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A PURIFICATION PROCESS OF FEEDSTOCKS FOR RENEWABLE FUEL PRODUCTION

Examiners: Professor Tuomas Koiranen
D.Sc. (Tech.) Andrea Gutierrez

ABSTRACT

Lappeenranta-Lahti University of Technology LUT
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A purification process of feedstocks for renewable fuel production

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The second-generation renewable fuel is produced by catalytic hydrotreatment process from renewable feedstocks. The catalysts in the process are sensitive to get poisoned and deactivated by contaminants in small concentrations. In this thesis, the purification process of feedstocks for renewable fuel production is studied. The aim of the work was to investigate and determine the effect of process parameters in the purification of different feedstocks.

Experimental part was performed in batch and continuous reactors. The concentrations of impurities were measured before and after the purification. The results of the purification process were analyzed by MODDE Pro data-analytics software. The purification results achieved with the batch equipment were verified with the continuous one.

As a result of the work, it was noticed that the feedstocks and their original concentration of impurities had a significant impact on the efficiency of the purification process and the process operation parameters.

TIIVISTELMÄ

Lappeenrannan-Lahden Teknillinen Yliopisto LUT
LUT School of Engineering Science
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Raaka-aineiden puhdistusprosessi uusiutuvan polttoaineen tuotantoon

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Uusiutuvaa toisen sukupolven polttoainetta tuotetaan katalyyttisellä vetykäsittelyprosessilla uusiutuvista raaka-aineista. Prosessin katalyytit ovat herkkiä myrkyttymään ja deaktivoitumaan kontaminanttien vaikutuksesta jo pienillä pitoisuuksilla. Tässä diplomityössä tutkitaan raaka-aineiden puhdistusprosessia uusiutuvan polttoaineen tuotantoon. Työn tavoitteena oli tutkia ja määrittää prosessiparametrien vaikutusta eri lähtöaineiden puhdistuksessa.

Kokeellinen osa suoritettiin panostoimisella sekä jatkuvatoimisella reaktorilla. Epäpuhtauksien konsentraatiot mitattiin ennen ja jälkeen puhdistuksen. Puhdistusprosessin tuloksia käsiteltiin MODDE Pro data-analyysiohjelmalla. Panosreaktorin puhdistustuloksia verifioitiin jatkuvatoimisen reaktorin puhdistustuloksilla.

Työn tuloksena huomattiin, että raaka-aineilla ja niiden alkuperäisillä epäpuhtauksien konsentraatioilla oli merkittävä vaikutus puhdistusprosessin tehokkuuteen ja prosessin operointiparametrien arvoihin.

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ABBREVIATIONS

ASTM	American Society for Testing and Materials
BC	Brassica carinata
BOD	Biochemical oxygen demand
CFR	Cooperative Fuel Research
CMC	Critical Micelle Concentration
CN	Cetane Number
COD	Chemical oxygen demand
CTO	Crude Tall Oil
DMDS	Dimethyldisulfide
DOE	Design of Experiments
DTO	Distilled Tall Oil
EDTA	Ethylenediaminetetraacetic acid
EIA	Environmental Impact Assessment
FA	Fatty Acid
FAE	Fatty Acid Ester
FAME	Fatty acid methyl ester
FFA	Free Fatty Acids
HDS	Hydrodynamic separation
HDT	Hydrotreatment process
HPL	Hydratable phospholipid
HVO	Hydrotreated vegetable oil

ICP-OES	Inductively Coupled Plasma Optical Emissions Spectrometry
IQT	Ignition Quality Tester
KFT	Karl Fisher titration
MLR	Multiple linear regression
NDIR	Nondispersive infrared detector
NERC	Northern European Research Center
NHPL	Non-hydratable phospholipid
ODt	Oven Dry ton
PL	Phospholipid
PLS	Partial least squares regression
RA	Rosin Acid
TA	Tall Oil
TG	Triglyceride
TN	Total nitrogen
TOC	Total organic carbon
TOFA	Tall Oil Fatty Acid
TOH	Tall Oil Heads
TOP	Tall Oil Pitch
TOR	Tall Oil Resin
TPP	Three Phase Partitioning
W/O ratio	Water/Oil ratio

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1. INTRODUCTION

Background of the work, main goal of the work and basic structure are introduced in this Chapter. A research question of the work is also determined.

1.1 Background of the work

There are different types of green fuels developed in the world. The first-generation biodiesel and the second-generation advanced renewable diesel fuels are two different products. Both can be produced from same raw materials, but the products differ in many ways such as chemical compositions, production process, quality and usefulness.

Biodiesel is a mono alkyl ester of the vegetable oil which is done by catalyzed transesterification reaction of the oil with an alcohol. The product is known as fatty acid methyl ester (FAME). (Sonthalia and Kumar, 2019) FAME cannot be directly used in conventional diesel engines in high concentration mixes with fossil-based diesel or as itself. Problems may occur because of poor cold flow properties, self-life and amount of impurities. (Neste Oyj, 2016)

Advanced renewable diesel fuel is produced by hydrotreatment process. The other name for the renewable diesel is hydrotreated vegetable oil (HVO) because it is done by using hydrotreatment (HDT) processing technique where the liquid is produced in high temperatures and pressures and in presence of catalyst and hydrogen. The product is environmentally and engine efficiently advantageous having high cetane number (CN), low density, great cold flow properties and good blending ability with conventional diesel fuel. (Sonthalia and Kumar, 2019)

Hydrotreatment process is a step in the renewable diesel fuel production where triglycerides are converted into hydrocarbons by deoxygenation. Hydrocarbons can further be used as a feedstock in renewable fuel production. (Kubička and Horáček, 2011) According to Anthonykutty et al., (2015) catalytic hydrotreatment process is an efficient method for improving the content of bio-based oils reducing the content of oxygenates (S, N, O) in the oil.

Other feedstocks than vegetable oils can be used such as Crude Tall Oil (CTO). UPM uses CTO as a feedstock in UPM BioVerno renewable diesel fuel production. UPM BioVerno can be used even without blending with conventional diesel fuel in diesel engines decreasing greenhouse gas emissions up to 80%. (UPM-Kymmene Oyj, 2019a)

Different catalysts are used in hydrotreatment process. Most widely used catalysts industrially are supported CoMo and NiMo. (Anthonykutty et al., 2015) Impurities in oil feeds have a critical impact by deactivating the catalyst. It is the reason why it is important to reduce and minimize the amount of different impurities in the feedstock oil of renewable diesel fuel.

Kubička and Horáček (2011) investigated rapeseed vegetable oil where sulfided CoMo catalyst was used in a reactor. Effects of different amounts of phosphorus, alkali metals and sulfur were studied and their impact on the catalyst deactivation. It was noticed that alkali metals decrease the activity of the catalyst gradually. Deposition of alkali metals on the surface of the catalyst produces electronic effects and reduces the efficiency of the hydrogenation process by blocking and poisoning the active side of the catalyst particles. It was realized that the presence of calcium in particular led to the deactivation of the catalysts in the process.

According to Kubička and Horáček (2011) the effect of phosphorus containing compounds is significant on catalyst deactivation. Phosphorous compounds affect the decomposition of phospholipids to phosphoric acid which starts the oligomerization reaction having a remarkable impact on the deactivation of catalyst.

Silicon compounds have also remarkable impact on deactivation of catalyst in catalytic HDT process. According to Pérez-Romo et al., (2012) the deposition of silicon in the catalyst affect the accumulation of silicon compounds on the catalyst surface deactivating the catalyst and shortening the catalyst lifetime.

1.2 Goals and delimitations

The main goal of this Master's thesis is to find answers to research question that is shown in Figure 1.

Research question

?

- How to obtain efficient purification results by determining suitable process parameters in a new purification process for different feedstocks in renewable fuel production?

Figure 1 The research question of the thesis

There is large availability of feedstock possibilities for the renewable fuel production in the world. The literature part of this thesis focuses on the Crude Tall Oil, Soybean acid oil and vegetable oils. Non-edible vegetable oils such as Brassica carinata and Jatropha curcas are presented more detail.

1.3 Structure of the thesis

This Master's thesis consists of literature part and experimental part. The purpose of the literature part is to investigate suitable feedstocks for renewable fuel production e.g. non-edible vegetable oils, acid oils and CTO. Existing production technologies for all raw material groups are described, chemical compositions are presented, and impurities are discussed. Existing purification technologies are discussed and compared.

Two reactor set-ups were used to investigate the process in laboratory scale. One of the set-ups is a batch system (biofuels reactor 5, BFR5) and the other one is a continuous system (biofuels reactor 7, BFR7). These systems are used to screen different operation parameters. Critical parameters identified are temperature, water/oil ratio and pH. The amount of impurities in the product oil compared to the feedstock is used to address the success of the purification operation at the different conditions.

Based on the laboratory scale results, demo plant is used to confirm the data. Based on the BFR5 and BFR7 results, predictions are made for demo plant operation. The aim of the demo plant is to find an optimal operation window that purifies the feedstock to the desired levels suitable for hydrotreatment (HDT). The feedstock used as well as all products obtained in the purification process are analyzed at UPM's North European Research Center (NERC). At the end, conclusion of the results is presented with parameter proposals. Finally, proposal for further research is made.

I LITERATURE PART

In the literature part UPM-Kymmene Oyj is introduced. Vegetable oils, acid oils and CTO are described as suitable feedstocks for renewable fuel production. Their production processes, chemical compositions and impurities are discussed. Existing purification technologies are described. Finally, the introduction of the experimental part is presented including introduction of the laboratory set-ups, introduction of the analytical methods used for sample analysis, introduction of the MODDE Pro data analysis software and description of possible measurement uncertainties.

2. UPM-KYMMENE OYJ

This Chapter introduces UPM-KYMMENE Corporation, a large company at the area of forest industry. Overview of the company is summarized, and company's business strategy is presented. In this Master's thesis, interest is in the renewable diesel fuel production so biorefineries and especially biofuel department is on focus.

2.1 General overview

UPM in its current form was born in 1995 as a result when Kymmene Corporation, Repola Ltd and its subsidiary United Paper Mills Ltd reported about their merger. The new corporation started its official business operations on 1 May 1996. However, UPM can be considered as a traditional operator in Finland having long roots in forest industry. First actions originate from 1870s when first sawmills and paper mills started to operate. The pulp production got started in 1880s, paper production in 1920s and plywood production in 1930s. (UPM BIOFORE, 2015)

The company consists of about one hundred smaller units which have been independent companies before the corporation was created. (UPM BIOFORE, 2015) Nowadays UPM is a large and global company having 19 000 employees working around the world. The company has 54 production plants in 12 countries concentrated in Europe where 62 % of all global business activity is taken place. The corporation has 12 600 customers located in 110 different countries. UPM's sales by market in 2018 was 10,483 million €. In 2018, company's sales grew by 5 % and comparable EBIT increased by 17 %. (UPM-Kymmene Oyj, 2018b)

UPM-KYMMENE OYJ consists of six business areas offering different renewable and biodegradable products for many different market areas. These business unit groups are: UPM Biorefining, UPM Energy, UPM Raflatac, UPM Specialty Papers, UPM Communication Papers and UPM Plywood. Besides of these six business areas the company has also Other Operations-business group. Main components in the seventh group are UPM Biochemicals, UPM Biocomposites and Wood sourcing & forestry. The company offers also forest services for forest owners and investors. (UPM-Kymmene Oyj, 2019b) This work is related to the UPM Biorefining business unit and more closely UPM Biofuels.

2.2 Strategy

UPM offers sustainable solutions towards nowadays global megatrends. Importance of wood fibres, biomolecules, industrial residues and side streams use as raw material of renewable products is increasing. In the bio-forest industry, UPM has been a forerunner producing renewable and sustainable products already decades and creates nowadays green alternatives for nonrenewable fossil market in its six business areas. (UPM-Kymmene Oyj, 2019e) UPM has divided its strategy into following five strategic focus areas which are shown in Figure 2. The target is to create value by means of all these areas. (UPM-Kymmene Oyj, 2018b; Pesonen, 2018)

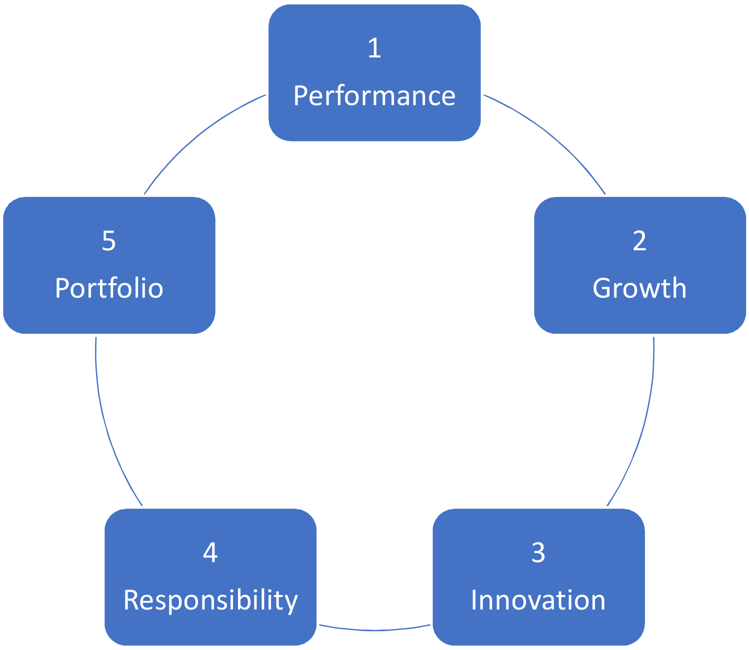


Figure 2 Strategic focus areas of UPM (UPM-Kymmene Oyj, 2018b)

2.3 UPM Biorefining

UPM Biorefining business area consist of UPM Pulp, UPM Timber and UPM Biofuels which are integrated together. Timber residues are used in pulp production and CTO is achieved as a by-product from the pulp production. UPM uses CTO as a raw material in renewable UPM BioVerno diesel fuel production. (UPM-Kymmene Oyj, 2018b)

UPM has three pulp mills, four timber plants and one biorefinery in Finland (UPM-Kymmene Oyj, 2019d). UPM has also one pulp mill in Uruguay and the company has planned to invest in new pulp mill in central Uruguay. Capacity of the new mill would be annually about 2 million tonnes of pulp. Eucalyptus will be used as a feedstock in the new plant. (UPM-Kymmene Oyj, 2018a) An investment agreement between UPM and the Republic of Uruguay is signed already in November 2017 (UPM-Kymmene Oyj, 2017).

Regarding this thesis high interest is in the UPM Biofuels business. UPM produces second generation BioVerno diesel and naphtha for road and sea transportation in its biorefinery in Lappeenranta. BioVerno diesel can be used in all diesel engines and renewable naphtha can be utilized for instance as a bio-component in gasoline or as a substitute component for the fossil-based materials in petrochemical industry (UPM-Kymmene Oyj, 2019d). The annual production of biofuels is about 100,000 tons. The plant in Lappeenranta is the first commercial wood based biorefinery in the world. (UPM-Kymmene Oyj, 2019g)

UPM plans to build a new biorefinery to Mussalo harbor in Kotka. The capacity of the new plant will be about 500,000 tons of advanced fuels from different sustainable non-edible feedstocks. Produced fuels will be suitable for road, sea and air transportation and the plant will produce also potential raw material for chemical industry. In October 2018, UPM Biofuels completed the environmental impact assessment (EIA) for the plant. (UPM-Kymmene Oyj, 2018b)

The large number of feeds, their amounts, and their difference in quality makes the development of purification methods crucial for the long-term operation of the downstream processes planned for the new UPM’s biorefinery. Thus, new, simple processes should be developed, tested and optimized at different scales before the commercial scale can be reached.

3. VEGETABLE OILS

The most common and widely available raw materials for renewable fuel production are edible oils such as soybean, rapeseed, canola, sunflower, coconut, corn and palm oil. However, the use of edible oil as feedstock for renewable fuel is problematic because it creates competition with food industry lowering the capacity of food production. (Koh and Ghazi, 2011) Due to the reasons mentioned, edible vegetable oils are not suitable in UPM company for biofuels production. Thus, in this work the focus is on non-edible vegetable oil alternatives for renewable diesel fuel production.

3.1 History of vegetable oils as renewable fuel feedstock

The history of vegetable oil as a potential diesel fuel is long. The use of vegetable oil in diesel engine was investigated in the same era when diesel engine was developed by Rudolf Diesel in the late 1800s. (Gupta and Demirbas, 2010) Until the late 1940s many studies were published regarding the use of vegetable oils as fuel in diesel engines. Petroleum fuel was globally inexpensive and highly available material between 1950s and 1970s. Therefore, the interest in the use of vegetable oils as a transportation fuel was relatively low. The energy crisis in 1973 changed attitudes and interest in alternative fuel sector increased, among them different vegetable oil species took its part in the investigation of the first-generation biodiesel raw materials. (Knothe and Dunn, 2005)

Many vegetable oils were investigated at early times such as palm oil, soybean oil, cottonseed oil and castor oil. The results were promising, and it had been seen that vegetable oils have high potential as fuel for diesel engines. Despite of high potential in diesel engines, it was early noticed that vegetable oils caused engine problems especially when used in direct-injection engines. The biggest problem realized was the high viscosity of crude vegetable oils which causes coking in injectors leading to poor atomization and bigger operational problems in engines. (Issariyakul and Dalai, 2014)

In the early 1980s sunflower oil-based methyl esters were used to reduce the viscosity of vegetable oil. Viscosity of esters are remarkable less than crude vegetable oil, being close to conventional fossil-based diesel fuel. (Knothe and Dunn, 2005; Knothe, 2010) However, according to Gupta and Demirbas (2010) the commercial production did not begin until the late of 1990s.

3.2 Global potential of vegetable oils as renewable fuel feedstock

There is a large amount of technically potential crop species available to provide oil for renewable fuel industry around the world. According to Gupta and Demirbas (2010), there are more than 350 different crops around the world which can be used to produce oil. However, crops have significant differences in oil content, supply chain possibilities and production technologies. Hence, only few of the species are justified to have a globally large-scale production. According to Bart et al., (2010) there are four crucial selection criteria of vegetable oil for fuel production: availability, cost, oil quality as a raw material for fuels and product shelf-life. Unlike fossil-based raw material, different regions in the world have their own vegetable oil species depending on their geographical location. (Woiciechowsk et al., 2016)

About 80% of the whole global vegetable oil production comes from four oil crops: Palm, soybean, rapeseed and sunflower which are the most used raw materials for industrial vegetable oil production. (Woiciechowsk et al., 2016)

Increase of global production of vegetable oils from year 2000 to 2018 is shown in Figure 3. According to the statistic, the average annual grow rate from year 2000 to year 2019 has been around 5% expect the year 2012 when global production decreased by 0.58 million metric tons. In 2000 the total production was about 90.5 million metric tons. The annual production in 2018 was 203.8 million metric tons. Thus, during the 18 years the amount of annual production has achieved an increase of over 125%.

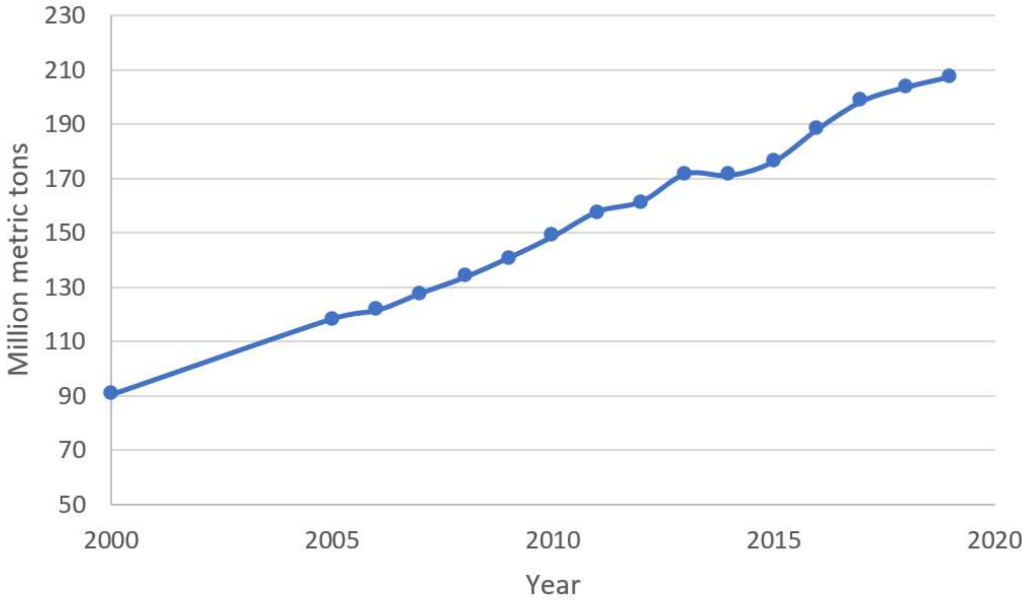


Figure 3 Global production of total vegetable oils in million metric tons from 2000 to 2018. (Statiska, 2019a)

Global annual consumption of common vegetable oils is shown in Figure 4. It can be seen that four major oils: palm oil, soybean oil, rapeseed oil and sunflower oil have significant roles in annual total consumption. According to Statiska (2019a), the growth of consumption has been almost constant from year 2013 to year 2019. When comparing the annual growth of palm oil and soybean oil in year 2017, the global consumption of palm oil was 65.15 million metric tons and consumption of soybean oil was 57.05 million metric tons. The percentual annual growth for palm oil was approximately 6.8% and for soybean oil about 4.5%, respectively.

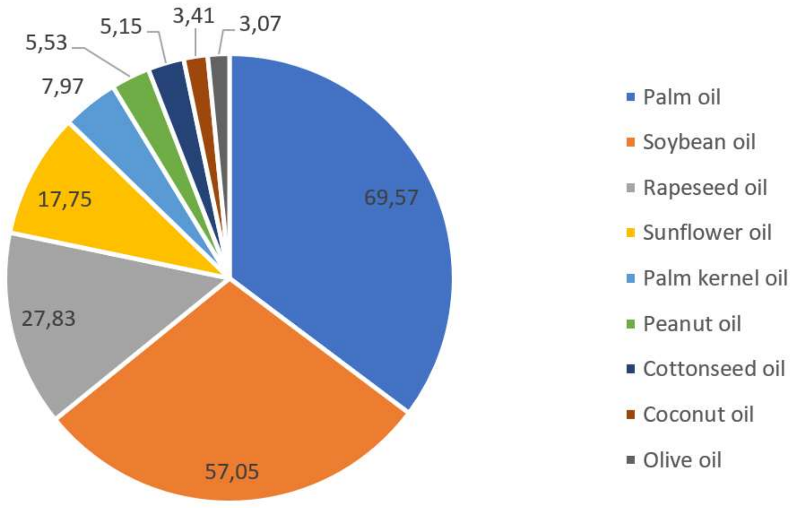


Figure 4 Consumption of major vegetable oils worldwide in million metric tons by oil type in 2018/2019. (Statiska, 2019b)

There are large differences in oil yields among crop species. Table 1 shows the achieved oil yields (liter oil/ha) from the common vegetable oils.

Table 1 Oil yield from the common crops (Pinzi and Dorado, 2011)

Crop	**Oil yield, [l/ha]**
Soya	446
Brassica carinata	594
Sunflower	972
Jatropha	1892
Palm	5950

The oil yield for palm crop is the highest from the major vegetable oil species. However, the yields of non-edible Brassica carinata and Jatropha curcas make them suitable as sustainable raw materials for the production of renewable fuels. Especially with Jatropha, high oil yield can be obtained. Brassica carinata has not as high yield as Jatropha but it has higher oil yield than soybean crop has.

3.3 Non-edible vegetable oils suitable as feedstocks

Brassica carinata and Jatropha curcas are described in this Chapter as suitable feedstocks for renewable fuel production.

3.3.1 Brassica Carinata

Ethiopian mustard i.e. Brassica carinata (BC) is a crop belonging to the family of the genus Brassica. It is one of the 35 species of the Brassica group which is the third important feedstock of vegetable oil in the world after palm oil and soybean oil. (Anjum et al., 2012) BC is especially developed to be a sustainable raw material for second generation biofuel production. As a non-edible vegetable oil, it is not affecting food industry by decreasing the capacity. (Basili and Rossi, 2018)

UPM have contracts with farmers in Uruguay who operate with BC. BC seems to be a suitable crop rotation species, creating incomes also outside summer, the most important growing season. During winter-time 2018, only 30 % of all crop fields were utilized in Uruguay. (Puoskari, 2018) Therefore, BC might be a good feedstock for renewable fuel production increasing raw material availability and income of farmers.

According to Zegada-Lizarazu and Monti (2011) crop rotation by BC has several benefits. Besides the efficient use of soil resources and capacity, crop rotation defend soil from dryness and can improve amelioration of the soil. It has been also investigated that the crops of Brassicaceae family have ability to phytoremediate soils by absorbing, accumulating and detoxifying contaminants (Basili and Rossi, 2018). A drawback for crop rotation by BC is the possibility of creating diseases such as sclerotinia if rotation is done with other energy crops. (Zegada-Lizarazu and Monti, 2011)

BC oil is collected from the seeds by extraction. Seed yields can vary in different plants due to soil composition and geographical location being about 2 tons of seeds/ha in average. (Basili and Rossi, 2018) According to Del Gatto et al., (2015) BC is farmed also in Italy. Even inside the country, there are remarkable differences in seed yields in average having a distinct variation among the north-middle-south plantation sectors. Naturally, the oil contents per hectare of plant varies also between the locations and is usually ranging from 30 to 50 % of the seeds (Basili and Rossi, 2018).

3.3.2 Jatropha curcas

Jatropha originally comes from tropical America. Nowadays there are plants efficiently growing also in many different locations in tropic and subtropic areas in Asia and Africa. The seeds and the extracted oil include phorbol esters and cursin which are toxic for humans (Abdulla and Pogaku, 2012). Seeds containing oil can be used for fuel production. (Nazir et al., 2012) According to Abdulla and Pogaku (2012) the main factors of the seed yield in plants are rainfall, type of soil, fertilizers in soil, genetics, the age of the plant and handling during the propagation.

The oil from Jatropha seeds has positive properties for renewable fuel production. Jatropha oil has a cetane number (CN) up to 51 which is higher than the CN in fossil-based diesel fuel. (Koh and Ghazi, 2011) CN is an important dimensionless number which describes the ignition quality of fuel. CN for fuels is usually defined using a Cooperative Fuel Research (CFR) engine or an Ignition Quality Tester (IQT). American Society for Testing and Materials (ASTM) standard D613 is normally used in CFR method. (Kessler et al., 2017)

3.4 Recovery methods of vegetable oils

Crude vegetable oil is usually recovered by extraction from seeds. This is the first and crucial step in the production of the renewable fuels (Basili and Rossi, 2018). The commercial extraction technologies of oils can be roughly divided into three classes: mechanical, solvent and enzymatic. (Sharma et al., 2018)

As a guideline for the two first mentioned methods, the mechanical extraction is suitable for seeds containing more than 20% of fatty matter and allows a residual matter content up to 15%. Chemical solvent extraction is suitable when values are lower than the ones mentioned above. The extracted oil is the same for both methods, but they differ in by-products generated. Mechanical extraction produces proteins and chemical solvent extraction produces flour. (Basili and Rossi, 2018)

Two commercial extraction technologies exist for BC vegetable oil. Mechanical cold-pressure based method and chemical extraction method where a solvent is used. Both methods have their own benefits depending on the feedstock seeds.

After extraction stage the oil refining process is used to convert the BC oil into the final product. In the refining step, foreign harmful substances will be removed. The part of crude oil consists of glycerine which increases the viscosity. High viscosity may create challenges in using of oils in diesel engines. (Basili and Rossi, 2018)

The other part of the BC is straw which is not used in renewable fuel production. Nevertheless, it has a significant and commercial target of use. Via steam explosion, cellulose and hemicellulose of the straw are used in Biofine process to produce chemicals such as ethyl levulinate and formic acid. Lignin can be combusted to produce electricity. (Fiorentino et al., 2014)

There are several commercial methods available for oil extraction of oil from Jatropha seeds such as mechanical press extraction, chemical solvent extraction, three phase partitioning extraction and supercritical extraction. The average oil yield in the extraction of Jatropha is between 1.5 and 2.5 tons/ha depending on the method used. (Nazir et al., 2012) Before extraction, oil seeds must be dried for weeks or in oven to decrease their water content. In conventional mechanical pressing extraction, seeds can be used as such. In the chemical solvent extraction, only powdered kernels are suitable for the extraction process. (Abdulla and Pogaku, 2012).

According to studies, one of the useful and potential technology is a Three-phase partitioning (TPP) extraction with combined enzyme pretreatment and sonication. This technology is efficient and gives a high-quality oil from Jatropha seeds. The overall yield can be up to 97 % in 2 hours. However, the main drawbacks of the process are the high energy consumption of sonication and the high cost of the enzymes. (Nazir et al., 2012; Abdulla and Pogaku, 2012)

The fruit of Jatropha can also be used in many ways. In the extraction of Jatropha oil seeds, seedcake can be utilized as a by-product of the process. When toxic compounds are removed, nutritious protein-based seedcake can be used as animal feed. (Nazir et al., 2012)

After extraction of oil, oil refining process is used to convert the oil to usable form. Industrially both chemical and physical refining processes are used and there are available many modified methods for both refining processes. In chemical refining process crude oil is pre-treated with acid and then neutralized with caustic. The caustic reacts with FFAs producing soap which is then separated from the oil by centrifugation. Separated oil is then usually washed with water and bleached. (Gupta, 2008)

In physical refining process crude oil is degummed and bleached. Degumming is used to decrease significantly the trace metals and phosphorus content. Bleaching removes the impurities which are still left in the oil. There are many degumming and bleaching technologies industrially used in the world. (Farr, 2012) These technologies are introduced more in Chapter *6.1, Purification technologies of vegetable oils*.

3.5 Chemical composition of vegetable oils

Crude vegetable oils consist mostly of triglycerides having commonly a share over 90 % of the oil. The amounts of triglycerides vary depending on the plant. Besides triglycerides, vegetable oils contain minor compounds that can be separated into two groups: oil soluble compounds and oil insoluble compounds. (Sharma et al., 2018) Table 2 presents the fatty acid contents in typical vegetable oils. Three major fatty acids can be determined according the Table: palmitic acid (16:0), oleic acid (18:1) and linoleic acid (18:2). The numbers present chemical structures of different fatty acids. First number in fatty acid composition describes the number of carbon atoms in the fatty acid chain and the second number tells the number of double bonds in the chain.

Table 2 Fatty acid composition in different vegetable oils. Xx shows the number of carbon atoms and y describes the number of double bonds. (Gupta and Demirbas, 2010)

Fatty acid (xx:y)	**Palmitic 16:0**	**Palmitoleic 16:1**	**Stearic 18:0**	**Oleic 18:1**	**Linoleic 18:2**	**Linolenic 18:3**	**Others**
Palm	42.6	0.3	4.4	40.5	10.1	0.2	1.1
Soybean	11.9	0.3	4.1	23.2	54.2	6.3	0
Rapeseed	3.8	0	2.0	62.2	22.0	9.0	0
Sunflower seed	6.4	0.1	2.9	17.7	72.9	0	0
Peanut	11.4	0	2.4	48.3	32.0	0.9	4.0
Cottonseed	28.7	0	0.9	13.0	57.4	0	0
Coconut	7.8	0.1	3.0	4.4	0.8	0	65.7
Olive	5.0	0.3	1.6	74.7	17.6	0	0.8

Figure 5 presents the common fatty acid content of BC vegetable oil. Erucic acid (22:1), linoleic acid (18:2) and linolenic acid (18:3) are the main fatty acids in BC. The fatty acid content of BC differs when compared to common major vegetable oils presented in Table 2. For example, the total content of palmitic acid, oleic acid and linoleic acid in BC oil is 29.6 % from the total content of fatty acids. BC vegetable oil consist of mostly unsaturated long-chain fatty acids.

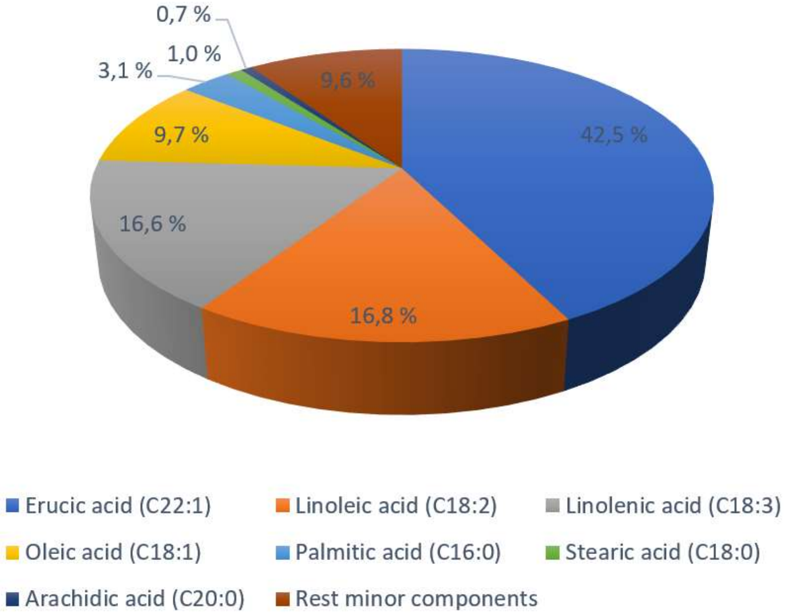


Figure 5 Fatty acid content of Brassica Carinata. (Cardone et al., 2003)

Table 3 presents the fatty acid composition of crude Jatropha curcas oil. It can be seen that unsaturated oleic acid is the one having the highest content of total fatty acids in Jatropha curcas oil. Besides oleic acid, the other major fatty acid in Jatropha curcas oil is unsaturated linoleic acid. Saturated palmitic and stearic fatty acids can have also total content up to 25 wt.-% from total fatty acids.

Table 3 Fatty acid content of crude Jatropha curcas oil. (Berchmans and Hirata, 2008)

Fatty acid	**Chemical structure**	**Wt.-%**
Oleic acid	C18:1	34.3-45.8
Linoleic acid	C18:2	29.0-44.2
Palmitic acid	C16:0	14.1-15.3
Stearic acid	C18:0	3.7-9.8
Palmitoleic acid	C16:1	0-1.3
Linolenic acid	C18:3	0-0.3
Arachidic acid	C20:0	0-0.3
Behenic acid	C22:0	0-0.2
Myristic acid	C14:0	0-0.1

3.6 Impurities in vegetable oils

Vegetable oils includes several impurities which affect the further hydrotreatment process in renewable fuel production. Metals are important impurities in vegetable oils. The plants assimilate metals from soil and water used during their growing period. Another reason for the presence of metals is the transferring of metals from the materials used during storage and transportation of the oils. (de Oliveira et al., 2012)

The triglycerides and fatty acids present in the vegetable oils can be hydrotreated in the presence of a catalyst (alumina supported CoMo or NiMo) and hydrogen at high temperatures (up to 400 °C) and pressures (up to 150 bar). In the process, hydroxyl groups are cleaved, and double bonds are saturated. Because of the long hydrocarbon chain, the product obtained mainly in the diesel range but also a lighter fraction (gasoline fraction) is produced.

The catalysts used in the hydrotreatment process are very sensitive to alkaline metals. These metals deposit on the surface of the catalyst blocking the pores and active sites not allowing the sites to be available for the hydrotreatment reaction. Furthermore, the presence of silicon in the feed reacts at the reaction conditions forming silicon oxides on the surface of the catalyst. Thus, it is very important that the concentration of alkaline metals and silicon in the feed is kept below 10 ppm to ensure the long-term operation of the hydrotreatment catalyst.

Crude vegetable oils include many impurities such as hydratable and non-hydratable phospholipids which affects the quality of oil and further processing. Besides phosphatides, a significant contaminant group is metals from salts of phosphatidic acids. These metals are mostly calcium, magnesium, potassium, aluminum, iron and copper. Calcium and magnesium salts of non-hydratable phosphatidic acids are especially presented in vegetable oils. (Copeland and Blecher, 2005) Alkaline metals (sodium, potassium, calcium and magnesium) in vegetable oils form sediments and cause problems in the renewable fuel production processes. It is also known that metals catalyze undesired oxidation and polymerization reactions of hydrocarbons. (Banga and Varshney, 2010).

Pal et al., (2015) investigated phosphorous content in crude sunflower oil. The crude oil contained 6.15 ppm of phosphorus. After degumming and neutralization processes the phosphorus content was near zero. Bianchi et al., (2011) investigated different sustainable feedstocks for fuel production. According the study non-edible vegetable oil from brassica juncea seeds contain less than 4 ppm of phosphorus. On the other hand, according to Copeland and Blecher (2005) conventional water-degummed vegetable oil can contain up to 150 ppm of phosphorus. Same vegetable oil included 1 ppm of iron, 50 ppm of magnesium and 80 ppm of calcium.

The mentioned concentrations above indicate that there are huge differences in phosphorous concentration between vegetable oils. Some oils can contain already before purification process desired ≤ 10 ppm of phosphorous and other oils hundreds of ppm.

Farzin and Moassesi (2014) investigated the metal contents of four different edible oils: olive oil, canola oil, sunflower oil and soybean oil. Table 4 shows the minimum and maximum values obtained in the metal determinations.

Table 4 Minimum and maximum metal concentrations in edible oils. (Farzin and Moassesi, 2014)

	Ni [ppm]	**Mn [ppm]**	**Cu [ppm]**	**Zn [ppm]**	**Fe [ppm]**	**Ca [ppm]**	**Mg [ppm]**
Vegetable oils min-max	0.91 - 2.17	0.14 - 1.76	0.18 - 0.68	3.58 - 9.54	7.78 - 28.93	21.42 - 78.52	5.34 - 36.49

It can be seen in Table 4 that iron, calcium and magnesium are the metals with the highest concentrations in edible oils. Calcium and magnesium amounts are the most important ones concerning HDT process as they deposit on the catalyst causing its deactivation. The maximum amount of alkaline metals in the feed to HDT process is recommended to be less than 10 ppm. Thus, according to the concentrations of calcium and magnesium reported in edible oils, the concentrations of these metals need to be decreased before the oil can be hydrotreated.

Knoll and Knopp (2007) also investigated the concentration of phosphorus, calcium and magnesium in soybean oil using ICP-OES. The results are presented in more detail in the Appendix I, Table 28. A total of 23 oils extracted from different varieties of plants were analyzed. The concentrations were determined for crude soybean oil and degummed soybean oil. In the report, remarkable differences were noticed in the qualities and properties of oils obtained from different plants. Depending on the feedstock, the phosphorus content of crude soybean oil ranged from 448.5 to 1286.0 ppm, calcium varied from 55.7 to 167.7 ppm and magnesium ranged from 51.5 to 151.7 ppm. (Knoll and Knopp, 2007) Due to the high concentration of metals and phosphorus in soybean oil, further purification steps are needed to remove the impurities before hydrotreatment.

De Oliveira et al., (2012) investigated the concentration of silicon in vegetable oils. In Table 5 are presented the concentrations of silicon for a corn, soybean and sunflower oil. Conventional ICP-OES analytical method was used in the quantification of silicon. Table 5 shows that the concentration of silicon is below 1 ppm in the study performed with edible oils.

Table 5 Concentration of silicon in ppm in corn oil, crude soybean oil and sunflower oil. (de Oliveira et al., 2012)

Vegetable oil	Concentration of silicon [ppm]
Corn oil	< 0.6
Crude soybean oil	0.71
sunflower oil	< 0.6

The concentrations of metals, phosphorus and silicon mentioned in studies reported in this Chapter were determined for edible oils. Due to the lack of information of non-edible oils, it can be assumed that same concentration levels exist in non-edible oils. Alkaline metals and phosphorus seem to have critical impact on purification process, whereas the significance of the concentration of silicon is low.

4. ACID OILS

Acid oils are by-products produced in vegetable oil refining. They are produced after the degumming of crude vegetable oil in the alkali deacidification process i.e. neutralization process. In the neutralization step soapstock (SS) is produced which is obtained as by-product together with high concentrations of water and soap. Acid oils contain mostly free fatty acids (FFAs), acylglycerols, pigments and other lipophilic compounds (Haas et al., 2003). (Watanabe et al., 2007; Deivajothi et al., 2018)

Acid oils can be obtained from many different vegetable oils. However, this Thesis focuses only on acid oils obtained from soybean oil refining because soybean acid oils are used as a raw material in the experimental part of this Thesis. Traditionally, acid oil obtained in the soybean refining process is used in the production of low-quality soaps and as animal feed. Its high availability, low cost and industrially unutilized situation makes the feedstock a potential for second generation renewable fuel production. (Tripathi & Subramanian, 2017) In 2005 SS from soybean oil refining cost about 0.11 US$ per kg which corresponded to about 20% of the price of crude soybean oil (Haas, 2005).

4.1 Production of acid oil

Soya acid oil is a by-product in chemical refining process of soybean oil. The crude vegetable oil is extracted from the seeds and the acid oil is produced in the saponification and acidification steps. (Tripathi and Subramanian, 2017)

Figure 6 presents the process how acid oils are obtained as by-products in vegetable oil refining process.

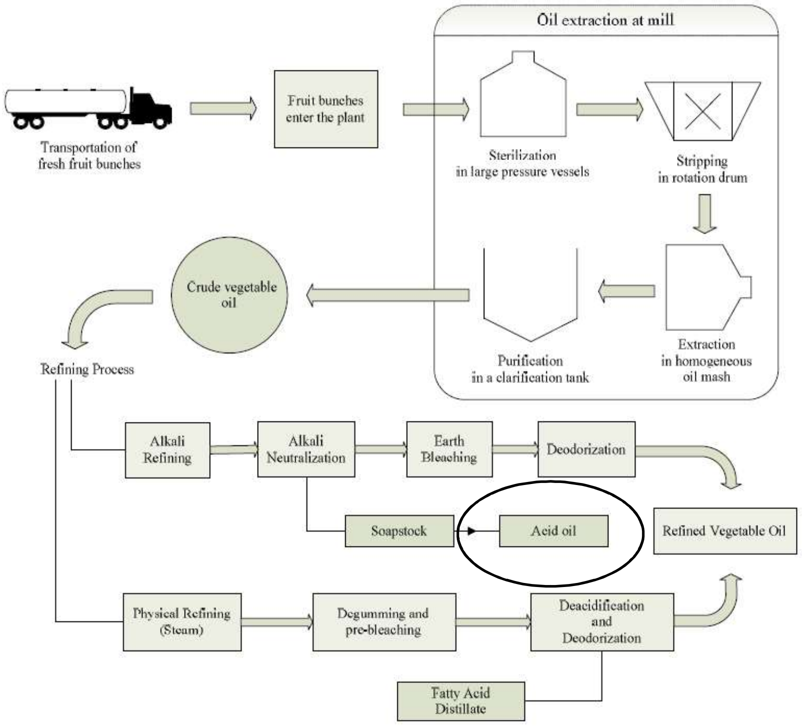
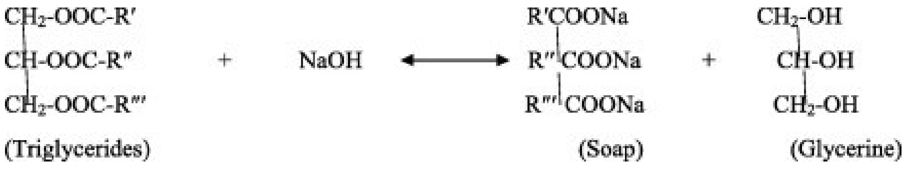


Figure 6 Process flow chart for the conventional vegetable oil refining process where acid oil is obtained as by-product. (Piloto-Rodriguez et al., 2014)

The saponification reaction is used to convert the crude soybean oil to soap and glycerine using sodium hydroxide as a saponifying agent. In the process, not only soap and glycerine are produced but also triglyceride (TG) and free fatty acids. Equations (1) and (2) describe the chemical reactions that happen during the saponification. In the Equation (1) triglycerides react with sodium hydroxide forming glycerine and soap. Glycerine and soap can be separated by using centrifugation. In the Equation (2), free fatty acids react with sodium hydroxide forming soap and water. (Tripathi and Subramanian, 2017; Morshed et al., 2011)



$$\begin{array}{lcccccc} CH_2\text{-}OOC\text{-}R' & & & & R'COONa & & CH_2\text{-}OH \\ CH\text{-}OOC\text{-}R'' & + & NaOH & \longleftrightarrow & R''COONa & + & CH\text{-}OH \\ CH_2\text{-}OOC\text{-}R''' & & & & R'''COONa & & CH_2\text{-}OH \\ \text{(Triglycerides)} & & & & \text{(Soap)} & & \text{(Glycerine)} \end{array} \quad \text{(Eq. 1)}$$

$$\begin{array}{lcccccc} R''''\text{-}COOH & + & NaOH & \longleftrightarrow & R''''\text{-}COONa & + & H_2O \\ \text{(Free fatty acid)} & & & & \text{(Soap)} & & \text{(Water)} \end{array} \quad \text{(Eq. 2)}$$

(Morshed et al., 2011)

After saponification reaction acidification takes place. The chemical reaction that happens in the acidification is presented in Equation (3). In the reaction, sodium salts of FFAs i.e. soap is converted to FFAs by using an acid as catalyst. In the process, free fatty acids are separated from the aqueous sodium chloride fraction and then washed with water and further dried.

$$R''''COONa + HCl \leftrightarrow R''''COOH + NaCl \qquad \text{(Eq. 3)}$$

Produced FFAs i.e. acid oil can be then further converted into renewable fuel. According to Li et al., (2010), the share of soapstock obtained as by-product in vegetable oil refining is about 5 % of the whole oil fed to the refining process. Because of low cost and great availability of acid oil, they have a significant potential as feedstock in renewable fuel production.

4.2 Chemical composition of acid oil

The chemical compositions and impurities presented in acid oils depend on the feedstocks used and on how they are processed. Acid oil are predominantly long chain FFA mixtures containing small amount of mineral acids (1-2%), phospholipids and sterols (8-10%) and some amount of free moisture (5-8 %). Depending on the composition, acid oils have their own characteristic odor and brown color. (Kulkarni et al., 2008)

Crude acid oils have significant differences in physical and fuel properties when compared with conventional fossil-based diesel fuel. Due to the oxygen-rich nature and chemical structure of different compounds, heating values are lower while viscosity and ignition rates are higher than in conventional diesel fuels. Viscosity is one of the main factors affecting the use of crude acid oils in diesel engines besides their impurities. Thus, viscosity must be reduced before acid oils can be used as fuel raw material. (Kulkarni et al., 2008)

The major fatty acids of soybean acid oil are presented in Table 6. Unsaturated oleic acid is the main fatty acid of the oil having 47.5 wt.-% of the total fatty acid content.

Table 6 Fatty acid content of soya acid oil (Tripathi and Subramanian, 2017)

Fatty acid	**Chemical structure**	**Wt.-%**
Oleic acid	C18:1	47.5
Linoleic acid	C18:2	24.83
Palmitic acid	C16:0	8.2
Linolenic acid	C18:3	4.97
Stearic acid	C18:0	3.77

5. CRUDE TALL OIL

Crude tall oil (CTO) is a relatively low-cost and important by-product generated in Kraft pulping process (Adewale & Christopher, 2017). It is a dark, viscous and odorous liquid which is a significant feedstock in the production of sustainable fuel alternatives. (Lee et al., 2006)

Quality, yield, and composition of CTO depends on many factors: type of wood species used in the pulping process, geographic location, storage time and storage type. It is also important to mention that the amount of timber residues and time of the year also impact the properties of CTO. (Adewale et al., 2017) According to Laxén and Tikka (2008), a concentration of extractives in wood decreases during storage because of biological activity. A low-level activity occurs in winter time while the level of activity increases in summer time. Also, the longer a tree grows, more extractives can be obtained.

The average yield of the CTO varies between 30 and 50 kg/ton of pulp (Alén, 2011). Table 7 presents typical tall oil (TA) yields in different locations.

Table 7 Typical tall oil yields in different production locations. (Laxén and Tikka, 2008; Isotalo, 2004)

Location	***Tall oil, [kg/ODt of wood]***
USA, Coastal	26
USA, Southwestern	32
Canada	12
Sweden	25
Northern Finland	40-50
Southern Finland	20-30

The amount of heartwood increases when going to the north. It mainly explains the difference in amounts of tall oil between Northern and Southern Finland (Isotalo, 2004). Besides pine, birch and/or spruce is usually added to the Kraft pulping process in Finland to produce CTO mixtures. Depending on the mixture content, adding of other wood sources than pine locally lowers total amount of tall oil fraction obtained from the Kraft pulping process. (Laxén and Tikka, 2008)

Wood extractives are the main components of CTO. Figure 7 shows the average chemical composition of pine wood. It can be noticed that the percentage of extractives in Scots pine wood is approximately 5 wt.-% of the total content of wood. However, according to Aho and Fatehi (2017), softwood such as Pine may contain extractives up to 10 wt.-% of wood.

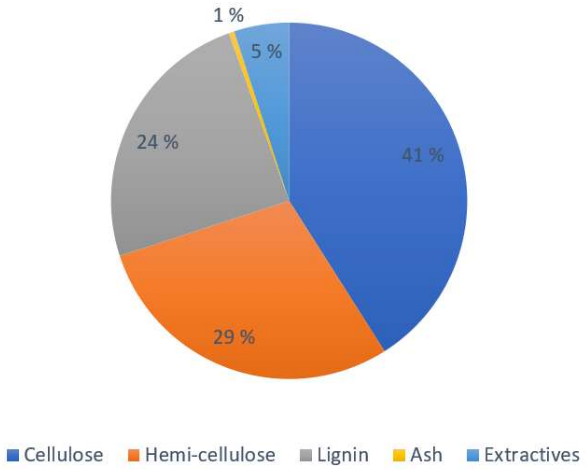


Figure 7 The average chemical composition of Scots pine (Isotalo, 2004)

Extractives are known as mixtures of three main components: resin acids, fatty acids and neutral unsaponifiable fractions. Unsaponifiable compounds are fractions which do not form soap in an alkaline solution. These compounds do not have any commercial or industrial use yet. (Aro and Fatehi, 2017)

Figure 8 presents the main composition of wood extractives in more detail. Neutral compounds consist of waxes, hydrocarbons, free alcohols and phenolic compounds. Fatty acids can be divided into two groups: free fatty acids and fatty acid esters.

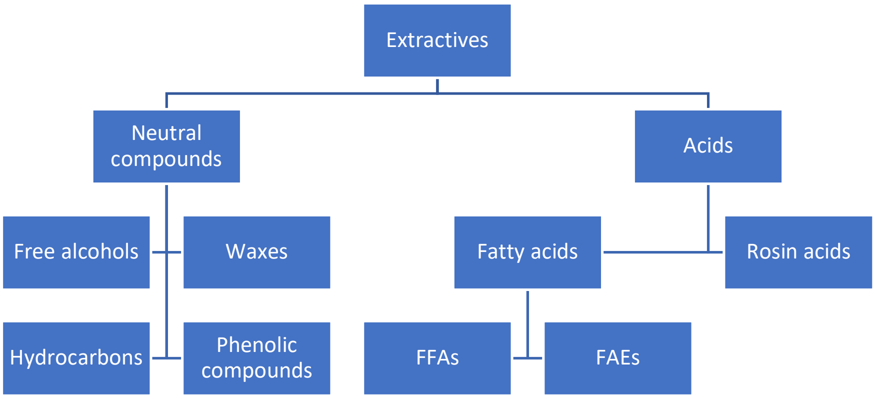


Figure 8 Composition of wood extractives. (Isotalo, 2004)

5.1 Production of Crude Tall Oil

The commercial tall oil production process is integrated into the Kraft pulping process (Aro and Fatehi, 2017). CTO production process can be divided into three major parts: the isolation of tall oil soap from black liquor, the production of crude tall oil from tall oil soap and finally the purification of tall oil and its applications.

In the Kraft cooking process acidic wood extractives are saponified with sodium hydroxide in the highly alkaline soup. Equation (4) describes the saponification reaction where fatty acid esters (FAEs) hydrolyses and free fatty acids (FFAs) are saponified. (KnowPulp, 2011)

$$R - COOH + NaOH \rightarrow R - COONa + H \qquad \text{(Eq. 4)}$$

In the white liquor fatty acids and rosin acids form sodium salts which are commonly known as soap. The soap forms soap micelles in critical micelle concentration (CMC) which are soluble in weak black liquor. Micelles begin to form when fatty and resin salts aggregate together. The concentration varies depending on several aspects: The soap is more soluble in the black liquor at high temperatures. The solubility of soap in black liquor is at its minimum value when the residual effective alkali is about 8-11g NaOH/l depending on the FA-RA ratio. The bigger ratio lowers the solubility of soap in black liquor. However, both salt types are needed in micelle formation. Many studies have been performed and has been found that when dry solid content of the liquor is 33 wt.-%, viscosity problems start to occur. High viscosity complicates the rising of the soap to the surface of the black liquor. According to Laxén and Tikka (2008), the optimal dry solid content is between 28 and 32 wt.-% to achieve the best separation efficiency. Therefore, achieving the most efficient separation, the separation step is operated in the evaporation plant (Isotalo, 2004). The minimum solubility of soap is typically 2-5 kg CTO/t of black liquor. The amount differs significantly depending on the soap composition. (Laxén and Tikka, 2008)

During evaporation, the concentration of dry solids in black liquor increases and soap rises to the surface. After settling, the crude soap can be separated by skimming or decantation. On the other hand, during evaporation, extractives of the wood separate from biomass (Mkhize et al., 2015). (Laxén and Tikka, 2008)

Separated soap continues to the next step of the CTO production which is acidification. The acidification is done in batch or in continuous process. In Finland, the continuous process is commonly used in the industry. In this step, the separated soap is acidified usually with sulfuric acid or waste acid from the chlorine dioxide plant which contain sulfuric acid. Acidification can be done also with CO_2. This process needs pressures up to 70 bars to achieve 100% acidulation efficiency. CO_2 is commercially used as a pre-acidification agent in a step performed at 10 bar pressure. Approximately, 30% acidification efficiency is achieved in this step. This pre-acidulation is then followed by sulfuric acidification. (KnowPulp, 2011)

In the acidification process, fatty and resin soaps are transformed into carboxylic acids. The chemical reaction of the acidulation is presented in Equation (5). (Laxén and Tikka, 2008)

$$2R - COONa + H_2SO_4 \rightarrow 2R - COOH + Na_2SO_4 \qquad \text{(Eq. 5)}$$

There are several commercial sulfuric acid acidification processes in the world, both batch and continuous. The yields and type of common processes are shown in Table 8. The main difference among these processes are the yields that can be reached.

Table 8 Commercially available sulfuric acid acidification processes in CTO production. Batch, centrifuge, decanter and HDS (hydrodynamic separation) (KnowPulp, 2011)

	Batch	**Centrifuge**	**Decanter**	**HDS**
Yield	70-80	95-98	70-85	95-98
Process type	Batch	Continuous	Continuous	Continuous

During the acidification process, organic material such as unsaponifiable compounds dissolve in fatty and resin acids. After the acidification step, CTO contains large number of impurities such as mother liquor, fibers, lignin and sulfuric acid. These impurities are removed by washing. (KnowPulp, 2011)

After washing and settling, three different layers are obtained. CTO is the lightest fraction, so it rises to the top of the reactor tank and is separated. (Aro and Fatehi, 2017) The separated CTO is then dried to lower its water content to under 1.5 wt.-%. Low water contents are desired for an effective distillation of CTO in further processing. (KnowPulp, 2011)

5.2 Chemical composition of Crude Tall Oil

Fatty acids in CTO are typically long-chain mono carboxyl acids. Oleic, palmitic and linoleic acid have the biggest share of the total fatty acids. Resin acids in CTO are tricyclic organic acids. The most presented resin acids are abietic and pimaric acids. Smaller amounts of other resin acids also present. It is common for resin acids to have the same tricyclic basic structure. Figure 9 shows the structures of most common resin and fatty acids of CTO. (De Bruycker et al., 2014; Aro and Fatehi, 2017)

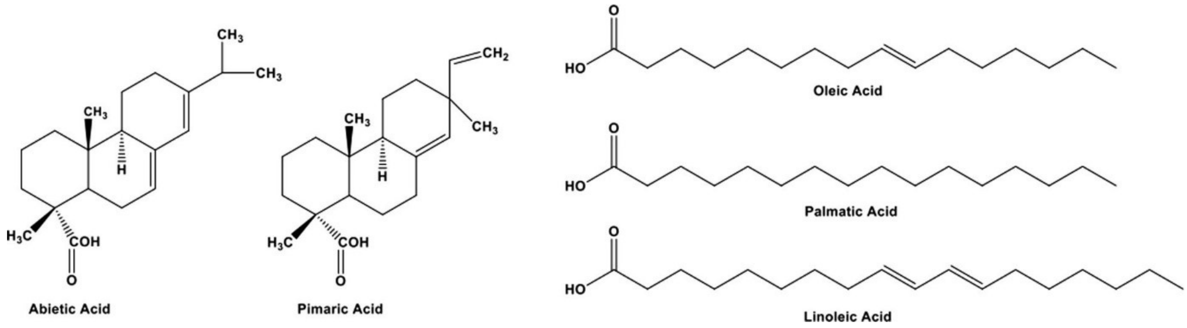


Figure 9 Most common rosin acids and fatty acids of CTO. (Aro and Fatehi, 2017)

The composition of CTO for different wood species is presented in Table 8. According to Laxén and Tikka (2008), the acid number for pine wood CTOs varies from 160 to 165 (mg KOH/g) which is distinctly bigger when compared to the CTO made from spruce and birch. Acid number for birch CTO is lowest being 110 (mg KOH/g). The quality of the CTO is mostly determined by value of acid number. Birch is a wood species that has CTO with low acid number and therefore low market prices when compared to e.g. CTO from pine wood. Birch also has significantly higher concentration of unsaponifiable neutral compounds (30%) when compared to pine (7%) or spruce (10%). Furthermore, birch CTO does not include resin acids at all. Thus, birch wood is less suitable than pine wood for crude tall oil production. In general, softwood is a better raw material for CTO production when compared to hardwood. (Isotalo, 2004)

Table 9 shows the composition of the mixture of pine and birch CTO which is compared to the composition of pine, spruce and birch CTO. The composition and acid number of the CTO mixture can be estimated depending the amounts of pine and birch sources used in CTO production and their properties. The amount of acid number of the mixture is lower than CTO from pine by 30 (mg KOH/g). On the other hand, the amount of unsaponifiable material increases 8 % when compared to CTO from pine.

Table 9 Roughly determined composition of CTO made from different species of wood (Isotalo, 2004)

		Pine	**Spruce**	**Birch**	**Pine/Birch (50/50)**
Acid Number	Mg KOH/g	160	140	110	130
Resin acids	%	40	25	0	25
Fatty acids	%	53	65	65	60
Unsaponifiable material	%	7	10	30	15

5.3 Impurities in Crude Tall Oil

CTO contains many impurities which cause problems during the CTO processing and may have a significant impact on the yield of desired products. Typical contaminants in CTO are residual mineral acids, mostly sulphuric acid, salts and soaps of alkali metals, salts and soaps of alkaline earth metals, transition metals, fibers and organic lignin compounds. Most of the impurities found in CTO come from black liquor. The efficiency of the separation of CTO from brine during the Kraft cooking process determines the concertation of the different impurities in CTO. (Stigsson et al., 2014) According to Hazelton et al., (2015) the amount of metal impurities in CTO is also due to corrosion of the equipment used in different unit operations.

CTO also contains ash which can cause deactivation and poisoning of the catalyst used in the hydrotreatment. The name ash is given to contaminants such as inorganic alkaline metal compounds (sodium, potassium), silicon, phosphorus, calcium and iron compounds. (Knuuttila et al., 2015) According to Adewale and Christopher (2017) the ash content in CTO is around 0.45 wt.-%.

According to laboratory data from Tuomola (2012), CTO consist of many elements where sodium, calsium, phosphorous, iron, potassium and silicon are the most important ones. Ash content of the analyzed sample was 15% wt.-%. In Table 10 is presented the result from elemental analysis of typical CTO.

Table 10 Elemental analysis of CTO. Ash content of the analyzed sample is 15 wt.-%. (Tuomola, 2012)

Element	Amount in CTO, [ppm]
Sodium, Na	35500
Calcium, Ca	10100
Phosphor, P	1860
Potassium, K	1230
Silicon, Si	920
Iron, Fe	510

In Table 11 is shown an example of the CTO impurity contents. Used feedstock is depitched CTO. Depitched CTO is obtained from the CTO distillation process where tall oil pitch (TOP) fraction is separated (Aro and Fatehi, 2017). It can be seen in Table 10 and Table 11 that there is a significant difference between CTO and depitched CTO in contents of impurities. However, the content of sodium and phosphorus are over 10 ppm in depitched CTO which indicates that those are some of the significant factor elements in purification process.

Table 11 Amounts of impurities in the CTO. (Mikulec et al., 2012)

Material	Amount in CTO, [ppm]
Sulphur, S	1610
Sodium, Na	27.7
Potassium, K	6.5
Calcium, Ca	1.1
Magnesium, Mg	0.1
Phosphorus, P	22.7

6. PURIFICATION OF OILS

Different purification technologies have been developed for different oils during the time. Technologies differs significantly depending on the oils used and properties of them. Generally, different technologies are used to vegetable oils and crude tall oil.

6.1 Purification technologies of vegetable oils

Different purification technologies have been developed to remove impurities from vegetable oils to enable the use of them in the hydrotreatment process. However, the basic structure of the purification processes usually consist of degumming and bleaching processes.

6.1.1 Degumming

Crude vegetable oils contain impurities which need to be removed when using vegetable oils as raw material in the production of renewable fuels. Degumming is a suitable process for the removal of the gummy substances. According to Knuuttila et al., (2015) degumming is a standard procedure in removal of phospholipids (PL) and metals from vegetable oils which contain high concentrations of gum. The share of phospholipids in gums is remarkable. (Sharma et al., 2018)

It is investigated that phospholipids reduce the activity of the catalyst in the hydrotreatment process. phospholipids block the active sites and pores in the surface of the catalyst. (Salam et al., 2018)

As gummy materials have higher density than the oil molecules, so they can be separated using gravity settling in the process known degumming. As a result, gum settles at the bottom of the settling tank whereas oil rises to the top of the tank. The purified oil can be then separated by filtration. Some disadvantages of the process are the long duration of the settling procedure and the process is not totally effective and some amount of gum remains after the process. (Sharma et al., 2018)

The phospholipids in vegetable oils can be divided into two groups depending on their water solubility. The two groups are hydratable phospholipids (HPLs) and nonhydratable phospholipids (NHPLs). According to Sharma et al., (2018) most of the phospholipids presented in vegetable oils are hydratable. The HPLs can be removed from the crude oil by treating it with water. In the treating, HPLs are hydrated with water and forms a heavy phase that is separated from the oil by centrifugation. After the centrifugation, NHPLs needs further treatment with acids where acid reacts with NHPLs making it soluble in water. (Gupta, 2017b) NHPLs are complex mixtures of metallic species. Addition of an acidic chemical reagents forces them to hydrolyze into HPLs and metallic cations which can be then removed by water degumming methods. (Sharma et al., 2018)

Degumming technologies can be divided into two groups depending on the nature of phospholipids. In industries exist many different degumming technologies such as water degumming, chemical degumming, membrane degumming and enzyme degumming. (Sharma et al., 2018)

HPLs can be removed from crude vegetable oil by water degumming method where water is absorbed by HPLs which leads to separation. From all phospholipids present in the oil, only HPLs can be removed by water degumming. Only small fraction of NHPLs may be removed by this technology. (Gupta, 2017b) Usually water degumming is first used which helps the further removal of NHPLs in acidic conditions. (Sharma et al., 2018)

In industry, both batch and continuous commercial water degumming are used. Oil agitation tanks are used in batch degumming methods, followed by centrifugation to separate the phases. In the continuous process, oil and water are preheated to about 80 ºC and pumped to pipeline agitator. After the holding time, the liquid is pumped into a centrifuge where the residue and oil phase are separated. Crude lecithin can be separated from the residue. This compound can be used e.g. as a food additive. The separation of lecithin increases the profitability of the purification process. (Sharma et al., 2018)

As mentioned above, NHPLs cannot be removed from oil by water degumming methods because they are not soluble in water. More complicated processes and different agents are needed for the separation of NHPLs. These processes are commonly divided into chemical, physical and biological depending on the chemical reagents used, the size-difference of phospholipids and triglycerides and the structure of PLs in vegetable oil. (Sharma et al., 2018)

In chemical degumming, a chemical reagent is used to increase the hydratability of the phospholipids. Citric acid and phosphoric acid are mostly used. Citric acid forms a complex compound with metal ions in NHPLs and phosphoric acid creates a precipitate with metal ions. Besides the two mentioned acid degumming, there are other commercial chemical degumming methods in the world such as TOP degumming, soft degumming and dry degumming processes. TOP degumming is a two-step process where first phosphoric acid is used in the deformation of phosphatide-based metals and then a base is used to neutralize acid and form soap. The neutralized acid and metals can be separated by centrifugation when the oil containing low amounts of phospholipids is obtained. (Sharma et al., 2018) The word TOP in this situation is an acronym which comes from Dutch words “Totaal Ontslijmings Process” meaning total degumming process (Zufarov et al., 2008).

In soft degumming, ethylenediaminetetraacetic acid (EDTA) is used as chelating agent which reacts with NHPLs and forms a metal-EDTA complex as a result which is hydratable. Then the oil is separated from the aqueous phase by centrifugation. (Gupta, 2017b) In the dry degumming, strong acids are used to displace weaker acids from salts. (Sharma et al., 2018)

Membrane technologies are also used in degumming of oils and they can fully or partly replace conventional degumming processes (de Souza et al., 2008). Important benefits of membrane degumming are high energy efficiency, less water and chemicals needed, no wastewater produced and low energy consumption (Vavra and Farr, 2012). According to de Souza et al., (2008), some other benefits are low oil losses, possible combination of degumming and bleaching steps into one efficient refining process and use of steam at low operating temperatures which decrease energy consumption.

Separation process by membrane technology is physically pressure-driven process which is based on the particle sizes. In the crude vegetable oil, the differences between sizes and molecular weights of the oil constituents such as triglycerides and phospholipids are small which is challenging for the efficiency of the process. (Manjula and Subramanian, 2006)

Enzyme degumming process is a new process developed in 1990s and known as EnzyMax. Enzymatic degumming is a potential alternative technology for removal of phospholipids from oil. Major benefits of the process are decreasing of wastes, low energy consumption, low chemical consumption and increasing yields when compared to traditional degumming technologies such as water degumming and acid degumming. (Dayton and Galhardo, 2012) According to Sharma et al., (2018) no oil losses occurs because there is no production of soap stocks. However, enzymatic degumming has some drawbacks. It decreases the oxidation stability and increases the concentration of peroxides in crude vegetable oil. Worse oxidation stability may have an impact on the production of renewable fuels. (Sharma et al., 2018)

The principle of the enzymatic degumming is to transform NHPLs to HPLs. The process is efficient for crude oils that contain relatively low levels of phosphatides. For the crude vegetable oils with high content of phosphatides water degumming is preferred before the enzymatic degumming. (Dixit and Kanakraj, 2010)

The enzymes (hydrolytic) break the ester bonds hydrolyzing the phospholipids generating phosphoric compounds and free fatty acids are released without affecting the triglycerides in oil. The method is efficient for the purification of oils especially when the desired total amount of phosphorus in the purified oil is below 10 ppm (Jiang et al., 2015). (Sharma et al., 2018)

6.1.2 Bleaching

Bleaching is the next step after degumming in crude vegetable oil purification process. According to Kuuluvainen et al., (2015) bleaching is an important final step in the processing of vegetable oils before the hydrotreatment step needed in the production of renewable fuels. Bleaching is a physical treatment where still remaining contaminants affecting the quality of oil are removed. Remove compounds are e.g. residuals of non-hydratable phospholipids, nitrogen compounds, traces of metals such as calcium, sodium, iron and magnesium, color matter from the chlorophyll and oil decomposition products such as aldehydes, ketones, polymers, and other non-triglyceride compounds produced during oxidation of oil (Gupta, 2017a; Kruger et al., 2017). All the impurities mentioned can be removed using an adsorbate. Possible adsorbates are for example silica, activated carbon and bleaching clays. Van der Waal’s forces are created between the impurities and the active part of the adsorbate. The impurities accumulate in the adsorbate and a clean oil is obtained as a product. (Gupta, 2017a)

Effectiveness of the bleaching process depends on several factors. The size of the contact area between oil and surface of the adsorbate is an important one. Other factors are temperature of oil and contact time between the surfaces. (Gupta, 2017a)

In the dry bleaching, the oil is treated with adsorbate. Commonly used adsorbates are acid activated or neutral clays. Acid activated clay is the most efficient alternative for the removal of trace metals and color structures. Neutral clays do not remove remaining phospholipids from oil at all. In such cases, water degumming is needed as prewashing followed by vacuum drying before bleaching step. (Gupta, 2017a)

The pretreated oil and the clay are mixed together under vacuum to avoid the oxidation of the oil. Modern plants are all working under vacuum. The oil and adsorbate are kept in good contact from 30 to 45 minutes. Citric acid or phosphoric acid can be added as catalyzing agent improving the removal of trace metals and the total purification efficiency. After the suitable reaction time, the bleached oil is filtered, cooled and stored. (Gupta, 2017a)

Bleaching process can be done also in wet conditions. It is a suitable technology for chemically refined and water degummed oils. Differences between dry and wet bleaching processes are in moisture content. In the dry bleaching, the moisture content of the feed is below 0.1 wt.-% whereas in the wet bleaching process the moisture content can be between 0.4 and 0.5 wt.-%. Thus, the vacuum drying step before the wet bleaching process can be avoided but it must be performed in the case of dry bleaching. (Gupta, 2017a)

6.2 Purification technologies of Crude Tall Oil

Degumming and bleaching technologies which are conventional methods for purification of vegetable oils are not suitable for crude tall oil. According to Čmolík and Pokorny (2000) when degumming and bleaching are performed separately, the degummed oil should have a maximum of 30 ppm of phosphorus for the bleaching step to be efficient. According to the data from Tuomola (2012) phosphorus concentration in CTO is significantly higher than 30 ppm. Thus, highly efficient degumming is needed which is challenging to achieve. Thus, alternative processes are needed for the purification of CTO.

6.2.1 Distillation

When CTO is separated from black liquor it can be used as such or distillated into single fractions based on the volatilities of the compounds present in CTO mixture. The commercial separation process includes three separation stages where five different fractions can be obtained. Before distillation, water and volatile compounds are collected in an evaporator. These volatile products are called tall oil heads (TOH). Heavy part separated in the evaporator is called tall oil pitch (TOP). TOP consists of non-volatile components. After the evaporation, the main product is sent to the first distillation column. Rosin acids are separated from the bottom of the first distillation column. The bottom stream is called tall oil rosins (TOR). Upstream of the column is sent to the second distillation column where the rest of volatile compounds are removed and added to the stream of volatile components from the evaporator (TOH). Remaining compounds are sent forward to the third distillation column where tall oil fatty acids (TOFA) is obtained as an overhead stream and distilled tall oil (DTO) as a bottom stream. (Aro and Fatehi, 2017) Fatty acids and resin acids cannot be separated effectively in one stage. Hence, an intermediate distillation stage is used where DTO is separated. DTO consist of about 30 wt.-% of resin acids, 65 wt.-% of fatty acids and 5 wt.-% of other compounds. Conventional production process of CTO is presented in the Figure 10 and Figure 11 shows the composition of the distillation fractions of CTO. (Wansbrough, 2008)

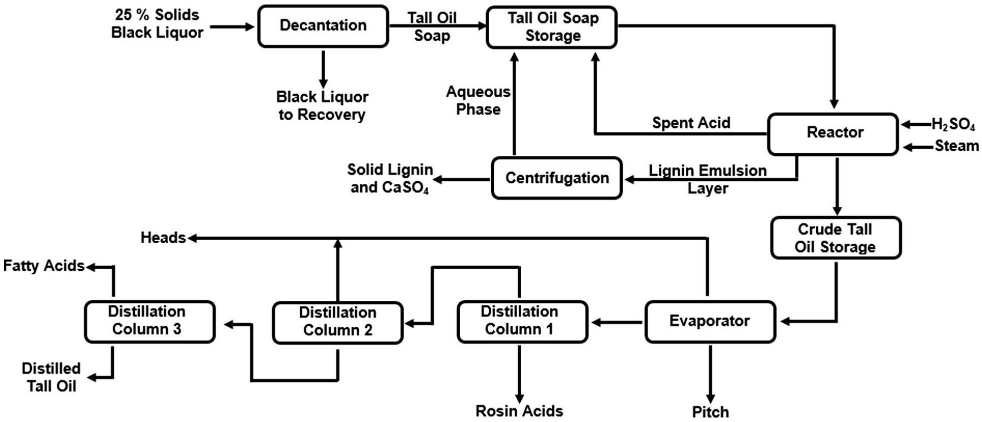


Figure 10 A block flow diagram of commercial tall oil production process which is integrated into the Kraft pulping process. (Aro and Fatehi, 2017)

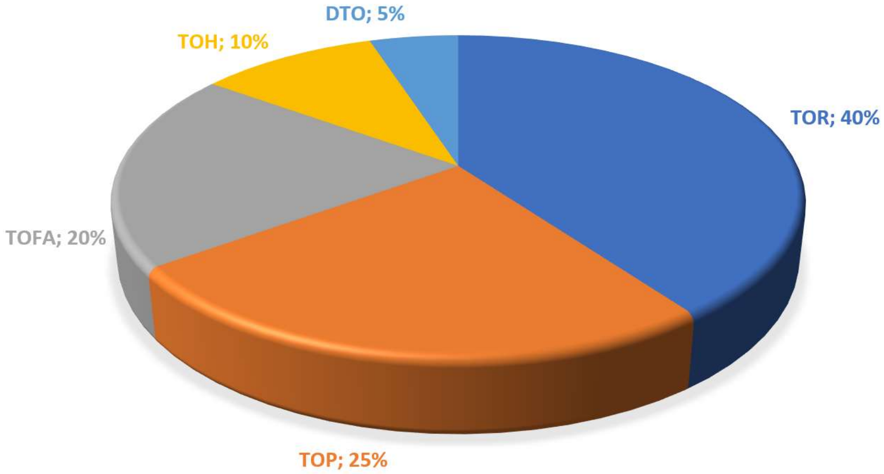


Figure 11 Share of five fractions in CTO distillation process. The fractions are Tall oil resins (TOR), Tall oil pitch (TOP), Tall oil fatty acid (TOFA), Tall oil heads (TOH) and Distillate tall oil (DTO) (Wansbrough, 2008)

According to Nousiainen et al., (2013) (US10240095) in the evaporation process light compounds such as crude sulphate turpentine (CST) and heavy compounds (TOP) are separated and the rest of the CTO is suitable to be used in catalytic hydrotreatment process. Figure 11 shows that suitable raw material for renewable fuel production is about 65% of the total CTO. According to Knuuttila et al., (2015), the conventional purification process is an expensive and inefficient way to produce feedstock for renewable fuel production where high product yield and CTO utilization rate are difficult to achieve because only a part of the total CTO is utilized in the fuel production.

Some patents disclose new ideas regarding the pretreatment of CTO and other renewable feedstocks to improve the removal of impurities before catalytic process e.g. hydrotreatment.

6.2.2 Other purification technologies

Petri and Marker (2006) introduced a process (EP1728844 A1) to produce diesel fuel from renewable feedstocks by hydrogenation and deoxygenation. Their process includes also the pretreatment of the raw materials. They presented three ways to purify feedstock. One pretreatment step is to use ion-exchange resin which is put in contact with the feedstock. The used resin is an acidic ion-exchange resin which is packed in a reactor where oil flows through it. Another technology described to remove contaminants is a mild acid wash where acid, such as sulfuric, nitric or hydrochloric acid is contacted with oil in a reactor either in batch or continuous operation. The third method for removal of metals uses alumina guard beds. These guard beds can contain demetallation catalysts such as nickel or cobalt. (Petri and Marker, 2006)

Perego et al., (2009) patented (EP2084245 B1) the process to produce hydrocarbon fractions from sustanable materials such as tall oil using hydrodeoxygenation (HDO) and hydroisomerization. Before HDO, CTO needs to be purified to remove affecting impurities. According to the patent, not only ion-exchange resins and acid washing are suitable technologies for the removal of alkaline metals and alkaline earth metals but also adsorption on suitable materials can be used. For instance, percolation technologies can be used in a column packed with acid earth or clays such as montmorillonites, bentonites etc. (Perego et al., 2009)

Knuuttila et al., (2015) presented a method (US9024095 B2) for producing fuel components from CTO. The method includes pretreatment followed by HDO. The pre-treatment, purification step, is done by washing the CTO with a liquid followed by a separation step. This step can be done either in batch or continuous mode. After pretreatment, the purified CTO is sent directly to the HDO reactor.

In the washing step, pure water or water with additives such as complexing agent, adsorbent or organic weak acid can be used as a washing liquid. An alternative for complexing agent is for instance ethylenediaminetetraacetic acid (EDTA). In case, a solid adsorbent is used, activated alumina is seemed to be a suitable alternative. When weak organic acid is used as an additive, acetic acid or oxalic acid are good alternatives to be used. Weak organic acids are suitable in the process as they disperse phospholipids in the oil without increasing the amount of inorganic salts in the oil. (Knuuttila et al., 2015)

Separation of the purified CTO from the aqueous solution is done by gravity in a washing vessel or in a single settling tank. Otherwise, separation can be achieved by centrifugation or by a combination of both technologies. (Knuuttila et al., 2015)

7. INTRODUCTION OF THE EXPERIMENTAL PART

In the experimental part the work is focused on the new purification process. Using this process, the target is to investigate and find suitable parameters to achieve high quality of CTO product having minimum amount of impurities. Before reaching the commercial scale, the new process is tested at different scales: batch (100 ml), continuous (200 ml/h), and demo (200 kg/h)

The hydrotreatment catalysts only tolerate ppm levels of impurities (≤ 10 ppm metals, ≤ 10 ppm silicon and ≤ 10 ppm phosphorus). The target is to identify the operation parameters that produce an oil with the desired levels of impurities, also get information about usability and reliability of the pilot plant and how this information correlates to the demo plant.

7.1 Purification method

The new purification process is presented in Figure 12. Clean water and dirty oil are fed counter to an empty reactor. In the reactor, water and oil are mixed and the water-soluble impurities in the oil transfer to the water. Thus, a clean oil stream containing some water and a dirty water stream containing some oil are obtained.

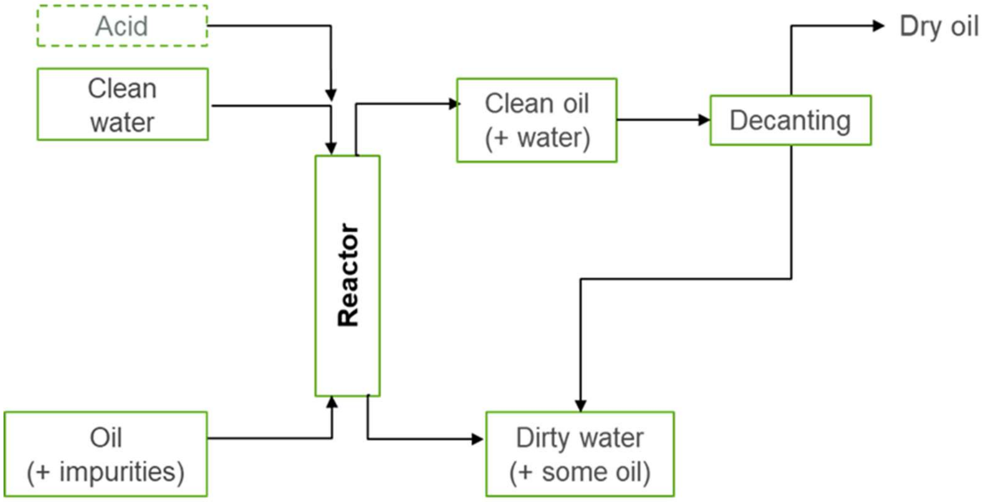


Figure 12 A block diagram of the purification method

The main parameters that can affect the efficiency of the purification are water/oil ratio, temperature, residence time and pH. The presence of acid makes challenging the material selection during the scale up of the process.

The process was tested in batch scale and based on the results obtained, and on the process presented in Figure 12, a continuous reactor setup was built (BFR7). CTO, Brassica carinata and soybean acid oil have been used as a feedstock. Impurity level of feeds have remarkable differences depending on the raw material used.

The success of the purification is evaluated comparing the levels of impurities before and after the process. For this, the metal content of feeds, purified oil and aqueous fraction are measured together with other determinations. Investigated elements are shown in Figure 13.

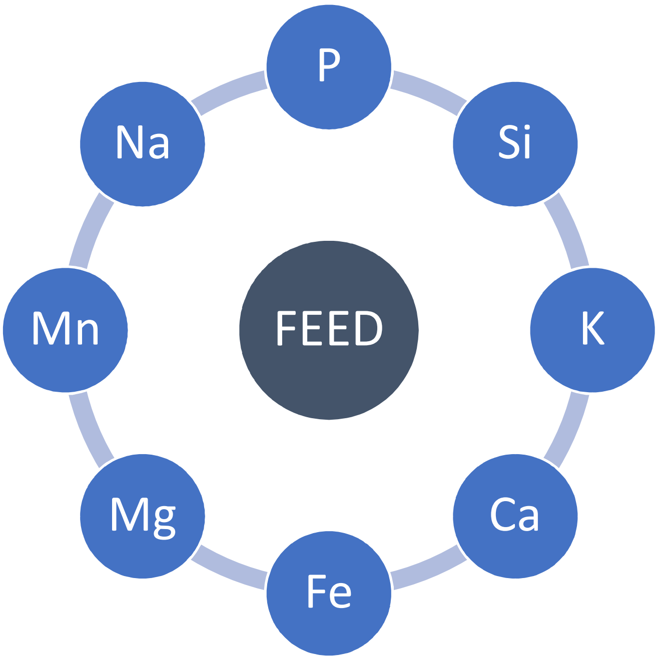


Figure 13 Elements analyzed in feed and product samples

7.2 Laboratory set-ups

Both batch reactor and continuous reactor are used in the experimental part. There are significant differences and limitations between the two set-ups.

7.2.1 Batch reactor

Biofuels reactor 5 (BFR5) is a 100 ml batch reactor. The autoclave reactor is made of acid resistant alloy (Hastelloy C-276) and it can be operated at a maximum temperature of 400 C and a maximum pressure of 300 bar. The feeds are weighted before the tests, the reactor is closed, and the heating and mixing are started. Acid, sulfuric acid was added in different concentration (0.5 to 1.5 wt.-% of total feed).

After the test, the reactor is cooled down to room temperature. The gas sample is collected, then the reactor is opened, and liquid samples are obtained. In the case of these tests, the reactor was flushed with nitrogen to eliminate all traces of oxygen and therefore avoid oxidation side reactions and ensure that the reactants were in the liquid form throughout the test. Then the mixing and the heating to the desired temperature were started. After the reaction time (from 0.5 h to 3 h), the reactor was cooled down, opened and samples were collected. The gas samples contained mainly nitrogen thus, it can be concluded that no cracking or other type of reactions occur during the tests. The reactor was emptied, and the oil and water fractions were separated (gravity and centrifugation) and characterized.

7.2.2 Continuous reactor

Biofuels reactor 7 (BFR7) is a continuous laboratory scale reactor used to test the purification. The reactor is based on the counter-flow of the oil and the water used in the procedure. The temperature in the reaction area of the reactor is around 180 °C. The reaction area which is above the oil/water interface is always filled by oil. Oil is fed into the reactor from the bottom of the reactor and it leaves the reactor from the top of the reactor. Water is fed into the reactor at the top of the reactor by help of sinter and mixing pump. Sinter drips the water into the fine droplets. Droplets go down through the oil filled reactor and ends up to the oil/water interface.

The measurement of the interface between oil and water is carried out by measuring hydrostatic pressure difference. Pressures are compared between water/oil tube and a tube filled with water. Heights for both tubes is 50 cm. The lower water/oil interface exists the higher pressure-difference is obtained.

The measurement of the interface between water and oil determines the water outflow. Water flows off the reactor using cascade control system either from the middle of the pressure difference-water/oil tube or from the top of the water tube. Water can be flown out also from the both ways at the same time. Oil flows of the reactor from the top of the reactor according to back-pressure controller.

Both treated oil and washing water are fed into the product vessels where they can be emptied manually. Samples were taken from both containers at known intervals of time and set for characterization.

7.3 Analytical methods for samples

All the samples obtained from the BFR5, BFR7 and demo plants are analyzed at NERC. Used sample handling methods concerning to this work are ICP-OES for metal determinations and Karl Fisher Method (KF) for moisture detection i.e. determination of water content of samples. Besides total organic carbon (TOC), chemical oxygen demand (COD), biochemical oxygen demand (BOD) and total nitrogen (TN) are determined for samples but they are outside of the scope of this Master's Thesis.

7.3.1 Thermo iCAP ICP-OES

ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometry) is used in this work to determine metal elements and concentrations of them in CTO and other oils which are soluble in xylene such as soybean acid oil. The determination process is based on the standard ASTM D5185:13e1.

The principle of the ICP-OES technology is that every element in the sample emit light in the characteristic wavelengths which are known for each single element. In the process, fine sample is sprayed into plasma torch. Temperature of the plasma ranges between 6000 and 10000 K. Thus, a solvent in the sample evaporates and elements atomize and partially ionized. Because of the high temperature, atoms and ions get excited and emit electromagnetic radiation at wavelengths characteristic for each element. The radiation is led to semiconductor detectors where the intensity of radiation is measured. The intensity of the emission determines the concentration of the element in the sample. (UPM-Kymmene Oyj, 2019c)

In Table 12 is presented quantification limits for elements. In the Table are shown only the elements which are remarkable regarding this work.

Table 12 Quantification limits (mg/kg) for elemental analysis by ICP-OES

Element	**Quantification limit, mg/kg**
Calcium, Ca	0.1
Iron, Fe	0.1
Potassium, K	2
Magnesium, Mg	0.01
Manganese, Mn	0.01
Sodium, Na	1
Phosphorus, P	1
Silicon, Si	1

7.3.2 Karl Fisher titration (KFT)

Karl Fisher titration (KFT) is a common analytical method for the determination of water content in wide range of liquid materials. In this work, KFT is used to determine water content in CTO. According to Bernreuther (2007), it is very effective method especially for samples with low amount of water. The principle of the KF titration is based on the Bunsen Reaction between iodine and sulfur dioxide in an aqueous condition. (EMD Chemicals Inc., 2019) The measurements are performed based on the PCTM 4C standard where determinations limits are 0.5-10 %

In Equations (6) and (7) are presented the two reactions that happen in the KFT.

$$\mathrm{ROH} + \mathrm{SO_2} + \mathrm{R'N} \rightarrow [\mathrm{R'NH}]\mathrm{SO_3R} \qquad \text{(Eq. 6)}$$

$$[\mathrm{R'NH}]\mathrm{SO_3R} + \mathrm{H_2O} + \mathrm{I_2} + 2\mathrm{R'N} \rightarrow 2[\mathrm{R'NH}]\mathrm{I} + [\mathrm{R'NH}]\mathrm{SO_4R} \qquad \text{(Eq. 7)}$$

where		
	ROH	alcohol
	SO_2	sulfur dioxide
	R’N	Base
	$[R'NH]SO_3R$	alkylsulfite salt
	H_2O	Water
	I_2	Iodine
	2[R'NH]I	Hydroiodic acid salt
	$[R'NH]SO_4R$	Alkylsulfate salt

In the Equation (6), alcohol reacts with sulfur dioxide and base to form intermedious product called alkylsulfite salt. According the Equation (7), the alkylsulfite salt is then oxidized to alkylsulfate salt by iodine. The reaction equation shows that the oxidation reaction consumes water. (EMD Chemicals Inc., 2019)

As the Equation (7) shows water and iodine are consumed in the same ratio in the KFT. When all water is consumed in the process, the amount of surplus iodine is detected by the titrator's indicator electrode. The end-point of the titration is determined by the signal of the indicator electrode. The amount of water in the sample can be then calculated by using the concentration of iodine in the KFT reagent and the amount of KFT reagent consumed in the titration process. (EMD Chemicals Inc., 2019)

7.4 MODDE Pro software in data analysis

Analyzing of the experimental data is made by MODDE Pro. MODDE Pro is a data analytics tool for Designing of Experiments (DOE). In the analysis, Partial least squares regression (PLS) model is used. (Umetrics, 2019) PLS is an enlargement from the multiple linear regression (MLR) model. The function of the linear model is to describe the relationship between dependent variables (response) Y and predicted variables X's regarding the simplest Equation (8) below: (TIBCO Software Inc, 2019)

$$Y = b_0 + b_1X_1 + b_2X_2 + \cdots + b_nX_n \qquad \text{(Eq. 8)}$$

Where	b0	Regression coefficient for the intercept
	bi	Regression coefficients (1,2..n) from the data

Figure 14 presents an example of the summary of fit in the MODDE Pro analysis tool. It consists of four bars: R2, Q2, model validity and model reproducibility.

- *R2* is the percent of the variation of the response explained by the model. It is a measure of fit telling how well the model fits the data.
- *Q2* is the percent of the variation of the response predicted by the model according to cross validation. Q2 shows that how well the model predicts new data. Poor Q2 number exists if model reproducibility and/or model validity is poor.

- *Model validity* is a test of diverse model problems. A value less than 0.25 indicates statistically significant model problems and lack of fit. Model validity might be also low in good models (Q2 is high) due to sensitivity in the test or good replicates.
- *Model reproducibility* is the variation of the response under the same conditions, often at the center points, compared to the total variation of the response. When the model reproducibility is 1.0, the pure error is 0. It means that under the same conditions, the values of the response are identical. Whereas, the model reproducibility is 0, the pure error equals the total variation of the response. If the model reproducibility is below 0.5, pure error occurs and the validity of the model cannot be assessed. This result in low R2 and Q2 values.

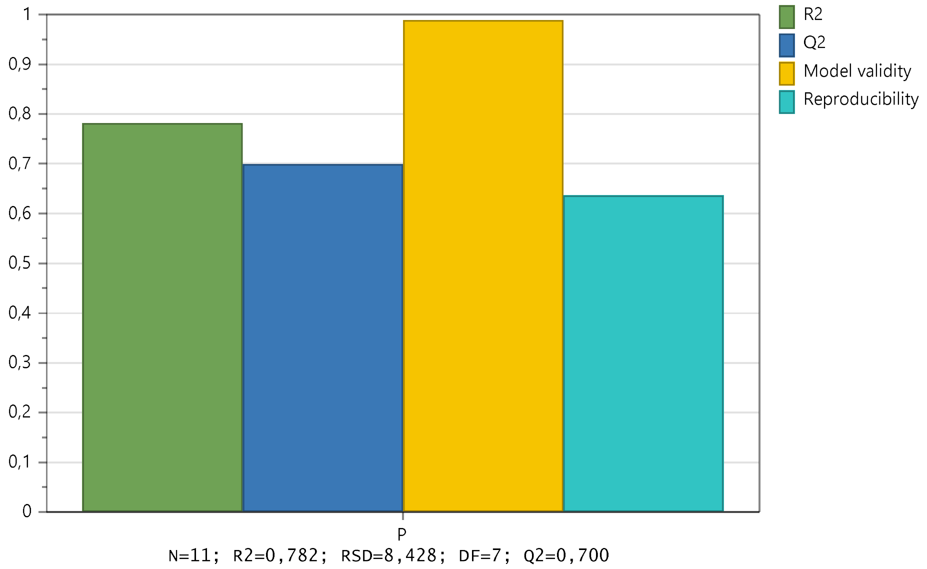


Figure 14 An example of the summary of fit

7.5 Measurement uncertainty

There are different sources of uncertainty in the operation of laboratory reactors. One measurement uncertainty is caused by the operators and their different way of working. This influences the preparation of reaction mixtures, heating times of reactors, calibration solutions and samples.

In the measurement of the metal content of feeds and samples, the main source of uncertainty for these samples is the sample itself as they are mixtures of several chemical compounds making the characterization by ICP-OES challenging. Furthermore, the same analytical method was used for CTO, acid oils and vegetable oils introducing even more uncertainty to the determinations, so the matrix effect was not taken into consideration.

All the samples were analyzed after purification processes however, sometimes they could not be analyzed immediately, and samples were stored which increase the possibility of layering of the sample. This influences the homogeneity of the samples. The age of the sample can have a significant vary which may have an impact on the structure of the sample. When samples are analyzed by ICP-OES, they should be fully homogenized to ensure accurate and reliable results.

Instrumental errors are also possible if, for example, calibration of the ICP-OES instrument is not done before the measurements or the calibration is no longer valid. Furthermore, low concentrations of metals can also be challenging or difficult to measure.

II EXPERIMENTAL PART

In the experimental part, analysis of the data from BFR5 and BFR7 is done by using MODDE Pro data analytics tool. Experimental planning is not done due to the already available data. Different feeds are used where concentrations of impurities vary significantly. All feeds have their own level of impurities. Depending on the concentration of elements in feeds and products, remarkable responses are chosen. If concentration of some impurity element is low (<10 ppm) in oil product, it is ignored in the data analysis to improve the model and analysis results. If concentration of an element is below detection limit, the concentration value 0 ppm is used in the calculations and analysis.

If low concentration of alkaline metals is remaining in oil product after purification, some of the analysis are done by groping alkaline metals into one group where total concentration (ppm) of alkaline metals is used in analysis.

After analysis, conclusion of the data analysis results are shown and discussed. Suitable process conditions are described for every raw material.

8. RESULTS

In this Chapter, results from the MODDE analysis are presented and discussed. Both BFR5 and BFR7 feeds are used and products are analyzed separately. Finally, conclusion of the BFR5 and BFR7 analysis are presented.

8.1 Analysis of BFR5 data

BFR5 data analysis includes a crude tall oil feed and a soybean acid oil feed. Each analysis includes different amounts of data points depending on the number of batches used. In every batch, the reaction time is 1 hour.

8.1.1 Feed: Crude Tall Oil

There are two CTO feeds available for BFR5. It was noticed that feed concentrations for phosphorus and silicon are close to each other, so data from two feeds can be combined. It can be noticed from the purification results presented in Appendix III, Table 31 and Table 32 that sodium, phosphorus and silicon are the only critical impurities while the concentration of other elements is negligible. As sodium is removed to below detection limits at the conditions tested, this element is not considered when analyzing the feeds. Thus, only the concentrations of phosphorus and silicon are considered in the data analysis. Table 13 presents the average concentration of phosphorus and silicon in the analysis feed.

Table 13 The average concentration of phosphorus and silicon in two CTO feeds

Silicon, Si	ppm	22.5
Phosphorus, P	ppm	23.8

Table 14 and Table 15 present the worksheets for both silicon and phosphorus analysis. Temperature, water to oil (w/o) ratio and acid content are factors in the analysis and concentration of silicon and phosphorus are the responses. The data analysis for silicon and phosphorus is done separately.

From Table 14 can be noticed that experiment number 2 (N2) is excluded from the analysis of silicon concentration. The reason for excluding can be found from Appendix V Figure 33 where the data fitting for the point is poor and it decreases the R2 and Q2 values in the model. The N2 can be also compared for example with N1 and N3. Acid content for every point is zero and w/o ratio ranging between 0.5 and 2.0. The silicon concentration for N2 is significantly bigger even though it should be probably between the concentration values of N1 and N3.

Table 14 The worksheet of the analysis of CTO purification results in BFR5. Temperature [°C], W/O ratio [-] and acid content [%] are factors and the concentration of silicon [ppm] is the response. Detection limit for silicon is 1 ppm.

Exp. No	**Exp. Name**	**Run Order**	**Temperature [°C]**	**W/O ratio [-]**	**Acid content [wt.-%]**	**Silicon, Si [ppm]**
1	N1	6	180	2	0	2.36
~~2~~	~~N2~~	~~4~~	~~180~~	~~1~~	~~0~~	~~19.3~~
3	N3	7	180	0.5	0	9.35
4	N4	5	180	1	0.5	0
5	N5	2	180	1	1	0
6	N6	9	180	1	1.5	0
7	N7	1	130	1	0.5	13.8
8	N8	8	140	1	0.5	13.3
9	N9	10	150	1	0.5	12.4
10	N10	3	130	1	1	13.4

All data points fitted the model for phosphorous well and there was no need to exclude any data points. Table 15 shows that the concentration of phosphorus is under 10 ppm in every data point. However, the data analysis shows trends on how the concentration changes in different operation conditions.

Table 15 The worksheet of the analysis of CTO purification results in BFR5. Temperature [°C], W/O ratio [-] and acid content [%] are factors and the concentration of phosphorus [ppm] is the response. Detection limit for phosphorus is 1 ppm.

Exp. No	**Exp. Name**	**Run Order**	**Temperature [°C]**	**W/O ratio [-]**	**Acid content [%]**	**Phosphorus, P [ppm]**
1	N1	4	180	2	0	0
2	N2	5	180	1	0	1.53
3	N3	8	180	0.5	0	0
4	N4	6	180	1	0.5	0
5	N5	2	180	1	1	0
6	N6	9	180	1	1.5	0
7	N7	3	130	1	0.5	7.75
8	N8	7	140	1	0.5	4.55
9	N9	1	150	1	0.5	2.19
10	N10	10	130	1	1	8.56

Figure 15 presents the model fitting and measured concentrations of silicon. Similarly, Figure 16 shows the fitting for observed and predicted concentrations of phosphorus. It can be seen in Figure 15 that the fitting of the model is good after the data point excluded above. R2 value is 0.93 and Q2 value is 0.83. In raw data, R2 value is 0.67 and Q2 value is 0.30.

Figure 16 shows that based on the values of R2 and Q2, it can be concluded that the fitting of the data is good having R2 value 0.93 and Q2 value 0.81.

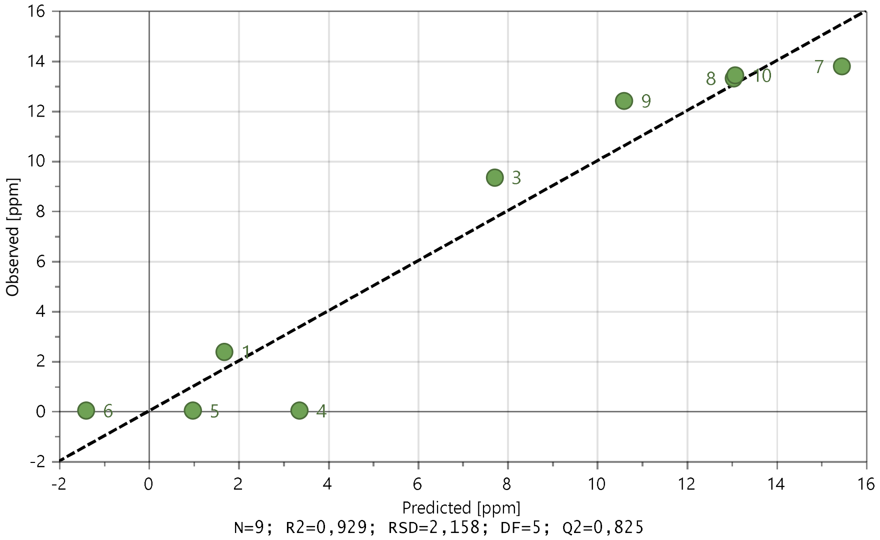


Figure 15 Observed and predicted concentrations of silicon [ppm] in CTO feed, BFR5

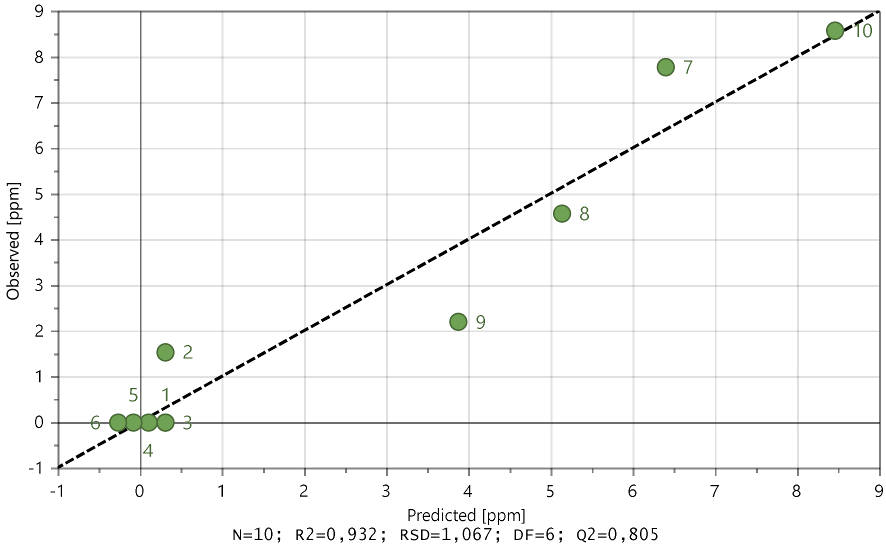


Figure 16 Observed and predicted concentrations of phosphorus [ppm] in CTO feed, BFR5

Figure 17 presents the concentration of silicon as a function of temperature, w/o ratio and acid content. Experiments with three different acid concentrations were performed to determine the effect of acid on the removal of silicon. It can be seen from the Figure 17 that increasing the temperature decreases the concentration of silicon in CTO product. Also, increase of w/o ratio decreases the concentration of silicon in CTO product. However, the impact of temperature seems to be bigger on silicon concentration than the impact of w/o ratio. It can also be seen that acid content has a distinct impact on the silicon concentration of the product. Increasing the acid content of process, lower temperatures w/o ratio can be used to obtain desired silicon concentration in the product.

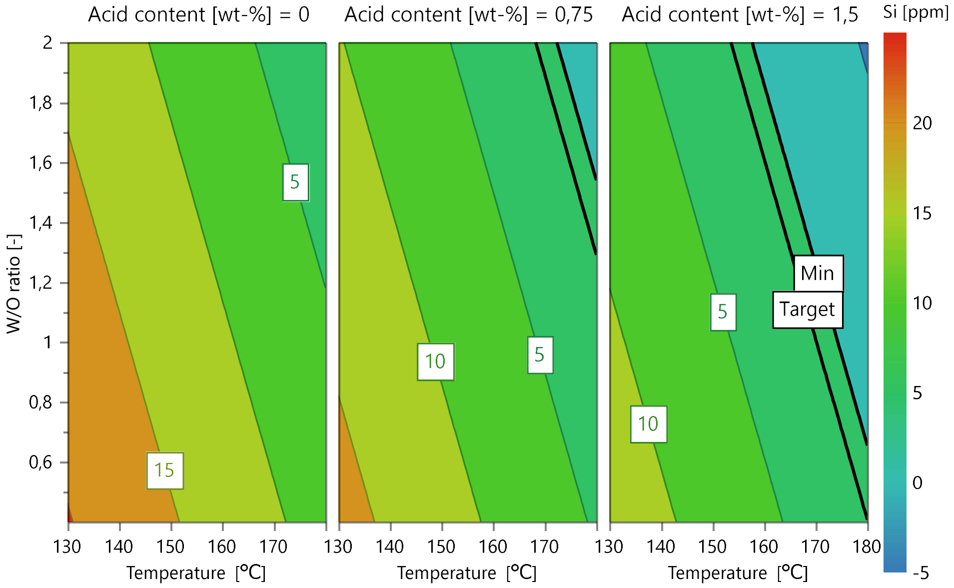


Figure 17 The concentration of silicon [ppm] as a function of temperature [°C] and w/o ratio [-]. Acid content [wt.-%] is kept in three values: 0, 0.75 and 1.5 wt.-%. R2 = 0.93, Q2 = 0.81. Concentration in the black target line is 1ppm.

Figure 18 presents the concentration of silicon as a function of temperature, w/o ratio and acid content. Figure 18 shows that temperature is the most critical parameter affecting the removal of phosphorus. It describes also that w/o ratio and acid content have no impact on phosphorus concentration in the product. The results are not reliable because it is expected that both w/o ratio and acid content affect the concentration of phosphorus.

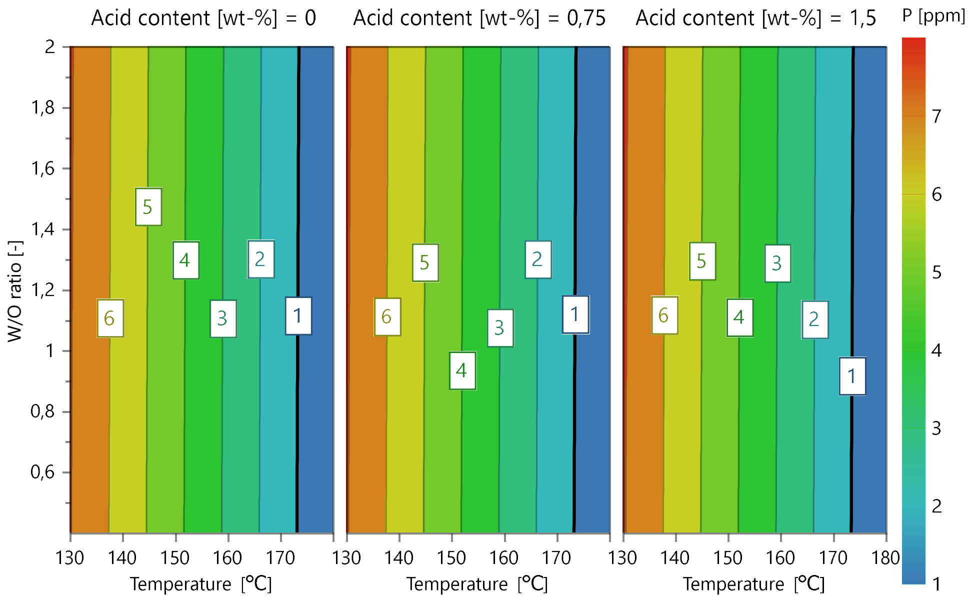


Figure 18 The concentration of phosphorus [ppm] as a function of temperature [°C] and w/o ratio [-]. Acid content [wt.-%] is kept in three values: 0, 0.75 and 1.5 wt.-%. R2 = 0.93, Q2 = 0.83

8.1.2 Feed: Soybean acid oil

Table 16 presents the concentration of impurities in the acid oil feed in BFR5. Table 16 shows that the concentrations of calcium, iron, potassium, magnesium and manganese are already in the feed at the desired value (<10 ppm). Thus, those can be excluded from the data analysis. The feed concentration of sodium, phosphorus and silicon are over 10 ppm and the concentration of phosphorus is over 400 ppm.

Table 16 The concentration [ppm] of impurities in the soybean acid oil feed

Calcium, Ca, ICAP	ppm	2.0
Iron, Fe, ICAP	ppm	2.5
Potassium, K, ICAP	ppm	3.6
Magnesium, Mg, ICAP	ppm	1.0
Manganese, Mn, ICAP	ppm	0.1
Sodium, Na, ICAP	ppm	13
Phosphor, P, ICAP	ppm	452
Silicon, Si, ICAP	ppm	11.5

In case of this feed, six batches are performed separately in different conditions. W/o ratio is kept constant 1:1 in every batch. Three different temperatures are used from 130 to 150 °C and acid content varying between 0.5 and 1 wt.-%. Table 17 presents the worksheet of the data analysis of acid oil purification results in BFR5. Data of the purification results are presented in the Appendix III Table 33. According to the data of the purification results, all the other elements expect phosphorus are obtained in low concentrations in every test performed. Concentration of phosphorus in the product oil is remarkable and ranging between 26.6 and 103 ppm. The lowest concentration value was obtained in the highest temperature and acid addition tested. Also, the concentrations of sodium and silicon were both < 1 ppm for every product obtained. Therefore, in the data analysis, only phosphorus is used. The analysis is performed by using temperature and acid content as factors and concentration of phosphorus as a response.

Table 17 The worksheet of the data analysis of soybean acid oil purification results in BFR5. Temperature [°C] and acid content [wt.-%] are factors and the concentration of phosphorus [ppm] is the response. W/O ratio [-] is kept constant. Detection limit for phosphorus is 1 ppm

Exp. No	**Exp. Name**	**Run Order**	**Temperature [°C]**	**W/O ratio [-]**	**Acid content [wt.-%]**	**Phosphorus, P [ppm]**
1	N1	5	130	1	0.5	103
2	N2	2	140	1	0.5	80
3	N3	4	150	1	0.5	52.9
4	N4	6	130	1	1	96.2
5	N5	3	140	1	1	75.3
6	N6	1	150	1	1	26.6

Figure 19 presents linear concentrations between the experimental data and model prediction. It can be seen from Figure 19 that both R2 and Q2 are high in the analysis. R2 value is 0.94 and Q2 value is 0.81. There are no outliers on the data so there was no need to exclude any data point.

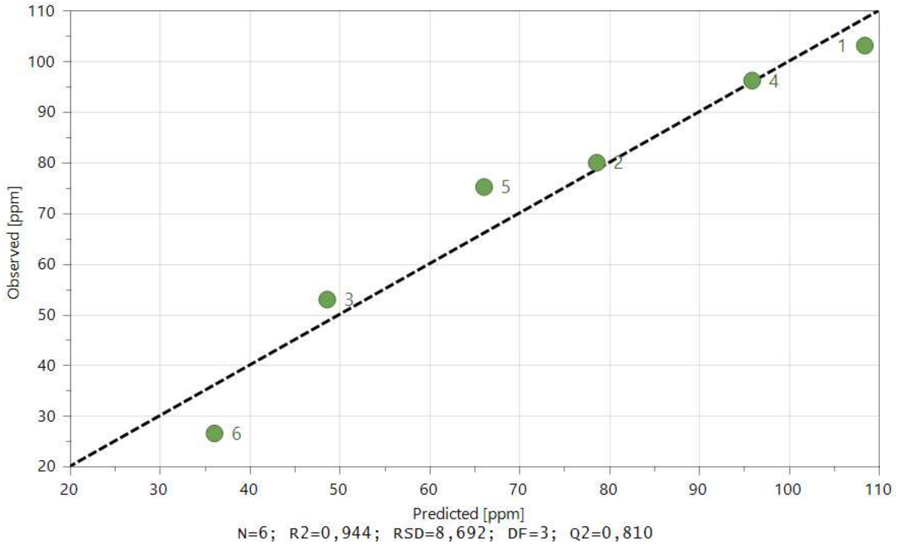


Figure 19 Observed and predicted concentrations of phosphorus [ppm] in Soybean acid oil feed, BFR5

Figure 20 presents the concentration of phosphorus as a function of temperature and acid content. Figure 20 shows that when the process temperature is < 160 °C, low concentration of phosphorus cannot be obtained without significantly increasing the acid content. The black line in Figure 20 is the target concentration for the phosphorus (10 ppm). It can be obtained already in 160 °C but over than 0.8 wt.-% acid content is needed. According the linear estimation model, it could be possible to obtain < 10 ppm of phosphorus in low acid content if temperatures around 170 °C are used. However, it is just a prediction because the experimental data for this feed does not include experimental tests where the acid addition was less than 0.5 wt.-%. Also, as acid improves the solubility of metals in water, the concentrations of sodium and silicon are expected to remarkably change even when very small amount of acid is added to the reaction mixture.

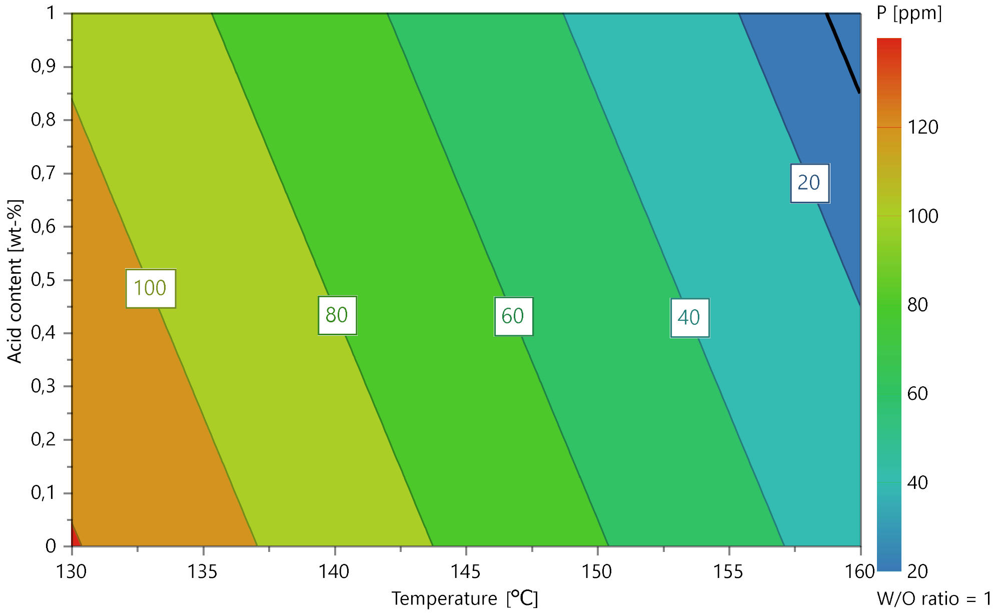


Figure 20 The concentration of phosphorus [ppm] as a function of temperature [°C] and acid content [wt.-%]. W/o ratio [-] is kept constant 1:1. R2 = 0.94, Q2 = 0.81. Concentration in the black line is 10 ppm.

8.2 Analysis of BFR7 data

BFR7 data includes different feeds. Used feeds are Crude tall oil, Brassica carinata and Soybean acid oil. All the feeds are analyzed separately in their own Chapters.

8.2.1 Feed: Crude Tall Oil

The concentration of impurities in the CTO feed used in the purification process by BFR7 is presented in Table 18.

Table 18 Concentration of impurities in the CTO feed

Calcium, Ca, ICAP	ppm	0.841
Iron, Fe, ICAP	ppm	1.3
Potassium, K, ICAP	ppm	5.7
Magnesium, Mg, ICAP	ppm	0.19
Manganese, Mn, ICAP	ppm	0.23
Sodium, Na, ICAP	ppm	47
Phosphor, P, ICAP	ppm	22.9
Silicon, Si, ICAP	ppm	17.4

The purification results can be found from the Appendix IV Table 34. According to the feed concentrations and purification results, the concentration of other elements except silicon are in desired values after every experiment performed. Therefore, only the concentration of silicon is taking part in the data analysis.

The worksheet of the analysis is presented in Table 19. Temperature and w/o ratio are working as factors and the concentration of silicon is the response. It is suitable to exclude one experiment from the total worksheet. N1 need to be excluded because the concentration of silicon is not logical with N2 and N3. Silicon concentrations in N1 should be probably near the N2 and N3 concentrations and between them.

Table 19 The worksheet of the analysis where temperature [°C] and w/o ratio [-] are factors and the concentration of silicon [ppm] is the response. Detection limit for silicon is 1 ppm

Exp. No	**Exp. Name**	**Run Order**	**Temperature [°C]**	**W/O ratio [-]**	**Silicon, Si [ppm]**
~~1~~	~~N1~~	~~8~~	~~171~~	~~0.29~~	~~7.99~~
2	N2	9	170	0.28	4.95
3	N3	10	172	0.28	4.08
4	N4	4	170	0.48	6.51
5	N5	11	171	0.48	6.09
6	N6	7	171	0.48	8.97
7	N7	6	171	0.48	8.63
8	N8	1	171	0.67	10.1
9	N9	2	171	0.66	9.82
10	N10	3	171	0.66	9.59
11	N11	5	171	0.66	9.48

Figure 21 presents the linearization of the observed and predicted silicon concentrations. R2 for the model is 0.84 and Q2 is 0.56. Figure 34 shows in the Appendix V the raw data before any excludes. In the raw data R2 value is 0.67 and Q2 value is 0.22. The critical improvement can be then obtained when only one data point is excluded.

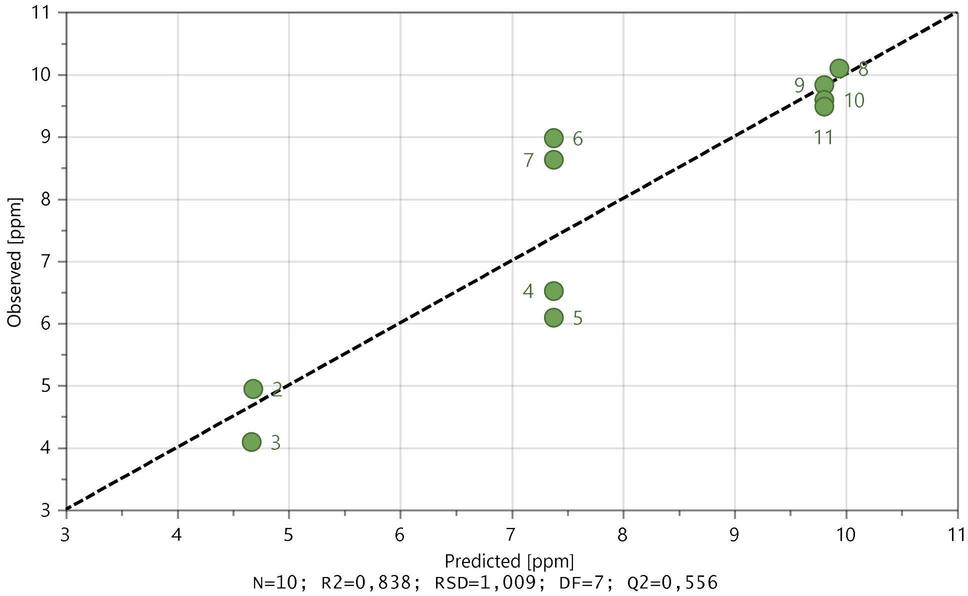


Figure 21 Observed and predicted concentrations of silicon [ppm] in CTO feed, BFR7

Figure 22 presents the concentration of silicon as a function of temperature and w/o ratio. Figure 22 shows that less than 5 ppm concentrations are obtained already at the lowest temperatures and w/o ratios tested. When the w/o ratio decreases, the concentration of silicon decreases. The raw data of the analysis is problematic. Clear differences in the product were obtained for small changes in temperature e.g. 170 and 172 °C, thus making temperature a critical parameter. To create a valid and more accurate model, a wider temperature range should be used.

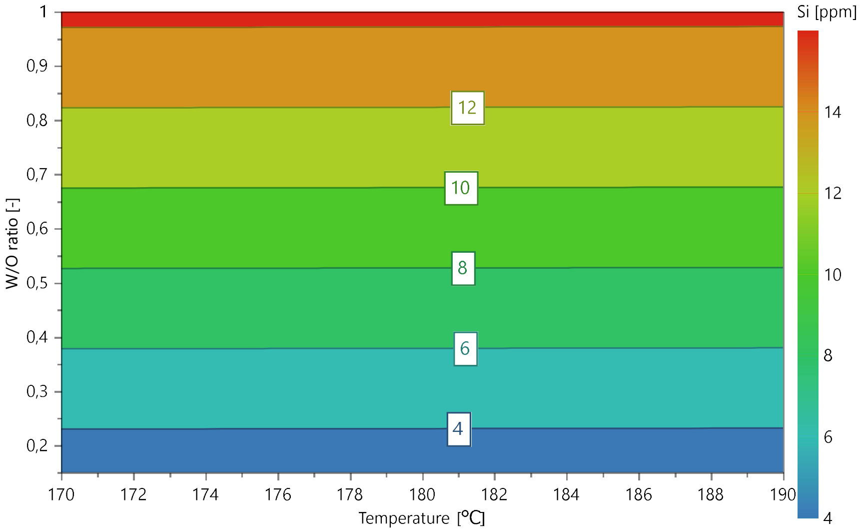


Figure 22 The concentration of silicon [ppm] as a function of temperature [°C] and w/o ratio [-]. R2 = 0.84, Q2 = 0.56

To better study the impact of temperature and w/o ratio on the concentration of silicon, another CTO feed was used. Table 20 presents the concentration of impurities in the CTO feed.

Table 20 Concentration of impurities in the CTO feed

Calcium, Ca, ICAP	ppm	<0.1
Iron, Fe, ICAP	ppm	1.3
Potassium, K, ICAP	ppm	<2
Magnesium, Mg, ICAP	ppm	0.302
Manganese, Mn, ICAP	ppm	<0.01
Sodium, Na, ICAP	ppm	65
Phosphor, P, ICAP	ppm	50.1
Silicon, Si, ICAP	ppm	30.9

According to the purification results in the Appendix IV Table 35, only concentration of silicon is bigger than desired concentration value in the purification product. Thus, only concentration of silicon is included in the analysis.

Table 21 shows the worksheet of the analysis where temperature and w/o ratio are factors and concentration of silicon is the response. Raw data fitting is found in Appendix V Figure 35. It shows that data fitting is poor without excluding data points. R2 value is 0.13 and Q2 value is 0.07. To improve the model, N4 and N5 are excluded from the analysis. N5 is excluded because high concentration difference compared to N6-N8. N4 is excluded because it highly outliner in the data fitting.

Table 21 The worksheet of the analysis where temperature [°C] and w/o ratio [-] are factors and concentration of silicon [ppm] is the response. Detection limit for silicon is 1 ppm

Exp. No	**Exp. Name**	**Run Order**	**Temperature [°C]**	**W/O ratio [-]**	**Silicon, Si [ppm]**
1	N1	11	175	1.02	19.9
2	N2	6	180	0.23	28.2
3	N3	4	180	0.46	27.7
~~4~~	~~N4~~	~~3~~	~~180~~	~~0.14~~	~~0~~
~~5~~	~~N5~~	~~5~~	~~182~~	~~0.21~~	~~7.43~~
6	N6	2	180	0.22	16
7	N7	1	182	0.2	14.8
8	N8	7	183	0.2	12.7
9	N9	9	183	0.15	5
10	N10	10	183	0.15	1.43
11	N11	8	183	0.09	5.08

Figure 23 presents the data fitting where observed and predicted concentrations are determined for silicon. R2 value is 0.84 and Q2 value is 0.66.

The concentration of silicon as a function of temperature and w/o ratio is presented in Figure 24. Figure 24 shows that increasing the process temperature decreases the amount of silicon in the product oil. Also, decreasing the w/o ratio (increasing the oil content), decreases the concentration of silicon in the oil product.

Both CTO feeds in BFR7 showed better purification efficiencies at smaller w/o ratio. According to Lenntech (2019a), water solubility of silicon and silicon compounds are low. Some compounds are totally insoluble with water. Thus, it is expected that w/o ratio has not significant effect on the removal of silicon.

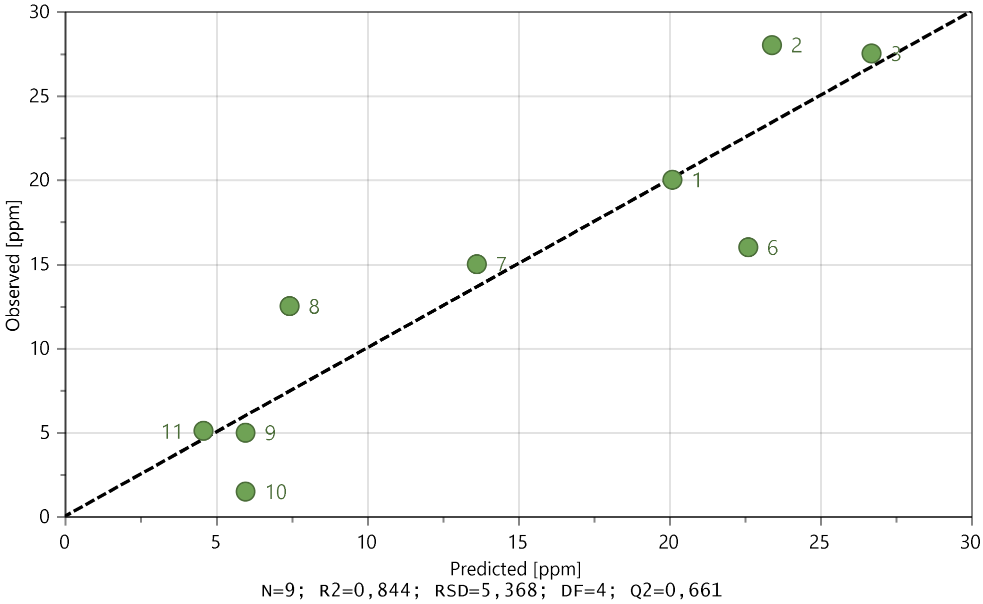


Figure 23 Observed and predicted concentrations of silicon [ppm] in CTO feed, BFR7

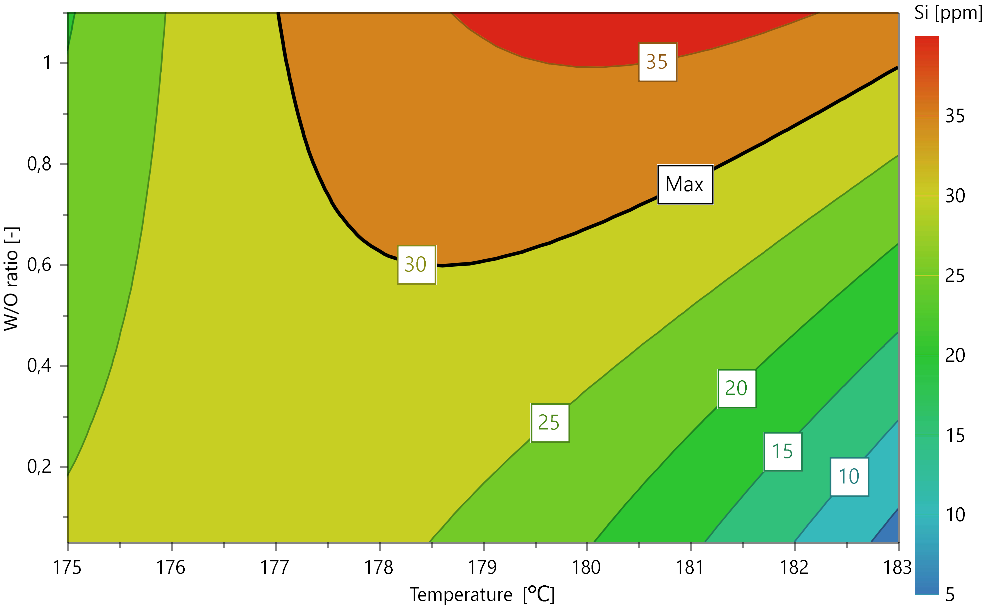


Figure 24 The concentration of silicon [ppm] as a function of temperature [°C] and w/o ratio [-]. R2 = 0.84, Q2 = 0.66

8.2.2 Feed: Brassica carinata

Table 22 presents the concentration of impurities in the feed of BC vegetable oil. It can be seen that the concentrations of calcium, magnesium and phosphorus are higher than desired values and therefore, the removal of these compounds is needed before the further processing of the oil.

Table 22 Concentration [ppm] of impurities in the feed

Calcium, Ca, ICAP	ppm	133
Iron, Fe, ICAP	ppm	1.6
Potassium, K, ICAP	ppm	<2
Magnesium, Mg, ICAP	ppm	20.1
Manganese, Mn, ICAP	ppm	0.79
Sodium, Na, ICAP	ppm	<1
Phosphor, P, ICAP	ppm	117
Silicon, Si, ICAP	ppm	<1

Table 23 and Table 24 present the worksheets of the data analysis of BC purification results from BFR7. Data of the purification results are shown in Appendix IV Table 36. According to the results, all the other elements except calcium and phosphorus were removed in all the tests performed and concentrations below the desired values were obtained. Therefore, only calcium and phosphorus were used in the analysis.

Table 23 The worksheet of the analysis where temperature [°C], w/o ratio [-] and acid content [wt.-%] are factors and the concentration of phosphorus [ppm] is the response. Detection limit for phosphorus is 1 ppm

Exp. No	**Exp. Name**	**Run Order**	**Temperature [°C]**	**W/O ratio [-]**	**Acid content [wt.-%]**	**Phosphorus, P [ppm]**
1	N1	3	176	0.8	0	15.8
2	N2	12	185	0.82	0	14.9
3	N3	6	187	0.8	0	11.4
4	N4	5	182	0.77	0	11.9
5	N5	11	183	0.77	0	18.3
6	N6	7	181	0.4	0	14.4
7	N7	1	182	0.42	0	17.8
8	N8	4	179	0.78	0.005	16.8
9	N9	8	179	0.76	0.005	12.7
10	N10	10	178	0.77	0.05	3.47
11	N11	2	178	0.76	0.05	0
12	N12	9	177	0.76	0.05	1.06
13	N13	13	150	0.8	0.005	22.1
14	N14	14	150	0.8	0.005	20.0

Table 24 The worksheet of the analysis where temperature [°C], w/o ratio [-] and acid content [wt.-%] are factors and the concentration of calcium [ppm] is the response. Detection limit for calcium is 0.1 ppm

Exp. No	Exp. Name	Run Order	Temperature [°C]	W/O ratio [-]	Acid content [wt.-%]	Calcium, Ca [ppm]
1	N1	3	176	0.8	0	23.9
2	N2	12	185	0.82	0	24.8
3	N3	6	187	0.8	0	18.8
4	N4	5	182	0.77	0	18.7
5	N5	11	183	0.77	0	28.2
6	N6	7	181	0.4	0	23.8
7	N7	1	182	0.42	0	28.5
8	N8	4	179	0.78	0.005	25.9
9	N9	8	179	0.76	0.005	20
10	N10	10	178	0.77	0.05	4.93
11	N11	2	178	0.76	0.05	1.75
12	N12	9	177	0.76	0.05	1.77
13	N13	13	150	0.8	0.005	29.6
14	N14	14	150	0.8	0.005	28.8

Figure 25 shows the model fitting for phosphorus concentration where observed and predicted concentrations are showed. It can be noticed that R2 value for the model is 0.91 and Q2 value is 0.83 without any data point excludes. Model fits well without the need to exclude data points.

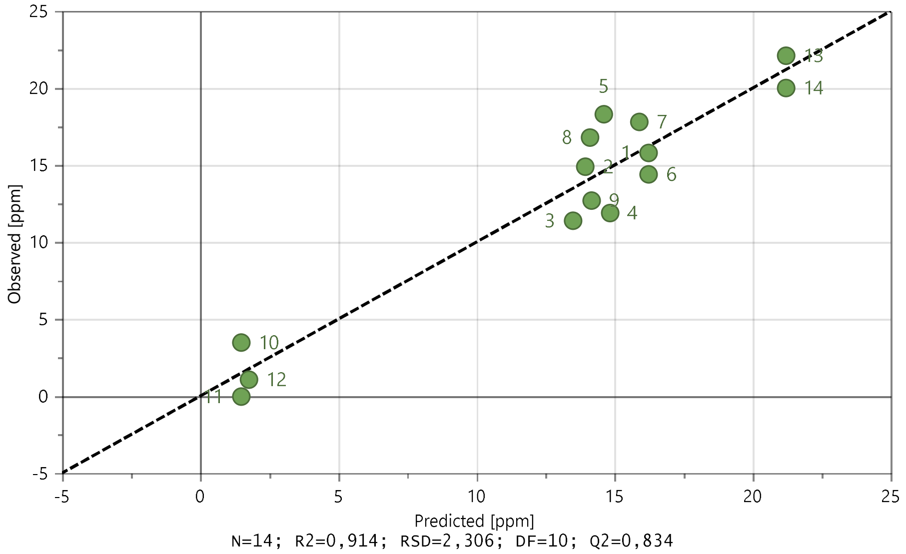


Figure 25 Observed and predicted concentrations of phosphorus [ppm] in BC feed, BFR7

Figure 26 presents the model fitting for calcium concentration where observed and predicted concentrations are compared and linearized. Such as in Figure 25, model is fitted well. R2 value is 0.92 and Q2 value is 0.86.

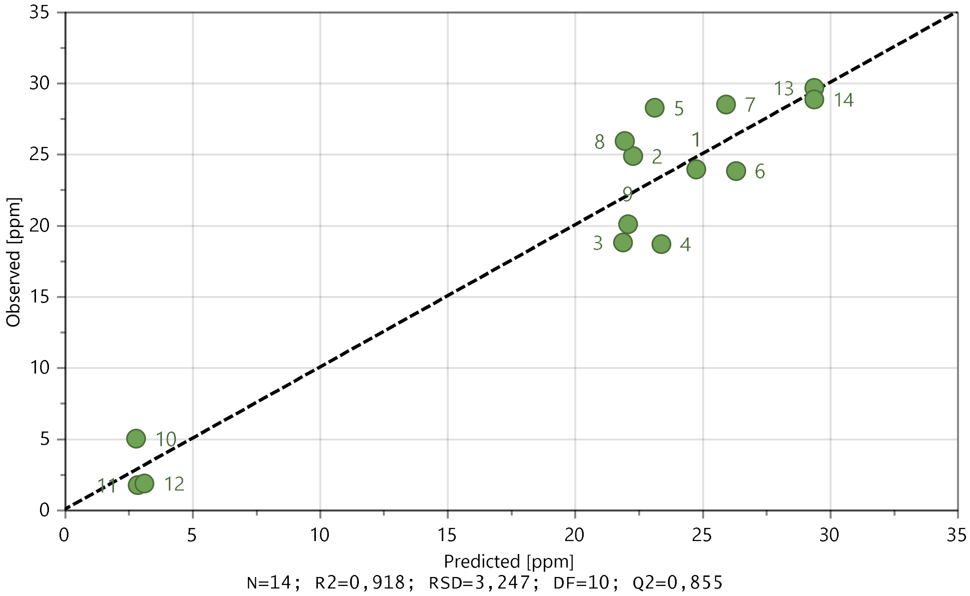


Figure 26 Observed and predicted concentrations of calcium [ppm] in BC feed, BFR7

Figure 27 presents the concentration of phosphorus as a function of temperature, w/o ratio and acid content. Used acid contents were 0, 0.025 and 0.05 wt.-%. The impact of acid addition on the concentration of phosphorus can be easily seen in Figure 27. When increasing the acid content, lower operation temperature can be used to obtain low concentration of phosphorus. When acid is not used, high concentration of phosphorus remains in the product. To obtain the desired concentration value for phosphorus without acid addition, higher process temperatures are needed than the ones tested, and this is not possible in the equipment used due to the other problems in the purification process.

Already 0.05 wt.-% of acid in the feed significantly decreases the concentration of phosphorus to low values. For example, in 165 °C, less than 6 ppm of phosphorus can be obtained even with low w/o ratio (< 0.5). Figure 27 shows also that the impact of w/o ratio on the concentration of phosphorus is not as significant as temperature and the addition of acid. However, when w/o ratio increases the concentration of phosphorus decreases.

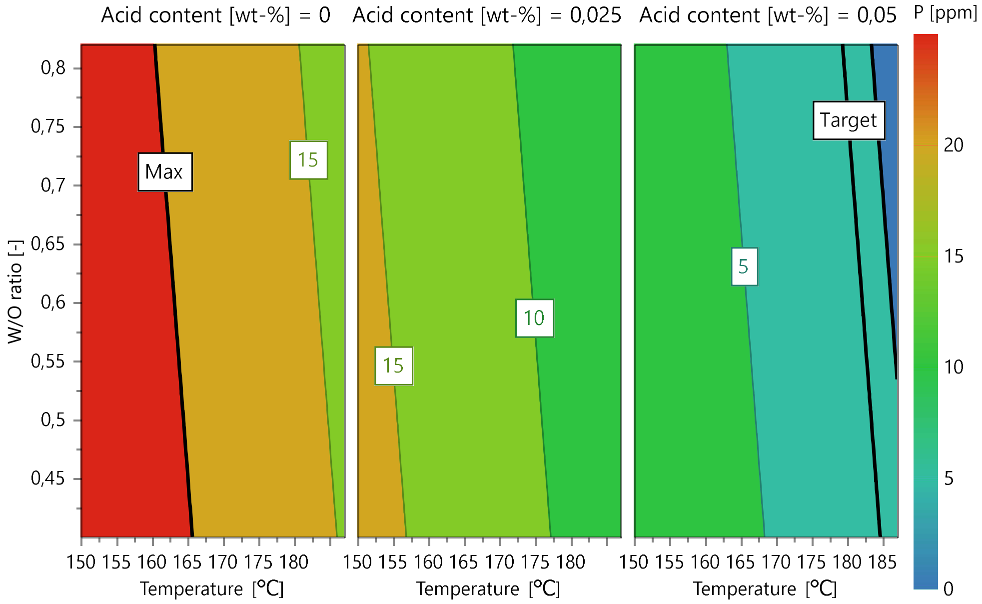


Figure 27 Concentration of phosphorus [ppm] as a function of temperature [°C], w/o ratio [-] and acid content [wt.-%]. R2 = 0.91, Q2 = 0.83

Figure 28 presents the concentration of calcium as a function of temperature, w/o ratio and acid content. Used acid contents are 0, 0.025 and 0.05 wt.-%. Figure 28 shows that acid content is the critical parameter also affecting the removal of calcium. When acid is not used in the process, it is not possible to obtain the desired concentration calcium in the product. When 0.05 wt.-% of acid is used, low concentrations of calcium are obtained at lower temperatures and lower w/o ratio. In general, increasing temperature and w/o ratio decreases the concentration of calcium in the product oil. According to Lenntech (2019b), calcium compounds are generally soluble in water. Thus, it is expected that increasing the water amount in the process, lowers the concentration of calcium in the oil product. Also, increasing temperature might improve the solubility of calcium in water.

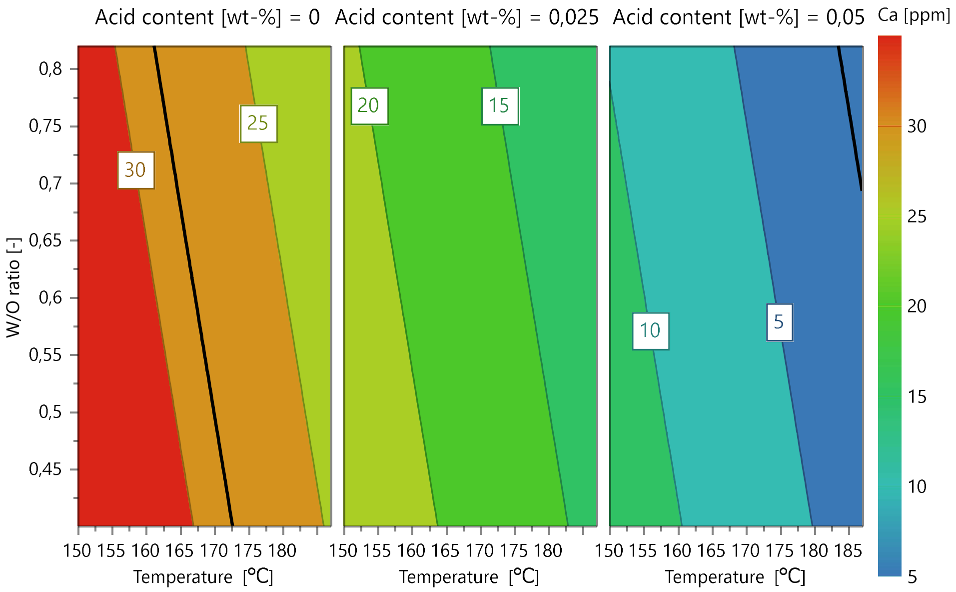


Figure 28 Concentration of calcium [ppm] as a function of temperature [°C], w/o ratio [-] and acid content [wt.-%]. R2 = 0.92, Q2 = 0.86

8.2.3 Feed: Soybean acid oil

Table 25 presents the concentration of impurities in soybean acid oil feed used in BFR7. It can be noticed that sodium, phosphorus and silicon are elements that need to be decreased to obtain desired concentration values (< 10 ppm). Especially the concentration of phosphorus needs remarkably decreased.

Table 25 Concentration of the impurities in the soybean acid oil feed

Calcium, Ca, ICAP	ppm	2.02
Iron, Fe, ICAP	ppm	2.5
Potassium, K, ICAP	ppm	3.6
Magnesium, Mg, ICAP	ppm	1.01
Manganese, Mn, ICAP	ppm	0.05
Sodium, Na, ICAP	ppm	13
Phosphor, P, ICAP	ppm	452
Silicon, Si, ICAP	ppm	11.5

The purification results are shown in the Appendix IV Table 37. According to the feed concentrations and purification results, the concentration of all the other elements expect silicon and phosphorus are low. Therefore, only silicon and phosphorus are used in the data analysis.

The worksheet of the data analysis for phosphorus concentration is presented in Table 26. In the analysis, temperature and w/o ratio are factors and the concentration of phosphorus is the response. Raw data includes 13 data points in overall. Raw data fitting is presented in the Appendix V Figure 36. According to Figure 36, R2 value in raw data fitting is 0.27 and Q2 value is 0.25. Thus, some points were excluded to improve the fitting. N10 is excluded because the control of temperature and w/o ratio was lost momentarily in the process. N5 and N11 were excluded because the differences between N3 and N4 values and other data points obtained for similar operation condition is big. By these exclude points, significant improvement of the model is achieved.

Table 26 The worksheet of the analysis where temperature [°C] and w/o ratio [-] are factors and the concentration of phosphorus [ppm] is the response. Detection limit for phosphorus is 1 ppm

Exp. No	Exp. Name	Run Order	Temperature [°C]	W/O ratio [-]	Phosphorus, P [ppm]
1	N1	8	180	0.2	34.9
2	N2	12	180	0.2	29.7
3	N3	6	180	0.4	34.7
4	N4	11	180	0.4	32.2
~~5~~	~~N5~~	~~5~~	~~180~~	~~0.41~~	~~7.81~~
6	N6	2	180	0.8	11
7	N7	3	178	0.81	10.8
8	N8	7	178	0.82	0
9	N9	13	178	0.82	0
~~10~~	~~N10~~	~~4~~	~~187~~	~~2.06~~	~~0~~
~~11~~	~~N11~~	~~1~~	~~180~~	~~0.42~~	~~1.36~~
12	N12	9	181	0.42	0
13	N13	10	181	0.42	0

Table 27 presents the worksheet of the analysis where temperature and w/o ratio are factors and the concentration of silicon is the response. Raw data includes also 13 data points. The raw data fitting is presented in Appendix V Figure 37. It shows that model fitting is poor when all data is used in the analysis. R2 value is 0.13 and Q2 value is 0.07. It can be seen that there are some distinct points that weaken the model. The concentration in N5 is significantly bigger when compared to N3 and N4. N10 is excluded also because of the loss of temperature and w/o ratio control during the experimental operation. N7 is excluded because of big difference in concentrations compared to N8 and N9. N12 is excluded because of remarkable difference compared to N3, N4, N11 and N13.

Table 27 The worksheet of the analysis where temperature [°C] and w/o ratio [-] are factors and the concentration of silicon [ppm] is the response. Detection limit for silicon is 1 ppm

Exp. No	**Exp. Name**	**Run Order**	**Temperature [°C]**	**W/O ratio [-]**	**Silicon, Si [ppm]**
1	N1	8	180	0.2	4.76
2	N2	12	180	0.2	5.35
3	N3	6	180	0.4	5.75
4	N4	11	180	0.4	6.01
~~5~~	~~N5~~	~~5~~	~~180~~	~~0.41~~	~~12.3~~
6	N6	2	180	0.8	9.64
~~7~~	~~N7~~	~~3~~	~~178~~	~~0.81~~	~~9.04~~
8	N8	7	178	0.82	0
9	N9	13	178	0.82	0
~~10~~	~~N10~~	~~4~~	~~187~~	~~2.06~~	~~0~~
11	N11	1	180	0.42	2.34
~~12~~	~~N12~~	~~9~~	~~181~~	~~0.42~~	~~0~~
13	N13	10	181	0.42	9.4

Figure 29 presents the model fitting where experimental data and predicted concentrations for phosphorus are shown. It can be seen that after excluding the data points mentioned above, good model fitting is obtained (R2 = 0.93 and Q2 = 0.86.)

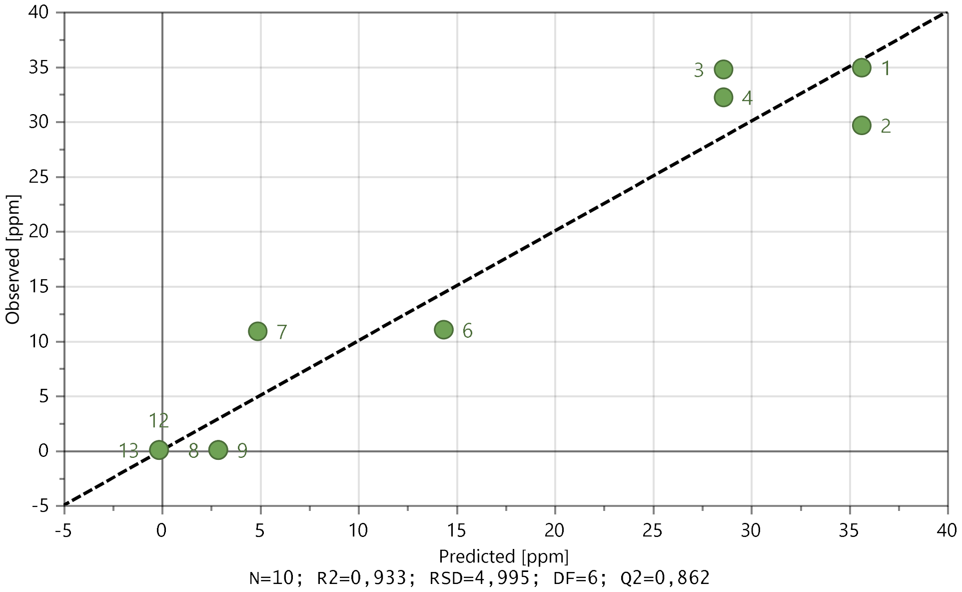


Figure 29 Observed and predicted concentrations of phosphorus [ppm] in soybean acid oil feed, BFR7

Figure 30 shows the model fitting for silicon concentration where experimental concentrations and predicted concentrations are shown in the linearization. R2 is 0.85 and Q2 is 0.75.

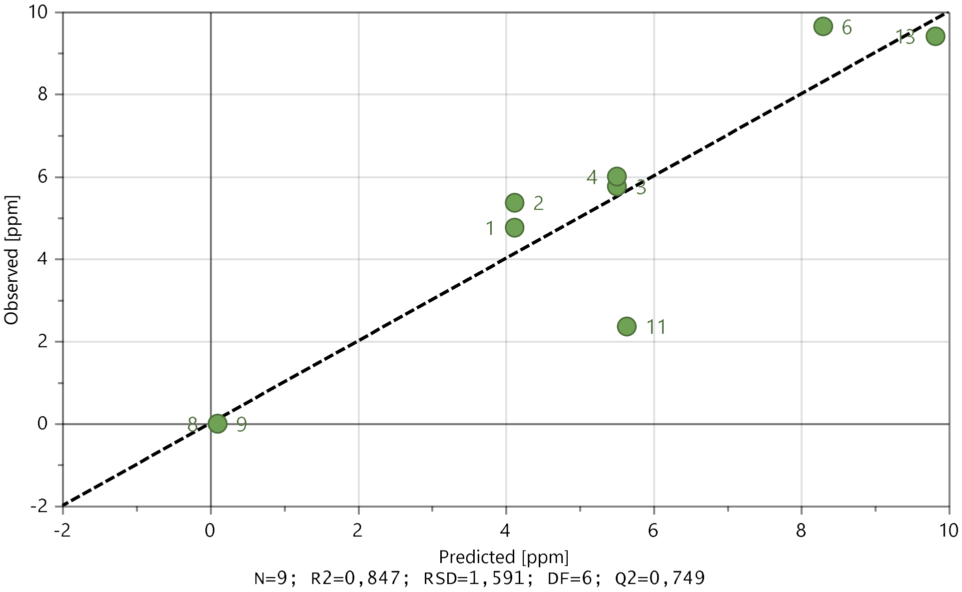


Figure 30 Observed and predicted concentrations of silicon [ppm] in soybean acid oil feed, BFR7

Figure 31 presents the concentration of phosphorus as a function of temperature and w/o ratio. Figure 31 shows that temperature is the most critical parameter affecting the removal of phosphorus. When acid is not used in the process, high temperature is needed to obtain low concentration of phosphorus in the product. If low temperatures (< 181 °C) are used, the w/o ratio must be high (~1:1).

A problem of the data is that there are no significant temperature differences among these experimental data points. Temperature ranges between 178 and 181 °C. This creates uncertainty in the analysis because phosphorus concentrations at low temperatures can only be just estimated.

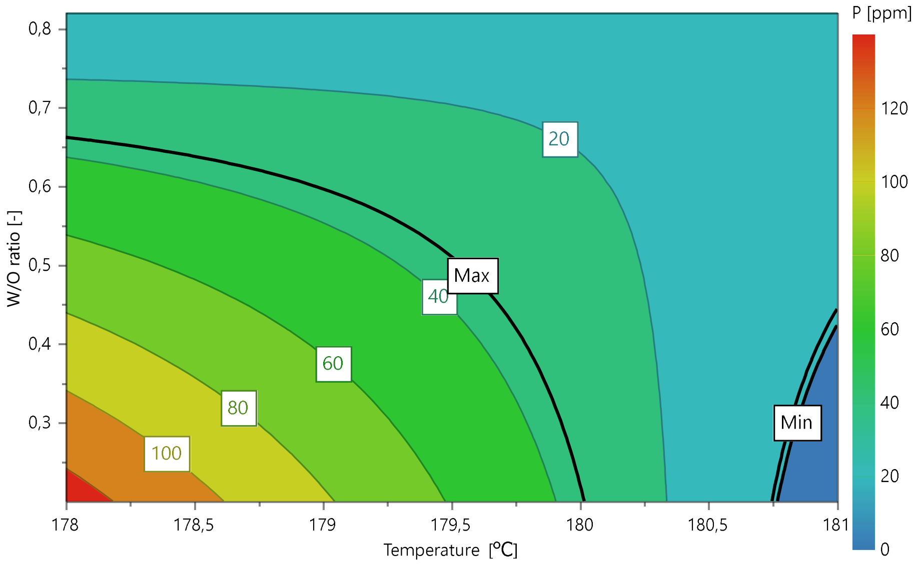


Figure 31 The concentration of phosphorus [ppm] as a function of temperature [°C] and w/o ratio [-]. R2 = 0.93, Q2 = 0.86

Figure 32 presents the concentration of silicon as a function of temperature and w/o ratio. The same uncertainty caused by temperature can also be seen in the case of the removal of silicon. The differences in temperature are small making temperature a critical parameter in the analysis and removal of the element. When process temperature is increased, the concentration of silicon in the product oil increases. Whereas, when w/o ratio is increased, concentration of silicon increases in the product oil. The impact of w/o ratio compared to temperature is remarkably smaller. Also, due to the water insolubility of silicon, can be expected that the impact of w/o ratio in the removal of silicon is low also in this case.

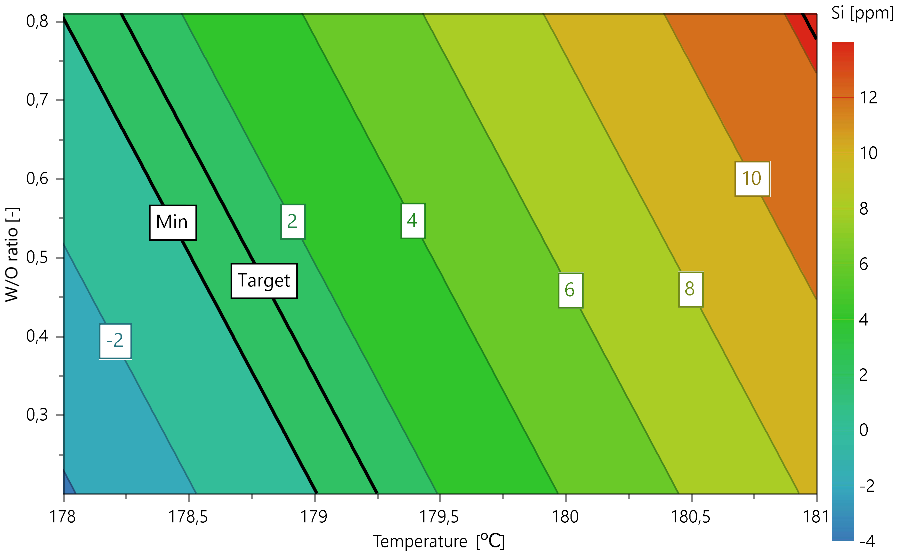


Figure 32 The concentration of silicon [ppm] as a function of temperature [°C] and w/o ratio [-]. R2 = 0.85, Q2 = 0.75

8.3 Conclusion of the MODDE analysis

Both BFR5 and BFR7 analysis show that phosphorus can be reduced even without acid addition when high process temperatures are used (> 170 °C). However, this depends on the concentration of this element in the feed. When the concentration of phosphorus is low, high purification efficiency is relatively easy to achieve. However, big concentrations of phosphorus in the feed, probably require the addition of acid for the complete removal.

BFR5 analysis shows that how acid addition affects the removal of silicon. It is easily noticed that increasing acid concentration in the process, increases the purification efficiency of silicon. Also, the higher temperature is, the more the concentration of silicon decreases. Thus, the use of acid allows high purification efficiencies. According to the BFR5 analysis, combination of acid addition and high temperature can reduce the concentration of silicon to below detection limit (< 1).

An impact of temperature in BFR7 can be difficult to determine because of limited temperature range among the data points. Another problem in the silicon analysis is the w/o ratio parameter. In BFR5 silicon concentration decreases when w/o ratio increases. In the analysis of data obtained in BFR7, when w/o ratio decreases, the concentration of silicon decreases. Thus, data analysis is difficult to provide by the limited data available.

The analysis indicates that acid addition is an important parameter for the removal of both phosphorus and calcium. If acid is not used, concentrations under 10 ppm cannot be obtained neither element. The needed temperature making the process difficult at commercial scale. Addition of low amounts of acid (e.g. 0.025 wt.-%) decreases the concentration of both, phosphorus and calcium, below the desired concentration (<10 ppm) using temperatures higher than 175 °C and w/o ratio higher than 0.55. In the same operation conditions, the concentration of calcium is about 16 ppm. To obtain also desired concentration for calcium, higher addition of acid or bigger temperature is needed.

Thus, some acid is needed to remove all impurities to the desired concentrations. When 0.05 wt.-% of acid is used in the process, good results are obtained. For example, in a condition where process temperature is 160 °C and w/o ratio is 0.5, less than 10 ppm of calcium was obtained. In the same conditions, the concentration of phosphorus was around 7 ppm. Both concentrations decrease further when higher temperatures were used. It can be easily noticed that even low amount of acid has a significant impact on both concentrations. It can be assumed that if 0.1 wt.-% of acid is used in the process, very low concentrations can be obtained for the phosphorus and calcium in temperatures between 160 and 170 °C.

Feed concentrations of phosphorus in both analyses is 452 ppm and the concentration of silicon in the BFR7 analysis is 11.5 ppm. Both BFR5 and BFR7 analysis indicate that increase of temperature decreases the concentration of phosphorus in the product. Acid was used in the BFR5 analysis but not in tests performed in BFR7. Surely acid has an impact on phosphorus removal, but based on this study, temperature seem to be the critical operation parameter. Even with acid and 1:1 w/o ratio, low concentration of phosphorus are not obtained. Based on the analyses of the data produced with BFR5, temperatures over 170 °C are needed to obtain the desired concentration of phosphorus when w/o ratio is 1 and acid content relatively low.

As mentioned, acid was not used in BFR7. It has been noticed that in case of low w/o ratio and low operation temperature, high concentration of phosphorus exists in the product oil. When process temperature is set to be around 180 °C, good purification efficiency of phosphorus is obtained. It can be assumed that already low amount of acid addition in the process significantly improves the purification efficiency of phosphorus and desired concentrations of phosphorus are obtained in lower temperatures (< 180 °C) and w/o ratios.

Concentration of silicon is also analyzed by the data produced in BFR7. According the data analysis, low concentrations of silicon compounds are already achieved at low w/o ratio. Model shows that silicon concentration decreases to low values already when temperature is decreased from about 181 °C to 179 °C. Acid was used in the BFR7 analysis and silicon concentration in the product was under 1 ppm for every data point. Thus, it can be assumed that small amounts of acid are needed to ensure silicon removal.

Challenges in the modelling and interpretation of the models was created by the narrow temperature range tested in BFR7. Thus, the real effect of temperature of the purification cannot be determined using the existing data.

8.3.1 Predictions to the demo plant

Demo plant was operated using w/o ratio 0.5 and 1 and temperatures between 160 and 170 °C without addition of acid. Based on these conditions and the models obtained for the purification of CTO in batch and continuous reactors, complete purification of alkaline metals was achieved in CTO. As acid was not used, silicon was expected to remain in the oil. As presented in Table 38, Appendix VI, the purification levels achieved with the demo plant are according to the model predictions.

9. CONCLUSION

The aim of the work was to investigate a new purification method of feedstocks for renewable fuel production. Existing commercial technologies are not economically or technically suitable for important raw materials of renewable fuel production. The main goal in the work was to find out impacts of process parameters (temperature, w/o ratio and pH) on impurity concentrations in product oil of the purification process. Investigated impurity elements were calcium, iron, potassium, manganese, magnesium, sodium, phosphorus and silicon and desired impurity concentrations were ≤ 10 ppm. It was researched in the literature part that alkaline metals, phosphorus and silicon are the most significant elements that are found from the feedstocks, poisoning and blocking catalysts in hydrotreatment process. It was also realized that there are remarkable differences in impurity contents between feedstocks.

The purification operations were done by Biofuels reactor 5 (BFR5) and Biofuels reactor 7 (BFR7). BFR5 is a batch process and BFR7 is a continuous process. Both reactors are operated in laboratory scale. The aim was to confirm the batch process results by continuous process results. Used feedstocks were crude tall oil (CTO), soybean acid oil (AO) and Brassica carinata oil (BC). Every feed included different concentrations of impurities. Results from CTO purification processes by BFR5 and BFR7 were used to predict and compare the results with demo plant purification results. Data analysis of purification results were done by MODDE Pro simulation tool.

As a conclusion of all the analysis, it was seen that there are remarkable differences in process conditions between different feedstocks. In the analysis results, it was noticed that all the other elements except phosphorus and silicon can be removed easily from CTO. Removal of phosphorus needs relatively high temperature. Acid addition is needed if the concentration of phosphorus in feed is high. Acid addition and temperature increase decreases also the concentration of silicon in the product.

In case of soybean acid oil, phosphorus content was reduced when temperature increased in both BFR5 and BFR7 analysis. It was noticed that temperature of the process has a strong impact on the concentration of phosphorus. The operation temperature can be lowered (< 180 °C) when a small amount of acid is used in the process.

Brassica carinata was processed in continuous system and it was realized that phosphorus and calcium concentrations were high in the product. According to analysis performed, it was noticed that small amount (≥ 0.05 wt.-%) acid addition decreases both phosphorus and calcium concentrations and desired concentration values are obtained already in ≤ 170 °C.

Demo plant was operated in 160 and 170 °C and it was seen that all the other elements but silicon were removed. In same conditions, the same results were obtained in BFR7 operation. It can be assumed that addition of acid decreases the silicon concentration to desired value also in demo plant.

9.1 Recommendations for future research

For future research there are couple of things that need to be studied more. It has been noticed in this thesis work that use of acid in the purification process is necessary to obtain desired impurity concentration values for all elements. More work needs to be done to find out optimal acid contents in the process for every feedstock used.

A recommendation for the future research is to study more the impact of different conditions to silicon concentration. The data used in this thesis does not give a totally reliable results from silicon concentration in different conditions, especially in variation of w/o ratio.

Only some predictions to demo operations with small amount of data was done in this thesis. More predictions need to be done in future when bigger amount of data is available from the demo plant operations.

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APPENDIXES

APPENDIX I	Concentration of phosphorus, calcium and magnesium in soybean oil
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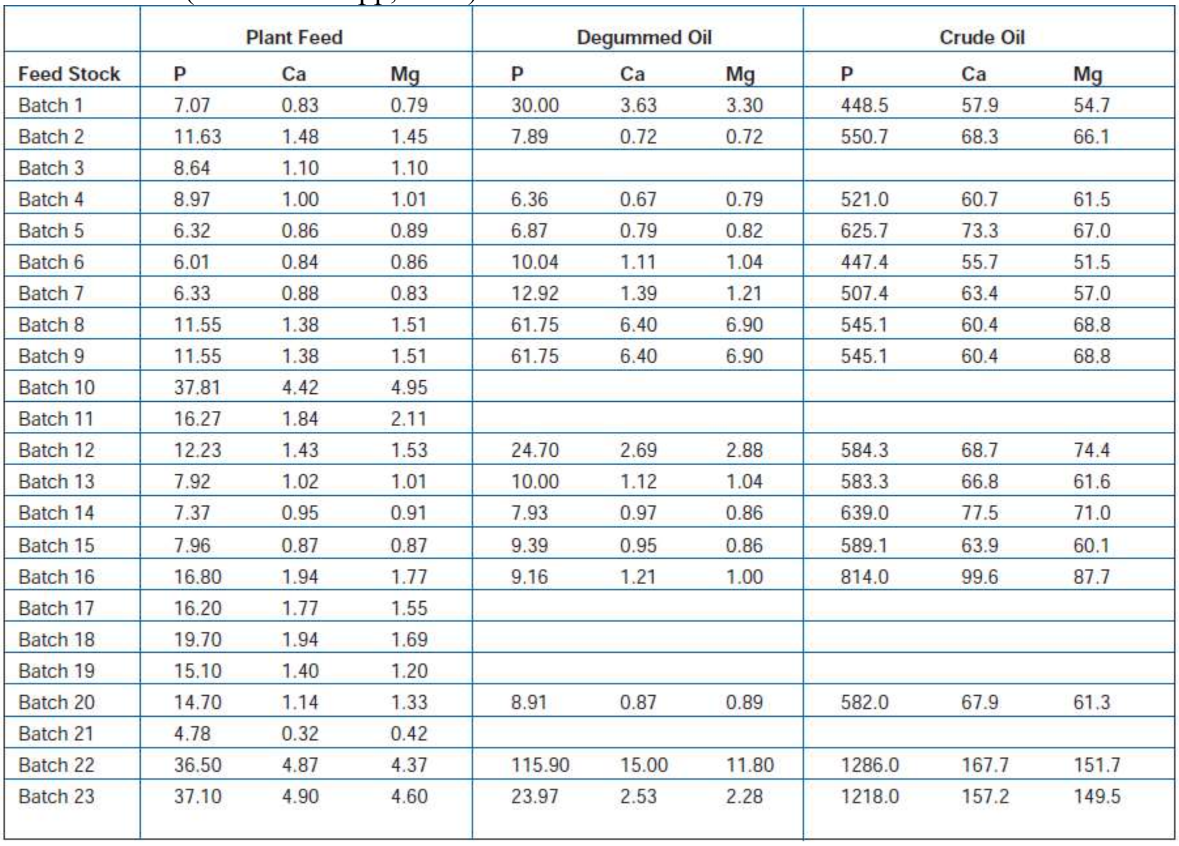
Concentration of phosphorus, calcium and magnesium in soybean oil

Table 28 Concentration of phosphorus, calcium and magnesium in soybean oil. (Knoll & Knopp, 2007)



	Plant Feed			**Degummed Oil**			**Crude Oil**		
Feed Stock	**P**	**Ca**	**Mg**	**P**	**Ca**	**Mg**	**P**	**Ca**	**Mg**
Batch 1	7.07	0.83	0.79	30.00	3.63	3.30	448.5	57.9	54.7
Batch 2	11.63	1.48	1.45	7.89	0.72	0.72	550.7	68.3	66.1
Batch 3	8.64	1.10	1.10						
Batch 4	8.97	1.00	1.01	6.36	0.67	0.79	521.0	60.7	61.5
Batch 5	6.32	0.86	0.89	6.87	0.79	0.82	625.7	73.3	67.0
Batch 6	6.01	0.84	0.86	10.04	1.11	1.04	447.4	55.7	51.5
Batch 7	6.33	0.88	0.83	12.92	1.39	1.21	507.4	63.4	57.0
Batch 8	11.55	1.38	1.51	61.75	6.40	6.90	545.1	60.4	68.8
Batch 9	11.55	1.38	1.51	61.75	6.40	6.90	545.1	60.4	68.8
Batch 10	37.81	4.42	4.95						
Batch 11	16.27	1.84	2.11						
Batch 12	12.23	1.43	1.53	24.70	2.69	2.88	584.3	68.7	74.4
Batch 13	7.92	1.02	1.01	10.00	1.12	1.04	583.3	66.8	61.6
Batch 14	7.37	0.95	0.91	7.93	0.97	0.86	639.0	77.5	71.0
Batch 15	7.96	0.87	0.87	9.39	0.95	0.86	589.1	63.9	60.1
Batch 16	16.80	1.94	1.77	9.16	1.21	1.00	814.0	99.6	87.7
Batch 17	16.20	1.77	1.55						
Batch 18	19.70	1.94	1.69						
Batch 19	15.10	1.40	1.20						
Batch 20	14.70	1.14	1.33	8.91	0.87	0.89	582.0	67.9	61.3
Batch 21	4.78	0.32	0.42						
Batch 22	36.50	4.87	4.37	115.90	15.00	11.80	1286.0	167.7	151.7
Batch 23	37.10	4.90	4.60	23.97	2.53	2.28	1218.0	157.2	149.5

Example of the BFR7 calculations

In the example dry sodium content in purified CTO is calculated. Feedstock used in the process is CTO from the UPM Lappeenranta Biorefinery which is washed with distilled water.

A Table below presents the concentration of impurities in CTO before the purification process. The quantification limits are set for each element. If the concentration is below quantification limit either in feed or in the product, the value 0 is used in the calculations. For example, in the feed below, concentration of calcium, potassium and manganese are 0 ppm in the calculations.

Table 29 Concentration of impurities in the CTO feed before the purification process

Calcium, Ca, ICAP	ppm	<0,1
Iron, Fe, ICAP	ppm	1,3
Potassium, K, ICAP	ppm	<2
Magnesium, Mg, ICAP	ppm	0,302
Manganese, Mn, ICAP	ppm	<0,01
Sodium, Na, ICAP	ppm	65
Phosphor, P, ICAP	ppm	50,1
Silicon, Si, ICAP	ppm	30,9

The concentrations below are obtained by ICP-OES analytical method.

Analysis of oil product: sodium 6.1 ppm

Water phase in oil product: sodium 46.5 ppm

Washing water phase: sodium 173 ppm

Parameters from the process:

Table 30 Process parameters

Data collection time	
Water feed mass, in	98,62 g
Oil feed mass, in	434,96 g
Total feed mass, in	98,62 g + 434,96 g = 533,58 g
Water output mass total	85,7 g
Oil product output mass total	443,3 g
Oil phase mass in oil product	431,7
Water phase mass in oil product	11,6
KF-water content of oil phase in oil product	2 %

Sodium amount (g) in feed:

$$434.96\ g * 65\frac{mg}{kg} * 10^{-6} = = 0.02827\ \mathrm{g} \quad \text{(Eq. 9)}$$

Sodium amount (g) in oil product's oil phase:

$$\frac{6.1\frac{mg}{kg}}{1000} * \frac{431.7\ g}{1000} = 0.00263\ g \quad \text{(Eq. 10)}$$

Sodium amount (g) in the water phase of oil product:

$$\frac{46{,}50\frac{mg}{kg}}{1000} * \frac{11.6\ g}{1000} = 0.00054\ g \quad \text{(Eq. 11)}$$

Total amount of sodium in oil output:

$$0.00263\ g + 0.00054\ g = 0.00317\ g \quad \text{(Eq. 12)}$$

Sodium amount (g) in washing water:

$$\frac{173\frac{mg}{kg}}{1000} * \frac{85.7\ g}{1000} = 0.01483\ g \quad \text{(Eq. 13)}$$

KF- water content of oil phase in oil product is measured to be 2 %. Water mass in the oil phase is calculated then according the equation:

$$0{,}02 * 431{,}7\ g = 8.634\ g \quad \text{(Eq. 14)}$$

Total mass of dry oil product can be calculated according the equation:

$$431.7g - 8.634\ g = 423.066\ g \qquad \text{(Eq. 15)}$$

Sodium amount (g) in dry oil product:

$$423.066\ g * 6.1\frac{mg}{kg} * 10^{-6} = 0.00258\ g \qquad \text{(Eq. 16)}$$

Sodium concentration (ppm) in dry oil product:

$$\frac{0.00258\ g}{423.066\ g} * 10^{6} = 6.10\ ppm \qquad \text{(Eq. 17)}$$

Sodium concentration (ppm) in water phase of oil:

$$\frac{0.00054}{11.6} * 10^{6} = 46.50\ ppm \qquad \text{(Eq. 18)}$$

Sodium concentration (ppm) in washing water:

$$\frac{0.01483}{85.7} * 10^{6} = 173\ ppm \qquad \text{(Eq. 19)}$$

Mass balance of Sodium:

$$\frac{0.00263\ g + 0.00054\ g + 0.01483\ g}{0.02827\ g} * 100\ \% = 63.7\ \% \qquad \text{(Eq. 20)}$$

Impurity concentrations in different oil products in BFR5

Table 31 Purification results of CTO feed in BFR5

BFR5	Unit	FEED	Temperature	w/o	Time	Acid, %	Oil	Aqueous
		CTO	180	2	1h	0		
Alkaline metals	ppm	65,2					24,07	33,55
Si	ppm	27,6					2,36	5,52
P	ppm	24,7					0	10,8
		CTO	180	1	1h	0		
Alkaline metals	ppm	65,2					3,26	103,26
Si	ppm	27,6					19,3	9
P	ppm	24,7					1,53	20,7
		CTO	180	0,5	1h	0		
Alkaline metals	ppm	65,2					6,5	125,44
Si	ppm	27,6					9,35	16,5
P	ppm	24,7					0	41,6
		CTO	180	1	1h	0,5		
Alkaline metals	ppm	65,2					13,84	28,25
Si	ppm	27,6					0	12,9
P	ppm	24,7					0	21,1
		CTO	180	1	1h	1		
Alkaline metals	ppm	65,2					12,28	40,4
Si	ppm	27,6					0	13,7
P	ppm	24,7					0	21,1
		CTO	180	1	1h	1,5		
Alkaline metals	ppm	65,2					1,13	76,95
Si	ppm	27,6					0	14,4
P	ppm	24,7					0	20,7

Table 32 Purification results of CTO feed in BFR5

BFR5		FEED	Temperature	W/O	Acid, %	Oil	Aqueous
		CTO	130	1	0,5		
Calcium, Ca	ppm	0,841				<0,1	2,27
Iron, Fe	ppm	1,3				0,15	3,74
Potassium, K	ppm	5,7				<2	6,71
Magnesium, Mg	ppm	0,19				<0,01	0,212
Manganese, Mn	ppm	0,23				<0,01	0,558
Sodium, Na	ppm	47				<1	55,7
Phosphorus, P	ppm	22,9				7,75	19,5
Silicon, Si	ppm	17,4				13,8	5,9
		CTO	140	1	0,5		
Calcium, Ca	ppm	0,841				<0,1	2,11
Iron, Fe	ppm	1,3				<0,1	3,97
Potassium, K	ppm	5,7				<2	6,65
Magnesium, Mg	ppm	0,19				<0,01	0,213
Manganese, Mn	ppm	0,23				<0,01	0,567
Sodium, Na	ppm	47				<1	54,6
Phosphorus, P	ppm	22,9				4,55	24,1
Silicon, Si	ppm	17,4				13,3	6,2
		CTO	150	1	0,5		
Calcium, Ca	ppm	0,841				<0,1	2,14
Iron, Fe	ppm	1,3				<0,1	5,21
Potassium, K	ppm	5,7				<2	6,51
Magnesium, Mg	ppm	0,19				<0,01	0,218
Manganese, Mn	ppm	0,23				<0,01	0,66
Sodium, Na	ppm	47				<1	54,7
Phosphorus, P	ppm	22,9				2,19	26,6
Silicon, Si	ppm	17,4				12,4	6,9
		CTO	130	1	1		
Calcium, Ca	ppm	0,841				<0,1	1,87
Iron, Fe	ppm	1,3				<0,1	4,62
Potassium, K	ppm	5,7				<2	5,59
Magnesium, Mg	ppm	0,19				<0,01	0,179
Manganese, Mn	ppm	0,23				<0,01	0,596
Sodium, Na	ppm	47				<1	48,4
Phosphorus, P	ppm	22,9				8,56	16,7
Silicon, Si	ppm	17,4				13,4	5,3

Table 33 Purification results of acid oil feed in BFR5

BFR5		FEED	Temperature	W/O	Acid, %	Oil	Aqueous
		AO	130	1	0,5		
Calcium, Ca	ppm	2,02				<0,1	2,95
Iron, Fe	ppm	2,5				0,21	3,81
Potassium, K	ppm	3,6				<2	5,1
Magnesium, Mg	ppm	1,02				<0,01	1,4
Manganese, Mn	ppm	0,05				<0,01	0,117
Sodium, Na	ppm	13				<1	17,7
Phosphorus, P	ppm	452				103	342
Silicon, Si	ppm	11,5				<1	0,853
		AO	140	1	0,5		
Calcium, Ca	ppm	2,02				<0,1	4,82
Iron, Fe	ppm	2,5				<0,1	5,14
Potassium, K	ppm	3,6				<2	5,41
Magnesium, Mg	ppm	1,02				<0,01	1,59
Manganese, Mn	ppm	0,05				<0,01	0,179
Sodium, Na	ppm	13				<1	25,5
Phosphorus, P	ppm	452				80	399
Silicon, Si	ppm	11,5				<1	0,888
		AO	150	1	0,5		
Calcium, Ca	ppm	2,02				<0,1	3,79
Iron, Fe	ppm	2,5				<0,1	5,99
Potassium, K	ppm	3,6				<2	5,32
Magnesium, Mg	ppm	1,02				<0,01	1,58
Manganese, Mn	ppm	0,05				<0,01	0,26
Sodium, Na	ppm	13				<1	24,3
Phosphorus, P	ppm	452				52,9	431
Silicon, Si	ppm	11,5				<1	0,734
		AO	130	1	1		
Calcium, Ca	ppm	2,02				<0,1	3,91
Iron, Fe	ppm	2,5				0,26	13,2
Potassium, K	ppm	3,6				<2	5,31
Magnesium, Mg	ppm	1,02				<0,01	1,65
Manganese, Mn	ppm	0,05				<0,01	0,839
Sodium, Na	ppm	13				<1	24,2
Phosphorus, P	ppm	452				96,2	376
Silicon, Si	ppm	11,5				<1	1,13

		AO	140	1	1		
Calcium, Ca	ppm	2,02				<0,1	3,86
Iron, Fe	ppm	2,5				<0,1	13,6
Potassium, K	ppm	3,6				<2	5,38
Magnesium, Mg	ppm	1,02				<0,01	1,62
Manganese, Mn	ppm	0,05				<0,01	0,84
Sodium, Na	ppm	13				<1	24,5
Phosphorus, P	ppm	452				75,3	419
Silicon, Si	ppm	11,5				<1	0,927
		AO	150	1	1		
Calcium, Ca	ppm	2,02				<0,1	3,68
Iron, Fe	ppm	2,5				<0,1	13,6
Potassium, K	ppm	3,6				<2	5,21
Magnesium, Mg	ppm	1,02				<0,01	1,53
Manganese, Mn	ppm	0,05				<0,01	0,858
Sodium, Na	ppm	13				<1	23,8
Phosphorus, P	ppm	452				26,6	454
Silicon, Si	ppm	11,5				<1	0,945

Impurity concentrations in different oil feeds and products in BFR7

Table 34 Purification results of CTO in BFR7

Temperature	C		171	170	172	170	171	171	171	171	171	171	171
W/o ratio	-		0,289063	0,277132	0,280464	0,481553	0,479691	0,481625	0,48249	0,669884	0,659048	0,660305	0,660305
Acid content	wt-%		-	-	-	-	-	-	-	-	-	-	-
		FEED											
Calsium, Ca, ICAP	ppm	0,841	0,14	0	0	0	0	0	0	0	0	0	0
Iron, Fe, ICAP	ppm	1,3	0,25	0,28	0,23	0,2	0,17	0,16	0,16	0,22	0,18	0,14	0,14
Potassium, K, ICAP	ppm	5,7	0	0	0	0	0	0	0	0	0	0	0
Magnesium, Mg, ICAP	ppm	0,19	0,025	0	0	0	0	0	0	0	0	0	0
Manganese, Mn, ICAP	ppm	0,23	0	0	0	0	0	0	0	0	0	0	0
Sodium, Na, ICAP	ppm	47	0	0	0	0	0	0	0	0	0	0	0
Phosphor, P, ICAP	ppm	22,9	0	0	0	0	0	0	0	0	0	0	0
Silicon, Si, ICAP	ppm	17,4	7,99	4,95	4,08	6,51	6,09	8,97	8,63	10,1	9,82	9,59	9,48

Table 35 Purification results of CTO in BFR7

Temperature	C		175	180	180	180	182	180	182	183	183	183	183
W/o ratio	-		1,02	0.23	0.46	0.14	0.21	0.22	0.2	0.2	0.15	0.15	0.09
Acid content	wt-%		-	-	-	-	-	-	-	-	-	-	-
		FEED											
Calsium, Ca, ICAP	ppm	<0,1	0	0,31	0,181	0,232	0	0	0	0	0	0	0
Iron, Fe, ICAP	ppm	1,3	1,2	2,9	0,92	0,85	0,38	0,57	0,26	0,14	0,61	0,55	0,58
Potassium, K, ICAP	ppm	<2	0	0	0	0	0	0	0	0	8,8	0	3,6
Magnesium, Mg, ICAP	ppm	0,302	0,06	0,048	0	0	0	0	0	0	0,082	0	0,016
Manganese, Mn, ICAP	ppm	<0,01	0,04	0,09	0,02	0	0	0	0	0	0,09	0	0,02
Sodium, Na, ICAP	ppm	65	0	6,1	3,8	0	0	0	0	0	4,9	1,8	5,2
Phosphor, P, ICAP	ppm	50,1	0	0	0	0	0	0	0	0	0	0	1,11
Silicon, Si, ICAP	ppm	30,9	19,9	28,2	27,7	0	7,43	16	14,8	12,7	5	1,43	5,08

Table 36 Purification results of Brassica carinata oil in BFR7

Temperature	C		176	185	187	182	183	181	182	179	179	178	178	177	150	150
W/o ratio	-		0.8	0.82	0.8	0.77	0.77	0.4	0.42	0.78	0.76	0.77	0.76	0.76	0.8	0.8
Acid content	wt-%		0	0	0	0	0	0	0	0.005	0.005	0.05	0.05	0.05	0.005	0.005
		FEED														
Calsium, Ca, ICAP	ppm	133	23,9	24,8	18,8	18,7	28,2	23,8	28,5	25,9	20	29,6	28,8	4,93	1,75	1,77
Iron, Fe, ICAP	ppm	1,6	2,8	2,7	1,8	1,6	2,1	0,77	0,78	0,85	0,58	1,1	0,81	0,56	0,17	0,11
Potassium, K, ICAP	ppm	<2	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Magnesium, Mg, ICAP	ppm	20,1	1,38	1,5	1,35	1,45	2,41	1,59	1,99	1,66	1,27	1,92	1,84	0,377	0,157	0,159
Manganese, Mn, ICAP	ppm	0,79	0,18	0,22	0,19	0,2	0,3	0,15	0,2	0,19	0,15	0,24	0,22	0,03	0	0
Sodium, Na, ICAP	ppm	<1	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Phosphor, P, ICAP	ppm	117	15,8	14,9	11,4	11,9	18,3	14,4	17,8	16,8	12,7	22,1	20	3,47	0	1,06
Silicon, Si, ICAP	ppm	<1	2,12	2,7	2,98	3,03	0	3,11	2,32	0	0	0	1,23	1,06	1,17	1,24

Table 37 Purification results of Soybean acid oil in BFR7

Temperature	C		180	180	180	180	180	180	178	178	178	187	180	181	181
W/o ratio	-		0.2	0.2	0.4	0.4	0.41	0.8	0.81	0.82	0.82	2,06	0.42	0.42	0.42
Acid content	wt-%		-	-	-	-	-	-	-	-	-	-	-	-	-
		FEED													
Calsium, Ca, ICAP	ppm	<0,1	0	0	0	0	0	0	0	0	0	0	0	0	0
Iron, Fe, ICAP	ppm	1,3	0,22	0,14	0,17	0,15	0,2	0,13	0	0,26	0,24	0,32	0	0	0,17
Potassium, K, ICAP	ppm	<2	0	0	0	0	4,3	0	2,6	0	0	0	0	0	0
Magnesium, Mg, ICAP	ppm	0,302	0,011	0	0	0	0,042	0	0	0,012	0	0	0	0	0,043
Manganese, Mn, ICAP	ppm	<0,01	0	0	0	0	0,03	0	0	0	0	0	0	0	0,04
Sodium, Na, ICAP	ppm	65	0	0	0	0	2,6	2	1,7	0	0	0	0	0	0
Phosphor, P, ICAP	ppm	50,1	34,9	29,7	34,7	32,2	7,81	11	10,8	0	0	0	1,36	0	0
Silicon, Si, ICAP	ppm	30,9	4,76	5,35	5,75	6,01	12,3	9,64	9,04	0	0	0	2,34	0	9,4

Model fitting of raw data

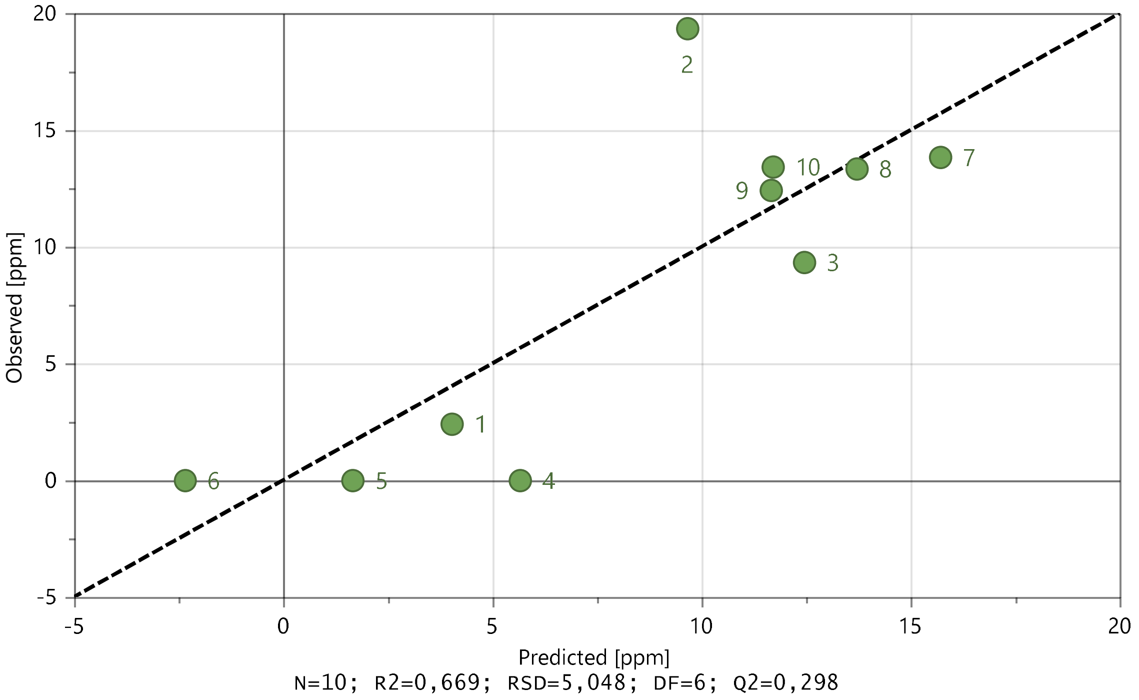


Figure 33 Observed and predicted silicon concentration in CTO feed, BFR5. The raw data points without any data point excludes

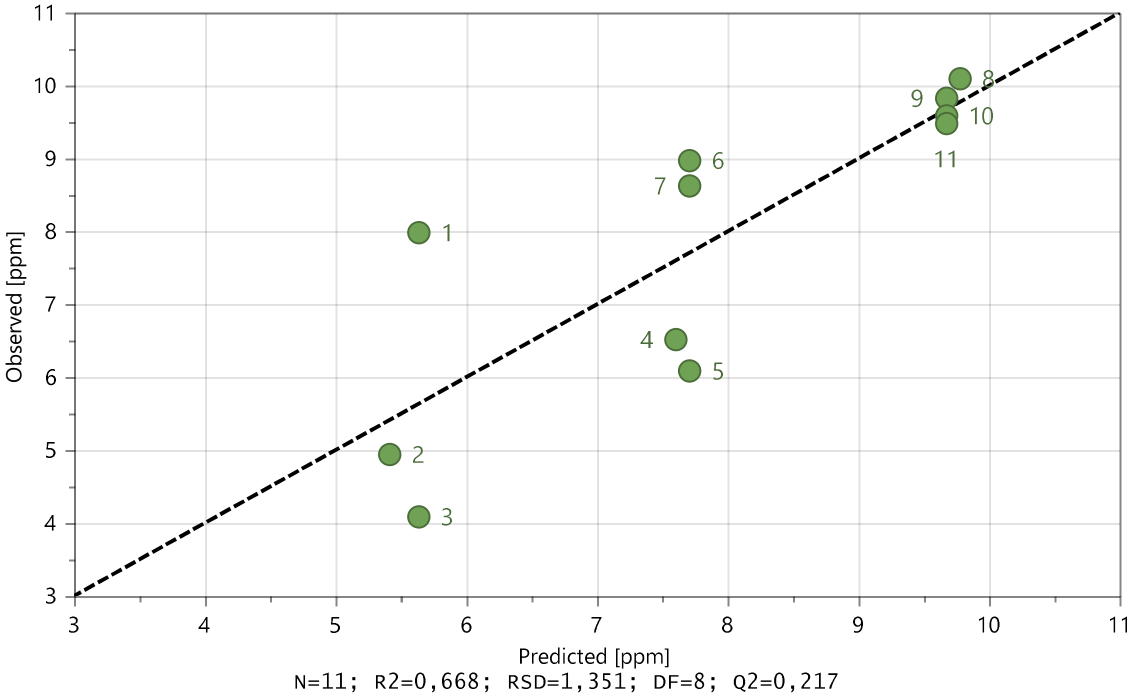


Figure 34 Observed and predicted silicon concentration in CTO feed, BFR7. The raw data points without any data point excludes.

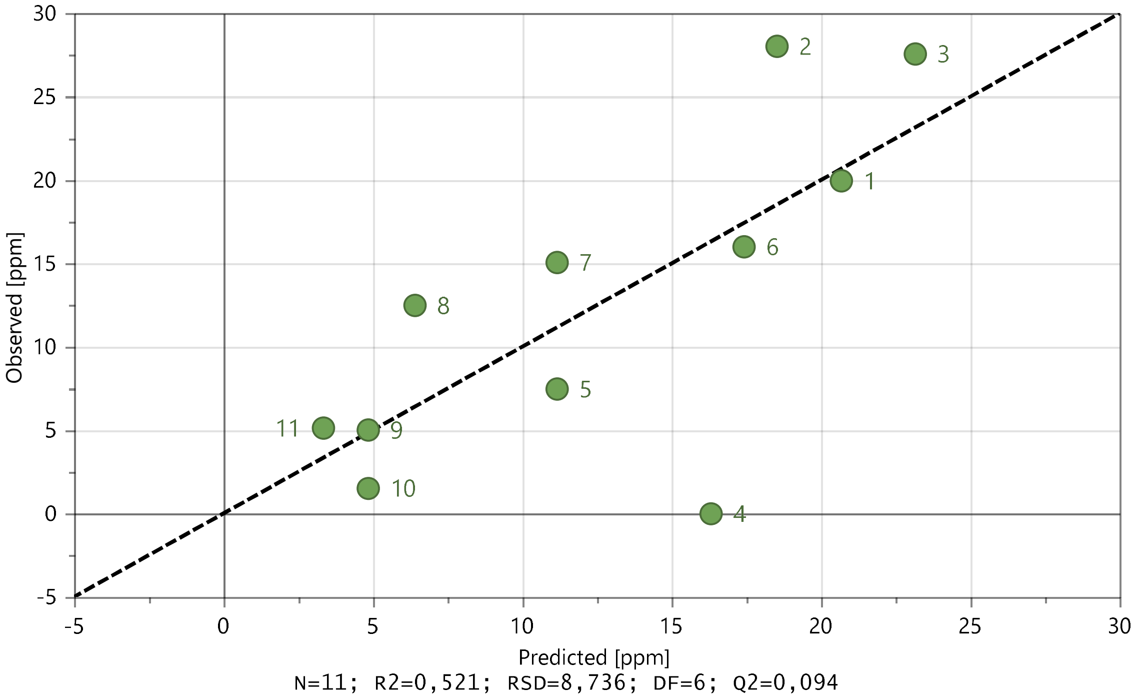


Figure 35 Observed and predicted silicon concentration in CTO feed, BFR7. The raw data points without any data point excludes.

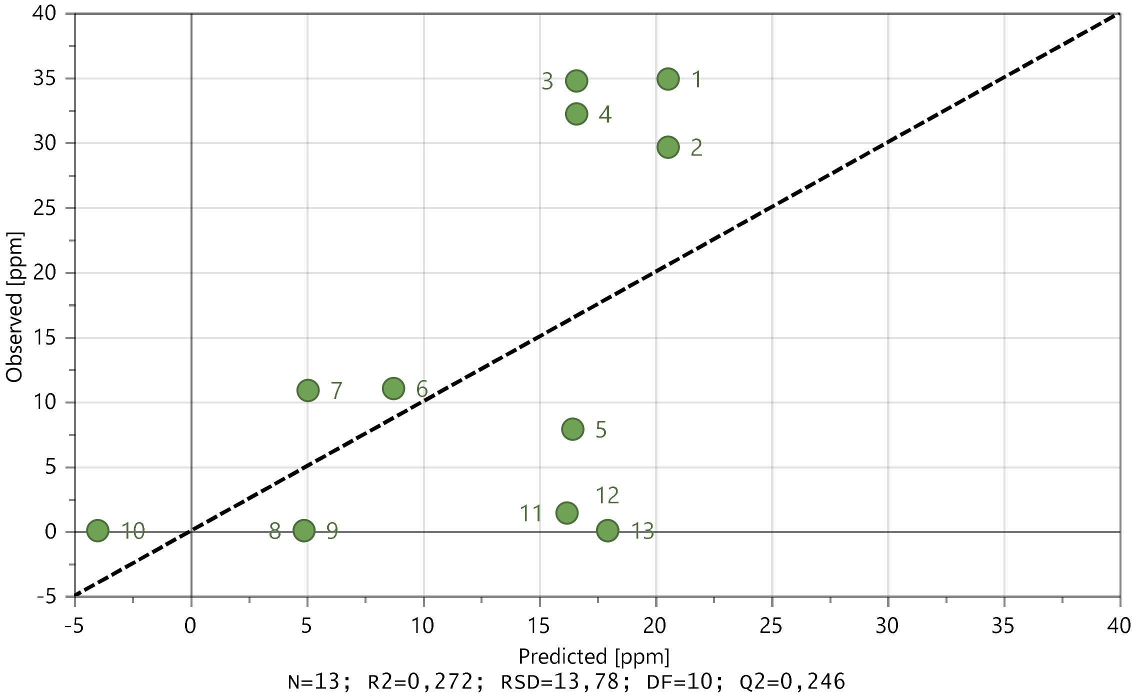


Figure 36 Observed and predicted phosphorus concentration in soybean acid oil feed, BFR7. The raw data points without any data point excludes.

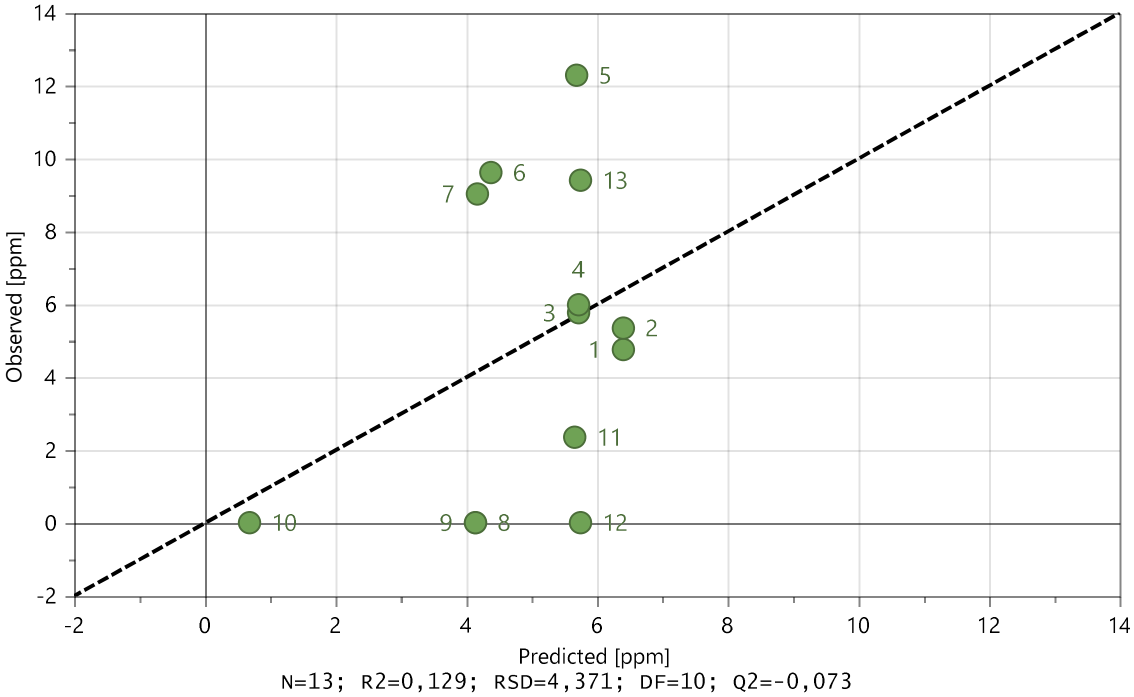


Figure 37 Observed and predicted silicon concentration in soybean acid oil feed, BFR7. The raw data points without any data point excludes.

Demo plant data

Table 38 Demo plant purification results

Demo		FEED	Temperature	W/O	Acid, %		
		CTO	170	1	-		
Calcium, Ca	ppm	0.25	<0,1				
Iron, Fe	ppm	3.6	1.4				
Potassium, K	ppm	3.8	<2				
Magnesium, Mg	ppm	<0,01	<0,01				
Manganese, Mn	ppm	0.02	<0,01				
Sodium, Na	ppm	33	11				
Phosphorus, P	ppm	11.6	<1				
Silicon, Si	ppm	82.6	78.6				
		CTO	170	0,5	-		
Calcium, Ca	ppm	0.25	0.129	<0,1	<0,1	<0,1	0.102
Iron, Fe	ppm	3.6	1.1	0.93	0.85	1	1.2
Potassium, K	ppm	3.8	<2	<2	<2	<2	<2
Magnesium, Mg	ppm	<0,01	0.058	0.036	<0,01	<0,01	0.022
Manganese, Mn	ppm	0.02	0.04	0.02	<0,01	<0,01	0.02
Sodium, Na	ppm	33	<1	<1	<1	<1	<1
Phosphorus, P	ppm	11.6	<1	<1	<1	<1	<1
Silicon, Si	ppm	82.6	51	53.6	52.7	53.9	53.1
		CTO	160	0,5	-		
Calcium, Ca	ppm	0.25	<0,1	<0,1	<0,1	0.111	<0,1
Iron, Fe	ppm	3.6	0.83	0.51	0.61	0.51	0.43
Potassium, K	ppm	3.8	<2	<2	<2	<2	<2
Magnesium, Mg	ppm	<0,01	<0,01	<0,01	<0,01	0.012	0.013
Manganese, Mn	ppm	0.02	<0,01	<0,01	<0,01	0.02	0.02
Sodium, Na	ppm	33	<1	<1	<1	<1	<1
Phosphorus, P	ppm	11.6	1.02	<1	1.04	<1	<1
Silicon, Si	ppm	82.6	55	54	54.6	55.7	56