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Water Contamination in Petroleum Refinery Processes

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ABSTRACT

This study was conducted to assessment the environmental impacts in petroleum refineries due to the different processes. The paper presents the data obtained during a case study was achieved in Tobruk petroleum refinery. The main petroleum products of the refinery represented by diesel, light naphtha, heavy naphtha and kerosene with maximum production capacity concerning 21,500 bbl/day. The results of the study revealed that the waste water affected by high concentration of hydrocarbons. The heavy metals are also determined and represented by V, Fe, Ni and Cu with low contents in crude oil. Also the pollutants parameters in the disposal water e.g. biochemical oxygen demand, chemical oxygen demand, total organic carbon, suspended solids, phenols, ammonia and sulphides are determined, and the results are compared with other refinery types. The concentration of these parameters are higher than the standard values that recommended by Environmental Protection Agency (EPA), at the same time these values are less if they are compared with the other refinery types.

Keywords : Oil Refinery, Distillation, Refinery Products, Water Pollution, Disposal Water, Drainage Water, Water Quality, Pollutants Parameters.

I. INTRODUCTION

Increasing global energy require, which is estimated to reach 44% over the next few decades, leads to the processing of oil, a complex mixture of organic fluids called crude oil and natural gas, and wastewater generation from oil are important issues [2].

The coal requires little processing before its (conventional) use for direct combustion purposes. Also the natural gas requires little or no processing. In comparison, when crude oil is pumped from the ground, it may contain several hundred individual components, which range from liquids of very low boiling points to solid waxes. Crude oil could be used as a boiler fuel to make steam for process heating or electric power generation, but it is only marginally more desirable than coal (because of the convenience of handling liquids rather than solids). No other device can make efficient use of a substance having such a complex mixture of components [9].

The approach to making the best use of petroleum is first to separate it into a small group of compounds. This is done in a petroleum refinery, schematically (and simplistically) illustrated in Figure 1. The numbers given in parentheses for the yields of different products are only approximate. They can vary considerably with the type of crude oil refined and with the conditions of operation of the refinery [18].

In principle, it is possible to separate each component of petroleum one-by-one, though this might take many repetitive distillation operations. However, to do so would be both very wasteful and prohibitively expensive [10]. For example, suppose we had a supply of crude oil that contained 0.5% octane. Octane, C_8H_{18}, is a component of gasoline. If for some reason we wanted to use pure octane as a motor vehicle fuel, we would require 4.8 million barrels (some 200,000,000 gallons) of crude oil to produce 1,000,000 gallons of pure octane, after many distillation steps to purify the octane. On the other hand, 20% of a good crude oil might yield gasoline on simple distillation. Making 1,000,000 gallons of gasoline would require only 119,000 barrels of crude oil. This upgrading of crude oil into products tailored to meet specific consumer needs is what we mean by *refining*.

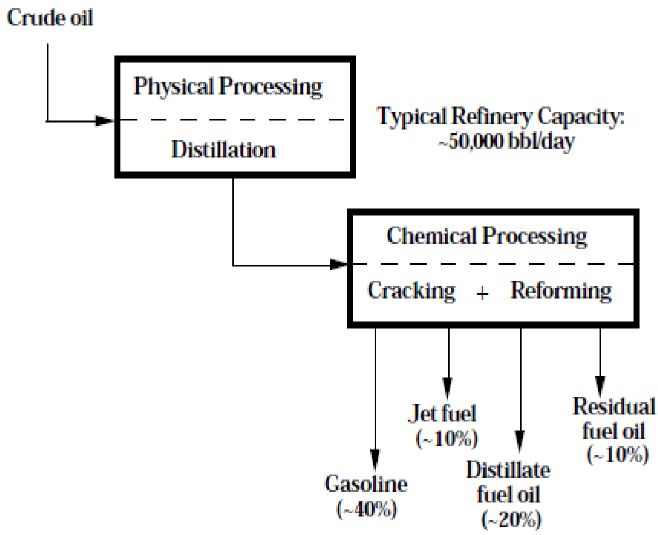

Fig. 1: Schematic representation of a petroleum refinery

The project of Tobruk oil refinery has been implemented by the National Petroleum Institution to satisfy some requirements of petroleum products. The job of refinery facility is to separate the crude oil into different products, the processes of separation take place under atmospheric distillation. The maximum capacity of production about 21,500 bbl/day. The main petroleum products of the refinery are diesel, light naphtha, heavy naphtha and kerosine.

II. MATERIAL AND METHODS

The study has been carried out on the refinery, where the samples are collected periodically and chemically analyzed in refinery labs. The concentration of metals determined by using some analytical techniques such as Atomic Absorption Technique and Flame Photometer.

The polluted parameters in the waste water of cooling tower are estimated. These parameters include: Biochemical oxygen demand (BOD), chemical oxygen demand (COD), total organic carbon (TOC), suspended solids (SS), phenols, ammonia and sulphide [15].

III. REFINING PROCESSES AND WASTEWATER SOURCES

There are three main sources of wastewater contamination at the refinery: (1) recycling of sulfurous oil and treatment of petroleum products with alkalines, which gives highly concentrated sulfurous alkaline wastewater; (2) complex processing of oil and gas to produce synthetic products generates wastewater with organic acids, alcohols, phenols, etc.; and (3) processes of desalination and dehydration. In the final source, wastewater contains demulsifiers and sulfonaphthones. All these substances are sources of harmful production, which leads to environmental pollution [16].

The following discussion is intended to provide an overview of refining operations by describing the steps in the refining of crude oil and the various products that can be made in a modern petroleum refinery. It is also intended to summarize the wastewater sources associated with various refinery operations.

The purpose of this discussion is to explain some of the technical references to refining in the accompanying report on wastewater pollution prevention opportunities in the refining industry. The refinery processes are discussed in the general sequence in which crude oil flows through the refinery. Emphasis is placed on the purpose of each processing step and its interactions with other processes.

Figure 2 is a flow chart of a representative refinery having most of the major processing units available to the industry today. As this figure indicates, refining is a complex operation. First, there are multiple options for feeding different feedstocks to various units.

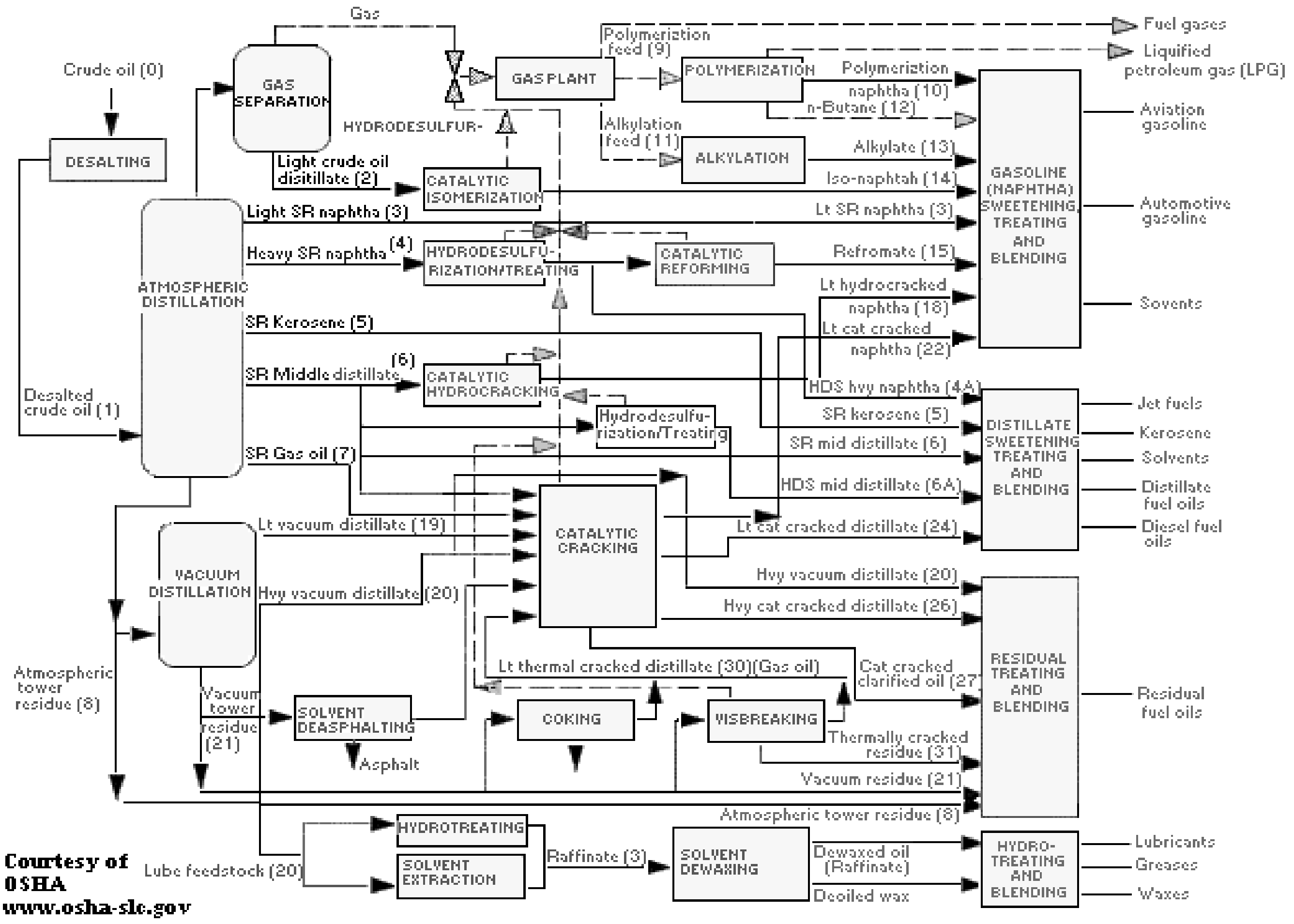

Fig. 2: Schematic flow chart of a complex refinery

Intermediate streams can usually be processed in more than one unit depending on the target slate of products that the refinery finds most profitable to produce. Second, there are many different crude oils available to refiners. The capacities and other characteristics of the various units in the refinery will limit the number of crude oils that are suitable for a given refinery. Conversely, the specific mix selected from this group of suitable crude oils will affect how various units are run in terms of the feed rates and operating parameters needed to produce the desired products [11].

However, Figure 3 shows the amounts of wastewater in some refinery processes. The highest amount of wastewater produced in crude distillation and catalyting cracking processes.

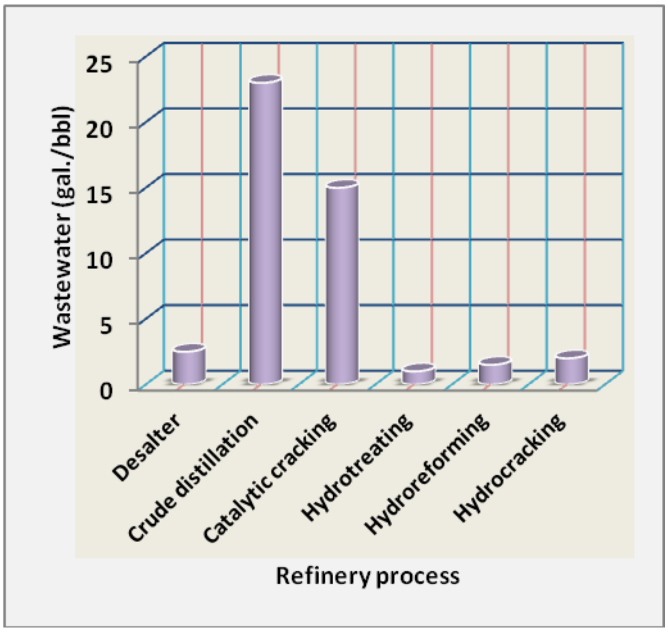

Fig. 3: Quantity of wastewater in refinery processes

IV. SOURCES OF WASTEWATER IN PETROLEUM REFINERY

The highest profit from crude oil is obtained by processing crude oil in a refinery into a variety of products. In excess of 2,500 refined products are produced, counting liquefied petroleum gas (LPG), kerosene, gasoline, diesel fuel, jet fuel, lubricants, waxes and bitumen [1]. In the meantime, the petrochemical industry obtains its raw materials from refined products, which are converted into valuable products such as plastics, synthetic materials and agrochemicals [20]. Large amounts of water are consumed in oil refineries for cooling systems, crude oil desalination, distillation and water treatment, and during maintenance and shutdown [1].

A reference [3] carried out refineries as either hydroskimming or complex. A hydroskimming refinery comprises three sub units: a distillation unit in which crude oil is fractionated into various components, a reforming unit for reformate production and a desulfurization unit for reducing the sulfur content of some fractions such as kerosene and naphtha. A complex refinery incorporates a catalytic cracking unit additional to the hydroskimming refinery. Regardless of configuration, the waste effluent is the overall contribution of the units involved in crude oil processing. An extensive programme for the identification of major process and utilities wastewater streams and quantification of these streams relative to the total wastewater generated from all refinery processes. Conversion processes include thermal and catalytic cracking, steam reforming, isomerization, alkylation and lube oil units, whereas treatment processes include naphtha and gas oil desulfurization, sour water strippers and catalyst regeneration units [3-5].

Refinery processes consume large amounts of water, and this makes them the main source of organic contaminants in wastewaters [20–21]. On the average, processing a barrel of crude oil consumes 65–90 gallons (246–341 l) of water [6]. Therefore, the oil industry will continue to discharge toxic waste into the marine environment. A decreased productivity of algae (a very important link in the food chain) was observed for water bodies receiving these effluents [8]. Table 1 summarizes the main pollutants in different petroleum refining units.

TABLE 1. Major Water Sources in Petroleum Refining Processes (adapted from [1]).

Unit	Wastewater major pollutants
Crude desalting	Free oil, ammonia, sulfides and suspended solids
Crude oil distillation	Sulfides, ammonia, phenols, oil, chloride, mercaptans
Thermal cracking	H_2S, ammonia, phenols
Catalytic cracking	Oil, sulfides, phenol, cyanide, ammonia
Hydrocracking	High in sulfides
Polymerization	Sulfides, mercaptans, ammonia
Alkylation	Spent caustic, oil, sulfides

V. TREATMENT OF WASTEWATER IN PETROLEUM REFINERY

The treatment of the wastewater is a key to the sustainable and acceptable industrial growth. Petroleum industries and refineries are important from economic growth point of view. The wastewater from these industries mainly contains oil, organic matter and other compounds [2].

Industrial wastewater treatment is important study area in environmental engineering. The treatment of petroleum and petrochemical wastewater is widely studies area of research. These streams are difficult to treat due to large concentrations of oil [4]. The petroleum and petrochemical wastewater treatments are classified effectively into three types; physical, chemical and biological treatment processes. However, the treatment required a typical application of the integrated system due to the complexity of characteristics of petroleum wastewater [2].

Depending on the type of crude oil, composition of condensate and treatment processes, the characteristics of refinery wastewater vary according to a complex pattern [4]. Industrial sectors like paint, pigment, sugar, distilleries, pharmaceutical, leather, fine chemicals, additives, textile, oil, wood, plastic etc. face the problem of efficient and low cost treatment methods. Various biological methods are found useful in treating organic matter [12, 13, 17].

VI. METAL CONTAMINANTS IN CRUDE OIL

All crude oils contain trace quantities of naturally occurring metals. Other than crude oil trader or proprietary oil company crude oil assay information, very little data have been published on the specific metal content of crude oils. In 1999, member companies in cooperation with the Petroleum Environmental Research Forum published a study that involved 26 crude oils from various parts of the world. Crude oils, which ranged in API gravity from 12° (very heavy crude oil) to 46° (very light crude oil), were examined with respect to 18 metals [14].

The results of the study indicated that many metals are present at such low levels that there is no need to consider them as chemicals of concern for purposes of site characterizations and risk assessments at sites where accidental and/or historical crude oil releases have occurred. Mercury is by far the most significant metal in crude oil and is of concern to refiners not only as a pollutant but also as a cause of corrosion of processing equipment.

VII. PETROLEUM UTILIZATION

Petroleum utilization is a much more complex process. This is illustrated in Figure 4. In particular, the preparation of petroleum before it is sold to the consumers is very extensive. The reason for this is that, despite their similar elemental composition, the chemical structure of different crude oils may be very different, as discussed above. Furthermore, a large number of different products are obtained from the petroleum refinery, this is illustrated in Figure 4, and most of them are used as fuels. A small but very important fraction is used as the basis for the (petro) chemical industry which gives us such indispensable products as plastics, pharmaceuticals and textiles.

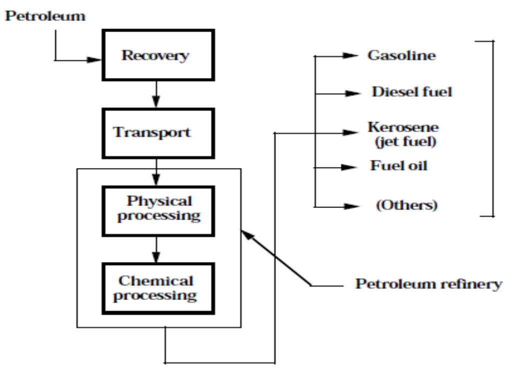

Fig. 4: Pathways to petroleum utilization

VIII. RESULTS AND DISCUSSION

The results that obtained from chemical analyses of water samples in different oil refinery units reveal a wide variation of physical and chemical parameters measurements.

The pH values are determined in some refinery units which including: tank water unit, Cooling tower, steam condensate and boilers that exhibit variation results. The average values are 6.5, 9.5, 6.2 and 7.0 respectively (Table 1).

TABLE 1: Concentration of Chemicals in Refinery Wastewater

Refinery unit	pH	Conductivity (μs/cm)	Chloride (Cl^-) ppm	Total iron (Fe) ppm	Sulphites (Na_2SO_3)	Nitrite ($NaNO_2$) ppm
Water tank	6.5	2095	5	0.5	3	210
Cooling tower water	9.5	1250	80	0.6	5	750
Boiler water	7.0	646	71	0.12	14	150
Steam condensate	6.2	7	10	1	1	1

Figure 5 presents the variation values of pH, chloride, total iron and sulphites in some refinery units. The conductivity has been determined for the cooling water, tank water, boiler water and steam condensate.

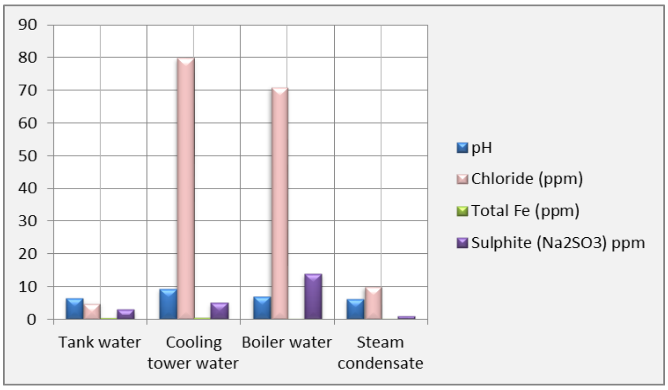

Fig 5: Concentration of chemicals in refinery units

The highest value is recorded in water tank (2095 μs/cm), while the lowest value in steam condensate (7.0 μs/cm) (Table 1). Figure 5 illustrates the concentration of chemicals in refinery units, while Figure 6 shows the variation of conductivity and nitrite in the refinery units. The highest value of nitrite is recorded in cooling tower water.

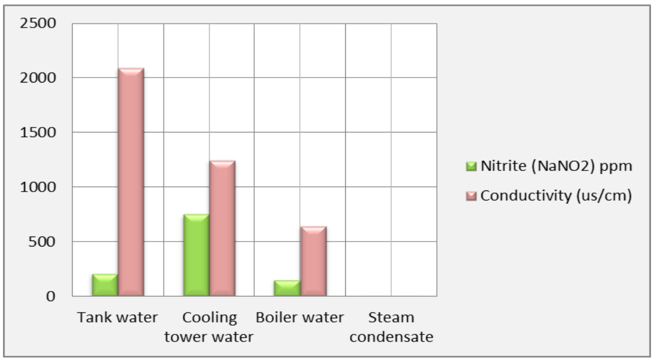

Fig. 6: Variation of conductivity and nitrite in refinery units

The waste cooling water has been analyzed to determine the average content of oil through one year. Figure 7 depicts a comparison between the content of oil in inlet and outlet water in cooling tower through one year. It is obvious that the wastewater contain high contents of oil than the inlet cooling water this is attributed to the high pollution of water by hydrocarbons. Consequently it must be eliminate from these oils before disposal wastewater into the surface water to avoid pollution risks.

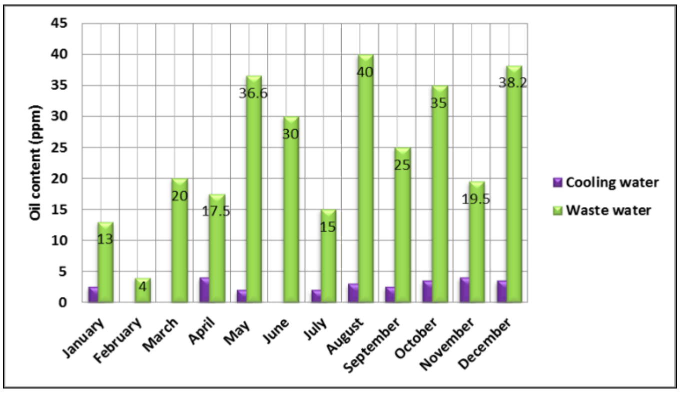

Fig. 7: Oil content in inlet and outlet water in cooling tower.

In addition to the previous physical and chemical parameters, some others pollutants parameters e. g. biochemical oxygen demand (BOD), chemical oxygen demand (COD), total organic carbon (TOC), suspended solids (SS), phenols, ammonia and sulphide are estimated in the waste water [15], as well as the volume of polluted water being produced in oil refinery (Table 2).

TABLE 2: Pollutants Parameters of Wastewater in Oil Refineries (adapted from [9]).

Refinery type	Polluted water volume bbl/oil bbl	BOD_5	COD	TOC	SS	Phenol	Ammonia	Sulphide
		Kg/1000 bbl polluted water						
Atmospheric distillation	62	25.5	42	16.5	44	0.150	19.5	0.02
Light cracking	80	31.20	44.01	20.25	54.30	7.45	22.60	0.97
Heavy cracking	90	29.5	55.04	22.05	62.90	5.70	24.50	0.85
Lubricated oils	120	40.0	85.9	17.50	115.2	2.50	34.80	-
Petrochemicals	110	30.2	73.40	25.07	80.04	3.25	51.45	0.445
Refinery complex	230	35.20	52.06	25.40	70.95	0.65	31.25	0.719
EPA (2006)	-	20	30	10	30	-	12	-

***1 kg/1000 bbl = 6.3 mg/l**

These parameters are compared with another different types of oil refinery distillation systems such as light cracking refinery, heavy or strong cracking, lubricated oils, petrochemicals and refinery complex (Table 2).

The results of analysis reveal that the concentration of these pollutants in atmospheric distillation in Tobruk oil refinery is lower than the other refinery systems, but it is still above Environmental Protection Agency (EPA) [7] recommended standard values (Table 2). So it must be reduce the concentration of these pollutants through treatment processes before the disposal to Bay water. The variation in these concentrations is illustrated in Figure 8.

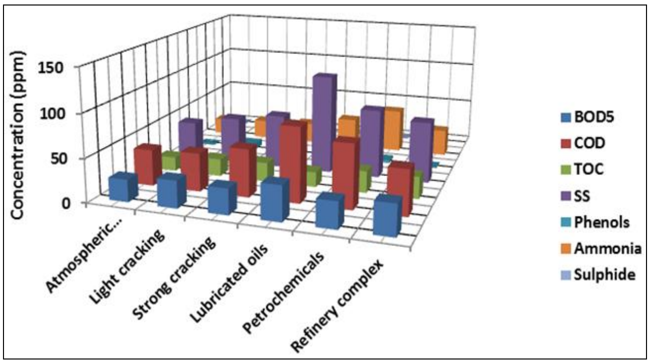

Fig. 8: Pollutants parameters of refinery waste water and other refinery systems

However, the obtained analyses are correlated with the standard levels recommended by EPA as shown in Figure 9.

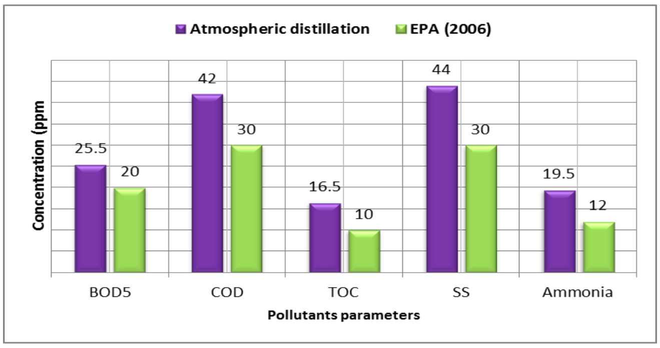

Fig. 9: Correlation between pollutants parameters and EPA standard values

The water volume being produced from the refinery also has been compared with the other ones (Table 2). It is obviously that the lowest volume produced from atmospheric distillation (62 bbl/day) and the highest amount of water volume produced in refinery complex (230 bbl/day) Figure 10.

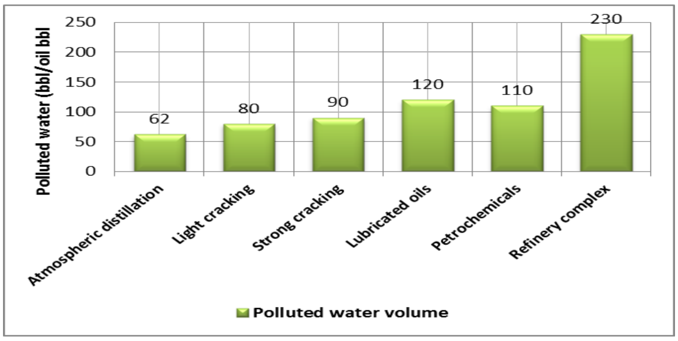

Fig. 10: Polluted water volume in the oil refinery

The heavy metal content in the wastewater represented by V, Fe, Ni and Cu. They show variation in their concentration with low contents. This may be attributed to their lower content in crude oil Figure 11.

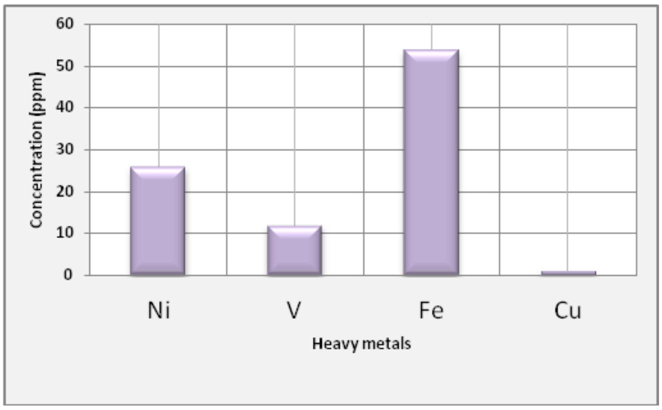

Fig. 11: Metals content in wastewater

IX. CONCLUSION

The most refinery units produce different amounts of wastewater due to the variable of refinery processes. The distillation process is the highest one which consumed a great quantity of water.

Some physical and chemical parameters exhibit high values in refinery units such as conductivity, sulphides and chlorides, particularly in cooling tower and boilers. These high contents will lead to the increase of pollutants concentrations in waste water.

The pollutants parameters e. g. BOD_5, COD, TOC, SS, and ammonia are exceed the standard levels recommended by EPA, so they must be reduced to acceptable limits. These parameters are low concentration in atmospheric distillation refinery comparing with the other types of refinery systems. Also, the amount of polluted water being produced from atmospheric distillation refinery is less than the other ones.

The heavy metals represented by nickel, iron, vanadium and cupper show low concentration in the wastewater. This may be due to their lower content in the crude oil.

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