DOKUZ EYLÜL UNIVERSITY

GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

WASTE MANAGEMENT ON THE TREATMENT OF OLIVE OIL BLACK LIQUOR BY VACUUM DISTILLATION

by

Onur CEBECİ

September, 2005

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A thesis Submitted to the
Graduate School of Natural and Applied Sciences of
Dokuz Eylül University
In Partial Fulfillment of the Requerements for
the Degree of Master of Science in Environmental Engineering,
Environmental Science Program

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ACKNOWLEDGEMENTS

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ABSTRACT

Olive mill effluents constitute a serious environmental problem in the Mediterranean Sea region due to the unique features associated with this type of agricultural waste. Therefore, it is not surprising that research efforts have been directed towards the development of efficient treatment technologies including various physico-chemical, biological and combined processes.

Olive oil mill wastewater (OMW- black liquor) have high organic matter, suspended solids and lipid contents. Many scientists work on efficient and cost effective treatment alternatives. To achieve this goal, several alternatives and their combinations were tested including the chemical, mechanical, physical, biological and thermal methods.

Here, OMW is accepted as a high volume waste and distillation is applied as a volume reduction. Since OMW has a water content above 80%, the volume of the waste to be treated is also high. The goal of the study is to decrease the amount of the waste to be treated by using different distillation temperatures for determining the ideal distillation temperature and mode to obtain a distillant with low COD concentration and high volume to obtain a more concentrate residue with less water content and high organic fraction.

As a conclusion it is determinated that distillate black liquor in continious mode with distillate cooling is the best alternative.

Keywords: Olive oil mill wastewater (OMW), distillation, black liquor, volume reduction

ZEYTİNYAĞI KARASUYUNUN VAKUM DİSTİLASYON YÖNTEMİ İLE ARITILMASINDA ATIK YÖNETİMİ

ÖZ

Zeytinyağı tesisleri çıkış suları bu tür tarımsal atıkların kendine özgü özellikleri nedeni ile Akdeniz bölgesinde önemli bir çevresel problemi oluşturmaktadırlar. Bu nedenle, bu tür suların arıtımında çeşitli fiziko kimyasal, biyolojik ve bir arada kullanılan prosesleri kapsayan etkin arıtma teknolojilerinin geliştirilmesi konusunda pek çok araştırmanın yürütülmesi şaşırtıcı değildir.

Zeytinyağı karasuyu organic madde içeriği, askıdaki katılar ve yağ içeriği bakımından yüksek değerler göstermektedir. Pekçok araştırmacı etkin ve ucuz arıtma seçenekleri konusunda çalışmaktadır. Bu hedefi gerçekleştirmek üzere kimyasal, mekanik, fiziksel, biyolojik ve ısıl yöntemler ve bunların bir arada kullanılabilenleri araştırılmaktadır.

Burada, zeytinyağı karasuyu yüksek hacimli bir atık olarak ele alınmış ve hacimsel indrgeme amaçlı distilasyon (özümleme) uygulamasına gidilmiştir. Karasu % 80 su içerdiğinden arıtılması gereken atık miktarı da hacimsel olarak fazladır. Çalışmanın hedefi; farklı distilasyon (özümleme) sıcaklıkları ve modları denenerek yüksek hacimde ve düşük KOİ (Kimyasal oksijen ihtiyacı) konsantrasyonuna sahip distilat ile, su içeriği düşük fakat organik madde içeriği yüksek daha konsantre bir kalıntı elde edecek en uygun sıcaklığı bulmaktır.

Çalışma sonunda soğutmalı ve sürekli olarak uygulanan distilasyon en uygun model olarak belirlenmiştir.

Anahtar sözcükler: Zeytinyağı atıksuyu, distilasyon (özümleme) , karasu, hacimsel indirgeme.

CONTENTS

CHAPTER ONE
INTRODUCTION

1.1. Literature Review

Olive is an environmental friendly vegetable because of unnecessary of chemical usage for growing and less energy requirement for processing. "Olive mill wastewater (OMW) is a highly polluting wastewater generated during the extraction of oil from the fruit, an aqueous, dark, foul-smelling and turbid liquid, which includes emulsified grease, is easily fermentable and has a very high amount of organics (up to 15% by weight)" (Potoglou et al., 2003). The OMW has low pH , high electrical conductivity and high free polyphenol concentrations, because of the fact that olive pulp esters and glycoside hydrolysis are produced during oil extraction. "Generally, OMW wastewater has BOD (Biological Oxygen Demand) values in the range of 12 000–63 000 mg:l and COD (Chemical Oxygen Demand) values in the range of 80 000–200 000 mg/l. These values are around 200–400 times higher than a typi-cal municipal sewage." (Al-Malah et al., 2000).
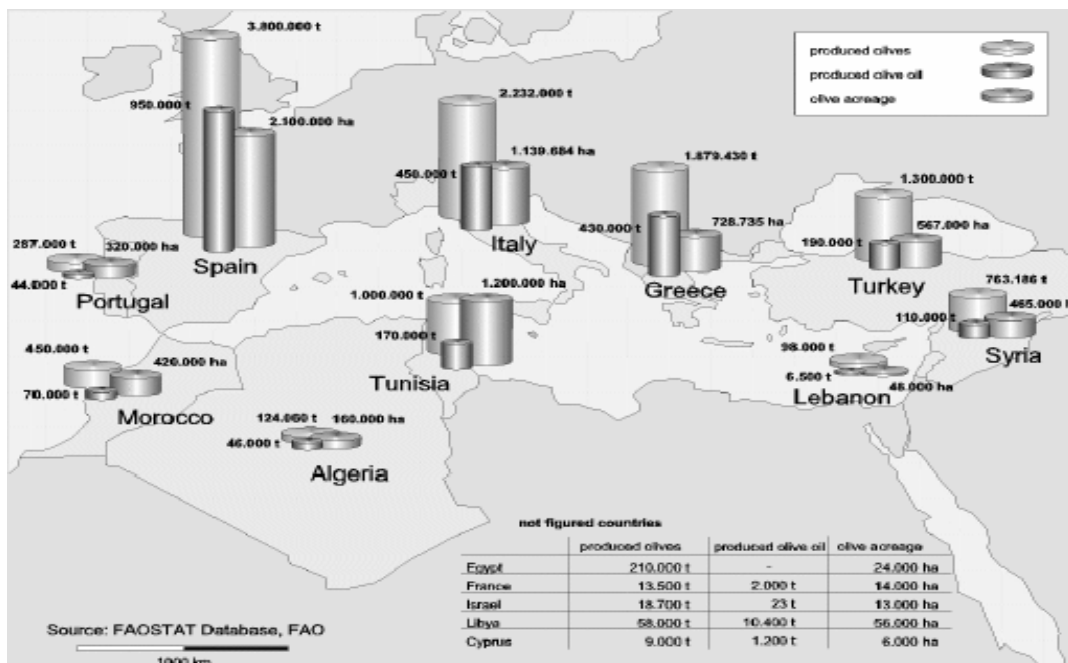
Figure 1.1. Olives and olive oil production in the Mediterranean area during 1998 (Skerratt & Ammar, 1999).

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Table 1.1 Composition of olives (Project Improlive, 2000).

Constitutents	Pulp(%)	Stone(%)	Seed(%)
Water	50-60	9,3	30
Oil	15-30	0,7	27,3
Constituens containing nitrogen	2-5	3,4	10,2
Sugar	3-7,5	41	26,6
Cellulose	3-6	38	1,9
Minerals	1-2	4,1	1,5
Polyphenols (aromatic substances)	2-2,25	0,1	0,5-1
Others	-	3,4	24

Olives have been cultivated in the short harvesting season lasting between November and April. The wastewaters produced during oil extraction generate a significant amount of organic pollution. The total amount of wastewater generated by the production of olive oil in the olive growing countries of the Mediterranean (Over 95% of the olive trees (805 millions) and over 97% of the agricultural area dedicated to growing olive is in excess of $30 \times 10^6\,\mathrm{m}^3$ per year. "Turkish olive oil trees cover 4% of the overall agricultural areas in Turkey. The olive oil production in the regions of Turkey are 75–80% in the Aegean area, 10% in the Mediterranean area and around 10% in the areas of Marmara and South East Anatolia." (Gurbuz et al., 2004). "The seasonal polluting load of olive-oil production is equivalent to about that of 22 million people per year since the COD value of the wastewater is about 80 g l and its volume produced from 1 ton olive is about 0,8 ton." (Aktas et al., 2001). OMW constitute an important environmental pollution problem in Mediterranean contries such as Turkey Greece, Spain, Italy, Morocco, Lebanon, Portugal, Tunisia and Israel.

1.2 Oil Production

Steps of the oil production process can be simply listed as follows;

1.2.1. Delivery

"The olives are delivered and stored in the yard in collection boxes. This offers the possibility to determine the quality and rate of yield, and serves as basis for the settlement of accounts between the oil mill and olive farmer. The production plant is fed in charges. The olives are filled in baskets, transported by donkey carts to the soil funnel and from thereby a belt conveyor to the first processing stage"(Tunca, 2004).

1.2.2 Washing of the olives

The olives are filled in charges into a soil funnel and transported by a belt conveyor into a sucking device, where leaves, wood particles and other disturbing solids are removed. Subsequently they are cleaned in a washing plant. In some plants the washing water is recycled into the process after sedimentation of the solids or filtration. In other plants the olives are directly processed without being washed. For washing of the olives 100 - 120 l of water per 1000 kg of olives are required. With the help of a perforated vibrating screen they are transported into a funnel. By the funnel tip they get into the loading opening of an eccentric worm pump, which conveys them into a grinding device (Tunca, 2004).

1.2.3 Grinding

"The olives are ground up, together with their stones, and mixed into homogeneous pulp. This is carried out in a stone-mill consisting of a horizontally lying granite block with a granite millstone resting perpendicular to it. Metal mills and hammer mills are also used for this purpose. If frozen or very dry olives are processed, a small quantity of water is added (100 - 150 liter per 1000 kg of olives)" (Tunca, 2004).

1.2.4 Mixing/beating of the olive pulp

In downstream-arranged malaxeurs the pulp is mixed after adding of warm water. For further breakdown of the olive cells and to create large oil droplets, the pulp is beaten (Figure 1.2). For this purpose salt is often added which aids the osmotic breakdown of cells in the olives and so the separation of the oil and water from each other is eased. Beating of the olives is repeated several times. For oil extraction by centrifuges the pulp is heated to improve the separation process. After beating the pulp is further ground up. In a malaxeur up to 100 % water are added before conveying the pulp by an eccentric worm pump into the two-phase- or three-phase decanter. (Tunca, 2004)
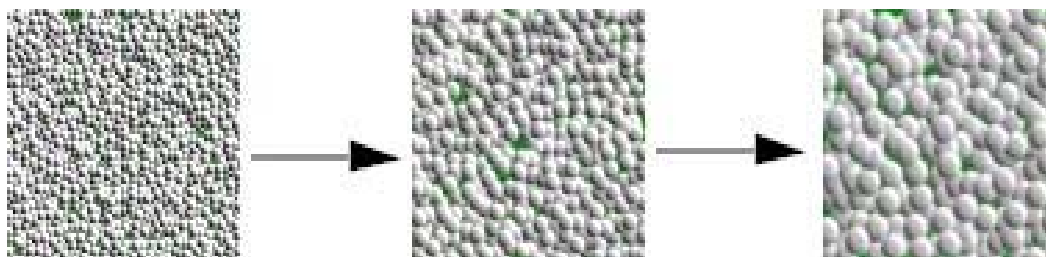
Figure 1.2. During mixing small oil droplets merge to form large drops, which can be squeezed out during pressing.(http://www.oliveoilsource.com/first_press-more_files/firstpressmanual.pdf)

1.2.5 Oil extraction and purification

Press-extraction is a mechanical process, involving the application of pressure to a stack of mats smeared with olive paste which are alternated with metal discs and placed on a frame that is fitted with a central spike (Figure 1.3). "Water and solids are thus separated from the oil and further centrifuged in order to recover residue oil. Oil is purified through clarification by sedimentation or filtration by vibrating screens. Wastewater streams are also clarified before disposal." (Caputo et al., 2003). BOD_5 and COD concentration of wastewater in this process 90-100g/l and 120-130g/l, respectively. This also has inherent environmental problems associated with it, in that although it produces no wastewater (margine) as such, it combines that wastewater that is generated with the solid waste (grignon) to produce a single effluent stream of semi-solid (~30 % solid by mass). This doubles the amount of

"solid" waste requiring disposal, and it is not able to be composted or burned without some form of (expensive) pretreatment. It is also unsuitable for solvent extraction to produce more oil for soap manufacture (Skerratt&Ammar, 1999).

Solid plate
on top and bottom →

Paste sandwiched between
fitler mats and slotted plates →
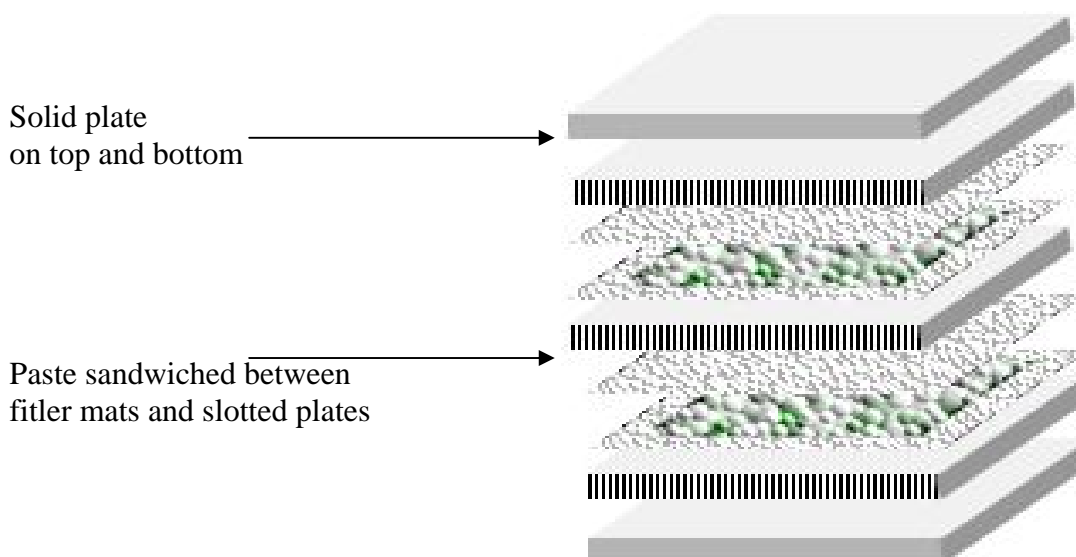
Figure 1.3. Pressing the paste (http : // www . oliveoilsource . com / first _ press-more _files / firstpressmanual.pdf)

"About 200 kg of oil result on an average from 1 ton of processed olives. To improve the separation of oil and pulp, biological or chemical aids can be added that attack the cell walls. With traditional presses the energy demand for olive oil extraction processes is 40-63 kWh per ton of processed olives, and 90 - 117 kWh with 3-phase decanters." (Tunca, 2004). "Residual solids from the purification step are mixed with those coming from the extraction process" (Caputo et al., 2003). "To enable the separation of small wastewater quantities and suspended solids that accompany the oil, 100 - 150 liter of water per 1000 kg of centrifuged oil are normally added to the purification process, which is achieved with the help of centrifugation" (Tunca, 2004).

1.2.5.1 Oil extraction Approaches

The 3-phase extraction method which in "pulp is processed into a 3-phase decanter where it is seperated into impure oil, liquid waste (OMW), and solid waste (OH) phases" (Caputo et al., 2003). was developed in the "70"s in order to reduce labour costs and increase processing capacity and yield whilst classical methods can process around 8-10 tonnes of olives per day, 3-phase continuous systems can process ~30 tonnes per day with a fraction of the labour requirement. Unfortunately, this technology also uses around 50 % more water than the simple pressing method (around 80-100 L of water per 100 kg of fruit processed) and generates around 50 % more wastewater per unit mass of fruit processed (~1,7 kg wastewater per kg olives processed compared to 0.9 in the classical method) (Lolos et al., 1994). The classical, 3-phase extraction method and are figured by Figure 1.4 and 1.5.

The 2-phase process (which uses much less water than the three-phase) was developed after the 3-phase process developed and so this method "mainly consists in a modification of the horizontal 3-phases centrifuge so that only 2-phase result (oil, sludge)" (Caputo et al., 2003). The 2-phase extraction method and are figured by Figure 1.6.
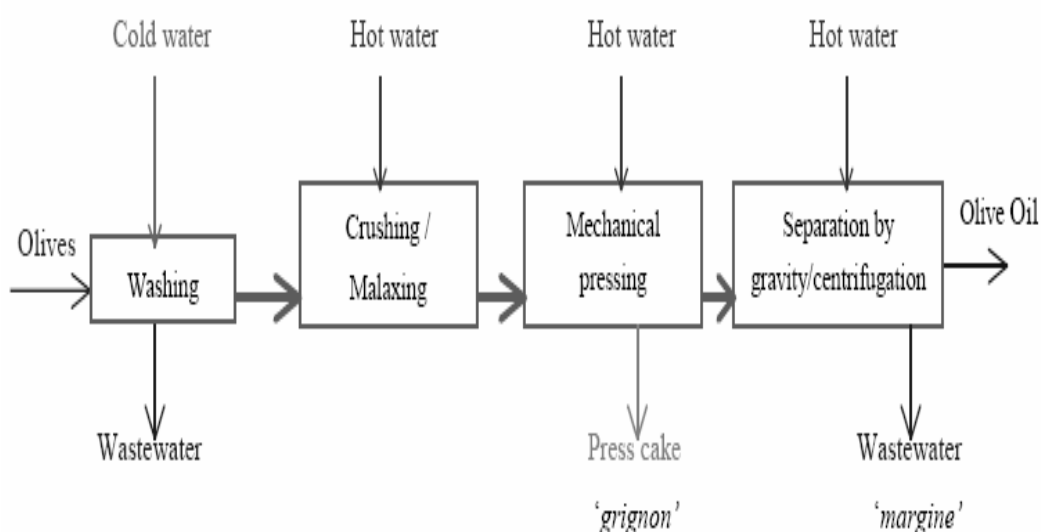
Figure 1.4. The pressure 'classical' extraction of olive oil (Skerratt&Ammar, 1999).
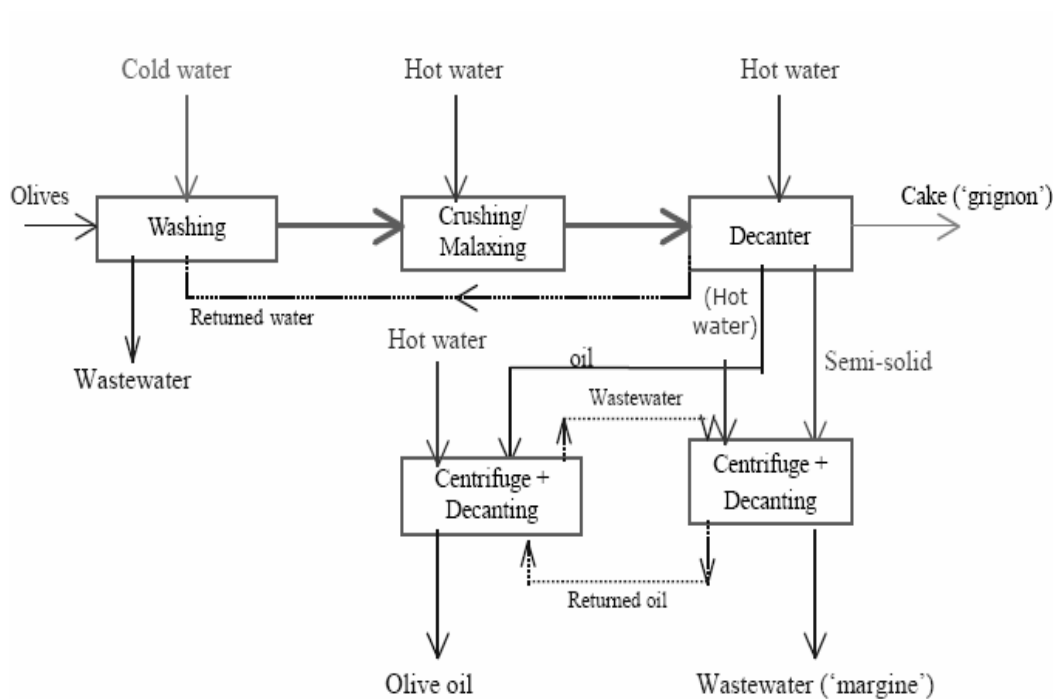
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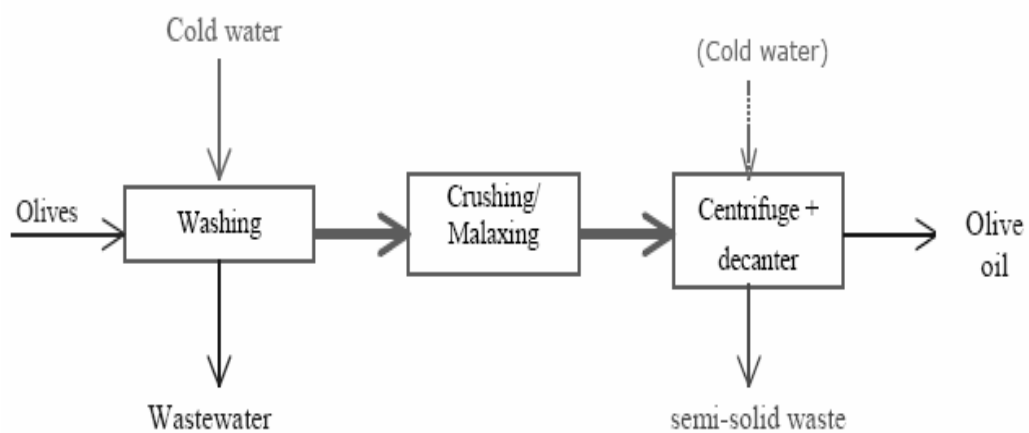
Figure 1.6. The 2-phase centrifugal extraction of olive oil (Skerratt&Ammar., 1999).

The mentioned extraction methods for olive oil production are compared in Table 1.2 and Table 1.3.

Table 1.2. Principles advantages and disadvantages of the pres, two-phase and three-phase systems. (http://cesonoma.ucdavis.edu/hortic/pdf/olive_oil_processing_influences_quality.pdf

System	Advantages	Disadvantages
Press	The old way romance factor, uses less energy, less cost to establish, produces relatively dry pomace.	Less capacity, require more labor, difficult to maintain cleanliness of mats, more paste and oil contact with oxygen.
3-phase decanter	Produces relatively dry pomace, easier to monitor extraction efficiency than 2-phase system, continuous flow.	Uses more water, needs more power to heat extra water, washes out too many polyphenols in some oils, produces a lot of waste water, needs 2 vertical centrifuges.
2-phase decanter	No-fruit-water effluent, oil has higher polyphenol content, uses less water, need only one vertical centrifuge, continous flow.	Produces very wet pomace, more difficult to determine extraction efficiency.

Table 1.3. The chracteristic properties of processes which uses in oilve oil production per 100kg of olive (Demicheli &Bontoux, 1996).

Type of Process	Process Water	Energy (MJ)	Wastewater Chracteristics	
			Volume (L)	COD(g/kg)
Press	0-40	3,3	40-50	90-130
3-phase decanter	50-70	5,8	90-110	60-90
2-phase decanter	0	0	5-10	10-15

1.2.6 Extraction of residual oil

The high-loaded wastewater from the three-phase decanter is treated by means of a vibrating screen and a centrifuge, the residual oil is extracted. The oil centrifuged twice flows into a collecting tank and is pumped by eccentric worm pumps in surface or underground storage tanks. The solid waste from oil extraction by pressing stil contains about 6 % oil, using the continuous three-phase decanter, still 4 % olive oil. The oil content in the solid-liquid mixture from the dual-phase decanting process is

2,5% to 3,5 %. In specialized plants the solvent extraction process is used for this purpose. First the waste is completely dried and then extracted using hexane as solvent. The dry residues can be used as concentrated fodder. In some extraction plants the stones are separated from the pulp after extraction and used as fuel for heating of the driers. The pulp is sold as fertilizer or fodder. In some oil mills the solid waste from the press is directly used as fuel for the heating of water. (Tunca, 2004)

A large comparison for olive oil extraction processes is summarized in Table 1.4. In addition to that, some parameters which olive mill wastewater has, and their typical values in conventional process and continious process are listed by Table 1.5.

Table 1.4. Comparative for the olive oil extraction process (Project Improlive, 2000).

Production Process	Input	Amount of Input	Output	Amount of Output
Traditional pressing process	Olives Washing water Energy	100kg $0,1-0,12m^3$ 40-63kWh	Oil Solid waste (25%water+6% oil) OMW(c. 88% water)	~200kg ~400kg ~600L
3-phase decanter	Olives Washing water Water for decanter To polish the impure oil Energy	1000kg $0,1-0,12m^3$ 0,5-1m3 ~10L 90-117kWh	Oil Solid waste (50% water + 4% oil) OMW (94% water + 1% oil)	200kg 500-600kg 1000-1200L
2-phase decanter	Olives Washing water Energy	1000kg $0,1-0,12m^3$ <90-117kWh	Oil Solid waste (60% water + 3% oil)	200kg 800-950kg

Table 1.5. Some parameters which OMW has, and their typical values in conventional process and continious process. (Skerratt & Ammar, 1999; Potoglou et al., 2003; Inan et al., 2004; Aktas et al., 2001; Galiatsatou et al., 2002; Caputo et al., 2003)

Parameter	OMW (conventional P)	OMW (continuous P)
PH	4,5-5,7	4,5-5,9
Dry matter g/l	15-266	10-161
Ash g/l	4,0-42,6	0,40-12,5
Cunductivity mS/cm	11,5	11,5
COD g/l	42-389	15-199
BOD g/l	90-100	30-50
Total Mineral SS %	1,5	0,4
Total solids %	12	3
Suspended Solids g/l,%	1-2, 0,1	6-9, 0,9
Total VSS %	10,5	2,6
Sugar %	2-8	1,0
Reducing sugars g/l	9,70-67,10	1,60-34,7
Oil g/l; %	0,2-11,5; 0,03-10	0,40-29,8; 0,5-2,3
Organic acids %	0,5-1,0	-
Polyalcohols %	1,0-1,5	1,0
Pektin,tannin etc. %	1,0	0,37
Total Polyphenols g/l	1,4-14,3	0,4-7,1
O-di phenols g/l	0,90-13,3	0,30-6,0
Hydroxy tyrosol mg/l	71-937	43-426
Total nitrogen %	2-5	0,28
Organic nitrogen g/l	0,15-1,1	0,14-0,97
Total phosphorus mg/l	157-915	42-495
Sodium mg/l	38-285	18-124
Potasium mg/l	1500-5000	630-2500
Calcium mg/l	58-408	47-200
Magnesium mg/l	90-336	60-180
Iron mg/l	16,4-86,4	8,8-31,5

Copper mg/l	1,1-4,7	1,1-3,4
Zinc mg/l	1,6-6,5	1,4-4,5
Manganese mg/l	2,2-8,9	0,9-5,2
Nickel mg/l	0,5-1,6	0,3-1,5
Cobalt mg/l	0,2-0,9	0,1-0,5
Lead mg/l	0,4-1,8	0,4-0,7

1.3. Treatment Methods of OMW

Various treatment methods for the treatment of OMW and olive residues can be used. The great variety of compounds of the wastes needs several technologies to remove the harmful compounds for the environment. Most of the following methods have been tested in laboratory scale and only some of them used in industrial scale. In the case of OMW the mostly used treatments are drying / evaporation, forced evaporation; dewatering with solar distillation, thermal treatment, biological treatment by fungi, aerobic treatment, anaerobic treatment; lagooning, adsorption; powdered activated carbon, filtration; sand filtration, membran filtration, ultrafiltration, precipitation / flocculation, evaporation, distillation, electrolysis, co-composting, advanced oxidation processes (AOP's) such as ozonation, hydrogen peroxide / ferrous iron oxidation (the so-called Fenton's reagent), and wet air oxidation, photocatalysis, sonocemical reduction, decolorisation, incineration, pyrolysis, gasification, several OMW treatment technologies have been developed aiming at the removal of the main toxic organic compounds (Erguder et al., 2000) etc. A lot factors must be considered to choose the treatment methods among investment, required area, specific training of the workers, noise and odor emissions, seasonal trouble.

"The difficulties of treatment of OMW are mainly related to; concentration and composition (presence of organic compounds), seasonal-localized production and low flow-rate. OMW are strong wastes containing high concentrations of phenolic compounds (up to 10 g/l depending on the type and origin of the effluent) and long-

chain fatty acids that are difficult to biodegrade, seasonal operation; which typically lasts between December and February for a time in two years.

1.3.1. Physical, Chemical and Physico-Chemical Treatment Methods

The presence in OMW of hardly or non-biodegradable and high values dissolved organic pollutants; COD, BOD, and phenolic content, asks for the adoption of chemical–physical treatments, such as adsorption, precipitation and occulation, characterized by the addition of specific chemicals (respectively activated carbon, polyelectrolites, occulants). Thus, even if high removal efficiencies are obtained, from an environmental point of view, problems arise from the disposal of large quantities of produced sludge. On the other hand, low investment and operational costs characterize such plants; therefore this technology is better suited for small-scale oil mills. (Caputo et al., 2003)

Various chemical, physical and physico-chemical treatment methods for the reduction of OMW and olive residues can be used. These are, evaporation, drying/evaporation, forced evaporation, dewatering with solar distillation, thermal treatment, filtration; membran filtration, ultrafiltration, membrane filtration, wet oxidation, precipitation / flocculation, adsorption, (Curi et al., 1998, Galiatsatou et al., 2002), distillation, electrolysis, co-composting, advanced oxidation processes (AOP's) such as ozonation; (Benitez et al., 1997; Andreozzi et al., 1998; Amat et al., 2003; Beltran-Heredia et al., 2000), photocatalysis (Poulios et al., 1999), hydrogen peroxide / ferrous iron oxidation (the so-called Fenton's reagent) (Rivas et al., 2001b) and wet air oxidation (Debellefontaine et al., 1994; Mantzavinos et al., 1996), sonocemical reduction (Atanassova et al., 2005), decolorisation, incineration, pyrolysis, gasification, several OMW treatment technologies have been developed aiming at the removal of the main toxic organic compounds (Erguder et al., 2000) etc. A lot factors must be considered to choose the treatment methods among investment, required area, specific training of the workers, noise and odor emissions, seasonal trouble.A membrane filter is shown by Figure 1.7.

(Potoglou et al., 2003), they used solar distillation for dewatering of OMW over a series of consecutuve days. (Turano et al. 2002) developed a 2-stage centrifugation–ultrafiltration process capable of reducing the total suspended solid, COD of OMW by 80% and 90%, respectively.

(Curi et al., 1980) have tested the treatment of OMW with a mixture of aluminum sulfate and ferric chloride, calcium hydroxide solution and also acidifying of the waste with hydrochloric acid solution. (Tsonis et al., 1989) have used calcium hydroxide, aluminium sulfate and magnesium sulfate for the chemical treatment of OMW. The effect of lime treatment of OMW was investigated by scientists, "In a chemical precipitation study in grease, lime precipitation was investigated. The sludge produced of the addition of 0,5-3 % CaO reduced the concentration of suspended solids in the vegetation waters by 28 % whereas 77 % of the oil and grease are distibuted in the precipitate fraction. The COD as well as the toxic load in terms of phenolic compounds are not strongly affected by the addition of CaO." (Lolos et al., 1994), "In another chemical treatment experiment, calcium hydroxide, magnesium sulfate and aluminum sulfate have been used. The values of COD have been determined after the treatment of OMW with the chemicals. The COD value dropped to 20-30 % with calcium hydroxide, when it was added until the pH of the waste reached 11." (Tsonis et al., 1989; Aktas et al., 2001) reported that after lime precipitation process, COD values of the wastewater samples could be reduced by 42-46 %. The average removal percentage of the other parameters are 29-47 % for total solids, 41-53 % for volatile solids, 74-37 % for reduced sugar, 95-96 % for oil-grease, 74-63 % for polyphenols, 38-32 % for volatile phenols and 61-80 % for nitrogenous compounds, respectively,

Adsorption is used to reduce soluble organic polluted in wastewater and also OMW. But it is not possible to use again "activated carbon" economically. Activated carbon needs to be incinirated after treatment and it is very expensive method and also there are a lot of air pollutant as a finally product. Curi et al., used adsorption on activated carbon to investigate the dark color removal of OMW. They did not report any values regarding the change in COD nor phenolic content of the treated samples.

A series of treatment steps composed of settling, centrifugation, and filtration was consecutively used to condition OMW by (Al-Malah et al., 2000). The filtrate was then subjected to a post-treatment process, namely adsorption on activated clay. Adsorption of phenols and organics is reversible and mainly due to hydrophobic interactions. The maximum removal of phenols was about 81%, while it reached about 71% for organic matter.

"Chemical oxidation using ozone or advanced oxidation technologies based on the generated of hydroxyl radical is a possible way to reduce COD and polyphenol content. In a study, chemical oxidation of OMW using ozone alone and combined with hydrogen peroxide or UV (UltraViolet) radiation was studied. COD reduction of 80 or 90 % was obtained with ozone doses between 3 and 4 g in the presence of 10^{-3} M initial hydrogen peroxide concentration or 254 nm UV radiation while total carbon concentrtion was between 40 and 60 %" (Beltran et al., 1999).

OMW, which is a toxic liquid, was treated by an electrochemical method using Ti/Pt as anode and Stainless Steel 304 as cathode. In this technique, $NaCl_4$ % (w/v) as an electrolyte was added to the wastewater and the mixture was passed through an electrolytic cell. Due to the strong oxidizing potential of the chemical produced (chlorine, oxygen, hydroxyl radicals and other oxidants) the organic pollutants were wet oxidized carbon dioxide and water. After 1 and 10 h of electrolysis at 0,26 A/cm^2, total COD was reduced by 41 and 93 %, respectively, total TOC was reduced by 20 and 80,4 %, VSS were reduced by 1 and 98.7 % and total phenolic compounds were reduced by 50 and 99,4 %. Also, the mean energy consumption was 1.273 kWh per kg of COD removed for 1 h and 12,3 kWh per kg of COD removed for 10 h. These results indicate that this electrolytic method of total oxidation of olive oil effluent is not feasible (Israilides et al., 1997).

OMW has to be completed by other processes, such as membrane filtration (e.g., reverse osmosis or ultrafiltration). Byproducts of this process are the concentrate from the filtration process and the membrane itself, which have to be disposed.

However, despite optimal COD reduction, this technology is hardly suited for the treatment of OMW in small-scale oil mills due to the very high investment and operational costs, high energy demand and rather complex process control that requires highly qualified personnel. (Caputo et al., 2003)

On the other hand, reverse osmosis or ultrafiltration methods could be used after sand filtration. Wastewater have two phase in membran filtration: Treated water and ratantate.

Figure 1.7. Membran filtration bank (http://www.energy.ca.gov/process/agriculture/ag_pubs/CEC-400-2000-901.PDF)

In convection drying heat is transferred to OH by means of hot gases. Water contained in OH evaporates and is conveyed by the hot gas flow. Examples of this type of dryer are drum dryers, belt dryers and fluidized-bed dryers. The resulting dried OH may be incinerated for energy production, reused in agriculture, or land filled, while the air emission must be treated appropriately. The main drawback is the

high energy demand. However, this disadvantage is justifiable against the background that the resulting final product can be reused for energy production. From an economic point of view, high investment and operating costs are associated to drying plants; moreover, to ensure trouble-free operations trained and qualified personnel is required. (Caputo et al., 2003)

"OH are incinerated together with additional fuel with the possibility of energy recovery and co-combustion with different waste types. Compared to other treatment, this process is very expensive considering the high cost of combustors and the associated air pollution control system." (Caputo et al., 2003)

1.3.2. Biological Treatment Methods of Olive Mill Wastewater

Biological treatments (aerobic, anaerobic, by fungi, trickling fitler etc…)are able to reduce BOD and COD concentrations and enable removal of organic and inorganic suspended solids, as well as phosphorous, nitrogen and ammonium compounds.

Aerobic microorganisms degrade a fraction of the pollutants in the effluent by oxidizing them with oxygen which is provided by an external source (either as air or pure oxygen). These microorganisms use most of the remaining fraction of the pollutants to produce new cells (termed biomass or sludge) which have to be removed from the water. Aerobic processes, such as activated sludge and trickling filters, are usually exploited to remove dissolved or colloidal pollutants from wastewaters at low concentration. They can operate efficiently only if the concentration of the feed is relatively low, of the order of 1 g COD/L. Higher concentration can be tolerated only if the plant operates at a long hydraulic retention time and / or with high recycle ratios (Boari et al.,1984). The high concentration of OMW makes it unsuitable for direct treatment by aerobic biological treatments. Besides, the aerobic treatment of concentrated wastewaters yields huge volumes of excess secondary sludge. When the COD concentration of the raw effluent reaches 50 g COD/L the volume of produced sludge (which has a solids concentration of the

order of 20-30 g Total Suspended Solids (TSS) /L) is comparable to the volume of the treated wastewater. (This is possible because the effluent has to be diluted prior to treatment with other effluents.)

Oil process is a seasonal production, huge amount of wastewater generates and OMW also have extremely high organic loading; all of these conditions make anaerobic treatment a very attractive option for the treatment of OMW's. (Capasso et al., 1992; Benitez et al., 1997; Subuh, 1999) studied anaerobic treatment; Subuh has conducted anaerobic digestion of OMW using laboratory scale Up-flow Anaerobic Sludge Blanket (UASB) reactor. He proved that removal efficiency of the soluble fraction of COD reached 76% using the UASB. (Hamdi et al., 1992; Martinez et al., 1993; Sabbah et al., 2001) studied different types of reactors were checked such as stirred-tank reactor, fluidized bed reactor and UASB reactor. UASB has showed promising technique of anaerobic treatment for OMW (Sabbah et al., 2004). (Sabbah, et al., 2003) achieved a 95% removal of the phenolic compounds present in OMW using sand filtration and subsequent treatment with powdered activated carbon in a batch system. This pretreatment for OMW was found to enhance the anaerobic activity of the sludge in the batch system significantly. Using the UASB reactor, COD removal efficiency reached 80-85% at a hydraulic retention time of 5 days. One further treatment option is the post-treatment of the effluents from anaerobic-aerobic reactors using mainly membrane systems so that treated OMW could be discharged directly to municipal wastewater treatment plants. Even if anaerobic technology has clear advantages including higher removal eficiency, lower excess sludge production (the quantity of produced excess sludge is 20 times lower than in the aerobic process), low space requirement, both aerobic and anaerobic processes can be adopted. The anaerobic process produces biogas(CH_4) valuable by-product that can be used to full the mill energy demand.

1.3.3. Other Treatment Methods

1.3.3.2. Natural Evaporation

Natural evaporation can be considered as a low-cost solution for the incorporation of the wastewater pollutants in the dried sludge Some applications in Greece are shown in Figure 1.8 and Figure 1.9. But due to long evaporation periods, this technique is technically and economically feasible only for low to moderate wastewater flows. The constraints in applying the natural evaporation to OMW have led to the forced evaporation technologies. The principle is based on the physical phenomena of forcing evaporation by the diffusion of the wastewater in dry air stream. This treatment alternative has the advantage of generating dried sludge that can be disposed off or reused as fertilizer, burning material,etc. (http://unpan1.un.org/intradoc/groups/public/documents/ARADO/UNPAN020869.pdf)

Figure 1.8. Natural evoparation in Greece.(Minos Project, 2004)

Figure 1.9. Natural evoparation in Greece.(Minos Project, 2004)

Evaporation lagoons have some disadvantages These are; the alteration of the groundwater quality characteristics due to infiltration, in the cases that the surface of the lagoon bottom is not lined with non-permeable materials, the annoyance in a significant area round the evaporation lagoons due to the discharge of strongly unpleasant odors and the aesthetic reduction of the surrounding area.

1.3.3.3. Composting

Composting is considered as one of the most suitable ways of disposing of unpleasant wastes and increasing the amount of organic matter that can be used to restore and preserve the environment. This process involves heterogeneous organic substrate in the solid state, evolves by passing through a thermophilic phase and a temporary relese of phytotoxin. After this process, CO_2, water vapour, mineral products and stabilized organic matter are produced. For this reason, composting is a practical and ecological way of recycling OMW. It is possible to transform OMW and olive residue added to a bulking agent into organic fertilizers or soil amenders with no phototoxic effects (Monteoliva-Sanchez et al., 1996).

Landscaping, and generally the sector of exterior design is a field where compost can be successfully applied. Basic prerequisite for the acceptance of this product from the landscaping sector is the performance of high quality standards. Quality standards include: The absolute absence of toxic heavy metals, the appropriate particle size, the neutral level of pH and finally the moisture level (<50%). More specifically compost can be used for:

- It replenishes the organic nutritional substances of the soil, sustains soil health and suspends soil desiccation and erosion.
- It improves and stabilizes soil pH.
- It improves the water holding capacity of soil.
- It emboldens soil worms activity and soil fauna in general, improving in this way soil aeration and soil enrichment with nutrients, decreasing at the same time the demand for chemical insecticides and fungicides.
- It improves soil structure, porosity and density. This characteristic increases soil aeration and soil water and nutrient holding capacity. As a result, heavy soils become lighter and easier to process, while the light soils increase their absorbency.
- It stores and releases gradually nutrients that are beneficial to plant growth producing healthy and rich harvest, decreasing at the same time the demand for chemical fertilization.
- It improves the plants roothold system.
- It favors the growth of microorganisms populations within the soil, and especially bacteria and fungus.
- It amplifies bacteria activity within the soil in order to suspend soil diseases.
- It improves the performance and the growing rate of seeds.
- It preserves the health of plants, animals and humans through-out the foodchain.
- It promotes sustainable practices, through the gradual abatement of chemical fertilizers and prevents the potential pollution of surface water and groundwater (Minos Project, 2004).

1.3.3.4. Land Treatment

Direct irrigation of soil with OMW to save water and fertilizer has long been proposed. Normally less than 800 m^3 / ha doses are used. Limitations of its use are due to the phytotoxic effect of OMW that is caused by its polyphenol and salt contents. However, average doses of OMW have beneficial effects such as increasing soil fertility, microbial population (especially N_2 fixing bacteria), improving the stability of the soil aggregates and in some instance crop yield. Land treatment of OMW needs a stretch of flat land close to the mill, where the soil has an adequate poro OMW, and avoiding stagnancy and runoff. Evaporation ponds caused serious negative effects such as odours, insect proliferation, leakages, infiltration and silting with sludges. However, the main problem with evporation ponds is their insufficient capacity (Cabrera et al., 1996).

1.3.3.5. Irrigation with OMW

Toxicologic properties of OMW is considered and land is watered on control. Italian scientists find out that watering with OMW is advantageous not only on olive trees but also vineyards and corns, in the event of land is irrigated with determined volume of OMW. (Oktav & Sengül, 2000).

Spanish scientists carried out that soils, which watering with OMW, have high concentration of heavy metals, organic compounds, total soluble nitrogen, phosphorus, salt but soil biological conditions is beter if land is irrigated with OMW of 1000m^3.hectare/year and OMW is treated.

1.3.3.6. Evaporation / Distillation

The goal of this process is the water separation by using a multistage evaporation system enabling heat recovery. The concentrate from the evaporation process has to be treated, before its disposal, generally by using biological treatments, such as aerobic digestion and an activated sludge process. Drawbacks arise from the high energy demand, considerable air emissions and complex control process that requires

qualified personnel. Moreover, from an economic point of view, even if economy of scale may be achieved, high operational costs are associated. Thus evaporation is a solution suited for industrial-scale oil mills only. (Caputo et al., 2003)

Most Mediterranean countries dispose of OMW in artificial evaporation ponds. In a study, the qualitative and quantitative evaluation of the phenolic content and the antibacterial properties of these residues are performed during evaporation in simulated evaporation ponds. No antibacterial effect was detectable in subsquent evaporation for 91 days. The evoporation of olive mill vegetation waters permits to pull down the polluting load to an extent superior to the 90 % in terms of COD (Di Gicomo et al., 1991).

In another study, samples of vegetation water from olive mills were separeted by evaporation into an aqueous liquid (80 – 90 % of the initial volume), a traditional biological process could then purify that, and a residue in which about 98 % of the organic load was concentrated. The properties of the concentrated vegetation water residue and of the olive husk suggested the possibility of using a mixture of the two as an efficient fuel to provide the heat for the evaporation stage (Saez et al., 1992).

The comparison of treatment methods for OMW are given by Table 1.6-1.10.

Table 1.6. Characteristics of OMW wastewater samples collected from a local olive mill (Al-Malah et al., 2000)

Test	Units	After Settlings	After Centrifugation	After Filtration
Temperature	C^o	35	35	35
Ph		4,52	4,87	5,15
Phenols	mg/l	3120	2940	1190
TDS	mg/l	42200	40540	35460
TSS	mg/l	21780	3100	600
Conductivity	µS/cm	7570	8470	10720
Alkalinity	mg/l	4,0	36,0	98,0
BOD5	mg/l	13250	11250	9350
COD	mg/l	320000	250000	240000
Volatile acids	mg/l	2740	2650	2570
Chlorides	mg/l	833	674	339
Density(22C^o)	g/l	0994	0,993	0,974

Table 1.7. First investment of OMW treatment plants (OMW Treatment Project, Sengul et. al., 2003)

Method/processes	First investment (Euro)	10 yılda geri ödemesi	Total Euro/m3
Forced mec. Evop. / lagoons	180722,89	18072,29	3,61
Physical / chemical Treatment + bio. + ultrafil.	150602,41	15060,24	3,01
Bio. Treat. (entegre)	180722,89	18072,29	3,61
Physical / Chemical + Revese Osmosis	138554,22	13855,42	2,77
Vacuum evoparation	96385,54	9638,55	2,75
Natural evoparation	30120,48	3012,05	0,86

Table 1.8.Operating investment of olive oil mill wastewater processes. (Project Improlive, 2000)

Method/process	Energy Euro/m^3	Chemical euro/m3	Worker Euro/m3	Vapor euro/m3	Total euro/m3
Mec.evop./ Lagoons	1,42	-	0,88	4,52	6,82
Phy/chem.+ Bio+ult.fil	5,15	2,06	1,47	-	8,68
Bio.Tret. (entegre)	1,28	2,40	2,53	-	6,21
Phy./Chem.+ Reverse osmosis	0,60	3,05	1,79	-	5,27
Vacuum Evop.	0,48	-	1,32	1,90	3,69
Natural evop.	0,07	-	0,05	-	0,05

Table 1.10. Combined chemical-biological treatment of OMW. (TP: Total Phenols, TC: Total Carbon.) (Mantzavinos & Kalogerakis, 2005)

Reference	Initial concentration	Chemical pretreatment	Biological degradation	Measure of biodegradability	Effect
Beltran-Heredia et al., 2001	COD=95 g/l, BOD_5=52 g/l, TP=1,5 g/l	Batch Fenton oxidation at $30C^0$ and various Fe^{2+} and H_2O_2 concentrations or continuous ozonation at residence times= 1,8–8,7 h and PO_3=0,35–1,21 kPa	Aerated microorganisms in batch reactors at $28C^0$	COD and total phenols removal, increase in biomass, Contois rate constants	+
Benitez et al., 1999	COD=34g/l (OME diluted about three times with distilled water)	Batch ozonation for 8h at PO_3=1.73 kPa and $20C^0$	Acclimated activated sludge in batch reactors at $28C^0$	COD removal, Grau kinetic constants	+
Andreozzi et al., 1998	COD=121,8g/l TC=34,2 g/l TP=6,2 g/l	Batch ozonation for 1–7 h	Anaerobic digestion with Mixed acclimated and non-acclimated sludge	Methane and volatile fatty Acids production yields	_
Benitez et al., 1997	COD=59,9 g/l TOC=8 g/l TP=1,12 g/l	Batch ozonation for 8h at PO_3=1,3 kPa and $20C^0$	Anaerobic digestion with immobilized acclimated biomass	Methane production yield	+

Table 1.9. Treatment of with various AOP (BODu: Ultimate BOD) (Mantzavinos & Kalogerakis, 2005)

Reference	AOP	Efficiency	Comments
Gernjak et al., 2003	Photo-Fenton with solar irradiation	74% COD and 87% phenols removal after 19 h with 5 mM Fe^{+2} and 20 g/l H_2O_2. With flocculation as pretreatment, COD and phenols removal increased to 89% and 100%. Initial COD=81 g/l	Solar photocatalysis over TiO_2 was less effective than photo-Fenton
Giannes et al., 2003	Electrolysis over Ti/Ta/Pt/Ir anode with NaCl as the electrolyte	71% COD removal after 8h, complete odor, color and suspended solids removal. Initial COD=45–60 g/l	Residual COD was toxic to daphnia manga and artemia salina
Vlyssides et al., 2003	Fenton followed by coagulation	~65% COD, ~30% BOD_5 and 100% total phenols removal after 2 h with 2 g/l $FeSO_4$ d $7H_2O$ and 5 ml/l H_2O_2 dosage at $20C^0$. Initial COD=80,3 g/l	COD/BOD5 ratio decreased from 3,1 to 1,79 following oxidation
Rivas et al. 2001a	Fenton	85–90% COD removal after 3–4 h with 10 mM Fe^{2+} and 1 M H_2O_2 at $50C^0$. Initial COD=14,7 g/l	Depending on the conditions, BOD/COD ratio increased or decreased after oxidation
Rivas et al., 2001b	Supercritical wet air oxidation	79% COD, 79% TOC and 98% total phenols removal after 18 s at $500C^0$ and 25 MPa. Initial COD=3,3 g/l	Addition of 0,2 M H_2 O_2 improved removal rates. OME was diluted ~50 times prior to oxidation
Rivas et al. 2001c	Subcritical wet air oxi with or without C uO/C or Pt/Al2 O3 catalysts and H2 O2	~50% COD removal after 6h at $180C^0$ and 7 MPa with either catalyst and ~30% without catalyst. Addition of 0,1 M H_2 O_2 improved removal by 15%. Initial COD=14,7 g/l	BOD_u/COD increased following oxidation with H_2O_2 but remained unchanged. OME was diluted ~10 times prior to oxidation
Benitez et al. 1999	Ozonation	22% COD removal after 8 h, complete total phenols removal after 2 h. Initial COD=34 g/l	OME was diluted ~3 times prior to ozonation
Israilides et al., 1997	Electrolysis over Ti/ Pt anode with NaCl as the electrolyte	93% COD, 80% TOC, 99,5% total phenols and 99% SS removal after 10 h. Initial COD=178 g/l	Mean energy consumption over 10h operation was 12,3 kWh/kg COD removed
Chakchouk et al. 1994	Subcritical wet air oxi	77% COD, 69% TOC and complete color removal after	Residual COD was aerobically degradable

CHAPTER TWO

MATERIALS AND METHODS

In this section, the sampling of OMW, the materials and the methods used for the analyses of the samples, and the experimental set up will be presented.

2.1. Sampling and Storage of OMW

OMW samples were collected in an industrial mill in Selçuk in İzmir. The oil manufacturing capacity of the plant is 2,5 tons per hour. The plant has a two-phase system. The sampling has done in February, 2004 which is the end of oil production season. The samples are immediately transferred to the laboratory and homogenized by using a kitchen blender and then kept in the laboratory freezer under +4°C until they are used.

2.2. Laboratory Methods Used for the Analyses

The OMW samples, distillates and the residues from the distillations are analysed for their pH, water content (WC), organic matter content (OMC), and water soluble Chemical Oxygen Demand (COD_d). The analytical methods used for the analyses are given in Table2.1.

2.3. Experimental Setup

A rotary evaporator with a vacuum pump is used for the distillation studies. The apparatus has four basic parts; the glassware part -that includes a sample reservoir (500ml), a condenser, and a distillate reservoir (500ml)-, a heater (IKA Werke HB4 Basic 50^0C-225^0C), a rotater (IKA Werke RV05 Basic 46-312 round per minute), and a vacuum pump (KNF NO26.1.2AN.18 P_{max}=2bar, 0,170 kW, 50 Hz and 0,85 A).

Table 2.1 The analytical methods used for the analyses

Parameters	Method	Procedure
pH	EPA Method 9045C	20 grams of sample is mixed with 20 ml of distilled water for 5 minutes and centrifuged at 4000 rpm for 10 minutes. The pH value of the supernatant is measured. NUVE NF 815 centrifuge and HANNAH HI 8314 pH meter is used for the experiments.
Water Content (WC)	Standard Methods, AWWA 1981	The sample dried at 105°C overnight and differences between the initial and final weights are used to determine the water content. MEMMERT Loading Modell 100-800 drying oven is used for the experiments.
Organic Matter Content (OM)	Standard Methods, AWWA 1981	The dried sample combusted at 550°C for 2 hours and differences between the initial and final weights are used to determine the organic matter content of dry portion. MEMMERT LM 100-800 furnace is used for the experiments.
Chemical Oxygen Demand (COD-Dissolved)	EPA Method 1310 and Standard Methods, AWWA 1981	Dried sample is extracted according to the EPA1310 and the supernatant is tested for COD with Closed Reflux Method given in Standard Methods.

200 ml blackliquor is used for each distillation and three different distillation temperatures is applied: 50°C, 70°C, and 90°C. Two sets of experiments are conducted as continious distillation and intermittent distillation, Intermittent extraction is applied to see the change in properties of distillate in time. Another application is to observe the change of distillation achievement with cooling distillate reservoir. For this purpose, the reservoir that the distillate is collected is sinked into a container which is full of ice during the extraction. The condenser system is cooled by tap water during the distillations. Since

the amount of distillate collected in unit time increases with increasing distillation temperature the distillation times are shorter in the distillations at 70°C and 90°C. The distillation modes used for the study and their features are summarized below in Table 2.2. The experiments are triplicated.

Table 2.2. Distillation modes applied in the study

Distillation Modes	Distillate Reservoir	Distillation Temperatures, °C	Distillation Time, min	Cummulative Distillation Time, min
Continious	Cooled	50	60	60
		70	45	45
		90	30	30
	Not Cooled	50	60	60
		70	45	45
		90	30	30
Intermittent	Cooled	50	15	15
			15	30
			15	45
			15	60
		70	15	15
			15	30
			15	45
		90	15	15
			15	30
	Not Cooled	50	15	15
			15	30
			15	45
			15	60
		70	15	15
			15	30
			15	45
		90	15	15
			15	30

During the experiments it was a question that if the vacuum outlet is a way for the volatile organics to escape from the system before they are condensate. To determine if

there is such stripping or not, a pipe with a diffuser at the other end is installed to the outlet of the vacuum pump and it is sinked into a 4 L cyclindirical container (water height is 40 cm) which holds distilled water. The pipe kept into the water and the allowed the vacuumed air from the system diffuse into the water during one experiment. At the end of the experiment the distilled water is analysed for its COD concentration to determine the possible organic load stipped from the system.

CHAPTER THREE

RESULTS AND DISCUSSION

In this part of the thesis the results of the experimental studies and the discussion of the results will be presented.

3.1. Results of the Experimental Studies

The initial properties of the blackliquor used for the experiments are given in Table 3.1.

Table 3.1. Properties of blackliquor

Parameter	Value
COD, mg/l	33250
Density, g/cm^3	1,017
Water Content, %	89,26
Organic Matter Content, % dw	85,70

Three set of distillation experiments are completed in the study. In each distillation pH, volume, and COD concentration of the distillate and water content, organic matter content, and COD concentration of the residue are determined in the laboratory.

The results of each distillation set are given in Tables 3.2, 3.3, and 3.4. below. The average of the data obtained from those sets are used in the discussion part to show the achievement of different distillation mode.

Table 3.2. The results of 1st distillation set

T°C	Cooling of distillate	Distillation Mode	Time, min.	Volume of Distillate, ml	Distillate COD, mg/l	Distillate pH	Water Content of Residue, %	Organic Matter Content of Residue, %	Residue COD, mg/l
50	YES	Intermittent	15	6	6400	3,6	87,4	88,2	14400
			30	7	5800	3,63			
			45	7	6200	3,64			
			60	8	5200	3,6			
		Continuous	60	41	6000	4,32	83,6	86	12820
	NO	Intermittent	15	17	9700	3,24	82,4	87	11660
			30	15	5400	3,23			
			45	13	4500	3,23			
			60	12	4100	3,23			
		Continuous	60	48	6900	3,23	83,9	79	13200
70	YES	Intermittent	15	23	8500	4,16	83,8	88,2	12000
			30	18	6100	4,81			
			45	19	5400	4,34			
		Continuous	45	87	7300	3,2	79,2	88	12060
	NO	Intermittent	15	25	10900	3,2	81,1	87	12060
			30	29	6500	3,18			
			45	32	5800	3,23			
		Continuous	45	72	11000	3,18	80,7	87	12480
90	YES	Intermittent	15	47	9400	3,23	82,4	85,4	8600
			30	42	4300				
		Continuous	30	110	10400	3,23	77	84,7	12380
	NO	Intermittent	15	56	10700	3,23	78,3	87	13780
			30	48	5700	3,2			
		Continuous	30	134	7400	3,23	81,3	78	12800

Table 3.3. The results of 2nd distillation set

T°C	Cooling of distillate	Distillation Mode	Time, min.	Volume of Distillate, ml	Distillate COD, mg/l	Distillate pH	Water Content of Residue, %	Organic Matter Content of Residue, %	Residue COD, mg/l
50	YES	Intermittent	15	9	7600	3,6	83,2	87,9	16800
			30	10	4300	3,6			
			45	11	2700	3,63			
			60	9	2500	3,57			
		Continuous	60	36	5600	3,6	83,5	88,3	12820
	NO	Intermittent	15	9	10400	3,24	84	89	11660
			30	9	11200	3,23			
			45	10	5800	3,23			
			60	11	5300	3,23			
		Continuous	60	39	8500	3,18	83,3	88,6	13200
70	YES	Intermittent	15	27	8700	4,14	80,7	88,2	2000
			30	25	4200	4,79			
			45	20	1700	4,28			
		Continuous	45	64	6500	4,28	81,3	90	12940
	NO	Intermittent	15	30	9700	3,2	80	88,9	12060
			30	29	6100	3,18			
			45	20	6000	3,18			
		Continuous	45	73	11000	3,22	81	88,9	12480
90	YES	Intermittent	15	62	6100	3,2	80,4	90,8	12200
			30	30	3200	3,2			
		Continuous	30	86	5600	3,2	81,1	91,4	12380
	NO	Intermittent	15	46	10000	3,18	80	90,1	13780
			30	42	6300	3,18			
		Continuous	30	84	9400	3,23	80,2	90,1	12800

Table 3.4. The results of 3rd distillation set

T°C	Cooling of distillate	Distillation Mode	Time, min.	Volume of Distillate, ml	Distillate COD, mg/l	Distillate pH	Water Content of Residue, %	Organic Matter Content of Residue, %	Residue COD, mg/l
50	YES	Intermittent	15	11	4800	3,23	86,8	87,2	18100
			30	12	4100	3,6			
			45	12	2800	3,63			
			60	11	3100	3,57			
		Continuous	60	54	5800	3,23	84,5	88,3	16100
	NO	Intermittent	15	13	4280	3,24	83,9	89	14800
			30	14	5520	3,23			
			45	14	6040	3,23			
			60	13	6520	3,23			
		Continuous	60	42	6400	3,18	87,3	88,6	14200
70	YES	Intermittent	15	24	7300	4,14	88,6	89,9	3000
			30	27	3900	4,79			
			45	24	2200	4,28			
		Continuous	45	74	6300	3,23	89,3	90,1	15400
	NO	Intermittent	15	31	4800	3,2	80,6	88,9	16900
			30	25	5760	3,18			
			45	28	-	3,2			
		Continuous	45	74	5720	4,18	82,3	88,9	13900
90	YES	Intermittent	15	66	6200	4,2	81,9	90,8	17000
			30	48	4100	4,14			
		Continuous	30	116	5800	4,2	81,3	91,4	15000
	NO	Intermittent	15	44	4960	4,32	81,1	90,1	-
			30	41	5000	4,2			
		Continuous	30	85	8400	4,2	77,4	90,1	16700

As mentioned before, vacuum pump outlet gas is diffused into the distilled water to determine the possible organics stripping by this way. At the end of 60 minutes distillation period, the COD content of the water in 4 L reservoir is determined and the result is found as 12mg/L. Total COD load stripped from the system by vacuuming is calculated as 48 mg, which can be neglected.

3.2. Discussion of the Results

Here, the result of the experiments are discussed according to the distillation modes and temperatures.

3.2.1. Intermittent Distillations

3.2.1.1. Intermittent Distillation at 50°C

Intermittent distillation is applied to see the change of volume and COD concentration of the distillate with time. This mode is tried in two cases; with and without distillate reservoir cooling.

3.2.1.1.a. Intermittent Distillation at 50°C - Distillate Cooled

The cummulative COD load of the distilates of this mode is presented in Figure 3.1. The equation on the graph is drawn by using the average of the data in three sets of experiments and it shown the linear relation between cummulative distillate COD load and time of distillation.
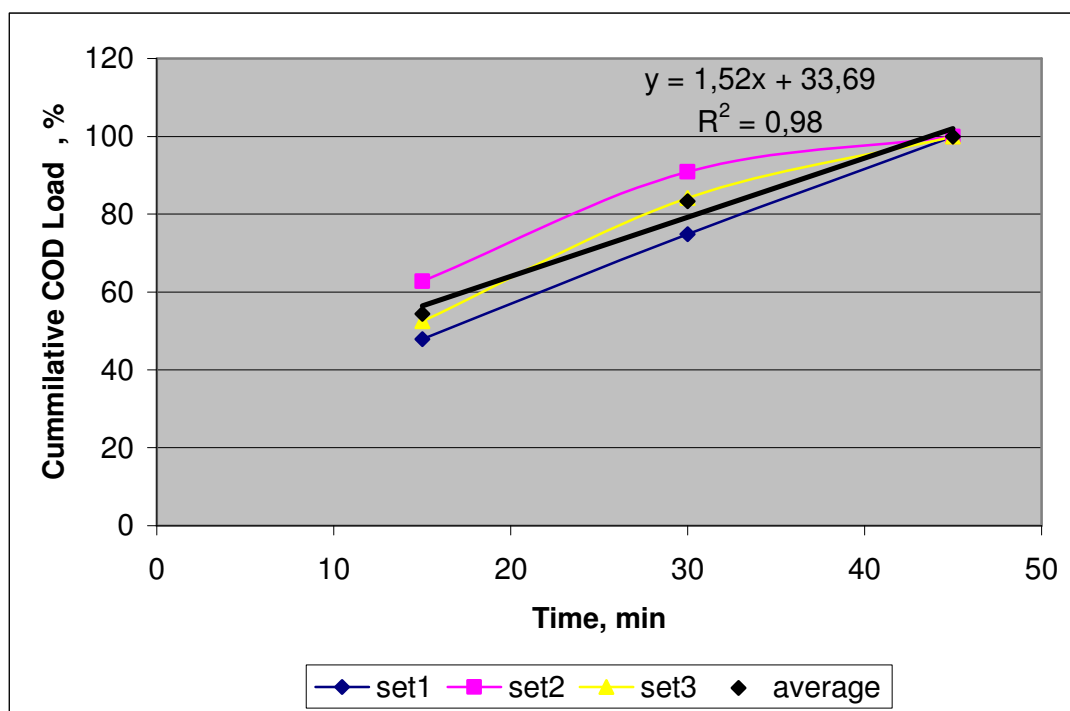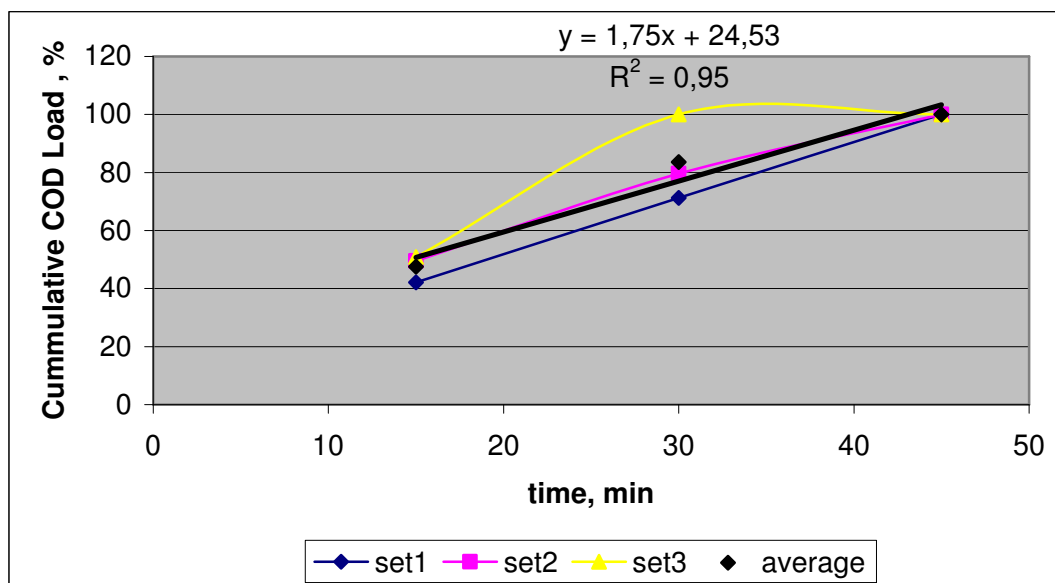
3.2.1.1.b. Intermittent Distillation at 50°C – No Distillate Cooling

The cummulative COD load of the distilates of this mode is presented in Figure 3.2. The equation on the graph is drawn by using the average of the data in three sets of

experiments and it shown the linear relation between cummulative distillate COD load and time of distillation.
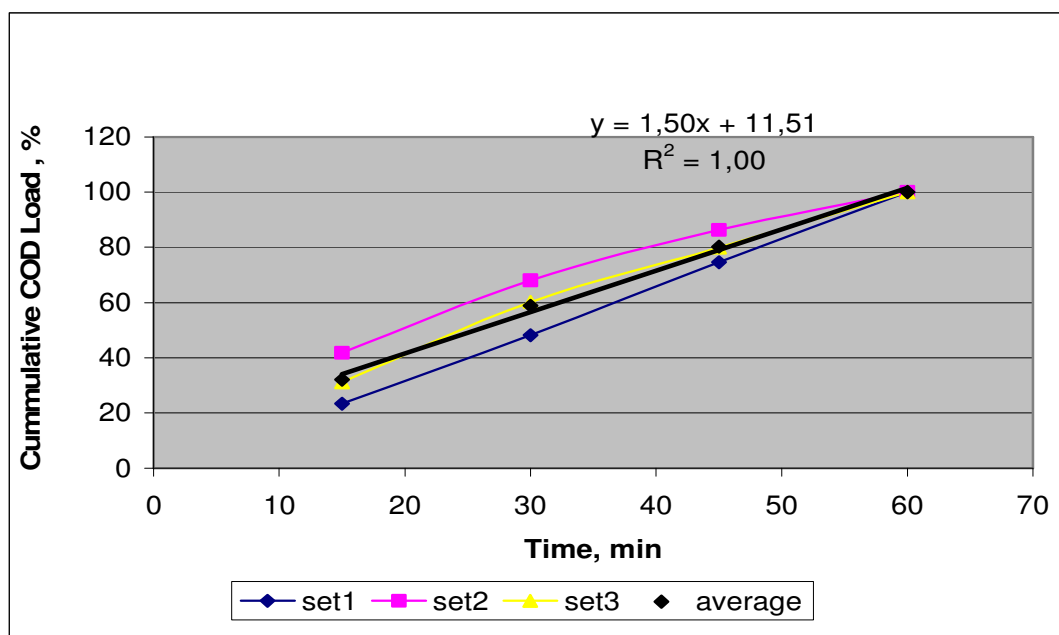
Figure 3.1. Intermittent Distillation at 50°C - Distillate Cooled
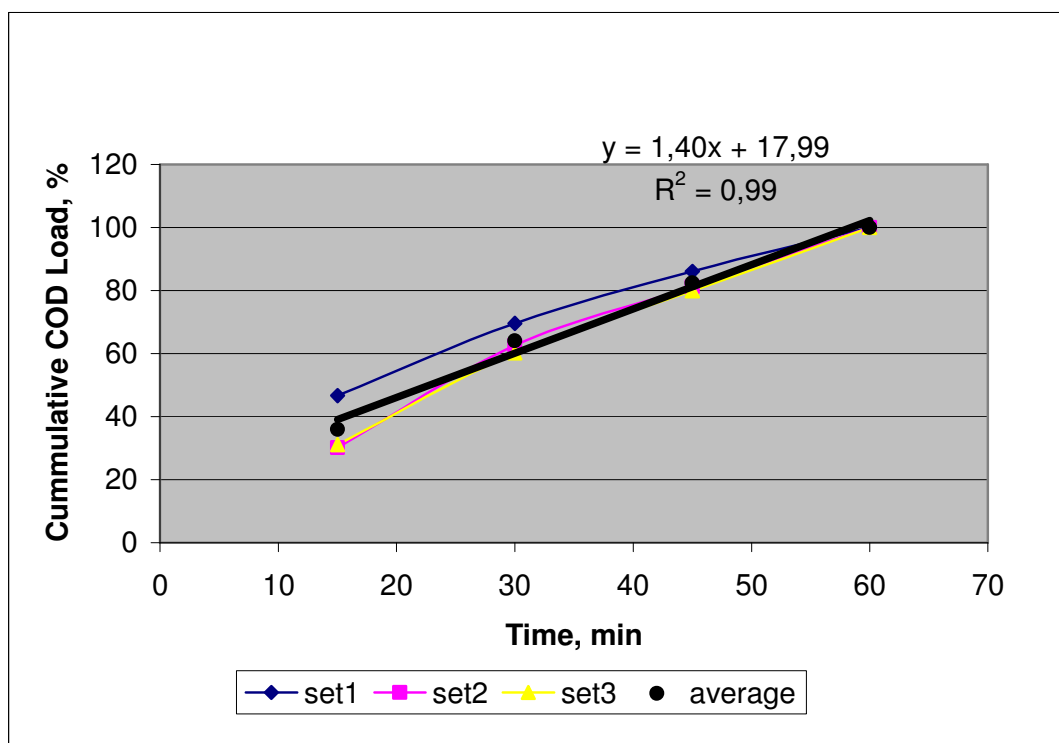
Figure 3.2. Intermittent Distillation at 50°C – No Distillate Cooling

As can be seen from the figures 3.1 and 3.2 the rate of COD accumulation in the distillates are very smilar in two cases.

3.2.1.2. Intermittent Distillation at 70°C

Intermittent distillation is applied to see the change of volume and COD concentration of the distillate with time. This mode is tried in two cases; with and without distillate reservoir cooling.

3.2.1.2.a. Intermittent Distillation at 70°C - Distillate Cooled

The cummulative COD load of the distilates of this mode is presented in Figure 3.3. The equation on the graph is drawn by using the average of the data in three sets of experiments and it shown the linear relation between cummulative distillate COD load and time of distillation.
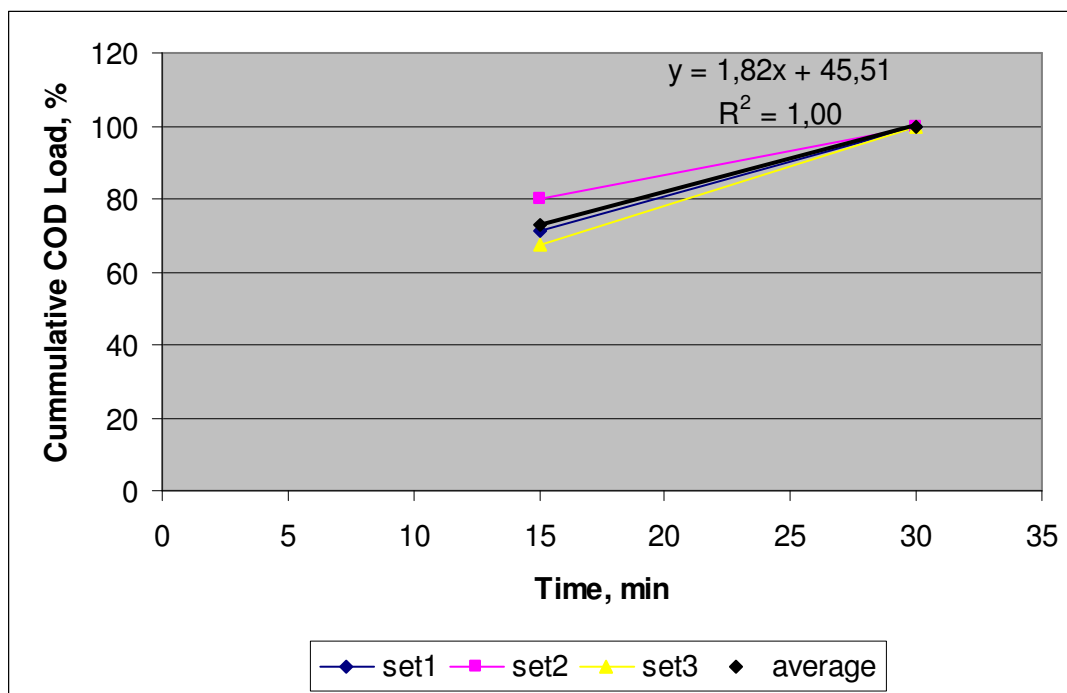

Figure 3.3. Intermittent Distillation at 70°C - Distillate Cooled

3.2.1.2.b. Intermittent Distillation at 70°C – No Distillate Cooling

The cummulative COD load of the distilates of this mode is presented in Figure 3.4. The equation on the graph is drawn by using the average of the data in three sets of experiments and it shown the linear relation between cummulative distillate COD load and time of distillation.
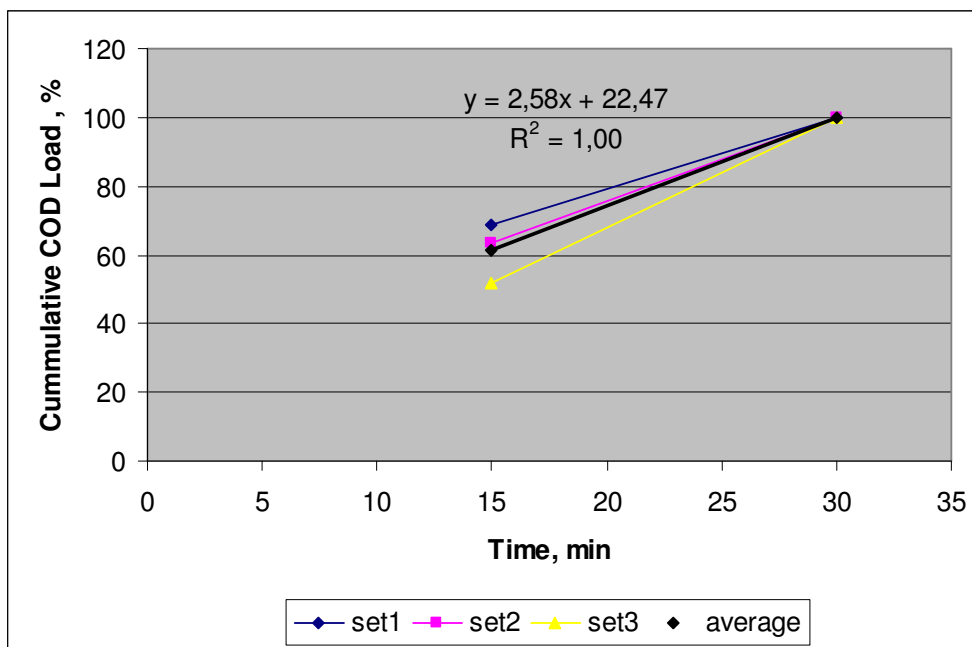

Figure 3.4. Intermittent Distillation at 70°C – No Distillate Cooling

Figures 3.3 and 3.4 shows that the changes of COD accumulation in cooled distillate is slower than the COD acculumation in the distillate which is not cooled. Another point draws attention is the COD removals from black liquor is faster in the distillations at 70°C then the distillations completed in 50°C.

3.2.1.3. Intermittent Distillation at 90°C

Intermittent distillation is applied to see the change of volume and COD concentration of the distillate with time. This mode is tried in two cases; with and without distillate reservoir cooling.

3.2.1.3.a. Intermittent Distillation at 90°C - Distillate Cooled

The cummulative COD load of the distilates of this mode is presented in Figure 3.5. The equation on the graph is drawn by using the average of the data in three sets of experiments and it shown the linear relation between cummulative distillate COD load and time of distillation.

Figure 3.5. Intermittent Distillation at 90°C - Distillate Cooled

3.2.1.3.b. Intermittent Distillation at 90°C – No Distillate Cooling

The cummulative COD load of the distilates of this mode is presented in Figure 3.6. The equation on the graph is drawn by using the average of the data in three sets of experiments and it shown the linear relation between cummulative distillate COD load and time of distillation.

Figure 3.6. Intermittent Distillation at 90°C – No Distillate Cooling

Figures 3.5 and 3.6 shows that the changes of COD accumulation in cooled distillate is significantly slower than the COD acculumation in the distillate which is not cooled. Another point draws attention is the COD removals from black liquor is faster in the distillations at 90°C then the distillations completed in 50°C and 70°C

These data show that if it is required to decrease the COD of the distillate, it is recommended to cool the distillate reservoir. Another determination is done according to the rates of COD load accumulations in distillates is higher the distillation temperatures, faster the COD load accumulation in the distillate. But here the ultimate decision should be taken after the exact COD concentration and loads in distillates are considered, not the rates.

3.2.2. Continious Distillations

Another case tried here is to complete the distillations without any break to see the possible differences with the intermittent cases. Since all the distillations are completed

in one step, the COD loads of the distillates are compared here by using the average data obtained for each distillation temperature (Table 3.5)

Table 3.5. COD loads of the distillates obtained in continious modes

Distillation Temperature, °C	Distillate Cooling	Distillation Time, min	Distillate COD Load, mg
50	YES	60	254
	NO	60	311
70	YES	45	506
	NO	45	673
90	YES	30	755
	NO	30	849

When the data in the table is reflected as a graphic (Figure 3.7), it is seen that COD loads of the distillates are increasing with increasing distillation temperature. Also, the COD of the distillate is lower in the distillates which are cooled during the distillation period.
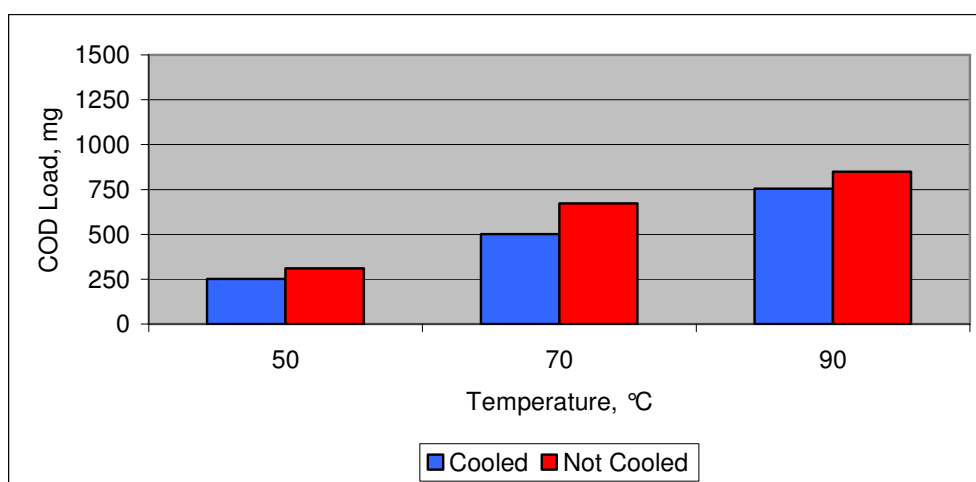
Figure 3.7. COD loads of the distillates in continious modes

3.2.3 Comparison of the Distillations According to Distillate Volume, Distillate COD Concentration, and Distillate COD Load

To decide about the best distillation mode may be possible to see the change of distillate volume, COD concentration, and COD load data in time together. Figures 3.8 and 3.9 present the mentioned data in one graph for different intermittent distillation temperatures.
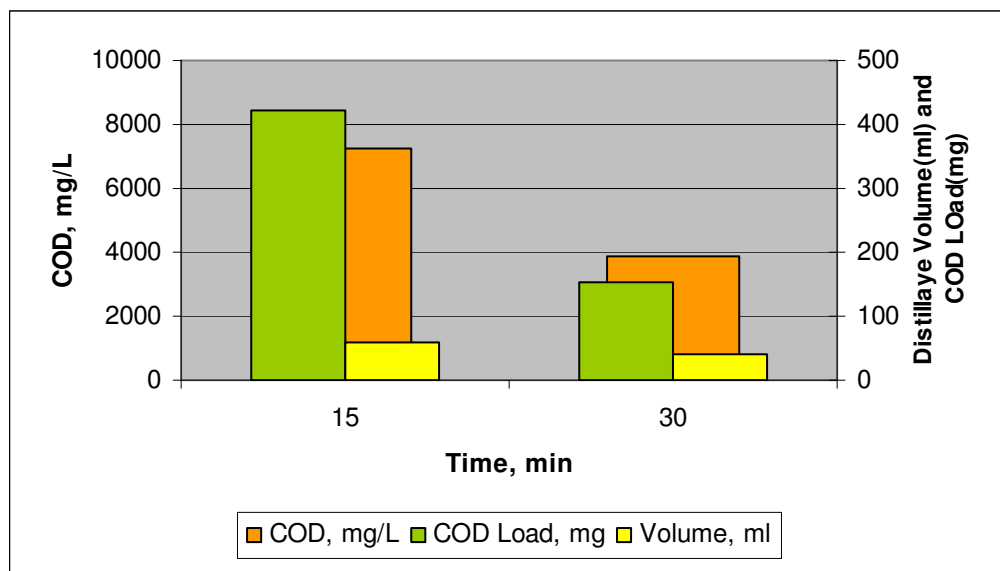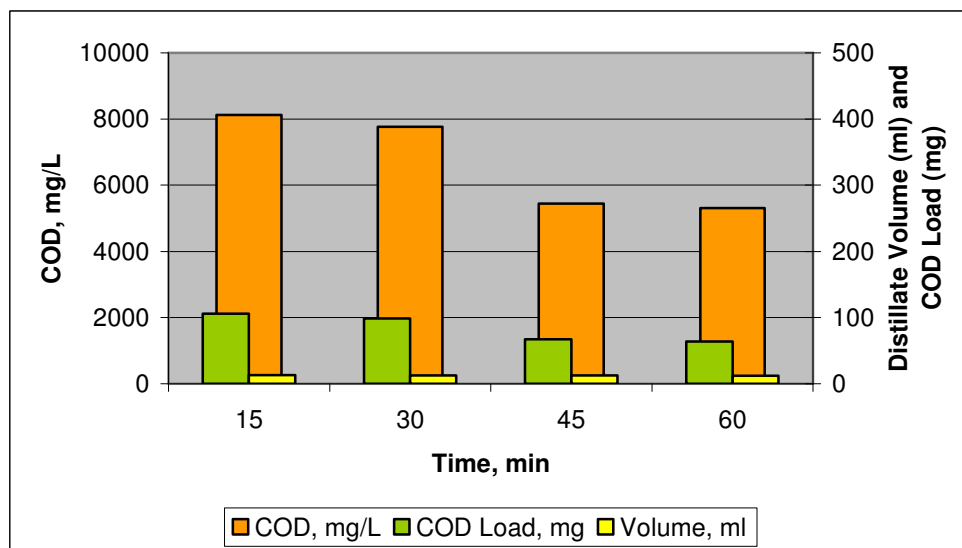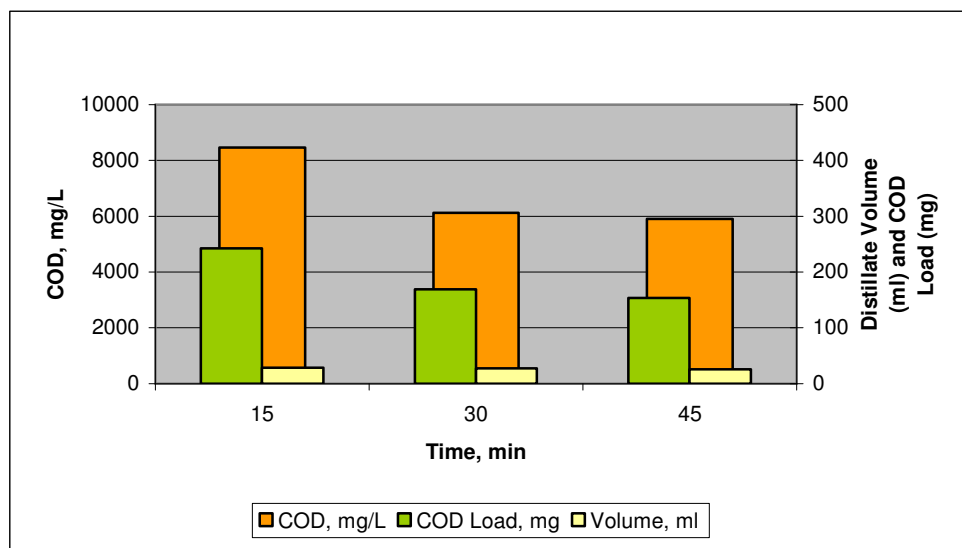
a) 50°C
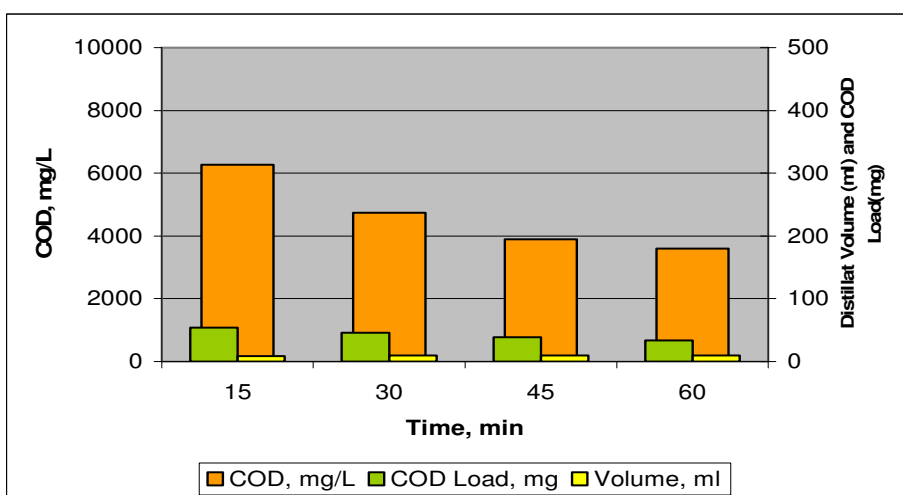
b) 70°C
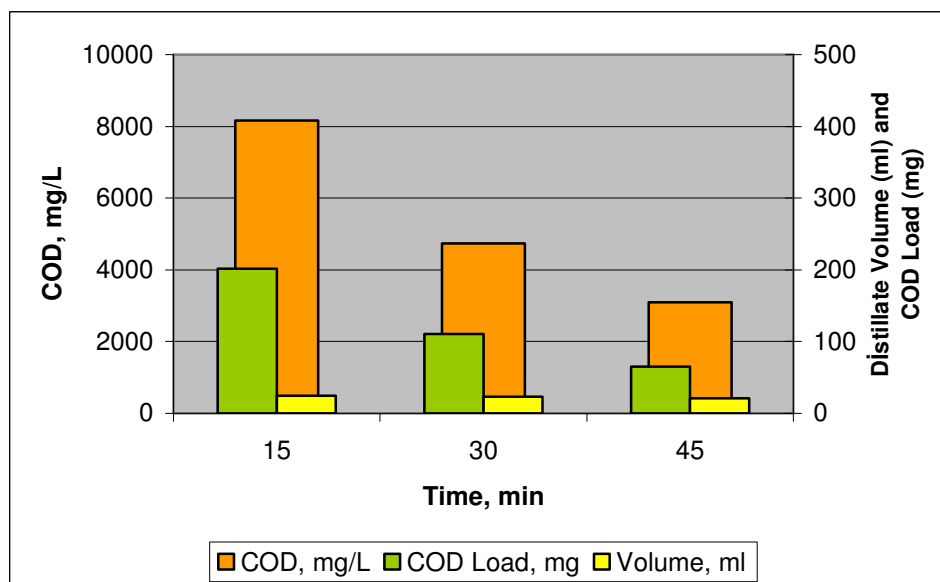
c) 90°C

Figure 3.8. Distillate volumes, COD concentrations, and COD loads for intermittent distillations when the distillate is cooled a) 50°C, b) 70°C, and c) 90°C

a) 50°C

b) 70°C

c) 90°C
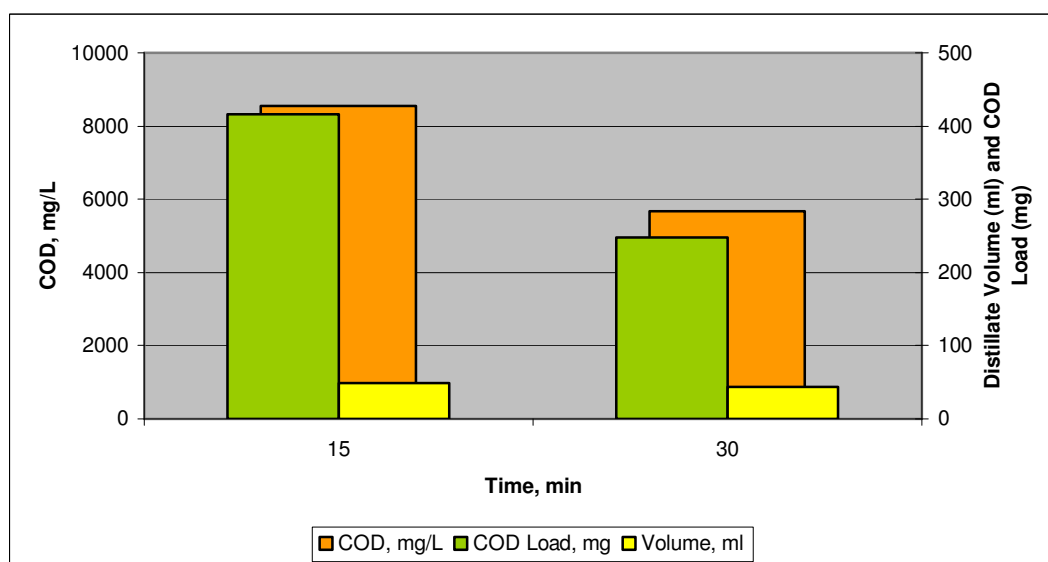
Figure 3.9. Distillate volumes, COD concentrations, and COD loads for intermittent distillations without distillate cooling a) 50°C, b) 70°C, and c) 90°C

From the Figures 3.8 and 3.9 it is seen that not only the COD loads of the distillates, but also the distillate volume and COD concentration is decreasing with time during the distillations. Another point cleared is the advantage of distilate cooling during the

distillations. The COD concentrations and distilate volumes in the distillations with distillate cooling are lower than the distillates without cooling. A further determination is as the distillation temperature rises cummulative COD load of the distillates increases. This situation is explained as rate of COD load change in the following table (Table 3.6).

Table 3.6. Increase of COD Load with Increasing Temperature and the Effect of Distillate Cooling

Distillation Temperature, °C	Cummulative COD Load of Cooled Distillates, mg	COD Load Increase, %	Cummulative COD Load of Distillates Without Cooling, mg
50	172,69 →	94 →	334,97
COD Load Increase, %	↓ 118		↓ 69
70	377,0 →	74 →	565,49
COD Load Increase, %	↓ 53		↓ 17
90	576,58 →	15 →	663,75

Since the goal of this study is to obtain maximum volume of distillate (V) with minimum COD concentration (C); the linear changes of distillate volume, COD concentration and COD load (L=C*V) with changing temperatures and the equations of these linear changes are presented in Figures 3.10, 3.11, and 3.12 for different distillation modes.
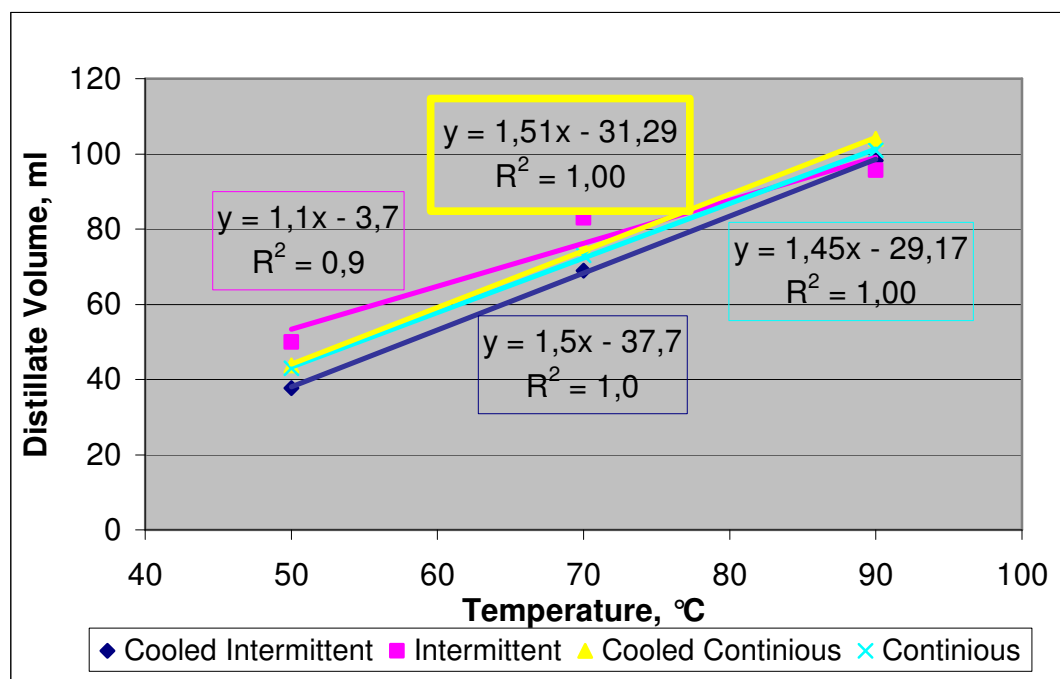
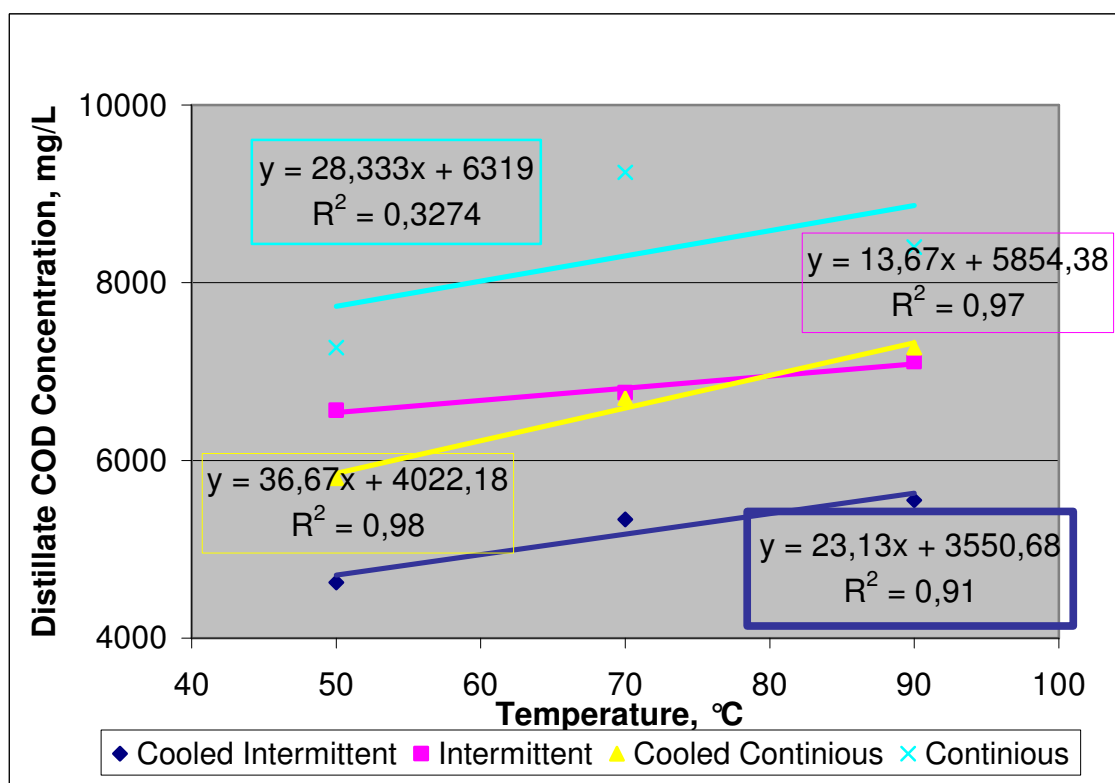Figure 3.10. Change of distillate volume with distillation temperature

Figure 3.10. Change of distillate COD concentration with distillation temperature
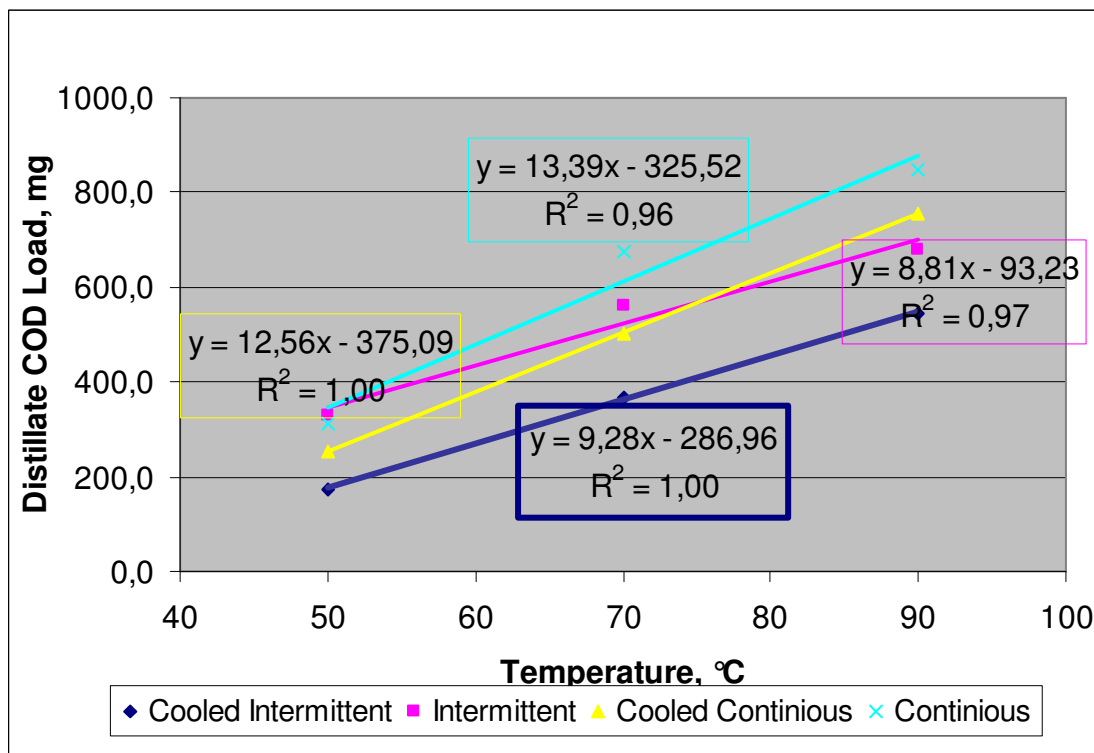
Figure 3.11. Change of distillate COD load with distillation temperature

Figure 3.9. shows that maximum distillate volume is collected in continious mode with distillate cooling. But in Figure 3.10. it is seen that minimum COD concentration is observed in the intermittent distillation with cooled distillate. When we looked at the COD loads again intermittent distillation with distillate cooling looks most beneficial mode and it is followed by conctinious mode with distillante cooling.

Here, we need to look at the leaks from the distillation system during the operation. At the beginning of the distillations the initial COD concentration of black liquor is 33250 mg/L and the volume is 200 ml. When the total COD loads in the distillates is substracted from the initial COD load of black liquor (6650 mg), the theorotical COD load of the residue is determined. The difference between the laboratory measured COD load of the residu and the theoretical COD load shows the leaks from the systems during distillations. Figure 3.12 shows the leaks from the system during the distillations.
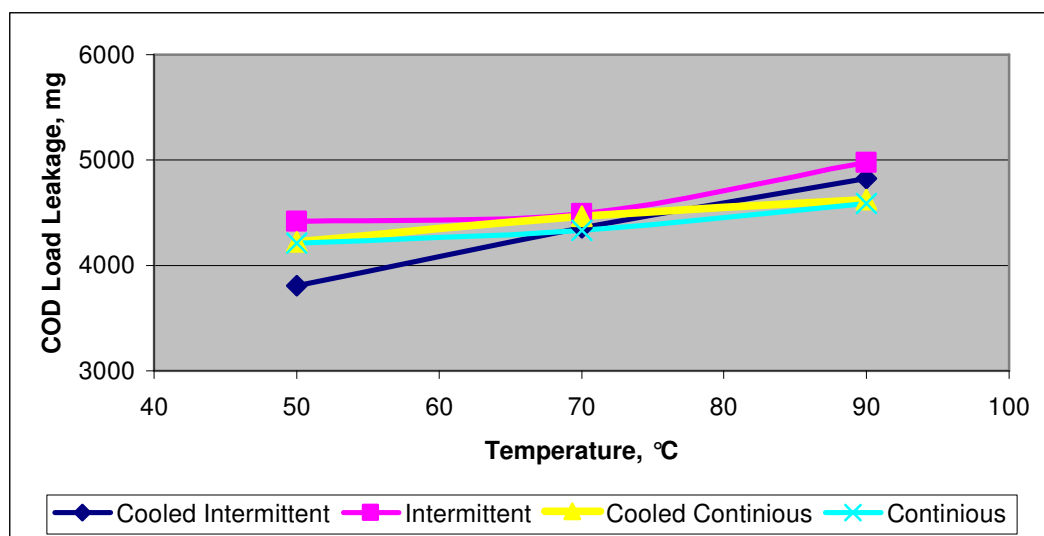
Figure 3.12. COD load leaks from the systems with changing distillation temperature

As can be seen in Figure 3.12. leaks from the system in intermittent modes are higher than the continious modes. Furthermore, the leaks are increasing with increasing distillation temperatures. When the leaks are taken into account, it is much meaningful to select the continious modes with distillate cooling.

3.2.4. The Relations of the Parameters in Residue

Here the relations between the parameters in residue is discussed. The calculated water content and measured water content of the residue is compared and the the results are given in Figure 3.13.
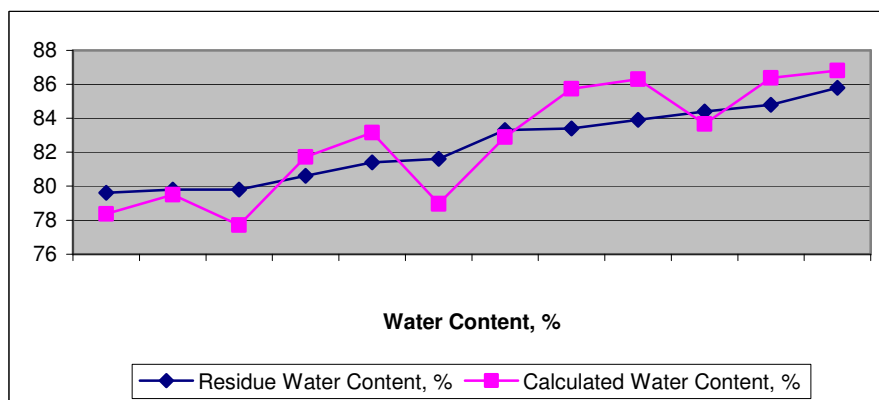
3.13. Comparison of calculated water content and measured waster content of the residue.

As can be seen from the Figure 3.13 calculated and measured water contents are very close to each other. Also the correlation between distillate volume and residue water content shows smilar trend (Figure 3.14).
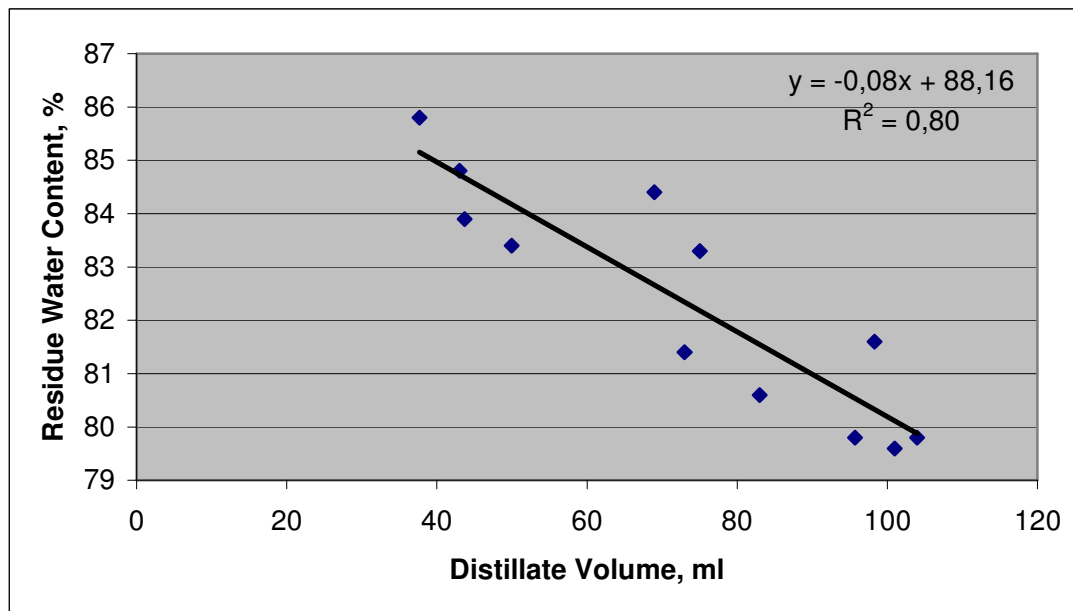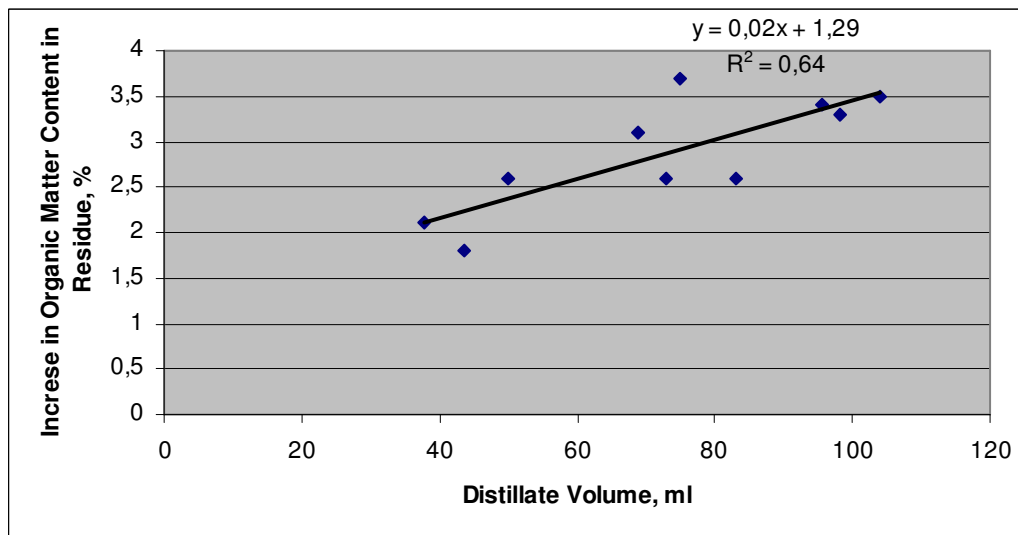

Figure 3.14. The correlation between residue water content and distillate volume

With incresing distillate volume the organic matter content of the residue is increasing as can be seen in Figure 3.15.

3.15. Organic Matter Content increase with incresing distillate volume

CHAPTER FOUR
CONCLUSIONS AND RECOMMENDATIONS

In this study distillation of black liquor is investigated as a waste volume reduction method. The goals of the study is to find the optimum temperature and mode to get maximum ditillate volume with minimum COD concentration.

It is found that;

- Distillate volume accumulated in unit time is increasing with increasing distillation temperatures
- Distillate volume is decreasing during the distillation period with time
- Distillate COD is increasing with increasing temperature
- Distillate COD is increasing during the distillation period with time
- Distillate COD is lower when the distillate reservoir is cooled
- Leaks from the system is increasing with increasing distillation temperatures and
- Leaks from the system is higher in intermittent modes

As a conclusion it is recommended to distillate black liquor in continious mode with distillate cooling. A moderate temperature should be choosen if the time of distillation is not limited because of energy savings.

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