



بسم الله الرحمن الرحيم

Sudan University science & Technology
Collage of petroleum & mining of Engineering
Department of Refining and Transportation Engineering



Refinery Wastewater Treatment:

Case Study Khartoum Refinery

معالجة المياه الملوثة في مصفاة الخرطوم

A Thesis submitted for partial fulfillment of the requirement for the
degree of Bachelor of Science in Refining and Transportation
Engineering

Presented by:

Alnaeem Adam Alnaeem Aldwo
Afif Gubran Barashi Albarashi
Badawi Tariq Badawi Ali
Mokhtar Hamid Mohammed Hamad
Sharnobi Mohammed Abdallah Almobark

Supervisor:

Dr. Zeinab Abdullah.

FEB 2022

الأهداء:

قال تعالى. (وَقُلْ اَعْمَلُوا فَسَيَرَى اللّهُ عَمَلَكُمْ وَرَسُولُهُ وَالْمُؤْمِنُونَ ۖ وَسَتُرَدُّونَ اِلَىٰ عَالَمِ الْغَيْبِ

وَالشَّهَادَةِ فَيُنَبِّئُكُمْ بِمَا كُنْتُمْ تَعْمَلُونَ) سورة التوبة الآية 105 صدق الله العظيم.

إلهي لا يطيب لي الليل إلا بشكرك، ولا يطيب لي النهار إلا بطاعتك، ولا تطيب لي اللحظات إلا بشكرك ولا تطيب لي

الآخرة إلا برويتك.

إلى من كلله الله بالهبة والوقار، إلا من علمني العطاء دون انتظار، إلا من أحمل اسمه بكل افتخار،

أرجو من الله أن يمد في عمرك ثمارك قد حان قطافها بعد طول انتظار.

والذي العزيز إلى ملاحي في الحياة إلى معني الحنان والتفاني إلى بسمة الحياة وسر الوجود.

والذي الغالية إلى من كان دعائها سر نجاحي زاد يقويني.

إخوتي وأخواتي إلى الشموع الموقدة التي تنير ظلمة حياتي من ساندوني ووقفوا معي وأنا أرتاد

المجد و الأفاق.

القادة العظماء الأجلء الأساتذة الصراة

زوجتي الحبيبة مستقبلا إلى من تحلى بالإخاء وتميزت بالعطاء، إلى منبع الصدق الصافي إلى من معما

سأسعد.

أبنائي وبناتي

إلى شهداء بلادي إلى من حلم بوطن شامخ لا رصاصة فيه تقتلهم، إلى الأرواح الذكية أصحابهم المهم،

من أطفاً الخدر شمعة أحلامهم المضيئة.

Acknowledgments

I acknowledge with gratitude the immense support given to me, all Through this research project, by teachers and doctor in the collage specifically: D. monira whom even to our visit to KRC, The man of the simulation A. ammar grate salaam for him.

*But foremost I highly indebted to our supervisor **Dr. Zeinab** whom, without her personal counseling and keen guidance, this research project would not have been accomplished, she outpaces all circumstances for us.*

Contents

الإهداء	I
Acknowledgments	II
Contents	III
List of Table	V
List of Figures	VI
Abstract	VII
List of Abbreviations	VIII
Chapter 1	1
1. Introduction:	1
1.1. In General:	1
1.2 Source of Water:	1
1.3 Source of Waste Water:	2
1.4 Water Pollution:	3
1.5. Major Type of Pollutants:	3
1.6. Statement of the Problem:	3
1.7. Research Objectives:	3
1.8. Scope of the Study:	4
Chapter 2	5
2.1. Background	5
2.1.1. The main sources of production unit:	5
2.1.2. Physical and Chemical Processes:	10
2.1.3. Waste water treatment method:	14
2.2. Literature Review:	24
Chapter 3	25
3. Research Methodology:	25
3.2 Sour water stripping unit:	33

Chapter 4	44
4. Results and Discussion:	44
4.1 The Results:.....	44
4.2 Discussion of Results:	46
Chapter 5	48
5. Conclusions & Recommendations	48
5.1 Conclusions:	48
5.2. Recommendations:	48
References:	50

List of Table

Table (2.1) physical and chemical process:.....	10
Table (2.2): Common refinery prevention and control techniques	21
Table (3.1) Average flow for waste water entering the wastewater treatment unit	25
Table (4.1) The physical quality of the MP effluents and comparison with National Sudanese standards and International standards.....	44
Table (4.2) The chemical quality of the MP effluents and comparison with National Sudanese standards and International standards.....	44
Table (4.3) The organics quality of the MP effluents and comparison with National Sudanese standards and International standards.....	44
Table(4.4) analysis results of waste water sample taken from monitory pond.....	45
Table (4.5) analysis results of simulation for sour water stripping unit.....	45
Table (4.6) the result of energy balance for flash tank	45
Table (4.7) energy balance for stripper.....	45

List of Figures

Figure Pages	Title
Figure 1.1	graphical distribution of the locations of water on Earth 2
Figure (2.1)	distillation column 6
Figure (2.2)	Delayed Coking unit 7
Figure 2.3	KRC 14
Figure (2.4)	API separator 16
Figure (2.5)	Dissolved air flotation—a typical DAF unit 18
Figure (2.6)	Induced air flotation (IAF) unit 19
Figure (2.7)	the configuration of a typical carbon adsorption system 21
Figure (2.8)	the typical chemical oxidation system. 22
Figure (2.9)	Biological sludge treatment 24
Figure (2.10)	Sour water stripping unit 29
Figure (3.1)	the condition require in separator 40
Figure (3.2)	the composition for feed to separator and the product composition 40
Figure (3.3)	heat exchanger condition 41
Figure (3.4)	heat exchanger design 41
Figure (3.5)	the design of stripper 42
Figure (3.6)	introduce the feed and product condition in stripper 43
Figure (3.7)	the temperatures for every stage in the column and the 44
Figure (3.8)	the composition of sour gases in the top of stripper 45
Figure (3.9)	the composition of gases and purified water in the stripper 46
Figure (3.10)	determine the overall design of sour stripping 46
Figure (3.12)	The energy balance for flash use excel 51
Figure (3.13)	show the energy balance for exchanger 52
Figure (3.14)	energy balance for stripper 53
Figure (4.1)	Comparison between organics concentrations in MP 52
Figure (4.2)	COD concentration at inlet of the unit compared with standard 53

Abstract

The aim of this research is to study how to treat the wastewater and sour water resulting from a petroleum refinery and to determine the characteristics of generated after treatment. The research identified the sources of wastewater pollutants, suitable treatment technologies, and its effect on the environment. Liquid waste produced was studied, the unit that used as well as to treat the waste, and the evaluation of the performance of these units. Laboratory tests were conducted to identify the characteristics of wastes in each stage and using hissy to simulate sour stripping unit to achieve high quality of purified water.

The analysis carried include: oil content, phenol content, Biochemical Oxygen Demand, Chemical Oxygen Demand, Ammonia - Dissolved Oxygen, Suspended Solid.

The results obtained revealed the following:

- The oil content can reach more than 20.000mg/l and this is more than The design capacity of the treatment unit but it can be reduced to less Than 10 mg/l after treatment.
- The waste water treatment unit works with capacity more than the Designed, so the efficiency of this unit is not enough.
- There is a lot of polluting effluent with concentration more than the Allowed (i.e. NH₃, pH)
- The above indicates some design problem and the study recommended To add additional units to solve the above mentioned problems and Obstacles.

List of Abbreviations

Abbreviations	Name	Page
LPG	Liquefied Petroleum Gas	5
TBP	True Boiling Point	6
ULSD	Ultra Low Sulphur Diesel	7
HDS	hydrodesulphurization	8
HDN	Hydro denitrification	8
HVGO	Heavy Vacuum Gas Oil	8
KRC	Khartoum Refinery Company	11
CNPC	China National Petroleum Corporation	11
MEM	Ministry Energy & Mining	11
CDU	Crude Distillation Unit	11
RFCC	Residue Fluidize Catalytic Cracking	11
REF	Catalytic Reforming	11
HDT	Diesel Hydro Treating	11
WWTB	Waste Water Treatment Plant	13
CPI	Corrugated Plate Interceptors	16
PPS	Parallel Plate Separators	16
DAF	Dissolved Air Flotation	16
IAF	Induced Air Flotation	17
SBR	Sequencing Batch Reactor	19
GAC	Granular Activated Carbon	20
ASS	Activated Sludge System	23

CBS	Central Bureau of Statistics	29
CPL	Central Petroleum Laboratories	29
MP	Monitoring Pond	29
BOD	Biochemical Oxygen Demand	30
COD	Chemical Oxygen Demand	30
TS	Total Solids	30
TDS	Total Dissolved Solids	30
TSS	Total Suspended Solids	30
BOD 5	Biochemical Oxygen Demand after 5 days	47
MEM	Ministry of Energy and Mining	47
WB/IFC	World Bank and International Finance Corporation	47
OME	Ontario Ministry of the Environment	47
MEF	Ministry of Environment and Forests	47
FEPA	Federal Environmental Protection	47

Chapter 1

1. Introduction:

1.1. In General:

Water is what humans need most to survive. Water has an important role in metabolic activities, such as ensuring the balance of heat in the body, transporting the nutrients taken into the body to the target destinations although often perceived to be pretty ordinary, water is the most remarkable substance. We wash in it, fish in it, swim in it, drink it and cook with it, although probably not all at the same time. We are about two-thirds water and require water to live. Life as we know it could not have evolved without water and dies without it. Droughts cause famines and floods cause death and disease. Because of its clear importance, water is the most studied material on Earth. It comes as a surprise, therefore, to find that it is so poorly understood, not only by people in general, but also by scientists working with it every day.

(Anon., n.d.)

1.2 Source of Water:

Water resources are natural resources of water that are potentially useful as a source of water supply 97% of the water on the Earth is salt water and only three percent is fresh water; slightly over two thirds of this is frozen in glaciers and polar ice caps.^[1] The remaining unfrozen freshwater is found mainly as groundwater, with only a small fraction present above ground or in is known as water rights the air. Natural sources of fresh water include surface water, under river flow, groundwater and frozen water. Artificial sources of fresh water can include treated wastewater (reclaimed water) and seawater, for example of sources water:

- Surface water
- Lacks and reservoirs
- Seasonal turnover
- Subsurface water
- Wells water

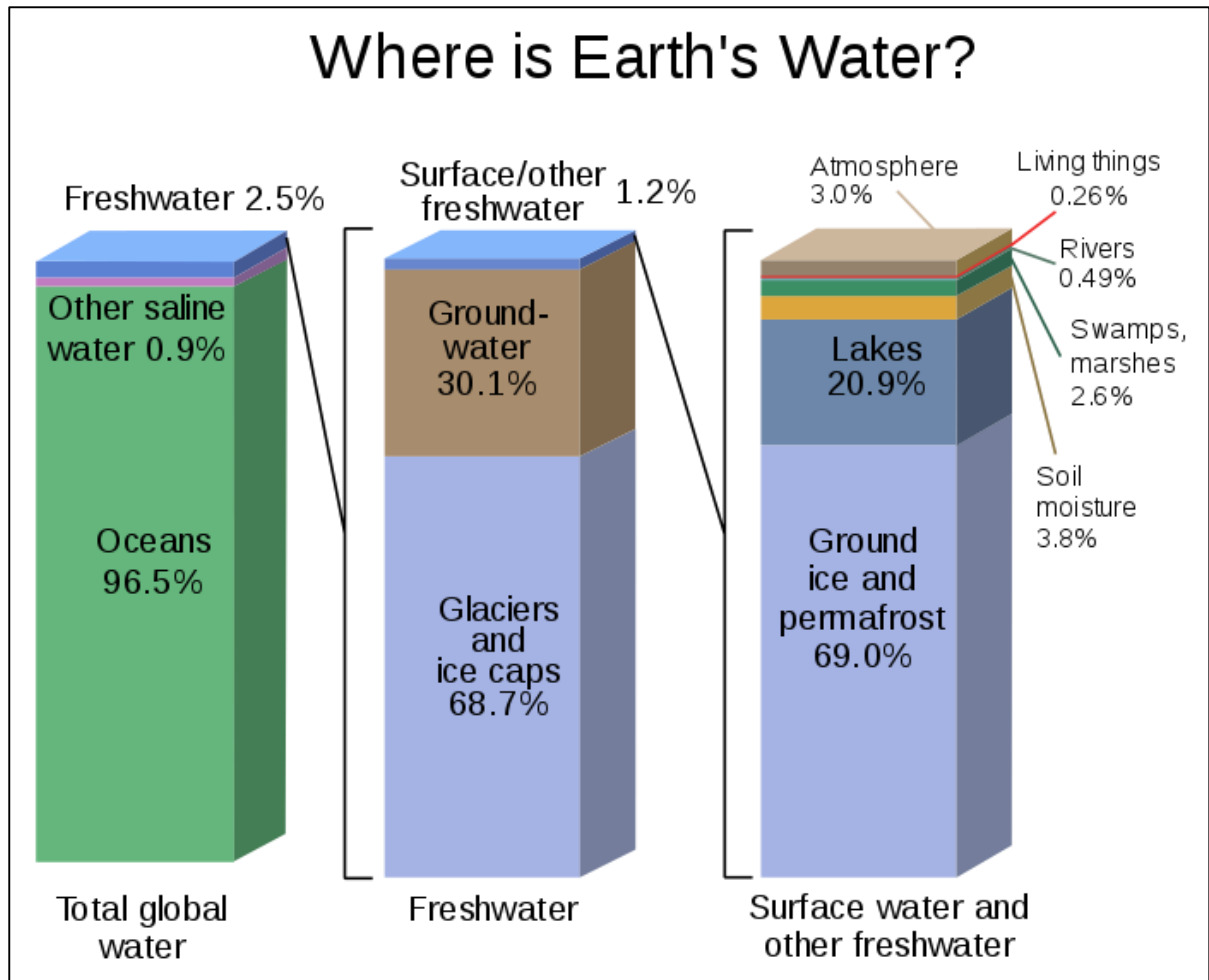


Figure 1.1 graphical distribution of the locations of water on Earth

. Only 3% of the Earth's water is fresh water. Most of it is in icecaps and glaciers (69%) and groundwater (30%), while all lakes, rivers and swamps combined only account for a small fraction (0.3%) of the Earth's total freshwater reserves

1.3 Source of Waste Water:

- Municipal
- Industrial (chemical industry, factories ...)
- Oil and gas refineries such as:
 - ❖ Crude oil storage
 - ❖ Desalting
 - ❖ Vacuum unit
 - ❖ Thermal and catalytic cracking
 - ❖ Hydrocracking
 - ❖ Reforming and hydro treating

(Anon., n.d.)

1.4 Water Pollution:

On the other hand, Contamination of streams, lakes, underground water, bays, or oceans by substances is harmful to living things. Water is necessary to life on earth. All organisms contain it; some live in it; some drink it. Plants and animals require water that is moderately pure, and they cannot survive if their water is loaded with toxic chemicals or harmful microorganisms. Water pollution can kill large numbers of fish, birds, and other animals, in some cases killing all members of a species in an affected area. People who ingest polluted water can become ill, and, with prolonged exposure, may develop cancers or bear children with birth defects Water is one of the most important natural resources being used in the process industry for instance, it is used for desalting crude oil in petroleum refineries, for liquid-liquid extraction in hydrometallurgy, as a cooling, quenching and scrubbing agent in the iron and steel industry, and for a variety of washing operations in the food and agricultural industries. The predicted scarcities of industrial water over the next few decades and the increasingly stringent environmental regulations for wastewater disposal will require efficient and responsible utilization of water in industry, one of the most industry its petroleum refineries industries (Awad, 2008)

1.5. Major Type of Pollutants:

The major water pollutants are chemical, biological, or physical materials that degrade water quality. Pollutants can be classed into eight categories, each of which presents its own set of hazards.

5.1. 1.Petroleum Products:

Oil and chemicals derived from petroleum are used for fuel, lubrication, plastics manufacturing, and many other purposes. These petroleum products get into water mainly by means of accidental spills from ships, tanker trucks, pipelines, and leaky underground storage tanks. Many petroleum products are poisonous if ingested by animals, and spilled oil damages the feathers of birds or the fur of animals, often causing death. In addition, spilled oil may be contaminated with other harmful substances, such as polychlorinated biphenyls (PCBs).

1.5.2. Heavy Metals:

Heavy metals, such as copper, lead, mercury, and selenium, get into water from many sources, including industries, automobile exhaust, mines, and even natural soil. Like pesticides, heavy metals become more concentrated as animals feed on plants and are consumed in turn by other animals. When they reach high levels in the body, heavy metals can be immediately poisonous, or can result in long-term health problems similar to those caused by pesticides and herbicides. (Awad, 2008)

1.6. Statement of the Problem:

The liquid effluents generated from Khartoum refinery, if not treated properly and disposed of in an environmentally acceptable manner, it can cause adverse environmental impacts on the surrounding environment.

1.7. Research Objectives:

Since water is a major liquid that used in separation processes in oil refineries it must be exploited in an optimum way so we will do this research that aimed to:

1. Minimize water wasting in oil refineries.
2. Study the properties of water extracted from several refining units.

3. Treatment of water to be used again in refining processes.

1.8. Scope of the Study:

The scope of this project is to give a comprehensive study for water system unit and sour water stripping unit.

The project will cover the following:

- 1- Analysis of water characteristics after treatment and determine the amount of composition that contaminate water to specify the quality of water.
- 2- Simulation
- 3- Material balance

Chapter 2

2.1. Background

The petroleum refining industry converts crude oil into more than 2500 refined products, including liquefied petroleum gas, gasoline, kerosene, aviation fuel, diesel fuel, fuel oils, lubricating oils, and feedstock for the petrochemical industry. Petroleum refinery activities start with receipt of crude for storage at the refinery, include all petroleum handling and refining operations, and they terminate with storage preparatory to shipping the refined products from the refinery. The petroleum refining industry employs a wide variety of processes. A refinery's processing flow scheme is largely determined by the composition of the crude oil feedstock and the chosen slate of petroleum products. The arrangement of these processes will vary among refineries, and few, if any, employ all of these processes. Petroleum refining processes having direct emission sources are presented on the figure in bold-line boxes. (Anon., n.d.)

2.1.1. The main sources of production unit:

2.1.1.1. Distillation column Units:

Distillation or fractionation models for planning and scheduling activities serve an important role in all decision-making problems inside the oil-refining sector. As the distillation units separate the crude-oil into various cuts or distillates and then distribute these to downstream transforming and treating units, all efforts to improve their quantity and quality predictions to avoid potential inconsistencies in the targets for scheduling and/or control applications is always worth pursuing. The driving force in most separation processes found in oil refining is the volatility difference between multiple light and heavy crude-oil components, which are of course temperature and pressure depended . distillation models in planning and scheduling problems rely on essentially mass and/or volume-basis material balances, where the crude oils are decomposed into several cuts based on what are known as true boiling point (TBP) temperature distribution curves for how yields and

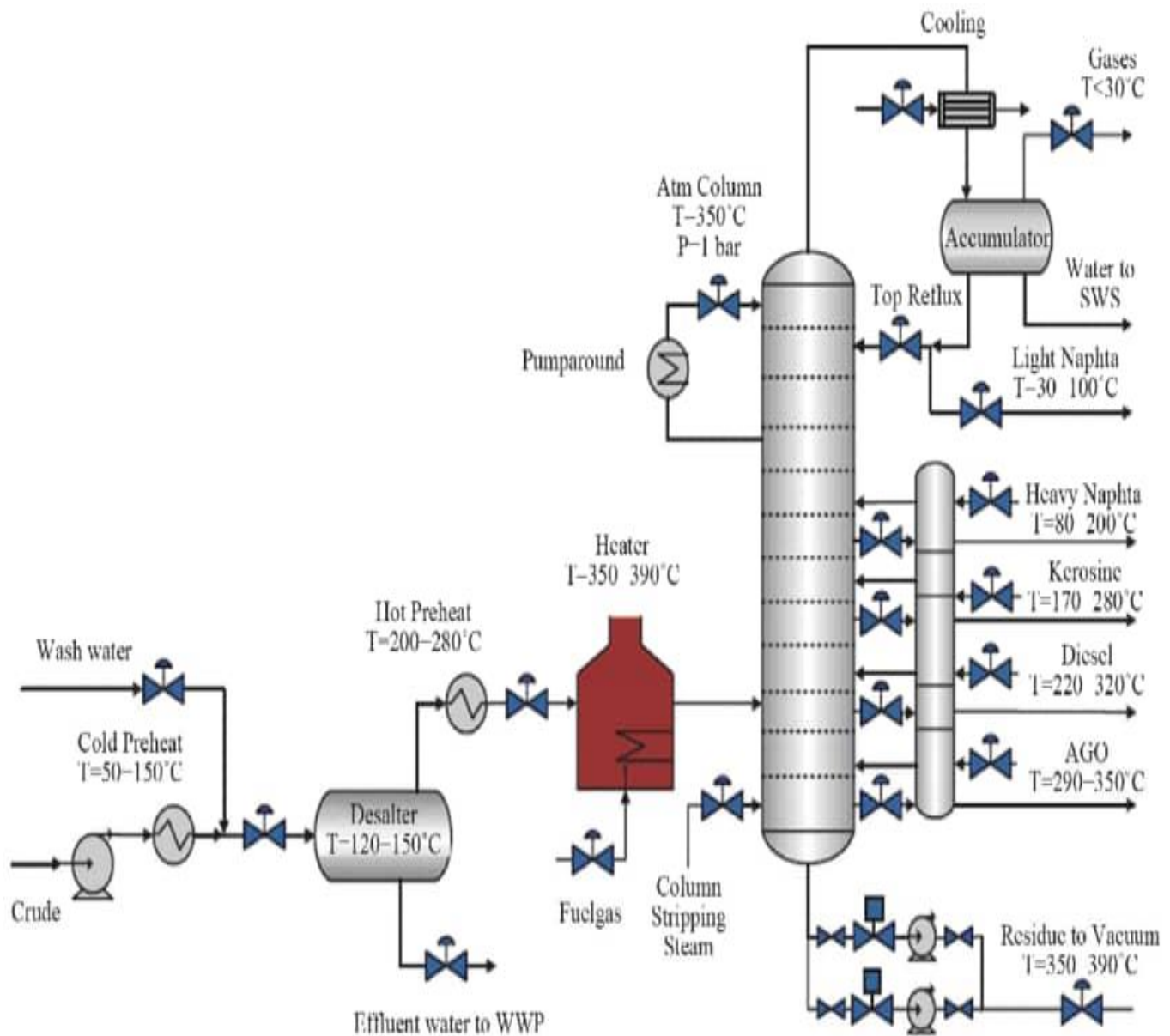


Figure 2.1 distillation column

other qualities are distributed as a function of TBP temperature. In this way, variations in material and property flows from these distillation processes can be modeled considering the column's known temperature distribution or profile (Zhang & Zhu, 2001).

2.1.1.2 Crude Oil Desalting unit:

Desalting is a water-washing operation performed initially at the production field and thereafter at the refinery site for additional crude oil cleanup. Crude oil often contains fine saline water droplets, salt crystals, suspended solids and traces of metals. Large amounts of dissolved salts can affect the crude refining process quite significantly. It can, for instance, foul heat exchangers, block pipe lines and generally affects the performance of other refinery equipment. In order to avoid salts-related problems, salts must be removed from the crude oil for this reason and to prevent corrosion, plugging, and fouling of equipment, electrical desalting plants are often installed in crude oil production units. Desalting involves mixing heated crude oil with washing water, using a mixing valve or static mixers to ensure a proper contact between the crude oil and the water, and then passing it to a separating vessel, where a proper separation between the aqueous and organic phases is achieved. (nasehi & sarraf, 2018) Since emulsions can be formed in this process, there is a risk of water carryover in the organic. In order to overcome this problem chemical demulsifiers are added to promote the emulsion breaking. When this operation is performed at a refinery, an electric field across the settling vessel is applied to coalesce the polar salty water droplets, and, therefore, a decreasing in water and salt content is achieved.

2.1.1.3 Delayed Coking unit:

The delayed Coker is the only main process in a modern petroleum refinery that is a batch-continuous process. The flow through the furnace is continuous. The feed stream is switched between two drums. One drum is on-line filling with coke, while the other drum is being steam-stripped, cooled, decoked, pressure checked and warmed up. The overhead vapors from the coke drums flow to a fractionator. This fractionator tower has a reservoir in the bottom where the fresh feed is combined with condensed product vapors to make up the feed to the Coker heater. (Industries, 2017)

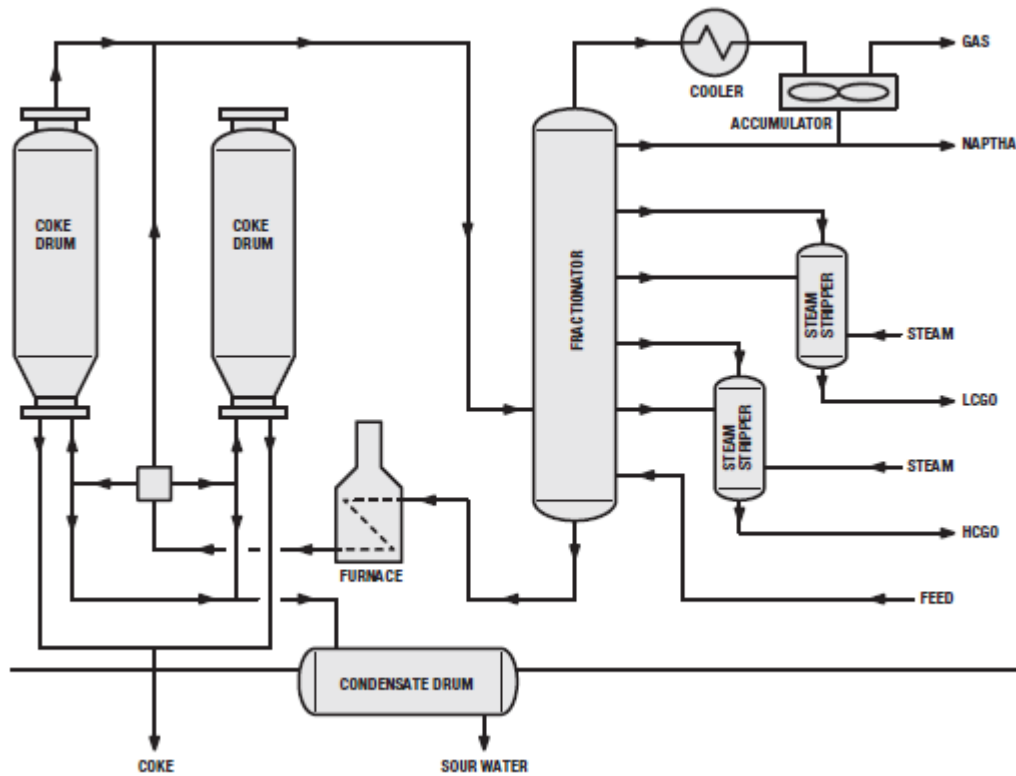


Figure 2.2 Delayed Coking unit

2.1.1.4 water system:

The traditional cooling water system can be regarded as an integrated system consisting of three main components: cooler network, cooling tower, and circulation water pump. The central unit of such system is the cooling tower in which hot water is cooled by air and returned to the process (Ljubica Matijašević, 2017)

2.1.1.5 Diesel Hydro treating :

Diesel Hydro treating is a major technology today with legislations enforcing improved diesel quality specifications. Presently, the technology is closely guarded and available only with few international licensors. It employs improved hydrodynamics and high active hydro treating catalyst. The technology offers the flexibility to upgrade middle range straight run distillates, Coker gas oil streams and light cycle oil from catalytic cracking to low sulphur, high cetane diesel suitable for meeting ULSD (Ultra Low Sulphur Diesel) pool requirement. Description of this process below

- Diesel feed is mixed with recycled hydrogen over a catalyst bed in a trickle bed reactor at temperature of 290-400°C and pressure of 35-125 kg/cm².
- The main chemical reactions are hydrodesulphurization (HDS), hydro denitrification (HDN), aromatic and olefin saturation.
- Reactor effluent is separated into gas and liquid in a separator. Gas is recycled back to the reactor after amine wash along with makeup hydrogen and liquid is sent to the stripper for removal of light gases and H₂S. (Ltd., n.d.)

2.1.1.6. Crude Oil Vacuum Distillation:

The vacuum distillation unit is the second main unit after the atmospheric distillation unit that processes atmospheric residue in any refinery. To extract more valuable distillates from the atmospheric residue, the residue from the atmospheric distillation unit is sent to the vacuum distillation unit. The objective of vacuum distillation is to separate the atmospheric residue into several fractions, including light vacuum gas oil (LVGO) and heavy vacuum gas oil (HVGGO). (Agrawal, 2018)

2.1.1.7. Naphtha catalytic reforming:

Naphtha catalytic reforming is one of the main processes of gasoline production with high octane number. Inactive catalysts and changing the products distribution is an important issue in this process. These units consist of three or four series fixed or movable catalytic bed reactors. Naphtha catalytic reforming is a process in which naphtha compounds with a low octane number are converted to high-octane gasoline compounds. In other words, mainly catalytic reactions of unbranched paraffin's in naphtha are converted to iso-paraffin and aromatics. Hydrogen and light hydrocarbons (C₁-C₄) are the process by-products.

Generally, the goals of catalytic reforming process are producing the high-octane gasoline, aromatics for petrochemical industries and the production of hydrogen for industrial uses such as hydrocracking and desulphurization. (Samimi & Shahbazi Kootenaiea, 2020)

2.1.2. Physical and Chemical Processes:

Table (2.1) physical and chemical process:

Physical	Chemical	
Distillation Solvent extraction Propane deasphalting Solvent dewaxing Blending	Thermal	Chemical
	visbreaking Delayed coking Flexi coking	Hydro treating Catalytic reforming Catalytic cracking Hydro cracking Catalytic dewaxing Alkylation Polymerization Isomerization

- Listed below are 5 categories of general refinery processes and associated operations:
 1. Separation processes
 - Atmospheric distillation
 - Vacuum distillation
 - Light ends recovery (gas processing)
 2. Petroleum conversion processes
 - Cracking (thermal and catalytic)
 - Reforming
 - Alkylation
 - Polymerization
 - Isomerization
 - Coking
 - Visbreaking
 3. Petroleum treating processes
 - Hydrodesulphurization
 - Hydrotreating
 - Chemical sweetening
 - Acid gas removal
 - Deasphalting
 4. Feedstock and product handling
 - Storage

- Blending
 - Loading
 - Unloading
5. Auxiliary facilities
- Boilers
 - Waste water treatment
 - Hydrogen production
 - Sulfur recovery plant
 - Cooling towers
 - Blow down system
 - Compressor engines

These refinery processes are defined below, and their emission characteristics and applicable emission control technology are discussed. (Awad, 2008)

2.1.2.1 Separation Processes:

The first phase in petroleum refining operations is the separation of crude oil into its major constituents using 3 petroleum separation processes: atmospheric distillation, vacuum distillation, and light ends recovery (gas processing). Crude oil consists of a mixture of hydrocarbon compounds including paraffinic, naphthenic, and aromatic hydrocarbons with small amounts of impurities including sulfur, nitrogen, oxygen, and metals. Refinery separation processes separate these crude oil constituents into common boiling-point fractions.

2.1.2.2. Conversion Processes:

To meet the demands for high-octane gasoline, jet fuel, and diesel fuel, components such as residual oils, fuel oils, and light ends are converted to gasoline and other light fractions. Cracking, coking, and visbreaking processes are used to break large petroleum molecules into smaller ones. Polymerization and alkylation processes are used to combine small petroleum molecules into larger ones. Isomerization and reforming processes are applied to rearrange the structure of petroleum molecules to produce higher-value molecules of a similar molecular size.

2.1.2.3. Treating Processes:

Petroleum treating processes stabilize and upgrade petroleum products by separating them from less desirable products and by removing objectionable elements. Undesirable elements such as sulfur, nitrogen, and oxygen are removed by hydrodesulphurization, hydrotreating, chemical sweetening, and acid gas removal. Treating processes, employed primarily for the separation of petroleum products, include such processes as deasphalting. Desalting is used to remove salt, minerals, grit, and water from crude oil feedstock before refining. Asphalt blowing is used for polymerizing and stabilizing asphalt to improve its weathering characteristics

2.1.2.4. Feedstock and Product Handling:

The refinery feedstock and product handling operations consist of unloading, storage, blending, and loading activities

2.1.2.5. Auxiliary Facilities:

A wide assortment of processes and equipment not directly involved in the refining of crude oil is used in functions vital to the operation of the refinery. Examples are boilers, waste water treatment facilities, hydrogen plants, cooling towers, and sulfur recovery units. Products from auxiliary facilities (clean water, steam, and process heat) are required by most process units throughout the refinery (Anon., n.d.)

2.1.2.6. Khartoum Petroleum Refinery:

Khartoum Refinery Company (KRC) Limited Figure (2.2) is a joint venture between China National Petroleum Corporation (CNPC) and the Ministry of Energy & Mining (MEM) of Sudan. The refinery started operating on May 2000. The main process units are Crude Distillation Unit (CDU) with maximum design capacity of 2.5 million tons of crude oil per year, Residue Fluidize Catalytic Cracking Unit (RFCC) with a design capacity of 1.800.000 tons a year, Catalytic Reforming Unit (REF) with design capacity of 15 thousand tons per year, and Diesel Hydro treating Unit (HDT) with 400 thousand tons per year designing capacity, Sour Water stripper with a design capacity of 400 thousand tons per year. The auxiliary utilities at the refinery constitute power generation station 36 megawatt, water purification and pumping, 1500m³/h, and wastewater treatment plant. The crude oil processing capacity is 2.5 million tons per year i.e. 50,000 bbl/d, expanded later when CNPC announced in July 2006, the completion of the Khartoum refinery expansion project, which doubled the refinery's capacity from 50,000 bbl/d to 100,000 bbl/d. The refinery processes Nile blend crude, which has a low sulphur content and high fuel-yield. The annual output is 2.2587 million tons of oil products such as unleaded gasoline, kerosene, jet fuel, diesel, fuel oil and liquefied gas.

Sources of wastewater associated with various units are Crude Tank: Crude oil normally contains traces of water, an average of 0.05% per weight. Therefore, water generated is about 3.75 tons/day; desalting, crude distillation unit (CDU), diesel hydro treating unit (DHT), residue fluid catalytic Cracking, utilities: cooling water system, power station, and boilers; other sources: rain water and cleaning "washing" water. (Khogali, 2005)



Figure2. 3 KRC

Caustic wastewater is acid neutralized and discharged into oily wastewater system. Sour water from all processing units is treated in sour water stripping unit with a capacity of 400,000 tone/year then sent into wastewater treatment plant. Oily water and alkaline water are sent to wastewater treatment plant. Sanitary wastewater from living area and offices is treated in cesspool then sent into wastewater treatment plant. Cooling towers water is also discharged into wastewater treatment plant. In the wastewater treatment plant (WWTP) of 300t/h capacity, wastewater received a primary treatment for gravity removal of floatable oil and settling of sludge, and secondary treatment to remove biodegradable pollutants. It is now allowed to enter into monitoring pond and then into oxidation ponds outside the refinery. (Awad, 2008)

2.1.2.7. Crude Oil Composition:

Crude oils are a naturally occurring complex mixtures of tens of thousands of different hydrocarbon molecules, and small amounts of other non- hydrocarbons and mineral impurities. Crude oils range in consistency from water to tar-libel solids and in color from clear to black. Some light crudes have specific gravities as low as 0.85, while others have specific gravities up to 1.15. Although the proportions of the elements in crude oils vary over fairly narrow limits, a wide variation in properties is found from the lightest crude oils to the highly asphaltic crudes. At the elemental level, oil consists of elements such as carbon 84-87%, hydrogen 11-14%, nitrogen 0.1-2% oxygen 0.1-2%, sulfur 1-3% and less than 1% each of metals and salts. Crude in the standard production and transpiration method, is inevitably associated with

dissolved water and salts. The physical characteristics and chemical composition of crude oil and the yields and properties of products or fractions prepared from it vary considerably and depend on the concentration of the various types of hydrocarbons as well as on the amount of heteroatoms (nitrogen, oxygen, sulphur, and metals) in it. The concentration of these constituents in crude oils varies according to its source and dictates their marketability. Of the crude oil constituents, 98% are organic. Due to the complex composition of crude oils, characterization by the individual molecular types is not possible, and elemental analysis is unattractive because it gives only limited information about the constitution of petroleum due to the constancy of elemental composition. Instead, hydrocarbon group type analysis is commonly employed. Knowledge of the distribution of major structural classes of hydrocarbons in crude oils is needed in various fields in the petroleum industry. Examples are studies related to reservoir evaluation, migration and maturity, degradation processes, processing, and environmental effects. The environmental impacts of the wastes generated in the petroleum refinery depend on amount and nature of pollutants released, which, in turn, depend, to a great extent, on the composition of the crude oil processed.

(Veenstra, 2000)

2.1.3. Waste water treatment method:

- Physical Treatment method
- Chemical Treatment method
- Biological treatment method

2.1.3.1. Physical Treatment methods:

2.1.3.1.1 First stage: separation (oil/water separators, API separators)

API separators are frequently used in the treatment of refinery wastewater which usually contains oil and oil-bearing sludge. Separators use the difference in specific gravity to allow heavier material to settle below lighter liquids.

Hydrocarbons that float on the surface are skimmed off, while the sludge that settles to the bottom is removed periodically. In a typical API separator, wastewater is first collected in a pretreatment section that allows sludge removal. A diffusion barrier slowly allows the wastewater to flow down the separator towards the outlet while the lighter oil fractions can be skimmed off. Flights and scrapers are sometimes used to remove heavier solids. Underflow baffle plates are usually used to prevent oil from escaping into the outlet section. Figure (2.3) shows a typical API separator.

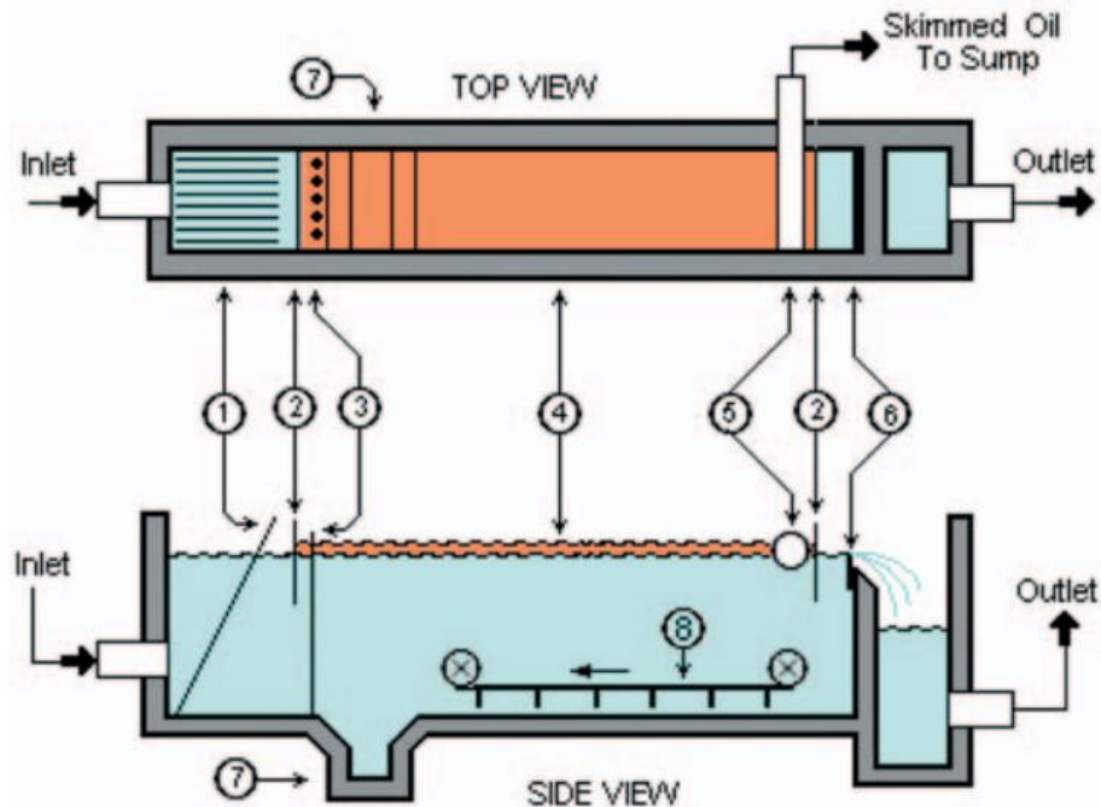


Figure 2. 4 API separator

1. Trash trap (inclined rods)
2. Oil retention baffles
3. Flow distributors (vertical rods)
4. Oil layer
5. Slotted pipe skimmer
6. Adjustable overflow weir
7. Sludge sump
8. Chain and flight scraper

Some of the performance-limiting factors relating to the API separators are listed and discussed below:

- Emulsified or dissolved oil that is usually present cannot be removed by an API Separator.
- High pH at the API separators can stabilize emulsions. Spent caustic streams should be either neutralized or routed directly to equalization in order to reduce pH at the API separators.

An API separator is an effective device for separating three phases (oil, solids and water) that are usually present in refinery wastewater. There are Some refineries that use corrugated plate interceptors (CPI) or parallel plate separators (PPS).

Both CPI and PPI separators tend to be smaller than a comparable API and require less plot space.

However, while these devices are very effective as two-phase separators (oil and water), they are less effective when a third phase (solids) are present.

The solids that are present in refinery wastewater tend to foul and plug the parallel plates resulting in the need for frequent maintenance. (IPIECA 5th Floor, 2010)

2.1.3.1.2. Secondary oil/water separation:

The effluent from the primary oil/water separation step is sent for further oil and fine solids removal to either a DAF unit or an IAF unit. The choice of whether to use a DAF versus an IAF unit is refinery specific, and needs to be evaluated based on the influent conditions and the required outlet conditions.

2.1.3.1.3 Dissolved air flotation (DAF):

The first step in a DAF system is coagulation/ flocculation. Dispersed particles (oil/solids) are stabilized by negative electric charges on their surfaces, causing them to repel each other. Since this prevents these charged particles from colliding to form larger masses, called flocks, they do not settle. To assist in the removal of colloidal particles from suspension, chemical coagulation and flocculation are required. These processes, usually done in sequence, are a combination of physical and chemical procedures. Chemicals are mixed with wastewater to promote the aggregation of the suspended solids into particles large enough to settle or be removed. (IPIECA 5th Floor, 2010)

Figure 1. Key Components of a Rectangular DAF System

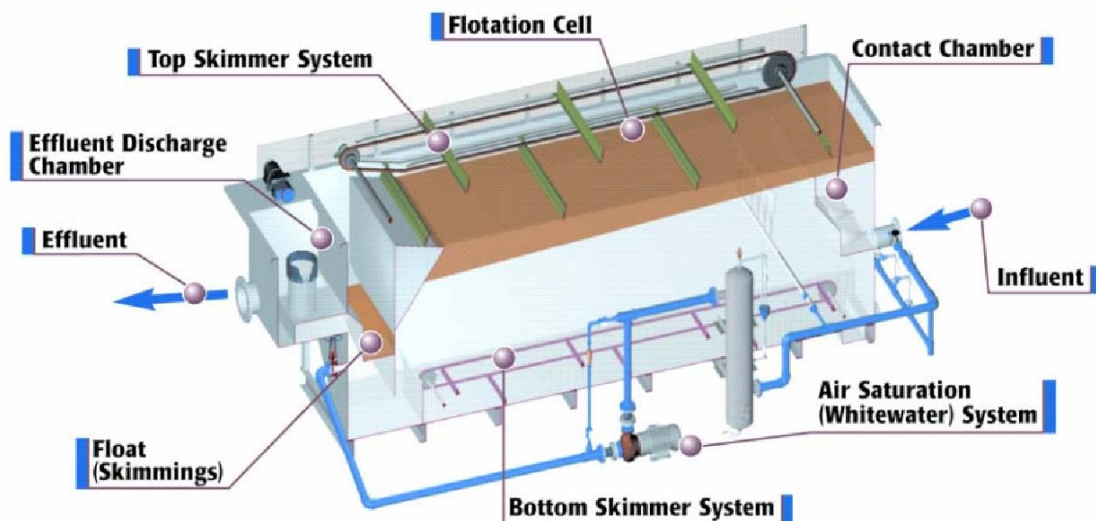


Figure2. 5 Dissolved air flotation—a typical DAF unit

In a DAF system, part of the effluent is recycled, pressurized, saturated with air and mixed with the Incoming feed. When the recycle stream is depressurized it releases the air bubbles which attach themselves to any free oil/solids contained in the feed

and float them to the surface of the vessel. The floated material is skimmed off and sent to Refinery slops after further dewatering. Some solids also settle to the bottom of the DAF where they are scraped off and removed periodically. (IPIECA 5th Floor, 2010)

2.1.3.1.4 Induced air flotation (IAF):

In an IAF unit, air is induced by a rotor-disperser mechanism, the spinning rotor acts as a pump and forces the fluid through the disperser openings and creates a vacuum in the stand pipe. The vacuum in the standpipe pulls the air and mixes it with the liquid. The liquid moves through a series of cells before leaving the unit and the float passes over the weir on one or both sides of the unit. The advantages of the IAF technique are compact size, low capital cost and the effective removal of free oil and suspended materials. The configuration of a typical IAF unit is shown in the Figure (2.5).

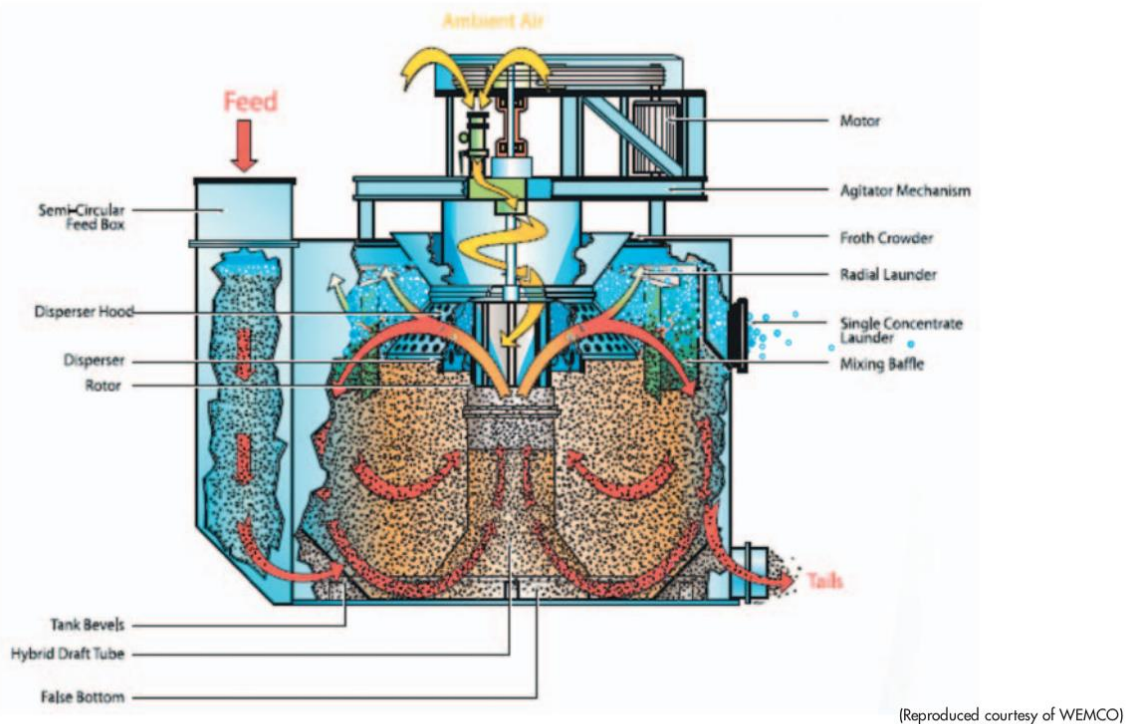


Figure2. 6 Induced air flotation (IAF) unit

Other types of dispersed gas flotation units exist, such as the hydraulic type, where effluent is pumped and educts vapor from the top, before being distributed to each cell via a striker plate to create smaller bubbles which again attract and pull oil out of suspension. Equalization system the objective of the equalization system is to minimize or reduce the fluctuations caused due to either sudden change of flow or composition in the wastewater treatment plant.

2.1.3.1.5. Sand filtration:

Effluent from the biological treatment system typically contains about 25 to 80 mg/l of suspended solids depending on the operating conditions in the clarifier. Refineries at many locations need to meet limits as low as 15 mg/l on a consistent basis. In these instances, one option is for the effluent from the clarifier to be filtered using sand filters. This process involves passing the

Wastewater through a filter bed comprised of a filter media. Dual media filters comprise a layer of anthracite over sand. The larger particles are trapped by the anthracite and the finer solids are held up in the sand. Periodically, the forward flow is stopped and the filter is backwashed to remove the trapped solids.

2.1.3.2. Chemical Treatment Methods:

2.1.3.2.1. Sequencing batch reactor:

A sequencing batch reactor (SBR) is a fill-and-draw semi-batch biological treatment alternative that employs aeration, sedimentation and clarification in a single reactor. The unit processes of aeration and sedimentation are common to both the SBR and activated sludge systems. In activated sludge systems the unit operations take place in different basins, while in the SBR the operations take place in sequential order in a common basin. Although still practiced in some refineries, SBR technology is increasingly uncommon and has limited application in refinery wastewater treatment.

2.1.3.2.2 Nitrification, or nitrification with DE nitrification

In some cases when a refinery site is required to meet tight ammonia or nitrogen limits, the biological treatment system could include either a nitrification (by the use of nitrifying bacteria) or a combined nitrification/DE nitrification step. The level of nitrogen compounds in refinery wastewater can be controlled by avoiding discharges of spent amines and proper removal of ammonia in the sour water stripper. If the concentration of nitrogen compounds is still too high to meet regulatory limits, then nitrification or nitrification/DE nitrification should be included in the biological treatment system.

Nitrification is the term used to describe the two-step biological process in which ammonia ($\text{NH}_4\text{-N}$) is oxidized to nitrite ($\text{NO}_2\text{-N}$) and the nitrite is oxidized to nitrate ($\text{NO}_3\text{-N}$). In denitrification, the nitrate is reduced to nitric oxide, nitrous oxide and nitrogen gas. Figure 25 shows the two arrangements that are used in these systems.

In the first system, the aeration/nitrification tank is followed by an anoxic tank where denitrification occurs. A food source (typically methanol) is added to this tank to aid in the process. In the second system, the anoxic tank is followed by the aeration/nitrification tank. In this case, the food source for the anoxic tank is the BOD in the incoming wastewater. A portion of the treated wastewater from the aeration tank is recycled so that the reduction of nitrates in the effluent can occur. (IPIECA 5th Floor, 2010)

2.1.3.2.3 Activated carbon

Removal of dissolved organic constituents from the refinery wastewater can be done by carbon adsorption. In general, activated carbon is usually applied as an effluent 'polishing' step (removal of residual organics) for wastewater that has been processed in a biological treatment system. This is because the carbon usage will be prohibitively high if it applied to the refinery wastewater.

In this process the wastewater is passed through a bed of granular activated carbon (GAC) where the organics in the wastewater are adsorbed by the carbon. The carbon bed is periodically regenerated to remove the organics from the exhausted carbon.

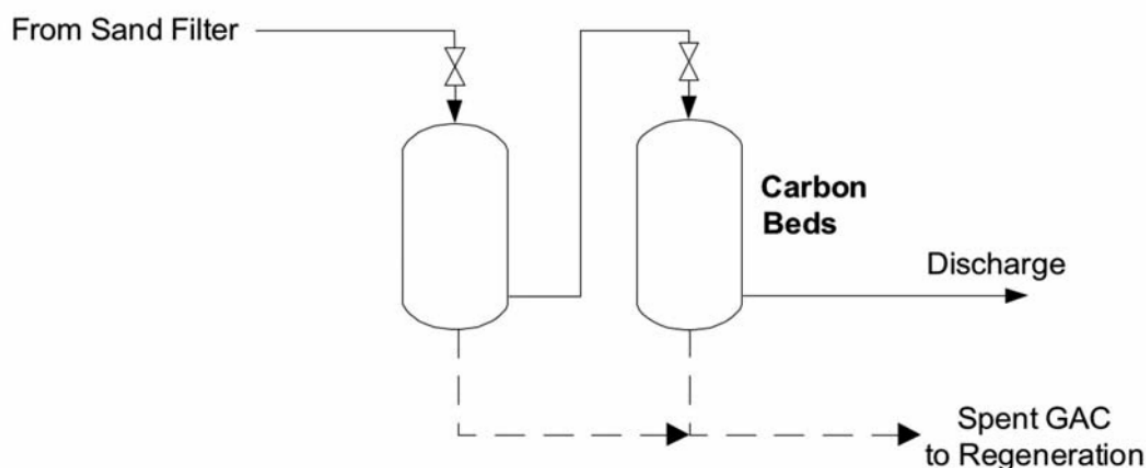


Figure 2.7 shows the configuration of a typical carbon adsorption system

2.1.3.2.4 Chemical oxidation:

Chemical oxidation in a refinery is generally used for reduction of residual COD, non-biodegradable compounds, and trace organic compounds. It is not common to have a chemical oxidation system in a refinery wastewater treatment plant; details of this approach are included in this document for information purposes. The following oxidation reagents are generally used in a chemical oxidation system:

- Hydrogen peroxide;
- Chlorine dioxide; and
- Ozone.

Chemical oxidation can be enhanced in some cases by the use of UV light as a catalyst, but this needs to be evaluated on a case-by-case basis.

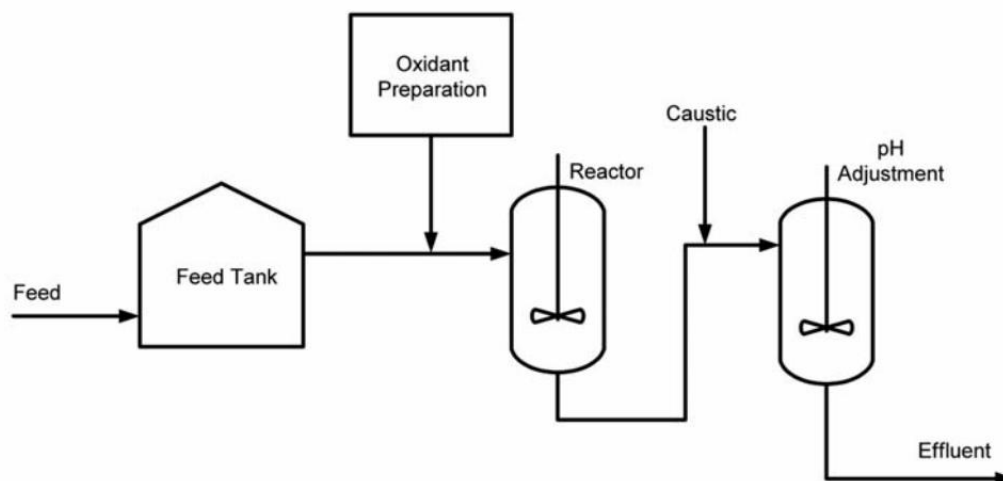


Figure 2.8 shows the configuration of a typical chemical oxidation system.

The feed is sent to the oxidation reactor via a feed tank which provides any surge capacity that is required.

2.1.3.3 Biological Treatment:

Biological processes utilize microorganisms (naturally-occurring, commercial, specific groups and acclimatized sewage sludge) to oxidize organic matter into simple products (CO₂, H₂O and CH₄) under aerobic, anaerobic or semi aerobic conditions. C: N: P ratio (100:5:1) is adequate for microorganisms to grow^{1, 22}. A study on biodegradation of petroleum oil by nematodes has identified *Bacillus* sp. as a primary degrader and cooperation with nematodes for degradation of pollutants²³. In a study using bio augmentation, activated sludge system (ASS) took only 20 days to achieve COD below 80 mg/l (84.2% COD removal efficiency) and NH₄⁺ -N concentration of 10 mg/l compared to non-bio augmented system, which needed an extra 10 days to reach similar effluent quality²⁰. Biological processes are classified as suspended-growth, attached-growth or hybrid processes. (ishak, et al., 2012)

2.1.3.3.1 Waste biological sludge:

Excess sludge that is produced in a biological system can be disposed of (after pretreatment) in several ways, depending on local regulations, including:

- Land farming;
- Landfills; and
- Off-site disposal.

Typical pretreatment of biological sludge is shown in Figure (2.8).

The biological sludge is sent to a thickener, which could be a gravity or DAF thickener, where water is separated from the sludge and returned to WWT, The sludge

from the Thickener is sent to an aerobic digester where air is added to digest the sludge. This step is essentially a volume reduction step to lessen the load on the downstream filter. In some cases the sludge from the Thickener is sent to the Filter. Several types of filters such as belt filter Presses, plate and frame filters etc... Can be used. The type of filter that is most appropriate will need to be evaluated on a case-by-case basis.

Figure 31 *Biological sludge treatment*

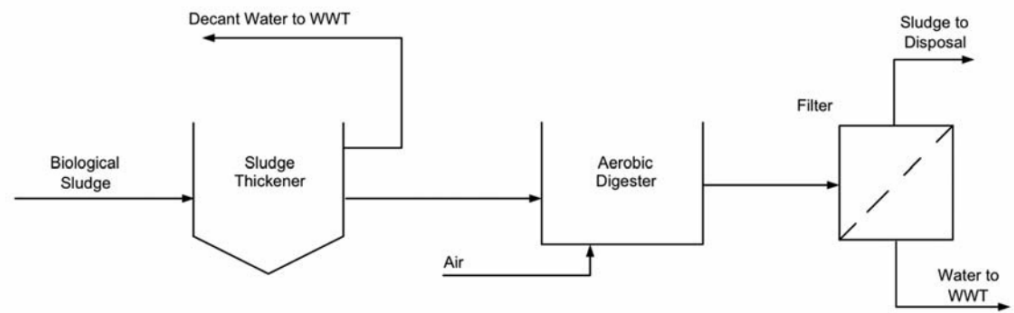


Figure2. 9 Biological sludge treatment

Table 1(2.2): Common refinery prevention and control techniques

(Awad, 2008)

	Oil& Grease	-oil skimming (API separators) -gravity separation (settling tanks and coalescing plate separators) -dissolved/induced air floatation(DAF/IAF) -Biological treatment
	Sulfides	-chemical treatment -clarification
Wastewater treatment	Organic compounds	-biological treatment -activated carbon adsorption -clarification

	Metals and solids	-source reduction --gravity separation (settling tanks and coalescing plate separators) -physical treatment (flocculation) -DAF/IAF -granular media Filtration
	Caustics & acids	Neutralization -clarification

2.1.3.4. Sour stripping unit:

There are several technologies for sour water treatments: with steam or flue gas in sour water strippers (SWS); conversion of the hydrogen sulfide to thiosulfates by air oxidation; or using vaporization and incineration. However, the reference document on best available techniques for mineral oil and gas refineries (Joint Research Center, 2003), only mentions the SWS; therefore, this technique is selected to be considered in this work. The main objective of the sour water treatments is to remove sulfides, achieving in normal conditions 85e99% of removal with feeds that typically have ammonia concentrations between 0.3 and 6% w/w and hydrogen sulfide concentrations between 0.3 and 10.4% w/w.

Ammonia is also stripped when no acid is added to the wastewater; then the efficiency depends widely on the stripping temperature and pH (Wong and Hung, 2006). The separation of ammonia from hydrogen sulfide has important advantages in the sulfur recovery units (SRU) eliminating problems such as catalyst deactivation, plugging in condensers and seals, lower operating factors and the diluent effect that increases the size of the unit.

Fig. 2 shows an outline of the studied process that corresponds to the sour water treatment plant of a refinery located in Germany, with a similar configuration to the Chevron WWT process (Wang et al., 2006). The model parameters were fitted in order to reproduce the operating data. Before the SWS the feed is pumped into flash drums to remove volatile hydrocarbon vapors and liquids.

Vapors are easily flashed off through a pressure controlled vent valve connected to a low pressure system. A weir permits liquid hydrocarbons to spill over into a separate compartment for reprocessing. After the flash drums, the sour water is often fed to a stabilization tank to increase the residence time to improve the hydrocarbon removal and minimize composition and flow rate fluctuations (Armstrong, 2003). In the studied plant, the sour water streams are grouped in three feeds coming from (1) the vacuum distillation, (2) from the fluid catalytic cracker (FCC) and amine regeneration fractionators, and (3) from the crude distillation unit. Besides, a stream with a low ethanol and ETBE content, coming from the same petrochemical complex, is added to the process. This water is also stripped with steam to recover a rich-gas in ethanol that

is dispatched to the FCC unit, while the treated water is sent to the ammonia recovery unit as fresh water supply. In the SWS, the downward flow of sour water contacts the ascending flow of stripping steam that removes the pollutants. In this way, the steam acts as the heating medium and at the same time as the stripping gas. The operating conditions in the stripping columns can vary from 200 to 250 kPa and from 80 to 135 °C. The plant has a two-stage system, with stripping and ammonia purification to enhance the recovery of sulfide and ammonia separately. In the first stripping stage, the high purity hydrogen sulfide recovered by overheads can be used for the Claus sulfur recovery unit. The bottoms streams contain almost all the ammonia and are sent to the ammonia stripper. (M. Torres, et al., 2012)

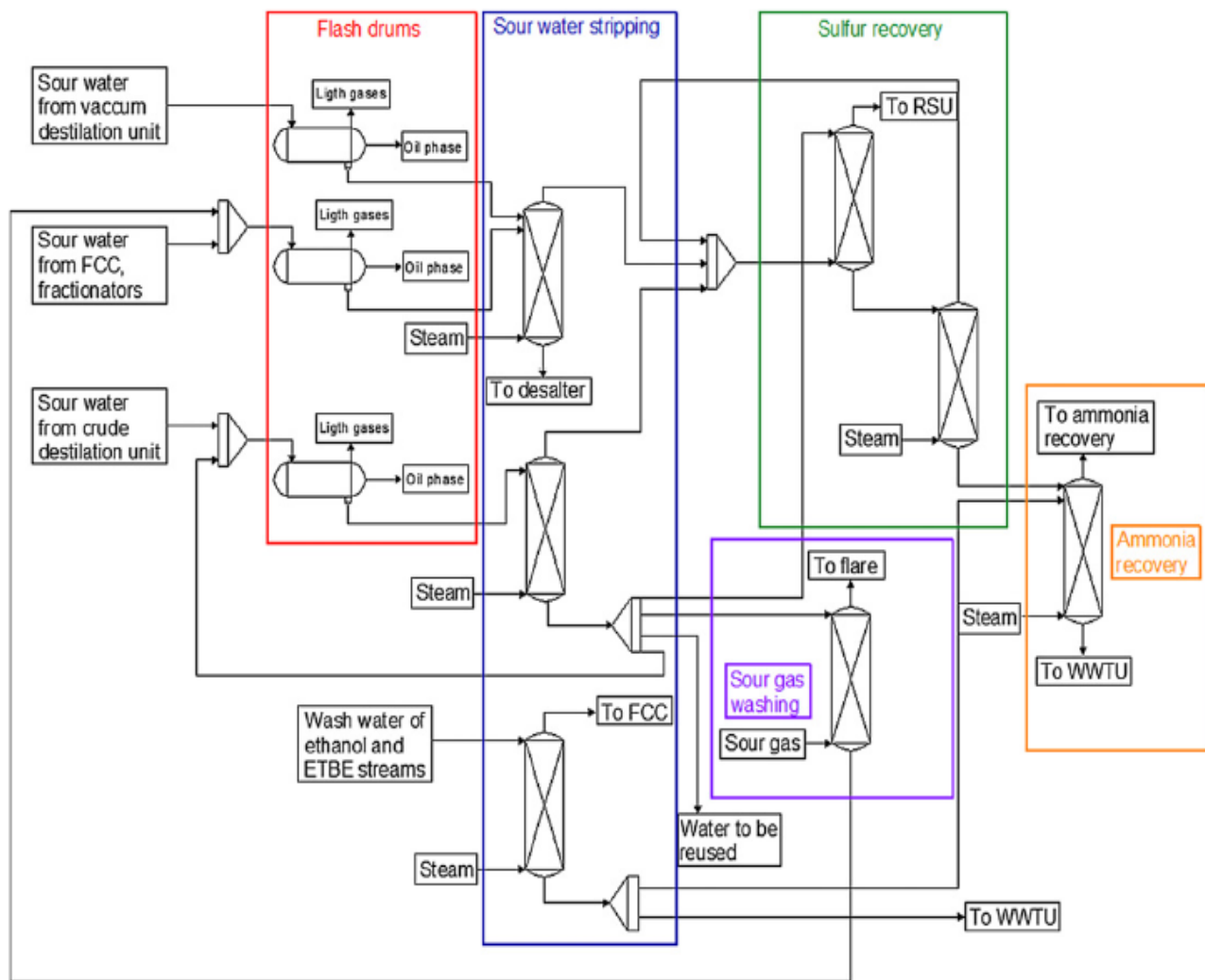


Figure 2.10 Sour water stripping unit

2.2. Literature Review:

In 2009 El-Gohary perform two treatment schemes were investigated. The 1st step in both schemes was chemical coagulation followed by precipitation in the 1st scheme and dissolved air flotation in the 2nd one. Ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), alum ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$) and ferrous sulfate ($\text{FeSO}_4 \cdot 6\text{H}_2\text{O}$) were used as coagulants. Lime (CaO) was used as coagulant aid and for pH adjustment. For C/P, the three coagulants investigated were found to be more or less similar in their performance. Maximum COD total removal obtained by ferric chloride, ferrous sulfate and alum was 75.8 ± 9.7 , 77.5 ± 9.6 and $76.7 \pm 9.9\%$, respectively. Corresponding BOD5 total removal values were 78 ± 15.8 , 78.7 ± 15.6 and $74.1 \pm 19.3\%$, respectively. However, the optimum dose of ferric chloride and alum was 600 and 700 mg/l while that of ferrous sulfate was 850 mg/l. Alum produced a voluminous sludge, but with the least solids content. Ferric chloride produced compact sludge with a good settle ability as reflected by the low sludge volume index (SVI) of 76.3 ± 28.8 ml/gTSS. In the coagulation–dissolved air flotation (C/DAF) experiments, the results showed that alum produced higher COD removal ($77.5 \pm 3.2\%$) as compared to ferric chloride ($71.6 \pm 2.9\%$) and ferrous sulfate ($67.7 \pm 3.7\%$).

A cost evaluation of the initial investment and the running costs using the different coagulants at their optimum operating conditions were calculated. The investment and running cost for C/P process is higher by 27.3 and 23.7% than C/DAF. (el-hohary & , 2009)

July 2013 Manal Abu Alhaija, Sulaiman Al-Zuhair a novel three-step process was developed and evaluated for the treatment of highly contaminated refinery wastewater. The process consisted of an electrocoagulation cell (EC), a spouted bed bioreactor (SBBR) with *Pseudonymous put idea* immobilized in polyvinyl alcohol gel, and an adsorption column packed with granular activated carbon produced from agricultural waste, specifically date pits. The units were evaluated individually and as combinations with different arrangements at different operating conditions to treat refinery wastewater with varying levels of contaminants. The EC unit was found to be effective as a pretreatment step to reduce the large concentrations of COD and suspended solid and reduce the load on the bioreactor and the adsorption column. At optimum conditions and unit arrangement, the process was able to reduce the concentration of COD, phenol and cresols by 97%, 100% and 100%, respectively. The process was found to be highly competitive in comparison with other combined systems used in the treatment of industrial wastewater and can handle highly contaminated refinery or industrial wastewater with relatively wide range of operating conditions. (abu alhaija, et al., 2013)

Chapter 3

3. Research Methodology:

This chapter describes the research methods used to obtain and process data to allow an empirical research assessment to be made of Khartoum refinery liquid effluent.

3.1 Waste Water Treatment Unit

3.1.1 Procedure and Process Technique

The sewage treatment unit of Khartoum Oil Refinery was put into production in 1999, the designed capacity of the unit is 300 m³/hr., includes alkaline containing sewage 40 m³/hr. and sulphur-containing sewage 37 m³/hr. The sewage after treatment is delivered to oxidation pond outside the plant. Capacity of the oxidation ponds: 650*650*0.5 m. the designed rate of evaporation 17.1 mm/d.

3.1.2 Source of waste water associated with various production units in the KRC: *Table 2(3.1) Average flow for waste water entering the wastewater treatment unit*

UNIT	OILY WAST (m ³ /h)
CDU	35
RFCC	10
SCR	0.8
DHT	10
OMS	13
PS	8.3
DCU	86

3.1.3 Research Design

Two designs are carried out in this study which are survey research which involved the field survey, and one -to- one interview and experimental research which involved samples collection and laboratory analysis.

3.1.3.1. Survey research:

Which involves the collection of data through personal Khartoum Refinery, including all units and oxidation ponds site.

3.1.3.2. Experimental research

Which involves sampling and laboratory analysis and investigation. Sediment samples were collected from oxidation ponds. Liquid effluent samples from both the the oxidation ponds and monitoring pond Effluent and sediment samples analyses were carried using appropriate referenced analytical methods.

Wastewater analyses were conducted by Khartoum Petroleum Refinery.

The wastewater samples were examined in accordance with the “Standard Methods for the Examination of Water and Wastewater, and the analyses were carried out for physical parameters (Temperature, pH, TS, TDS and TSS), inorganics (Alkalinity, Hardness, Chloride, Sulfate, Cyanide, Sulfide and Hexavalent Chromium), nutrients (Ammonia-Nitrogen, Nitrate-Nitrogen, Nitrite-Nitrogen and Phosphorus) and organics (BOD, COD, Oil & Grease, and Phenols). Temperature and pH were measured immediately after sample collection.

PH was measured by a pH Ultra meter 6P, Myron L Company, Carlsbad, CA. USA. Alkalinity was determined by Titration Method.

HACH DR/4000U spectrophotometer, CAMLAB limited, Cambridge, was used in all spectrophotometric determinations. BOD Incubator, Model 205, HACH, was used for BOD tests, whereas COD determination was performed using a COD reactor Model 45600, HACH.

3.1.7.1 Physical parameters:

Temperature

Temperature readings were taken immediately at the sampling site using a mercury thermometer.

pH

pH determination was immediately carried out at the site using a portable pH meter.

Total solids (TS)

100 ml of well mixed sample were evaporated in a reweighed porcelain dish in a steam bath, then dried to a constant weight in an oven at 103°C.

Calculation

$$\text{Mg T.S/L} = ((A-B) \times 1000)/V$$

Where:

A: weight of (dried solids + dish) in g.

B: weight of empty dish in g.

V: Volume of sample taken in ml.

Total dissolved solids (TDS)

200ml of well mixed sample were filtered into a 500 ml suction flask using a vacuum pump. 100 ml of the filtrate were transferred to a reweighed evaporating dish, and evaporated to dryness on a steam bath. Then the evaporated sample was dried in a drying oven at 180°C. mg TDS/L were calculated as in TS.

Total suspended solids (TSS)

The total suspended solids were determined by subtracting the total dissolved solids from the total solids calculated for each sample taken.

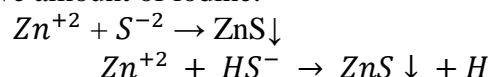
$$\text{TSS} = \text{TS} - \text{TDS}$$

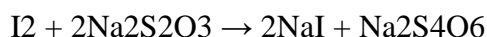
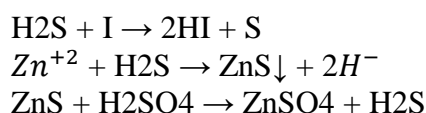
3.1.7.2 Inorganics

Sulfide (Iodimetry Method):

Principle:

Sulfide reacts with Zinc acetate to produce settling of white Zinc. Sulfide dissolve This settling in acid and let it react with standard Iodine, then use sodium Hyposulfite to titrate the excessive amount of iodine.





Instruments:

- Acid burette.
- Iodine flask.
- Vacuum pump, Buckner filter.
- Middle-speed quantitative filter paper.

Test steps:

- Pour 10ml of 10% Zinc acetate solution and 5ml of 1mol/l Sodium hydroxide solution into a sample-taking bottle of 250ml, take 250ml of water sample into this bottle to determine sulfide of water sample.
- Take 100ml of water sample with immobile liquid, use middle-speed filter paper and vacuum. Pump to filter white settling and wash sediment with distilled water. Put settling and filter paper into an Iodine flask of 250ml, add 50ml of distilled water. Agitate and break up filter paper sufficiently, then add 5.0ml of 1+5 sulfuric acid solutions as well as 10ml of 0.05mol/l Iodine water. Cover with a bottle block immediately and seal with distilled water, settle in a dark place for 5 minutes, titrate with 0.05mol/l sodium hyposulfite to light yellow, add 1ml of 1% facula indicator, continue titrating till blue disappears completely.
- Record consumption V_2 (ml) of Sodium hyposulfite, make a blank test in the same way.

Result:

$$S^{-2} \text{ (ML/L)} = \frac{(V_1 - V_2) * C * 16 * 1000}{V}$$

Where: $V_1 \equiv$ volume of Sodium hyposulfite standard solution for blank test (ml).

$V_2 \equiv$ volume of Sodium hyposulfite for titrating water sample (ml).

$V \equiv$ volume of water sample (ml).

Note:

In order to prevent the volatilization of hydrogen sulfide, immobile liquid (10ml of 10% Zinc acetate solution, 5ml of 1mol/l Sodium hydroxide solution are used to fix sulfide in water of 250ml) must be added into the sample-taking bottle before sample taking.

Ammonia- nitrogen

The method used for the determination of ammonia- nitrogen in the sample is the Nessler Method in which the mineral stabilizer complexes hardness in the sample and the polyvinyl alcohol dispersing agent aids the color formation in the reaction of nessler reagent with ammonium ions. A yellow color formed is proportional to the ammonia concentration and measured at 425 nm.

Reagents

- (a) Nessler Reagent : (mercuric iodide, sodium iodide, sodium hydroxide, demineralized water).
- (b) Mineral Stabilizer: (potassium sodium tartarate, sodium citrate, demineralized water).
- (c) Polyvinyl Alcohol Dispersing Agent.
- (d) Sodium Hydroxide Standard Solution (5.0N).

Calibration standard preparation

For ammonia calibration using the Nessler Method, standard solutions containing 0.5, 1.0 and 2.0 mg/L ammonia- nitrogen were prepared by pipetting 0.5, 1.0 and 2.0 ml of the 100 mg/L ammonia- nitrogen standard solution into three different 100 ml volumetric flasks and diluting to the mark with deionized water and mixing thoroughly.

Procedure

The sample was neutralized with 5.0 N sodium hydroxide standard solution before analysis. Deionized water was used as a blank and the standard solutions prepared above were used to adjust the calibration curve. A 25-ml mixing graduated cylinder was filled to the mark with the sample. Three drops of the mineral stabilizer were added and the stoppered cylinder was inverted several times for mixing. Then three drops of polyvinyl alcohol dispersing agent were added and the mixture was mixed. 1.0 ml of Nessler reagent was pipetted into the cylinder and the contents were mixed. A yellow color was developed and the solution was poured into the sample cell which was placed into the cell holder after a one minute reaction period. The result in mg/L ammonia expressed as nitrogen (NH₃-N) was recorded.

3.1.7.3 Organics:

Phenols

The 4- Aminoantipyrine Method was applied for the determination of phenols in the wastewater samples. It is capable to measure all ortho- and meta- substituted phenols. The sample is distilled to remove interfering substances such as oxidizing compounds, sulfur compounds, oils, and tars. The phenols present in the distilled sample react with 4- Aminoantipyrine in the presence of potassium ferricyanide to form a colored antipyrine dye that is then extracted from the aqueous phase with chloroform and the color is measured at 460nm. The sensitivity of the method varies with the type of phenolic compound. Since wastewater may contain various types of phenolic compounds the analytical results are expressed as mg/L of phenol (C₆H₅OH).

Reagents

(a) Methyl Orange Indicator : 0.5g/L solution.

(b) Phosphoric Acid Solution: 10% (v/v).

Principle:

Distil off sample and separate from disturbance matter and fixed agent by distillation. Distilled sample reacts with tetra aminoantipyrine in the medium with PH 10±0.2 and existence of Potassium ferri-Cyanide to produce orange antipyrine dye. After developing color, test absorbency at wavelength of 510nm with 30mm thick cell, expressed in phenol content mg/l.

Preparation of water without hydroxyl benzene (phenol):

Add 0.2g of active Carbon powder which has been activated at 200°C for 30 minutes after sufficiently shaking up, set for filtering with filter paper of double Layers and at medium speed. Add Sodium hydroxide and drop Potassium permanganate solution to make solution purple, transfer into glass vaporizer for Distillation to collect distillate service.

Instruments:

- 500ml whole glass vaporizer.
- Spectrophotometer.

Test steps:

- Transfer 250ml sample into 500ml glass vaporizer, add several glass balls to Prevent bumping add several drops of (0.5g/l) methyl orange indicator.
- Adjust with 1+9 Phosphorous acid solution to pH= 4 (solution indicates Orange), add 10% Copper sulfate solution of 5ml.
- Connect a condenser and heat for distillation till 225ml distillate is Produced, then stop heating and cool down, add 25ml distilled water without Phenol into distillation flask, then continue to distill till 250ml distillate is Produced.
- Take 50ml distillate into a 50ml color comparison tube, add 0.5ml Buffer Solution with pH= 10.7, shake up at this time pH is about 10 ± 0.2 , add 2% 4-Amonioantipyrine solution of 1ml shake up, add 8% Potassium ferri-cyanide Solution of 1ml, shake up sufficiently, settle for 10 minutes.
- At wavelength of 510nm with 20nm cell taking blank reagent as reference, Test the absorbency of the solution.
- At the same time, take 250ml distilled water without phenol with the same Test steps for blank test.

Result expression:

$$\text{Phenol content (mg/l)} = \frac{\text{Absorbance(reading)} * 197 * 0.11}{V}$$

V= Sample volume in ml

Oil and grease (Oil & G)

The method used is the Partition Gravimetric Method. The procedure involves the extraction of oil and grease with an organic solvent 1, 1, 1- trichloroethane. The two immiscible solvents (organic solvent and water) make separate layers. The solvent containing the oil and grease fraction of the wastewater is separated from the aqueous layer. It is dried and evaporated to determine the extractable residue by the gravimetric method.

Reagents

- (a) Extracting solvent: 1, 1, 1-trichloroethane, CCl₃-CH₃.
- (b) Na₂SO₄: anhydrous salt.

Procedure

All glassware were rinsed with 1, 1, 1-trichloroethane solvent to remove any traces of oil/grease. The boiling flask and clean glass beads were dried in an oven adjusted to 103°C for 1 hour, then cooled to room temperature in a desiccating cabinet and the flask with beads were weighed to a constant weight. 1 L of the sample was transferred to a separator funnel of 2 L capacity then, the sampling bottle was rinsed with 20 ml solvent and the washings were transferred into the separator funnel. This procedure was repeated three times and the separator funnel was vigorously shaken for 2 minutes. The solution was allowed to stand for 10 minutes for clear separation of the extracting solvent and the water layers. The extraction procedure was repeated and the solution was allowed again to stand for 10 minutes. The extracting solvent layer was passed into the pre-weighed boiling flask through a funnel with a Whitman paper

cone. The bottle was rinsed three times more with 60 ml of the solvent and each extraction layer was transferred to the boiling flask containing the first solvent layer. Then the solvent was evaporated to dryness in a distillation unit with the heating mantle adjusted at 70°C. The exterior of the cool boiling flask was carefully wiped with an absorbent clean cloth and a small amount of acetone to remove any traces of water and fingerprints. Then the boiling flask was placed in a desiccator for 1 hour and weighed immediately. The process of desiccating and weighing was repeated until a constant weight was obtained. A blank was run using 1 L deionized water following the same procedure as described for the sample.

Calculation:

$$\text{Oil/Grease, mg/L} = \frac{(A-B)-C}{\text{volume of sample,ml}} * 1000$$

Where:

A= total weight of (flask + beads + residue)

B= weight of (flask + beads)

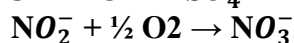
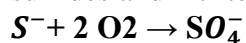
C = average blank determination (residue obtained from deionized water)

In the above procedure, 1L sample was taken for the determination of oil and grease content, hence the calculation was further modified as follows:

$$\text{Oil/Grease, mg/L} = (A-B) - C$$

Chemical oxygen demand (COD)

This is the quality of oxygen in mg/l and measure by reducing chemicals such as sulfides and nitrites is typified as follows:



Instruments:

- Reflux apparatus.
- Round bottom flask.
- 500-ml Erlenmeyer
- Volumetric cylinder.
- Glass beads.

Analysis steps:

- Place a 20ml sample in the round bottom flask; add 0.4 mercuric sulphate, and Add 10ml potassium dichromate solution .carefully add 30ml sulphric acid – Silver sulphate solution, mix after each addition.
- Add a few clean glass beads to prevent bumping and attack the flask to condenser. Reflux the mixture for 2 h Cool, and wash down the condenser with Approximately 25ml of distilled water
- Transfer the content to 500-ml Erlenmeyer flask, washing out the reflux flask 4 to 5 times with distilled water .Dilute the mixture to approximately 140ml .cool and titrate the excess dichromate with ferrous ammonium sulphate solution, add 2 or 3 drops of the ferroin indicator.
- Take as the end point the sharp color change from blue –green to brown.
- A blank consisting of 20ml of distilled water instead of the sample, together With the reagent, is refluxed and titrated in the same manner.

Calculation:

$$\text{COD mg/l} = (A - B) * C * 800 / \text{sample volume - ml} \dots\dots\dots(3.10)$$

Where:

A= Ferrous ammonium sulphate solution used for blank, ml

B= Ferrous ammonium sulphate solution used for sample, ml

C= Normality of ferrous ammonium sulphate solution.

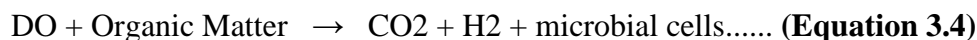
Biochemical oxygen demand (BOD)

The biochemical oxygen demand (BOD) determination is an empirical test in which standardized laboratory procedures are used to determine the relative oxygen requirements of water, effluents and polluted waters. Biochemical oxygen demand is the representation of the amount of oxygen required for microbial decomposition, i.e., complete aerobic decay and mineralization of biodegradable organic matter present in water or wastewater. The aerobic decomposition involves the breakdown of complex organic molecules into their simpler constituents that can serve as food for the growth and activity of microbes and liberate energy in the presence of dissolved oxygen (DO).

The aerobic decomposition of organics takes place in two stages:

(a) Carbonaceous oxidation: This is the first stage in which mainly the carbonaceous (carbon fraction) matter is oxidized. Generally it reaches to maximum stabilization in five days (**Equation 3.4**):

Bacteria



Protozoa

(b) Nitrogenous oxidation: In this second stage, nitrogenous (nitrogen – containing) substances such as ammonia are attacked by bacteria and develop a demand of oxygen as shown in **Equation 3.5** below:

Nitrifying



Bacteria

For the purpose of wastewater treatment, the first stage oxygen demand is considered BOD because the maximum carbonaceous components of organic matter are stabilized. The stabilization is maximum (96%) in five days (**Tomar, 1999**), hence the term BOD is generally represented as BOD₅ which means the oxidation of organic wastewater in five- days at 20°C. The extent of oxidation of nitrogenous compounds during the five - day’s incubation depends on the presence of nitrifying bacteria. Usually during this period the nitrogenous oxidation does not begin because nitrifying bacteria are not available in sufficient number in primary effluent. However, for samples of secondary effluent and for samples of polluted waters the interference from nitrogenous demand can be prevented by an inhibitory chemical.

Reagents

(a) Phosphate buffer solution: 8.5g KH₂PO₄, 21.75g K₂HPO₄, 33.4g Na₂HPO₄.7H₂O, and 1.7g NH₄Cl were dissolved in 500 ml DDW and diluted to 1 L (pH 7.2).

(b) Magnesium sulfate solution: 22.5g MgSO₄.7H₂O were dissolved in DDW and diluted to 1L.

Testing procedure

(a) Seeded dilution water: 2mL of seed per 1mL of diluted sample. Used for dilution of samples.

(b) Sample preparation and pretreatment: Sample temperature was adjusted to 20 °C, then pH to 7.0 to 7.2 using sulfuric acid solution.

(c) Sample dilution: 30 mL sample were added to individual BOD bottles using a wide - tip volumetric pipettes. Each BOD bottle was filled approximately two-thirds full with dilution water. Appropriate amounts of seeds suspension and nitrification inhibitor were added to the individual BOD bottles which are then completely filled with dilution water, sealed, and stoppered carefully without entrapment of air bubbles.

(d) BOD measurement: For each sample, one 300 mL glass stoppered BOD bottle filled with diluted sample and the other with dilution water only as a blank, were prepared. The initial DO was measured immediately in the two bottles using a DO probe with replacement of displaced contents with sufficient diluted sample or dilution water to fill the bottles, which were stoppered tightly, and water sealed. The bottles were incubated for 5 days at 20°C. Each sample was done in duplicate.

After 5 days of incubation, DO was determined in all sample dilutions, and in all blanks using the membrane electrode method. BOD was calculated as follows:

$$\text{BOD}_5, \text{ mg/L} = \frac{(D_1 - D_2) - (S)V_s}{P}$$

Where:

D₁ = DO of diluted sample immediately after preparation, mg/L.

D₂ = DO of diluted sample after 5 d incubation at 20°C, mg/L.

S = oxygen uptake of seed, DO/mL seed suspension added per bottle, (S = 0 if samples are not seeded).

V_s = volume of seed in the respective test bottle, mL.

P = decimal volumetric fraction of sample used; 1/P = dilution factor.

3.2 Sour water stripping unit:

3.2.1 Outline of the Unit:

The sulfur-containing sour water stripper of Khartoum Refinery is capable of treating 65 tons of sour water each year. The stripper consists of three parts: the deaeration, deposition and deoiling of sulfur-containing sour water; single column stripping (ammonia extraction of side line) of sulfur-containing sour water; and ammonia make-up

3.2.2. The process in hysys:

Using aspen hysys to design sour water stripping unit has been achieve.

Sour water enter to flash tank to separate the light gases with little amount of energy then the bottom stream enter to heat exchanger to obtain heat for separation process in stripper, in stripper the stream of sour water will separate to light sour gases in the top of stripper after cooling in stripper's condenser and purified water with little amount of ammonia in the bottom.

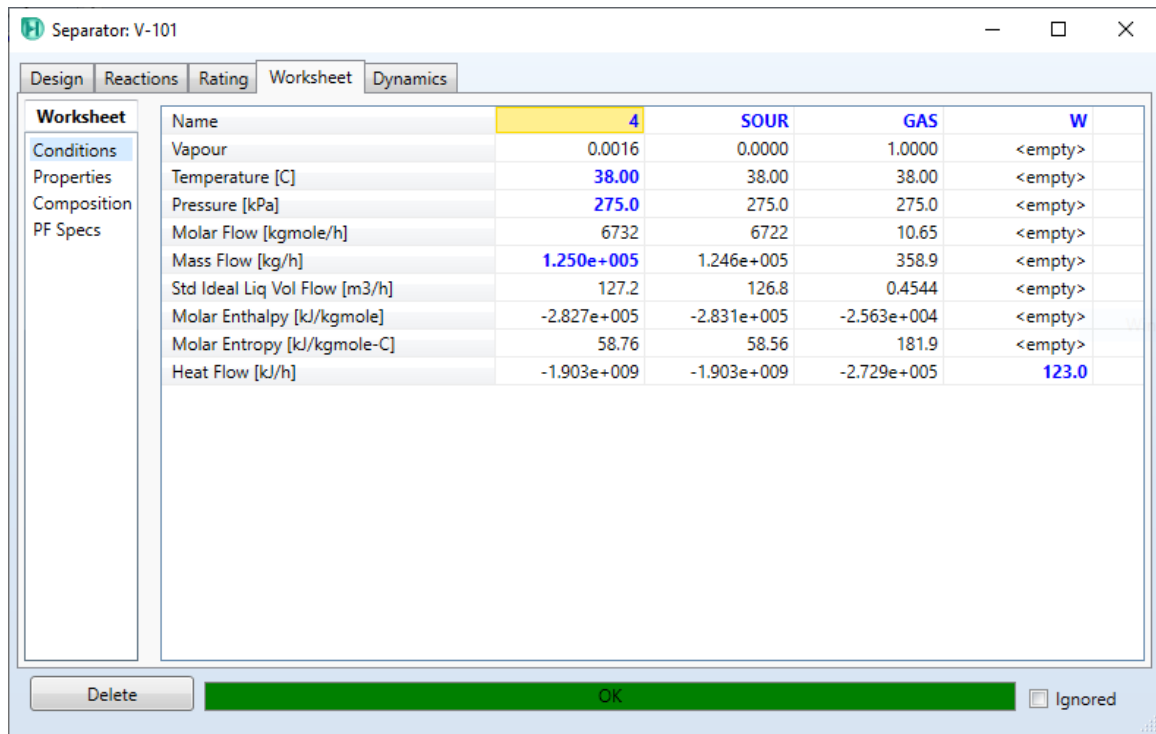


Figure 3.1 the condition requires in separator

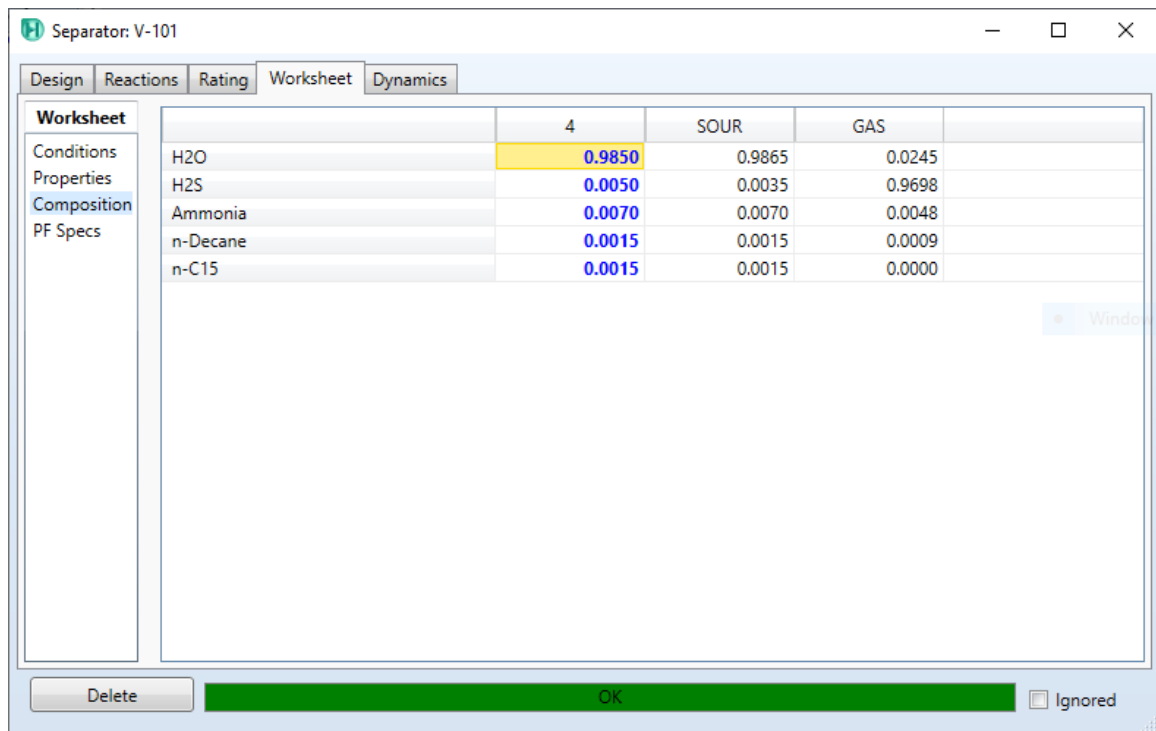


Figure 3.2 the composition for feed to separator and the product composition.

Feed of sour water entered heat exchanger to obtain heat and the condition introduce in the figure below:

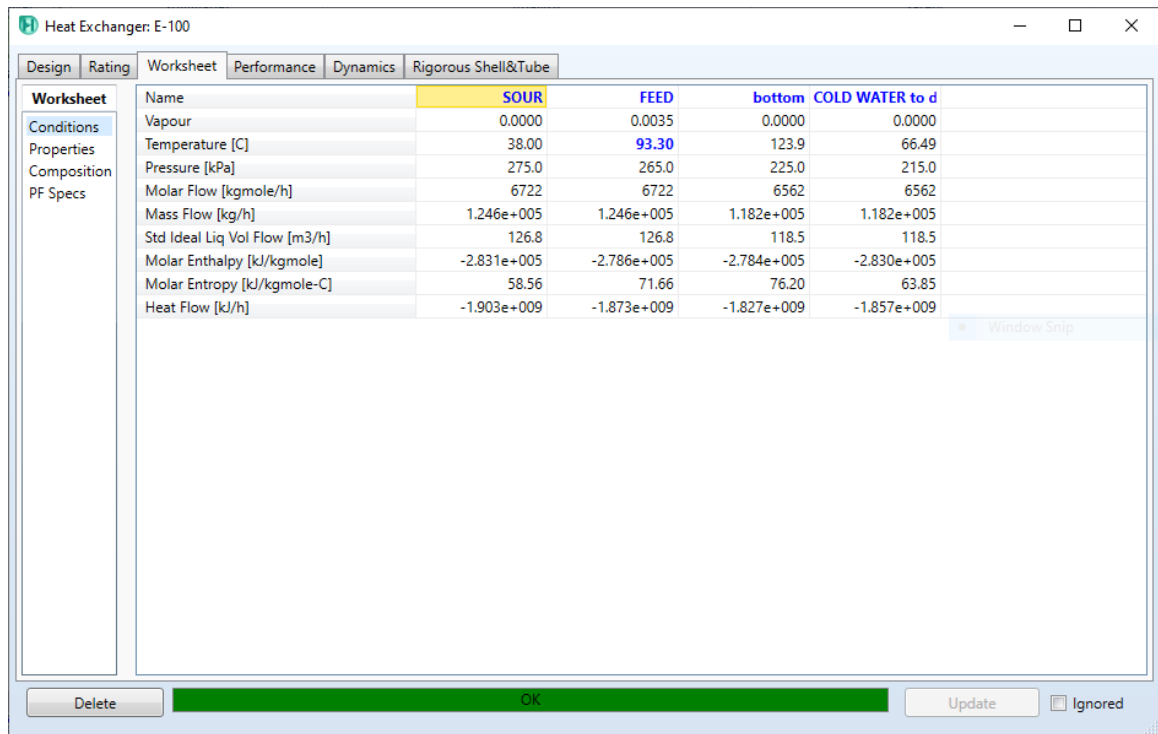


Figure 3.3 heat exchanger condition

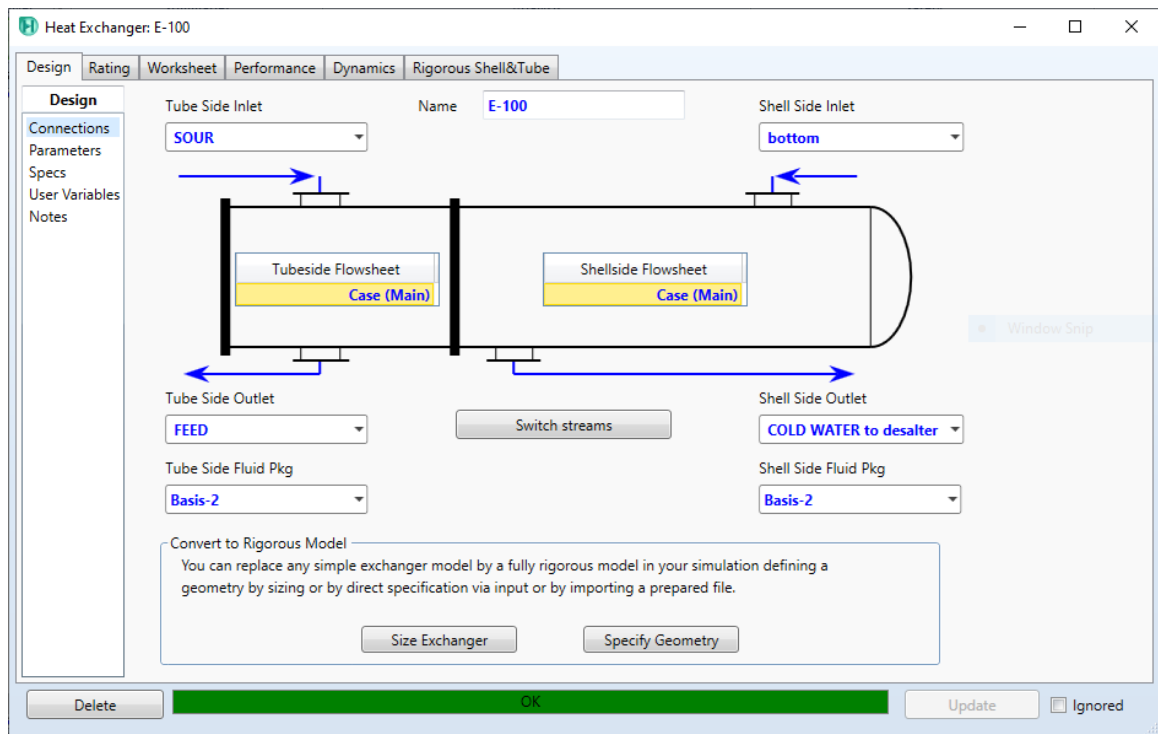


Figure (3.4) heat exchanger design

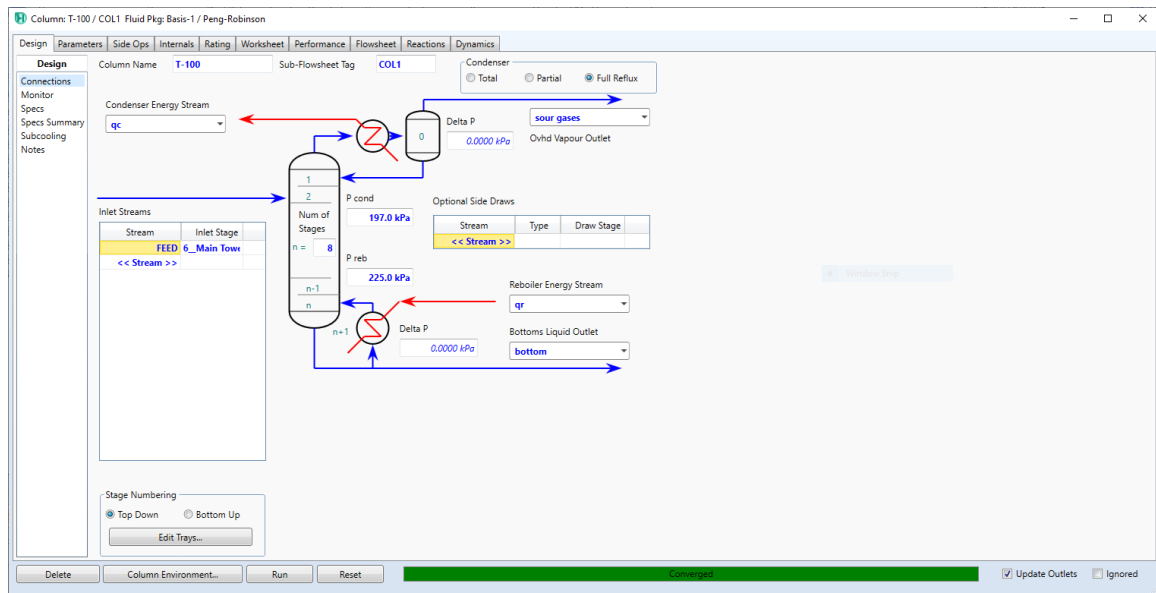


Figure (3.5) the design of stripper

Then the hot feed inter stripping unit to stripping the sour gases on the top of the column and in the bottom we have purified water the details in the figure (3.2)

Column: T-100 / COL1 Fluid Pkg: Basis-1 / Peng-Robinson

Design	Parameters	Side Ops	Internals	Rating	Worksheet	Performance	Flowsheet	Reactions	Dynamics
Worksheet									
Conditions									
Properties									
Compositions									
PF Specs									
Name	FEED @COL1	sour gases @COL1	bottom @COL1						
Vapour	0.0035	1.0000	0.0000						
Temperature [C]	93.30	96.45	123.9						
Pressure [kPa]	265.0	197.0	225.0						
Molar Flow [kgmole/h]	6722	159.7	6562						
Mass Flow [kg/h]	1.246e+005	6424	1.182e+005						
Std Ideal Liq Vol Flow [m3/h]	126.8	8.297	118.5						
Molar Enthalpy [kJ/kgmole]	-2.786e+005	-1.549e+005	-2.784e+005						
Molar Entropy [kJ/kgmole-C]	71.66	225.5	76.20						
Heat Flow [kJ/h]	-1.873e+009	-2.474e+007	-1.827e+009						

Figure 3.6 introduce the feed and product condition in stripper

The gases in the top condensing and stripping to burn in the incinerator.

In the bottom we have reboiler to the degree of the bottom heat to continue process and turn away the sour gases to the top and the purified water return to heat exchanger to heat the sour water and cold itself the it reused to wash the crude in desalter unit or other unit according to the quality of purified water.

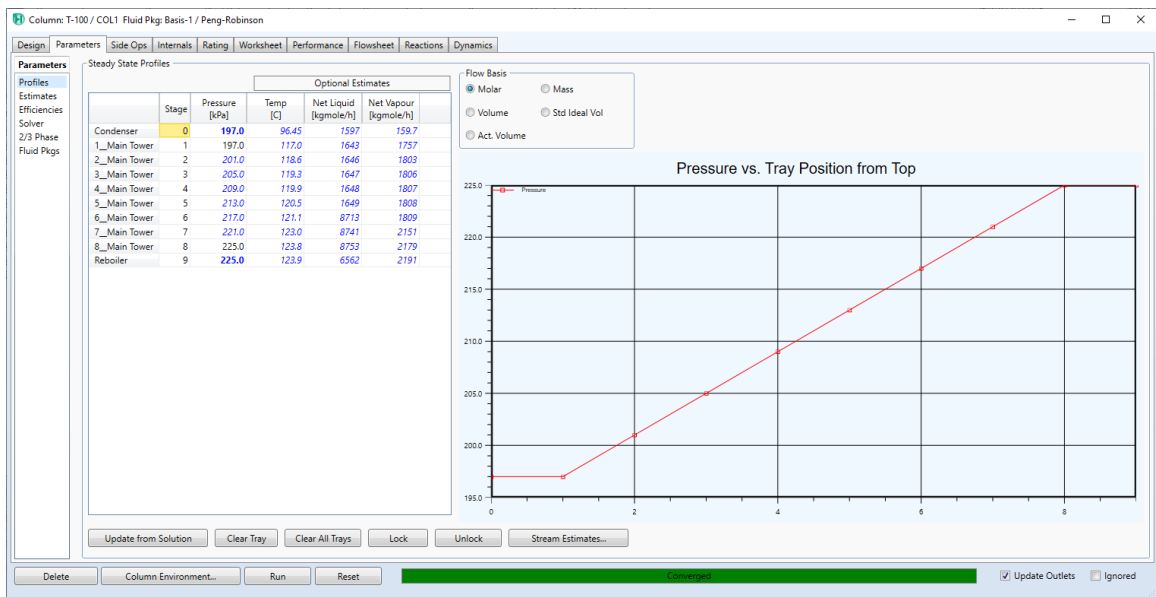


Figure (3.7) the temperatures for every stage in the column and the pressure gradient.

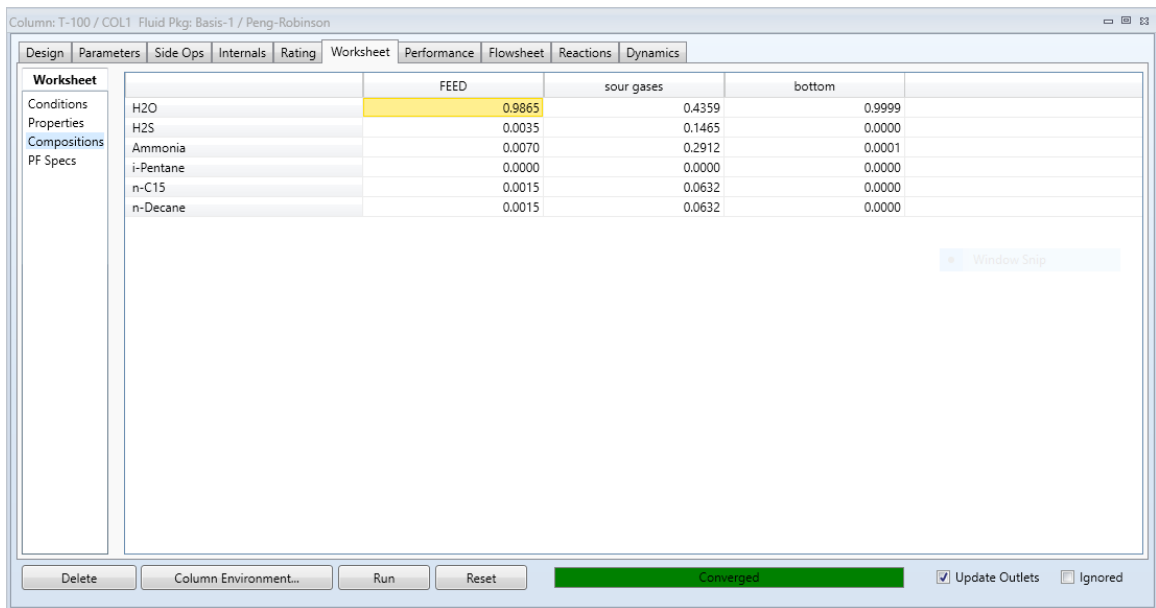


Figure (3.8) the composition of gases and purified water in the stripper

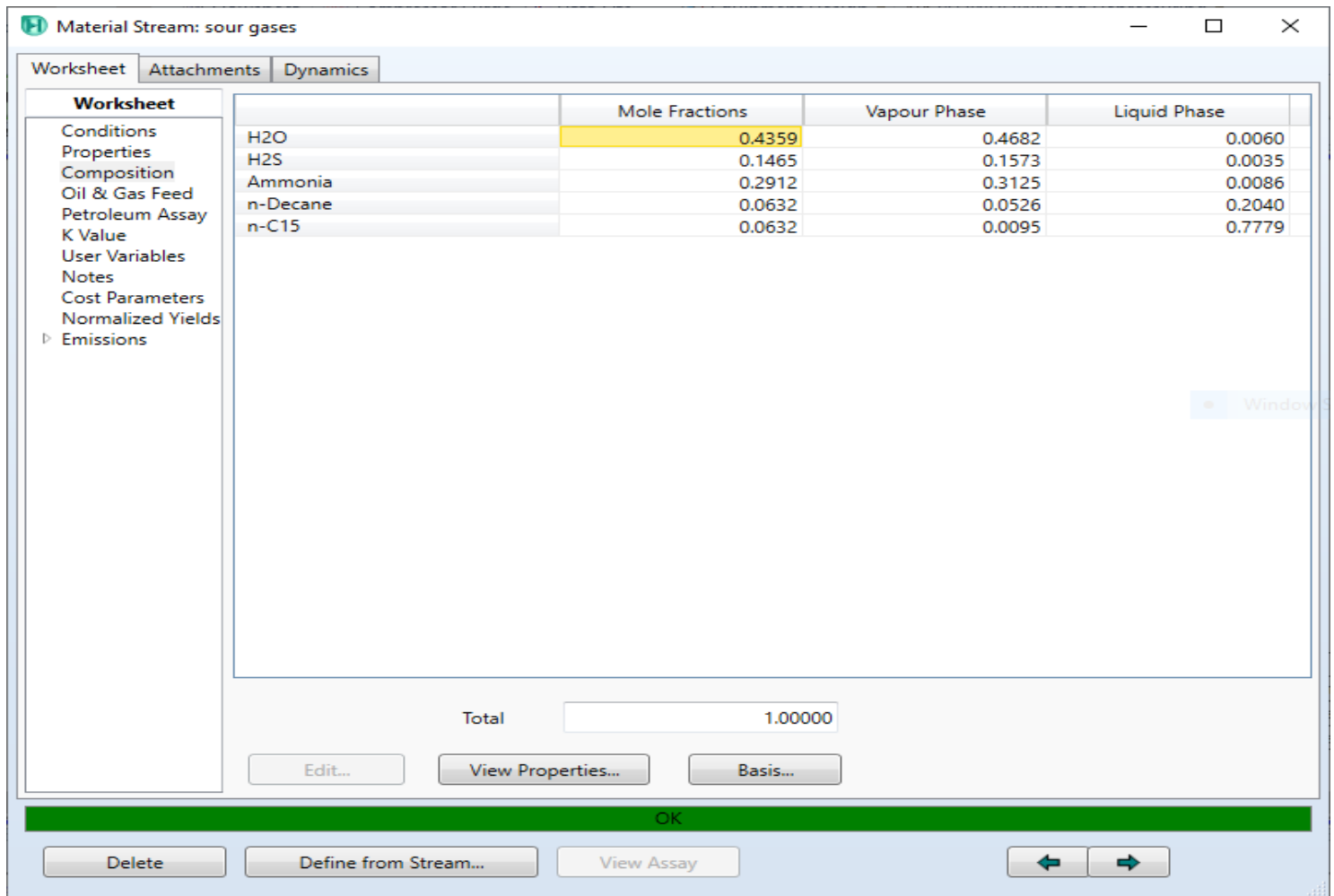


Figure (3.9) the composition of sour gases in the top of stripper

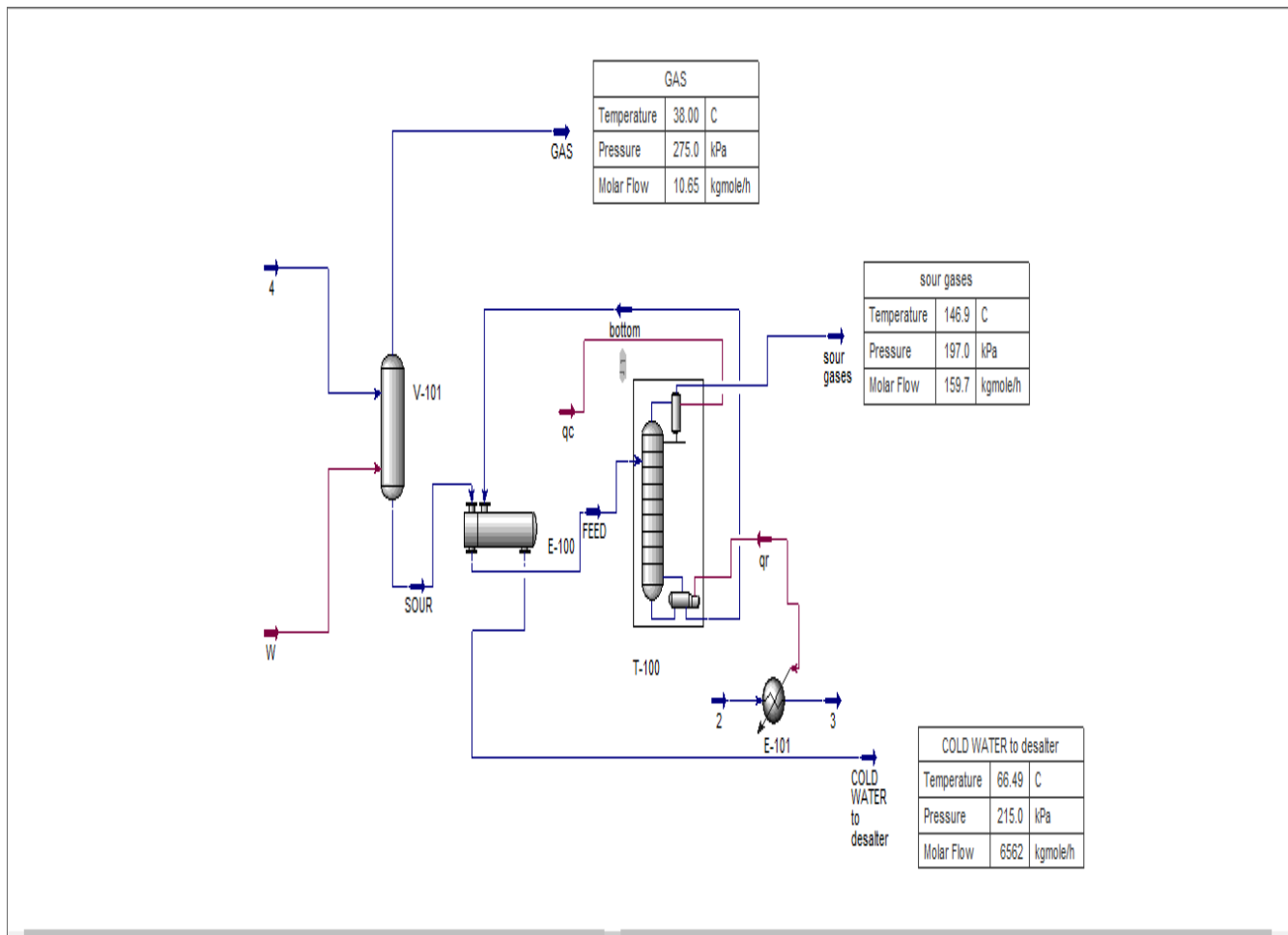


Figure (3.10) determine the overall design of sour stripping unit contain heat exchanger, stripper, reboiler, condenser and return the bottom to heat the feed.

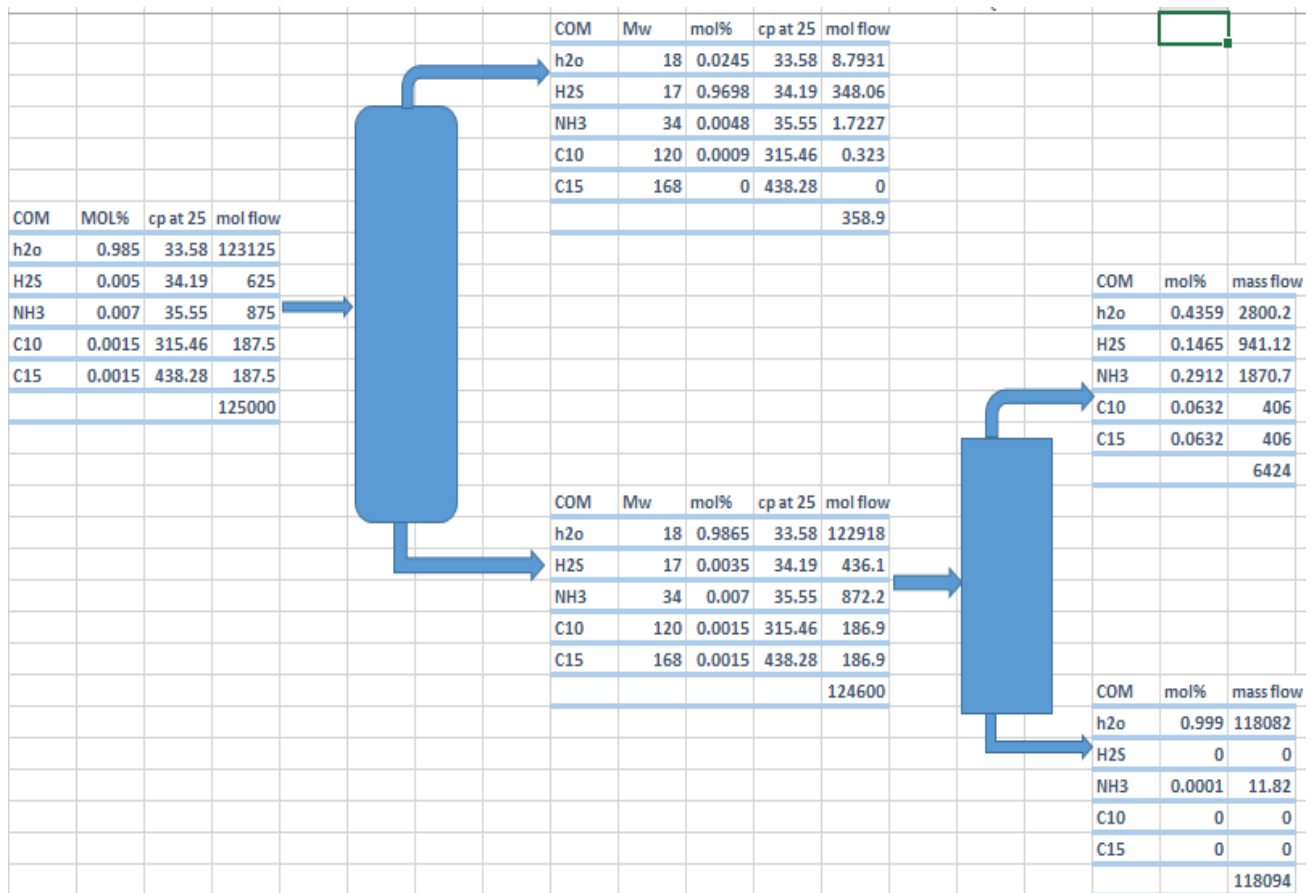
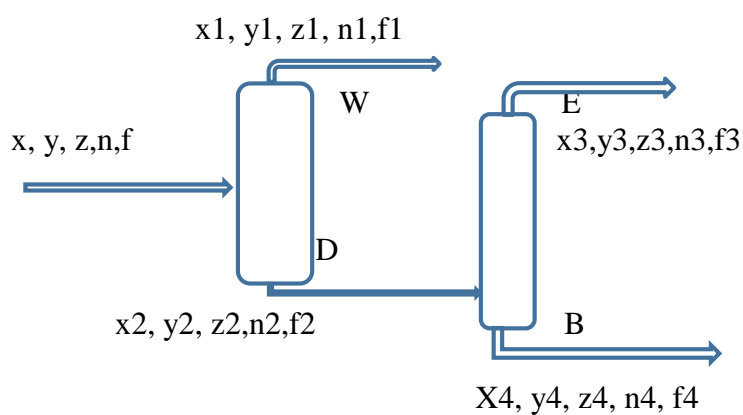


Figure (3.11) the material balance in excel

3.2.4 Material balance:



component	Symbol
H2O	X
H2S	Y
NH3	Z
n-C10	N
n-C15	F

OVER ALL MATERIAL BALANCE

$F = W + E + B$ (1)

$F = W + D$ (2)

$D = E + B$ (3)

Component material balance:

For h2o

$F \cdot x = x_1 \cdot W + x_3 \cdot E + x_4 \cdot B$ (4)

$F \cdot x = x_1 \cdot W + x_2 \cdot D$

For H2S

$F \cdot y = y_1 \cdot W + y_3 \cdot E + y_4 \cdot B$ (5)

$F \cdot y = y_1 \cdot W + y_2 \cdot D$

For NH3

$F \cdot Z = z_1 \cdot W + z_3 \cdot E + z_4 \cdot B$ (6)

$F \cdot Z = z_1 \cdot W + z_2 \cdot D$

For decane

$F \cdot n = n_1 \cdot W + n_3 \cdot E + n_4 \cdot B$ (7)

$F \cdot n = n_1 \cdot W + n_2 \cdot D$

For n-c15

$F \cdot f = f_1 \cdot W + f_3 \cdot E + f_4 \cdot B$ (8)

$F \cdot f = f_1 \cdot W + f_2 \cdot D$

The feed was 112500kg/h

For h2o

$0.985 \cdot 12500 = 0.0245 \cdot W + 0.4359 \cdot E + 0.999 \cdot B$

$0.985 \cdot 12500 = 0.0245 \cdot W + 0.9865 \cdot D$

For H2S

$0.005 \cdot 12500 = 0.9698 \cdot W + 0.1465 \cdot E + 0.00 \cdot B$

$0.005 \cdot 12500 = 0.9698 \cdot W + 0.1465 \cdot D$

For NH3

$0.007 \cdot 12500 = 0.0048 \cdot W + 0.2912 \cdot E + 0.0001 \cdot B$

$0.007 \cdot 12500 = 0.0048 \cdot W + 0.007 \cdot D$

For decane

$0.0015 \cdot 12500 = 0.0009 \cdot W + 0.632 \cdot E + 0.00 \cdot B$

For c15

$0.0015 \cdot 12500 = 0.0632 \cdot E$

If the feed was 12500

$W = 19.5 \text{ kg/h} \quad D = 12480.5 \text{ kg/h} \quad E = 296 \text{ kg/h}$

$B = 12184.5$

The amount of sour in bottom:

$H_2S = 0 \quad NH_3 = 1.218 \text{ kg/h} \quad H_2O = 12172.2 \text{ kg/h}$

The amount of sour in the top

$H_2S = 43.364 \text{ kg/h} \quad NH_3 = 86.19 \text{ kg/h} \quad H_2O = 129 \text{ kg/h}$

3.2.5 The energy balance:

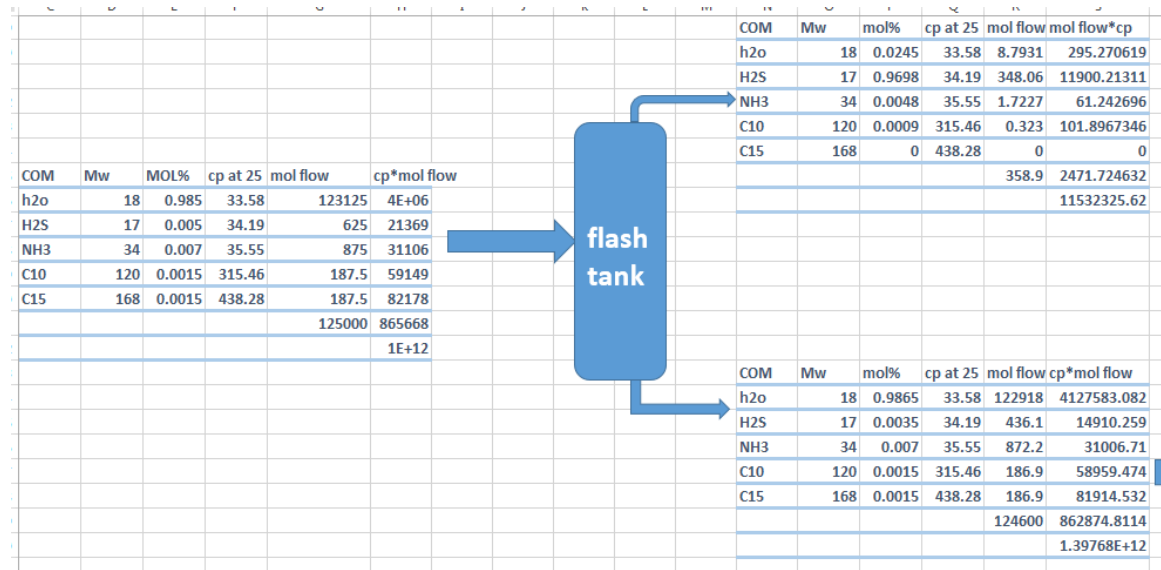


Figure (3.12) The energy balance for flash use excel

Heat flow in = Heat flow out
 Heat flow = $C_p \cdot m \cdot \Delta T$

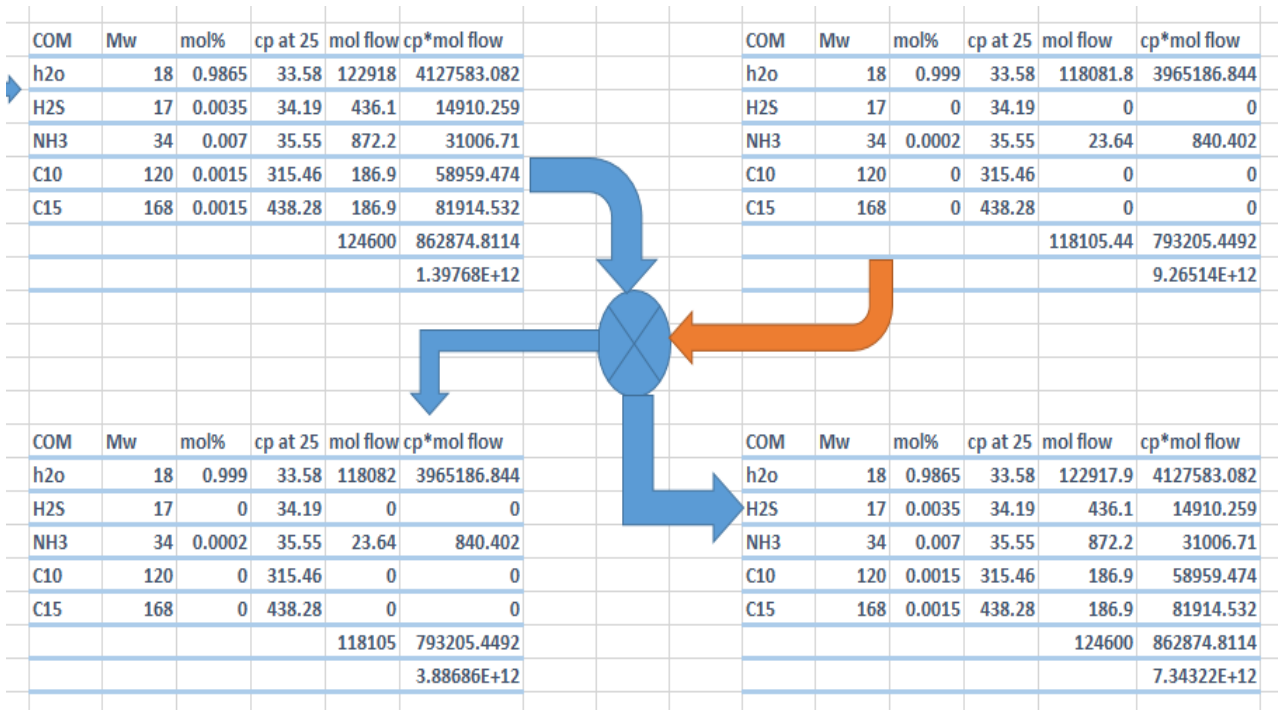


Figure (3.13) show the energy balance for exchanger

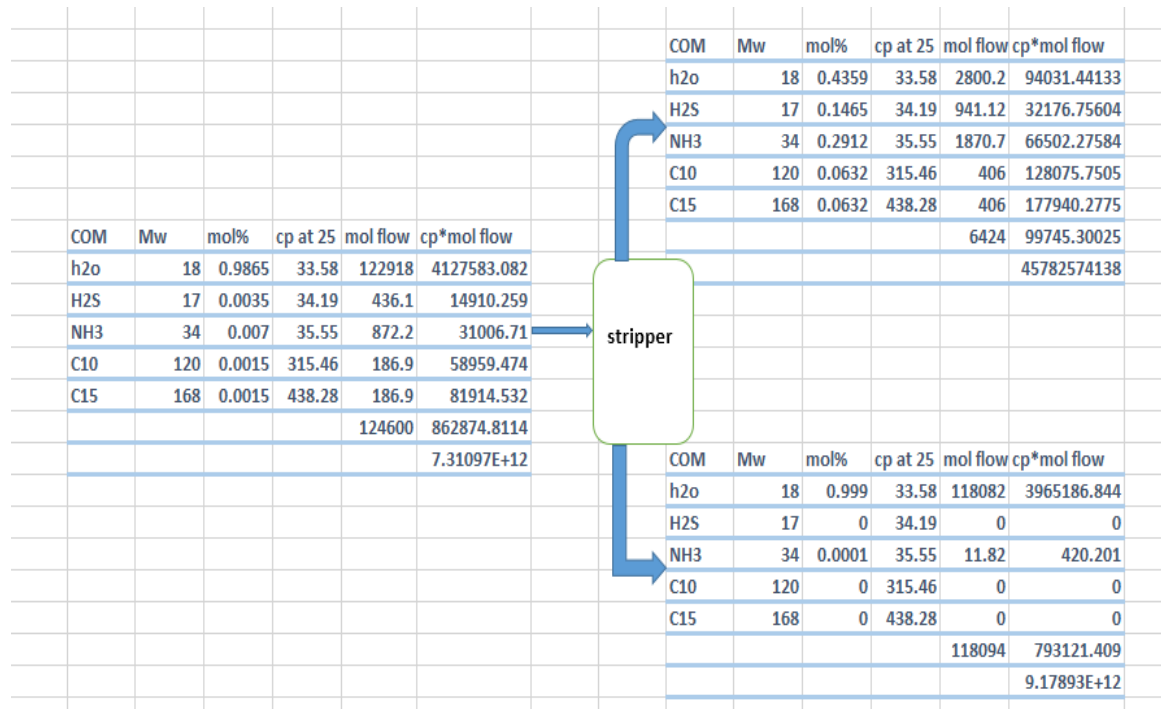


Figure (3.14) energy balance for stripper

Chapter 4

4. Results and Discussion:

The results obtained from the analysis which have been already mentioned in the last chapter are shown as below:

4.1 The Results:

4.1.1 Monitoring Pond (MP) Effluent Quality:

Table 3.1 *The physical quality of the MP effluents and comparison with National Sudanese standards and International standards.*

Parameter	Unit	Result	MEM	WB/IFC	OME	MEF	FEPA
pH	-	8.4	6-9	6-9	5.5-9	6-8.5	6.5-8.5
TS	Mg/L	314	-	-	-	-	-
TDS	Mg/L	258	-	-	-	-	200
TSS	Mg/L	56	-	30	15	20	30

Table 4.4 *The chemical quality of the MP effluents and comparison with National Sudanese standards and International standards.*

Parameter	UNIT	Result	MEM	WB/IFC	OME	MEF	FEPA
sulfide	Mg/l	9.07	1.0	1.0	-	0.50	0.2
Ammonia	Mg/l	83.1	15	10	10	15	10

Organics:

The results of the MP effluent analyses for organic pollutants content (BOD, COD, Oil and grease, and Phenols) are presented in Table (3). Organic characteristics of the treated effluent did not comply with the permissible limits, except for oil and grease which comply with all, but not with Indian guidelines.

Table 4.3 *The organics quality of the MP effluents and comparison with National Sudanese standards and International standards.*

Parameter	unit	result	MEM	WP/IFC	OME	FEPA
BOD5	Mg/l	<60	20	30	-	10
COD	Mg/l	<600	100	150	200	40
OIL&G	Mg/l	7	10	10	10	10
Phenols	Mg/l	39.72	0.5	0.2	0.2	0.5

4.1.2 Oxidation Ponds Effluents Quality

The oxidation ponds at Khartoum refinery are the final disposal terminals of treated wastewater discharged from the wastewater treatment plant (WWTP) through monitoring pond (MP). It is important here to note that Khartoum Refinery untreated effluents were bypassed from time to time and redirected to pond (C) instead of normal path where effluents are conveyed from MP through pipeline to pond (A) then pond (B) and lastly pond (C) (field observations).

Table 4.4 analysis results of waste water sample taken from monitory pond

Oxidation pond	PH Mg/l	Oil Mg/l	COD Mg/l	SS Mg/l	Sulfide Mg/l	Ammonia Mg/l	Phenol Mg/l	BOD Mg/l
A	9.9	5.2	570	144	0.109	14	0.069	8.00
B	8.1	4.1	144	102	0.002	2.08	0.039	3.00
C	7.7	3.5	280	390	0.274	2.28	0.049	5.00

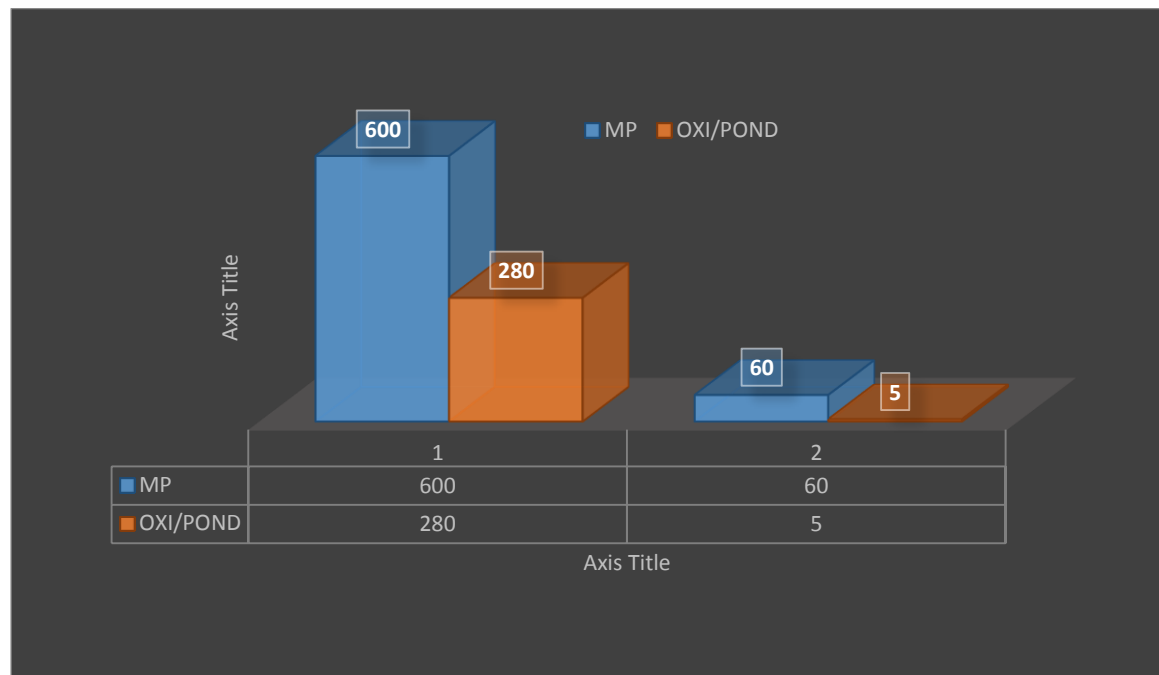


Figure (4.1) Comparison between organics concentrations in MP effluent and the oxidation ponds effluents.

4.1.3 Sour water stripping unit:

Table 4.5 analysis results of simulation for sour water stripping unit

item	Sour stream	Before treated			After treated		
		ammonia	Sulfide	pH	ammonia	sulfide	pH
unit	Kg/h	Mg/l	Mg/l		Mg/l	Mg/l	
	12500	8750	6250	9.7	99.3	0	9.81

Table (4.6) the result of energy balance for flash tank

item	Sour feed	Gases	Sour water
unit	K j/k mole	K j/k mole	K j/k mole
Enthalpy	1e+12	1e+7	1.3e+12

Table (4.7) energy balance for stripper

item	Sour water	Sour gases	Purified water
unit	K j/k mole	K j/k mole	K j/k mole
Enthalpy	7.3e+12	4.5e+10	9.17e+12

4.2 Discussion of Results:

4.2.1 Sour water stripping unit:

- Sour water enter the unit with high concentration of ammonia (6738.8mg/l) And leave the unit as a purified water with concentration about (99 mg/l) But it must be less than 200, since this will affect the biochemical treatment Unit

- And enter the unit with concentration of sulfide (3304mg/l) and leave the Unit as purified water with the range of permission.

- The heat flow for the stream of sour feed low so addition energy must be adding

4.2.2 Waste water treatment unit:

- The oil content in the effluent is 3.5mg/l which is in the permissible limit (10mg/l) that indicate good oil removal by API separator and dissolved air Floatation.
- Ammonia nitrogen is one of the major pollutants found in refinery effluents.

It was found in large concentrations above the permissible limit .the Observed ammonia is (87.3mg/l) which much higher than (15mg/l) Recommended for refinery effluents .the increase in the ammonia Concentration because of the following reason:-

- the concentration of the influent is greater than the unit design limit
- The COD value of the effluent discharge did not meet the effluent limitation Standard, the observed value of COD is (141mg/l) which is higher than Maximum standard limitation (100mg/l) the increasing of the concentration is Due to the following reason:-
- The concentration of the influent is greater than the unit design limit.
- Design configuration of the unit

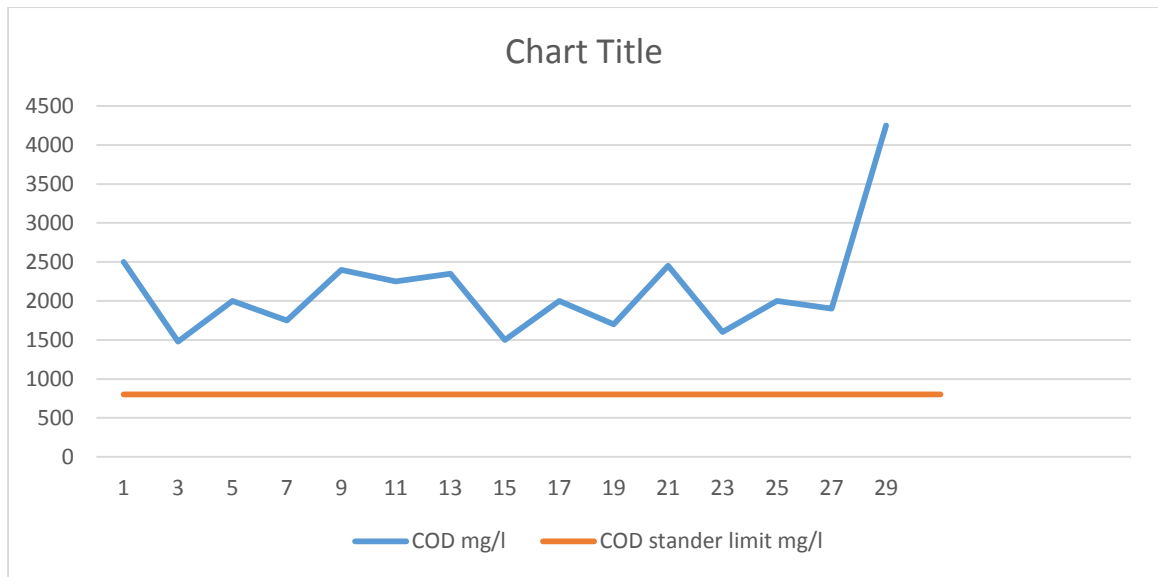


Figure (4.2): COD concentration at inlet of the unit compared with standard inlet

- Phenol content in the effluent is about 0.05 mg/l in oxidation pond which is less than the maximum permissible limit (0.5mg/l), this indication of a good unit performance for removal of phenol.

Chapter 5

5. Conclusions & Recommendations

5.1 Conclusions:

- Waste water treatment unit is being operated with a capacity greater than design capacity.
- Oil content, phenol, NH₃, enter the unit with very high concentration, above The design limit.
- NH₃, PH, COD concentration in the effluent are above the permissible limit Which is a very important problems that faces this unit.
- Oil content, phenol, pH in the effluent are within the permissible limit.
- As general the efficiency of the unit is not enough.
- Disposal of the contaminated oil and ammonia is done in bad ways and against environmental laws.
- Some modifications in the design of waste water treatment process are been Considered to improve the performance of the unit.

5.2. Recommendations:

- Treat contaminated oil it must be treated instead of disposing it in dumping Area.
- Sell ammonia or as another alternative one can burn it instead of dissolving in Water and disposal in dumping area. Because excessive ammonia has a great Effect on ground water, soil and aqueous life.
- Control the influent wastewater quality by controlling the wastewater effluent From processes units.
- Use zeolite instead of activated carbon, the results showed that the zeolite Performed some better in removal of ammonia compounds than activated Carbons.
- expand the capacity of the unit

• Oil water separator API:

Dose the flocculants in case of high oil content from the processes Units, there is a provision that will speed up the oil separation in the API thus compensating the need for extra retention time.

- Use timer for skimming or skim continuously.
- Reduce Oil content.
- Reduce COD.
- Lower SS.

• Dissolved Air Floatation Unit DAF:

Rehabilitate the skimmer with installing timer or skim continuously- thin Sludge blanket-visual inspection.

Rehabilitate the pressurized dissolved air system to produce fine bubbles -

Lower SS pH adjustment – lower chemical consumption. Apply the Proposed DAF chemical program.

- **The DAF chemical program:**

Supplement coagulant by flocculants through metering pump dosing skit (Preparation, feeding tanks) interlocked with the influent flow.

- **turning into anoxic out-come**

Reduce COD- heterotrophic bacteria, -3kg organic/kgN.
Aeration tank.

Increase DO level at the pond outlet, (+2.86kgO₂/kgN)

References:

- 1- M. Torres, C., Gadalla, M. & M. Mateo-Sanz, J., 2012. An automated environmental and economic evaluation methodology. *Journal of Cleaner Production*.
- 2- abu alhaija, m., al-zuhair, s. & h. el-naas, m., 2013. evaluate of three step process for the treatment of petroleim refinery wastewater. *journal of enviromental chemical engineering*.
- 3- Agrawal, A., 2018. Crude Oil Vacuum Distillation. 4.
- 4- Anon., n.d. <https://en.m.wikipedia.org/wiki/water>. [Online] [Accessed 9 2021].
- 5- Anon., n.d. https://en.m.wikipedia.org/wiki/water_resources. [Online] [Accessed 10 2021].
- 6- Anon., n.d. *petroleum refining1-us environmental protection agency*. [Online] [Accessed 11 2021].
- 7- Awad, R. H., 2008. *Refinery wastewater treatment Case study Khartoum Refinery*, khartoum: B.Sc. chemical Engineering.2004.
- 8- el-hohary & a. t., 2009. comparative study between chemical coagulation(c/p) versus coagulation/dissolved air flotation for pre-treatment of personal care product waste water. *desalination*.
- 9- Industries, C. M., 2017. delayed_coking. 2.
- 10- IPIECA 5th Floor, 2. B. R. L. S. 8. U. K., 2010. *Petroleum refining waste/wastewater use and managment*. s.l., s.n.
- 11- ishak, i., a. m. & a. M. H. I., 2012. refinery waste water biological treatment. *journal of specific and industrial research* , Volume 71.
- 12- Khogali, H., 2005. *The environmental impact of gaseous by-products and pollutants in wastewater at Khartoum Refinery..* khartoum, Thesis in Environmental Studies. Institute of Environmental Studies, University of Khartoum.
- 13- Ljubica Matijašević, I. D., 2017. Analysis of Cooling Water Systems in a Petroleum Refinery. *Chemical and Biochemical Engineering Quarterly*, 5.
- 14- Ljubica Matijašević, n.d.
- 15- Ltd., E. I., n.d. *DIESEL HYDROTREATING TECHNOLOGY*. [Online].
- 16- nasehi, s. & sarraf, m. j., 2018. Study of Crude Oil Desalting Process in Refinery.
- 17- Samimi, A. & Shahbazi Kootenaeia, A. H., 2020. Kinetic Overview of Catalytic Reforming Units (Fixed. *Department of Chemical Engineering, Mahshahr Branch, Islamic Azad University*, 5.
- 18- Veenstra, J. a. M. K., 2000. *An overview of US and international regulations regarding hydrocarbons in water effluents*. New Mexico,, s.n.

19- Zhang, J. & Zhu, X. X., 2001. G. P. A Level-by-Level Debottlenecking Approach in Refinery Operation.