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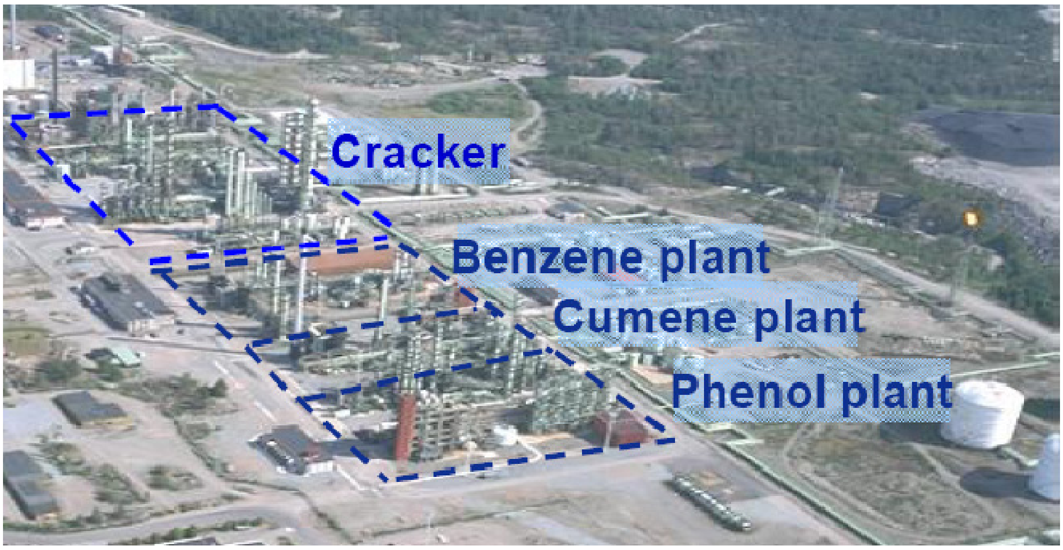

Reduction of Waste Water Loads at Petrochemical Plants

Master of Science Thesis in the Master Degree Programme, Industrial Ecology –for a Sustainable Society

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Göteborg, Sweden, 2011

MASTER’S THESIS

Reduction of Waste Water Loads at Petrochemical Plants

A study of components present in petrochemical waste water, their origin and their contribution to chemical oxygen demand.

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Cover: Borealis Polymers Oy Petrochemical plants located in Porvoo, Finland, p 4
[Chalmers Reproservice]
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Preface

The work was carried out in Borealis Polymers Oy in Porvoo (Finland) between December 2010 and June 2011. The thesis was instructed by Vincent Soudant from Borealis and Gregory Peters from Chalmers University of Technology.

First I want to thank Jari Koivumäki (Borealis) for providing me the opportunity to do this project.

I am very thankful for my supervisor Vincent Soudant for engagement for supporting this project. Your advices and guidance for this project were very valuable.

I'm also thankful to Gregory Peters for your constructive comments and flexibility during the project.

My gratitude goes also to everybody working in the Phenol and Aromatics and in the Cracker. I am so thankful for all the advice, help and encouragement I received during the project. You had always time to help me. I owe special thanks for Jari Syri (Borealis) for your support during the project.

I am so grateful to my mother Leena and father Juha. You have always supported me and been there for me in everything I have decided to do. Your encouragement has meant so much to me.

Finally I want to thank my dear boyfriend Jukka. You were my tower of strength.

Abstract

This Master's thesis was done for Borealis Polymers Oy in co-operation with Chalmers University of Technology.

The research concentrated on the load of petrochemical waste waters. Borealis' Petrochemical plants consist of cracker, butadiene, benzene, cumene and phenol plants. There are two waste water systems in Borealis Polymers Petrochemical plants: phenolic waters (PW) and oily waters (OW) which were studied separately. The phenol plant discharges its waste water to both systems, while other plants discharge only to OW-system.

The loads of waste waters were assessed with two methods. The first method was chemical oxygen demand and the second method was to assess the quality of waste water streams from plants. Chemical oxygen demand (COD) was studied with theoretical oxygen demand (ThOD) analysis. The quality of different waste water streams were assessed by taking samples from waste waters generated in the plants.

In phenolic waters, the ThOD was mostly caused by methanol and phenol. In OW-system the contribution to COD-load was divided more equally between all the components found in the waste waters. Petrochemical waste waters contain a variety of different components, so ThOD analysis based only on known components did not give a full answer how different sorts of chemicals contribute to COD. On average the determined ThOD was one fifth of measured in COD in phenolic waters and one third of measured COD in oily waters.

In the phenol plant the load originated from the effluent stripper and methylhydroperoxide (MHP) reactor to the phenolic waters. When the quality of waste waters was studied, the MHP-reactor was the main contributor to the load to biological treatment feed, biolsy. It is recommended that the known components should be analysed also from the outlet of the MHP-reactor continuously. The waste water from the MHP-reactor contained high concentrations of cumene and phenol. Also because of the high phenol and cumene content of the water, it should be treated either in effluent stripper or in the OW-stripper.

The cracker was responsible for benzene, toluene, xylenes and phenol load to oily waters system. The phenol and aromatics were responsible for methanol, and total nitrogen load. The known components should be continuously analysed from all the main waste water sources; the diluting steam generator, the NaOH and FCC washing steps, the carbonyl wash, the OW-stripper and the ejector waters. The streams that contained high hydrocarbon concentrations should be treated in OW-stripper and streams that contained phenol should be treated in effluent stripper.

The reduction of load is difficult even impossible if the reduction concentrates only on the total load, measured either from pit 27 in case of the OW-system or from the biolsy in case of phenolic waters. Firstly the variety of components in the final stream increases because waste waters from different plants are aggregated. The reduction of different kinds of components is difficult, because of different nature of components. In the final stream also the components are diluted, which also makes the reduction of components more difficult. The reduction of components can be more efficient if it is carried out at the origin of the load.

Keywords: Petrochemical waste water, chemical oxygen demand, theoretical oxygen demand

Abbreviations

ACE	Acetone
ACN	Acetonitrile
BTX-components	Benzene, toluene, xylenes
BU	Butadiene
BZN	Benzene
C	Cracker
COD	Chemical oxygen demand
CUM	Cumene
DOC	Dissolved organic carbon
EG	Ethylene glycol, glycol
ESTD	External standard technique
FCC	Fluid catalytic cracking
GC	Gas Chromatography
GC-MS	Gas Chromatography-Mass spectrometry
ISBL	Inside battery limit
ISTD	Internal standard technique
MET	Methanol
MHP	Methyl hydro peroxide
NaOH	Sodium hydroside
OSBL	Outside battery limit
OW	Oily water
PHE	Phenol
Ppb	Parts per billion
Ppm	Parts per million
ThOD	Theoretical oxygen demand
TOL	Toluene
TOT. HC	Total hydrocarbons
TOT. N	Total nitrogen
XYL	Xylenes

Letters

a	Correlation factor for Theoretical oxygen demand
b	Molecular oxygen demand of component i per mole component i
c_i	Concentration of component i
M_i	Molar mass of component i

1 Introduction

The Borealis Polymers Oy plants are located at Kilpilahti industrial area about 17 km by road southwest from the City of Porvoo. The direct distance from Porvoo downtown is about 11 km and from Helsinki downtown to the northeast about 35 km. The Kilpilahti area is dedicated to industrial activities only and around the area there is a zone which is not allowed to be used for housing. The closest industrial plants are the Neste Oil Power plant (CHP) and refinery to the north of the Petrochemical plants and the StyroChem Finland Oy polystyrene plant to the south of the Petrochemical plants. Other industrial companies at the area are Oy AGA Ab (nitrogen, oxygen, and other gases), Oy Innogas Ab (LPG), Gasum Oy (LNG), M-I Finland Oy (Flow improver chemicals) and Grace Catalyst AB (catalyst carriers). The Ashland Finland Oy polyester plant is located in the east corner of the Plastic plants area. Locations of different plants are shown in Figure 1.

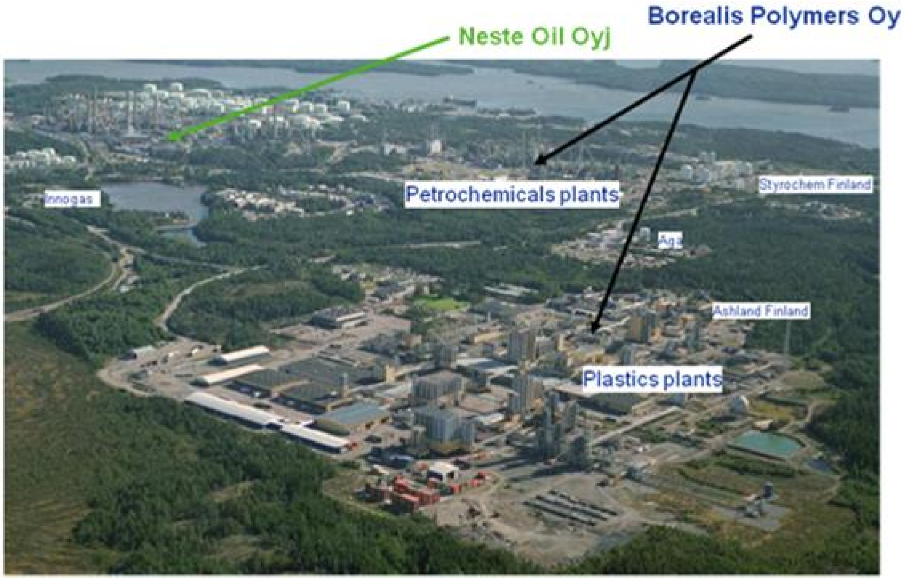

Figure 1 **Locations of different companies in the Kilpilahti industrial area. Artificial lake Hackalandet is located next to Innogas. Water for the process is taken from Hackalandet.**

Raw water for the process is taken from Mustijoki-river, which it is situated north of Kilpilahti. Its discharge point into the Gulf of Finland is outside the city of Porvoo in Kulloonlahti.

Raw water for the process is used for making steam for example. Waste water from the Petrochemical plants is first transferred to Neste Oil's waste water treatment unit and then discharged to Svartbäckinselkä. Sea water from the Gulf of Finland is used for indirect cooling. Sea cooling water is provided by an underground tunnel to heat exchangers where it cools a secondary cooling water loop. The sea cooling water discharge point is located in Svartbäckinselkä in the Porvoo archipelago. The secondary cooling water is used by the refinery, plastics and Petrochemical plants.

Production in the Petrochemical plants

Borealis' Petrochemical plants consist of the phenol and aromatics unit as well as the cracker. The phenol and aromatics plants produce phenol, acetone, benzene and cumene. The cracker produces ethylene, propylene and butadiene. The integration of petrochemical processes in Porvoo and location of different production plants are shown in Figure 2 and in Figure 3.

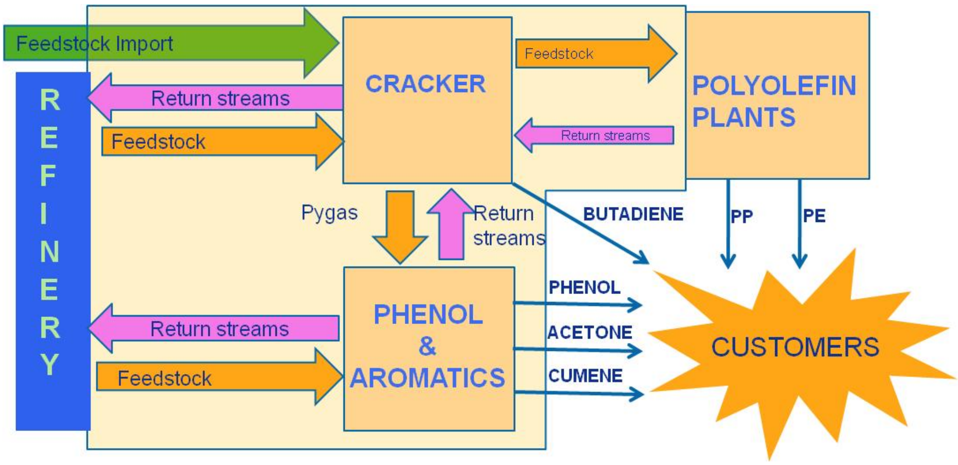

Figure 2 Figure shows the integration of The Neste Oil refinery and the Borealis. (Borealis Polymers 2010)

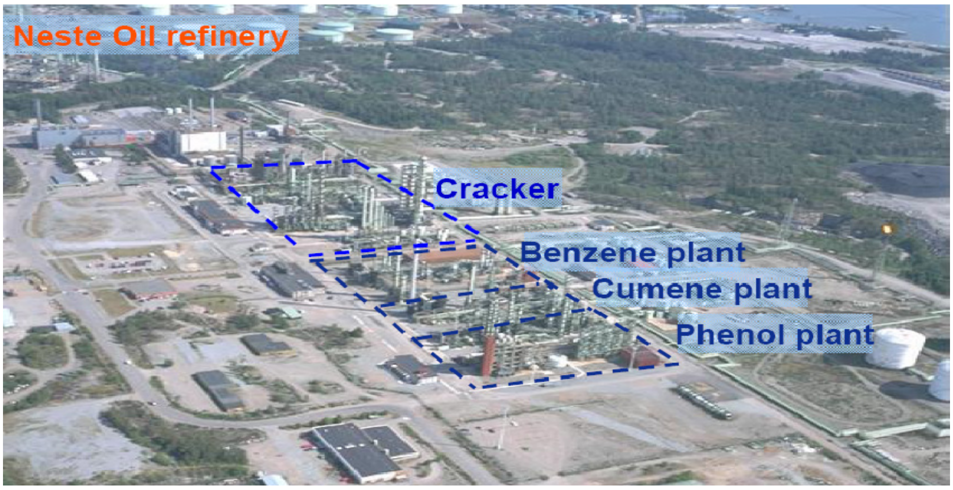

Figure 3 Petrochemical plants are located next to each other. Part of Neste Oil refinery can be seen in the upper part of the picture. Products from the cracker (ethylene, propylene, and butadiene) are transferred to plastic plants via pipelines. (Borealis Polymers 2010)

Production is continuous and products are transferred to customers in the Kilpilahti area via pipelines. Products delivered further away are transported by tank trucks, trains or ships. In addition to production plants in the Petrochemical plants, there are also feedstock and product tank areas. Feedstock and product tank areas are located to the right side of the production plants in Figure 3.

Feedstock are supplied by Neste Oil refinery or imported. Utilities needed in the production (steam, pressurized air, process water, cooling water and electricity) are produced by Neste Oil, Borealis or by other neighboring companies.

Waste water systems

The Borealis' plastic plants treats its own waste waters, but the Petrochemical plants discharge waste waters to Neste Oil's waste water treatment plants. The Neste Oil and The Borealis have a reciprocal agreement on the quality of waste waters. Waste water from Borealis has to fulfill some quality requirements before it can be discharged to the active carbon or to the biological treatment plant. The costs of the treatment is based on the quantity and load of the waste waters.

The waste water system in the petrochemical plant is divided into four physically different systems: Two systems for process waste waters, one for sanitary water and one for cooling water (Koski 1994). Two systems for process waters are phenolic waters and oily waters. The Phenol plant discharges its phenol containing waste water to phenolic waters. The cracker, butadiene, benzene, cumene and part of waste water from phenol plant are discharged to oily waters. Sanitary waters are discharged straight to biological treatment and will not be covered in this study. Sewerage systems are underground steel constructions, except for phenolic waters, which is on the ground (Borealis Polymers Oy 2007).

2 Goal and Scope

Knowledge of the existing systems was scattered, so this master's thesis was intended to collect and combine information about waste water sources to phenolic waters system and to oily waters system under one document. The waste water systems were analyzed under normal operation conditions. Oily waters and phenolic waters were examined separately, since these systems are not connected. The functionality of different analyzing systems of components or parameters was not included in the study. Phenomena taking place inside the process was left out as well as operation of Neste Oil's treatment plants.

2.1 Phenolic waters

For the phenolic waters system the goal was to find answers for following questions

- What is the quality of waste waters formed in process units?
- Which components in the biological feed stream, Biolsy, contribute to build-up of COD? Is it possible to find out the main contributing component with parameters Borealis analyze?
- What are the possibilities to reduce waste water load (without building own water treatment plant) based on the information of waste water quality acquired during the master thesis?

2.2 Oily waters

For the oily waters system the goal was to find answers for following questions

- What is the quality of waste waters formed in plants?
- Is there demand for new distribution of streams? Could some of the streams that are now treated in activated carbon plant, be treated more efficiently in biological treatment plant? This considers mainly phenol and nitrogen components found in the streams.
- Which components in the final stream (measured from pit 27) of OW-system contribute to the build up of COD? Is it possible to find out the main contributing component with parameters Borealis analyze?
- What are the possibilities to reduce waste water load (without building own water treatment plant) based on the information of waste water quality acquired during the master thesis?

3 Literature review

Literature review of waste waters from petrochemical plants was carried out in order to acquire information of what kind of waste waters originate from petrochemical plants and what components can be found in waste waters.

3.1 Components in petrochemical effluents

Industrial waste waters contain organic and inorganic pollutants. Waste water treatment facilities are nowadays effective to reduce the amount of pollutants in the waste water, but for example industrial accident may cause single release. (Botalova, et al. 2009) To be able to reduce the polluting effect on waste waters it is significant to know the quality of waste waters. The problem with industrial effluents is the great diversity of different chemicals and their isomers in waste waters which makes it difficult to reduce efficiently different pollutants from waste waters. Organic components presented in waste waters from petrochemical plants are usually hexanes, heptanes, higher alkanes, benzene, xylenes, acetonitrile, acrylonitrile, methanol, butanol, ethylene glycol, phenol and formaldehyde. (Danana Goud, Parekh and Ramakrishnan 1985) Botalova *et al.* had discovered in their studies for example pesticides, mono- and polycyclic hydrocarbons, polychlorinated biphenyls, phosphorous and sulphur containing compounds in petrochemical effluents. In Italy 16 different polyaromatic hydrocarbon compounds were found in low concentrations (1-5 µg/l) from petrochemical waste waters. (Botalova, et al. 2009) Lu *et al.* (2006) found more than 75 different hydrocarbons from the waste water from oil refinery including aliphatic hydrocarbons, aromatic hydrocarbons and heterocyclic hydrocarbons. 28 of these 75 hydrocarbons were detected in high concentrations in many sampling points. High-molecular-weight organic acids (HMWOA) which are aliphatic acids and aromatic acids were also found. (Botalova, et al. 2009)

The effects of different chemicals found in petrochemical effluents vary: petrochemical carbons may cause mutagenic activity, aromatic and PAH compounds may cause genotoxicity. Some of the pollutants are toxic at low concentrations. Also accumulation of different components to sediments or even to organisms is possible. (Castillo, et al. 1999) Botalova *et al.* (2009) states that there is overall lack of systematic investigations of petrogenic pollutants in industrial waste water and also their environmental relevance is not known. They also criticise that oil production industries and petrochemical industries concentrate too much on bulk parameters like total organic carbon (TOC), nitrogen (N), phosphorus (P), heavy metals and depending on their interests to some selected organic pollutants like chlorinated benzenes, phenols, estrogens, polyaromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), phthalates and tensides. EU has listed PAH components as priority components, which concentrations in waste waters need to be controlled. The problem is that the bulk parameters can quite easily be measured from waste waters but to analyze single compounds is difficult. (Sponza and Oztekin 2010)

Castillo *et al.* (1999) states that it is difficult to select the analyzing methodology and different standards because of the complexity of the samples. They studied effluents from various industries and found more than 50 different chemicals in industrial effluents from which almost half (21 chemicals) were present in petrochemical effluents. Castillo *et al.* found phenolic compounds, phthalates, aliphatic carboxylic acids, aromatic carboxylic acids, amines, alkanes and linear aliphatic alcohols. It is estimated that 70% organic components presented in total organic carbon (TOC) analyses cannot characterized. Castillo *et al.* (1999) came to conclusion that not all the chemicals in petrochemical effluents could be even identified.

3.2 Activated carbon waste water treatment efficiency

The literature review on activated carbon waste water treatment was conducted to find if some of the waste water streams, now treated in the activated carbon waste water treatment plant could be treated more efficiently in the biological waste water treatment. This considers only streams in the OW-system, which contain phenol and nitrogen.

In the activated carbon waste water treatment adsorption technology is used in removal of organic and inorganic contaminants from industrial effluents. A broad range of different materials can be used, but the material has to contain carbon (for example wood, coal, lignite, peat and coconut shells). Materials used in the activated carbon treatment have a large surface area, a micro-porous structure and high a degree of surface activity. Surface chemistry properties of materials can be differentiated with different activation practices. During activation, the less organized and loosely bound carbonaceous material is removed. This increases the inner particular surface and creates the porous structure because spaces between the elementary crystallites are created (Mohan and Pittman Jr. 2006).

The removal efficiency of the activated carbon treatment is dependent on the selected material, particle size, its activation practice and selected catalyst. Organic hydrocarbons, some heavy metals, biodegradable organic compounds and components not responsive to conventional biological treatment are suitable for activated carbon treatment. Also components toxic to conventional biological treatment like pesticides, phenols, and organic dyes can be treated in the activated carbon treatment. Also according to Hameed *et al.* (2008) the activated carbon waste water treatment is efficient in removal of phenol from the waste solution. The activated carbon can also remove soluble BTX-components (benzene, toluene and xylenes). The problem is that the activated carbon does not remove nitrogen. Waste water, containing residues of oil, is more suitable for activated carbon treatment than biological treatment, because oil in the effluent hinders the biological treatment in sewage works. (Marsh and Rodríguez-Reinoso 2006)

3.3 Chemical oxygen demand

The total load of Borealis' waste water to the Neste Oil's treatment plant is quantified by chemical oxygen demand. At the moment it is not known which components are included in the COD. Borealis is interested in identifying these, in order to know better how the COD could be reduced which would lead to lower costs.

This section first discusses the background of the COD method, then the relationship between actual COD and theoretical oxygen demand (ThOD) and finally the method to calculate the theoretical oxygen demand.

3.3.1 Background of COD method

Micro-organisms in natural water bodies consume oxygen when degrading organic matter to biomass. Biochemical oxygen demand (BOD) is a parameter which describes the oxygen consumption when micro-organisms “eat” organic mass. More organic load enters the water body, the more oxygen the micro-organisms will use for conversion. Large amounts of pollutants may cause oxygen loss in a water body and lead to harmful effects in nature so it is useful to know the oxygen consumption of waste water before discharge. BOD requires days to get the results and COD is used because it is a lot faster. So called standard methods for COD determination are open and closed reflux systems, where a strong oxidant is added to the water solution and is boiled in open or closed reflux for a few hours and then the amount of used oxidant is measured by titration methods. COD determination with standard methods take usually a few hours but colorimetric determination of COD require less than an hour. COD measures the organic content of solution (Belkin, Brenner and Abeliovich 1992). Due to its rapidity, the COD is used to measure the total amount of pollutants in water media. It is often used in water and waste water quality determination (Hu and Grassob, Water Analysis -Chemical oxygen demand 2005) .

The difference between the COD and the BOD is that in the COD, the amount of oxidant used for oxidation of organic components is measured, but BOD expresses the oxygen consumed by micro-organisms when the sample is kept five days in 20˚C degrees. The dissolved oxygen is measured in the beginning and in the end of the test and the oxygen consumption is the difference between amount dissolved oxygen in the beginning and in the end of the test. There is a correlation factor between the BOD and the COD so when the COD is known, the biochemical oxygen consumption in nature can be determined (Kwok, et al. 2005).

3.3.2 Determination of the COD

Usually a strong oxidant, like potassium dichromate, is used in this measurement. The standard method for determination of the COD is titration with open or closed reflux, where the sample is heated either in a closed or an open vessel in the laboratory. The sample is boiled for two hours in the presence of the oxidant. The amount of dichromate consumed can be determined when the difference in oxidant concentration in the beginning and in the end is determined. Potassium dichromate is considered to be the best oxidant because it has a strong oxidizing capability, it is applicable to many kinds of organic and inorganic matter and is easy to manipulate. Oxidation of inorganic components interferes with COD determination since they also consume dichromate.

In the oxidation process, the dichromate ion (Cr^{6+}) is oxidized to chromate (Cr^{3+}). The oxidation reaction of dichromate is shown in Equation 1 (Hu and Grasso, Chemical Oxygen Demand 2006).

Equation 1

$$Cr_2O_7^{2-} + 6e^- + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O$$

In practice, the colorimetric COD analysis is mostly used, which is a modification of the standard closed reflux method. In the colorimetric method, the change in dichromate and chromate concentration is measured as a colour change. The colour changes when the dichromate oxidation state is reduced from +6 (Cr^{6+}), which is orange, to chromates +3 (Cr^{3+}), which is green. The colour determination can be done in two different ways. One uses light of 420 nm wavelength, which determines the disappearance of Cr^{6+}. The other measures the absorbance at 600 nm to quantify Cr^{3+} (green). This method is based on the fact that the chromate ion strongly absorbs light with a wavelength of 600 nm, whereas dichromate has almost zero absorbance. Dichromate absorbs strongly at a wavelength of 420 nm, when chromate on the other hand absorbs weakly. It is recommended to use 600 nm wavelength when analyzing samples with high COD (between 100 and 900 $\mathrm{mg_{O_2}L^{-1}}$). The wavelength of 420 nm, which measures the decrease in absorbance, is recommended to be used with samples with a low COD (< 90 $\mathrm{mg_{O_2}L^{-1}}$). A decrease of absorbance directly correlates to Cr^{6+} concentration.

The COD values can be determined from a calibration curve. The desired range can be obtained by preparing standards with potassiumhydrogen phthalate. Different amounts of potassiumhydrogen phthalate are diluted in distilled (DI) water so that all volumes of the samples are equal. A reference liquid with only DI-water is also prepared. All standards are heated to 150 ºC degrees for a certain time to have time to react and their absorbance is measured against a blank sample when cooled to room temperature, giving a linear calibration curve (Hu and Grassob, Water Analysis -Chemical oxygen demand 2005).

3.3.3 Interferences with the COD method

Inorganic constituents interfere with the COD analysis. COD is used in determination of the organic content of a solution and inorganic compounds like ferrous, sulphide, manganese or nitrite in a sample give falsely high COD. This is because inorganic compounds and free halogens like S^{2-}, Br^{-}, I^{-}, Fe (II), Mn (II) and Ni(II) will be oxidized and hence reduce the dichromate in the sample solution (Hu and Grasso, Chemical Oxygen Demand 2006).

Halogen ions cause problems in combination with ammonia. On its own, ammonia does not contribute to the COD since it cannot be oxidized. Problems occur with free halogens because then ammonia creates falsely high COD (Lu, et al. 2006). Free halogens, like chloride and bromide ions, are usually considered as a group of chemicals which have the same effects and act similarly with different catalysts in the COD determination, but lately that was discovered to be wrong. While the interference of chloride can be corrected with certain catalyst the same catalyst does not correct the interference of bromide (Belkin, Brenner and Abeliovich 1992).

Different catalysts have been introduced to correct these interferences. Silver sulphate catalyst is added because otherwise long chain carboxylic acids will not be fully oxidized. The oxization may not be complete even when a catalyst is present (Baker, Milke and Mihelcic 1999). This may cause some problems if the waste water contains chloride because chloride reacts with silver sulphate and generate silver chloride, which precipitates from the solution and results in a negative interference. On the other hand, chloride, bromide or iodide may cause an overestimation of the COD when these react with dichromate. Mercury sulphate can be used to minimize this effect (Hu and Grasso, Chemical Oxygen Demand 2006).

Mercury sulphate can also be added to a sample to form a complex with chloride and in that way reduces its interference. Mercury sulphate, $HgSO_4$, forms a stable complex ($[HgCl]^{2-}$) with chloride. The problem is that it cannot be measured how much of the chloride reacts with mercury sulphate and how much is oxidized (Lu, et al. 2006). Belkin *et al.* (1992) has also demonstrated in their study that even though mercury sulphate works with chlorine it does not work with bromide.

Sulphuric acids and silver sulphate improve the oxidation of nitrogen compounds in the sample. Compounds including nitrogen, like ammonia (NH_3), may cause positive interference when high amounts of dichromate is used. Sulphuric acid may on the other hand improve the evaporation of volatile compounds from the solution and cause interference since only the compounds present in the solution are measured with COD (Baker, Milke and Mihelcic 1999).

The COD method is accurate for solutions containing more than 50 $mg\ O_2\ l^{-1}$ (Baker, Milke and Mihelcic 1999).

3.3.4 Correlation between ThOD and COD

Theoretical oxygen demand (ThOD) determines stoichiometrically the amount of oxygen needed to oxidise a compound to its end products including carbon dioxide, ammonia and water. Janicke (1983) tested 582 compounds of their oxidizabilities. Oxidizabilities were tested with permangate in acidic solution and with dichromate /H_2SO_4 both with and without using Ag^{+} as a catalyst. The dichromate method with the mercury catalyst was proved to be efficient in determining the COD most accurately. Organic compounds have the correlation of 100% between ThOD and COD. Due to this, Janicke (1983) suggested this method to be used in analyzing industrial effluents. With the permanganate method, on the other hand, correlation was only 10 %, meaning the COD value was only one tenth of ThOD and thus not suitable to be used when analysing industrial effluents (Janicke 1983).

COD can be estimated from ThOD by using Equation 2, where *a* is an empirical constant, thought to be between 0.95 and 1. This means that the real COD is between 95% and 100% of calculated ThOD. While Janicke (1983) gives an empirical constant to every compound separately, Baker *et al.* (1999) gathered different compounds into chemical classes and studied correlation of whole chemical classes.

Baker *et al.* (1999) did the study in order to make it easier for industries with a lot of chemicals, to calculate their COD. When the COD is determined from the ThOD for a chemical class it is important to know whether the empirical constant is near 0,95 or 1, and how well the ThOD correlate the real COD value for certain classes of chemicals. Baker *et al.* (1999) found out that an average value for *a* is 0,85 when standard deviation was 0,33 for all the 565 chemicals. But the value of the empirical constant is different for different kind of chemicals and it was found out that *a* varied between different chemical groups (Baker, Milke and Mihelcic 1999).

Equation 2

$$COD = a \cdot ThOD$$

Baker *et al*. (1999) studied the correlation of the ThOD and the COD for 565 components, which were divided into 64 different chemical classes. The background information was Janicke's study. A statistically reliable method to study how well the COD and the ThOD correlated for different chemical classes was constructed with help of mixed beta-normal distribution. The result was that the data were divided into six groups accordingly to how well the COD correlated to the ThOD. The six groups are: well-correlated aromatics, well-correlated non-aromatics, potentially well-correlated aromatics, potentially well-correlated non-aromatics, other aromatics and other non-aromatics (Baker, Milke and Mihelcic 1999).

Baker *et al.* (1999) had three criteria to select chemical classes to the "well-correlated" group. Firstly, there should be at least six chemicals in the class to leave out classes with only few chemicals. Secondly, there should be a 95% confidence that population mean of a would be between 0,95 and 1,1 for the class as a whole to make sure that the chemical class had a near the 1. A third criterion was that chemicals with a less than 0,8 or a more than 1,2 were only less than 10% of all chemicals in the class. The result was that 210 chemicals out of 565, representing 13 different classes, had a good correlation.

Baker *et al*. (1999) also studied the chemicals and chemical groups that did not fit into chemical classes that correlated well. They found out that some chemical classes had potential to also correlate well, with few exceptions. That is why they created two additional groups: potentially well-correlated aromatics and potentially well-correlated non-aromatics. Baker *et al.* (1999) used three additional criteria to select chemical classes into these groups. The chemical class was potentially well correlative if the class met all the criteria for well-correlated data, but had less than seven chemicals in the class. A chemical class that had data for between seven and 19 chemicals were potentially well correlated, if removal of one outlier allowed the class to meet the criteria for well-correlated data. A chemical class that had data for more than 19 chemicals, and met the criteria for well correlated data when two outliers were removed, could be classified as potentially well-correlated. There are altogether eight chemical classes presenting 67 chemicals in potentially well-correlated groups (Baker, Milke and Mihelcic 1999).

The study of Baker *et al.* (1999) declared that the COD for the chemicals, present in group one and group two (well-correlated data), equals directly to the ThOD. For chemicals in group three and group four (potentially well-correlated data) the COD can be estimated from the ThOD and no correlation for chemicals presented in group five and group six could be determined. With chemicals presenting group five or group six, the empirical constant a should be individually determined for every chemical. Important chemicals in group five are for example some hydrocarbons like benzene, toluene, xylenes and styrene. Important chemicals in group 6 were for example alkanes, alkenes and aldehydes. Baker *et al.* (1999) gives a full list of correlation factors for COD/ThOD of chemicals presented in groups five and six. Chemical classes according to their correlation are shown in Appendix A.

Compounds normally analyzed from Borealis' waste waters, their theoretical oxygen demand and their COD/ThOD correlation factor as well as class of correlation factor are given in Table 1.

Table 1 **Four of the components that Borealis analyzes from waste waters, belong to class 1 or class 2 components, which means that these components' COD correlate well with the calculated ThOD (Baker, Milke and Mihelcic 1999).**

Component	**Theoretical oxygen demand (ThOD)**	**Correlation factor , a, (COD/ThOD)**	**Class of correlation factor**
	$gO_2\ g_i^{-1}$	-	-
Acetone	2,20	0,92	4
Acetonitrile	1,56	0,92	4
Benzene	3,07	0,65	5
Cumene	3,19	0,76	5
Ethylene glycol	1,29	0,97	2
Methanol	1,50	0,97	1
m-xylene	3,16	0,58	5
o-xylene	3,16	0,72	5
Phenol	2,38	0,98	1
Propanols	2,66	0,97	2
p-xylene	3,16	0,5	5
Toluene	3,13	0,4	5
MHP	0,67		

3.3.5 Determination of the theoretical oxygen demand

The Thod can be obtained for different chemicals from different studies. Janicke covers most of the chemicals but not every chemical. Because the late arrival of the data and because theoretical oxygen demand was not determined for all the chemicals found in the waste waters, the ThOD was determined to every chemical with the method presented in study of the Baker *et al.* (1999).

Borealis' two waste water systems operate separately, but the technique to determine the COD is similar. To determine the oxygen consumption of all the components, the oxygen demands of single components were summed together and compared to measured COD.

Every component has its own ThOD which is consumed when one gram of a compound is oxidized to end products, hence the compounds concentration affects oxygen demand. Data of concentration of different chemicals in the waste water was obtained from Borealis' own database LIMS.

According to J. Lu *et al.* (2006), the residual ThOD is the sum of a single component's theoretical oxygen demand in a certain concentration (Equation 3).

Equation 3

$$\Sigma ThOD = \sum_{i}^{n} ThOD_i = \sum_{i}^{n} (ThOD_{0,i} \cdot c_i)$$

The total oxygen demand of a single component with a certain concentration is represented with $ThOD_i$ and it is determined with Equation 4. Concentration of a component is represented with c_i (Lu, et al. 2006).

Equation 4

$$ThOD_i = ThOD_{0,i} \cdot c_i$$

To determine the $ThOD_i$, the oxygen demand per one gram component *i* has to be determined. Oxygen demand per one gram component *i* is represented with $ThOD_{0,i}$ and determined with Equation 5 where b_i is the amount of oxygen consumed in moles per one mole component *i*, M_i is the molar mass of a single component *i, M_{O_2}* is the molar mass of an oxygen molecule.

Equation 5

$$ThOD_{0,i} = \frac{b_i}{M_i} \cdot M_{O_2}$$

According to Baker *et al.* (1999) the amount of oxygen consumed by single component *i* can be determined with Equation 6 (Baker, Milke and Mihelcic 1999).

Equation 6

$$b = n + \frac{m - k - 3j - 2i - 3h}{4} - \frac{e}{2} + 2i + 2h$$

Variables *n, m, k, j, i, h* and *e* can be determined with Equation 7. According to Baker *et al.* (1999), Equation 7 assumes that all compounds are oxidized totally to end products. For example organic nitrogen is converted totally to ammonia (NH_3) and carbon, phosphorus and sulphur are oxidized according to Equation 7. In Equation 7 the X represent the sum of all halogens.

According to Lu *et al.* (2006) it can be estimated that ferrum, manganese and nickel exist in waste water in the form of Fe (II), Mn (II) and Ni (II) and that they are oxidized to Fe (III), MnO_2 and Ni (III) respectively. Carbon and hydrogen are oxidized mainly to carbon dioxide and water. Halogen ions like Cl^-, Br^- and I^- are oxidized to Cl_2, Br_2 and I_2. Sulphur (S^-) is oxized to SO_4^{2-}.

Equation 7

$$C_nH_mO_eX_kN_jS_iP_h + bO_2 \rightarrow nCO_2 + \left(\frac{m - k - 3j - 2i - 3h}{2}\right) H_2O + kH_x + jNH_3 + iH_2SO_4 + hH_3PO_4$$

4 Methods

In this section the methods used to assess both waste water systems is presented.

4.1 Phenolic waters

4.1.1 Qualitative system analysis of phenolic waters

Qualitative system analysis of the phenolic waters concentrated on studying and determining the waste water sources to the biological feed stream biolsy. The method to find out the necessary information, familiarize oneself with existing documentation as well as to interview plant personnel.

4.1.2 Supplementary onsite measurement program of phenolic waters

According to the results of the qualitative system analysis (presented in the results section) the main contributors to Biolsy were outlet of MHP-reactor and outlet of effluent stripper (later on called stripper). Extra samples were taken on February 21st and 23rd and March 7th from these two origins as well as from biolsy. Samples were analyzed in Borealis' petrochemical's laboratory.

One litre of water from every sampling point was taken in a one-litre glass bottle. Samples were analyzed on the same day of sampling. Analyzing methods are described in section "Methods used in Borealis' petrochemical laboratory".

The MHP-reactor outlet had a sampling unit. The glass bottle was placed in a vortex in the sampling unit and the bottle was filled with water by pressing the handle, as shown in Figure 4.

Figure 4 Sampling unit of the MHP-reactor's outlet

The stripper also had a sampling unit. A glass bottle was placed under the nozzle and a valve was opened to get the sample. The sampling unit of the stripper is shown in Figure 5.

Figure 5 Stripper sampling point.

The sampling unit of the biolsy is shown in Figure 6. The glass bottle was placed on a liftable level and lifted tightly to the sampler. The water sample was pumped to the bottle with a manual pump.

Figure 6 **Sampling unit of the biolsy**

4.1.3 Supplementary external measurement program of phenolic waters

The results of the supplementary onsite measurement program of the phenolic waters established a need for more specific analyzing, than could be performed in the Borealis' petrochemical laboratory, for two reasons. Firstly, the ThOD calculations did not equal to the measured COD. Secondly, the quality of waste waters from different sampling points could not be analyzed accurately enough for this study in the Borealis' petrochemical laboratory.

The sampling points remained the same in the supplementary external measurement program. Two set of samples were sent to SGS Inspection Service. The first sample was taken on March 7th and the second on April 5th. Samples were taken in two one-litre glass bottles and in one 100 millilitre Dopac-bottle from biolsy, the outlet of the MHP-reactor and the outlet of the stripper. 100 ml sample bottle was filled so that there was no space for air. This is important in order to analyze volatile organic compounds, which escape from water to airspace due to their hydrophobic nature. Both sets of samples were sent to analyzing during the day the samples were taken.

Figure 7 **Pictures of the waste water samples from right are: the biolsy (BIOLSY), outlet of the stripper (DA-18920) and outlet of the MHP-reactor (DC-18920)**

4.2 Oily waters

4.2.1 Qualitative system analysis of OW-system

Waste waters system for oily waters was much more complicated than phenolic waters because all five plants discharge water to the OW-system. The qualitative system analysis of the OW-system studied waste water sources in the different plants. The method to find out necessary information was to familiarize oneself with existing documentation as well as to interview plant personnel.

4.2.2 Supplementary onsite measurement program of OW-system

According to the results obtained from the qualitative system analysis of the OW-system, four sampling points were selected: outlet of the diluting steam generator in the cracker, outlet of the acetonitrile (ACN) recovery column in the butadiene plant, outlet of the OW-stripper in the benzene plant and the pit 27 which is the last checkpoint for Borealis' OW-system's waters before the water goes to the Neste Oil's active treatment plant. In the beginning of March, the weather was still cold enough so there were neither melting waters nor rain waters entering the system. Supposedly all water that entered the OW-system came from these three process water sources, so analysis of these three sources should give a picture of how the total load is distributed between the plants. Samples were analyzed in Borealis' petrochemical's laboratory. Analyzing methods are described in section "Methods used in Borealis' petrochemical laboratory".

The diluting steam generator was selected since it is the discharge point of the cracker's process water to the OW-system. The water is contaminated with process chemicals and the flow is continuous (Hyrsylä 2010).

Figure 8 **Sampling point of the diluting steam generator**

A water sample from the butadiene ACN-circulation was seen as important since this is the only place that discharges directly to the system from the butadiene plant (Hyrsylä 2010).

Figure 9 **Acetonitrile recovery column sampling point**

The outlet of the OW-stripper was selected since the most of the load from the benzene and the cumene plants go through the OW-stripper before being discharged to the OW-system. The OW-stripper situated in the benzene plant is not same with effluent stripper situated in the phenol plant. A sampling point was selected to find out the aromatics contribution to the total load. No distinction between the benzene and the cumene plants was necessary since neither of these processes have process water circulation.

Figure 10 OW-stripper outlet sampling unit

4.2.3 Supplementary external measurement program of the OW-system

More specific analyzing of waste waters discharged to the OW-system was needed for two reasons. Firstly, the theoretical oxygen demand calculations did not equal the measured chemical oxygen demand. Secondly, the quality of the waste waters from different sampling points could not be analyzed accurately enough for this study in the Borealis' petrochemical laboratory. A new waste water research plan was constructed for the OW-system and according to that, new sampling points were chosen. Selection of sampling points was based on the OW-system analysis and on meetings and negotiations with plant managers, engineers and process plant operators. The number of sampling points increased from four to twelve. The sampling method was also changed according to requirements. Instead of taking the samples from the outputs of the different process units, different pits in the OW-sewer were selected. Pits were selected as sampling points because a snapshot method in sampling was used. The snapshot method was used in order to get all the samples from similar process conditions. Taking the samples from the outputs was not possible for the snapshot method because of non-simultaneous nature of discontinuous flows. Taking samples from the outputs would also have increased the number of samples significantly. One example of a sampling point is shown (the pit BZN-1), since all the sampling points were similar. Only the pit OSBL-15 was not a weir dam type pit, but a normal pit without weir dam. All the main water sources to the OW-system are gathered in Appendix F.

Three sets of samples were sent to SGS Inspection Service. The first set of samples was taken on Mars 28th, the second set on April 4th and the third set on April 12th. The processes are large, so a retention time of one week was selected because it takes time before changes in process conditions result in changes in the waste water quality. If all samples were taken very closely to each other, during one week, it would not matter whether there were one or three sets of samples taken since all the samples would present the same process condition. In every three sets, every plant was working under normal process conditions.

On March 28th the cracker had a heat exchanger wash and water from washing was discharged to C-10. On April 4th there was a little hydrocarbon leakage from some of the plants, and it was detected along the OW-systems ISBL-branch which goes through all plants. Sample date April 11th had to be changed to April 12th because the shut-off valve after outlet of pit BZN-2 was closed and had to be opened and the system needed time to normalise before it could be analyzed.

The volume of one water sample was 2,1 litres. Two litres of water were taken to either two one-litre glass bottles or to four half-litre glass bottles. Also a 100 millilitre sample was taken into a Dopac-bottle. The Dopac-bottle was filled so that there would be no air, in order to prevent separation of volatile compounds dissolved in water. All other places except outlet of the OW-stripper were taken from the pits. In the OW-stripper the bottle was placed in the sampling unit as described before and shown in Figure 10. A glass bottle was placed in the sampler and dropped to the pit with help of a drag-line. The sampler was dropped to a one meter depth in those sampling points that had a high level of water (pit-27, BU-1, BZN-1, and C-13). In other sampling points there was less water and sampling was a little bit more difficult. The sampling procedure is shown in Figure 11.

Figure 11 The glass bottle was dropped into the pit and lifted out with help of a drag-line.

During the study, the valve in the outlet of OSBL-13 was closed, all the water from aromatic side goes through the OW-stripper and pit BZN-1 and does not enter OSBL-branch. BZN-1 is so called weir dam.

The weir dam type pit is illustrated in conceptual drawings in Figure 12 and Figure 13. Figure 14 shows the weir dam BZN-1. First water is led to the reservoir side of the pit which is not directly connected to the sewer system. The water level will rise in the reservoir and then finally flow over the weir dam and join the OW-system's ISBL-branch in the by-pass side. The reservoir side collects the water from a particular plant or area, while the main stream runs on the bypass side. Water level on the bypass side is in much lower level than on the reservoir side.

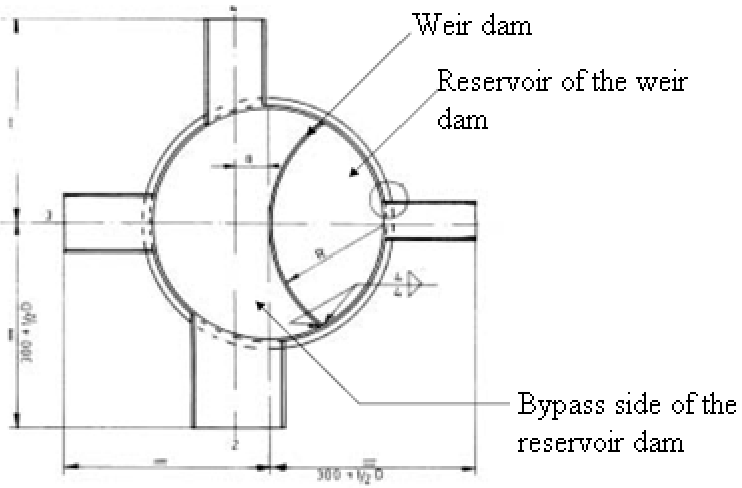

Figure 12 Conceptual drawing of a weir dam type pit. This figure present the weir dam type pit from above.

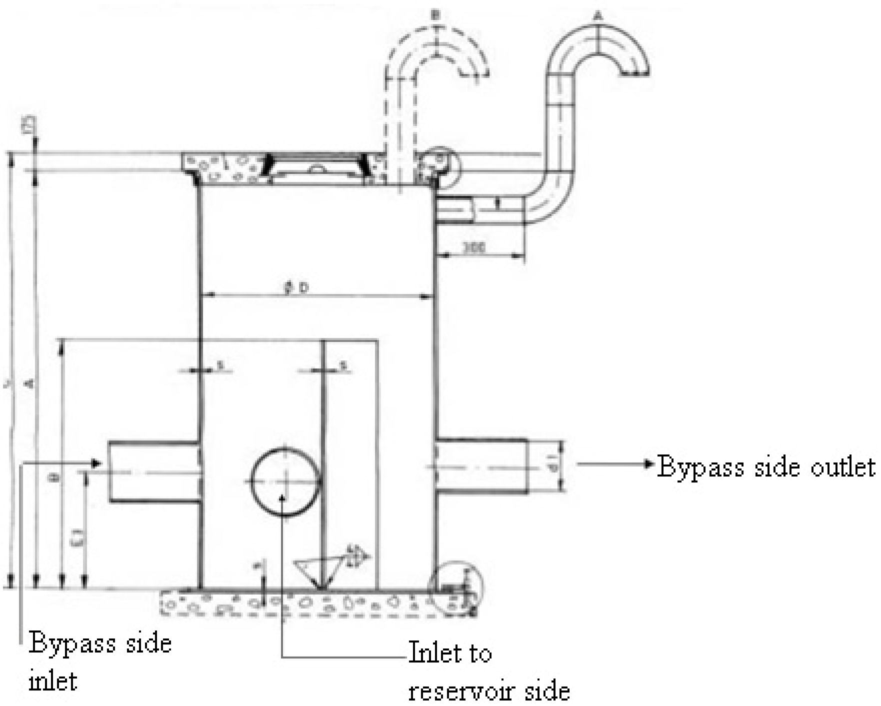

Figure 13 **Conceptual drawing of a weir dam type pit from the side.**

Figure 14 **Reservoir of pit BZN-1 has higher water level, when reservoir has reached the maximum water level, it will flow over weir dam.**

From the benzene plant, the OW-stripper was also selected to be one of the sampling points. This was done in order to separate the contribution of load between process plants on the aromatics side. Rain water from spill basins of the aromatic's feedstock tanks, water from benzene and cumene processes, rain water from paving areas and part of the rain water from the benzene's ISBL-areas paving are treated in the OW-stripper. Waters from the aromatics side that are not treated in the OW-stripper, are another part of the benzene's paving waters, all rain water from paving areas in the cumene plant, rain water from paving area in phenol plant that do not have phenol contamination possibility and ejector waters from the phenol plant. The ejector waters are discharged to the OW-system via pit PHE&CUM-15. Selection of sampling points OW-stripper and pit PHE&CU-15 was based on the need to separate origin of components entering the OW-system from the aromatics side.

Selection of the pit BU-1 was based on the result from the OW-system analysis that all the waters from the butadiene plant go through the BU-1. The pit BU-1 is also a weir dam type pit where the water from the butadiene plant enters the ISBL-branch when it flows over the weir dam.

Both the ISBL and the cracker branch collect waters from the cracker. The cracker has four side branches which connect to the cracker branch, which again interconnects to the ISBL-branch. The cracker has also four side branches that interconnect straight to the ISBL-branch so its waters do not enter tothe OW-system through one pit. To assess the cracker's contribution to total load, and how load is distributed inside the cracker, four sampling points were selected: C-8, C-9, C-10 and C-13.

One sample was taken from the OSBL-branch to get an idea of what kind of components may enter the system from the OSBL-area. A sample was taken from the pit OSBL-15 since all the waters from the OSBL-area go via this pit. Shut-off valve on the outlet side of OSBL-13 is closed so no waters enter the OW-system from the aromatics side via the OSBL-branch. All components entering the OW-system from the OSBL-branch originate in the cracker.

Also Neste Oil's power plant discharges its waters to the OW-system. Because of difficulties in sampling, as well as the confusion of the marking of the pits, the sampling point was not always the same. On March 28th the sample was taken from the pit 22, but since there was not enough water, an additional sample was also taken from the pit 24 (old type pit). On April 4th the sample was taken from the pit 23 which is situated next to the pit 24 and on April 12th the sample was taken both from the pit 23 and the pit 24. The problem with the pit 23 is that there is a lot of oil and the water level is low for taking samples. The problem with pit 24 is that the load from the power plant cannot be separated from other load from Borealis' side.

The last sampling point in the OW-system was pit 27, the last checkpoint for analysis of the quality of waste waters entering the activated carbon treatment plant. In Borealis' ongoing analysis of waste waters, fractional sampling is used since it gives a more whole picture of the waste waters. Fractional sample could not be used in this case since there was not enough material in the sample.

Samples left Borealis either during the same day or in the day after, for analysis. Samples taken on March 28th left Tuesday 29th of March as well as samples taken on April 4th left Borealis the day after. The last set taken on Tuesday April 12th was sent to analysisduring the same day.

Figure 15 Water samples from the first set on 28th of March (the OW-system)

4.3 Waste water analyzing methods

4.3.1 Methods used in Borealis' petrochemical laboratory

Borealis's petrochemical's laboratory's analysis methods are described in this section. All the results from the analysis were fed manually to laboratory software LIMS. Waste waters analysis in Borealis consisted of determination of pH, dissolved organic carbon (DOC), total nitrogen, volatile organic hydrocarbons, water soluble compounds (methanol, acetone and acetonitrile) and chemical oxygen demand.

pH-determination was done with Metrohm pH meter 744 which measure both pH and temperature of the water. The sample did not need to be prepared, the analyzer was placed in the water and the result read from the screen.

The colorimetric-method was used for determination of the COD_{Cr}. Cr means that it was the dichromate method. The analyzer consisted of incubator (HACH Dr Lange HT200S) and colorimetric analyzer (HACH Dr Lange DR2800). 2 ml of water was taken if the sample could be considered as rather clean (basically this concerned samples from the OW-system), and injected to the HACH LCK 514 tube. If the water sample was expected to contain more pollutants (phenolic waters), then 0,2 ml of sample was injected to the HACH LCK 914 tube. In both cases, HACH-tube was first shaken and then placed in incubator. The COD-tube was kept for 15 minutes in 150 ºC degrees in incubator. When the tubes were cooled down they were placed in spectrophotometer, where the colour of the solution was analyzed with 605 nm wavelength. The theory of colorimetric determination is explained in section “Determination of the COD”. The COD result was given in milligrams per litre (Borealis Polymers 2008).

The phenol concentration of the water sample was measured with the spectrophotometric method. A sample of 1 ml injected into a 50 ml volumetric flask, and 20 ml of disodium tetraborate, 1 ml of 4-aminoantipyrine and 1 ml of ammoniumpersulphate were added. Alkaline aminoantipyrine solution formed a red or red-brownish colour with phenol and phenolic compounds. The water samples were left for five minutes to react. After five minutes, the graduated glass was filled with distilled water so that the total sample volume was 50 ml. Also a blank solution was prepared the same way, only waste water was left out. Phenol concentration was analyzed with spectrophotometric determination (UV-VIS spectrophotometer). Wavelength 505 nm was used to measure colour appearance. The method was suitable for a phenol concentrations of 10-250 mg/kg. Higher phenol concentrations used only 0,2 ml of sample in the analysis (Borealis Polymers 2000).

Total organic carbon, dissolved organic carbon and total nitrogen were measured with a gas chromatograph (GC). The GC method is a physical separation method between two phases. One of the phases is stationary while the other is the carrier phase. The stationary phase remains stationary while the carrier phase is moving into a defined direction. Components’ affinity to the stationary phase result in different retention times, which were captured by the detector (Borealis Polymers 2000). A sample of 20 ml was filtered and injected into an ampoule. A GC-tubing was inserted into the ampoule. The right method was selected from the computer and the analyzer sucked the right amount of sample and analyzed total organic carbon, dissolved organic carbon and total nitrogen. A standard was set to the analyzer once a day, which night shift operators took care of (Wörlin 2011).

Volatile organic hydrocarbons like benzene, toluene, styrene, xylenes and cumene were analyzed with the head-space method and external standard technique (ESTD). An amount of 10 mg of sample was injected into the ampoule. The ampoule was placed into the analyzer where hydrocarbons dissolved in water were vaporized. Gas phase was then automatically injected to the GC. GC measures the amounts of different components in the waste water.

Acetonitrile, methanol and acetone concentrations were analyzed with different GC. Methanol and acetonitrile were analysed also with help of an internal standard technique (ISTD). Used carrier was nitrogen (Borealis Polymers 2000). An amount of 20 mg of sample was injected into the ampoule and five millilitre of ISTD-solution or five microlitre of n-butanol was added. The sample was shaken and 0.4 µl was manually injected into the GC.

4.3.2 Methods used in Neste Oil’s laboratory

Waste water quality of the phenolic waters was analyzed in Neste Oil’s laboratory (Fortum in 2004) in November 2004 and in Mars 2005.

Organic components were analyzed from waste waters. In 2005, also nitrite, nitrate, sulphate, phosphate, chloride and bromide were analyzed. Phenol, methanol and COD were not analyzed because these parameters were not requested. The results are partly quantitative. Analysing methods were gas chromatography and gas chromatography mass spectrometry (GC-MS). The calibration was performed on ketones and carboxylic acids in general. Other analyzed parameters are quantified with ketone calibration.

4.3.3 Methods used in SGS Inspection Service’s laboratory

Waters analyzed in the SGS Inspection service are not discussed in depth. Analyzed parameters and methods used by SGS Inspection Service are listed in Table 2.

Table 2 **Analysing methods in the SGS Inspection Service**

Parameter	Method
Volatile organic compounds	ISO 11423-1
Polyaromatic hydrocarbons	SFS-ISO 18287
Oily hydrocarbons	SFS-EN ISO 9377-2
Water soluble compounds	EPA-8015
Phenols	SO 8165-2
Volatile fatty acids	In House HPLC/UV
Anions	DIN EN ISO 10304-1
Total nitrogen (NO3, NO2, Kjeldahl-nitrogen)	DIN EN 25663
Formaldehyde	HPLC DNPH (internal method)
Chemical Oxygen demand (CODcr)	DIN 38409-41
Solid matter	SFS-EN 872
Metals in water	ISO 11885
pH	SFS 3021
Alkalinity	SFS 3005
Mercury	SFS-EN 1483

5 Results and discussion

5.1 Phenolic waters

5.1.1 Waste water sources to the phenolic waters

Phenolic waters originated only from the phenol plant. The water is used in the processes in cleavage product wash and sodium hydroxide (NaOH) wash, where hydrocarbons are washed from process stream. These process units are integrated and water from these sources exits to biolsy (biological treatment feed stream) through an effluent stripper (from now on only called stripper). When cumene is oxidized in the phenol process, small amounts of effluent streams that contain biocides are formed. Biocides are broken down in the MHP-reactor. The water from the MHP-reactor is discharged straight to biolsy.

5.1.2 ThOD analysis for the components present in the phenolic waters

The known components are the components Borealis continuously analyses from the waste water. Results from the biological treatment feed stream, biolsy, were analyzed. As it can be seen from Figure 16, the chemical oxygen demand is mainly between 10 000 and 15 000 $mgO_2\ L^{-1}$ during the studied period.

The variation between April and June is a result of a shutdown in the phenol plant. The shutdown started in the beginning of April and lasted about month, but influenced the waste water COD load up till the beginning of June. Waste water data was first studied so that first all the data was included, from the studied period year 2010 and the same data was studied in such a way that the shut down time was neglected to get results which are more representative for normal operating conditions.

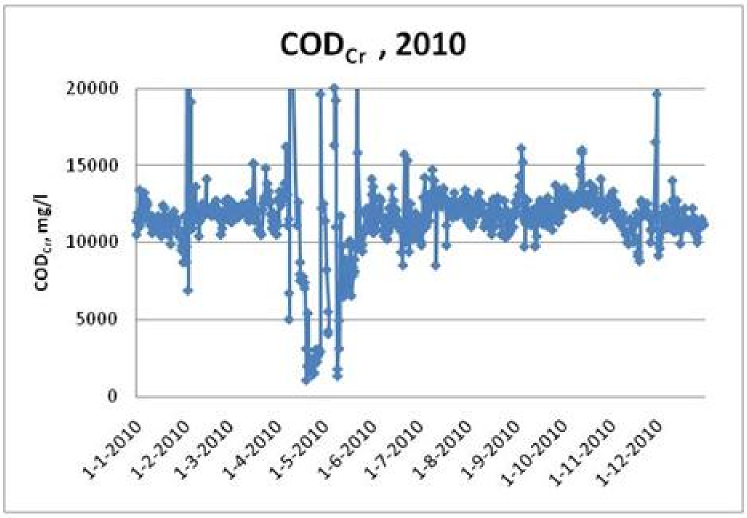

Figure 16 COD load variation in Biolsy during the studied period.

The concentrations of the components and the correlation between concentration and COD

First the variation of COD-values was studied in order to find out whether the concentration changes of one component in the waste water would respond to the variation of COD-load in the biological feed stream. Concentrations of different chemicals were studied to find out if there was a correlation between some of the components and COD.

In Figure 17, Figure 18, Figure 19 and Figure 20 the COD and the concentration of different components analyzed from waste water are shown. These figures show that there is no seasonal variation.

The concentration differences of the components are quite large and because of that the results are shown in separate figures. Methanol and phenol concentrations and COD-load during studied period are shown in Figure 17 and in Figure 18.

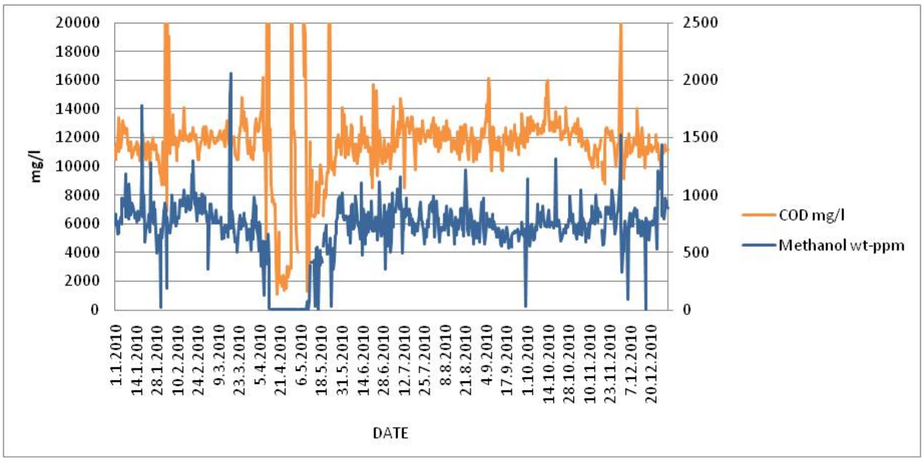

Figure 17 Methanol concentration and COD variation during the studied period. Methanol is shown on the secondary axis.

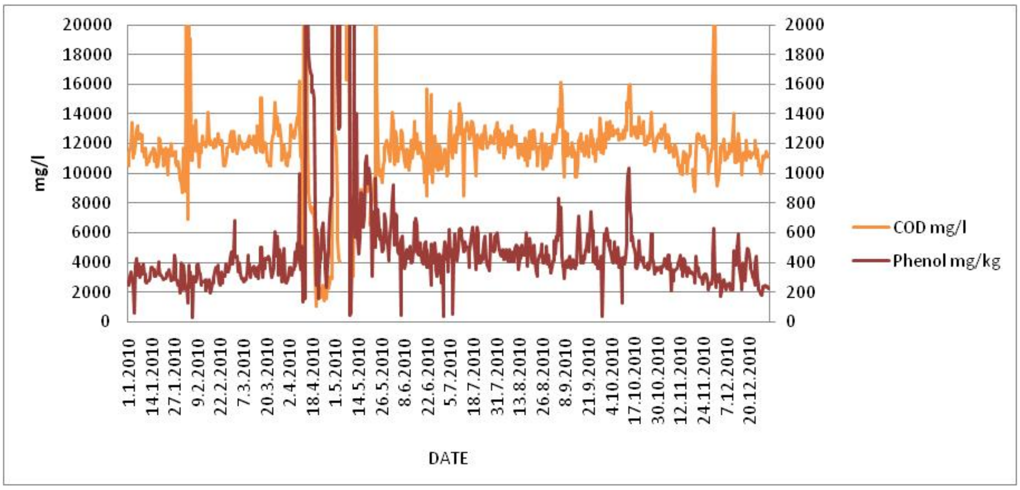

Figure 18 Phenol concentration and COD variation during the studied period. Phenol is shown on the secondary axis.

Volatile organic compounds appear in concentrations of 0.1 $mgO_2\ L^{-1}$ during the studied period. Few exceptions can be found, and these did not seem to have any impact on the COD load, mainly because these were in low concentrations. Only the concentration of cumene increased in waste waters now and then. Variation of volatile hydrocarbons concentrations are shown in Figure 19.

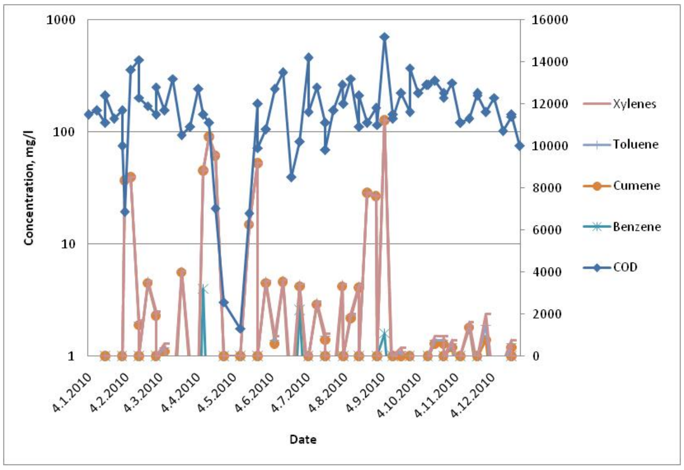

Figure 19 Concentration changes of volatile organic compounds in waste water and COD variation in studied period. Concentrations of the components are shown on the primary axis and the COD variation on the secondary axis.

Concentration of ethylene glycol was under 20 ppm and concentration of acetone was under 100 ppm during the studied period (see Figure 20).

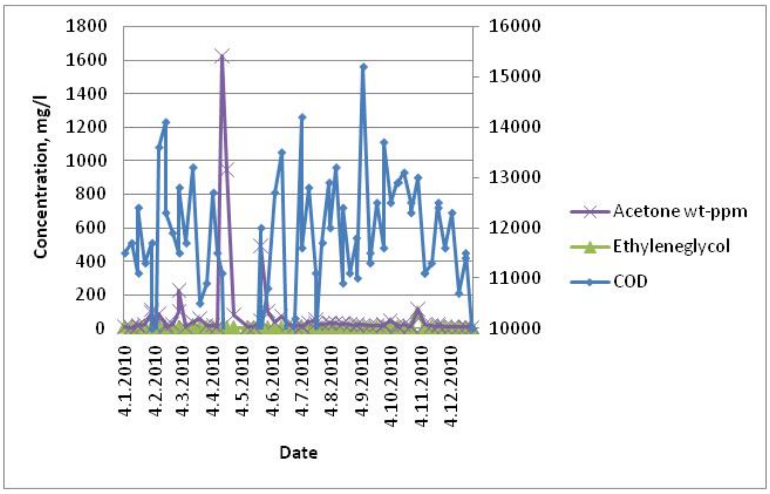

Figure 20 Concentration of acetone and ethylene glycol and COD variation in studied period. COD variation is shown on secondary axis.

In Figure 21 it is shown that while COD increases, the concentration of phenol increases as well, while methanol concentration do not change significantly. This indicates that the concentration of phenol affects COD. Again, there are different components with different concentrations so figures are studied separately.

The regression "R square or R^2" describes the fit of the data, if is it near zero the data cannot be used to make a correlation between data, and if the R^2-value of the data is one, it is possible to make a fit to describe the correlation between concentration of components and COD.

Phenol and methanol were the components present in highest concentrations in biolsy. It was of interest to examine if one could make a fit based on concentrations of these components could be determined, so that COD could be predicted with help of concentrations of components. The results are shown in Figure 21 for phenol, and in Figure 23 for methanol.

In Figure 21 the phenol concentration and the COD variation seem to have two different trends (marked with two red lines in the figure). Both correlate with COD but differently. One ascends straight up while the other increases more linearly. Because of this different behaviour the data points do not fit to the trend line, but are dispersed instead. The result is that a fit cannot be done, because similar concentrations of phenol may result in very different COD-load.

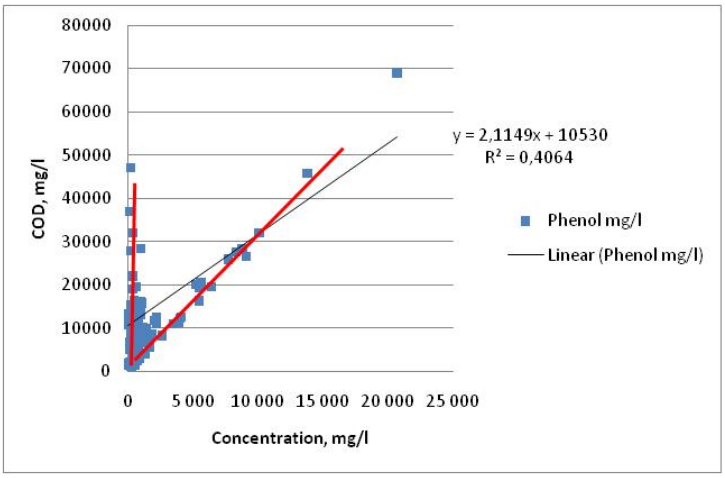

Figure 21 Phenol's concentration was mostly under 10 000 ppm. The data points are spread and no useful fit between concentration of phenol and COD-value can be done.

When the shutdown time is neglected, most of the COD values set between 17 000 ppm and 8000 ppm. Altogether five COD values were outside these limits: four highest COD values were over 19 000 ppm and one ,the smallest, COD value was 6800 ppm. These values could be considered as outliers and where removed to get more reliable data of how phenol and COD variation correlated. The values of phenol concentrations were more evenly distributed after the reduction of shutdown time and the outliers (see Figure 22). Editing the data this way did not make it more usable for predicting the COD value from phenol concentration, but gave an answer that COD values ascending straight up result from shutdown time. Comparing Figure 21and Figure 22, one may conclude that the correlation apparent in the concentration data only occurs during the shutdown, presumably when very high concentrations of phenol mask the effects of other chemicalcomponents.

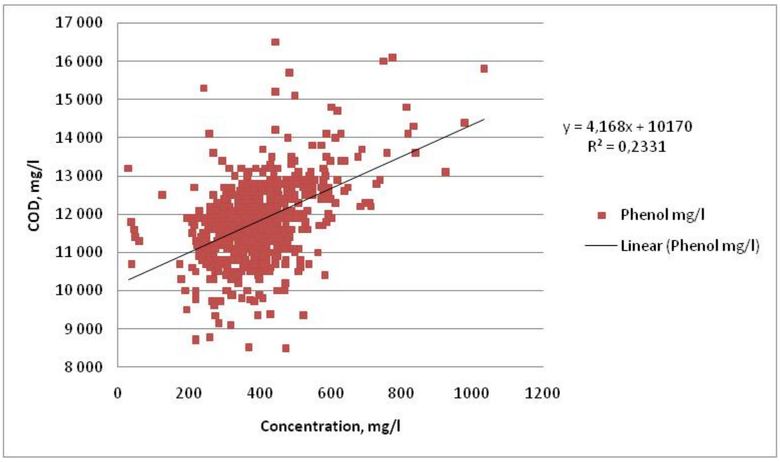

Figure 22 Phenol concentration variation against COD variation when the shutdown time is neglected.

The methanol concentration values were also very scattered from studied period and correlate with COD variation poorly as seen from Figure 23. The shutdown time was not neglected.

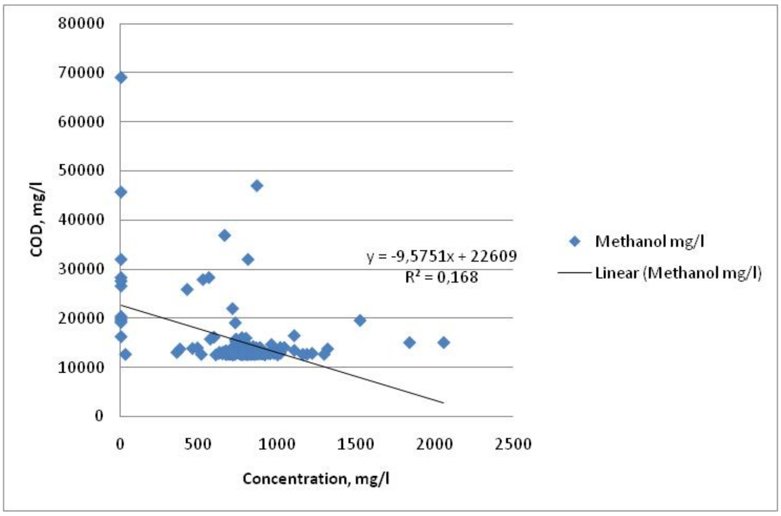

Figure 23 Methanol had concentration mainly between 500 and 1500 mg l^{-1} during the studied period. The data points are very spread out, which means that with similar methanol concentrations, the COD varies significantly.

Also the trend lines of bulk parameters, like dissolved organic carbon, total nitrogen and total hydrocarbons does not fit the data reliably enough that the variation of COD could be estimated from concentrations of these parameters (see Figure 24). Even the dissolved organic carbon (DOC), which should clearly correlate with COD does not correlate; the data points are very scattered. DOC concentration in less than 5000 mg l^{-1} gave an COD-load close to 40 000 mgO_2 L^{-1}but DOC concentration around 10 000 mg l^{-1} gave a COD load less than 20 000 mgO_2 L^{-1}.

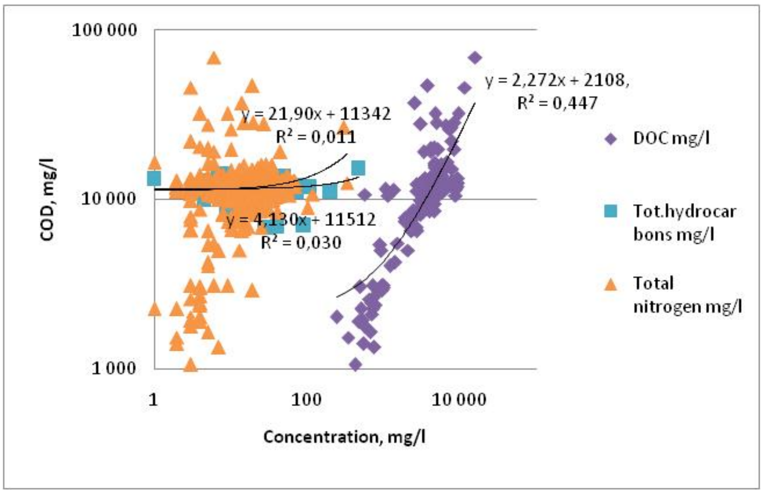

Figure 24 **Concentration of bulk parameters and COD variation. Concentration of bulk-parameters cannot be used to make a prediction of COD variation because values are so scattered. DOC values match quite well with the trendline (R^2=0,447), in contrary to total hydrocarbons (R^2= 0,03) and total nitrogen (R^2=0,011).**

The poor correlation of datapoints and trendlines was thought to be due to the outliers caused by shutdown time of a plant, but as seen from Figure 25 and Figure 26, the trendlines do not fit to the data points even when the shutdown time is not included. Phenol was already studied before, but the correlation of other parameters are shown in these figures. This means that similar concentrations of for example methanol may give different COD loads. According to the results shown in Figure 25 the methanol concentration of 1000 $\mathrm{mg\,l^{-1}}$ may give a COD load between 10 000 $\mathrm{mgO_2\ L^{-1}}$ and 15 000 $\mathrm{mgO_2\ L^{-1}}$.

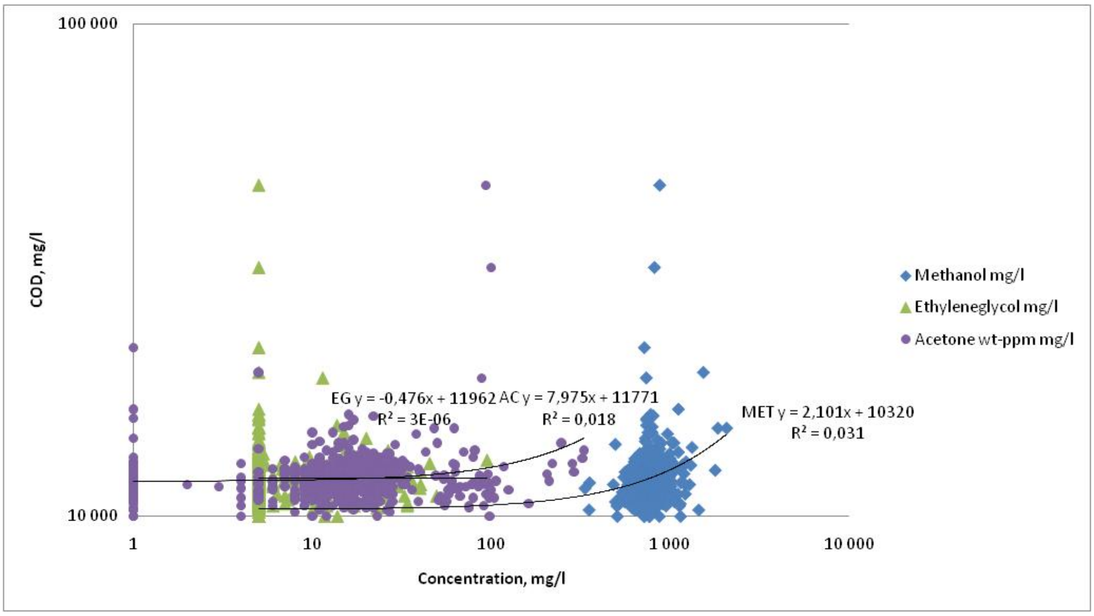

Figure 25 **Methanol, ethylene glycol and acetone concentrations plotted against the COD variation. The concentrations of components cannot be used to make a prediction of COD-load even when the shutdown time is neglected.**

So called BTX-components (benzene, toluene and xylene) are present at waste waters in very low concentrations (see Figure 26). Only data that contains information about concentration of BTX-components and cumene in the waste water was taken into consideration and the stoppage time was neglected from this data. Concentration of these components were below 0,5 $\mathrm{mg\,l^{-1}}$ even though the COD load varied between 6 000-16 000 $\mathrm{mgO_2\ L^{-1}}$. The concentration of these components did not contribute to the COD-load variation, mainly because these were present in low concentrations. Concentration of benzene varied between 0,1-2,5 $\text{mg}\,\text{l}^{-1}$, but mostly the concentration was under one milligram per litre.

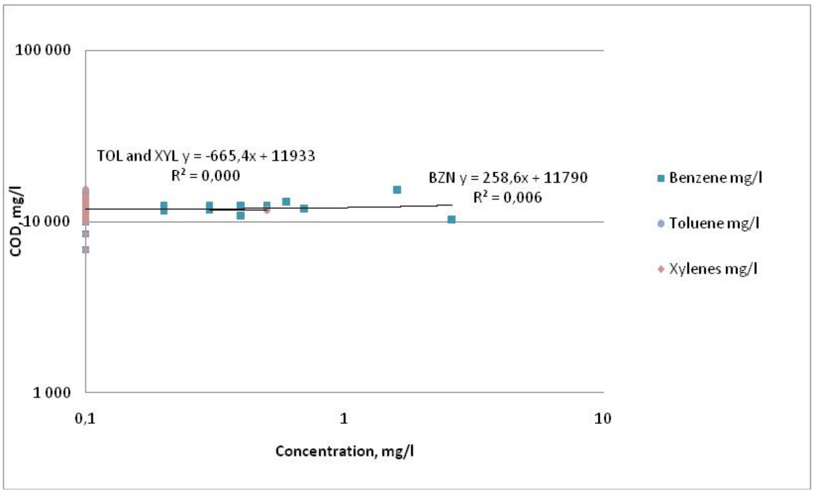

Figure 26 **Concentration of BTX-components plotted against COD-variation. There was no correlation between concentrations and COD-variation.**

No correlation could be found by studying only the concentration of the components and the COD- load. The problem was that the cumulative effect of components presented in waste waters could not be studied this way. The cumulative effect of components to COD-load variation was studied with ThOD-analysis.

Oxygen consumption per mole component and the ThOD for every component are given in Table 3. Only components analyzed during the studied period of 2010 are shown in Table 3. Bulk parameters like total nitrogen, total hydrocarbons and DOC are left out because those were sum components, and if the sum component total hydrocarbons had been included in addition to benzene, toluene, xylenes and cumene, the importance of these components would have been calculated twice. This would have led to incorrect results and conclusions.

Table 3. **Oxygen demand and theoretical oxygen demand of components Borealis analyses from waste water. Methanol and phenol have low molecular theoretical oxygen demand compared to cumene, toluene and xylenes.**

Analyte	Oxygen demand per mol i	Theoretical oxygen demand
	b, $(mol\ O_2\ mol_i^{-1})$	ThOD, $(gO_2\ g_i^{-1})$
Methanol	1,5	1,50
Phenol	7	2,38
Ethylene glycol	2,5	1,29
Acetone	4	2,20
Benzene	7,5	3,07
Cumene	12	3,19
Toluene	9	3,13
Xylenes	10,5	3,16

The total ThOD determined was on average only one fifth of the COD. In Figure 27 the ThOD value and its respective COD value were plotted when ThOD increases from smallest to largest value in x-axis. The shutdown time was excluded from this data set, otherwise the annual data set from 2010 was used. The ThOD value cannot be used for predicting COD variation with equation shown in Figure 27, because most of the COD values were outside the trendline (R^2=0,06).

The positive finding was that the COD load is not caused only by phenol, which is a toxic component. The negative fact was that then it is not fully known which other components there is in the waste water that contribute to the COD load.

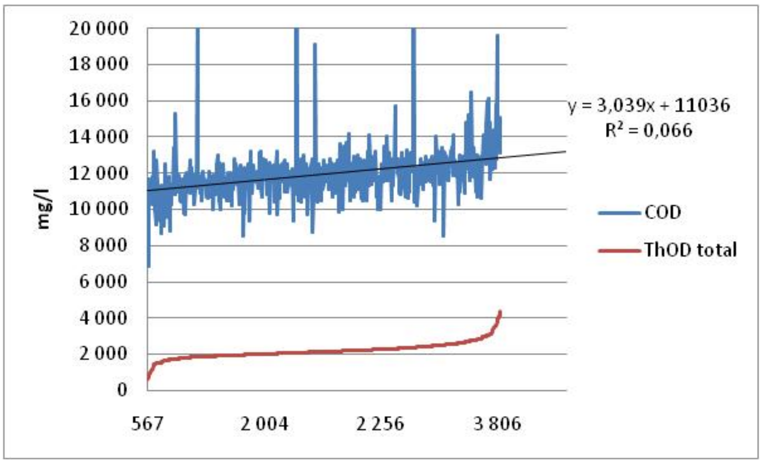

Figure 27 **The ThOD grows from smallest to highest value and the respective COD is plotted to the same figure. Measured COD value varied mostly between 10 000 and 15 000 $mgO_2\ L^{-1}$, while calculated ThOD variation did not reach similar. These two parameters did not even behave similarly.**

When the same data was plotted in a way that ThOD-load increased from smallest to highest the COD load showed interestingly having two main trends. When ThOD exceeded 1 000 $mgO_2\ L^{-1}$, some of the COD values increased linearly while some of COD values ascended sharply upwards (shown with red lines in Figure 28). This behaviour disappeared when the shutdown time was neglected and only the data points that all components were analysed were taken into consideration. This is shown in Figure 29. Phenol and methanol were the main components causing the ThOD load, and as shown previously in Figure 21and Figure 22, also the phenol concentration had similar kind of behaviour before the shutdown time was neglected. This determines that these two main trends were caused by phenol.

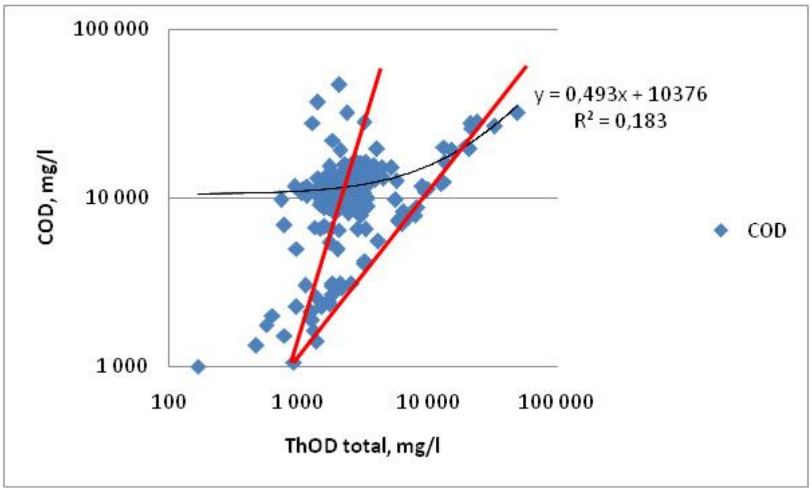

Figure 28 **ThOD and its respective COD plotted in another way. ThOD cannot be used to predict the COD-load when only methanol, phenol, acetone, benzene, toluene, xylenes and cumene are analyzed in the waste water.**

ThOD analysis results are gathered in Table 4. The maximum results of COD and ThOD are in the same scale, but otherwise the values differ significantly. COD and ThOD maximum values are close to each other, then phenol is the only component found from waste water that peaks. Minimum COD is about 100 times higher than minimum ThOD. Median determines the value which separates higher half from lower half (50% of values higher than median and 50% of values lower than median). Medians of the COD and the ThOD are not even in the same scale, the same holds for average values of the COD and the ThOD.

The error in percentage is used for describing how close the COD and the ThOD values are to each other. The error percentage makes it possible to compare different the COD and the ThOD values with each other better.

The error describes the proportion of different between the COD and the ThOD of the COD in percentages: $(\mathrm{COD} - \mathrm{ThOD}) \cdot \mathrm{COD}^{-1} \cdot 100\%$. If the ThOD is close to the COD, the error is small and opposite. Concentrations of the components and their respective ThOD's are given in Appendix C. On average the error between the COD and the ThOD is 78%, which illustrate that these two values which should be equal are not even close to each other.

Table 4 **The ThOD analysis results of components measured from the biolsy compared to the measured COD.**

Parameter	COD	ThOD total
	mg/l	**mg/l**
Minimum	1 060	168
Maximum	69 000	49 841
Median	11 700	2 133
Average	11 559	2 506

The proportion of how different components contributed to the ThOD varied during the studied period. In general methanol and phenol are the two main contributors to the ThOD in the phenolic waters. The contribution of methanol and phenol together range from the minimum contribution of 57% to the maximum contribution of 100% of total ThOD. On average methanol and phenol contribute equally to the ThOD, but there are a lot of variation among the results as seen in Table 5. Minimum contribution of methanol to ThOD was 0% but maximum contribution was 89%. The contribution of phenol ranges from a minimum 5 % to a maximum of 100 % contribution.

Table 5 **The effect of methanol and phenol to the ThOD is significant in the phenolic waters.**

Parameter	ThOD total	ThOD Met&Phe	Metanol and phenol share of total ThOD	Share of methanol	Share of phenol
	mg l^{-1}	**mg l^{-1}**			
Minimum	168	159	57%	0%	5%
Maximum	49 841	49 273	100%	89%	100%
Median	2 133	2 081	98%	52%	45%
Average	2 446	2 339	96%	49%	47%

When all the data was analyzed, the contribution of benzene, toluene, xylenes and cumene was zero and so was also the contribution of acetone and ethyl glycol. Methanol, phenol, acetone and ethyleneglycol are measured from the biolsy twice a day but benzene, cumene, toluene and xylenes less frequently. The data that did not contain information on these less frequently measured components were neglected to make sure that these missing values did not distort the results. Simultaneously, also the shutdown time data was neglected. This reduced the number of data points from 600 to the 30. COD value ranged between 6 000-16 000 $\mathrm{mgO_2\ L^{-1}}$ while ThOD remains around 2000 $\mathrm{mgO_2\ L^{-1}}$. The fit between measured COD and calculated ThOD did not improve by neglecting the data as described above.

When the shutdown time was neglected and only data points that all the parameters were analysed (also benzene, cumene, toluene and xylenes) were taken into consideration, the ThOD values represent better the COD and the linear correlation of these two parameters can be seen. This is shown in Figure 29.

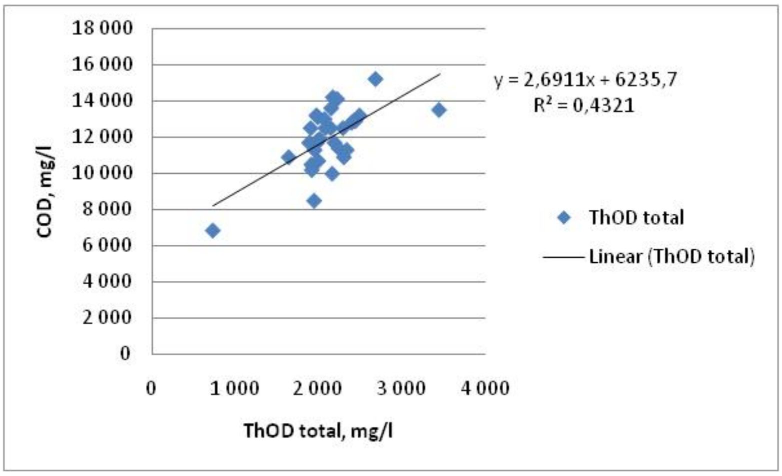

Figure 29 **ThOD and COD correlation when the shut down time was not included. ThOD correlates better with the COD, when shutdown time is neglected.**

As it is shown in Table 6 the reduction of data points do not change the result, the phenol and methanol are still contributing most of the ThOD of phenolic waters.

Table 6. **Proportion of parameters contributing to the ThOD. Methanol and phenol are the main components contributing to the ThOD.**

	ThOD total	ThOD Met+Phe	ThOD other than Met + Phe	Met and Phe share of total ThOD	MET	PHE	EG	AC	BZN	CUM	TOL	XYL
	mg/l	mg/l	mg/l									
min	736	594	8	81%	39%	21%	0%	0%	0%	0%	0%	0%
max	3 451	3 275	444	100%	79%	55%	6%	9%	0%	16%	0%	0%
median	2 088	1 987	51	97%	54%	43%	0%	2%	0%	0%	0%	0%
average	2 128	2 043	85	96%	54%	41%	1%	2%	0%	1%	0%	0%

By determining the ThOD, only one fifth of measured COD can be determined. If ThOD would have equalled with the COD, it would have facilitated that which of the measured components build-up the COD. It is clear that with components now measured from biolsy, only one fifth of the load can be analysed with help of the ThOD. If Borealis wants to concentrate on components normally measured from biolsy, a suggestion is to concentrate on phenol and methanol in order to reduce load. If Borealis wants to reduce the load significantly, more analysis is needed in order to find out which other components there might be contributing to the load, because the measured components from biolsy do not give a full answer to the question of which components are responsible for COD load in waste waters.

5.1.3 Results of the supplementary onsite measurement program of phenolic waters

5.1.3.1 Origin of the components present in the phenolic waters

The results of the supplementary onsite measurement program are used both in the load determination and in the ThOD-analysis. The final results are shown in this section of supplementary onsite measurement program, but all the primary results are shown in Appendix D.

In supplementary onsite measurement program, waste water samples were taken from biolsy and from two main water sources: the MHP-reactor and the stripper. Acetonitrile and propanols were analyzed in addition to phenol, methanol, acetone, ethylene glycol, cumene, benzene, toluene and xylenes. Methanol and phenol were the components present in the highest concentrations for every analyzing occasion. Methanol and phenol concentrations in the outlet of the MHP-reactor were higher than from the stripper. Cumene and total hydrocarbons also seemed to originate from the MHP-reactor. The stripper was the main origin of total nitrogen present in the phenolic waters. Concentration of acetone varied from 1 ppm to 18 ppm, but surprising results is that acetone seemed to enter the biolsy from somewhere else than from the MHP-reactor or from the stripper because its concentration was higher in biolsy than any of the source streams. Acetone might have entered the biolsy with waters collected from paving or from ground water. The origin of ethylene glycol and acetonitrile cannot be traced. Most probably acetonitrile is not even present in the waste water. The acetonitrile concentration of 5 ppm is the minimum limit set to the laboratory software LIMS. If the acetonitrile concentration is zero, or less than 5 ppm, it displays the concentration as 5 ppm, because that is the best accuracy possible to get with the selected method. The origin of benzene, xylenes and toluene cannot be traced, for the same reason, except that the limit is 0,1 ppm. Due to this accuracy problem, the external measurement program was needed in order to be able to analyze components with lower concentrations, to assess where the load originate from. The values presented in Table 7 are given as an average of three analyses.

Table 7 Results of onsite measurement program of the phenolic waters. Concentrations of components are given in mg l^{-1}.

Component	Sampling point		
	Biolsy	Stripper	MHP-reactor
Methanol	446	52	4 880
Phenol	323	203	1 867
Ethyleneglycol	5	8	5
Acetone	10	6	2
Benzene	0,3	2	0,1
Cumene	0,1	0,1	39
Xylenes	0,1	0,1	0,1
Toluene	0,1	0,1	0,1
Acetonitrile	5	5	5
Propanols	1	1	1
Tot.hydrocarbons	3	3	65
Total nitrogen	18	17	1
DOC	4 412	2 965	17 350
COD	11 740	9 463	46 467

5.1.3.2 ThOD analysis for the waste water sources in the phenolic waters

Due to the poor correlation between the COD and the ThOD in the biolsy, the ThOD analysis was conducted for waste water sources discharging also to the biolsy. The error between the ThOD and the COD did not decrease when the source streams were analyzed in addition to the biolsy. The error in the outlet of the MHP-stripper was less than the error in other streams. This resulted probably from the fact that components were present in higher concentrations in the MHP-reactor's outlet or that the outlet of the MHP-reactor did not contain as much unknown components as outlet of the stripper. All results from the onsite supplementary measurement program are shown in Appendix D. The supplementary onsite measurement program results are gathered in Table 8, where the average of results from three separate analyses is taken.

Table 8 **The error between the ThOD and the COD did not decrease when ThOD analysis was performed to waste water sources. Results are shown in mg O_2 L^{-1}.**

Parameter	Sampling point		
	Biolsy	Stripper	MHP-reactor
COD	11 740	9 463	46 467
ThOD Met&Phe	1 414	562	11 754
ThOD total	1 458	597	11 898
Error	88%	94%	73%

Analyses of samples taken straight from the outlet did not give any reliable additional information of why the calculated the ThOD does not equal the COD.

5.1.4 Results of the supplementary external measurement program of phenolic water

5.1.4.1 Origin of the components present in the phenolic waters

The results shown in here are the average of the two times analysed, all results are shown in Appendix D.

Methanol originated only from outlet of the MHP-reactor, the amount from there is much higher than from the stripper (see Table 9). Both the MHP-reactor and the stripper streams contained phenol so the origin of phenol could not be limited to one source only. Acetone originated from both sources, higher concentration was found in the outlet of the stripper. Cumene was the only volatile organic component of all analyzed volatile components that could be found in significant concentration. The origin for cumene was the MHP-reactor (see Table 9). Benzene and toluene were found from the outlet of the MHP-reactor in higher concentration than from the stripper. Xylenes are not present at all in the phenolic waters. Also the amount of total volatile hydrocarbons (TVOC C5-C10) was significantly higher in the outlet of the MHP-rector than in the outlet of the stripper. Cumene results show an interesting non-correlation: cumene concentration in the biolsy in the first analyzing occasion was 170 µg/l when cumene concentration in the MHP-reactor outlet was 27 000 µg/l and from the stripper 2.2 µg/l. In the other analyzing occasion, the cumene concentration in the biolsy had increased to 1200 µg/l, while the cumene concentration from the MHP-reactor had dropped to 7000 µg/l and from the stripper the concentration is under detection limit 2 µg/l at the same time. So the cumene concentration increase in the biolsy could not be explained by higher concentration in outlet of the MHP-reactor or stripper. The COD from the MHP-reactor is almost four times higher than from stripper.

Table 9 **Origin of components present in the biolsy. Results are average results based on two separate analyzing occasions.**

Analyte Name	Unit	Sampling point		
		Biolsy	Stripper	MHP-reactor
Methanol	mg/l	780	<2	6 950
Phenol	µg/l	154 000	37 365	900 145
Acetone	mg/l	31	41	12
Isopropylbenzene (Cumene)	µg/l	685	<2	17 000
Benzene	µg/l	<2	<2	9
Toluene	µg/l	<2	<2	6
m+p-Xylene	µg/l	<4	<4	<4
o-Xylene	µg/l	<2	<2	<2
TVOC C5-C10	µg/l	1 045	56	21 500
COD	mg/l	12 500	9 750	37 600
pH	-	10	5	13

5.2 Oily waters

5.2.1 Waste water sources to the oily waters

In this section the water sources to the OW-system are described. The water sources in ISBL-areas, as well as information about discharge points of these sources, and the opportunities to lead water to the OW-stripper are also presented in Table 23 in Appendix F.

The cracker and the butadiene plant have water circulation, but there is no process water circulation in the benzene and cumene plants. Water circulated in the phenol plant is discharged to another system. There are also numerous continuous and irregular sources of water to the OW-system from different plants in addition to water which have been used in water circulations.

The OW-system has three main branches which are shown in Figure 30 with thick black lines. To make different branches more easily distinguish, branches were named to OSBL-, ISBL- and cracker-branch. The OSBL branch collects water from outside battery limit area (OSBL). Waters collected in the OSBL branch are mainly rain waters from spill basin areas and from paving areas. Two other branches cover the inside battery limit area (ISBL), which means the production plants. The cracker branch covers part of the cracker only. Both the OSBL-branch and the cracker branch interconnect with the ISBL-branch so that in the end there is only one branch leading to the Neste Oil's activated carbon treatment. Also the power plant operated by Neste Oil Oy lead its waste waters to the OW-system.

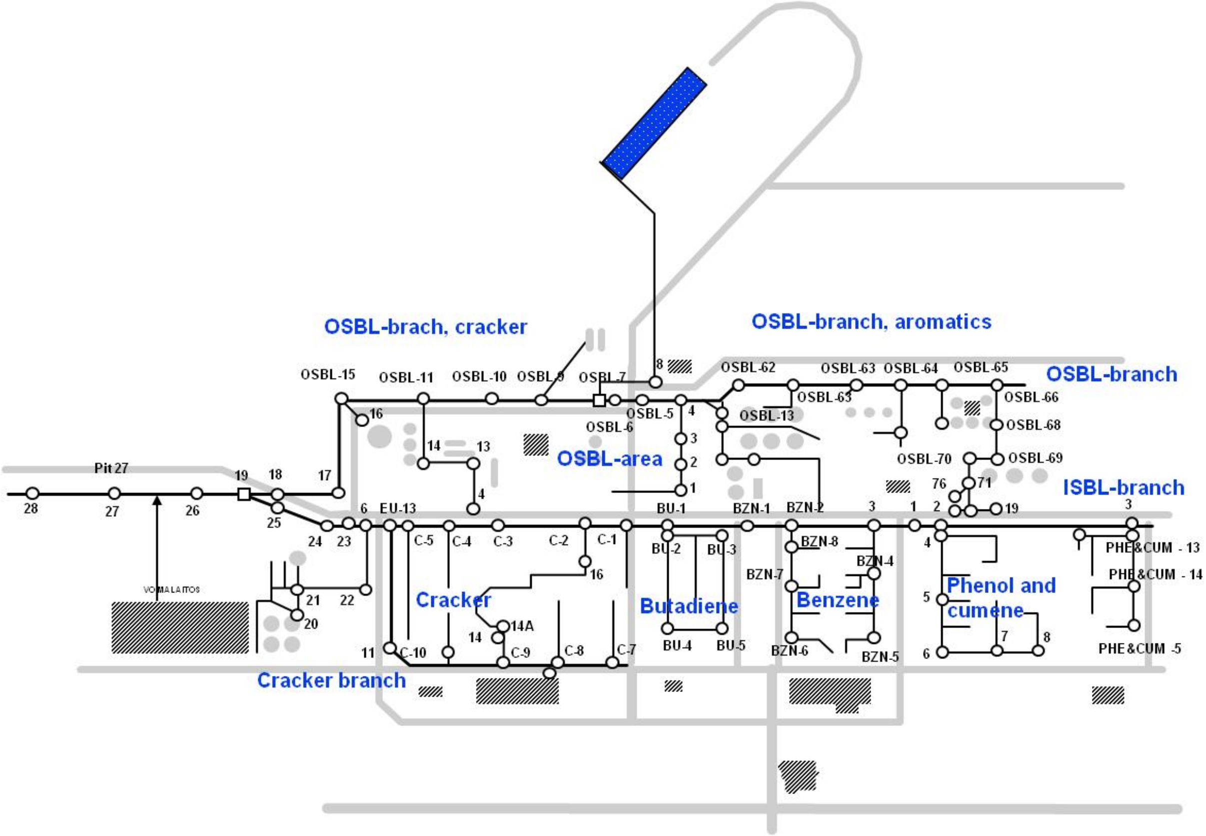

Figure 30 **Three main branches, the OSBL-, ISBL- and cracker branch, of the OW-system. Cracker branch covers only part of the cracker, the ISBL branch covers all production plants and the OSBL branch covers the feedstock, intermediate and product tank areas.**

The cracker

Clean condensate is fed to, and dirty condensate discharged from, the diluting steam generator in the cracker. Clean condensate is clean condensed steam from Neste Oil's power plant, and dirty condensate is condensed steam used in the process. Clean condensate is mixed with recycled condensate in the diluting steam generator and heated before it is being fed to the cracking furnaces. Steam is used in the furnaces to make cracking more efficient, by making circumstances milder and by increasing the retention time. Raffinate exits from furnaces at 800ºC degrees, after which it is cooled down in numerous process steps before finally being circulated back to the dilution steam generator. The water is cooled down before it is drained (Hyrsylä 2010). Process water discharged from the diluting steam generator enters a side branch which interconnects to the cracker branch in pit C-10. Normally water is being discharged directly to the OW-system, but it can also be fed to the OW-stripper. There is neither a flow meter nor a monitoring where it could be monitored whether water is fed to the OW-stripper or not (Pynnönen 2010).

The cracker also has a sodium hydroxide wash and a FCC-wash (FCC means fluid catalytic cracking), which use clean condensate and hence discharge water contaminated with process chemicals directly to the OW-system. Raffinate (process stream) is washed with 6 % sodium hydroxide and water. The water is used to reduce the sodium hydroxide residues. The FCC-washer is identical with the sodium hydroxide washer (Hyrsylä 2010). Used wash water from both washers is collected to tank, which discharges waters to the OW-sewer via pit C-9. There is no flow metering or monitoring, which shows whether the water is fed to the OW-stripper or not (Pynnönen 2010).

There are three steamers which discharge to the pit C-9. The amount of water, directly discharged to the OW-system, from all steamers is about 0,5 m^3 per hour. Water is used also as sealant solution in one of the steamers and discharged to the OW-system via same pit. Water used as sealant solution is clean condensate and discharge rate approximately 0,5 m^3 per hour (Pynnönen 2010).

One reboiler discharges the condensate to the ISBL branch via pit C-2. Steam fed to the reboiler has not been in contact with process chemicals because it is used for warming up the reboilers. Amount of flow is approximately 0,5 m^3 per hour. This waste water stream can also be discharged to the OW-stripper (Pynnönen 2010).

There are no continuous flows to pit C-4 normally. At the moment (from December 2010 onwards) a heat exchanger discharges its condensate to the OW-system, the amount is about two to three tons per hour (Pynnönen 2010).

There is also a continuous flow from emergency the showers. Altogether showers introduce a two cubic meter load per hour to the OW-system (Pynnönen 2010).

Rain water from the paving area near cracking furnaces and water originating from the furnace shut downs are discharged to a side branch connected to the ISBL branch via pit C-5. There are ten furnaces in the cracker which discharge water to this side branch. During the shutdown of the furnaces, condensate from steam generators is unloaded to side branch. Approximately, there is one furnace shut down once a month and load generated during the shut down is about 10 m^3. There are a lot of different types and sizes of heat exchangers, so a total amount of water from heat exchangers could not be determined more specifically (Pynnönen 2010).

Regeneration steam from the acetylene converters is led to a drip condenser where it is cooled down with sea water and the condensate is led to the OW-system. It is directly discharged to the OW-system via pit C-7. The amount of water led to system is about 25 m^3 per hour during regeneration, and regeneration time is about 40 days per year, so the total load annually is about 24 000 m^3 (Pynnönen 2010). Another drip condenser cools down the regeneration steam (methane in this case) used in the feedstock dryers. The condensate formed in this condenser is discharged to the pit C-9. The condensate could be discharged to the OW-stripper as well (Pynnönen 2010).

Regeneration steam used in the DPG-reactors and in acetylene absorbers is condensed with sea water, and discharged to the pit C-9. Water feed is not automatically adjusted, so accurate amount is difficult to estimate. The amount of water led to the system is about 20 m^3 per hour during regeneration, and regeneration time about 16 days per year. (Pynnönen 2010).

Dirty condensate (DC) from reboilers and heat exchangers can, depending on process conditions, be led to the OW-system from different places in the cracker, but it happens very rarely (Hyrsylä 2010).

The butadiene plant

The butadiene plant uses five (5) bar steam in carbonyl wash. The amount of steam used is about 4-5 tonnes per hour. Raw material in butadiene plant is C_4-stream from the cracker, and water is used to reduce carbonyl from the feedstock stream. Water from the carbonyl washer is led to butadiene's flaring basin. It can be estimated that all water fed to the wash is also discharged to the OW-system. Water is discharged from flaring basin to the pit BU-1 and further to the OW-system (Hyrsylä 2010).

The butadiene process discharge waste water to the OW-system also from acetonitrile solution circulation. Water is discharged from the ACN-recovery column to the OW-system. Flow from the ACN-recovery column is continuous (Hyrsylä 2010).

The Phenol and Aromatics

The phenol and Aromatics (from now on mentioned as the aromatics) consist of benzene, cumene and phenol plants. The benzene and cumene plants do not have any water circulation and, hence no continuous flows to the OW-system. Very small amounts of humidity enter the process (concentration in parts per million -scale) with the feedstock and it will be removed in different stages of the processes (Palosaari 2010). Water that separated during the processing is collected to a hydrocarbon separation tank. From the separation tank, the waters are led via the OSBL branch to pit OSBL-13 and to the OW-stripper situated in the benzene plant (Saukonoja 2011). Waste water from the phenol plant is mainly collected to another waste water system, but there is a continuous flow from the phenol plant also to the OW-system. The ejector waters, water from evaporators and rain water from paving in the phenol plant, enter the OW-system from the phenol plant. Steam is used in steam jet vacuum ejectors for pressure adjustment. It is discharged to the OW-system via the pit PHE&CU-15. In the evaporator, steam is used in liquid ring pumps. Water is circulated in the evaporator, which creates vacuum in the steamer (Kainulainen 2010). These two streams are not processed in the OW-stripper normally, but will be processed if the valve on outlet side of BZN-2 is closed (Saukonoja 2011).

All paving waters from the cumene plant are led to the OW-system without treatment in the OW-stripper. Part of the paving waters from the benzene ISBL area are treated in the OW-stripper and some waters are not. Those that are treated in the OW-stripper are collected in pit BZN-2 to the reservoir side of the pit. Water from the reservoir side is led to the OW-stripper. Paving waters from the phenol plant, which are collected to the OW-system, are not treated in the OW-stripper.

There is a shut-off valve on outlet side of pit BZN-2. Normally this valve is open and waters are operated as described above. When the valve is closed, the surface in the by-pass side of the BZN-2 will rise to the reservoir side of the pit BZN-2, hence all waters from the benzene, cumene and the phenol plants are treated in the OW-stripper as well as waters from the aromatics OSBL area. When the valve is closed on the discharge side of the BZN-2, waters treated in the OW-stripper (ie. all waters) are not led to the by-pass side of the BZN-2 but to an extra bypass pipeline, which connects the pits BZN-2 and BZN-1 (Saukonoja 2011). The pit BZN-2 is shown in Figure 31 and in Figure 32.

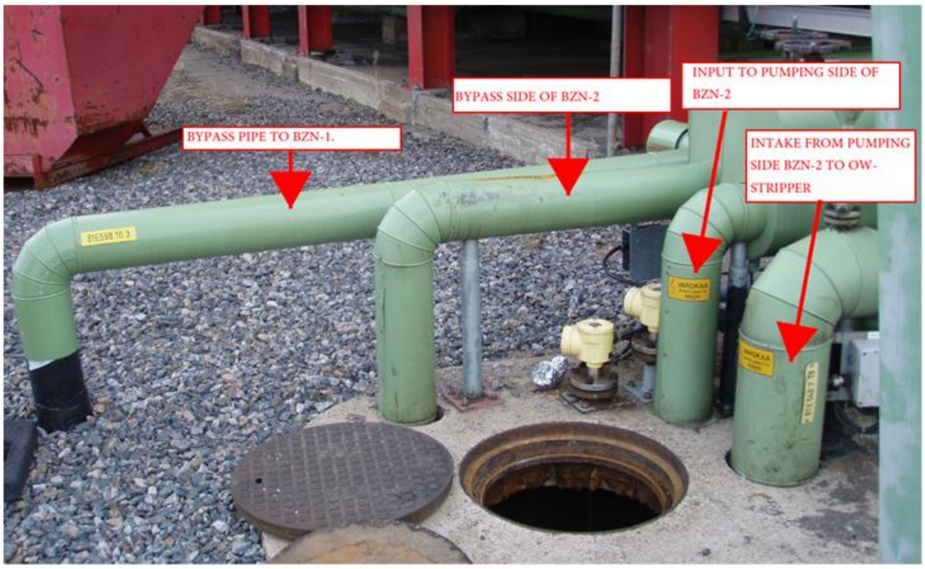

Figure 31 **Pit BZN-2**

Figure 32 **Pit BZN-2 shown from inside**

Outside battery limit waters

The OSBL branch covers the intermediate storage tank areas of the cracker, butadiene, benzene, cumene and phenol production units. The OSBL branch can be divided into two sections: the cracker's side and aromatics' side, which are shown in Figure 33. When valve situated on the outlet of OSBL-13 is closed, all waters from the pit OSBL-13 are treated in the OW-stripper before led to the OW-system, and only the cracker causes load to the OSBL branch. If the valve is open, all waters will bypass OSBL-13 and continue along the OSBL branch to the activated carbon treatment. All other tanks, which also belong to the aromatics, are part of the same system (Saukonoja 2011).

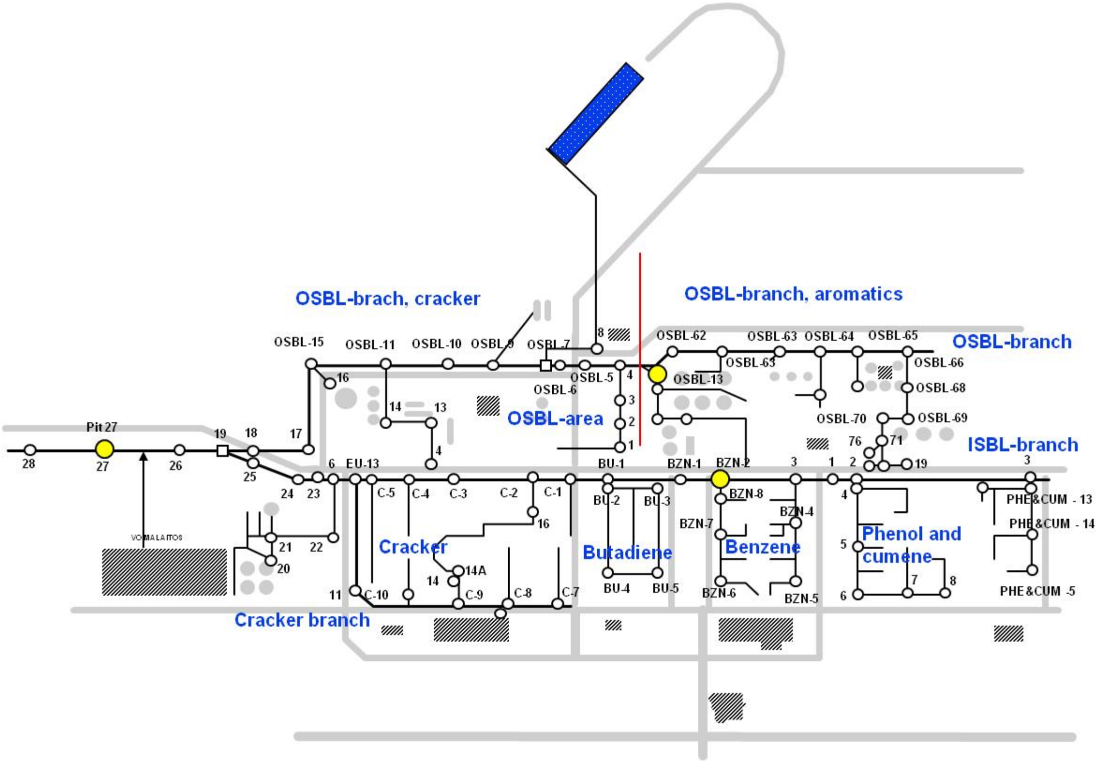

Figure 33 Important pits (BZN-1, OSBL-13 and pit 27) in OW-system are shown with yellow colour. Distinction between cracker's side and aromatics' side of OSBL branch is shown with red line.

An extra branch from the OSBL branch begins from the pit OSBL-7. Through this branch, water can be led straight to the sea water tunnel in case of exceptional high load, or due to problems in the system (Saukonoja 2011). This side branch will be used only in exceptional cases and it is equipped with hydrocarbon monitoring system.

Water from the cracker flaring basin is discharged to the OW-system via pit OSBL-9 but can also be led to the OW-stripper. The water has been in contact with flaring gases and contains residues of process chemicals, and is therefore the main contributor to the load coming from the OSBL branch. Water is discharged to the OW-system every third day and an approximation of the amount is 50 m^3 per week. Surface level metering starts and stops the emptying of the tank. There is no monitoring, neither of the quality of water nor of the amount of water led to the OW-system. Also water from the washing place, where for example heat exchangers can be washed, create irregular load to the OSBL branch. Otherwise the waters sewed via the OSBL branch are rain waters from spill basin areas of tanks and rain water from paving areas (Pynnönen 2010).

5.2.2 ThOD analysis for the components present in the oily waters

The known components of oily waters are the components continuously analyzed from oily waters. These components are methanol, phenol, acetone, ethylene glycol, acetonitrile, propanols, benzene, cumene, toluene, and xylenes. In addition to that also parameters DOC, COD, total nitrogen, total hydrocarbons and pH is analysed. The only component analyzed from waste water that was not included in the study was oil. This was because it is not know what kind of oil it is. It was also present in very low concentrations (0,1 ppm) and hence not included in the study.

The COD in the OW-system varies between 700-1 300 $\mathrm{mgO_2\ L^{-1}}$ (as shown in Figure 34) during the studied period of year 2010.

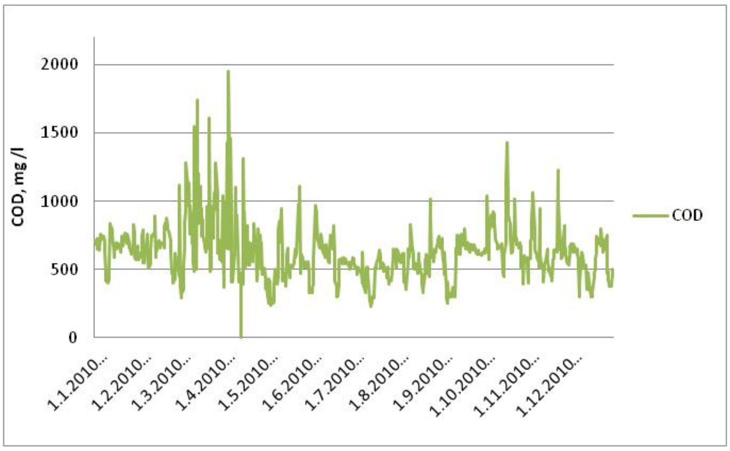

Figure 34 **COD variation at the OW-system's sampling point, pit 27, during studied period.**

In the OW-system, it was first studied if there is any significant compound, which variation would correlate to COD variation. The oily waters and the concentrations of components found in the oily waters are different to phenolic waters due to the different nature of the system. That is why the findings obtained from analyzing phenolic waters could not be used when the OW-system was analysed.

Methanol, phenol, acetone, acetonitrile and ethylene glycol concentrations and their linearizations are shown in Figure 35 against the COD variation. None of the components show clear correlation with COD-variation (data scattered). For example when methanol concentration was 100 ppm in the waste water the COD was varied between $700\ \mathrm{mgO_2\ L^{-1}}$ or over $1000\ \mathrm{mgO_2\ L^{-1}}$, hence the data is scattered and it cannot be used to make a fit or adaption to predict the COD-variation (see Figure 35 and Figure 36). This applied for all the components.

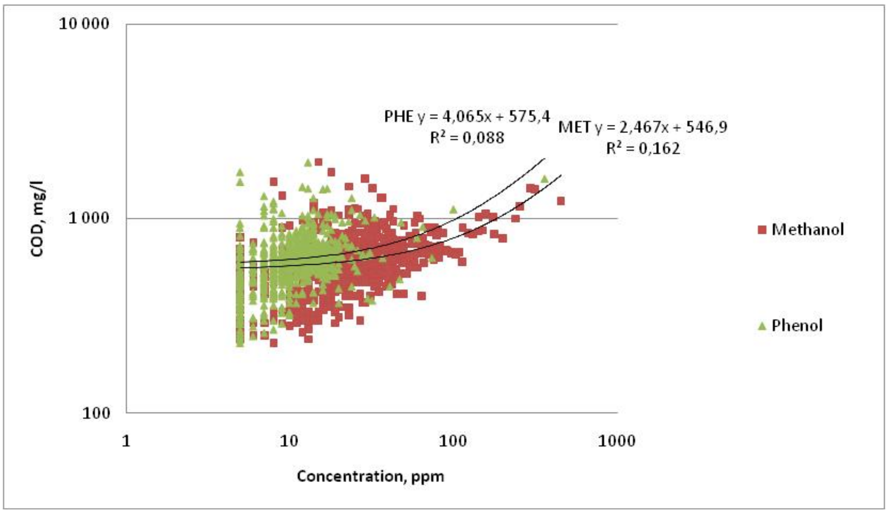

Figure 35 **Variation of concentration of methanol and phenol and the simultaneous variation of COD. The COD cannot be predicted directly from the concentration of methanol or phenol.**

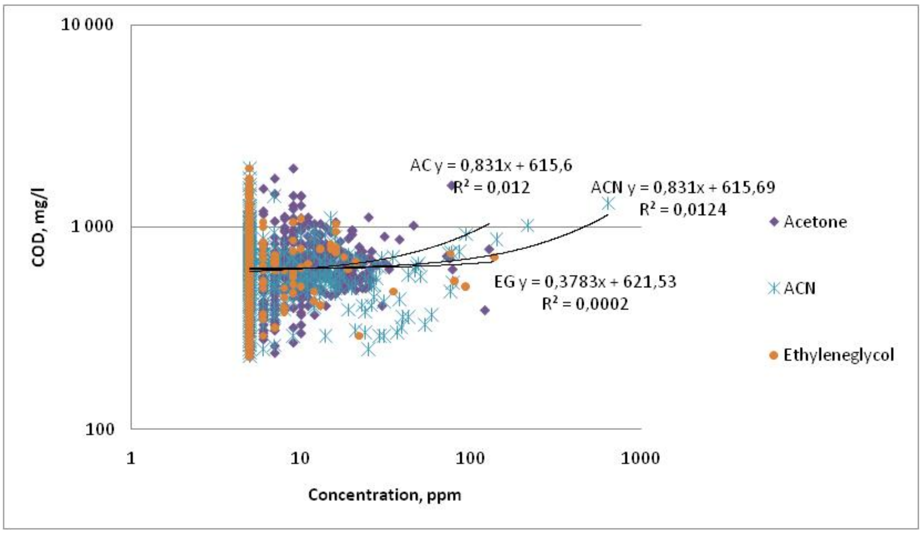

Figure 36 **Concentration variation of acetone, ACN and ethyleneglycol and the simultaneous variation of COD. The COD cannot be predicted directly from the concentration of any of these components in the waste water.**

The non-correlation of concentration of hydrocarbons with the COD is shown in Figure 37. Benzene has the highest concentration of BTX-components, but its concentration changes did not have clear correlation with the COD variation. When benzene concentration was 7 mg/l, the COD value was either more than 1000 $\mathrm{mgO_2\ L^{-1}}$or less than 1000 $\mathrm{mgO_2\ L^{-1}}$, which determines that benzene (or other BTX-components) did not affect to the COD-variation.

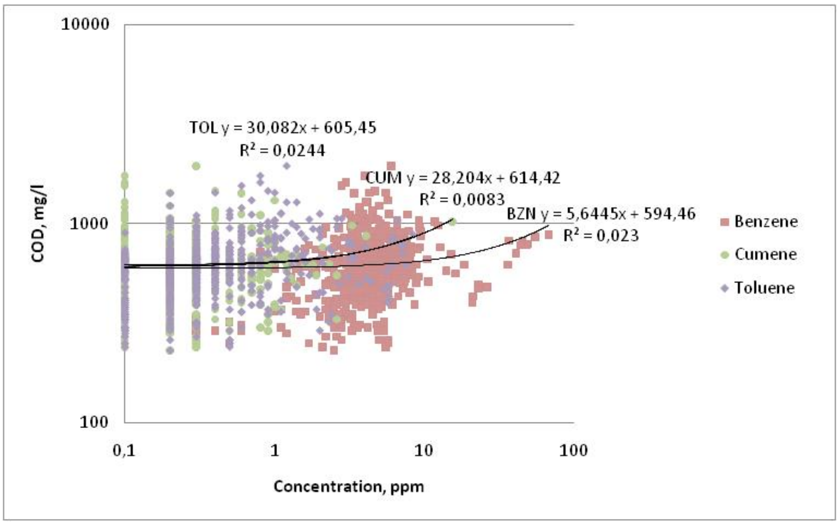

Figure 37 **The COD variation with different concentration of benzene, cumene and toluene. The COD cannot be predicted from hydrocarbon concentrations present in the waste water in the OW-system because there is no clear correlation between the amount of these components in the water and the COD.**

As shown in Figure 38 the dissolved organic carbon (DOC) data points has the better correlation than other bulk parameters: total nitrogen and total hydrocarbons.

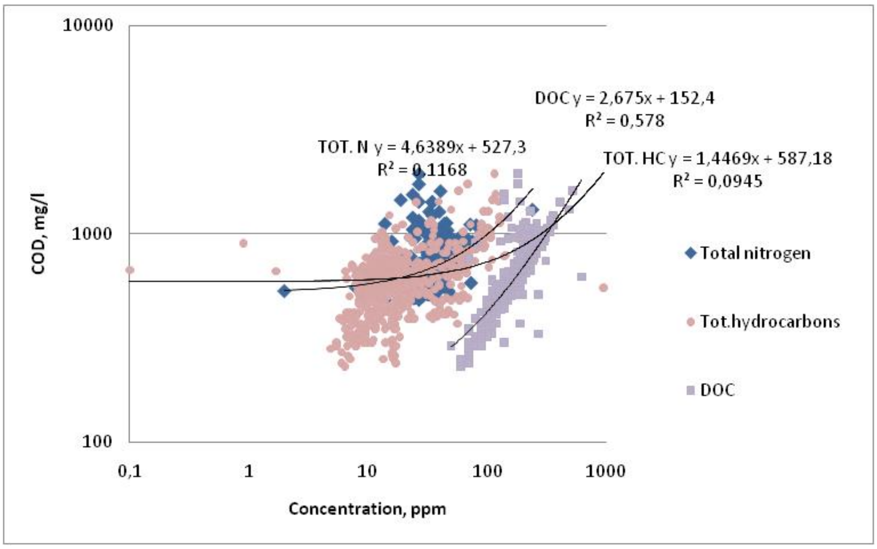

Figure 38 **The COD variation with different concentration of bulk parameters. The DOC predicts the COD value better than other bulk parameters.**

The phenol plant had shutdown during the studied period, as mentioned before, but its significance in the OW-system was considered to be small, because only ejector waters and part of the paving waters enter the OW-system from the phenol plant. That is why the shutdown time was included when oily waters were studied. The nitrogen load in the OW-system was thought to come from cracker and that is why the total nitrogen is treated as 2-aminoethanol, since most of the nitrogen load from the cracker plant is 2-aminoethanol (Soudant 2011).

The determined ThOD did not explain the contribution of different components to the COD, because the total ThOD did not behave like the COD did (shown in Figure 39). When the ThOD is set to go from lowest to highest value, and the corresponding COD drawn into the same figure it can be seen that these two parameters did not behave similarly.

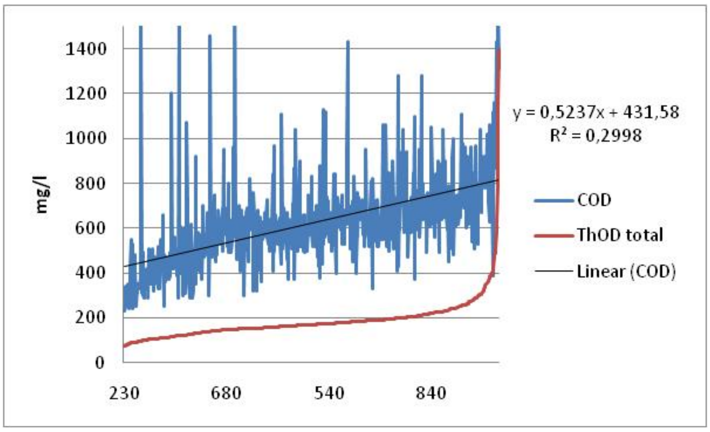

Figure 39 **The ThOD and its respective COD is shown. When the ThOD goes from lowest to highest value, the respective COD do not behave similarly, hence the ThOD could not be used in determining the COD.**

The ThOD values varied mostly between 200-400 mg O_2 L^{-1}, while the measured COD varied between 400-800 mg O_2 L^{-1} (see Figure 40).

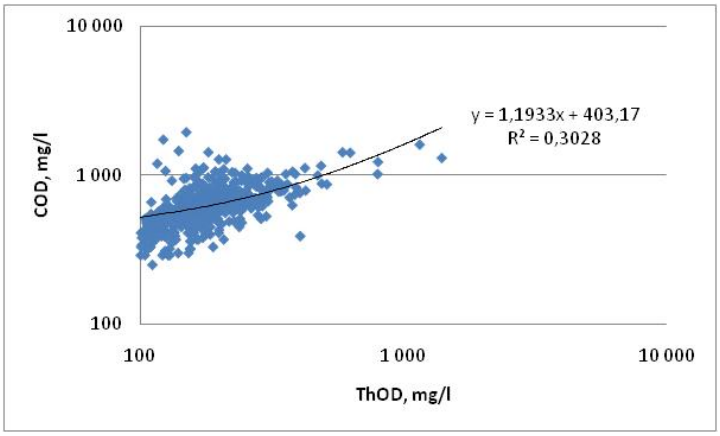

Figure 40 **The correlation between the ThOD and COD shown in different way. COD cannot be predicted with help of ThOD, because values are so scattered.**

On average, the ThOD value is one third of the measured the COD (see Table 10). The median also shows the different centres of the values: the COD has median value 620 mg O_2 L^{-1} and ThOD only 170 mg O_2 L^{-1} so the ThOD median is also only one third of the COD. The results shown in Table 10 are based on study of over 600 data points during the studied period of year 2010.

Table 10. **The minimum, maximum, median and average values of the COD and ThOD. On average the calculated ThOD is less than one third of the COD.**

	COD	ThOD total
	mg O_2 L^{-1}	mg O_2 L^{-1}
Minimum	230	74
Maximum	1950	1398
Median	620	170
Average	624	185

Aminoethanol (AE), methanol (MET), phenol (PHE), acetone (AC) and acetonitrile (ACN) contributed the most to ThOD of known components. In the OW-system, the contribution of cumene (CUM), toluene (TOL) and xylenes (XYL) were minimal. Benzene (BZN) on the other hand, reached maximum contribution of 48% and it also had the ThOD values significantly higher than cumene, toluene and xylenes. Benzene had the ThOD values higher than other similar components. This results purely from concentration differences of these components in the waste water, because ThODs of benzene, cumene, toluene and xylenes are very similar. The concentrations and theoretical oxygen demands of all the comonents can be seen from Appendix H.

Table 11. **The minimum, maximum, median and average contibution of known components to the ThOD.**

	ThOD total, mg/l	AE	MET	PHE	AC	ACN	EG	PRO	BZN	CUM	TOL	XYL
Minimum	74	0%	1%	1%	1%	1%	0%	0%	0%	0%	0%	0%
Maximum	1398	54%	85%	74%	71%	72%	48%	11%	47%	8%	10%	31%
Median	170	23%	22%	15%	12%	5%	4%	2%	8%	0%	1%	0%
Average	185	23%	24%	15%	13%	8%	4%	2%	9%	1%	1%	1%

The COD and the ThOD may vary because there might be other components present in the waste water, which are not analyzed continuosly. There may also be components that interfere with either the COD measurement, by causing falsely high COD (like halogens do with ammonia), or there might be inorganic compounds that falsely give a too high COD by reacting with the oxidant in the COD analysis. These things are not possible to know only by relying on the parameters continuously analysed from the oily waters. If Borealis want to reduce the load by concentrating only on known components, they should concentrate on 2-aminoethanol, methanol, phenol, acetone, acetonitrile, glycol and benzene concentrations in the waste water.

5.2.3 Results of the supplementary onsite measurement program of the oily waters

5.2.3.1 Origin of known components present in the oily waters

Waste water from outlets of the diluting steam generator, the acetone recovery column and the OW-stripper were selected to represent the contribution from the cracker, the butadiene plant and the aromatics, respectively. The OW-stripper was in use on March 9th, but the waste water from the OW-stripper was not discharged to the OW-system, but was instead circulated to prevent the freezing of the OW-stripper during the cold winter. Because of that the results of the OW-strippers outlet stream analysts on March 9th, did not represent the normal operation; the results from analysts on March 3rd were used instead in the ThOD analysis. An average of two analysts are gathered in this section, but all the primary results are shown in Appendix I.

The outlet of the OW-stripper is not the same as the outlet of effluent stripper described when phenolic waters were studied. The OW-stripper is situated in the benzene plant and only waters that originate in plants connected to the OW-system can treated in the OW-stripper. According to results from sampling on March 9th, the OW-stripper works and was capable of removing the components other than methanol.

2-aminoethanol (as total nitrogen), methanol and phenol load originated in the cracker (see Table 12). The load from the cracker was higher than the load from the aromatics. The origin of glycol, acetone, propanols, benzene, cumene, toluene and xylenes cannot be determined with needed accuracy in the Borealis petrochemical laboratory. The COD and the DOC concentrations are highest in the outlet of the dilution steam generator and second highest in the outlet of the OW-stripper. Total hydrocarbon load overall, originated primarily in the aromatics and secondly in the cracker.

The concentrations of acetonirtile, acetone, benzene, cumene, toluene and xylenes were higher in pit 27, than in the studied outlet streams. It indicates that these components could enter the OW-system outside the studied streams, or the load accumulated when the streams from all plants were combined. The butadiene plant causes only total nitrogen load to the OW-system according to this measurement.

Table 12 Results of supplementary onsite measurement program of oily waters. Results are shown in $\mathrm{mg\,l^{-1}}$.

Component	Sampling point			
	Pit 27	Cracker	Butadiene	Aromatics
Total nitrogen	41	66	48	42
Methanol	20,5	36	5	3299,5
Phenol	10	31,5	5	17,5
Acetonitrile	27	5	5	5
Glycol	5	5	5	5
Acetone	6,5	5	5	5
Propanols	1	1	1	1
Benzene	5,8	0,1	0,1	0,1
Cumene	0,4	0,1	0,1	0,1
Toluene	0,6	0,1	0,1	0,1
Xylenes	0,35	0,15	0,1	0,1
Tot.hydrocarbons	15,4	5,75	0,1	10,3
DOC	170	260	70	930
COD	590	865	215	5380

5.2.3.2 ThOD analysis for the waste water sources in the oily waters

ThOD analysis was conducted to examine whether the ThOD and the COD values would be closer to each other directly in the discharge point of different outlets. At this point the waters have not been in contact with each other or diluted.

The COD load was highest from the cracker, second highest from the aromatics and lowest from the butadiene plant. The ThOD analysis of these streams determined that components causing the ThOD load varied. In the butadiene plant the highest contributor were, in order of magnitude, phenol, acetone, acetonitrile, methanol and glycol. In the aromatics the greatest contributors were phenol, acetone, toluene, methanol and cumene. The biggest contributors to the ThOD build-up from the cracker were, 2- aminoethanol, phenol and methanol. In the pit 27 the acetonitrile was the largest contributor, 2-aminoethanol the second largest and methanol the third largest on the first analyzing occasion. On the second analyzing occasion, the largest was 2-aminoethnanol, the second largest was methanol and the third largest phenol. Primary results are shown in Appendix I.

The results shown in Table 13, show that the ThOD and the COD are no closer to each other even when the water was analysed before waters mix with each other, or get diluted due to other water sources discharges. The error between the COD and ThOD was largest in the aromatics, which could indicate that most of the unknown components causing the COD were coming from aromatics. However, the error is high in the cracker and the butadiene plants as well. The lowest ThOD and COD error was found when the ThOD analysis was performed for samples taken on March 9th from outlet of the OW-stripper. The error was only 2%, this was because the water sample contained only methanol and ThOD value of methanol correlated well to actual the COD of methanol (methanol is well correlative component according to Baker *et al.* (1999)) and resulted in very low error value. This proved that the ThOD analysis method for estimating the COD works generally when there is mainly one component present in the stream. Interesting was also that when methanol concentration is high, also the COD was high, over 10 000 mg O_2 L^{-1}.

Table 13 **Results of ThOD analysis of known components present in waste water sources of oily waters**

Parameter	**Sampling point**			
	Pit 27	**Cracker**	**Butadiene**	**Aromatics**
COD, mg/l	590	865	215	565
ThOD total, mg/l	196	245	49	49
Error, %	66%	72%	77%	91%

5.2.4 Results of the supplementary external measurement program of oily waters

5.2.4.1 Origin of components present in the oily waters

The results shown in Table 14 are average of three separate analyzing occasions. All results of supplementary external measurement program of oily waters can be found from Appendix J.

First it was analyzed how the load was distributed between production plants: the cracker, the butadiene, the aromatics (containing benzene, cumene and phenol plants) and the OSBl area. Then the distribution of load inside the cracker and the aromatics was analyzed. When the concentration was under detected limit, it was set as zero. If the average value from three separate analyzing occasions was less than detection limit, it is shown in tables as below detection limit, for example in Table 14 the methanol concentration in every analyzing occasion was under 2 mg l^{-1} from butadiene plant.

The origin of methanol load was the aromatics. Most of the phenol originated from the cracker and the aromatics. What was an interesting was that phenol concentration was higher in waste water from the cracker than from the aromatics. It would be recommended that phenol plant treated their waste water in the stripper if it is possible. Acetone enters the system from all production plants, but originates most from the butadiene plant.

Benzene concentration is 100 times larger than the concentration of second biggest component toluene in water sample taken from the pit 27. Benzene and toluene originate from the cracker, while isopropyl benzene (cumene) originate from the aromatics. Benzene and toluene concentrations from the cracker are seven times higher than from the aromatics. Cumene originate from both the cracker and the aromatics, but can be found in 100 times higher concentrations in samples taken from the aromatics. No volatile organic compounds are introduced from butadiene plant. The load from the OSBL branch can be determined as load from the cracker since other plants do not charge waste water to the OSBL branch at the moment.

Total nitrogen originated mostly from the aromatics. The total nitrogen present in the crackers water sample most probably represents 2-aminoethanol and in the butadiene's water sample it represents acetonitrile.

The COD load is highest from production plants. It was surprising that butadiene plants's COD load equals to load from the cracker even though many single components analyzed are found in very low concentrations from the butadiene's water sample. Only total nitrogen and acetone concentrations were equal to the concentrations from water samples from other plants.

Table 14 Origin of the new components found in the waste water.

Component	Unit	Sampling point				
		Pit 27	Ethylene	Butadiene	Aromatics	OSBL-branch
Methanol	mg/l	30	44	<2	137	4
Phenol	mg/l	32	7	0	7	0
Acetone	mg/l	8	11	18	11	<1
Benzene	µg/l	7 367	14 000	2	2 130	375
Toluene	µg/l	737	1 400	<2	208	126
Isopropylbenzene	µg/l	340	1 540	<2	15 333	1 147
m+p-Xylene	µg/l	48	80	<4	49	52
o-Xylene	µg/l	28	38	<2	23	35
TVOC C5-C10	µg/l	8 800	17 000	16	20 667	2 003
Total nitrogen	mg/l	37	32	18	36	9
Ph	-	12	12	8	12	7
COD	mg/l	450	590	567	833	46

5.2.4.2 Origin of components in the cracker

All pits analysed in the cracker (C-8, C-9, C-10), other than the OSBL-15 discharge to the C-13. Water sample taken from the C-13 represents the load that build up in the cracker's ISBL area. The water sample from the OSBL-15 is included under the crackers contribution because it is the only plant discharging water to the OSBL branch. Components and their concentrations that are present in the cracker's waters are gathered to Table 15. The results shown in table 15 are an average results of three separate measurements, all results are shown in Appendix J.

Methanol load originated mostly from C-9 and secondly from C-10, which indicates that these components originate from washings steps and from the process water circulation. The cracker was the main origin of benzene and toluene. These components were introduced to the OW-system via the pit C-9. Origin for all volatile organic hydrocarbons is not the process water as thought but instead the washing steps since highest concentrations were found from the pit C-9. Also the bulk parameter total volatile organic hydrocarbons (TVOC C5-C10) show similar result. Highest COD concentrations were not surprisingly found from the C-9 and the second biggest COD concentration in the C-10.

Table 15 Origin of the new components in the cracker.

Component	Unit	Sampling points in the cracker				
		C-13	C-8	C-9	C-10	OSBL-15
Methanol	mg/l	44	<2	82	12	1,83
Phenol	mg/l	7	0,001	0,20	15	0,04
Acetone	mg/l	11	<1	38	4	<1
Benzene	µg/l	14 000	<2	193 333	19	375
Toluene	µg/l	1 400	<2	18 667	6	126
Isopropylbenzene	µg/l	1 540	<2	23	<2	1147
m+p-Xylene	µg/l	80	<4	883	9	52
o-Xylene	µg/l	38	<2	367	12	35
TVOC C5-C10	µg/l	17 000	19	213 333	400	2 003
Total nitrogen	mg/l	21	4	16	69	9
pH in water	-	11,7	7,2	11,9	10,2	7,2
COD(Cr)	mg/l	590	46	987	670	46

5.2.4.3 Origin of the components in the aromatics

Aromatics contributed most to methanol, total volatile organic hydrocarbons, and total nitrogen. The results are shown in Table 16. The results shown in Table 16 are an average results of three separate measurements, all results are shown in Appendix J.

Methanol and acetone were introduced to the OW-system with ejector waters. Aromatics plant is the main contributor of cumene to the OW-system. Also the biggest total volatile organic hydrocarbon load was found in samples of ejector waters. Cumene was the factor why total hydrocarbon load from aromatics and from ejector waters was so high. The ejector waters had cumene concentration almost two hundred times higher than the outlet of OW-stripper. The next biggest volatile organic chemicals from aromatics were benzene and toluene. Benzene load is evenly distributed between the two sources in aromatics. Toluene concentrations in both water sources is very low but found from sample which reflect the total load from aromatic side, this indicates that either toluene built-up outside analyzed places or accumulated in the OW-system. Xylenes are either found in very low concentrations (under 100 ppb) or not found at all from water samples.

OW-stripper was the main origin for phenol and total nitrogen. Waters fed to the OW-stripper should not contain any phenol. The phenol concentration in water coming from OW-stripper varied between 8-15 ppm. This indicates that maybe the cracker discharges some of its waters to the OW-stripper anyway, because it is unlikely that phenol would originate from benzene or cumene plants. There is no possibility to monitor whether the cracker lead its waste water to the OW-stripper or not.

Table 16. Origin of the new components in the aromatics.

Component	Unit	Samplin point		
		Aromatics	OW-stripper	Ejector waters
Methanol	mg/l	137	3	603
Phenol	mg/l	7	11	0,02
Acetone	mg/l	11	<1	64
Benzene	µg/l	2130	36	13
Toluene	µg/l	208	<2	<2
Isopropylbenzene (cumene)	µg/l	15 333	42	17 667
m+p-Xylene	µg/l	49	<4	<4
o-Xylene	µg/l	23	2	<2
TVOC C5-C10	µg/l	20 667	103	20 000
Total nitrogen	mg/l	36	40	N.A.
pH in water	-	12,1	8,8	4
COD(Cr)	mg/l	833	523	1667

6 Conclusions

6.1 Common conclusions

The impression in the beginning was that the measured COD was reliant on parameters normally analyzed from waste waters: methanol, phenol, acetone, ethylene glycol, benzene, toluene, cumene, xylenes, total nitrogen, total hydrocarbons and dissolved organic carbon. First the COD variation was studied against the concentration variations of different components.

The problem with studying only these correlations was that the cumulative effect could not be characterized. ThOD analysis was performed for single components normally analyzed from waste waters: methanol, phenol, acetone, ethylene glycol, benzene, cumene, toluene and xylenes. ThOD-analysis was selected because it ought to reflect the cumulative effect and then a function to describe the COD variation should have been feasible according to the literature review. When ThOD analysis was performed for selected parameters described above, the COD-value did not follow the same trend with ThOD, hence the COD could not be determined with help of calculating ThOD for selected parameters. What was found was that ThOD method predicts the COD value when there is only one high concentration of one component, but does not predict COD if there are a lot of components present in low concentrations.

The COD load could not be determined by analysing the components Borealis had chosen as part of the regular monitoring program. Borealis has to analyze other components as well. When more accurate analysis of quality of water is performed more research is needed to find out how the interplay of different components affects COD load. The ThOD method does not take into account the different kind of interferences of halogens but instead assume that all halogens interfere with the COD as chlorine does. In the literature it is discussed that different halogens affect COD differently and the interference cannot be diminished only with one catalyst. The ThOD analysis does not take into account the halogen interference with ammonia. Halogen in presence of ammonia may cause falsely high COD. The ThOD does not take into account inorganic compound and anions which also may be oxidised (use oxidant) and that way cause falsely high COD. Anions may cause falsely high COD-values. The COD of waste waters containing phenolic compounds needs much more analytical attention. Overall there should be more scientific research to understand the source of the COD load in waste waters of refineries and petrochemical plants. According to my literature research the COD of phenolic waters does not necessarily decrease when phenol is treated, but stays the same and the contribution of other phenolic components or other components present in waste waters from oil plants and petrochemical plants increase their contribution. According to J.lu *et al.* (2006) it is not fully know why the COD is so high in petrochemical waste waters.

6.2 Phenolic waters

The water circulation in phenol plant was studied and only waters discharged to biological treatment in Neste Oil were included. It was found out that there are three main waste water sources to biological treatment feed stream, biolsy, because of effective water circulation. The water used in process is effectively circulated through different process steps where water is used and finally processed in effluent stripper before discharge to biolsy. The other water source is the MHP-reactor and third is the basin, where all the paving waters are collected. The result from qualitative analysis of phenolic waters was to analyse outlet of the MHP-reactor and the effluent stripper to find from where different components originate to biolsy.

The ThOD analysis for phenolic waters showed that the ThOD was on average only fifth of the COD. Because of this the contribution of different components to the COD load could not be determined. Methanol and phenol were the main contributor to the ThOD load in phenolic waters and other measured parameters had none or very little contribution to ThOD.

In the supplementary onsite measurement program the water samples were taken in addition to biolsy also from the outlets of defined main water sources (the stripper and the MHP-reactor) primarily to find the origins of load and secondly to exclude the influence that waters are mixed and diluted in final stream biolsy. Based on an analysis including all the components, one may conclude that methanol, phenol and cumene originates from the MHP-reactor. Also the highest COD load was from the MHP-reactor. The error between the ThOD and the COD was analyzed to find out if calculated ThOD was closer to measured COD. The error became smaller in the outlet of the MHP-reactor, but got bigger in the outlet stripper compared to error in biolsy. This may be due to the higher concentration of components in the outlet of the MHP-rector. According to results from external measurement program, the MHP-reactor was the origin of all other load than acetone.

6.3 Oily waters

The water circulation and different sources for waste water in all plants were analyzed. It was found that the cracker had about 15 different water sources, from which the most important were the diluting steam generator and waste water discharge from the sodium hydroxide and the FCC washers. The diluting steam generator discharges the water used as diluting steam in cracking process. From the butadiene plant, the main and only continuous waste water origin was the acetonitrile recovery column. From the benzene and the cumene plants almost all waste waters are discharged through the OW-stripper, waters that are not, are paving waters. The phenol plant discharges part of its paving waters and ejector waters to OW-system.

The ThOD analysis was performed for OW-systems waters. On average ThOD determined for analyzed parameters is one third of average COD. With help of only given parameters the COD contribution could not be determined in OW-waters. The main contributors to ThOD in the OW-system were 2-aminoethanol, methanol, phenol, acetone, ethylene glycol and benzene.

At the moment most of the principal contributors to the load are analysed, but these analyses do not help when the total load is studied, because different components or parameters are analyzed. That is why the old analyses could not be used in the study, but a new analyzing scheme, the supplementary onsite measurement program, was implemented. According to the onsite measurement program nitrogen, phenol and methanol originate from water used in the cracking process. Origin of ethylene glycol, acetone, propanols, benzene, cumene, toluene and xylenes is not possible to determine reliably. Also the concentration of contaminants in the water samples taken from the pit 27 were higher than in the studied streams which indicated that these components enter the system somewhere else than from studied process units. ThOD analysis performed for the streams measured in the onsite measurement program showed that the error between the ThOD and the COD minimised. ThOD shows it predicts the COD well when there is only component in the stream. Low error was determined (2%) in outlet of OW-stripper, when only methanol was present in waste water. Measured COD was load highest from outlet of diluting steam generator, second highest from the OW-stripper and lowest from the outlet of the butadiene's carbonyl wash.

In the external measurement program first it was determined which components are coming from which plants. Methanol originates from the aromatics, but also a small amount from the cracker. Acetone originates mostly from the butadiene plant, but also from the aromatics and the cracker. Benzene has its highest concentration in pit 27 of all volatile hydrocarbons analyzed and it biggest contributor is the cracker. Toluene also originates in the cracker while cumene comes from the aromatics. Phenol originates both from cracker and aromatics, but mostly from the cracker.

In the cracker the highest concentrations of components were found in from sample taken from C-9. This indicates that the sodium hydroxide wash and the FCC-wash could be the origin of these components. Also the steam condenser discharges to the same pit, which can be the origin of the load as well. Methanol, benzene and toluene were found at their highest concentrations in pit C-9.

In the aromatics most of the components enter the OW-system with waste water discharged from ejectors. All other components analyzed were introduced to OW-system with waste water from ejector other than acetone and total nitrogen.

Only the quality of the waters was studied, because adequate information about flow rates from different waste water sources was not available. If water is discharged a little here and there, now and then, without any monitoring it is not possible to gasp the total picture, neither possible to design suitable methods to reduce the load. At the moment the flow rates of pit 27, outlet of diluting steam generator, acetonitrile recovery column outlet and outlet of OW-stripper have flow monitoring. Flows from few other process units can also be traced by assuming that input equals to output. The total flow determined from these sources do not equal to the amount of total flow in pit 27 as it should. The simplest way to reduce the load is to cut down the amount of water fed to the waste water system and because of that it is also important know amount of water discharged from different places.

The OW-system, which covers all the five different plants, is a large system. It seemed that personnel in different plants knew well their own specific area, but there was lack of an overall picture of how the system works. Without an overall picture of how the system works it not possible to design effective and cost efficient load reduction solutions.

7 Recommendations

7.1 Common

1. More research is needed to find out how the interplay of different components present in the waste waters affects the COD.

2. It should be studied whether the COD is falsely too high because of the interplay of different components or because of the inert material. COD does not differentiate the inert material from the biologically available material, which the BOD does. Whether the COD is falsely too high or not could be therefore studied with BOD-analysis.

7.2 Phenolic Waters

1. Start analysing the quality of the waste water from the outlet of the MHP-reactor

2. Treat the water from the MHP-reactor either in the effluent stripper or study the possibility to treat it in the OW-stripper.

7.3 Oily waters

1. Start analysing the same components from all the main waste water sources.

2. Group together flows with similar component content.
    - i) One solution could be for example to group together flows with high hydrocarbon content (like water used in the NaOH and the FCC washers and water from the cracker flaring basin) and their treatment in the OW-stripper. If it is not possible to treat all the waste water in the OW-stripper, then it should be determined which of the sources should be the most important to be treated in OW-stripper. Once the changes are done also an enhanced monitoring program should be implemented to monitor which flows are sent to the OW-stripper and how they affect the overall input and output loads associated with the OW-stripper.
    - ii) Another solution could be treatment of phenol containing waste water in effluent stripper (for example the outlet of the diluting steam generator).

3. Start monitoring more properly when and from where the water is discharged to the OW-system.
    - i) Monitoring the flow rates from the washing steps in cracker, the cracker flaring basin, and the butadiene flaring basin should be started.
    - ii) It is also recommended to start monitoring the overall flow rates from the cracker, the butadiene plant and the phenol and aromatics. These could be monitored from the pits C-13, BU-1 and BZN-1 from the cracker, the butadiene and the aromatics, respectively.

4. If new waste water treatment process units are designed these should be placed near the contaminant source.

5. Cracker and butadiene plant should mark their pits correctly. At the moment pit C-7 is marked as pit C-9 in the cracker and pit BU-1 is named as BU-2.

6. It would be good idea if there was one person responsible for the whole OW-system.

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Appendix A

Chemical classes according to Baker *et al. (1999)*

Table 17. Chemical classes divided according to the information how well their COD correlates to ThOD. (Baker, Milke and Mihelcic 1999)

Group number	Groupe type	Number of chemicals in the group	Chemical class	COD/ThOD correlation		Low end of 90 % and 95% confidence bound[1]
				mean	std.dev	
1	Well correlated aromatics	113 (6 classes)	Sulphonic acids	0.98	0.092	0.96;0.90
			Phenols and phenol ethers			
			Alcohols, aldehydes and ketones			
			Carboxylic acids			
			Amines and nitriles			
2	Well correlated non-aromatics	97 (8 classes)	Alcohols	0.97	0.082	0.92;0.90
			Nitrile esters with phoshate, sulfate, silicate substituent			
			Unsaturated carboxylic acids			
			Acetates and acrylates			
			Multisubstituted alcohols and ether alcohols			
			Saturated dicarboxylic acids			
			carbohyrates			
			Terpenes, sesqui- ja diterpenes			
3	Potentially well correlated non-aromatics	29 (2 classes)	Chloro-, nitro- and aminophenols	0.93	0.18	0.80;0.59
			Thiocompunds			
4	Potentially well correlated non-aromatics	38 (6 classes)	Nitriles	0.92	0.23	0.75;0.22
			Ketones and hydroxyketones			
			Amino acids			
			Diketones			
			Hydroxy di- and tricarboxylic acids			
			Polycyclic ring structure with nitrogen sustituted into aromatic ring			
5	Other aromatics	79 (8 classes)	Azo compounds			
			Non-benzene hydrocarbons			
			Hydrocarbons			
			Halogenated aromatic hydrocarbons			
			Nitro and chloro-nitro aromatic hydrocarbon			
			Quinones			
			Triphenylmethane derivates			
			Condensed ring aromatic hydrocarbons			
6	Other non-aromatics	209 (35 Classes)	Alkenes			
			Alkynes			
			Multiple unsaturated hydrocarbon			

		Alkenol Alkynol Ether, halogen ether, oligoether Thioalcohol and derivates Thioethers Nitroalkanes Silicon and metal organic Aldehydes Saturated acids Furans with two heteroatoms and derivative Six-sided ring with heteroatom and derivative Bicyclic hetero-systems Alkaloid Aliphatic alkane Aliphatic halogen alkane and alkene Glycerinesthers Halogenalcohol, halogenated acid and acid ester Hydroxy acid Aldehyde and ketoacid Unsaturated acid Ketoacid and carbon acid derivative Thio-carbon-acid derivative Iso-and thicyanate Aliphatic sulfone, sulfoxide, sulfonic acid Aliphate amines and imines Acyclic cycloalkane and cycloalkene Bicyclic alkanes Steroids Furan and derivates Condensed rings of furan-, thiphene- and pyrrol Derivates of cycloparafin and olefinen Synthetic polymers			
all	565	64	0.85	0.33	0.64;0.38

NA= Data does not fit into beta-normal model. Chemical-specific data in Baker *et al.*(1999)

1) 90% or 95 % confidense that any of the chemicals in this group has a COD/ThOD above the "mean" value. This value does not include the removal of an anticipated laboratory error other than for groups 1 and 2.

Appendix B

Calculation of ThOD

According to Baker *et al.* (1999) the amount of oxygen consumed by single component *i* can be determined with Equation 9. Letters *n, m, k, j, i, h* and *e* can be determined with Equation 8. According to Baker *et al.* (1999) the Equation 8assumes that all compounds are oxidized totally to end products. Letters inform how many molecules there is of element *i* in component *i*.

Phenol's chemical formula is C_6H_6O

Equation 8

$$C_nH_mO_eX_kN_jS_iP_h + bO_2 \rightarrow nCO_2 + \left(\frac{m-k-3j-2i-3h}{2}\right)H_2O + kH_x + jNH_3 + iH_2SO_4 + hH_3PO_4$$

According to Equation 8

n=6
m=6
e=1
k=0
j=0
i=0
h=0

When *n, m, k, j, i, h* and *e* are used in Equation 9, the amount of oxygen molecules needed to oxidise phenol into end products can be determined.

Equation 9

$$b = n + \frac{m-k-3j-2i-3h}{4} - \frac{e}{2} + 2i + 2h$$

Determination of oxygen consumption for phenol is shown with Equation 10.

Equation 10

$$b_{PHE} = 6 + \frac{6-0-3\cdot 0-2\cdot 0-3\cdot 0}{4} - \frac{1}{2} + 2\cdot 0 + 2\cdot 0 = 7\frac{mol\ O_2}{mol\ PHE}$$

Table 18. Chemical formulas and determined oxygen demand for different components.

Component	Composition	Oxygen demand per one mole component i
		b
Methanol	CH4O	1,50
Phenol	C6H6O	7,00
Acetone	C3H6O	4,00
2-Aminoethanol	C2H7NO	2,50
Benzene	C6H6	7,50
Cumene	C9H12	12,00
Propanols	C3H8O	5,00
Toluene	C7H8	9,00
Total Nitrogen	N	0,00
Xylenes	C8H10	10,50

Determination of $\mathrm{ThOD}_{0,\mathrm{i}}$ is shown with Equation 11, where b_i is the amount of oxygen consumed in moles per one mole component i, M_{O_2} is the molar mass of oxygen molecule and M_i themolar mass of component i. Molar mass can be calculated with help of chemical formula.

Equation 11

$$ThOD_{0,i} = b_i \cdot \frac{M_{O2}}{M_i}$$

An example of Theoretical oxygen demand calculations for phenol is shown with Equation 12.

Equation 12

$$ThOD_{0,i} = 7{,}00 \frac{mol\ O_2}{mol\ PHE} \cdot \frac{31{,}98\ \frac{g\ O_2}{mol\ O_2}}{94{,}10\ \frac{g\ PHE}{mol\ PHE}} = 2{,}38 \frac{g\ O_2}{g\ PHE}$$

Results for oxygen demand per one mol component i, molar mass and theoretical oxygen demand are gathered in Table 19.

Table 19 Oxygen demand per one mole component i, molar mass and theoretical oxygen demand.

Component	Composition	Oxygen demand per one mole component i	Molecular weight	Theoretical oxygen demand
		b	Mi (g/mol)	ThODi (gO2/gi)
Methanol	CH4O	1,50	32,03	1,50
Phenol	C6H6O	7,00	94,10	2,38
Acetone	C3H6O	4,00	58,07	2,20
2-Aminoethanol	C2H7NO	2,50	61,08	1,31
Benzene	C6H6	7,50	78,11	3,07
Cumene	C9H12	12,00	120,20	3,19
Propanols	C3H8O	5,00	44,10	3,63
Toluene	C7H8	9,00	92,14	3,12
Total Nitrogen	NH3	0,00	17,03	0,00
Xylenes	C8H10	10,50	106,17	3,16

Equation 13

$$\mathrm{ThOD_i} = \mathrm{ThOD_{0,i}} \cdot \mathrm{c_i}$$

For example, if the concentration of phenol is 360 mg/l in waste water sample, the theoretical oxygen demand determination with phenol concentration of 360 mg/l is shown in Equation 14. The total theoretical xygen demand was determined by summing the single theoretical oxygen demand together.

Equation 14

$$\mathrm{ThOD_{PHE}} = \mathrm{ThOD_{0,PHE}} \cdot \mathrm{c_{PHE}}$$

$$= 2{,}38 \frac{mg\ O_2}{mg\ PHE} \cdot 360 \frac{mg\ PHE}{l\ H_2O} = 856{,}8\ \frac{mg\ O_2}{l\ H_2O}$$

The results of ThOD calculations are shown in Appendix C and in Appendix H.

Appendix C

ThOD-analysis for components present in biolsy.

Concentrations of different components and theoretical oxygen demand they caused in stream biolsy in phenolic waters are shown in Figure 41, Figure 42, Figure 43, Figure 44, Figure 45, Figure 46 and Figure 47. Studied period was year 2010.

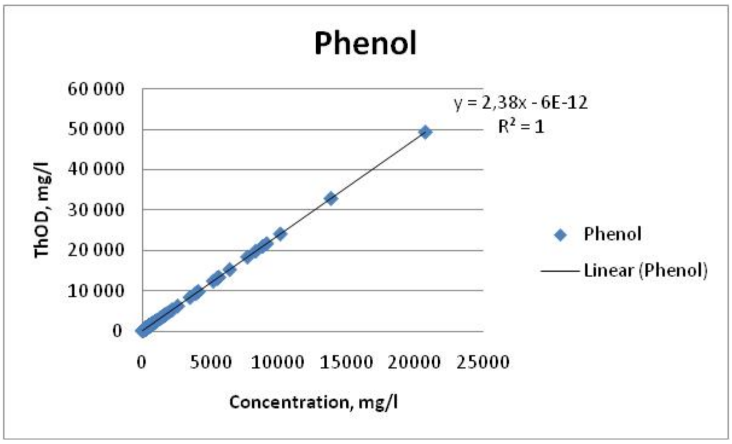


Figure 41 **Phenol concentration in studied period varied between zero and 25 000 mg l^{-1} and calculated ThOD between zero and 50 000 mg l^{-1}.**

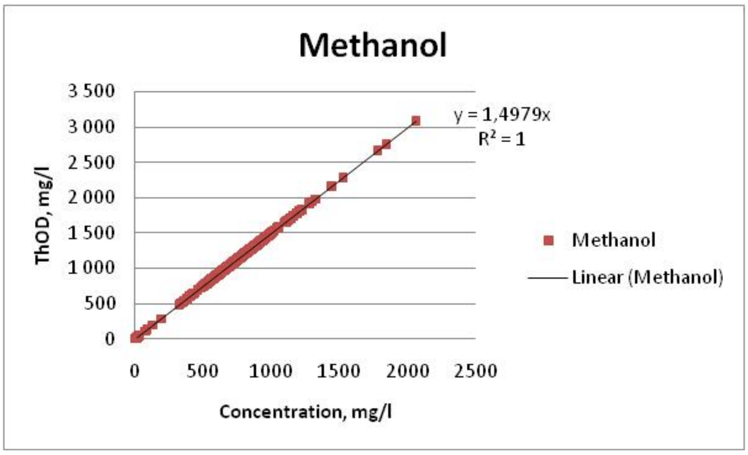


Figure 42 **Methanol concentration varied between zero and 2500 mg l^{-1} and ThOD it casued varied between zero and 3000 mg l^{-1}.**

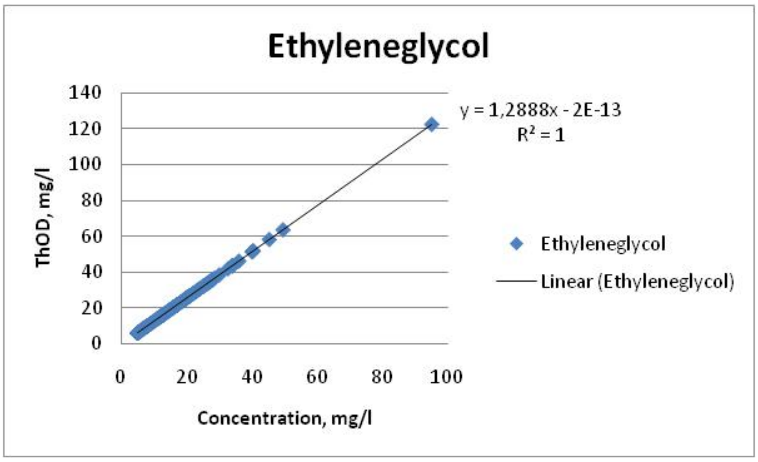


Figure 43 Concentration of ethylene glycol varied between zero and 100 mg l^{-1}, most of the time it was under 60 mg l^{-1} and hence caused ThOD between zero and 120 mg l^{-1}.

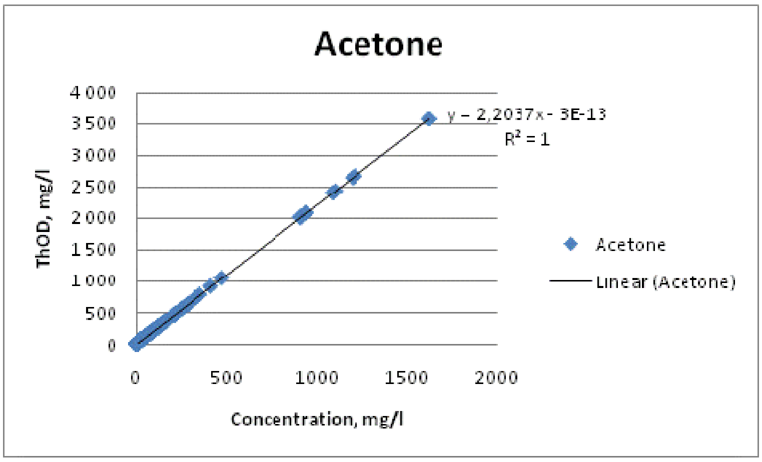


Figure 44 Acetone concentration varied in studied period between zero and 2000 mg l^{-1} and caused ThOD between zero and 3500 mg l^{-1}.

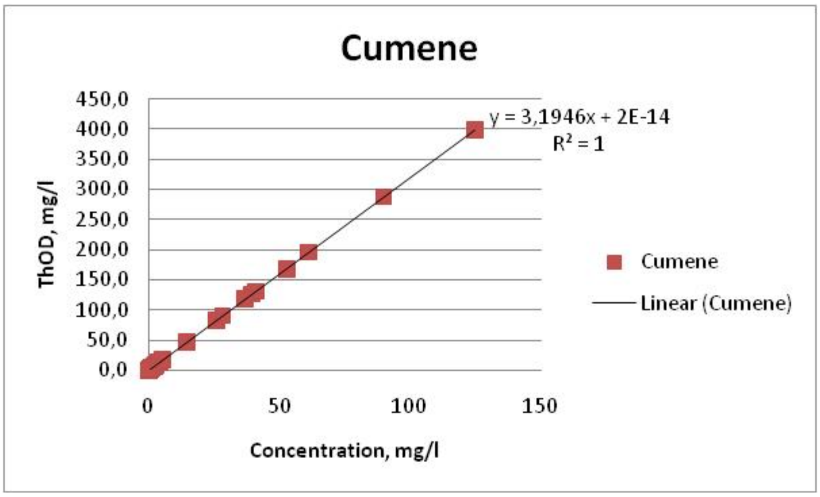


Figure 45 Cumene concentration stayed under 150 mg l^{-1} under studied period and it caused ThOD maximum 400 mg l^{-1}.

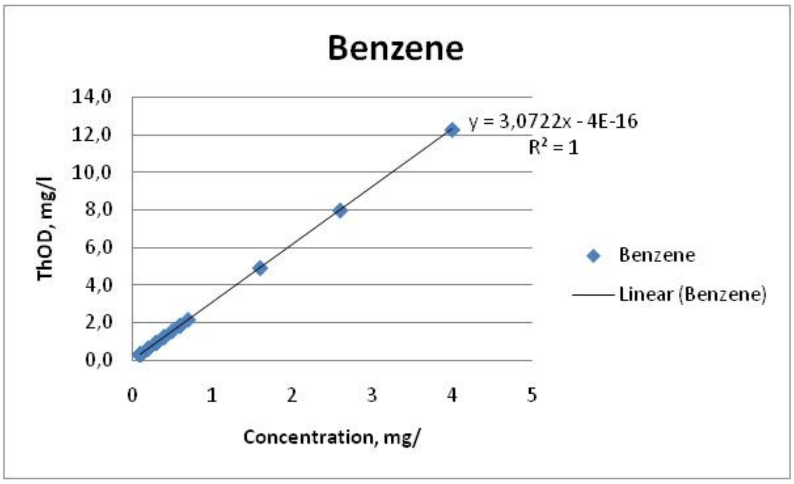


Figure 46 Benzene concentration was under 5 mg l^{-1} under studied period and caused ThOD between zero and 12 mg l^{-1}.

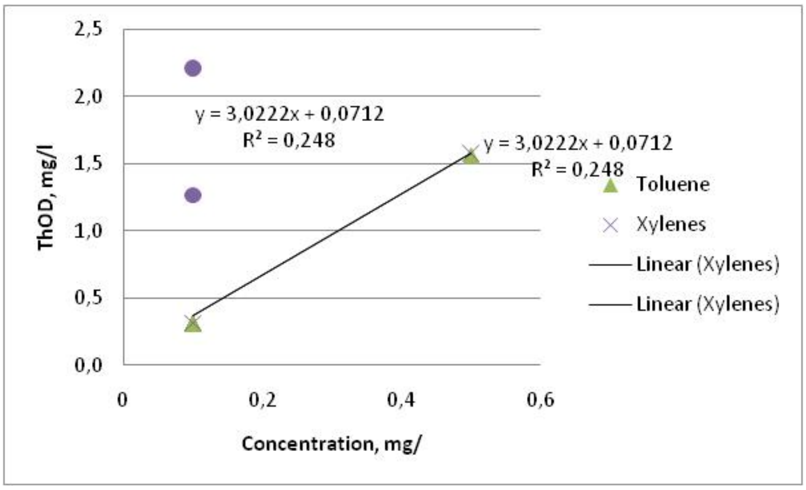


Figure 47 Toluene and xylenes (o-, m-, and paraxylene) concentration stayed under 0,6 mg l^{-1} and caused ThOD less than 2,5 mg l^{-1}.

Appendix D

Supplementary onsite measurement program

Results of supplementary onsite measurement program of phenolic waters

Table 20. Results of supplementary onsite measurement program. Concentrations of components is shown in mg l^{-1}

Component	21.2.2011			23.2.2011			7.3.2011		
	Biolsy	Stripper	MHP-reactor	Biolsy	Stripper	MHP-reactor	Biolsy	Stripper	MHP-reactor
Methanol	78	5	4 955	360	53	4 412	901	99	5 272
Phenol	233	193	1 135	368	212	1 500	368	204	2 967
Ethyleneglycol	5	5	5	5	5	5	5	15	5
Acetone	1	1	1	12	1	1	18	15	5
Benzene	0,3	3,2	0,1	0,5		0,1	0,1	0,1	0,1
Cumene	0,1	0,1	56,6	0,1		36	0,1	0,1	25,4
Xylenes	0,1	0,1	0,1	0,1		0,1	0,1	0,1	0,1
Toluene	0,1	0,1	0,1	0,1		0,1	0,1	0,1	0,1
Acetonitrile							5	5	5
Propanols							1	1	1
Tot.hydrocarbons	1,3	4	82	3,9		60	4,9	1,5	53,9
Total nitrogen	24			13	14	1	16	20	1
DOC	3 500			4 815	2940	19 450	4 920	2 990	15 250
COD	9 520	8 770	52 500	11 700	9420	49 700	14 000	10 200	37 200

ThOD-analysis results for onsite supplementary measurement program of phenolic waters.

Concentrations of different compounds, their theoretical oxygen demands and contribution to total ThOD in phenolic waters.

Table 21. ThOD analysis for water sources in phenolic waters system.

SAMPLING POINT	Component	Original results, mg/l			ThOD, mg/l			ThOD, %		
		21.02	23.02	07.03	21.02	23.02	07.03	21.02	23.02	07.03
Biolsy	Methanol	78	360	901	117	539	1 350	17%	39%	59%
	Phenol	233	339	368	555	807	876	81%	58%	38%
	Ethyleneglycol	5	5	5	6	6	6	1%	0%	0%
	Acetone	1	12	18	3	37	55	0%	3%	2%
	Benzene	0,3	0,5	0,1	1	2	0	0%	0%	0%
	Cumene	0,1	0,1	0,1	0,3	0,3	0,3	0%	0%	0%
	Ksylenes	0,1	0,1	0,1	0,3	0,3	0,3	0%	0%	0%
	Toluene	0,1	0,1	0,1	0,3	0,3	0,3	0%	0%	0%
	Acetonitrile			5			7,8			0%
	Propanols			1			3,6			0%
	Tot.hydrocarbons	1,3	3,9	4,9						
	Total nitrogen	24	13	16						
	DOC	3500	4460	4920						
	COD	9520	11700	14000						
	ThOD Met&Phe				671	1 346	2 225			
	ThOD total				683	1 392	2 300	100%	100%	100%
	Error				93%	88%	84%			
Stripper	Methanol	5	53	99	7	79	148	2%	13%	21%
	Phenol	193	212	204	459	505	486	94%	85%	68%
	Ethyleneglycol	5	5	15	6	6	19	1%	1%	3%

	Acetone	1	1	15	3	3	46	1%	1%	6%
	Benzene	3,2		0,1	10		0	2%	0%	0%
	Cumene	0,1		0,1	0,3		0,3	0%	0%	0%
	Ksylenes	0,1		0,1	0,3		0,3	0%	0%	0%
	Toluene	0,1		0,1	0,3		0,3	0%	0%	0%
	Acetonitrile			5			7,8			1%
	Propanols			1			3,6			1%
	Tot.hydrocarbons	4		1,5						
	Total nitrogen		14	20						
	DOC		2940	2990						
	COD	8770	9420	10200						
	ThOD Met&Phe				467	584	634			
	ThOD total				487	593	712	100%	100%	100%
	Error				94%	94%	93%			
MHP-reactor	Methanol	4955	4412	5272	7 422	6 609	7 897	72%	64%	52%
	Phenol	1135	1500	2967	2 701	3 570	7 061	26%	35%	47%
	Ethyleneglycol	5	5	5	6	6	6	0%	0%	0%
	Acetone	1	1	5	3	3	15	0%	0%	0%
	Benzene	0,1	0,1	0,1	0	0	0	0%	0%	0%
	Cumene	56,6	36	25,4	180,8	115,0	81,1	2%	1%	1%
	Ksylenes	0,1	0,1	0,1	0,3	0,3	0,3	0%	0%	0%
	Toluene	0,1	0,1	0,1	0,3	0,3	0,3	0%	0%	0%
	Acetonitrile			5			7,8			0%
	Propanols			1			3,6			0%
	Tot.hydrocarbons	82	60	53,9						
	Total nitrogen		1	1						
	DOC		19450	15250						
	COD	52500	49700	37200						
	ThOD Met&Phe				10 124	10 179	14 959			
	ThOD total				10 315	10 304	15 074	100%	100%	100%
	Error				80%	79%	59%			

Appendix E

External measurement program of phenolic waters

Table 22. Results of external measurement program of phenolic waters

Component	Unit	1.set			2. set		
		Biolsy	MHP-reactor	Stripper	Biolsy	MHP-reactor	Stripper
Methanol	mg/l	990	8 100	<2	570	5 800	<2
Phenol	mg/l	240	1 800	1	68	0,3	74
Acetone	mg/l	34	13	68	28	11	14
Isopropylbenzene (Cumene)	µg/l	170	27 000	2	1 200	7 000	<2
Benzene	µg/l	<2	14	<2	<2	3,1	<2
Toluene	µg/l	<2	5,80	<2	<2	<2	<2
m+p-Xylene	µg/l	<4	<4	<4	<4	<4	<4
o-Xylene	µg/l	<2	<2	<2	<2	<2	<2
TVOC C5-C10	µg/l	290	36 000	60	1 800	7 000	52
COD	mg/l	14 000	37 200	10 200	11 000	38 000	9 300
pH	-				9,8	12,9	5,4

Appendix F

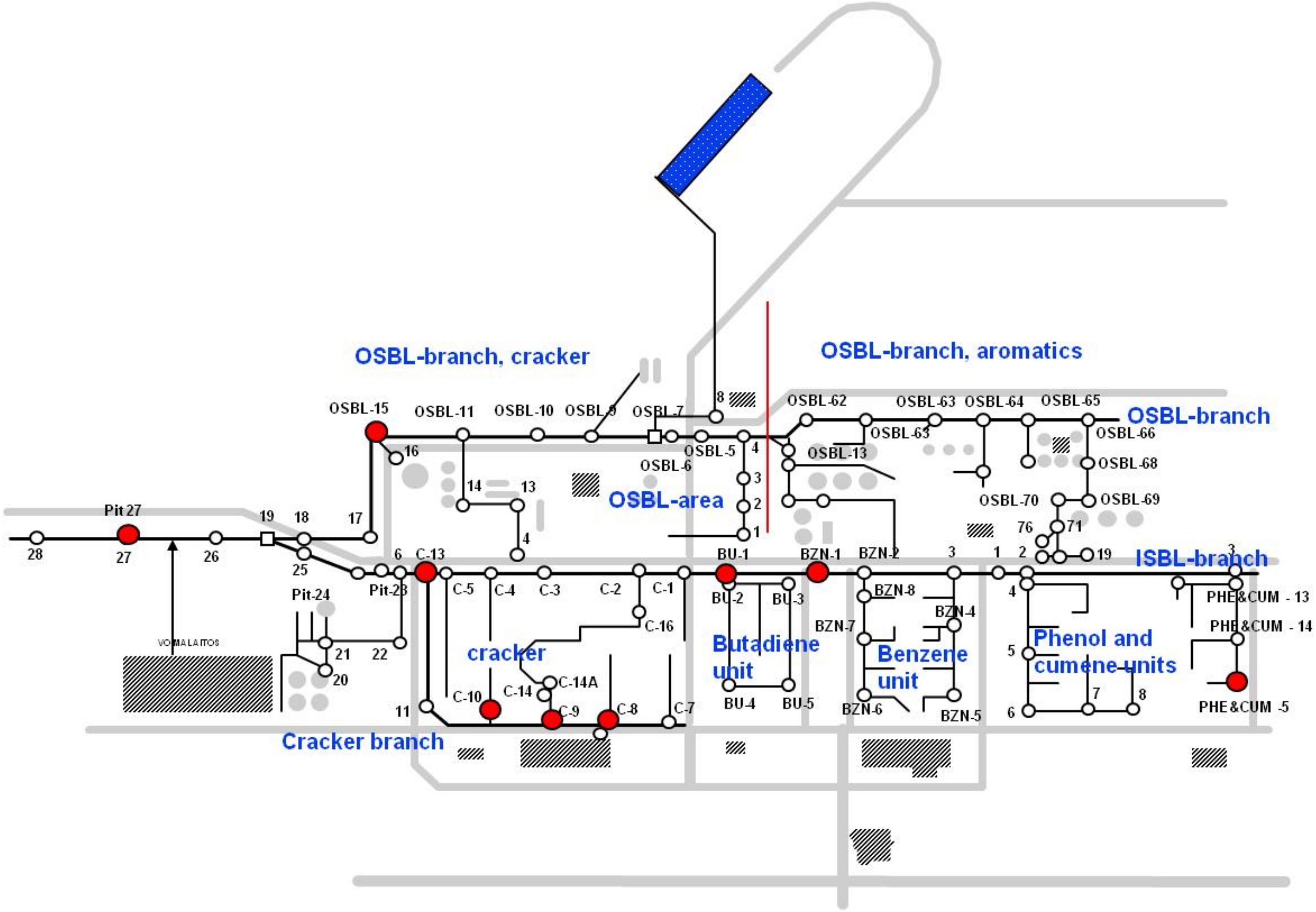
Main water sources to the oily water system

Table 23. Water sources to the OW-system from ISBL-areas.

Plant	Water Source	Discharge to OW-system via pit
Cracker	Water from diluting steam generator	C-10
	Collection tank for water from NaOH-wash and from FCC-wash	C -9
	Steam condenser	C -9
	Sealant water from condenser	C -9
	Reboiler	C -2
	Condensate from heat exchanger	C -4
	Condensate from drip condenser	C -7
	Drip condenser. Condensated regeneration steam.	C -9
	Another drip condenser	C -9
	Flaring tank.	OSBL-9
	Distillation column	
	Dirty condensate from reboilers and heat exhangers	
	Cylinders and haet exchangers	C -5
	Emergency shower	C -3
	Emergency shower	C -10
Butaidiene	ACN-recovery column	BU-1
	Flaring basin	BU-1
	Emergency shower	BU-1
Benzene and cumene	OW-stripper	BZN-2
Phenol	Ejector waters	PHE&CU-15

Appendix G

Sampling points of external measurement program of oily waters. Sampling point OW-stripper is not marked in the figure because it is not a pit.



Appendix H

Results of ThOD-analysis of oily waters

Concentration of components present in OW-system in pit 27 and their theoretical oxygen demands are shown in Figure 48, Figure 49, Figure 50, Figure 51, Figure 52, Figure 53, Figure 54, Figure 55 and Figure 56.

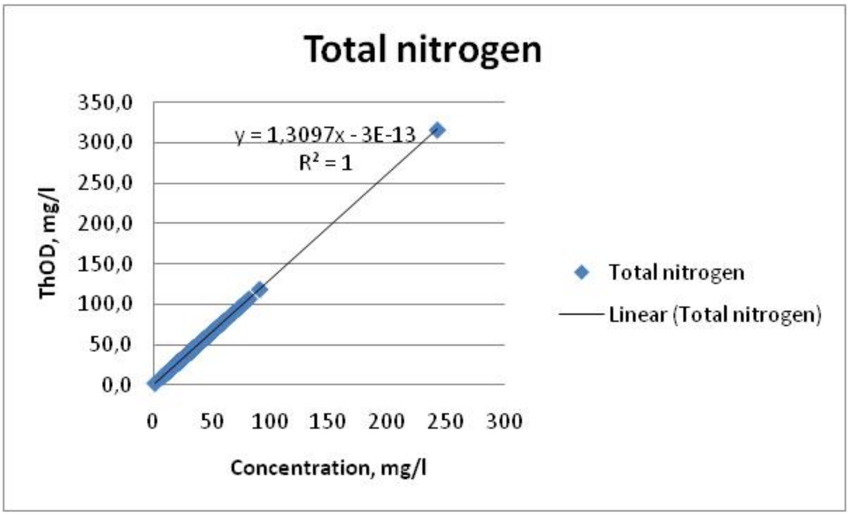


Figure 48 Total nitrogen concentration varied between zero and 300 mg l^{-1} and caused ThOD between zero and 350 mg l^{-1}. The total nitrogen was treated as 2-aminoethanol.

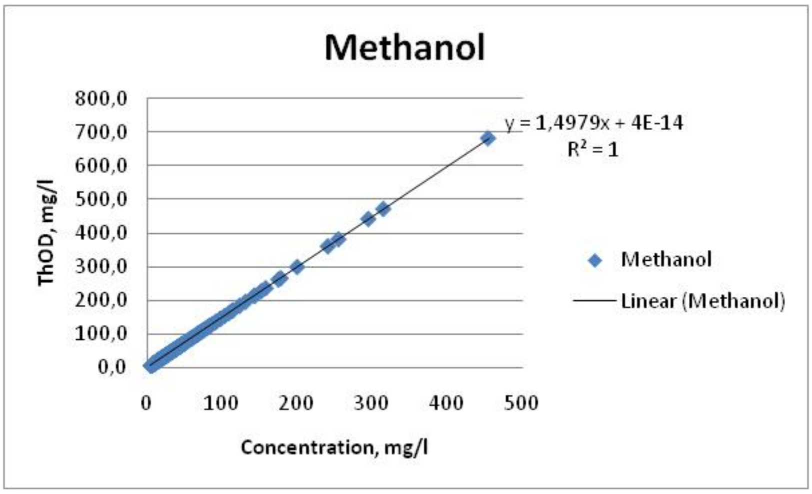


Figure 49 Methanol concentration in OW-system varied between zero and 500 mg l^{-1}, when its maximum in Biolsy stream was 2500 mg l^{-1}.

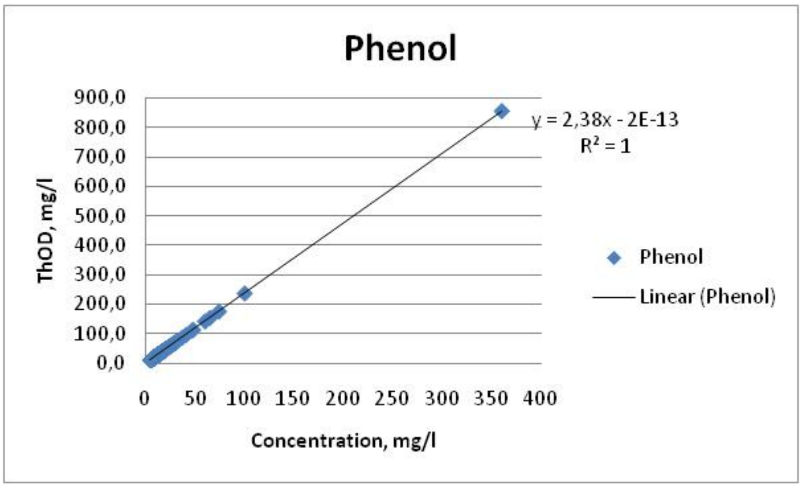


Figure 50 Phenol concentration stayed mostly under 150 mg l^{-1} in OW-system under studied period.

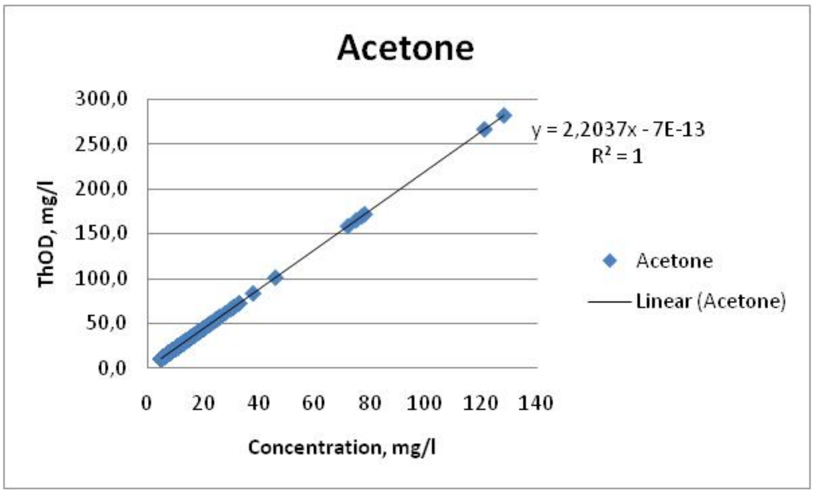


Figure 51 Acetone concentration in OW-system stayed mostly under 100 mg l^{-1}, when in biolsy the amount was three times higher. ThOD caused by acetone remained under 300 mg l^{-1}.

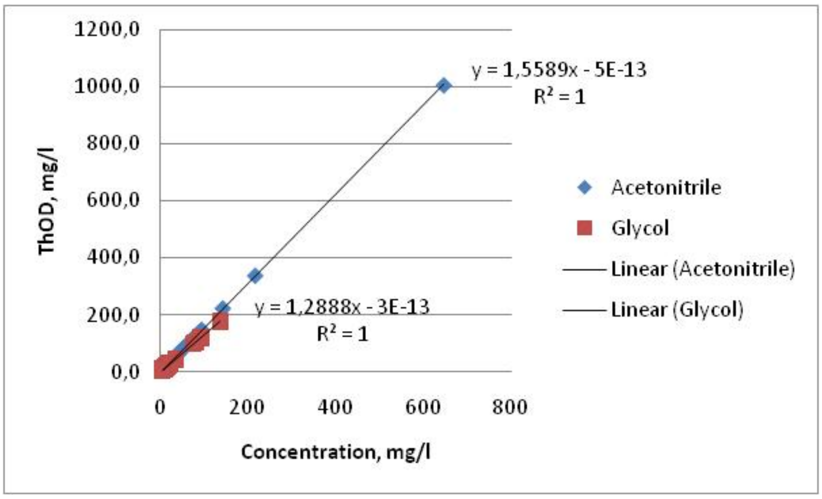


Figure 52 Ethylene glycol and acetonitrile were found mostly under concentration 200 mg l^{-1} and ThOD caused but these components remained mostly under 400 mg l^{-1}.

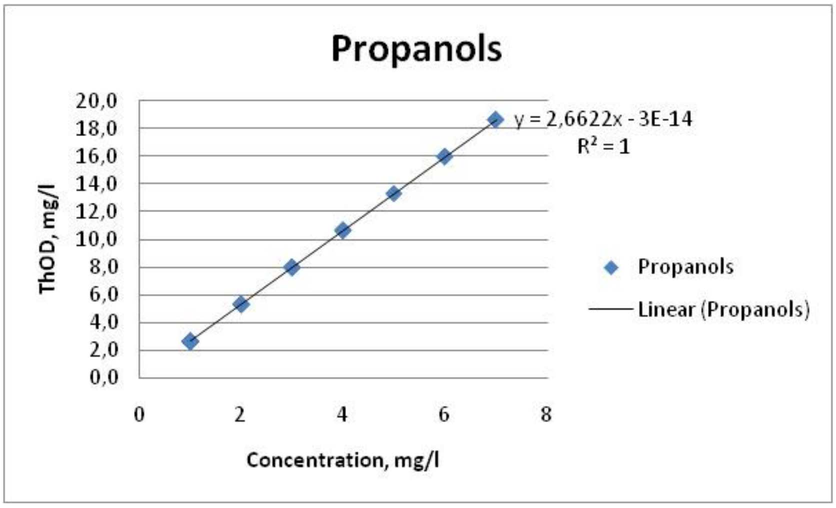


Figure 53 Propanols are only measured from oily waters normally. The concentration remained under 8 mg l^{-1} and caused ThOD under 20 mg l^{-1}.

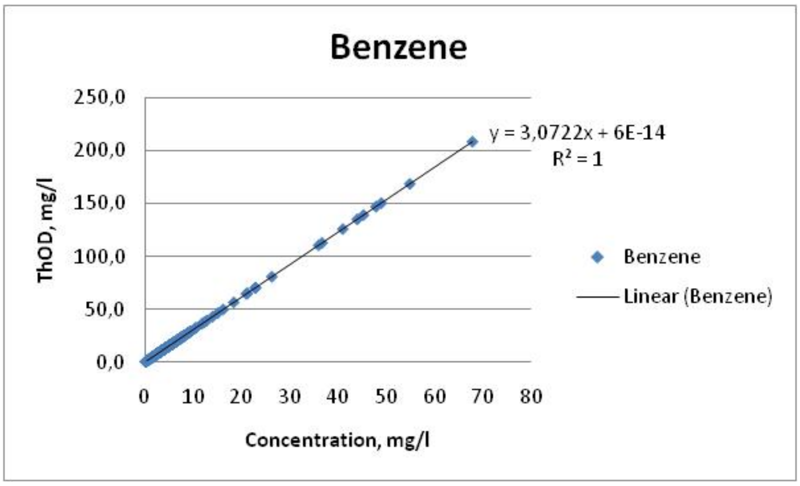


Figure 54 Benzene concentration in oily waters varied between zero and 80 mg l^{-1}, compared to concentration in biolsy which was only under 5 mg l^{-1}.

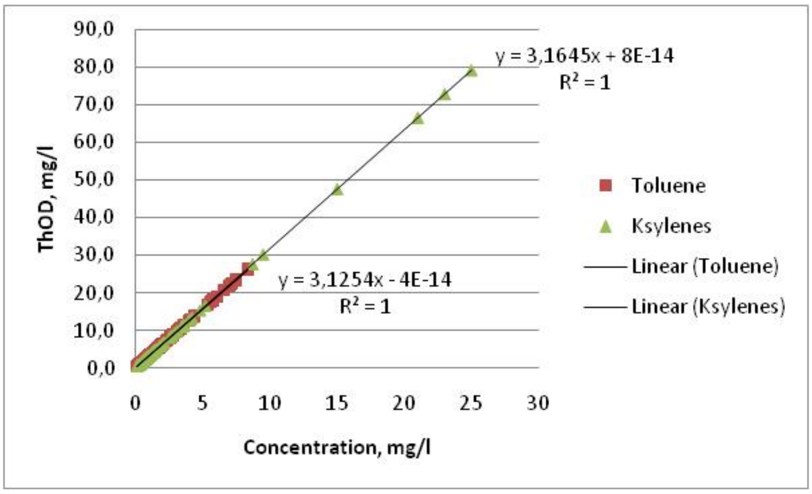


Figure 55 Toluene was found in concentrations under 10 mg l^{-1} and xylenes under 25 mg l^{-1} in oily waters. These components were found in biolsy in less than 1 ppm concentrations.

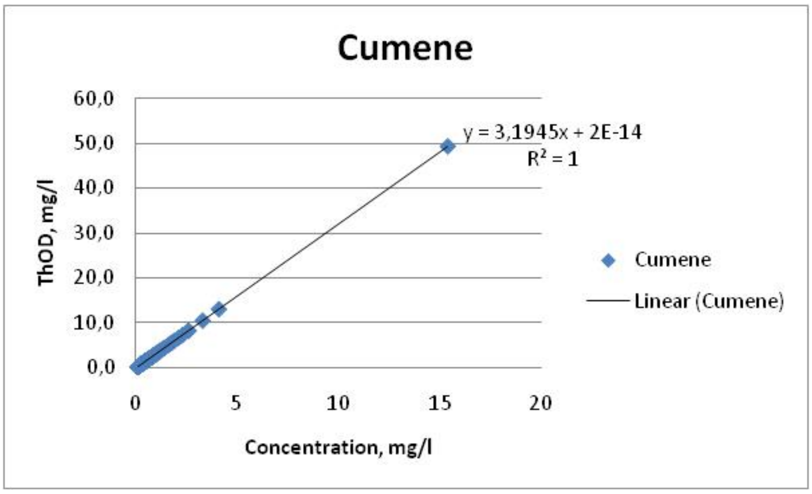


Figure 56 Cumene concentration remained mainly under 5 mg l^{-1} and caused ThOD under 15 mg l^{-1} in oily waters when in biolsy its concentration was more than 100 mg l^{-1}

Appendix I

Results of supplementary onsite measurement program of oily waters.

Table 24. Origin ogf components present in the pit 27 according to onsite measurement program.

Component	2.3.2011				9.3.2011				3.3.2011
	Pit 27	Cracker	Buta	Aro	Pit 27	Cracker	Buta	Aro	Aro
Total nitrogen	37	66	45	20	45	66	51	64	19
Methanol	15	21	5	5	26	51	5	6594	5
Phenol	7	31	5	10	13	32	5	25	8
Acetonitrile	48	5	5	5	6	5	5	5	
Glycol	5	5	5	5	5	5	5	5	5
Acetone	5	5	5	5	8	5	5	5	1
Propanols	1	1	1	1	1	1	1	1	
Benzene	3,2	0,1	0,1	0,1	8,4	0,1	0,1	0,1	0,1
Cumene	0,3	0,1	0,1	0,1	0,5	0,1	0,1	0,1	0,1
Toluene	0,2	0,1	0,1	0,1	1	0,1	0,1	0,1	0,2
Xylenes	0,1	0,1	0,1	0,1	0,6	0,2	0,1	0,1	0,1
Tot.hydrocarbons	10,6	1,5	0,1	0,3	20,2	10	0,1	20,3	19
DOC	130	250	80	160	210	270	60	1700	170
COD	480	840	230	560	700	890	200	10200	570

Results of ThOD-analysis of onsite supplementary measurement program of oily waters

Table 25. Results of ThOD analysis of waste water sources to the oily waters system.

SAMPLING POINT	Component	Concentration, mg/l			ThOD, mg/l			ThOD percentage		
		2.3	3.3	9.3	2.3	3.3	9.3	2.3	3.3	9.3
Butadiene	Total nitrogen	45		51	0		0	0%		0%
	Methanol	5		5	7		7	15%		15%
	Phenol	5		5	12		12	25%		25%
	Acetonitrile	5		5	8		8	16%		16%
	Glycol	5		5	6		6	13%		13%
	Acetone	5		5	11		11	23%		23%

	Propanols	1		1	3		3	5%		5%
	Benzene	0,1		0,1	0,3		0,3	1%		1%
	Cumene	0,1		0,1	0,3		0,3	1%		1%
	Toluene	0,1		0,1	0,3		0,3	1%		1%
	Xylenes	0,1		0,1	0,3		0,3	1%		1%
	Tot.hydrocarbons	0,1		0,1						
	DOC	80		60						
	COD	230		200						
	ThOD total				49		49	100%		100%
	Error				79%		76%			
OW-stripper	2-aminoethanol	20		64	0	0	0	0%	0%	0%
	Methanol	5	5	6594	7	7	9877	12%	20%	99%
	Phenol	10	8	25	24	19	59	39%	52%	1%
	Acetonitrile	5		5	8	0	8	13%	0%	0%
	Glycol	5	5	5	6	6	6	11%	18%	0%
	Acetone	5	1	5	11	2	11	18%	6%	0%
	Propanols	1		1	3	0,0	3	4%	0%	0%
	Benzene	0,1	0,1	0,1	0,3	0,3	0,3	1%	1%	0%
	Cumene	0,1	0,1	0,1	0,3	0,3	0,3	1%	1%	0%
	Toluene	0,1	0,2	0,1	0,3	1	0,3	1%	2%	0%
	Xylenes	0,1	0,1	0,1	0,3	0,3	0,3	1%	1%	0%
	Tot.hydrocarbons	0,3	19	20,3						
	DOC	160	170	1700						
	COD	560	570	10200						
	ThOD total				60	37	9966	100%	100%	100%
	Error				89%	94%	2%			
Cracker	Total nitrogen	66		66	86,44		86,44	39%		32%
	Methanol	21		51	31,46		76,39	14%		28%
	Phenol	31		32	73,78		76,16	33%		28%
	Acetonitrile	5		5	7,79		7,79	4%		3%
	Glycol	5		5	6,44		6,44	3%		2%
	Acetone	5		5	11,02		11,02	5%		4%
	Propanols	1		1	2,66		2,66	1%		1%
	Benzene	0,1		0,1	0,31		0,31	0%		0%
	Cumene	0,1		0,1	0,32		0,32	0%		0%
	Toluene	0,1		0,1	0,31		0,31	0%		0%

	Xylenes	0,1	0,2	0,32	0,63	0%	0%
	Tot.hydrocarbons	1,5	10				
	DOC	250	270				
	COD	840	890				
	ThOD total			221	268	100%	100%
	Error			74%	70%		
Pit 27	2-aminoethanol	37	45	48,46	58,94	25%	30%
	Methanol	15	26	22,47	38,95	12%	20%
	Phenol	7	13	16,66	30,94	9%	16%
	Acetonitrile	48	6	74,83	9,35	39%	5%
	Glycol	5	5	6,44	6,44	3%	3%
	Acetone	5	8	11,02	17,63	6%	9%
	Propanols	1	1	2,66	2,66	1%	1%
	Benzene	3,2	8,4	9,83	25,81	5%	13%
	Cumene	0,3	0,5	0,96	1,60	0%	1%
	Toluene	0,2	1	0,63	3,13	0%	2%
	Xylenes	0,1	0,6	0,32	1,90	0%	1%
	Tot.hydrocarbons	10,6	20,2				
	DOC	130	210				
	COD	480	700				
	ThOD total			194	197	100%	100%
	Error			60%	72%		

Appendix J

Results of supplementary external measurement program of the oily waters.

Plant contribution

Table 26. Origin of components present in the pit 27. Contribution of different process plants.

Component	Unit	First set of samples					Second set of samples					Third set of samples				
		Pit 27	Cracker	Buta-diene	ARO	OSBL -15	Pit 27	Cracker	Buta-diene	ARO	OSBL -15	Pit 27	Cracker	Buta-diene	ARO	OSBL -15
Methanol	mg/l	24	26	<2	160	7	30	62	<2	130	4	35	44	<2	120	<2
Acetone	mg/l	8	12	28	11	<1	5	8	12	10	<1	11	12	15	12	<1
Phenol	µg/l	11000	7200	33	7000	41	83001	8400	1	6300	4	2700	5600	280	7400	62
Benzene	µg/l	8800	19000	<2	1500	400	6500	13000	4.8	4700	15	6800	10000	2,3	190	710
Toluene	µg/l	600	1400	<2	150	110	720	1500	<2	440	28	890	1300	<2	35	240
Isopropylbenzene	µg/l	250	620	<2	16000	1900	420	2600	<2	17000	240	350	1400	<2	13000	1300
m+p-Xylene	µg/l	45	64	<4	40	57	42	95	<4	97	20	56	82	<4	9,7	78
o-Xylene	µg/l	26	35	<2	18	40	27	43	<2	47	12	31	37	<2	4,7	52
TVOC C5-C10	µg/l	10000	21000	27	22000	2900	8000	17000	22	24000	410	8400	13000	<20	16000	2700
COD(Cr)	mg/l	460	550	600	960	63	390	580	560	860	21	500	640	540	680	55
Total nitrogen	mg/l	28	28	9	45	4	48	35	14	37	5	34,43	<3	31,02	27	17,12
pH in water	-						11,7	11,7	8,2	12,7	7,2					

Table 27. Origin of components present in the pit 27 from the cracker.

Component	Unit	1. set					2. set					3. set				
		C-13	C-8	C-9	C-10	OSBL-15	C-13	C-8	C-9	C-10	OSBL-15	C-13	C-8	C-9	C-10	OSBL-15
Methanol	mg/l	26	<2	41	10	7	62	<2	56	17	4	44	<2	150	8	<2
Acetone	mg/l	12	<1	38	4	<1	8	<1	30	5	<1	12	<1	47	4	<1
Phenol	µg/l	7 200	1	320	13 000	41	8 400	3	< 1	22 000	4	5 600	< 1	290	11 000	62
Benzene	µg/l	19 000	<2	230 000	25	400	13 000	<2	180 000	15	15	10 000	<2	170 000	17	710
Toluene	µg/l	1 400	<2	15 000	5,4	110	1 500	<2	21 000	6	28	1 300	<2	20 000	7,5	240
Isopropylbenzene	µg/l	620	<2	25	<2	1 900	2 600	<2	18	<2	240	1 400	<2	26	<2	1300
m+p-Xylene	µg/l	64	<4	700	8,9	57	95	<4	850	10	20	82	<4	1 100	7,5	78
o-Xylene	µg/l	35	2,4	300	11	40	43	<2	360	15	12	37	<2	440	11	52
TVOC C5-C10	µg/l	21000	32	250000	320	2900	17000	<20	200000	520	410	13000	24	190000	360	2700
Total nitrogen	mg/l	28	3	3	40	4	35	5	5	80	5	<3	4,46	39,27	85,67	17,12
pH in water	-						11.7	7.2	11.9	10.2	7.2					
COD(Cr)	mg/l	550	62	890	530	63	580	21	770	640	21	640	56	1300	840	55

Table 28. Origin of components present in the pit 27 from the phenol and aromatics.

Component	Unit	1.set			2. set			3. set		
		Aromatics	OW-stripper	Ejector waters	Aromatics	OW-stripper	Ejector waters	Aromatics	OW-stripper	Ejector waters
Methanol	mg/l	160	<2	690	130	5	570	120	5	550
Acetone	mg/l	11	<1	72	10	<1	58	12	<1	62
Isopropylbenzene (cumene)	µg/l	16 000	4,2	15 000	17 000	120	19 000	13 000	2,7	19 000
Benzene	µg/l	1 500	14	13	4 700	73	16	190	22	11
Toluene	µg/l	150	<2	<2	440	3	<2	35	<2	<2
m+p-Xylene	µg/l	40	<4	<4	97	7	<4	9,7	<4	<4
o-Xylene	µg/l	18	2	<2	47	4	<2	4,7	<2	<2
TVOC C5-C10	µg/l	22 000	37	18 000	24 000	230	19 000	16 000	42	23 000
Phenol	µg/l	7 000	11 000	15	6 300	15 000	23	7 400	8 000	18
Total nitrogen	mg/l	45	59	N.A.	37	20		27	41	N.A.
pH in water	-				12.1	8.8	4.0			
COD(Cr)	mg/l	960	750	1 900	860	350	1 700	680	470	1 400