppm
Feed 2_2	LOD	630	LOD	LOD	290	28	LOD	LOD	59	0.51	530
Blank / 130 °C	LOD	670	LOD	LOD	260	36	LOD	LOD	58	LOD	263
commercial adsorbent 3 / 25 °C	LOD	620	28	LOD	280	27	LOD	5.9	60	0.69	240
commercial adsorbent 3 / 65 °C	LOD	620	10	LOD	250	24	LOD	15	60	LOD	235
commercial adsorbent 3 / 130 °C	LOD	400	4.1	LOD	180	17	LOD	6.2	45	LOD	210

Table XIII Calculated Cu, Fe, Na, Pb, Si, Sn, Ca, Mg, P, Zn, and Cl reduction values from the temperature dependence tests.

sample name:	R(Cu), %	R(Fe), %	R(Na), %	R(Pb), %	R(Si), %	R(Sn), %	R(Ca), %	R(Mg), %	R(P), %	R(Zn), %	R(Cl _{tot}), %
Blank / 130 °C	-	-8.1	-	-	13.3	-44.0	-	-	0.0	-	40.9
commercial adsorbent 4 / 25 °C	-	7.5	-	-	11.5	33.3	-	-	12.1	-	6.8
commercial adsorbent 4 / 65 °C	-	11.9	-	-	19.2	36.1	-	-	12.1	-	7.2
commercial adsorbent 4 / 130 °C	-	47.8	-	-	30.8	52.8	-	-	20.7	-	8.4
Blank / 130 °C	-	-6.3	-	-	10.3	-28.6	-	-	1.7	-	50.4
commercial adsorbent 3 / 25 °C	-	7.5	-	-	-7.7	25.0	-	-	-3.4	-	8.7
commercial adsorbent 3 / 65 °C	-	7.5	-	-	3.8	33.3	-	-	0.0	-	10.6
commercial adsorbent 3 / 130 °C	-	40.3	-	-	30.8	52.8	-	-	25.0	-	20.2

Table XIV Calculated capacities of Fe, Si, Sn, P, and Cl from the temperature dependence tests.

sample name:	q(Fe), g/kg	q(Si), g/kg	q(Sn), g/kg	q(P), g/kg	q(Cl _{tot}), g/kg
commercial adsorbent 4 / 25 °C	0.5	0.3	0.1	0.1	0.2
commercial adsorbent 4 / 65 °C	0.8	0.5	0.1	0.1	0.2
commercial adsorbent 4 / 130 °C	3.2	0.8	0.2	0.1	0.2
commercial adsorbent 3 / 25 °C	0.5	-0.2	0.1	0.0	0.2
commercial adsorbent 3 / 65 °C	0.5	0.1	0.1	0.0	0.3
commercial adsorbent 3 / 130 °C	2.7	0.8	0.2	0.1	0.5

Adsorption kinetics test

Table XV Used feed, serie number, separation material, separation material and oil weighings for adsorption kinetics test.

feed:	serie:	SM:	m(SM), g	m(oil), g
2	1	commercial adsorbent 4	70.03	700

Table XVI Sampling time, amount of oil left in batch, concentrations of Cu, Fe, Na, Pb, Si, Sn, Ca, Mg, P, Zn, and Cl for the adsorption kinetics test.

t, min	m(oil in batch), g	c(Cu), ppm	c(Fe), ppm	c(Na), ppm	c(Pb), ppm	c(Si), ppm	c(Sn), ppm	c(Ca), ppm	c(Mg), ppm	c(P), ppm	c(Zn), ppm	c(Cl _{tot}), ppm
0	-	LOD	640	1	LOD	280	28	LOD	LOD	56	LOD	500
2	700	LOD	680	1.2	LOD	220	28	LOD	LOD	56	LOD	243
5	687	LOD	700	1.3	LOD	220	28	LOD	LOD	56	LOD	240
10	674	LOD	700	1.2	LOD	210	28	LOD	LOD	54	LOD	238
15	661	LOD	690	3.2	LOD	200	29	LOD	LOD	53	LOD	234
30	648	LOD	710	2.3	LOD	190	37	LOD	LOD	51	LOD	227
60	635	LOD	710	4	LOD	170	37	LOD	LOD	50	LOD	224
120	623	LOD	720	3.9	LOD	160	38	LOD	LOD	48	LOD	223
180	610	LOD	740	5.3	LOD	160	39	LOD	LOD	47	LOD	220
240	597	LOD	770	5.9	LOD	160	40	LOD	LOD	46	LOD	225
300	584	LOD	810	6.5	LOD	160	41	LOD	LOD	46	LOD	234

Table XVII Sampling time, masses of Fe, Si, Sn, P, and Cl left in the oil for adsorption kinetics test.

t, min	m(Fe), mg	m(Si), mg	m(Sn), mg	m(P), mg	m(Cl _{tot}), mg
0	448	196	20	39	350
2	476	154	20	39	170
5	481	151	19	38	165
10	472	142	19	36	160
15	456	132	19	35	155
30	460	123	24	33	147
60	451	108	24	32	142
120	448	100	24	30	139
180	451	98	24	29	134
240	459	95	24	27	134
300	473	93	24	27	137

Fixed bed experiment

Table XVIII Used feed, serie number, separation material, and separation material weighing for the fixed bed experiment.

feed:	serie:	separation material, SM:	m(SM), g	m(oil), g
2	1	commercial adsorbent 4	90,0	-

Table XIX Sampling time and concentrations of Cu, Fe, Na, Pb, Si, Sn, Ca, Mg, P, Zn, and Cl for fixed bed experiment.

t, min	c(Cu), ppm	c(Fe), ppm	c(Na), ppm	c(Pb), ppm	c(Si), ppm	c(Sn), ppm	c(Ca), ppm	c(Mg), ppm	c(P), ppm	c(Zn), ppm	c(Cl _{tot}), ppm
0	LOD	212	LOD	LOD	296	26	LOD	LOD	58	LOD	525
6	LOD	190	3	LOD	163	26	LOD	LOD	22	LOD	164
7	LOD	195	2	LOD	179	26	LOD	LOD	31	LOD	190
10	LOD	200	3	LOD	180	27	LOD	LOD	38	LOD	210
19	LOD	207	2	LOD	204	25	LOD	LOD	39	LOD	230
36	LOD	210	3	LOD	210	22	LOD	LOD	49	LOD	240
53	LOD	210	3	LOD	220	27	LOD	LOD	51	LOD	245
62	LOD	210	3	LOD	220	22	LOD	LOD	52	LOD	250
91	LOD	210	3	LOD	230	27	LOD	LOD	54	LOD	250
100	LOD	210	3	LOD	230	23	LOD	LOD	56	LOD	250
112	LOD	210	3	LOD	230	24	LOD	LOD	57	LOD	255
116	LOD	210	4	LOD	230	24	LOD	LOD	56	LOD	250
120	LOD	210	4	LOD	230	25	LOD	LOD	57	LOD	250

Table XX Sampling time, masses and volumes of oil flown through the bed volumes, and concentrations of Si, P, and Cl for fixed bed experiment, $\rho(oil) = 0.86 \text{ g mL}^{-1}$, $V(\text{bed}) = 140 \text{ mL}$.

t, min	m(oil through the bed), g	V, mL	BV, -	c/c ₀ (Si), -	c/c ₀ (P), -	c/c ₀ (Cl), -
0	-	-	-	-	-	-
6	11.6	14	0.1	0.709	0.393	0.656
7	21.4	25	0.2	0.778	0.540	0.760
10	37.9	44	0.3	0.783	0.667	0.840
19	74.9	87	0.6	0.887	0.681	0.920
36	145.4	169	1.2	0.913	0.860	0.960
53	207.1	241	1.7	0.957	0.895	0.980
62	241.4	281	2.0	0.957	0.912	1.000
91	316.6	368	2.6	1.000	0.947	1.000
100	345.7	402	2.9	1.000	0.982	1.000
112	376.4	437	3.1	1.000	1.000	1.020
116	386.6	449	3.2	1.000	0.982	1.000
120	396.7	461	3.3	1.000	1.000	1.000

FTIR spectra

Table XXI Calibrated and estimated concentrations for Si, P, and Cl. Thermo Scientific Nicolet iS10 ATR-FTIR, background correction done, wavenumber region 4000–650 cm⁻¹.

sample name:	sample:	c (Si) _{CAL.} , ppm	c (Si) _{EST.} , ppm	c (P) _{CAL.} , ppm	c (P) _{EST.} , ppm	c (Cl) _{CAL.} , ppm	c (Cl) _{EST.} , ppm
Blank / 130 °C	1	260	215	58	51	263	239
Feed 2_1	2	300	302	58	60	445	465
commercial adsorbent 4 / 25 °C	3	230	230	51	52	245	255
commercial adsorbent 4 / 65 °C	4	210	198	51	49	244	211
commercial adsorbent 4 / 130 °C	5	180	173	46	48	241	210
Feed 2_2	6	290	309	59	60	530	444
commercial adsorbent 3 / 25 °C	7	280	258	60	58	240	300
commercial adsorbent 3 / 65 °C	8	250	230	60	53	235	293
commercial adsorbent 3 / 130 °C	9	180	211	45	51	210	266
Untreated feed	10	286	278	56.8	60	316	310
Filtered (0.45 µm) feed	11	288	275	57.2	60	255	237
Fixed bed, t = 9.97 min	12	180	203	38	41	210	257
Fixed bed, t = 36.47 min	13	210	210	49	50	240	230
Fixed bed, t = 52.75 min	14	220	215	51	51	245	248
Fixed bed, t = 61.87 min	15	220	218	52	50	250	227
Fixed bed, t = 91.08 min	16	230	230	54	52	250	246
Fixed bed, t = 100 min	17	230	227	56	53	250	249
Fixed bed, t = 112 min	18	230	237	57	57	255	234
Fixed bed, t = 116 min	19	230	243	56	56	250	270
Fixed bed, t = 120 min	20	230	227	57	55	250	209
FEED, kinetics test	21	280	310	56	66	500	456
Kinetics test, 2 min	22	220	260	56	65	243	357
Kinetics test, 5 min	23	220	257	56	63	240	393
Kinetics test, 10 min	24	210	245	54	62	238	339
Kinetic tests, 15 min	25	200	227	53	60	234	309
Kinetics test, 30 min	26	190	207	51	57	227	298
Kinetics test, 60 min	27	170	186	50	54	224	295
Kinetics test, 120 min	28	160	146	48	46	223	240
Kinetics test, 180 min	29	160	121	47	43	220	247
Kinetics test, 240 min	30	160	106	46	44	225	78
Kinetics test, 300 min	31	160	100	46	48	234	164