Original Research Article

Effect of Thermodynamic Parameters on the Concentration of Pollutants in Produced Water from Crude Oil Production

ABSTRACT:

Thermodynamic parameters such as temperature and pressure of petroleum reservoirs are among the most important physical characteristics which are required to effectively produce crude oil from the reservoirs. Oil and gas reservoir pressures determines if external energy is required to force well fluids out of the reservoir; the temperature of the reservoir determines the flow characteristics of the produced fluid through the tubing and along the flowline by its influence on the viscosity of the fluid. The produced fluid is made up of produced water, crude oil and natural gas. Produced water contains several substances which at certain concentrations could pose health threats to living organism in the environment. Local regulatory authorities do not allow discharge of produced water to the environment except the prescribed limits for selected pollutants contained in the produced water are not exceeded. This has led to post-production treatment of produced water in most crude oil production facility in order to meet these limits. This treatment increases the cost of production of crude oil thereby reducing the profitability of crude oil production process. It is believed that thermodynamic parameters such as temperature and pressure are capable of either decomposing or altering the structure of some pollutants thereby reducing their concentration in the produced water at the end of the production process. This research has employed an environmental process engineering simulator (Aspen HYSYS) to determine which thermodynamic variables of temperature and pressure could be altered in combination to reduce the concentration of pollutants in produced water to meet the regulatory limits prior to discharge.

Keywords: Produced water, pollutant concentration, production process, crude oil, thermodynamic parameters, environmental process engineering

1. INTRODUCTION

Crude oil does not exist alone in the reservoir; it exists with either natural gas, formation water or both. When crude oil and natural gas is brought to the surface through the production processes, this water is also brought to the surface alongside hydrocarbons. This water may originate as natural water in the formations holding oil and gas or can be water that was previously injected into those formation through secondary recovery techniques like water flooding (injection water) or steam flooding (condensation water) [1]. There is also possibility of some additional water from other formations adjacent to the hydrocarbon-bearing layers to become part of the produced water that comes to the surface [2]. Produced water is therefore a mixture of injected water, formation water, production chemicals, and hydrocarbons [3,4,5,6]. The composition of produced water depends on the chemistry of the rocks or the geologic formation, lifetime of the reservoir, and the type of hydrocarbon produced [4]. The varied nature of the composition of produced water from different sources is shown in table 1.

Table 1. Concentration (µg/l) ranges for several metals in produced water from Scotian Shelf and the Grand Banks in Canada compared to produced water in the Gulf of Mexico, the North Sea and Offshore Nigeria.

Metal	Gulf of Mexico[16]	North Sea[16]	Scotian Shelf[16]	Grand Banks[16]	Offshore Nigeria
Arsenic	0.5-31	0.96 – 1.0	90	<10	NA
Barium	81,000 - 342,000	107,000 – 228,000	13,500	301 – 354	NA
Cadmium	<0.05 – 1.0	0.45 – 1.0	<10	<0.02 -0.04	NA
Chromium	<0.1 – 1.4	5 – 34	<1 – 10	<1	0.8 -10
Copper	<0.2	12 – 60	137	<5	1 - 60
Iron	10,000 – 37,000	4,200 -11,300	12,000 – 28,000	1,910 – 3,440	220 – 5,000
Lead	<0.1 – 28	0.4 – 10.2	<0.1 – 45	0.09 – 0.62	<1 – 120
Manganese	1,000 – 7,000	NA	1,300 – 2,300	81 -565	NA
Mercury	<0.1 – 0.2	0.017 – 2.74	<10	NA	NA
Molybdenum	0.3 – 2.2	NA	NA	<1	NA
Nickel	<1.0 – 7.0	22 – 176	<0.1 420	1.7 – 18	NA
Vanadium	<1.2	NA	NA	<0.1 – 0.6	NA
Zinc	10 – 3,600	10 – 340	10 – 26,000	<1 – 27	10 - 215

Source: Neff et al., 2002.

Although produced water has a complex composition, its constituents can be broadly classified into organic and inorganic compounds. These comprise several thousand compounds that vary in concentration between wells [7,8] and over the lifetime of a well; including dissolved and dispersed oil components, aromatic hydrocarbons, alkylphenols, grease, heavy metals, radionuclides, production chemicals, dissolved formation minerals, salts, dissolved gases (including CO_2 and H_2S), scale products, waxes, microorganisms, and dissolved oxygen [9,10,11,12,13,14]. Produced water can also contain large amounts of organic material, particles, inorganic salts, and low molecular weight organic acids like acetic acid and propionic acid and can have high levels of sulphur and sulphide. The injected water component of produced water can bring traces of added chemicals such as biocides, corrosion inhibitors, scale inhibitors, emulsion breakers, coagulants flocculants and oxygen scavengers to the surface [15,16]. Sulphate reducing bacteria may also be present in produced water [17].

There are various chemical constituents that could be present in the produced water. These chemicals, individually or collectively, could have significant impact on the environment. Some of the impacts include disruption of physiological and behavioural activities of the aquatic life, bioaccumulation, and deterioration of physical environment [18]. The major constituents of concern in produced water are the salt content (often expressed as salinity, conductivity, or total dissolved solids [TDS]), oil and grease (which could be found in the form of free oil, dispersed oil or dissolved oil), inorganic and organic toxic compounds (which may have been introduced through production chemicals or by leaching of formation rock or hydrocarbon) and naturally occurring radioactive materials. The composition of produced water affect how they are treated, used, and/or disposed [19].

Produced water receives various types of treatment before it is disposed or reused. The treatment and disposal techniques proposed for produced water depends on the location (offshore or onshore), the composition of the produced water, the local legislations concerning produced water and the overall crude oil production philosophy of the company. The treated produced water could be re-injected (including injection for enhanced recovery, disposal or sent to offsite commercial disposal), discharged to the water body, evaporated or re-used for beneficial purposes (irrigation, dust and ice control on the road) [4,20]. The choice of treatment process or technology depends on how clean the produced water is required to be before it is sent to it destination. For example, produced water must be treated to remove oil and grease and toxic chemicals before discharging it to the ocean from an offshore platform. Produced water that is discharged to onshore freshwater rivers must be further treated to reduce salt content [8]. Water that is injected for either enhanced recovery or for disposal is treated in a different way from water that is discharged. The treatment processes used prior to injection are designed to remove free oil, solids, and bacteria. Chemicals are often used to enhance treatment processes and to protect underground formations and equipment.

The Environmental Guidelines and Standards for Petroleum Industry in Nigeria (EGASPIN), a legislation of the Department of Petroleum Resources (Nigeria's oil and gas industry regulator) mandates that produced water be treated to acceptable limits prior to disposal, re-injection or reuse [21,31]. The capital and operating costs associated with most produced water treatment systems could be high therefore the need for economical management of produced water in oil fields is critical [4,22]. In the management of produced water, onshore and offshore oil and gas operators are faced with numerous challenges which include exceeding discharge oil concentrations, plugging of lines, valves and orifices due to deposition of inorganic scales, growth of bacteria that plug lines and valves or result in formation of harmful products and plugging of disposal wells and producing formations by solid particles and suspended oil droplets [23].

Several techniques and materials have been employed to remove oil and other pollutants from produced water. Raw eggshell has been employed and it was reported to be effective [24]. CPC modified barley straw, activated carbon, bentonite, carbonized rice husk, walnut shell and fatty acid grated banana trunk have been used in several research works to removed oil and other pollutants from produced water [25,26,27,28,29,30]. Most of these research methods were not able to meet the regulatory limits for discharge of the treated produced water. The commonly used conventional treatment schemes which employ numerous technologies still achieve inconsistent results as the continual changing of inlet conditions often limit their effectiveness. The use of heavy doses of chemicals by conventional systems is also creating an ongoing economic and chemical management burden for the oil and gas industry [22]. Modern hydrocarbon recovery systems have shown to be more effective than the conventional solution through the provision of operational flexibility, reduction of lost energy, savings on chemical additives, low maintenance cost with fouling, elimination of excursions and generally higher efficiencies [22]. The costs of these modern treatment schemes are however very prohibitive especially for marginal fields.

In order to avoid the cost-prohibitive produced water treatment methods that can make crude oil production in marginal field unviable, a combination of variation of the thermodynamic variable of temperature and pressure have been applied on the production process until the treated produced water meet the limits using process simulation with Aspen HYSYS. The result of this research may be applied to design of crude oil production process or to the debottlenecking of existing production process to meet the discharge or disposal limits for produced water set by local authorities without post production treatment.

2. MATERIALS AND METHODS:

2.1 Case Study Process Plant

The Izombe Flow Station (IFS), which is currently operated by Addax Petroleum Development Nigeria Limited, is an onshore crude oil and natural gas facility located Oil Mining Lease (OML) 124 in Izombe, Oguta Local Government Area of Imo State, Nigeria. The flow station, which was commissioned on 6 June 1975, is a complete self-sufficient facility containing Oil and Gas Production and Processing Systems: Oil Production Process; Gas Compression and Re-injection Systems; and Produced Water Re-injection Unit.

Figure 1. The Izombe Flow Station Manifold

IFS was originally designed to receive 37,000 barrels per day of well fluids from Izombe, Ossu, Njaba and Jisike fields. However, the current crude oil production of the facility is 3,300 barrels per day and the crude oil - produced water ratio is 0.3. The reservoir fluids from the various oil wells which flow into the facility through the manifold (Figure 1) are separated into their three components: oil, gas and water; and each component is further processed for final disposition. Crude oil is processed for export, natural gas is compressed to be used as either fuel, lift gas or re-injection gas while produced water is prepared for disposal through injection to the available injection wells.The flow station houses 48 mmscfd capacity compressors which are made up of eight units: six (6) low pressure (LP) and two (2) high pressure (HP) compressors. The compressed gas is used as lift gas for Izombe and Ossu gas-lifted wells. Excess of the compressed gas is re-injected into gas disposal well.

2.2 Produced Water and Reagents:

Samples of produced water were collected from three points at the Izombe flow station on Friday, November 17, 2017. Three samples of varying sizes were collected in the recommended containers at each point. The samples for physio-chemistry analysis were collected in two-litre plastic containers. The samples for metals and cations were collected in 300 ml plastic bottles while the samples for hydrocarbon concentration check were collected in 1000 ml Amber Glass bottles. The samples for metals and cations and those for hydrocarbons were preserved with 3ml Nitric acid and 4ml Sulphuric acid respectively. The sample points are the production manifold, the outlet of the line heater and the inlet of the water injection pump. The sample at the production manifold is aimed at obtaining the condition of the produced water on arrival at the flow station prior to treatment. The samples from the outlet of the line heater are expected to show the effect of heat on the pollutants while the last samples collected at the inlet of the water injection pump are expected to reveal the effect of further treatment on the pollutant's concentrations prior to the disposal of the produced water into a selected reservoir. Tables 2 and 3 below show the average conditions under which the samples were collected, and the initial characteristics of the produced water samples as determined in the laboratory respectively.

Table 2. Sample collection conditions

Points of Collection	Time of Collection	Collection Point Pressure (psi)	Collection Point Temperature (^oC)
Production Manifold	14:25 hrs	48	39
Outlet of Line Heater	14:35 hrs	23	52
Inlet of Water Injection Pump	14:45 hrs	14.7	37

Table 3 Characteristics of produced water at the point of collection.

Parameters	Manifold	Line Heater	WIJ Pump
PH	7.10	6.97	6.68

Oil Content (ppm)	3,000	146	84
Total Dissolved Solids (mg/litre)	17,100	16,600	12,400
Chemical Oxygen Demand (mg/litre)	43	36	30

2.3 Method:

The collected samples were subjected to laboratory analysis to determine the concentrations of some selected pollutants in the samples. Different analytical approaches were employed in the process. The results of the laboratory tests are shown in Table 4 below:

Table 4. Results of the laboratory tests on samples collected at various points on Izombe Flow Station on 17 November 2017.

S/N	Sample Parameter	Analytical Method	Concentration at Manifold (mg/l)	Concentration at Line Heater (mg/l)	Concentration at WIJ Pump (mg/l)
1	pH	pH Meter	7.10	6.97	6.68
2	Benzene	GC (FID)	0.50	0.19	0.02
3	Toluene	GC (FID)	0.52	0.15	0.08
4	Phenol	HACH DR 3900	0.72	0.21	0.12
5	Lead	AAS (FLAME)	1.25	0.98	0.41
6	Chromium	AAS (FLAME)	0.89	0.81	0.67
7	Phosphate	HACH DR 3900	0.03	0.12	0.14
8	Ammonia	HACH DR 3900	10.65	7.90	5.50
9	Nitrates	HACH DR 3900	20	22.89	16.94
10	TDS	TDS Meter	17,100	16,600	12,400
11	Chlorides	Titrimetry	6,000	5,500	5,200
12	Salinity	Titrimetry	9,900	8,665	7,175

In the analysis, the pollutants were considered as parameters in the produced water samples which were analysed following American Society for Testing and materials (ASTM) standard methods recommended in the Standard Methods for the Examination of water and Wastewater by American Public Health Association (APHA) [32] and Recommended Practice for Analysis of Oilfield Waters (API RP – 45) [33]. The concentrations of the of the hydrocarbon pollutants (BTEX) in the produced water was determined by Gas Chromatography with Flame Ionisation Detector (GC -FID) but phenol, phosphates, nitrates and ammonia concentrations were determined by HACH DR 3900 spectrophotometer. The concentrations of the metals in the produced water were determined by Flame Atomic

Absorption Spectroscopy (Flame AAS). The chlorides and salinity content were determined by titrimetry.

2.4 Environmental Process Simulation:

Aspen Hysys 6.2 has been used for this simulation. *Hysys* is designed and manufactured by Aspen Technology Incorporated in the United States of America. It is a software with integrated steady state and dynamic modelling capabilities where the same model can be evaluated from either perspective with full sharing of process information. The process engineering software provides extremely powerful approach to steady state modeling. It has been designed to allow for the use of multiple property packages, creation of pre-built templates and use of multiple flowsheets. Figure 2 is a flowsheet for the path of produced water in the crude oil production process. Soave-Redlich-Kwong (SRK) was the base property package selected for this simulation. The pollutant compositions were expressed in mass fraction. Some of the pollutants include chromium, iron, copper, lead, phosphate, and zinc.

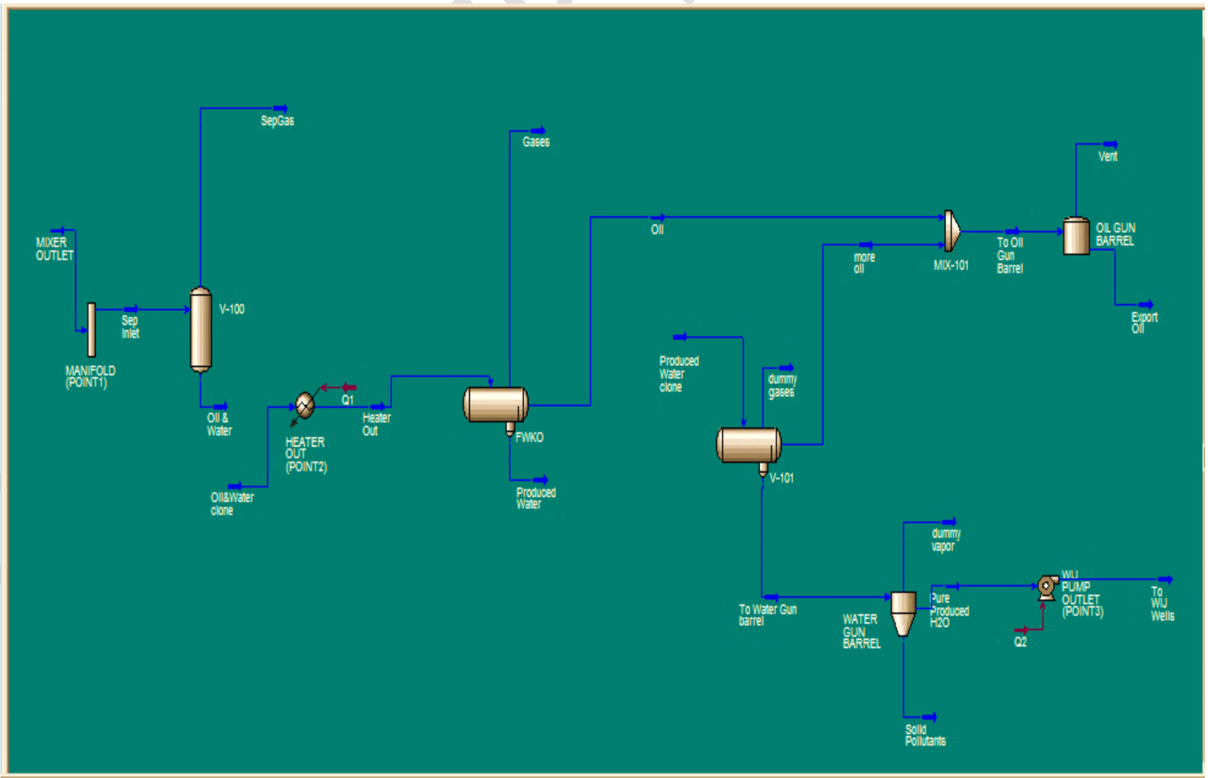

Figure 2. Process flow diagram of the facility showing the three sampling points

3. RESULTS AND DISCUSSION

The samples of produced water were analysed in IESL Laboratories, Port Harcourt, Rivers State, Nigeria. It is a standard laboratory which is also approved by the Department of Petroleum Resources, Nigeria's oil and gas industry regulator. The results of the effects of temperature and pressure from process simulation are found below.

3.1. Effect of temperature on the concentration of pollutants:

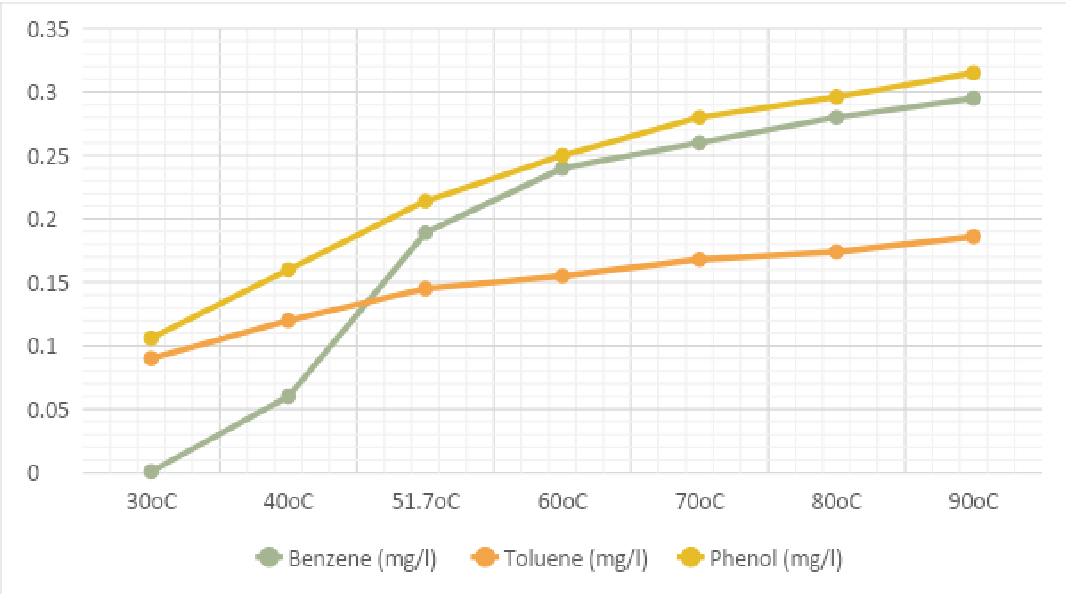

Figure 3a. Concentrations of hydrocarbon pollutants at different temperatures at the heater outlet.

3.2. Effect of pressure on the concentration of pollutants:

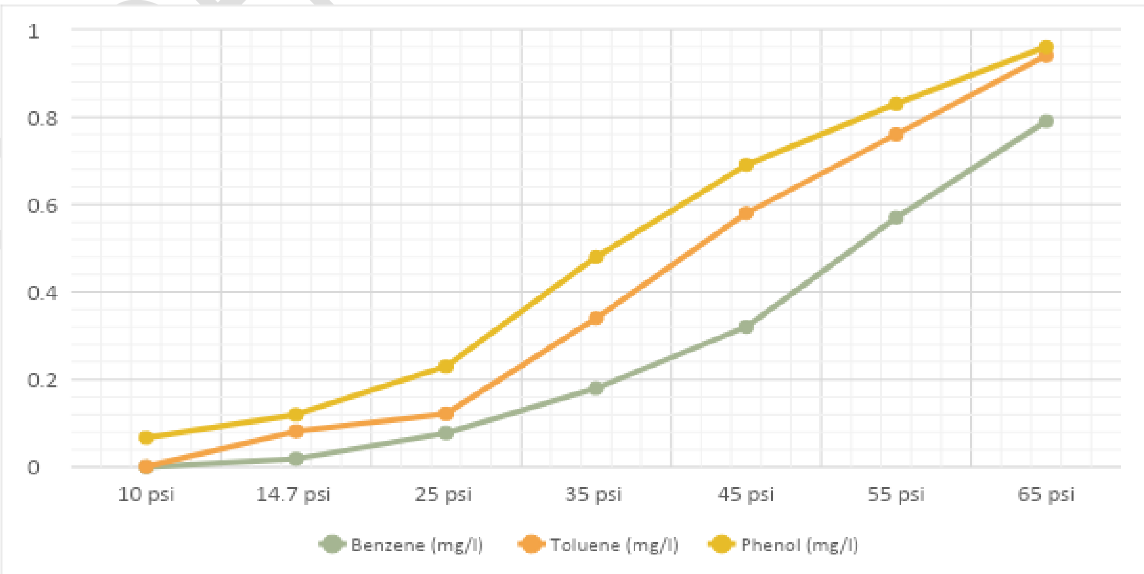

Figure 3b. Concentrations of hydrocarbon pollutants at different pressures at the WIJ pump.

3.3. Effect of temperature and pressure combination on concentration of pollutants:

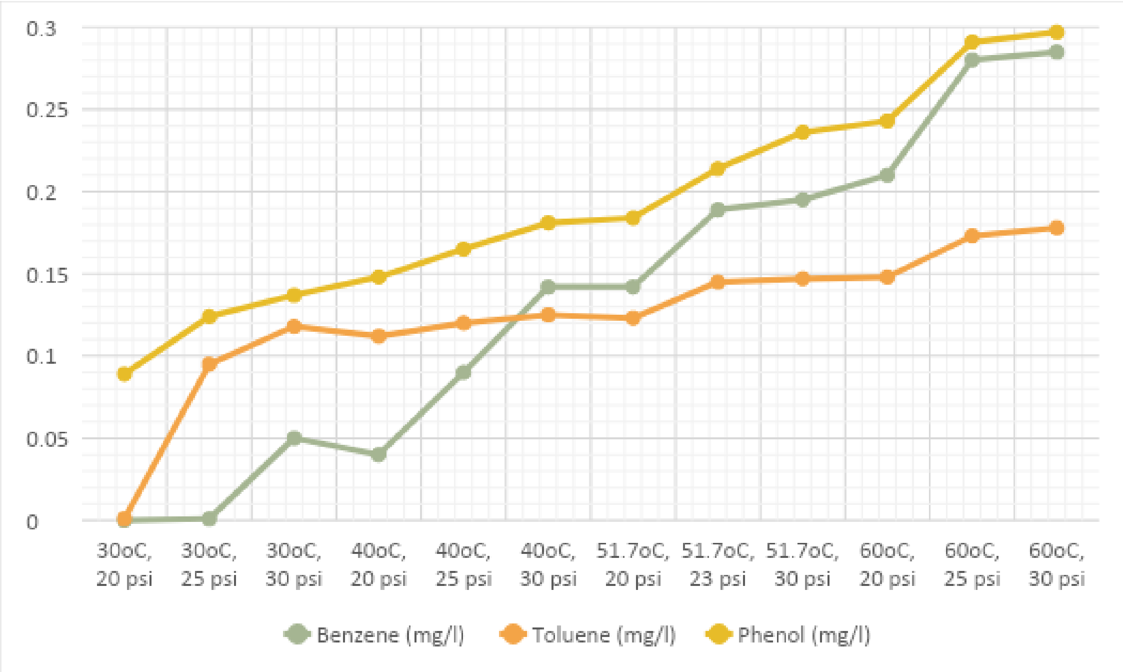

Figure 3c. Concentrations of hydrocarbon pollutants at various pressure and temperature combinations at the heater outlet.

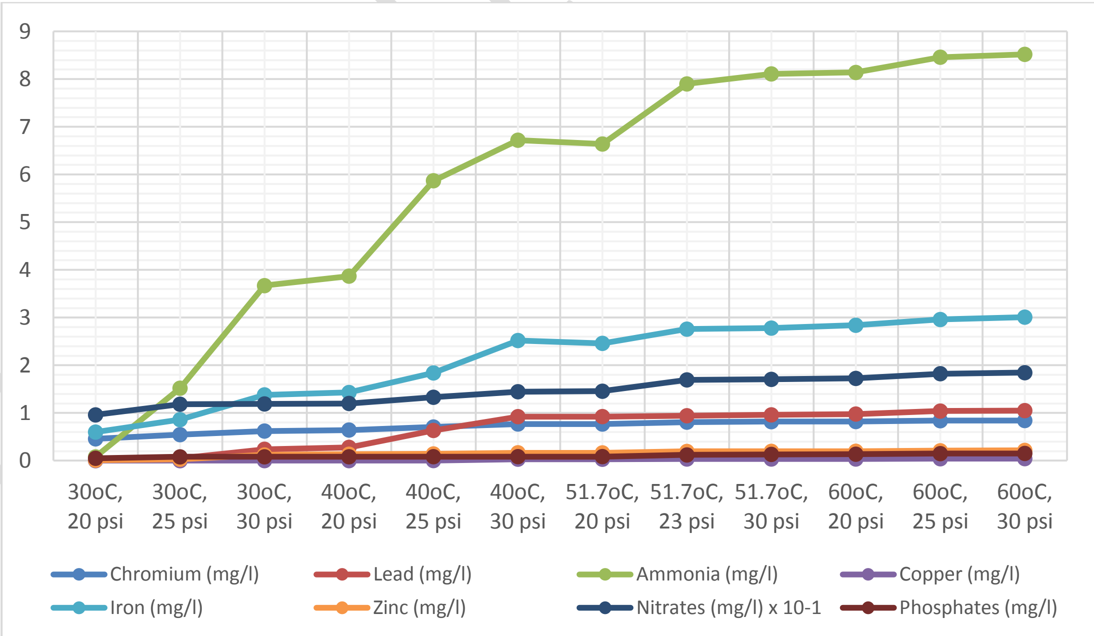

Figure 3d. Concentrations of other pollutants at various pressure and temperature combinations at the heater outlet.

3.4. Analysis of results

The results obtained from the simulations have been grouped according to the similarity in behavior, chemical compositions or test methods of the pollutants. The pollutants whose concentrations are above the regulator's limits at the WIJ pump were considered priority since disposal of produced water at these conditions will attract sanctions and fines from the regulator. Pressures and temperatures have been varied at the selected points along the production process within the design limits of the facility and the effect of these variation on the concentrations of the pollutants for many pressure-temperature combinations recorded. Figures 3a and 3b show that concentrations of hydrocarbon pollutants increased rapidly beyond 14.7 psi while the concentrations of other pollutants increased marginally under the same condition at the WIJ pump. Using this guide, temperature - pressure combination simulations were conducted at the heater outlet. The results are shown in Figures 3c and 3d.

The thermodynamic variables of temperature and pressure have been found to affect the concentration of each of the pollutants in the produced water at the sampling points. The concentrations of the pollutants generally decreased along the production process from the manifold to the WIJ pumps. Figures 4a and 4b below indicate that the concentrations of benzene, lead, ammonia and chromium at the WIJ pumps exceeded the Department of Petroleum Resources' limits.

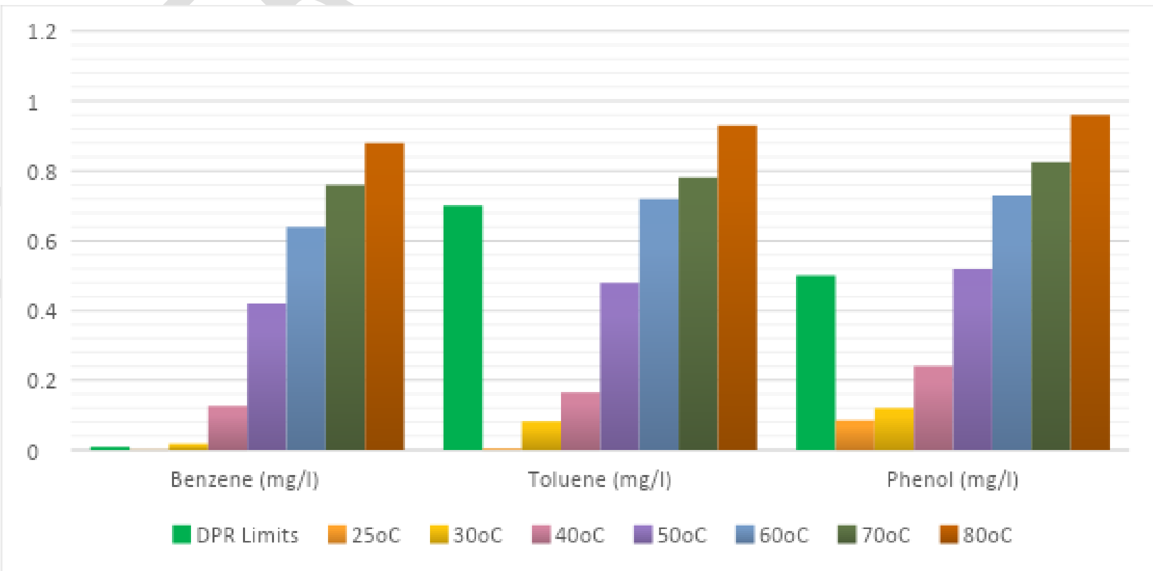

Figure 4a. Concentration of hydrocarbon pollutants against the regulator's limit at various temperatures at the WIJ pump

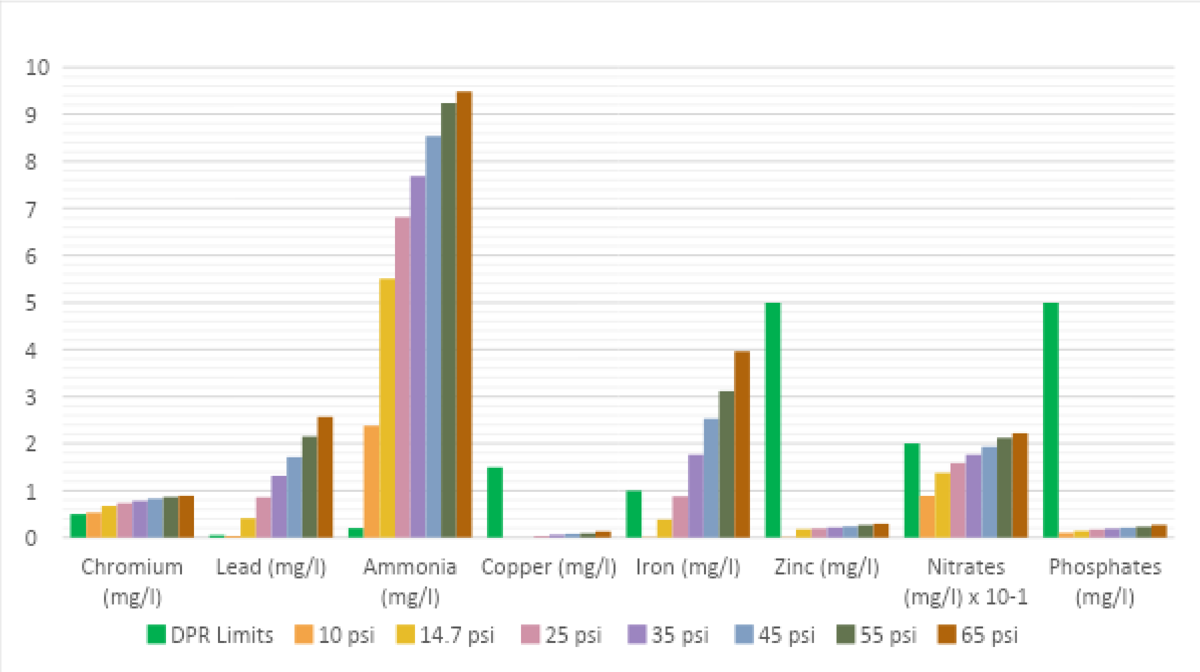

Figure 4b. Concentration of other pollutants against the regulator's limit at various pressures at the WIJ pump.

The results of the simulation process showed that although the concentration of the pollutants decreases along the production process, it increases with temperature and pressure increase at the sample points on the production process. The various components of the production process are designed to operate within temperature and pressure range hence the simulation considered these design range for the thermodynamic variables. The results of the simulation process showed that the temperature of 30°C and pressure of 20 psi at the heater outlet is the optimal condition since it gave the best results which met the regulator's limits for all pollutants (Figures 4c and 4d). Moreover, the Free Water Knock Out (FWKO) vessel which receives the fluid from the line heater can operate at these conditions.

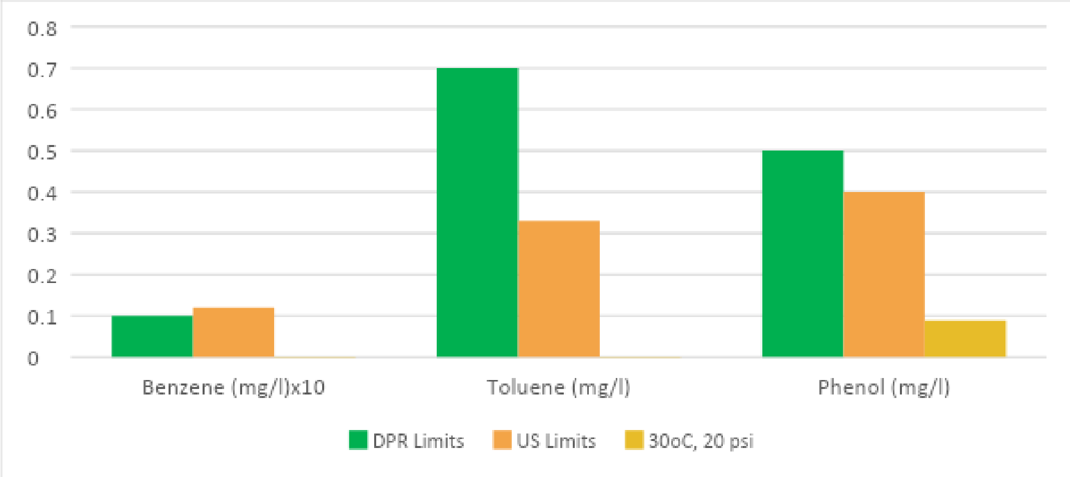

Figure 4c. Concentrations of hydrocarbon pollutants at optimum conditions (30^{o}C,20psi) against Nigeria's and USA's regulatory limits

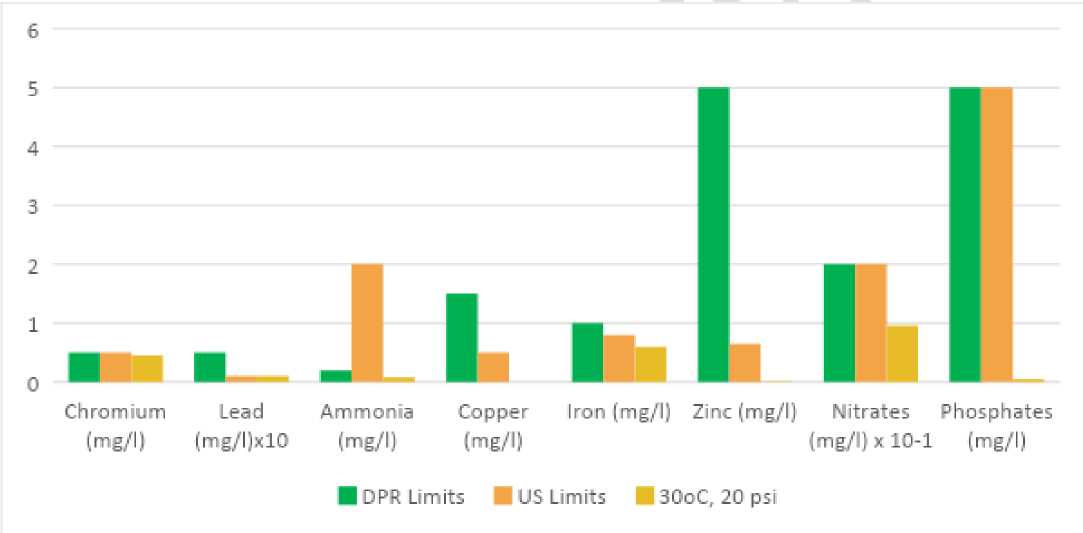

Figure 4d. Concentrations of other pollutants at optimum conditions (30^{o}C,20psi) against Nigeria's and USA's regulatory limits

4. CONCLUDING REMARKS AND OUTLOOK

Environmental process simulation using Hysys 6.2 has been used to show that temperature and pressure variables could reduce the concentration of pollutants in produced water from crude oil production to meet the limits acceptable for disposal by the regulator. The produced water sample at the manifold represent the composition of the produced water before introduction into the flowstation, the sample collected at the heater outlet indicates the composition of the produced water at the mid-point of the production process while the samples collected at the Water Injection (WIJ) pump represents the state of the produced water at the end of the production process prior to disposal. The laboratory results indicate decrease in the concentration of the pollutants in the produced water along the production process but inability to meet the discharge limit set by the regulator hence the need for the research. There were challenges to ensure that quality data on the concentrations of the pollutants in the produced water were used for simulation but some quality control measures like contamination checks and repetition of tests were employed in the laboratory to ensure that good quality data were obtained. The results of the work suggest that there is an optimal point (temperature, pressure) at the which the pollutant concentration is reduced to the minimum without incurring production losses. This result is required to save the cost involved in further treatment of produced water and thereby improves the cost per barrel of produced crude especially for ageing oil fields. The effect of other variables like residence time and production chemicals on the concentration of the pollutants in produced water prior to discharge could also be studied.

COMPETING INTERESTS DISCLAIMER:

Authors have declared that no competing interests exist. The products used for this research are commonly and predominantly use products in our area of research and country. There is absolutely no conflict of interest between the authors and producers of the products because we do not intend to use these products as an avenue for any litigation but for the advancement of knowledge. Also, the research was not funded by the producing company rather it was funded by personal efforts of the authors.

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