

# Characterization of Produced Water from Petroleum Hydrocarbons Terminal

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## Abstract

Produced water (PW) is the largest by product of oil and gas extraction. It contains both organic and inorganic components that can harm the environment. However, the PW contents are different according to the area it is produced. There are a few factors that can affect the content compositions such as type of reservoir, geographic location of field, geologic formation, type of hydrocarbon being produced and lifetime of the proposed reservoir. This study analyses the contents via PW characterization which has been collected from five different sampling points from a petroleum hydrocarbon terminal. The characterization conducted includes pH, turbidity, salinity, total suspended solid (TSS), total dissolved solid (TDS), chemical oxygen demand (COD), biochemical oxygen demand (BOD), dissolved oxygen (DO), total oil and grease (TOG), polycyclic aromatic hydrocarbon (PAHs) analysis and MP-AES test which is to study the element content in the PW. Results shows that the PW characteristic of each PW samples varies based on different sampling point. PW samples with higher amount of oil content affect others characteristic of the sample. Most of the samples were found not meeting the standard of EQA1974.

**Keywords**— Produced water (PW), organic and inorganic content, COD, BOD, TOG

## Introduction

Malaysia produces 762,168.43 barrels per day of oil (as of 2016) and ranking 25th in the world. Oil and gas production will keep increasing as it has a high demand in energy consumption. An expected increase of 37% in energy demand is projected by 2040 [1]. However, as of July 2021 the production has declined to 489.34 thousand barrels per day [2]. This might happen due to the pandemic Covid 19. Oil and gas industry are facing a challenge where there is a byproduct from the extraction of the crude oil. The biggest contributor to the byproduct of oil and gas production is PW which can be defined as the water from subsurface formations that is brought to the surface during oil and gas extraction [3]. It also can be classified and treated as wastewater [4]. PW can be produced from two types of process in the oil and gas exploration which are

extraction and water injection [5]. A mixture of oil and water from the surrounding of oil well is extracted during the extraction process while for the second process, water is injected in the oil well to bring the oil closer to the surface. Hence, the water injected also becomes produced water. Global PW production is estimated at around 250 million barrels per day compared with around 80 million barrels per day of oil production. As a result, water to oil ratio is around 3:1 that is to say water cut is 70%. This statement is supported by report from K. Guera et. al [3] where they stated that 7 to 10 barrels, or 280 to 400 gallons, of water are produced for every barrel of crude oil. From this total generation of PW, about 40% will be discharged into the environment [6]. As presented in Figure 1, the global PW production from year 1990 to 2015 keep increasing along

with the increasing demand of oil and gas demand.

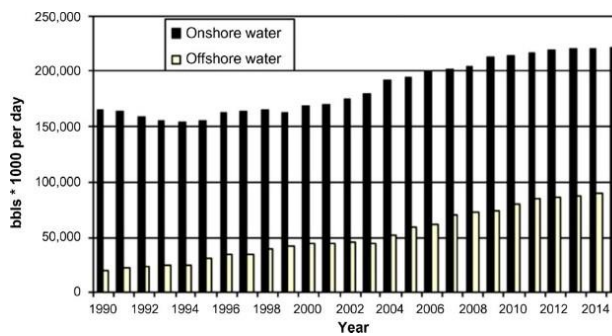


Figure 1: Global onshore and offshore produced water production [6]

Figure 2 is the sketch of a typical reservoir where there is layer of water, oil, and gas. The water layer can naturally exist in the subsurface rocks, and it also can be formed from reinjection of water into the reservoir. Reinjection of water is needed to maintain hydraulic pressure and to enhance oil recovery since the extraction of oil and gas will reduce the reservoir pressure [7]. This process is known as water flooding, in order to enhance the oil recovery [8]. The water will be produced together with hydrocarbon mixture and will be separated at the surfaces. PW can be generated from both conventional and unconventional sources [7]. Conventional sources are the sources that can be directly extracted from the reservoir while unconventional sources are trapped in reservoirs. Unconventional sources of oil and gas need specialized techniques and tools to extract the product, such as the extraction of shale oil, tight gas, and shale gas.

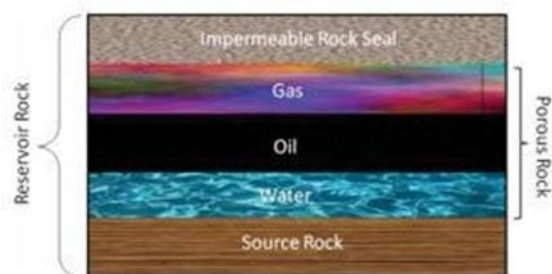


Figure 2: Sketch of typical reservoir [5]

Characteristic of PW are varies depending on few factors including type of reservoir, field geographic location, geologic formation,

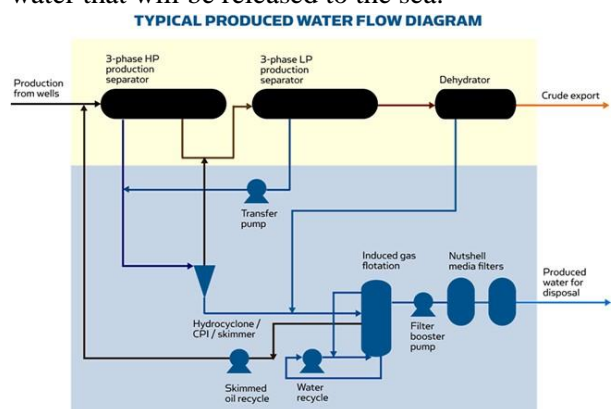
different hydrocarbon being produced and lifetime of the proposed reservoir [9]. It is studied that PWs discharged from gas/condensate platforms are 10 times more toxic compared to PW discharged from oil wells. However, in terms of volumes, oil production discharged more PW than gas production [7]. The characteristic of PW such as pH, conductivity, alkalinity, hardness, total suspended solid (TSS), total dissolved solid (TDS), oil and grease (O&G) and chloride are the examples of physicochemical properties of PW that need to be considered in the characterization. Generally, PW holds dispersed oil, dissolved organic compound (including organic acids, PAHs, phenol, some volatiles), treatment chemicals (that is used as corrosion inhibitor and reverse emulsion breakers), solid particles, anaerobic bacteria and heavy metal [9]. Presence of dispersed oil in PW is due to inability of hydrocarbon to dissolve in water. Hence, the oil will be dispersed in PW as emulsion or separated in two phase, oil and water. The dispersed oil mainly contains polycyclic aromatic hydrocarbon (PAHs) and some of heavier alkyl phenols where these contents are toxic to the environment [7].

The main objective of this study is to characterize produced water sample that has been collected from a crude oil terminal with 5 different sampling point and to analyze the produced water whether they meet the standard of EQA1974. Materials and methods

### Produced water collection

Produced water used in this study was collected from a petroleum hydrocarbon terminal. There are 5 samples of produced water, collected from five different sampling points. Generally, a crude oil production process flow will be involving separators to separate gas, crude oil and produced water. Figure 3 shows the typical produced water flow diagram. Crude oil from offshore will undergo three phase separators, gas will be separated to HP flare and vapour recovery compression system, crude oil will go to the refineries while PW will go through treatment before being disposed to the sea.

According to crude oil field production facility process flow diagram provided by C. Dumitran et al [10] PW line will be divided into three; PW that will be re-injected into well, slurry and water that will be released to the sea.



**Figure 3 Typical produced water flow diagram [11]**

### Produced water characterization

A few tests were carried out for the characterization of PW. It included turbidity, salinity pH, total dissolved solid (TDS), total suspended solid (TSS), total oil and grease (TOG), chemical oxygen demand (COD), biochemical oxygen demand (BOD), dissolved oxygen (DO), MP-AES for element contents and PAHs analysis. All tests were run according to the standard method; USEPA for turbidity and PAHs analysis, ASTM D1293 for pH, salinity and DO, ASTM D5907 for TDS and TSS, ASTM D7678 for TOG and ASTM D6238 standard COD and BOD. Results and discussion

Based on the Table 2, S3 had the highest turbidity, followed by S4, S5, S1 and S2. S3 had the highest turbidity because it was a bottom flow from separator where it had a lot of sediment. On the other hand, S5 was the last pit point before the produced water will be released to the sea. According to EPA water quality standard, a standard turbidity for clear water is around 50 NTU. Therefore, S5 did not meet the standard and can be categorized as polluted. Based on the result, only S2 followed the standard.

In order to protect the aquatic life, the standard pH should be ranging from 6.5 to 9. By referring to Table 2, only S2 and S3 fell into the

range with pH value of 6.63 and 6.72 respectively. However, the pHs for the other samples did not have significant outrange values. They only differed for about 0.1 to 0.3 which supposed to not give great impact to the aquatic life. Total dissolved solids (TDS) contained inorganic salts such as calcium, magnesium, potassium, sodium, bicarbonates, chlorides, and sulfates and also small amounts of organic matter that were dissolved in water. TDS for each sample fell in the range of standard TDS for sea water where the range was from 500 to 30,000 ppm. Most suspended solids were made up of inorganic materials, though bacteria and algae could also contribute to the total solid concentration. These solids included anything drifting or floating in the water, from sediment, silt, and sand to plankton and algae. Total suspended solid could also be measured by naked eyes by looking at the color of the samples. Higher amount of TSS lead to higher turbidity. The term "oil and grease" can be defined as chemicals containing aliphatic and aromatic hydrocarbons.

Total oil and grease in the produced water could also contribute to the number of PAHs as they exist in the oil. S3 contained the highest amount of oil and grease, while S2 had the lowest. This result was expectable by referring to the condition and turbidity of the produced water sample. TOG should be in the range of 100 mg/L according to the standard. Therefore, all samples did meet the standard for TOG. COD is the total of oxygen utilised to chemically oxidize organic water contaminants to inorganic end products. The higher amount of oxygen consumed conclude that the water is higher contaminated. The most contaminated sample was S3 as it had the highest amount of COD, which was 19220 mg/L. As S3 was the bottom flow of separator, the water sample might carry a lot of contaminant that make it had the highest COD. COD for all samples had exceed the range of COD for clean water where it supposed to be below 100 mg/L. Different case for BOD where S5 hold the highest BOD compared to the others. This might happen because of the effect from scale inhibitor (SI)

injection. For PAHs analysis, most of PAHs content were below 5 µg/L. Obvious present of PAHs can be seen in sample 3 where it contained 122 µg/L of naphthalene and 31 µg/L of phenanthrene, while other PAHs content are in range of below 10 µg/L and 5 µg/L. As stated before, S3 had the most oil content where it

leads to higher PAHs content compared to other samples since PAHs will be present in the presence of oil. Table 4 is the summary of element content in the produced water samples. Three significant element presents are manganese (Mg), iron (Fe) and Zinc (Zn).

Table 2: Characterization of produced water

Sample name	Turbidity (NTU)	pH (-)	Salinity (Ms/cm)	TDS (mg/L)	TSS (mg/L)	TOG (ppm)	COD (mg/L)	BOD (mg/L)	DO (mg/L)
S1	136	6.23	14.89	15884	103.33	168.33	2467	7.750	3.41
S2	50.07	6.63	12.63	13660	100	25.00	3257	7.947	5.20
S3	7776.7	6.72	10.72	11730	2344.098	474.33	4158	8.120	2.46
S4	864.67	6.32	9.02	10012	130	206.33	3414	8.217	4.10
S5	215.33	6.33	10.98	12012	140	136.33	2357	8.333	5.83

Table 3: PAHs analysis

Parameters	S1	S2	S3	S4	S5
Naphthalene, µg/L	<5	<5	122	<5	<5
Acenaphthylene, µg/L	<5	<5	<5	<5	<5
Acenaphthene, µg/L	<5	<5	<5	<5	<5
Fluorene, µg/L	<5	<5	<5	<5	<5
Phenanthrene, µg/L	<5	<5	31	<5	<5
Anthracene, µg/L	<5	<5	<5	<5	<5
Fluoranthene, µg/L	<5	<5	<5	<5	<5
Pyrene, µg/L	<5	<5	<5	<5	<5
Benz(a)anthracene, µg/L	<5	<5	<5	<5	<5
Chrysene, µg/L	<5	<5	<5	<5	<5
Benzo(b)fluoranthene, µg/L	<10	<10	<10	<10	<10
Benzo(k)fluoranthene, µg/L	<5	<5	<5	<5	<5
Benzo(a)pyrene, µg/L	<5	<5	<5	<5	<5
Indeno(1,2,3.cd)pyrene, µg/L	<5	<5	<5	<5	<5
Dibenz(a,h)anthracene, µg/L	<5	<5	<5	<5	<5
Benzo(g,h,i)perylene, µg/L	<5	<5	<5	<5	<5

Table 4: Element content in produced water

Elements	Concentration (mg/l)				
	S1	S2	S3	S4	S5
Cd	-0.015	-0.016	-0.015	-0.011	0.029
Cr	-0.043	-0.044	-0.044	-0.042	-0.034
As	-0.015	-0.017	-0.017	-0.01	0.04
Pb	-0.004	-0.001	-0.006	-0.009	0.003
Cu	-0.088	-0.086	-0.088	-0.08	-0.066
Mn	0.031	0.015	0.012	0.139	0.354
Ni	-0.209	-0.157	-0.146	-0.556	-1.714
Zn	0.02	0.011	0.01	0.08	0.452
Fe	0.023	-0.038	-0.041	0.125	0.81



\*Negative value can be considered as 0 since it cannot be detected by the Atomic Absorption Spectroscopy (AAS)

### Conclusion

Physical characteristics of produced water from petroleum hydrocarbons terminal has been analyzed in this study. It was found that the location of the water sampling point affects the produced water content and their physical characteristics as the produced water samples had undergone pre different treatment processes. All samples did not meet the EQA1974 for COD and while for TOG and turbidity, only S2 met the standard. It was found that all samples except S3 met the standard for TSS. On the other hand, for TDS, all samples were found to meet the standard.

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