APPLICATION OF ENVIRONMENTAL PROCESS ENGINEERING FOR POLLUTANTS REDUCTION AND ENERGY SAVINGS IN CRUDE OIL PRODUCTION PROCESSES

BY

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DECLARATION

I declare that this thesis is my own work carried out by me, except where due acknowledgement has been made in the text and that it has not been submitted either in part or full for any other award than the degree of Doctor of Philosophy of the University of the West of England. Materials from other sources have been duly acknowledged and referenced in line with ethical standards, and the list of publications made from the thesis has been provided.

STANLEY E. NGENE

Signature …………………………

Date ……………………………….

ABSTRACT

Crude oil production generates pollutants whose management require capital and recurrent investment in energy-intensive treatment facilities. Produced water is the main pollutant and the volume generated increases as the oil wells get older. Benzene, toluene, lead, chromium, ammonia, naturally occurring radioactive materials and other compounds are found in produced water at levels higher than allowed by regulatory authorities thereby making the water toxic and raising the need for treatment prior to re-use or disposal. The application of process integration techniques on the production process with targets set on energy savings and pollutants reduction allowed the manipulation of thermodynamic variables of temperature and pressure by the research as an alternative route to achieve the reduction of the concentrations of pollutants in produced water to regulatory limit other than the deployment of the capital-intensive produced water treatment technologies.

Several samples of produced water were collected over a cumulative period of twelve months at onshore and offshore crude oil production facilities. Data resulting from laboratory analysis of these samples and information on the process plants including but not limited to design and operating parameters were used as input in Aspen Hysys 8.8 process simulation software to test the hypothesis of the research. The study has applied results from the “laboratory –

simulation – analysis" methodology to obtain results which indicate that temperature and pressure variation lead to decrease in the concentration of pollutants in produced water and subsequently savings in energy consumption of the production process. The change in concentration decreases across the production process. A temperature of 40^0C – 45^0C and operating pressure at the WIJ pump of the IFS (onshore facility), causes decrease in the concentration of toluene, ammonia and nitrates by 2.28×10^{-3} mg l^{-1} $^{o}C^{-1}$, 5.62×10^{-1} mg l^{-1} $^{o}C^{-1}$ and 1.41×10^{-2} mg l^{-1} $^{o}C^{-1}$ respectively. At the analyser exit of the offshore facility, a pressure of 20 – 30 psi and operating temperature causes the concentrations of toluene, phenol, lead, and chromium to reduce by 6.6×10^{-4} mg l^{-1} psi^{-1}, 2.86×10^{-3} mg l^{-1} psi^{-1}, 4.0×10^{-4} mg l^{-1} psi^{-1} and 5.0×10^{-4} mg l^{-1} psi^{-1} respectively. The best reduction in the concentration of pollutants was achieved by a combination of temperature and pressure at the line heater exit of the onshore facility and at the hydrocyclone inlet of the offshore facility. The concentrations in both cases were lower than the Nigeria oil industry's regulatory limits. Moreover, an annual energy savings of about 379,600KWh and 64,984 KWh could be achieved at the offshore and onshore production facilities respectively. The implication of the research study is that if constituent equipment on the production facility are subjected to the temperature and pressure recommended by the research, the final produced water leaving the facility will be good for disposal without further treatment thereby saving cost and energy for the production process.

DEDICATION

To God Almighty

– The unseen hand in every good success

To my father, Late Chief Samuel Ngene Igwe (Eziokwu bu Ndu)

– He sowed the seed but could not wait for harvest

To my mother, Mrs Grace U. Ngene

– She watered the seed sowed by her husband till harvest.

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PUBLICATIONS FROM RESEARCH

Journal Papers:

1. **Ngene, S.** and Tota-Maharaj, K. (2019) Reduction of Pollutant Toxicity Levels in Produced Water from Crude Oil Production Processes. *Kenya Engineer-Journal of the Institution of Engineers of Kenya*. 40 (1) pp. 34-37.

2. **Ngene, S**., Tota-Maharaj, K., Eke, P. and Hills, C. (2016) Environmental and Economic Impacts of Crude Oil and Natural Gas Production in Developing Countries. *International Journal of Economy, Energy and Environment*. 1(3), pp. 64-73.

3. **Ngene, S**., Tota-Maharaj, K., Eke, P. and Hills, C. (2016) Environmental Implications of Flaring and Venting in Crude Oil and Natural Gas Production. *International Journal of Environmental Monitoring and Analysis*. 4(6), pp. 154-159.

4. **Ngene, S**. and Tota-Maharaj, K. (2019) Effect of Thermodynamic Parameters on the Concentrations of Pollutants in Produced Water from Crude Oil Production. *Journal of Energy Research and Reviews*. 3(3), pp. 1-13. http://www.journaljenrr.com/index.php/JENRR/article/view/30101

5. **Ngene, S**. and Tota-Maharaj, K. (2020) The Influence of Production Chemicals on the Quality of Oilfield Produced Water. *Journal of Sustainable Development of Energy, Water and Environment Systems;* (Under Review).

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TABLE OF CONTENTS

CHAPTER THREE: PRODUCTION OF CRUDE OIL AND NATURAL GAS......................42

CHAPTER FOUR: ENVIRONMENTAL AND ECONOMIC EFFECT OF CRUDE OIL PRODUCTION…………………………………………………………………..........103

LIST OF FIGURES

LIST OF TABLES

LIST OF APPENDICES

LIST OF ABBREVIATIONS

GDP:	Gross Domestic Product
GRP:	Gross Regional Product
IEA:	International Energy Agency
UNPF:	United Nations Population Fund
OSPAR:	Oslo and Paris Commission
HVAC:	Heating, Ventilation and Air-Conditioning
LNG:	Liquified Natural Gas
GHG:	Greenhouse Gas
EPA:	Environmental Protection Agency
FPSO:	Floating, Production, Storage and Offloading
WIJ:	Water Injection
IFS:	Izombe Flowstation
EGASPIN:	Environmental Guideline and Standard for the Petroleum Industry in Nigeria.
DPR:	Department of Petroleum Resources
OFC:	Oilfield Production Chemical
MEG:	Monoethylene Glycol
DEG:	Diethylene Glycol
TEG:	Triethylene Glycol
API:	American Petroleum Institute

NORM:	Naturally Occurring Radioactive Material
ANSI:	American National Standards Institute
CFC:	Chlorofluorocarbon
HFC:	Hydrofluorocarbon
PFC:	Perfluorocarbon
GWP:	Global Warming Potential
VOC:	Volatile Organic Compound
NMHC:	Non-Methane Hydrocarbon
CRM:	Carbon Dioxide removal Method
SRM:	Solar Radiation Management
OML:	Oil Mining Lease
PW:	Produced Water
ASTM:	American Society for Testing and Materials
APHA:	American Public Health Association
BTEX:	Benzene Toluene Ethylbenzene and Xylene
GC-FID:	Gas Chromatography with Flame Ionisation Detector
TDS:	Total Dissolved Solids
NRTL:	Non-Random Two Liquid
FWKO:	Free Water Knock Out

CHAPTER ONE

INTRODUCTION

1.1 BACKGROUND TO THE STUDY:

The petroleum industry has been a vital source of energy to the world for the last six decades and will likely remain so in many decades to come; even under the most optimistic assumptions about the growth in alternative energy sources. It is believed that even if the use of renewable energy triples over the next 25 years, the world is still likely to depend on fossil fuels for at least 50 percent of its energy needs. The growing demand for energy in the world, believed to be fuelled by the dramatic population growth, could be attributed to industrialisation of emerging economies, increase in wealth in emerging markets, globalisation, and energy security concerns (*Chevron, 2014*). The world currently has over seven billion people and an average annual growth rate of 86 million people (*Roser et al., 2019*). The growth of the economies of the emerging markets (China, India etc) has influenced output and standard of living and thus the energy demand as consumers want cars, air conditioners, refrigerators, and other high energy consuming luxury machines. Although energy demand is typically driven by short-term considerations (e.g. Gross Domestic Product (GDP) growth, weather, transport needs), long-term concerns over energy security around the world have led to payment of high premium for energy assets. The world's economy has been developing with oil and gas as its lifeblood for over a hundred years (*Berdzanadze, 2015*). The upstream part of the oil and gas industry has become much more capital intensive over the past decade for both conventional and non-conventional sources of petroleum; mostly owing to depletion of cheaper conventional resources. The new reality in the industry therefore represents a fundamental change for the global economy, requiring greater capital to maintain oil supplies, and higher prices to sustain investment; even as the price of oil plummet (*Mueller et al., 2015*).

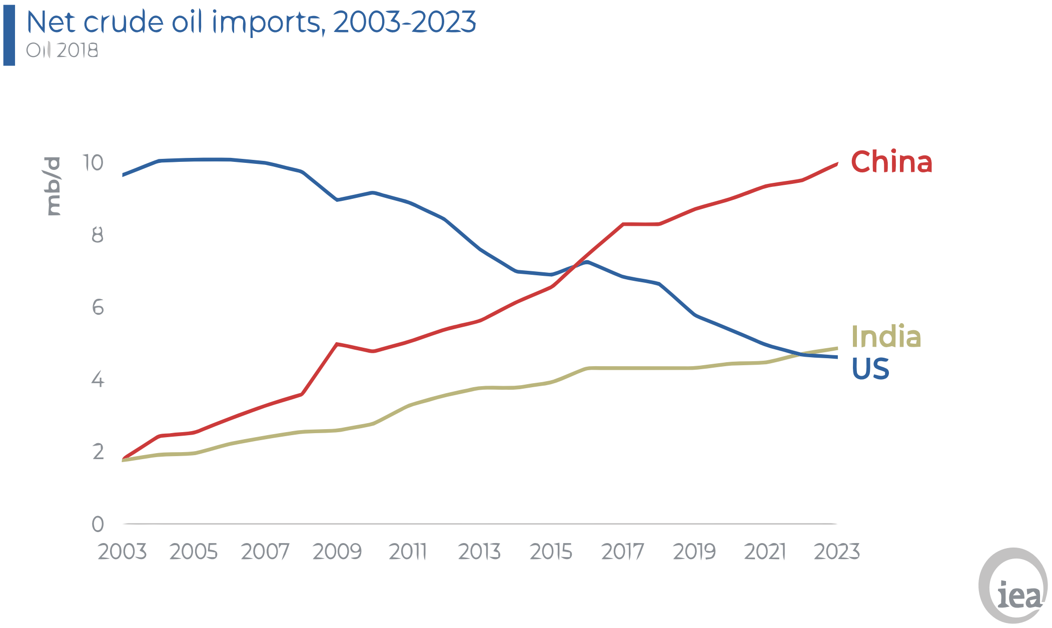


Figure 1.1: Net crude oil imports of the US, China and India (*IEA ,2018*)

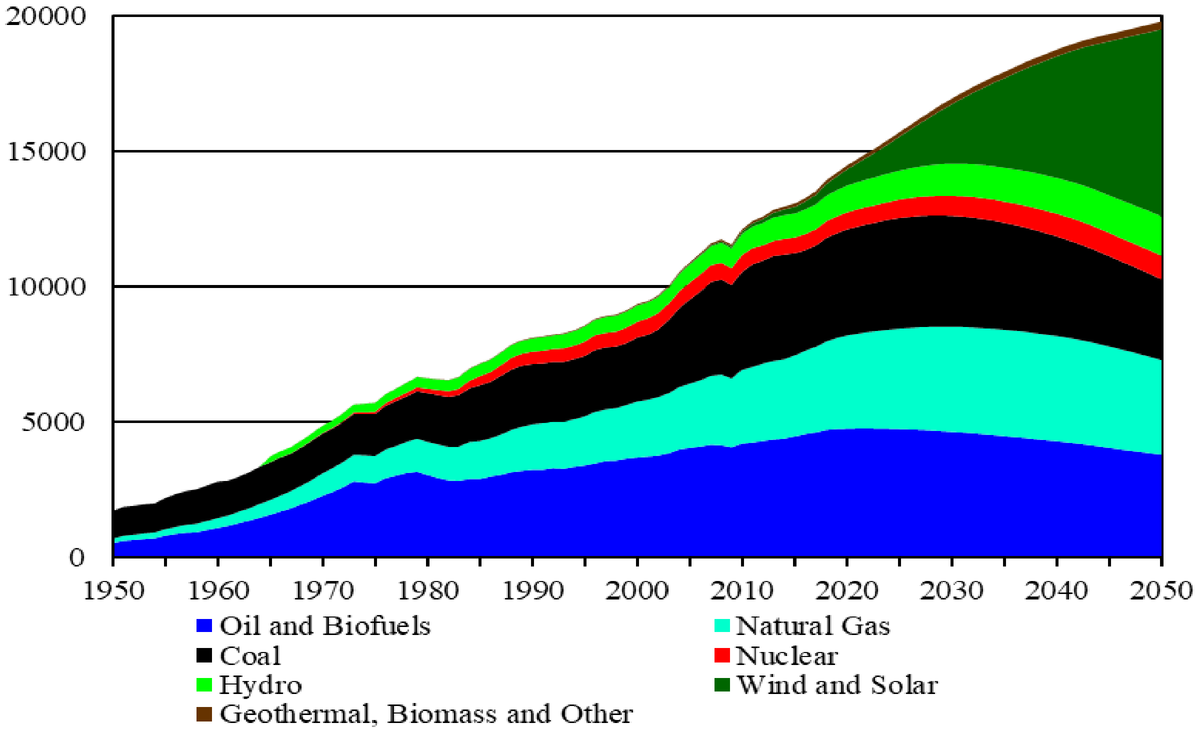


Figure 1.2: World primary energy consumption (1950 – 2050) (*Patterson, 2018*)

Oil and gas production consume enormous amount of energy, produces various types of wastes, and leads to emission of non-environmentally friendly compounds into the atmosphere. Apart from the normal energy demand of process facilities, a typical mature field would require a variety of production enhancing techniques that demand considerable energy input. These may include water injection for production aquifer pressure support, increased gas compression due to declining reservoir pressure, increased dependence on production lift techniques, increased complexity and reduced reliability of facilities operations arising from a variety of factors such as increasing volumes of water produced with oil production (*Vanner, 2005*). The energy consumption relative to oil and gas production increases at the later stage of the life of a field. The production facilities are normally designed to cater for this inherent "inefficiency".

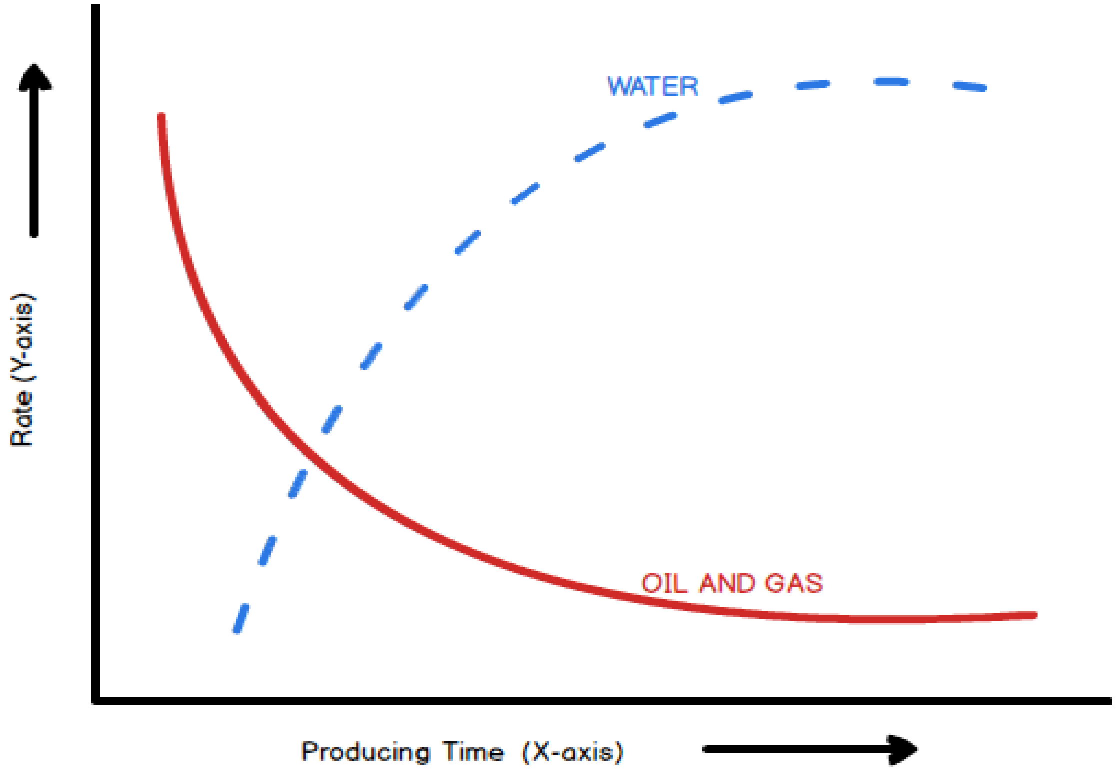


Figure 1.3: Produced water production over time in a conventional oil and gas well (adapted from *Veil, 2015*)

In general, produced water is seven to eight times greater by volume than oil produced at any oilfield (*Igwe et al., 2013*). Produced water may contain a wide variety of organic and inorganic pollutants, suspended solids, salt water used for water flooding, production chemicals, and low concentrations of hazardous substances that occur naturally in the reservoir, such as heavy metals, aromatic hydrocarbons, alkyl phenols and radioactive substances (*OSPAR Commission, 2009; Hansen et al., 1994*). The total volume of produced water estimated for 2012 in the United States is about 21.2 billion barrels (*Veil, 2015*). Additional production from the rest of the world is estimated at a volume of more than 50 billion barrels per year (*Duhon, 2012*). The volume of produced water generated is an immense challenge to oil and gas production especially in offshore petroleum platforms and it increases as the reservoir is depleted.

Leaks from oil and gas production equipment e.g. compressors, valves, pumps and flanges as well as routine venting results in emission of greenhouse gases especially methane into the atmosphere. The petroleum industry is the largest source of emission of volatile organic compounds in Canada (*Environment and Climate Change Canada, 2015*). It also emits oxides of nitrogen (NOx). These groups of chemicals contribute to the formation of ground–level ozone (smog). Exposure to ozone is linked to a wide range of health issues including aggravated asthma, increased emergency room visits, hospital admissions, and premature deaths *(Brunekreef et al., 2002)*. Elevated levels of Benzene have been detected near natural gas production sites (*Alvarez et al., 2012*). Other hazardous air pollutants like hydrogen sulphide and formaldehyde are also emitted from oil and gas production.

Table 1.1: World energy, economy, and climate change: 2000-2050 (2018 Scenario) (*Patterson, 2018*)

	2000	**2010**	**2020**	**2030**	**2040**	**2050**
World Energy Consumption (Mtoe):						
Oil and Biofuels	3,701	4,209	4,759	4,644	4,296	3797
Natural Gas	2,065	2,731	3,441	3,869	3,884	3,489
Coal	2,356	3,606	3,903	4,095	3,668	2,977
Nuclear	584	626	631	741	839	872
Hydro	601	777	986	1,177	1,321	1,454
Wind and Solar	7	85	597	2,198	4,484	6,892
Geothermal, Biomass and Other	42	86	146	210	249	284
Total	9,356	12,119	14,463	16,935	18,741	19,766
Gross World Product (trillion $)	63.3	91.3	129.5	175.0	222.5	268.6
Carbon Dioxide Emissions (Gt)	23.6	31.1	35.1	36.4	33.9	29.0
Global Temperature Anomaly (°C)	0.66	0.89	1.09	1.34	1.58	1.79

Although statistics show that production of oil and gas has been on the increase for over a decade, the demand has continued to outweigh the supply. From estimation, it has been found that to meet the projected increase in world oil demand, the total petroleum supply in 2030 is required to reach 118 million barrels per day from 80 million barrels per day as of the year 2003 (*Berdzanadze, 2012*). New oil and gas reserves have been discovered across the African continent including Kenya, Uganda, Tanzania, Mozambique and Ghana in the last few years. There have also been discovery of conventional oil and gas in Cyprus and billions of barrels of recoverable oil shale in Israel. In Asia, Vietnam and Papua New Guinea are among the latest countries to become oil and gas producers just like Guyana in South America. In some of these countries, production has already started; thereby subjecting more area of the world to the negative environmental effects of oil and gas production. Oil and gas deposits in deep offshore locations are being produced today. The production of non-conventional oil and gas deposits by fracking in shales has also brought another dimension into the challenges posed by oil and gas activities as the type of pollution generated by fracking varies from that due to normal conventional oil and gas production.

Several stringent environmental legislations on the production of oil and gas have been promulgated by various states and countries in order to preserve the hydrocarbon reserves, protect the people and the environment. These laws have significantly raised the cost that may be required to remedy the environmental effects that may result due to oil and gas production. The potential to pollute the environment increases as petroleum hydrocarbons continue to be used as the principal source of energy. When this type of pollution occurs, stemming from oil and natural gas production operations, it often results in huge disturbances and disastrous consequences for the biotic and abiotic component of the natural ecosystem (*Mueller et al., 1992*).

Waste produced in the process of oil and gas production poses a risk to the people and the environment. The release of gaseous pollutants to the atmosphere due to oil and gas production is also a threat to life. These challenges get tougher as the oil and gas fields being produced get older. Engineers have applied energy efficient and modern facilities in new production process plants and in existing plants, process integration and heat recuperation have been applied for reduction of energy consumption *(Rangaiah, 2016)*. Process integration techniques like pinch technology, a methodology for minimizing energy consumption of chemical process by calculating thermodynamically feasible energy targets (or minimum energy consumption) and achieving them by optimising heat recovery systems, energy supply methods and process operating conditions, has been applied to several process plants; and has been successful *(Kemp, 2007)*. Pinch analysis has been applied to improve energy efficiency of a mechanical pulp and paper mill (*Rhuohinen et al., 2010*). In offshore facilities, replacement of gas turbines with bottoming cycles have been found to produce up to 22 % savings in fuel consumption and 22 % CO_2 reduction (*Mazetti, 2013*). Heating, Ventilation and Air-conditioning (HVAC) equipment manufacturers have made great strides in the past 25 years, increasing the efficiency of components by as much as 40%. This has aided central plant optimisation in house cooling process to deliver energy savings of up to 60 % (*Klee et al., 2011*). Simulation and optimisation have been used to remove up to 75% of total produced CO_2 from steel plant flue gases using the conventional Methyl Ethyl Amine (MEA) based removal method (*Tobiesen et al., 2011*). Furthermore, Ferretti et al., (2008) found that Simulation based decisions in a steel plant may lead to a significant reduction (more than 20%) of the daily consumption of electric energy. Optimisation and modelling have been applied for energy savings and pollutants reduction in wastewater treatment plants (*Nolasco, 2014*); using performance indicator analysis as a basis (*Wennerholm, 2014*). In the fluid milk processing industry, decrease in energy use, greenhouse gas emissions and water use could be achieved through evaluations of the impact of the farm and off-farm processes involved in the production of a litre of milk. This may however be done more efficiently through the use of software tools for farm management simulation and process simulation (*Tomasula et al., 2014*); such optimisation using energy audit approach on the pasteurization process has produced about 18 % improvement in the process load as well as the process energy cost (*Modi et al., 2014*). Steam system efficiency optimisation following energy assessment of the J.R. Simplot Fertilizer plant in Pocatello, Idaho, United States of America (USA) saved approximately 75,000 MMBtu in annual fuel consumption (*Stluka et al., 2009*).

Process simulation and optimisation have been applied for energy efficiency and pollution reduction in cement plants (*Benhelal et al., 2012*), ethanol plants (*Ahmetovic et al., 2010*), crude distillation units of refineries (*Bandar et al., 2015*), pulp and paper mill (*Ji et al., 2012*) and Liquefied Natural Gas plants (*Sun et al., 2013*). Life Cycle Analysis (LCA) is today considered an appropriate method for accessing environment impact and selecting new technology to reduce emission for the steel industry (*Iosif et al., 2009*). For brown fields, oil and gas fields that have matured to production plateau or even progressed to declining stages, it becomes necessary to simulate and optimise the process incorporating economic effects e.g costs, yield, and long-term cost of ownership, with environmental effects e.g life cycle, sustainability and contingent cost analysis (*Kohlbrand, 1998*).

Process integration, a family of methodologies for combining several processes to reduce the consumption of resources or harmful emission to the environment, started as mainly heat integration simulation by the energy crisis in the 1970s (*Friedler, 2010*). One of the first related works was investigated by *Hohmann, (1971*). Bodo Linnhoff and his Supervisor, the Late John Flower, at the University of Leeds, United Kingdom (UK), continued with this research and in 1977 developed the basis of pinch technology which is now considered as the foundation of heat integration. The first publication of this work appeared in 1978 *(Linnhoff et al, 1978*). Similar works was being done in Japan around the same time (*Umeda et al., 1978, Umeda et al., 1979*). In the early 1990's, Nilsson and Sunden combined the MIND method with pinch technology. The pinch technology was focused on the thermal design while the MIND method focused on structural design to reach the best solution (*Nilsson et al., 1992,* *Nilsson et al., 1994*). The combination of MIND method and pinch technology was also used to study how the methods could be combined in the analysis of industrial energy systems and how total energy system of a mill is influenced by improved energy utilization (*Bengtsson et al., 2002*). In many studies, optimisation and simulation tools have been combined in such a manner that one of the tools are used at the start and the results that are obtained are then used in the second tool (*Mardan, 2012*). *Roy et al (2010)* have used optimisation and simulation techniques in order to optimise a system and obtain an approximate solution for a given set of input variables. The optimisation technique was used to minimize the size of wind-battery while the Monte-Carlo simulation was used to predict the system behaviour and validate the solutions provided by the optimisation technique.

1.2 PROBLEM STATEMENT:

Engineers, scientist and researchers have done so much work on pollutant reduction and energy savings in process plants. Several research projects at the commercial level and academically have also combined process simulation and optimisation techniques for this purpose in wastewater treatment plants, pulp and paper mills, cement manufacturing plants, steel mills, Liquefied Natural Gas (LNG) Plants and even in crude distillation units of the refinery. However, knowledge on the application of these principles to crude oil production in the upstream sector of the oil and gas industry is currently not available. This study seeks to apply a combination of process integration, simulation and optimisation on crude oil production process in the upstream sector of the petroleum industry. The research project will seek to:

i. Identify the various wastes streams and pollutants generated by crude oil production process and the risk they pose to man and his environment.
ii. Classify the sources of pollutant responsible for the creation of the waste streams and the key compounds responsible for these pollutions.
iii. Identify the effect of pollutant generation on energy loss from crude oil production process.
iv. Highlight the similarities and differences between the onshore and offshore production of crude oil.
v. Discover how the difference in the location of the production process impact on the design and the performance of the plant.
vi. Identify the peculiar difficulties likely to be encountered in attempt to control release of pollutants into the environment in offshore locations.
vii. Categorise the indicators that are suitable or irrelevant when comparing onshore and offshore production process plant and how they could be implemented.
viii. Study the variation of the energy requirement and performance of the production process plant over time and identify the main causes of the changes.

ix. Assess the possibilities of optimisation for energy savings through pollutants reduction in crude oil production process, with respect to thermodynamic, economic and environmental criteria.

x. Evaluate the effects of the various polluting compounds on the generation of pollutants in crude oil production process and determine the optimum mix required to generate the minimum waste stream or waste stream with minimum impact on the environment.

The result of this research project will be useful in the design and modification of production processes and other process plants where minimum impact on the environment and energy savings are desired. As a result of the promulgation of stricter environmental regulations by several countries, oil and gas companies have been paying so much on penalties for emission and waste discharge. This research will help operators comply with emission limits and handling of wastes in crude oil production.

1.3 RATIONALE, AIMS AND OBJECTIVES OF THE STUDY:

The rationale of the research project is to assess existing crude oil production process, identify the various ways through which pollutants and wastes are generated and thereafter released to the environment and suggest ways to manage these sources of release in order to optimise the energy efficiency of the process, check environmental effect and operate within the state's regulatory provisions. In the case of energy release or loss from the process through pollutants generation, the research will study the relationship and suggest the appropriate way to handle the pollutants to minimise energy loss so as to ensure it does not pose a threat to the environment.

The overall goal of the study is to evaluate the effect of a combination of optimisation and process simulation on process plants; relying on the results achieved to suggest an environmentally friendly and energy efficient model for the design of oil and gas production process plants.

The specific research objectives are to:

I. Apply a systematic framework for simulating, analysing and optimising existing and future crude oil production process plants;
II. Evaluate the efficiency of the combination of optimisation and process simulation techniques on waste / pollutants generation in crude oil production process;
III. Examine the relationship, if any, between the improvement in energy efficiency of crude oil production process and the volume of wastes / pollutants generated from the process;
IV. Generate generic models that describe adequately the crude oil production processes;
V. Investigate the thermodynamic, economic and environmental trade-off of crude oil production activities.

VI. Determine the energy savings due to the application of the research results on production facilities

1.4 OUTLINE OF THE THESIS CONTENT:

The thesis of the research work has been organised into nine chapters and outlined as follows:

Chapter 1: Introduction - This chapter gives the background to the study, statement of the problem, the outline of the thesis content and enumerates the rationale, aims and objectives of the research work.

Chapter 2: Origin and Composition of Crude Oil - In this chapter, the literature of the earliest discoveries and use of crude oil as well as the beginning of the petroleum industry has been reviewed. The theories behind the formation of crude oil and the composition of petroleum have also been discussed.

Chapter 3: Production of Crude Oil and Natural Gas - This chapter gives a detailed review of crude oil and natural gas production process including the roles of chemicals in the production process, the associated pollutants and wastes, the concepts of energy efficiency, energy savings, energy consumption and energy loss.

Chapter 4: Environmental and Economic Effects of Crude Oil Production - The economic benefits and environmental impacts of crude oil production are discussed in this chapter. The potential climate and human health concerns as a result of the release of natural gas, produced water and crude oil to the environment were discussed.

Chapter 5: Pollution Reduction and Energy Saving Processes - In this chapter the concept of process / system integration, energy / mass integration, process simulation and optimisation with respect to crude oil production have also been reviewed.

Chapter 6: Methodology and Materials - This chapter explains the materials and tools used for the study and the methods employed to achieve the set objectives including the general strategy.

Chapter 7: Results and Discussions - This chapter shows the documentation of the results obtained from all the stages of the research work: sampling and measurements, laboratory analysis, process simulation and optimisation. It also contains analysis of these results and application of them on case study processes.

Chapter 8: Conclusions and Recommendations - In this chapter, conclusions are drawn from the results obtained and the analysis made in the previous chapter. Based on these conclusions, areas for potential further studies were identified and recommendations made to that effect.

ORIGIN AND COMPOSITION OF CRUDE OIL

2.1 INTRODUCTION

Crude oil has been in use for over 5000 years. It was collected from seepages around rivers and hills at the earliest times and used in its natural state either for medicinal purposes or as oil in lamps. As the demand for crude oil increased, the search for it below soil surface started and subsequently the digging of wells for oil. More demands led to commercial search for crude oil and the establishment of companies primarily for the exploration and production of crude oil.

Figure 2.1: Earliest use of crude oil in lamps to provide light and heat (*source: AncientPages.com, 2018)*

Although some scientists have put forward theories to show that crude oil has inorganic origin, the hypothesis that it is of organic origin is the more generally accepted one. It is believed to have been formed from biological matters, left behind by very ancient lives which become subjected to high temperature under the absence of oxygen. Crude oil is principally made up of elemental carbon and hydrogen; also containing nitrogen, oxygen, sulphur in small amounts and traces of metals.

2.2 EARLY DISCOVERIES AND HISTORY OF THE OIL INDUSTRY

The ancient Sumerians, Assyrians and Babylonians used crude oil collected from large seeps at Tuttul on the Euphrates River as medicine for wound and as oil in lamps to provide light about 5000 to 6000 years ago (*Vagabond, 2009*). This represents the earliest recorded use of crude oil. Around the same time in Iran, between 6000 and 2000 BCE, the first discoveries of natural gas seeps were made *(Curley, 2011)*. At about four thousand years ago, asphalt was used in the construction of the walls and towers of Babylon *(Simanzhenkov and Idem, 2003)*. There were also great quantities of asphalt found on the bank of the River Issus, one of the tributaries of the Euphrates which exploited by the ancient Persians and Romanians, especially the upper levels of their society, for medicinal and lighting purposes. Petroleum was also used in ancient China more than 2000 years ago. Crude oil in its raw state without refining was first discovered, extracted, and used in China in the first century BCE. In addition, the Chinese were the first to use petroleum as fuel as the early as the fourth century BCE (*Gao and Kao, 2008*).

The world's earliest oil wells were drilled in China in the 4th Century around 347 AD. They had depths of up to about 800 feet (240 m) and were drilled using bits attached to bamboo poles (*Vogel, 1993*). The oil was burned to evaporate brine and produce salt. By the 10th century, extensive bamboo pipelines connected oil wells with salt springs. The ancient records of China and Japan are said to contain many allusions to the use of natural gas for lighting and heating. Crude oil was known as *burning water* in Japan in the 7th century (*Encyclopaedia Britannica, 11th Edition*).

Figure 2.2: Tar bubble at La Brea Tar Pits, California, USA (Weber, 2010)

The first streets of Baghdad, Iraq were paved with tar derived from petroleum that became accessible from the oil fields in the region. In the 9th century, oil fields were exploited in the area around modern Baku, Azerbaijan. In the 10th century these fields were in existence and by 13th century the output of the fields has reached hundreds of shiploads. Around this period, there was distillation of Petroleum as observed by the Persian alchemist, Muhammad Ibn Zakariya Razi (*Al-Hassan, 2008*). There was production of kerosene in the alembic (*al-ambiq*), *(Ajram, 1992*) which was mainly used for kerosene lamps (*Bilkadi, 1995*). Arab and Persian chemists also distilled crude oil to produce flammable products for military purposes. Distillation became available in Western Europe by the 12th century (*Riva Jr and Atwater, 2008*). It has also been present in Romania since the 13th century, being recorded as pacura (*Istoria Romania Vol II, P300, 1960*).

The earliest mention of petroleum in the Americas could be traced to Sir Walter Raleigh's account of the Trinidad Pitch lake in 1595. There was also the account of the visit of Joseph de la Roche d'Allion in 1642 to the oil springs of New York which was published in Gabriel Sagard's *Histoire du Canada*. The work of Peter Kalm, *Travels into North America*, published first in 1753 showing the map of the oil springs of Pennsylvania was also among the earliest account of petroleum in the Americas (*Encyclopaedia Britannica, 11th Edition)*.

Figure 2.3: (a) Aerial view of Trinidad's Pitch Lake, West Indies which covers 40 hectares and reported to be 75 meters deep.

Figure 2.3: (b) Tour-guide of Trinidad's Pitch Lake- the largest natural deposit of asphalt in the world (Source: Seaman, 2014)

In 1710 the Russian-born Swiss physician and Greek teacher, Eirini d'Eyrinys discovered asphaltum at Val-de-Travers, (Neuchatel). He established a bitumen mine, *de la Presta,* there in 1719 that operated until 1986 (*Stoddart, 1883*). In 1745 under the Empress Elizabeth of Russia the first oil well and refinery were built in Ukhta by Fiodor Priadunov. Through the process of distillation of the crude oil he received a kerosene-like substance, which was used in oil lamps by Russian churches and monasteries.

The modern petroleum industry began in the 19th century with the refining of paraffin from crude oil. The Scottish chemist, James Young, in 1847 noticed a natural petroleum seepage in the Riddings colliery at Alfreton, Derbyshire from which he distilled a light thin oil suitable for use as lamp oil, at the same time obtaining a thicker oil suitable for lubricating machinery. The first ever well drilled with percussion tools was drilled to a depth of 21 meters in 1846 in Baku (*Mir-Babayev, 2018*). It was drilled for oil exploration thirteen years before the Drake's well was drilled in Pennsylvania. Young, noticing that the oil was dripping from the sandstone roof of the coalmine, theorized that it somehow originated from the action of heat on the coal seam and from this thought that it might be produced artificially. Following up this idea, he tried many experiments and eventually succeeded, by distilling cannel coal at a low heat, a fluid resembling petroleum, which when treated in the same way as the seep oil gave similar products. Young found that by slow distillation he could obtain some useful liquids from it, one of which he named "paraffine oil" because at low temperatures it congealed into a substance resembling paraffin wax (*Russel, 2003*).

Abraham Pineo Gesner, a Canadian geologist developed a process to refine a liquid fuel from coal, bitumen and oil shale. His new discovery, which he named kerosene, burned more cleanly and was less expensive than competing products, such as whale oil. In 1850, Gesner created the Kerosene Gaslight Company and began installing lighting in the streets in Halifax and other cities. By 1854, he had expanded to the United States where he created the North American Kerosene Gas Light Company at Long Island, New York. Demand grew to where his company's capacity to produce became a problem, but the discovery of petroleum, from which kerosene could be more easily produced, solved the supply problem.

In 1846 the first oil well in the world was drilled in Asia, on the Aspheron Peninsula North-East of Baku by Major Alekseev (*Mir-Babayev, 2018*). Ignacy Lukasiewicz improved Gesner's method to develop a means of refining kerosene from the more readily available crude oil seeps in 1852 and the first crude oil mine was built in Bobrka, near Krosno in Central European Galicia (Poland) in 1854 (*Craig et al., 2018*). These discoveries rapidly spread around the world, and Meerzoeff built the first modern Russian refinery in the mature oil fields at Baku in 1861. At that time, Baku produced about 90% of the world's oil.

Edwin Drake’s 1859 well near Titusville, Pennsylvania is popularly considered the first modern oil well. Drake's well is probably singled out because it was drilled, not dug; because it used a steam engine; because there was a company associated with it; and because it touched off a major boom. However, the first well ever drilled anywhere in the world, which produced oil, was drilled in 1857 to a depth of 280 feet by the American Merrimac Company in La Brea in Southeast Trinidad in the Caribbean (*Down, 2018*). Additionally, there was considerable activity before Drake in various parts of the world in the mid-19th century. A group directed by Major Alexeyev of the Bakinskii Corps of Mining Engineers hand-drilled a well in the Baku region in 1846 (*Matveichuk, 2004*). There were engine-drilled wells in West Virginia in the same year as Drake's well (*McCain and Allen, 1994*). An early commercial well was hand dug in Poland in 1853, and another in nearby Romania in 1857. At around the same time the world's first, but small, oil refineries were opened at Jaslo, in Poland, with a larger one being opened at Ploiesti, in Romania, shortly after. Romania is the first country in the world to have its crude oil output officially recorded in international statistics, namely 275 tonnes. In 1875, crude oil was discovered by David Beaty at his home in Warren, Pennsylvania. This led to the opening of the Bradford oil field, which, by the 1880s, produced 77 percent of the global oil supply. However, by the end of the 19th century, the Russian Empire, particularly the Branobel company in Azerbaijan, had taken the lead in production. Samuel Kier established America's first oil refinery in Pittsburgh on Seventh avenue near

Grant Street, in 1853. In addition to the activity in West Virginia and Pennsylvania, an important early oil well in North America was in Oil Springs, Canada in 1858, dug by James Miller Williams (*Elford, 1982*). The discovery at Oil Springs touched off an oil boom which brought hundreds of speculators and workers to the area. New oil fields were discovered nearby throughout the late 19th century and the area developed into a large petrochemical refining centre and exchange (*May,1998*). The modern US petroleum industry is considered to have begun with Edwin Drake's drilling of a 69-foot (21 m) oil well in 1859 (*Gordon, 2008*), on Oil Creek near Titusville, Pennsylvania, for the Seneca Oil Company. The well originally yielded 25 barrels per day but the end of the year output was at the rate of 15 barrels per day. The industry grew through the 1800s, driven by the demand for kerosene for oil lamps. It became a major national concern in the early part of the 20th century; the introduction of the internal combustion engine provided a demand that has largely sustained the industry to this day. Early "local" finds like those in Pennsylvania and Ontario were quickly outpaced by demand, leading to "oil booms" in Ohio, Texas, Oklahoma, and California.

By 1910, significant oil fields had been discovered in the Dutch East Indies (1885, in Sumatra), Persia (1908, in Masjed Soleiman), Peru (1863, in Zorritos District), Venezuela (1914, in Maracaibo Basin), and Mexico, and were being developed at an industrial level. Significant oil fields were exploited in Alberta (Canada) from 1947. First offshore oil drilling at Oil Rocks (Neft Dashlari) in the Caspian Sea off Azerbaijan eventually resulted in a city built on pylons in 1949. Availability of oil and access to it, became of "cardinal importance" in military power before (*Encyclopaedia of the American Nation*) and after World War I, particularly for navies as they changed from coal, but also with the introduction of motor transport, tanks and airplanes. Such thinking would continue in later conflicts of the twentieth century, including World War II, during which oil facilities were a major strategic asset and were extensively bombed (*Baldwin, 1957*). In 1938, vast reserves of oil were discovered in the Al-Ahsa region along the coast of the Persian Gulf.

John D. Rockefeller, who began his career in refining, became the industry's first "baron" in 1865, when he formed Standard Oil Company. By 1879, Standard Oil controlled not only 90% of America's refining capacity, but also its pipelines and gathering systems. By the end of the 19th century, Standard Oil's dominance had grown to include exploration, production, and marketing. Today ExxonMobil is the successor company to Standard Oil. While Rockefeller was building his U.S. empire, the Nobel and Rothschild families were competing for control of production and refining of Russia's oil riches. In search of a global transportation network to market their kerosene, the Rothschild family commissioned the first oil tankers from a British trader, Marcus Samuel. The first of these tankers was named the Murex, after a type of seashell, and became the flagship of Shell Transport and Trading, which Samuel formed in 1897.

Royal Dutch Petroleum got its start in the Dutch East Indies in the late 1800s, and by 1892 had integrated production, pipeline, and refining operations. In 1907, Royal Dutch and Shell Transport and Trading agreed to form the Royal Dutch Shell Group. Further, in 1907 the discovery of oil in Iran by a British former gold miner and a Middle Eastern shah led to the incorporation of the Anglo-Persian Oil Company. The British government purchased 51% of the company in 1914 to ensure sufficient oil for the Royal Navy in the years leading up to World War I. The company became British Petroleum in 1954 and is now BP.

Today, these three companies: ExxonMobil, Shell, and BP are considered the original "super majors" of the oil and gas industry. In the United States, the 1901 discovery of the Spindletop field in Texas eventually spawned companies such as Gulf Oil, Texaco, and others. The dominance of the United States during this era was illustrated by the fact that regardless of where oil was produced in the world, its price was fixed at that of the Gulf of Mexico. Beginning with World War I, oil became a strategic energy source and a tremendous geopolitical prize. In the 1930s, Gulf Oil, BP, Texaco, and Chevron were involved in concessions that made major discoveries in Kuwait, Saudi Arabia, and Libya. Based on those discoveries, a cartel of seven companies was formed that controlled the world's oil and gas business for much of the twentieth century. Known as the Seven Sisters, they included: Exxon (originally Standard Oil), Royal Dutch/Shell, BP, Mobil, Texaco, Gulf, and Chevron.

2.3 ORIGIN OF CRUDE OIL AND NATURAL GAS

The search for the origin of petroleum dates to the 18th and early part of the 19th century, when the chemical nature of petroleum was not known. Abraham Gottlob Werner and supporters of neptunism in the 18th century considered basaltic sills as solidified oils or bitumen. While these concepts proved not solid, the primary idea of an association between petroleum and magmatism has then persisted as Alexander von Humboldt proposed an inorganic abiogenic hypothesis for petroleum formation after he saw petroleum springs in the Bay of Cumaux (Cumaná) in Venezuela. He is quoted as saying in 1804, "the petroleum is the product of a distillation from great depth and issues from the primitive rocks beneath which the forces of all volcanic action lie". As it is said above other prominent advocate of the abiogenic hypothesis included Dmitri Mendeleev (1834 -1907) and Marcelin Berthelot (1827-1907). The Soviet Russian geologist Nikolai Alexandrovitch Kudryavtsev also proposed the modern abiotic hypothesis of petroleum in 1950s. On the basis of his analysis of the Athabasca Oil Sands in Alberta, Canada, he concluded by denying the existence of "source rocks" that could form the enormous volume of hydrocarbons, and as consequence he offered abiotic deep petroleum as the most admirable explanation. (Humic coals have since been proposed for the source rocks. Others who continued Kudryavtsev's work are Emmanuil B. Chekaliuk, Petr N. Kropotkin, Georgi E. Boyko Vladimir B. Porfir'ev, and Vladilen A. Krayushkin. In the 21^{st} century, the most prominent supporter of the hypothesis are Astronomer Thomas G. and Jack Kenney.

Petroleum origin and formation had been discussed from two opposing theoretical hypothesis as a polarized topic of scientists' debates. These theories are abiogenesis and biogenesis. Abiogenesis explains that petroleum is of inorganic origin. It is the oldest of the theories and suggests that petroleum comes from the underneath part of the mantle very long time ago before the existence of life on earth (*Ceric, 2012*). The second hypothesis, biotic or organic origin suggests that petroleum is formed from biological matters, left behind by very ancient lives. These matters become subjected to high temperature under the absence of oxygen. The last hypothesis, biogenesis is currently accepted by many people due to how it is supported by various valid grounds while the first one is more doubtful. Its early supportive tenets lost their truth, especially when they fall in contraction with modern science.

2.3.1 Abiogenetic Origin of Petroleum:

Early in 16th century, a theory of the origin of oil stated that it resulted from very deep carbon deposits that have been around far longer than life on this planet. That theory, lately became known as the abiotic oil formation (AOF) theory, was largely ignored and forgotten until rather recently when a few people resurrected it and backed it with more theories.

As the earth existence is dated back to 4.5 billion years, the Abiotic theory is said to occur in that time, before the appearance of any form of life. The hypothesis is based on the fact that some of the harvested hydrocarbons and other associated substances have a very deep origin, indeed they are widely found in the universe. Methane is said to be present in the atmosphere of Jupiter, Saturn, Uranus, and other planets as well as moons and meteorites found in the solar system. Russian chemist and mineralogist Dimitri Mendeleev and scientists of the epoch have had a great influence supporting the hypothesis. "They propose that abiogenic methane reflects a cosmic organic inheritance that is subsequently released by the mantle and migrates towards the surface utilizing weaknesses in the crust such as plate" (*Sephton and Hazen, 2013*). Recently in 20th century, members of so-called "Russian-Ukrainian School" supported the hypothesis by stating that generated methane polymerizes into higher molecular weight hydrocarbons, which results into petroleum deposits, the fact that is also persuade by finding increased abundance of methane gas in the depth of petroleum basin. (*Sephton and Hazen, 2013*). The tenets supporting abiogetic origin of petroleum are in the following way.

a. The existence of methane on other planets of solar system, meteors, moons and comets.

b. The biogenic explanation fails to explain some of hydrocarbon deposit characteristics.

c. The crude oil distribution of metals fits better with upper serpentinised mantle, primitive mantle and chondrite patterns than the oceanic and the continental crust, and never shows any correlation with seawater.

d. The helium and other noble gas association with hydrocarbons.

e. Deep hydrocarbon seeps.

f. Hydrocarbon-rich areas tend to be hydrocarbon-rich at various levels.

g. Some proposed mechanisms of abiogenesis formation of petroleum.

2.3.2 Biogenetic Origin of Petroleum:

Biogenetic origin of petroleum suggests that petroleum come from a long-time decaying of died organisms such as planktons, zooplankton and other form of biological species under a subjection of high temperature. This hypothesis is currently accepted by many people around the world and it has many viable supporting grounds which fits well modern sciences. According to that hypothesis, very long time ago, the organisms (marine living things, terrestrial) died and buried and covered by silt in a sedimentary basin where they undergo a very slow and very long lasting physical and chemical transformation which involves processes such as diagenesis and kerogen formation.

The more conventional view of petroleum formation is that it formed when selected aliquots of biomass from dead organisms were buried in a sedimentary basin and subjected to diagenesis through prolonged exposure to microbial decay followed by increasing temperatures and pressures. Oxygen-poor conditions, produced by exhaustion of local oxygen levels by biomass decay and often sustained by physical barriers to oxygen recharge, are obvious enhancers for fossil organic matter preservation and passage into the geosphere. The major organic components in life are large, high molecular weight entities and the most resistant of these units are preserved in sediments, augmented by cross-linking reactions that polymerize and incorporate smaller units into the complex network. The high molecular weight sedimentary organic matter is termed kerogen from the Greek for "wax former." It is worth noting that not all of life's organic matter is reflected in kerogen. Even under relatively favourable conditions less than 1% of the starting organism, representing the most resistant chemical constituents, may be preserved *(Sephton and Haze, 2013)*.

The hypothesis of biotic origin of petroleum has many plausible evidences which can indeed allow scientists to simulate the production of petroleum (crude oil). Today advancements in science such as chemistry-knowledge about carbon and its compounds and geology make the hypothesis well understood and well useful. The most plausible evidence is the focus on the stage of what so-called "development of hydrocarbons", from peat to anthracite and equally from algae to oil.

Biotic origin of petroleum inspires the possibility of exhausting oil reserves while abiotic hypothesis assures quasi-unlimited supplies of oil and gas reserves leading to issues regarding energy renewability. The arguments on the biotic and abiotic origin of crude oil is driven by politics; with each group motivated by some hidden reasons which is for a particular interest.

The process of petroleum formation occurs in two steps:

Step 1: Diagenesis

Diagenesis is a process of compaction under mild conditions of temperature and pressure leading to the formation of kerogen. When organic aquatic sediments (proteins, lipids, carbohydrates) are deposited, they are very saturated with water and rich in minerals. Through chemical reaction, compaction, and microbial action during burial, water is forced out and proteins and carbohydrates break down to form new structures that comprise a waxy material known as "kerogen" and a black tar like substance called "bitumen". All of this occurs within the first several hundred meters of burial.

The bitumen comprises the heaviest components of petroleum, but the kerogen will undergo further change to make hydrocarbons and more bitumen.

Step 2: Catagenesis (or "cracking")

This process converts kerogen into crude oil and natural gas. As temperatures and pressures increase (deeper burial) the process of catagenesis begins, which is the thermal degradation of kerogen to form hydrocarbon chains. Importantly, the process of catagenesis is catalysed by the minerals that are deposited and persist through marine diagenesis. The conditions of catagenesis determine the product, such that higher temperature and pressure lead to more complete "cracking" of the kerogen and progressively lighter and smaller hydrocarbons. Petroleum formation, then, requires a specific window of conditions; too hot and the product will favour natural gas (small hydrocarbons), but too cold and the plankton will remain trapped as kerogen.

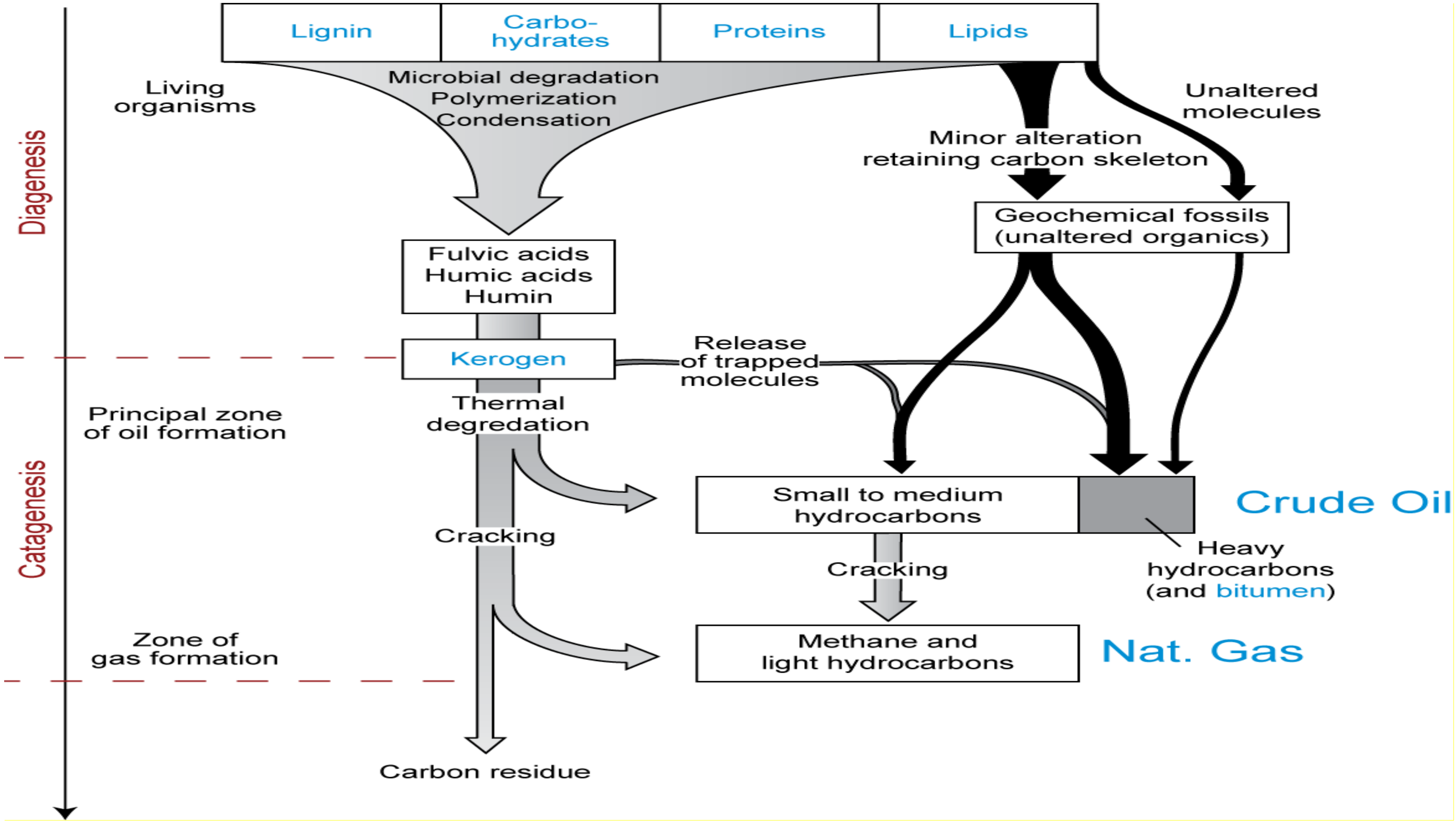


Figure 2.4: Steps in the formation of petroleum (adapted from *Tissot and Welte, 1984*).

There is a window of temperature that the zooplankton must find to form oil. If it is too cold, the oil will remain trapped in the form of kerogen, but too hot and the oil will be changed (through "thermal cracking") into natural gas. Therefore, the formation of an oil reservoir requires the unlikely gathering of three particular conditions: first, a source rock rich in organic material (formed during diagenesis) must be buried to the appropriate depth to find a desirable window; second, a porous and permeable (connected pores) reservoir rock is required for it to accumulate in; and last a cap rock (seal) or other mechanism must be present to prevent it from escaping to the surface. The geologic history of some places on earth makes them much more likely to contain the necessary combination of conditions.

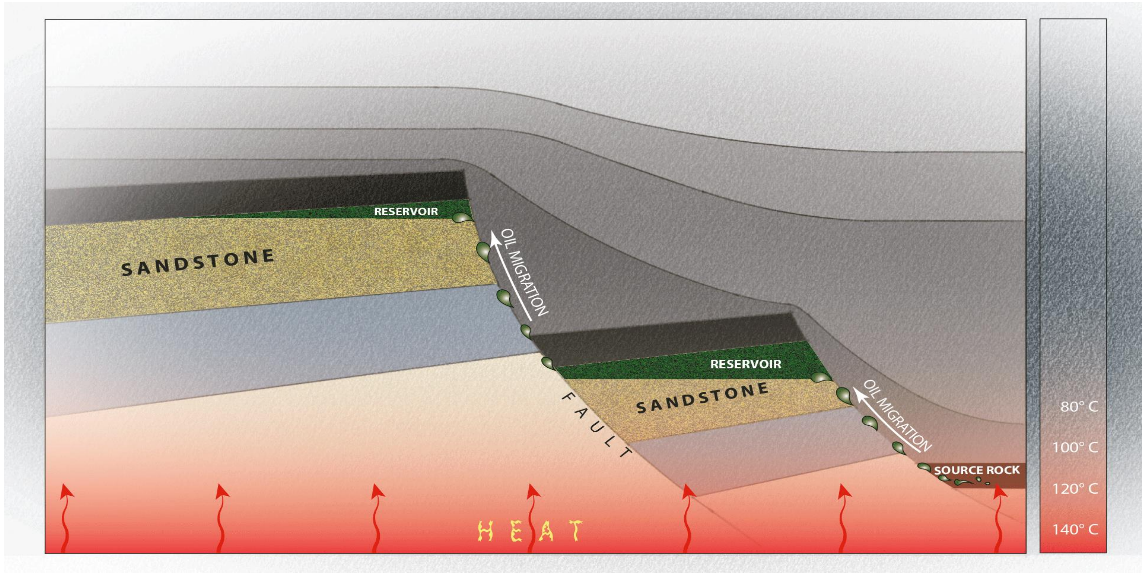


Figure 2.5: Illustration of the formation of crude oil and natural gas (Source: Norwegian Petroleum Directorate, 2019).

2.4 COMPOSITION OF CRUDE OIL AND NATURAL GAS

An oil well produces predominantly crude oil, with some natural gas dissolved in it. As a result of the lower pressure at the surface than underground, some of the gas will come out of solution and be recovered (or burned) as associated gas or solution gas. A gas well produces predominantly natural gas. However, because the underground temperature and pressure are higher than at the surface, the gas may contain heavier hydrocarbons such as pentane, hexane, and heptane in the gaseous state. At surface conditions, these will condense out of the gas to form "natural gas condensate", often shortened to condensate. Condensate resembles gasoline in appearance and is similar in composition to some volatile light crude oils (*Hidy and Hidy, 1955*). The proportion of light hydrocarbons in the petroleum mixture varies greatly among different oil fields, ranging from as much as 97 percent by weight in the lighter oils to as little as 50 percent in the heavier oils and bitumen (*Wall, 1988*). The hydrocarbons in crude oil are mostly alkanes, cycloalkanes and various aromatic hydrocarbons, while the other organic compounds contain nitrogen, oxygen and sulphur, and trace amounts of metals such as iron, nickel, copper and vanadium. Many oil reservoirs contain live bacteria (*Olivier and Magot, 2005*).

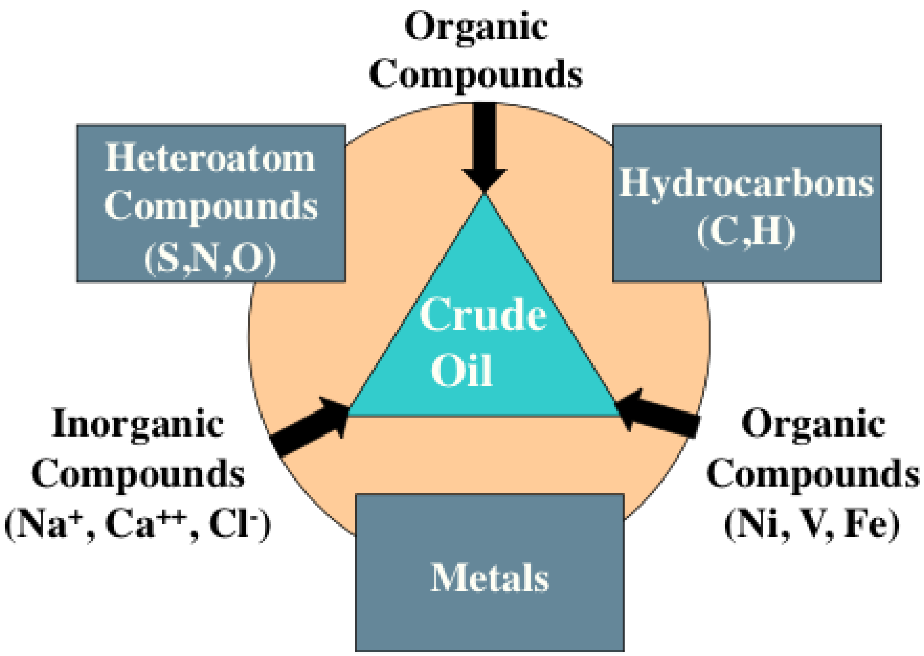


Figure 2.6: Illustration of the composition of crude oil (Source: Eser, 2018)

The exact molecular composition of crude oil varies widely from formation to formation, but the proportion of chemical elements varies over fairly narrow limits as follows (*Speight, 1999*):

Table 2.1: Elemental composition of crude oil (Source: Helmenstine, 2018)

S/N	**Element**	**% Range**
1	Carbon	83 – 87
2	Hydrogen	10 – 14
3	Nitrogen	0.1 – 2.0
4	Oxygen	0.05 – 1.5
5	Sulphur	0.05 6.0
6	Metals	<0.1

Typically, four different types of hydrocarbon molecules appear in crude oil. The relative percentage of each varies from oil to oil, determining the properties of each oil. This is shown in the Table 2.2.

Table 2.2: Hydrocarbon composition of crude oil by weight

Hydrocarbon	Average (%)	Range (%)
Alkanes (Paraffin)	30	15-60
Naphtenes	49	30-60
Aromatics	15	3-30
Asphaltics	6	Remainder

Table 2.3: Composition of natural gas (Source: Viswanathan, 2017)

S/N	Component	Typical Analysis (mole %)	Range (mole %)
1	Methane	95.0	87.0 – 97.0
2	Ethane	3.2	1.5 – 7.0
3	Propane	0.2	0.1 – 1.5
4	Iso-Butane	0.03	0.01 – 0.3
5	Normal Butane	0.03	0.01 – 0.3
6	Iso-Pentane	0.01	Trace – 0.04
7.	Normal Pentane	0.01	Trace – 0.04
8.	Hexane Plus	0.01	Trace – 0.06
9.	Nitrogen	1.0	0.2 – 5.5
10.	Carbon Dioxide	0.5	0.1 – 1.0
11.	Oxygen	0.02	0.01– 0.1
12.	Hydrogen	Trace	Trace – 0.02

2.5 SUMMARY

Crude oil has been in existence and use for over 5000 years. Crude oil collected from seepages were used for medicinal purposes and as oil in lamps. These early usages were recorded in the middle east. The Chinese also found and used crude oil around this same time.

The earliest oil wells were drilled in the 4th Century in China using bamboo poles (Vogel, 1993). There were various claims to the drilling of the first modern oil well: an oil well was drilled in 1846 in Baku with percussion tools to a depth of 21 meters for oil exploration (*Mir-Babayev, 2018*). It was also recorded that a commercial oil well was hand dug in Poland in 1853, and another in nearby Romania in 1857 (*Craig et al., 2018*). Edwin Drake's well which was drilled in 1859 near Titusville, Pennsylvania is popularly considered the first modern oil well. Drake's well is probably singled out because it was drilled, not dug; because it used a steam engine; because there was a company associated with it; and because it touched off a major boom (*Giddens, 1981*). However, the first well ever drilled anywhere in the world, which produced oil, was drilled in 1857 to a depth of 280 feet by the American Merrimac Company in La Brea (Spanish for "Pitch") in southeast Trinidad in the Caribbean (*Down, 2018*).

The origin of crude oil has been discussed from two viewpoints and attributed to either inorganic or organic sources. These theories are abiogenesis and biogenesis. Abiogenesis, championed by Berthelot and Mendeleev, explains that petroleum is of inorganic origin. It is the oldest of the theories and suggests that petroleum comes from the underneath part of the mantle very long time ago before the existence of life on earth. The second hypothesis, biotic or organic origin suggests that petroleum is formed from biological matters, left behind by very ancient lives. These matters become subjected to high temperature under the absence of oxygen. This hypothesis, biogenesis is currently accepted by many people due to how it is supported by various valid grounds while the first one is more doubtful.

Although the molecular composition of crude oil varies widely from formation to formation, the proportion of chemical elements varies over narrow limits and has been shown to be mainly made up of carbon and hydrogen. Other elements like nitrogen, oxygen, sulphur and metals exit in either small quantities or in traces. Crude oil is principally made up of alkanes, naphtenes, aromatics and asphaltics in various percentages by weight.

CHAPTER THREE

PRODUCTION OF CRUDE OIL AND NATURAL GAS

3.1 INTRODUCTION

Oil and gas production involve diverse activities, such as production of hydrocarbons from underground geologic formations; separation of natural gas, oil, and, water; and collection of gas from multiple wells through natural gas gathering pipeline systems. These activities require equipment such as tanks, piping, valves, meters, separators, dehydrators, pipelines, and gathering compressors. Apart from wastes that are generated alongside crude oil and natural gas production, there are also emission of greenhouse gases from these activities; either as leaks or intentionally. US EPA's GHG Inventory estimates that the oil and natural gas production segments emitted just under 3,500,000 metric tons of methane in 2012 (*McCabe et al, 2015*).

Oil is either pumped or pressure forced to the surface. Natural gases may be re-circulated to increase oil recovery rates. Water or steam flooding (including the use of potentially hazardous chemicals) of the reserve is commonly completed to induce movement of oil in the reservoir. The permeability of the bedrock (and hence recovery rate of oil and gas) may also be improved by fracturing using explosives or water, with a variety of chemical additives, at high pressure. Acids and other compounds are typically injected to prevent clogging. When extracting oil and gas the excess gases may be flared off to atmosphere (*Environmental and Social Risk Briefing, 2015*). These processes deliver oil and gas to meet our energy needs but can cause significant environmental and social impacts.

3.2 THE PRODUCTION PROCESS

Petroleum is naturally occurring solid, liquid or gaseous hydrocarbons which are trapped between impermeable geological layers underground; crude oil is a reference to the liquid petroleum while natural gas refers to the hydrocarbon gas mixtures (*Kiboub, 2011*). Methane constitutes the major component of natural gas; attaining up to 85% of the overall gas composition. Natural gas may also contain ethane, propane, butane, pentane and impurities like carbon dioxide, helium, nitrogen, and hydrogen sulphide in smaller quantities.

Crude oil and natural gas are usually trapped under pressure in the reservoir. The pressure, in most cases, are enough to push the crude out from the oil well to the surface of the earth. This natural flow of crude oil to the surface of the earth will continue if the pressure in the reservoir is high enough (*Ceric, 2012*). The crude oil and natural gas that flows from the reservoir to surface of the earth comes with impurities that need to be removed in order to meet sale specifications. The basic sediments (salt, mud and sand) and water in the crude oil is removed while the associated crude oil, water, H_2S, CO_2 and N_2 are removed in the case of natural gas (*Shimetti and Mukhtar, 2012*). The process of extracting hydrocarbons from the reservoir and separating the mixture of liquid hydrocarbon (crude oil), natural gas, water and solids; removing the constituents that are non-saleable and preparing the crude oil and natural gas for sale is called production (*Heminway, 2000*). Production sites often handle crude oil from more than one well. Oil is nearly always processed at a refinery; natural gas may be processed to remove impurities either in the field or at a natural gas processing plant.

Oil and gas reservoirs are found in both onshore and offshore location hence production could be either onshore or offshore. Onshore production is economically viable from a few tens of barrels a day upwards (*Devord, 2013*). Oil and gas are produced from several million onshore wells world-wide. Gas gathering network can become very large, with production from hundreds of wells, several hundred kilometres apart, feeding through a gathering network into a processing plant.

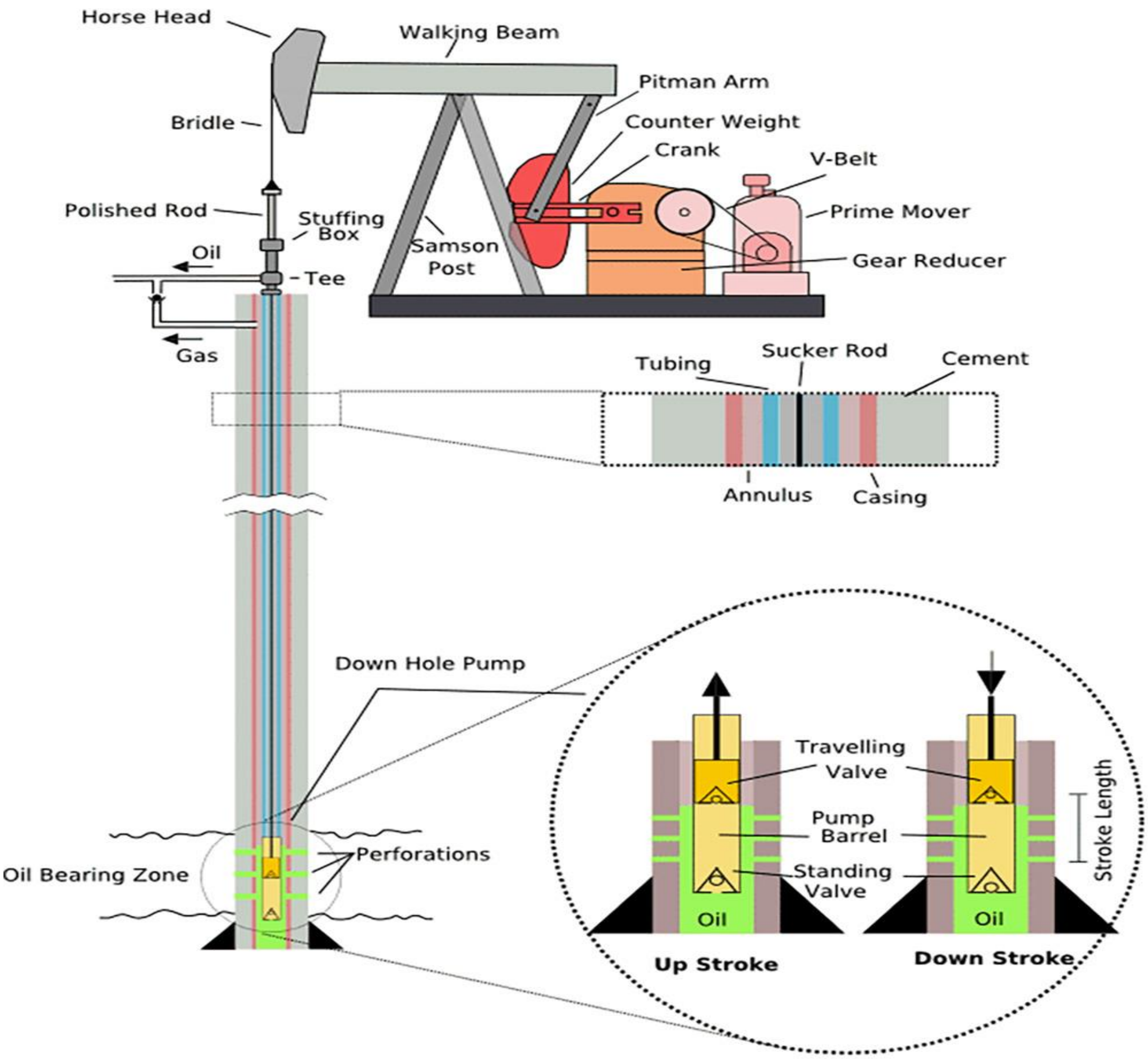


Figure 3.1: Crude oil production using the jack pump (Source: *UKOG, 2018*).

For the very small reservoirs, oil is simply collected in a holding tank and collected at regular intervals by tanker truck or railcar to be processed at a refinery. But onshore wells in oil rich areas which are also high capacity wells with thousands of barrels per day are connected to a flowstation where oil and gas separation is undertaken. Produced crude oil and natural gas is sent to the refinery and gas processing plant respectively from flowstation by pipeline. In some cases, the production may come from different fields or even different license owners. Metering and logging of individual well streams into the gathering network are very important tasks in this case.

Recently, very heavy crude, tar sands and oil shales have become economically extractible with new technology. Heavy crude may need heating and diluent to be extracted, tar sands have lost their volatile compounds and are strip-mined or could be extracted with steam (*Devord, 2013*).

In offshore locations, depending on size and water depth, a whole range of different structures is used. Some of the common offshore structures in shallow water complex are characterised by several independent platforms with different parts of the process and utilities linked with gangway bridges. Individual platforms could be described according to the service they render as wellhead platform, riser platform, processing platform, accommodations platform and power generation platform. In the last few years, we have seen pure sea bottom installations with multiphase piping to shore and no offshore topside structure at all replacing outlying wellhead towers. Directional drilling has been used to reach different parts of the reservoir from a few wellhead cluster locations.

Figure 3.2: Conductor supported production platform (Source: *Gill, 2019*)

Once a field is brought on production, good reservoir management is required to ensure that as much oil and gas as possible is produced as cost effectively as possible, with minimal waste and environmental impact. Early producers, relying on natural pressure and primitive pumps, recovered only about 10 percent of the oil in a given field (*Johnson and Transtrum, 1999*). They sometimes vented or flared natural gas produced in association with the oil. In contrast, today's producers use an arsenal of advanced recovery techniques to keep oil and gas resources flowing, enabling them to produce as much as 50 percent or more of the oil resources and 75 percent or more of the natural gas in a typical reservoir (*Johnson and Transtrum, 1999*).

3.2.1 Oil and Gas Process:

The oil and gas process refers to the suite of equipment that takes the reservoir fluids from the wellhead manifolds and delivers stabilized marketable products, in the form of crude oil, condensate or natural gas at the required specifications. The equipment to determine the quality and quantity of crude oil and natural gas produced, manage the produced waste within provisions of the state laws are also part of the components of the oil and gas process.

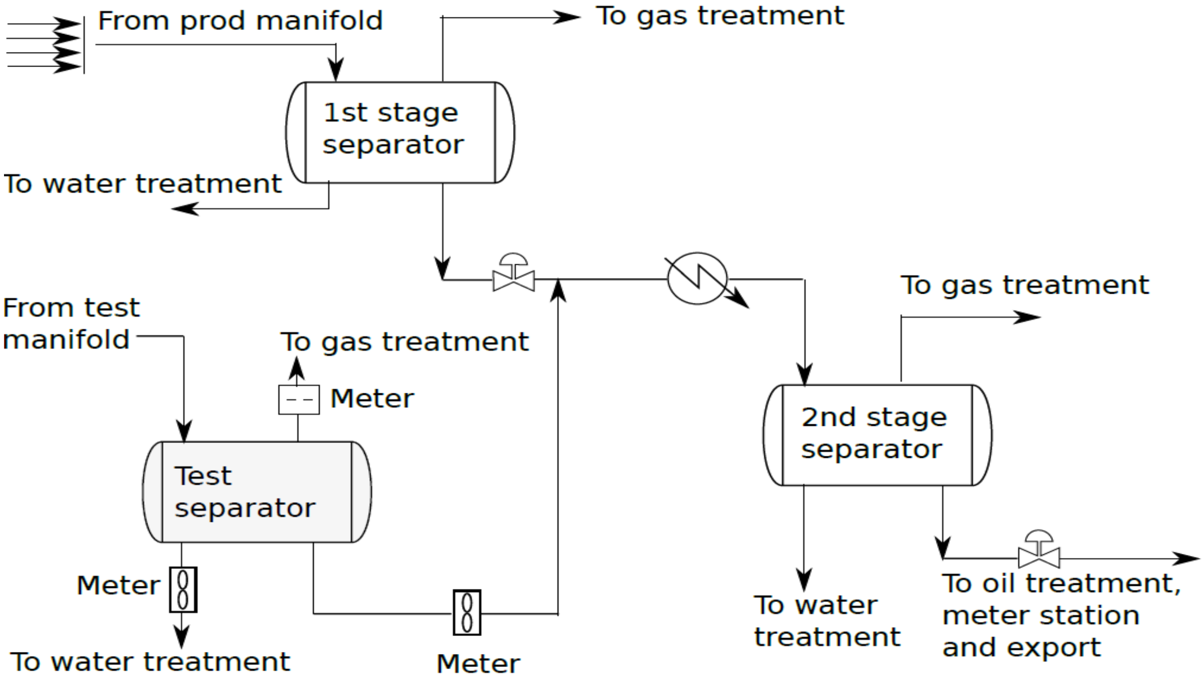


Figure 3.3: Simple crude oil production process (Source: *Devold, 2013*)

The case study facility is an onshore crude oil and natural gas facility originally designed to process 37,000 barrels of well fluid per day. The facility currently produces 3,300 barrels of crude oil per day. The flow station has oil and gas production process, gas compression and re-injection system and water re-injection unit. Case study 2 is an offshore Floating Production Storage and Offloading (FPSO) vessel, which is currently located in an average water depth of 14 metres in the eastern Niger Delta. It has a 27,000 barrel of oil per day production process and storage capacity for 360,000 barrels of crude oil. The FPSO currently produces 16,000 barrels of oil per day.

3.2.2 Fuel Gas Treatment and Flare System:

In both case study facilities, the natural gas from the various separation and treatment systems are gathered and directed into the Flare Knock Out Drum. The liquids are knocked out, collected and drained into the Off-Specification tank while the gas is sent to the flare. However, Non-Associated Gas is passed through the Fuel Gas Filter into the Turbine Fuel Gas Compressor Suction Scrubber. The stripped gas is either compressed through the Turbine Fuel Gas Compressor or sent to the flare. The compressed gas is filtered and sent to the Fuel Gas Pump Turbine while the liquid is recycled to the 2nd Stage Separator.

3.2.3 Water Injection System:

In case study 1, the produced water is pumped back into the reservoir through a water disposal well. The Water Injection (WIJ) pumps are used for this purpose. However, in case study 2, seawater is used for this secondary recovery operation. Seawater is mixed with hypochlorite and passed through coarse filters. The filtrate is mixed with process cooling water return, ferric sulphate and poly electrolyte and passed through fine filters. The filtrate from the fine filters is dosed with anti-foam and biocides and introduced into the deaerator. Water from the bottom of the deaerator is dosed with corrosion inhibitor, nitrate and scale inhibitor and then pumped through the water injection flowline into the designated water injection well. Oxygen scavenger is introduced into the deaerator through a recycled portion of the filtrate from the bottom of the deaerator.

3.2.4 Produced Water Treatment:

Only case study 2 is equipped with produced water treatment system. The produced water treatment system is made up of the produced water manifold, the produced water surge drum, the hydrocyclone, the produced water degasser and the produced water analyzer. In offshore locations, it is commonly recommended that the produced water from the separators be treated with hydrocyclones followed by gas floatation vessels. This arrangement is to ensure that the oil-in-water limits for discharge overboard is met. For instance, according to Nigeria's Environmental Guideline and Standards for Petroleum Industry in Nigeria (EGASPIN), the maximum amount of oil/grease in produced water allowed for discharge into water body is 40mg/l in Deep Offshore but decreases to 30mg/l in Offshore and Continental Shelf (EGASPIN 4.2.1, 2001) *Igwe et al, 2013*).

3.2.5 Produced Gas Treatment System:

Produced natural gas treatment could either be incorporated into the oil and gas production process or carried out in a separate treatment process. The processing of wellhead natural gas into pipeline-quality dry natural gas can be quite complex and usually involves several processes to remove: (1) oil; (2) water; (3) elements such as sulphur, helium, and carbon dioxide; and (4) natural gas liquids (*Tobin et al, 2006*).

3.3 BASIC COMPONENTS OF CRUDE OIL PRODUCTION FACILITY:

3.3.1 Manifold:

The manifold is a pipe or channel into which pipes, pipelines or flowlines gather or emanate from. It is the point where the flowlines from the various wells comingle. It is also the point from which the reservoir fluid is delivered into the process for separation into oil, gas and water. Manifolds get their names from their functions as depicted in names of the types of manifold: *Production Manifold*, *Test Manifold*, *Injection Manifold* etc.

3.3.2 Heat Exchangers / Steam Heaters:

The Heat Exchangers are very important heat transfer equipment in oil and gas production. There are usually two exchange fluid flowing through the Heat exchanger in order to transfer heat.

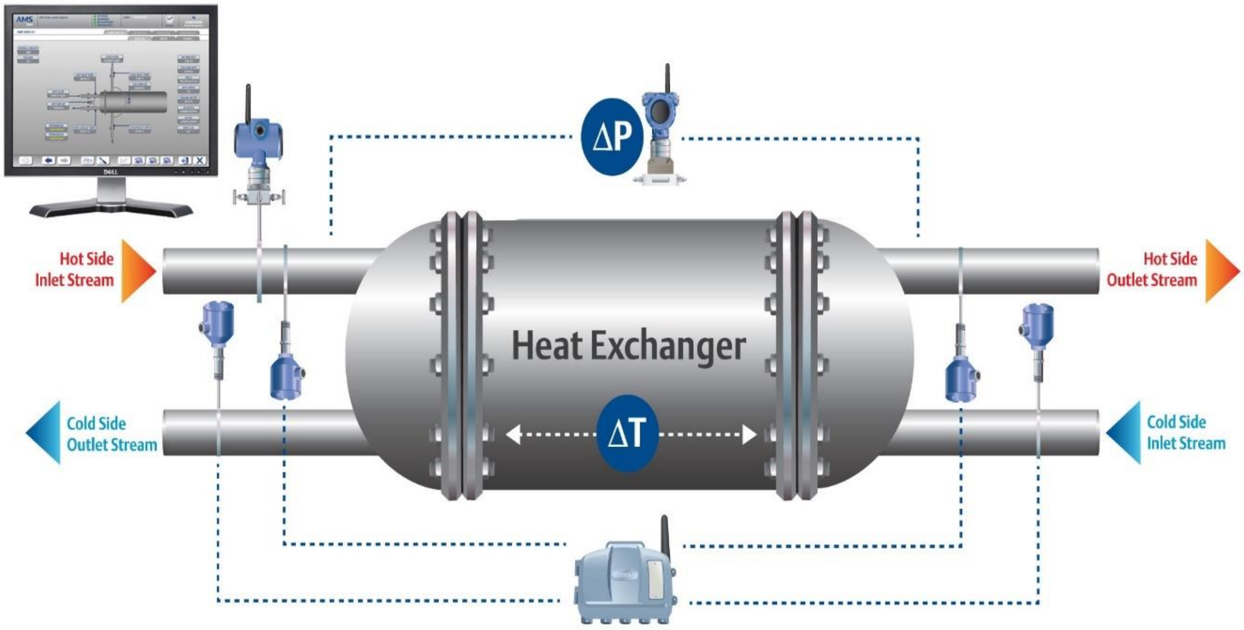


Figure 3.4: The Heat Exchanger (source: Industry Types, 2017)

In the production process, it could be used to increase the temperature of the well fluid as demonstrated by the Inlet Oil Heat Exchanger on the case study process. It could also be used to cool the temperature of the oil, the gas or the produced water as seen in the oil cooler, Flash Gas Compressor

Suction Cooler and Produced Water Cooler respectively on the case study process where sea water was used counter-currently to cool the fluids. Steam Heaters are used to increase the temperatures of fluids. On the case study process, all the Steam Heaters exchanged heat between the fluid and steam to raise the temperature of the fluid and thereby aid separation.

3.3.3 Separators:

There are usually many types of separators in oil and gas production process. They include:

a. ***Production Separators*:** There are usually two or three production separators in a typical oil and gas production process. The first two could be three-phase separators are used to separate oil, water and gas into their respective legs and the third a two-phase separator, which may be used as a Flash Drum or Scrubber.

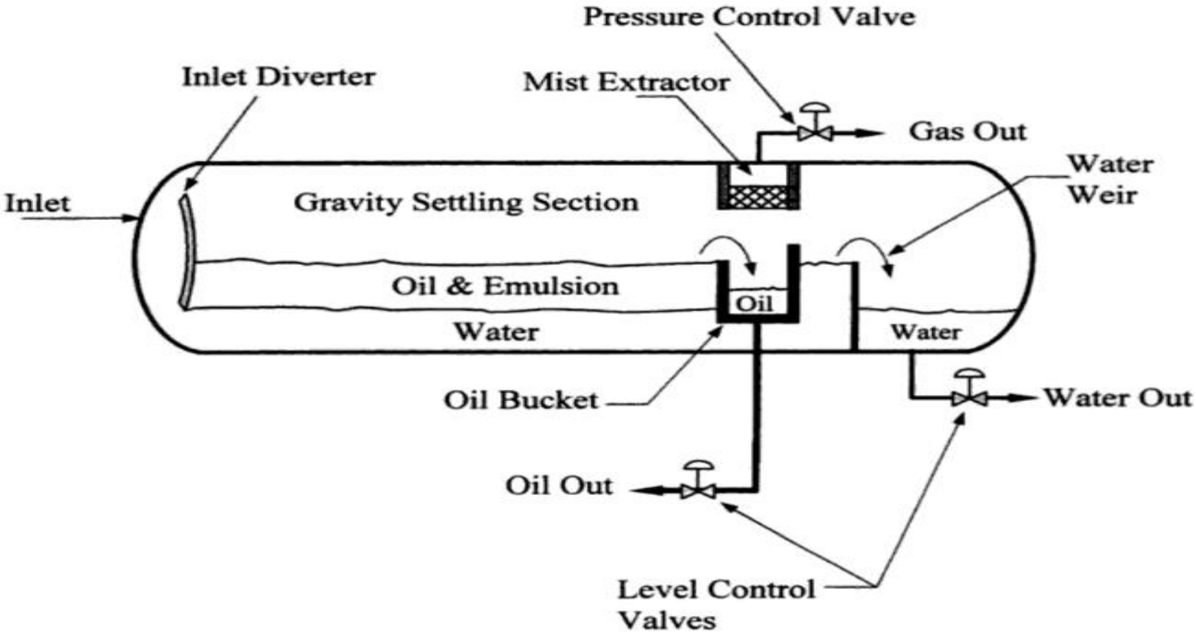


Figure 3.5: Parts of a three-phase separator (Source: Abdel-Aal et al., 2003)

- ***b. Test Separators*:** Test Separators, usually two-phase separators, are used to determine the production characteristics of the wells. They are used to ascertain the production of each well; the barrel of liquid produced per day, the barrel of oil produced per day, the volume of natural gas produced per day, the gas-oil-ratio of the well, the API Gravity of the crude etc.

- ***c. Electrostatic Coalescer*** *(Dehydrators/Desalters):* This vessel is applied as the final separation step to break up emulsion and removes interstitial water from the oil by the application of the principle of electrolysis. Electrostatic coalescers are also applied for desalting in order to reduce the crude oil's salt content.

d. ***Water Treatment System*:** Produced Water Treatment System is common in offshore production process. The Produced Water Hydrocyclone and the Produced Water Gas Floatation Vessel, which make up the water treatment system, are separators.

3.3.4 Pumps and Compressors:

Different types of pumps are used in the oil and gas production process to give energy to the liquids / fluids and aid flow through the facility. The pumps increase the pressures of the fluids and could be motorized or pneumatic. On the case study process, there are a few pumps which includes the oil transfer pump, the produced water return pump, the produced water discharge pump, the skimmed oil return pump etc. Compressors increase the pressure of gases by reducing the volume occupied by the gas. Some of the compressors on the case study process are the Flash Gas Compressor, the Turbine Fuel Gas Compressor etc.

3.3.5 Metering System:

There are usually two types of metering on the oil and gas production process: the production metering and the fiscal metering. Whereas the production meters are used to account for the produced oil and gas, the fiscal meters are used as export meters for the custody transfer of either crude oil or natural gas from the possession of one party to another. Turbine meters, Coriolis meters, Ultrasonic meters, Positive Displacement meters and Differential Pressure meters are some of the commonly used meters in oil and gas production process.

3.4 CHEMICAL USE IN THE PRODUCTION OF CRUDE OIL

The production, handling and transportation of crude oil require the use of various types of chemicals. These chemicals can be mixtures or formulations of various chemicals and could divided into various categories. For most of these chemicals, only trace amounts may remain in the crude oil as impurities until it reaches the refinery.

These oilfield production chemicals (OFCs) are complex formulations of many different chemicals. Often the constituent chemicals themselves are not pure chemical species but a mixture of reaction products, reactants, and diluents. The formulation usually has one or two primary ingredients that give the additive its main functionality. In addition, the formulation is specifically designed for each oilfield, and within the oilfield, for each well, and for each well the recipe may vary depending upon the time and the operating conditions. Crude from many wells / fields is combined such that it is nearly impossible to ascertain the resulting combination of OFCs used at a particular well oil at the terminal.

Apart from their use at the various stages of oilfield development: drilling, cementing, well completion, and well stimulation / workover, production chemicals are also widely used in oil and gas development and production activities to treat and prevent a range of common problems which may be encountered during normal operations. Production chemicals may be added at all stages of the production process, from the water injection phase in which the hydrocarbon resources are being extracted, through the oil-water separation phase, and including the transport phase where the recovered oil is sent to pipelines (*Schmeichel, 2017*). At the production phase, the flow of oil out of the well needs to be assured by preventing the deposition of hydrates, wax, asphaltenes, or scale. Chemicals provide a means for controlling such deposits. The presence of water, bacteria, and acids all result in a corrosive environment. Production of crude oil usually involves a significant bulk water phase; many (OFCs) are water-soluble by design. When used in continuous low dose injection they remain with the water phase at the upstream facilities. The production of oil usually involves its separation from water and gas. A small amount may be present in water droplets dispersed or partitioned in the oil phase as an impurity.

Additionally, chemicals may be needed during the transportation and handling of crude oil, e.g. in pipeline, tanker, or terminal. Drag reducing agents can be added in pipelines to improve flow. Pour point depressants, mercaptan scavengers, hydrogen sulphide scavengers are often added to cargoes in order to satisfy shipping or terminal requirements for stability.

3.4.1 Physicochemical Properties of Production Chemicals

Production chemicals are often complex mixtures of various compounds *(Veil et al., 2004)*, some of which are known to producers and operators, while many others remain proprietary to the chemical manufacturers for business reasons. Some of the common chemical components of production chemicals are identified below along with their chemical class and functions.

3.4.1.1 Scale Inhibitors:

These chemicals are used in oil production process to prevent the deposition of mineral scale that may occur in the pores of rock formations, in downhole pipework and in surface treating facilities.

3.4.1.2 Corrosion Inhibitors:

Aqueous acids are used to stimulate production from reservoirs expose oil production systems to the possibility of corrosion. Corrosion inhibitors are therefore required to protect the downhole pipework and vessels of oil production facilities. The common chemical components of these corrosion inhibitors are sodium sulphite, zinc carbonate, ammonium bisulphite, zinc chromate, diammonium phosphate.

3.4.1.3 Biocides:

Bacterial growth in waters associated with crude oil production is controlled using biocides. Biocides are water-soluble and removed with the water from crude. The common chemical constituents of biocides are gluteraldehydes, sodium hypochlorite, quaternary ammonium salts, oxyalkylated phenols, fatty diamines, thiazolines, carbamates, paraformaldehydes, dichlophenols.

3.4.1.4 Oxygen Scavengers:

Often used to mitigate corrosion problems in water injection systems, in hydrotesting and drilling.

3.4.1.5 Emulsion Breakers:

Production of oil also involves the production of large quantities of water. The natural surfactants present in the oil, water or other chemicals such as corrosion inhibitors may combine with the shearing effect from turbulent flow and pumps to create emulsions. Demulsifiers are used to resolve water-in-oil emulsions. The common chemical component of demulsifiers are oxyalkylated alkylphenols, aromatic hydrocarbons, glycols, cationic and non-ionic surfactants.

3.4.1.6 Antifoams Agents:

Foaming problems occur in many oilfield processes. Problems occur when gas breaks out from crude oil in separators, or in gas processing plants. The common chemical components of antifoam agents are silicones, flourosilicones, octyl alcohol, aluminium stearate, various glycols, and sulfonated hydrocarbons

3.4.1.7 Drag Reducing Agents:

High molecular weight oil-soluble polymeric compounds are added to fluids in crude oil pipeline to enhance flow and minimize pressure drop. A long pipeline can have more than one injection point

3.4.1.8 Hydrate Inhibitors:

Gas hydrates are formed when water molecules crystallize around hydrocarbon molecules at certain pressure and temperature combinations. They can plug flowlines and damage process equipment. In addition to specific chemicals, methanol or glycols (MEG, DEG, TEG) may be used to prevent crystallization of the water molecules. Alkyl triazines, amines, amine phosphonates are other chemicals that could be used as hydrate inhibitors.

3.4.1.9 Hydrogen Sulphide Scavengers:

Hydrogen sulphide in produced oil and gas poses safety and corrosion concerns. Scavengers bind the H_2S in a form that is stable in the liquid phase. The two types of scavengers common in the oil and gas industry are the zinc–containing chemicals and iron-oxide, Fe_3O_4. They can be added at oil production facilities or in transit in a pipeline or tanker.

3.4.1.10 Mercaptan Scavengers:

Low molecular weight (C_1-C_3) mercaptans have offensive odours and are toxic. It is necessary to remove and neutralize them. Mercaptan scavengers either oxidize the offending species or convert them to less-volatile molecules. Methane thiol, ethane thiol and 2-propane thiol are examples of mercaptan scavengers.

3.4.1.11 Paraffin Control Agents and Pour Point Depressants:

Crude oils may contain varying degrees of long chain paraffins or waxes that tend to form deposits if the oil is subjected to changes in temperature, pressure or other conditions. While dispersants / detergents are used to remove deposits already formed, inhibitors are known to interfere with wax crystal growth and formation.

3.4.1.12 Asphaltene Control Agents:

Asphaltenes can destabilize and precipitate out when temperature, pressure or oil composition changes. Chemicals are added to control asphaltene precipitation. Some constituents of common production chemicals tend to be polar and hydrophilic compounds, which are not as amenable to routine analysis as nonpolar, hydrophobic compounds (*McCormack et al, 2001)*, but are less prone to persist in the environment. Adding to the complexities of studying these mixtures, *Henderson et al.,1999* noted that in their study that it was not possible to differentiate between the toxic contribution of the production chemical and the crude oil content in the aqueous phase of produced water because the toxicological contribution of the oil could not be separately accounted for. With only general knowledge about the class of chemical constituents in a production chemical and the lack of suitable analytical methods, it is difficult to understand and predict the fate of these chemicals in the environment and therefore assess their potential impacts *(McCormack et al., 2001)*.

3.4.2 Production Chemical Use in Oilfields

Chemicals can be added either by continuous dosage or in batch treatments during crude oil production. The concentration of chemical left in the crude after production typically ranges from 10 – 200 ppm. These post-production chemicals help to control corrosion, scale, hydrogen sulphide, bacteria; help to prevent hydrate formation, wax deposition, asphaltene precipitation; and help to resolve emulsions. In other words, they are added to preserve the stability of crude oil during transport so that the crude can reach the refinery for conversion to products. Scale and corrosion inhibitors, defoamers, and demulsifiers are generally the most heavily used production chemicals (*AMAP, 2010*). A sample of production chemical use from the North Sea is presented in below (*Neff et al., 2011*).

Table 3.1: Production chemical use and discharge volumes from North Sea oil and gas platforms (Source: Neff et al., 2011)

Chemical	**Typical Use Concentration (ppm, v/v)**	**Phase Association of Chemical**	**Amount discharged to North Sea (t/y)**
Scale Inhibitor	3 – 10	Water	1143
Corrosion Inhibitor	25 – 100	Oil	216
H_2O/O_2 Scavenger	5 – 15	Water	22
Biocide	10 – 200	Water	81
Emulsion Breaker	10 – 200	Oil	9
Coagulant/ Flocculants	<3	Water	127
Gas Treatment Chemicals	Variable	Water	2846

Most offshore production platforms use at least two types of chemicals in their operations; only very few uses none (*Henderson et al., 1999*). With production process targeting improvement in the quality of crude for export, there are some indications that chemical use is becoming more significant and volumes used are increasing (*Henderson et al., 1999*). Moreover, it has been determined that chemical use tends to increase as oil field age (*Igunnu and Chen, 2014*).

Table 3.2: World demand for production chemicals, with projections to year 2021(Source: *Upstream Pumping, 2016*)

Region	**Million US Dollars ($)**				**% Annual Growth**	
	2006	**2011**	**2016**	**2021**	**2006-2011**	**2016-2021**
World	10,749	18,245	27,930	40,850	11.2	8.9
North America	5,580	10,240	15,270	21,100	12.9	8.3
United States	4,300	8,350	12,450	17,000	14.2	8.3
Canada & Mexico	1,280	1,890	2,820	4,100	8.1	8.3
Central & South America	650	1,220	2,300	4,050	13.4	13.5
Europe	1,460	1,890	2,560	3,650	5.3	6.3
Africa / Mid-East	1,531	2,430	3,850	5,850	9.7	9.6
Asia / Pacific	1,528	2,465	3,950	6,200	10.0	9.9

In their recent study on production chemical usage in the United Kingdom (UK), *La Vedrine et al., 2015* observed that the total quantity of discharged chemical product remained roughly the same over the study timeframe of 2000 through 2012. According to that study, over one million tonnes of chemical products were discharged between 2006 and 2012, and these included products ranging from non-hazardous to highly hazardous as per UK rankings, with the greatest discharge amounts from the gas hydrate inhibitor class (155,758 tonnes, or 29% of total chemicals discharged), followed by scale inhibitors (62,473 tonnes, or 12% of total), hydrogen sulphide scavengers (59,599 tonnes, or 11% of total), and corrosion inhibitors (52,185 tonnes, or 10% of total). Demulsifiers and biocides each contributed approximately 5% of the total chemicals discharged *(La Vedrine et al., 2015)*. A 2007 paper on chemical usage in the Artic reported similar findings on the use of chemical product classes, stating that scale and corrosion inhibitors, defoamers, and demulsifiers were the most widely used in that region, with smaller amounts of hydrogen sulphide scavengers, gas hydrate inhibitors, and a range of others *(AMAP, 2010)*.The discharge of particularly hazardous chemical components (sometimes referred to as substitutable substances) within chemical products was also reviewed as part of the *La Vedrine et al., 2015* study, and was found to have declined significantly in the 2000 through 2012 study period. The discharge of corrosion inhibitors accounted for the largest contribution of substitutable substance discharges. The corrosion inhibitor class products were discharged in relatively high volumes proportionally to other product functions (10% of total discharges) and their discharges have remained relatively constant despite containing the highest proportion of substitutable substances. *La Vedrine et al., 2015* report that attempts to replace the more toxic constituents in this product class with ones posing lesser risk have resulted in reduced product efficacy, thus explaining the relatively constant discharge rates in this product class while substitutable substance discharges have declined in total and in other product classes. Scale inhibitors contributed roughly 12% of total discharges and contained a high proportion of substitutable substance chemicals in 2006, although they were used in declining proportions between 2006 and 2012. The hydrogen sulphide scavenger class included a small and declining proportion of chemical constituents considered particularly toxic. Gas hydrate inhibitors have used minimal proportions of substitutable substances and are therefore considered to be low-risk chemicals (*La Vedrine et al., 2015*).

Veil et al., 2004 identified the production chemicals having the greatest aquatic toxicity risk for adverse effects in marine organisms as being corrosion inhibitors, biocides, and reverse emulsion breakers, which is generally consistent with the *La Vedrine et al* findings although the *Veil et al* study did not specify the approach used to make these determinations. *Veil et al* noted that these higher risk substances may undergo reactions prior to being discharged that reduce or eliminate their toxicity. While it is arguable that chemical composition and toxicity are highly variable for different formulations within the same chemical class, available literature suggests there are enough constituent similarities to make assertions about their relative toxicities in marine environments *(La Vedrine et al, 2015; Grigson et al., 2000; Henderson et al, 1999).*

3.5 POLLUTANTS FROM CRUDE OIL PRODUCTION

Crude oil and natural gas have become the main source of primary energy for the increasing world population; this dominance is expected to continue for several more decades (*Schmeichel, 2017*). Petroleum constitutes 39% of the used fossil fuels share whilst natural gas represents 23% of the total energy consumption source (*Hamed and Sulayman, 2009*). The benefits of consumption of petroleum comes with unavoidable environmental impacts that may be regional or global in scale, including air pollution, climate change, land and water pollution due to oil spills. Production of petroleum has caused local detrimental impacts to soils, surface and ground waters and the ecosystems (*Veil et al, 2004*). These impacts arose primarily from the improper disposal of saline water produced with oil and gas, from accidental and produced water releases and from abandoned oil wells that were orphaned or not correctly plugged (*Edwards, 1997*). The greenhouse gas (GHG) emissions and wastes generated from oil and gas activities are not only costly to the companies; they have negative and sometimes irreversible effects on the environment (*Richter and Kreitler, 1993*). They potentially contribute to global warming, depletion of biotic/abiotic resources and affect the health and safety of workers and host community.

3.5.1 Produced Water:

Produced water is the water found in reservoir along with crude oil and / or natural gas. When crude oil or natural gas is extracted from the reservoir, produced water comes to the earth surface with it. It is estimated to account for more than 98% of oil and gas production waste (*Kharaka et al, 1995*). This water is usually entrained with hydrocarbons which must be removed from the water to a certain limit prior to discharge. Produced water is generally re-injected into a well to enhance the oil and gas recovery by raising the down-hole pressure (*API, 2009b*); it can also be sent to evaporation ponds or be treated (*API, 2009c*). As the volume of hydrocarbons found in a reservoir decreases over the life of the field, the volume of produced water generally increases. Produced water also contains low concentrations of hazardous substances that occur naturally in the reservoir, such as heavy metals, aromatic hydrocarbons, alkyl phenols and radioactive substances. Produced water volumes from gas installations are low compared to volumes from oil producing installations but may contain higher concentrations of lead (*Kiboub, 2011*). Produced water may also contain residues of chemicals used to assist drilling, well maintenance and oil and gas separation.

3.5.2 Chemicals:

The use of chemicals is critical for production of crude oil and natural gas. The chemicals used in oil and gas production are discharged into the environment principally in produced water. Some of the crude oil and natural gas production operations where chemicals are used include:

- chemicals used in the actual production and processing of hydrocarbons including but not limited to demulsifiers, corrosion inhibitors, scale inhibitors, hydrate inhibitors, biocides, drag reducing agents, anti-foam agents, hydrogen sulphide scavengers, mercaptan scavengers etc;
- water injection chemicals;
- chemicals used to maintain pipelines and ensure pipeline integrity; these include dyes used for hydrotest of subsea pipelines, biocides and oxygen scavengers.

Chemicals discharged into the marine environment has led to acute or long-term toxic effect to marine organisms. Persistent and bio-accumulative chemicals can magnify in the food chain and result in high exposure levels for top predators like seabirds and marine mammals and for human seafood consumers (*Iversen et al, 2009*). Low concentrations of some substances are enough to interfere with the hormone and immune system and reproduction processes. Biological effects can extend beyond individual marine organisms to a whole population with adverse consequences for species composition and ecosystem structures.

3.5.3 Crude Oil:

Crude oil could be released into the environment from a variety of sources during oil and gas production. Crude oil in the produced water; either injected into the reservoir or discharged into the water body poses a threat to groundwater or marine life respectively. Equipment failure, disasters, deliberate acts and human error could lead to spill of oil on land or water (*Iversen et al, 2009*). The cost of clean-up of oil spill and remediation of the environment; either land or water is usually very high. There could also be leaks of crude oil from facilities, drop out oils when flaring, during well testing and well workovers but these are considered insignificant (*Anderson and Labelle, 2000*). The ecological implications of oil spill on the land or marine environment are massive and may include:

- coating the feathers of seabirds and fur of some marine mammals. This reduces their ability to provide buoyancy and insulation, leading to increased mortality.
- ingestion of oil with food by mammals and turtles may expose them to potential toxic effects and likely reduction in breeding success in birds and mammals.

- inhibition of growth of vegetation due to reduction of the moisture content of the soil and lowering of the soil's PH.
- health concerns on the residents likely due to use of water with traces oil and inhalation of the fumes.

3.5.4 Naturally Occurring Radioactive Materials (NORM):

Naturally occurring radioactive materials (NORM) in crude oil and natural gas production is caused mainly by ^{226}Ra and ^{228}Ra in produced water, the daughter products of ^{238}U and ^{232}Th respectively in reservoir rocks (*Fisher, 1998*). Uranium, radium, and thorium are dissolved in very low concentrations during normal reactions between water and rock or soil (*Zielinski and Otton*). The groundwater that coexists with deposits of crude oil and natural gas is rich in chloride; this enhances the solubility of other elements including the radioactive element, radium. Some of this saline, radium-bearing water is brought to the earth's surface with the crude oil and natural gas and must be separated and then disposed. The tanks and pipes that handle large volumes of produced water could become coated with scale deposits that contain radium (Otto, 1989).

The health effects of NORM are a function of the energy transmitted to the body as the α, β or γ radiation dissipates excess energy into living cells, which may result in cellular damage and genetic mutation (*IAOGP, 2016*).

Radioactive activity of produced water is typically very low but where large volumes of produced water are generated, the potential cumulative impact requires consideration (*Srebotnjak and Rotkin-Ellman, 2014*).

3.5.5 Air Pollutants:

Flaring, routine venting and leaks from components are responsible for the release of particulate matter, volatile organic compounds, hydrogen sulphide, respirable silica, oxides of nitrogen, methane and carbon dioxide into the atmosphere during the production of crude oil and natural gas (*Alvarez and Paranhos, 2012*). Flaring and venting of hydrocarbons which are considered safety operations are the main sources of most of the atmospheric emissions (*Kiboub, 2011*). Oil and gas production also require substantial power in order to extract, process and export hydrocarbons consequently power generation is also a major source of emissions (*Ubani and Onyejekwe, 2013*).

3.5.6 Heat and Light:

The flare from the crude oil and natural gas production process generate heat and light to the environment where it is located. Almost no vegetation can grow in the area directly surrounding the flare due to the tremendous heat it produces and the acid nature of the soil pH (*Kiboub, 2011*). A study undertaken in the Southern North Sea by the Netherlands has suggested that the chance that flaring directly impacts a flock of birds is small and only significant during the migration periods. However, the study estimates that about 10% of the total bird population crossing the North Sea is impacted in some way by light emitted from offshore installations (*Kiboub, 2011*).

3.5.7 Noise:

Noise from oil and gas production are usually from natural gas handling facilities and the flare. These facilities are designed not to exceed the noise limits but as they age, the emission to the environment increases and the potential to exceed set limits. Flare specifications are often written that require flares to operate at 85 dBa or less at the maximum rate (*Beck, 2010*). This limit has been violated in some production processes.

3.5.8 Installations and Pipelines:

Pipelines and installations used in the production of oil and gas are built on land and in water. These installations in the course of performing their primary functions release unwanted substances to the air, the sea or the land. Apart from pipelines, large number of production installations are being located on the seabed today.

3.6 PRODUCED WATER, CHARACTERISATION AND TREATMENT TECHNOLOGIES

Crude oil production involves the extraction of hydrocarbons from the reservoir and separating the mixture of liquid hydrocarbons, gas, water, and solids, removing the constituents that are non-saleable, and selling the liquid hydrocarbons and gas. Produced water is the major non-saleable constituents that are removed from the hydrocarbon mixture. Produced water removed from hydrocarbon mixture contain various substances that constitute pollutants to the environment and could be poisonous to the plant and animal lives. The presence of these pollutants in produced water makes it unusable and prevents it from being disposed into the environment. These are some of the few reasons for the treatment of produced water.

The engineering and installation of produced water treatment facilities are usually done to meet set expectations or standard. The final use of the treated produced water is considered in establishing treatment limits; produced water treatment for use in irrigation of farms require more treatment than produced water for disposal in offshore location. These produced water treatment facilities require huge capital investment. The process is also energy intensive thus the energy bill required to continue to run the process makes the crude oil production process less profitable.

3.6.1 Produced Water Treatment Process and Treatment Technologies:

Produced water treatment process is the route through which the harmfulness of produced water is decreased to a set limit for disposal or re-use. The main objectives of this process are the removal of free and dispersed oil, dissolved organics, micro-organism, algae and bacteria; removal of suspended solids and colloids, dissolved salts and minerals, dissolved gases and in some cases radioactive materials from the produced water *(Arthur et al., 2005)*. The selection of the produced water treatment method is normally a challenging problem that is steered by the overall treatment goal. The general plan is to choose the cheapest and most efficient method. To meet up with mentioned objectives, operators usually have applied many stands-alone in one combined technology: physical, biological and chemical treatment methods for produced water management and treatment *(Nasiri and Jafari, 2017)*. Produced water treatment methods are classified as either conventional or non-conventional. The conventional methods of produced water treatment are grouped under physical, chemical and biological methods. The commonly used physical methods are physical adsorption, sand filtration, cyclones, evaporation, and dissolved air precipitation (DAP). Some of the chemical methods are chemical precipitation, chemical oxidation, electrochemical process, photocatalytic treatment, Fenton process, treatment with ozone and demulsification. Aerobic and anaerobic micro-organisms have also been used for biological treatment of produced water and has been found to remove up to 90% of COD using Bacillus Spp. (*Li et al., 2005*). Conventional treatment methods can remove suspended particles with particle size of 5 micron or above; the disposal and injection regulations are however becoming more stringent and the conventional methods are not able to treat produced water to meet these new limits (*Li et al., 2005*). The membrane treatments, combination of systems and some commercial treatment processes are used to achieve results where conventional methods fail to meet the set limits.

3.6.1.1 Adsorption:

The adsorption process is the most commonly used conventional method for the treatment of produced water. Adsorption is applicable to all types of produced water irrespective of TDS and salt concentrations. It can significantly reduce heavy metals, TOC, BTEX and oil concentrations. A variety of materials are used for adsorption; they include zeolites, copolymer, organoclays, activated alumina, and activated carbon, which can remove iron, manganese, TOC, and other contaminants. Although chemical use is minimal, the adsorbent can be easily overloaded with large concentrations of organics, so this process is not always ideal for primary treatment but as a polishing process. The media also eventually become consumed with contaminants and must be disposed or regenerated using chemicals. Regeneration creates a liquid waste product that must be disposed. Media may require frequent replacement or regeneration depending on type and feedwater quality. The combination of activated carbon and organoclays proved to be more efficient in removing total petroleum hydrocarbons (TPH) *(Doyle and Brown, 2000)*. Copolymers reduce the oil content up to 85% *(Carvalho et al., 2002)*. Zeolites are efficient in removing BTEX compounds *(Janks and Cadena, 1992)*.

3.6.1.2 Media Filtration:

Sand, anthracite coal and walnut shells are the most commonly used media for treatment of produced water from crude oil production. It is a simple but effective method for treating produced water and can effectively remove oil, grease and total organic carbon (TOC). It can also be employed on highly salty water. Although energy consumption is minimal, the expected lifetime of filtration media is lower than other methods, with replacement required frequently, depending on media type and feed water quality. The process also requires a vessel to contain the media and pumps and plumbing to implement backwashes. Chemicals may also be required to increase particle size, enhance separation, and for media regeneration.

3.6.1.3 Hydrocyclones:

Hydrocyclones use physical method to separate solids (i.e. sand) and oil contents of produced water streams based on density difference. They are made from metals, plastics or ceramic, and usually have a cylindrical top and a conical base with no moving parts. The performance of the hydrocyclone is determined by the angle of its conical section *(Colorado, 2009)*. Hydrocyclones can remove particles in the range of 5–15 mm and have been widely used for the treatment of produced water *(Jain, 2010)*. Nearly 8 million barrels per day of produced water can be treated with hydrocyclones *(Svarovsky and Thew, 1992)*. They are used in combination with other technologies as a pre-treatment process. They have a long lifespan and do not require chemical use or pre-treatment of feed water. A major disadvantage of this technology is the generation of large slurry of concentrated solid waste.

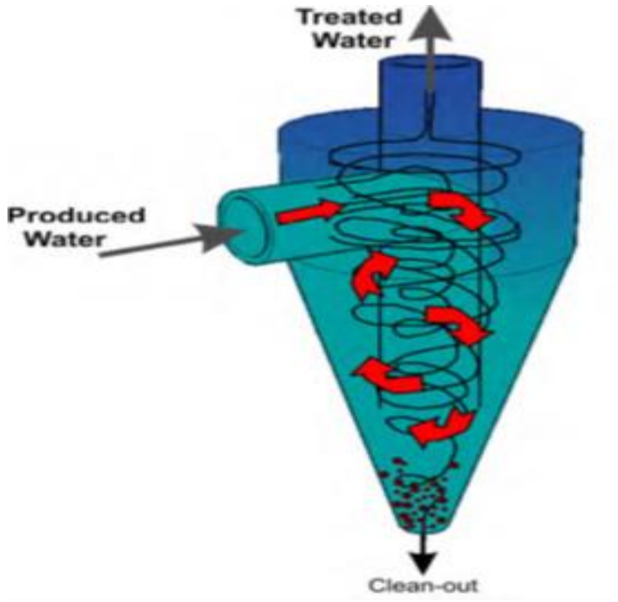


Figure 3.6: The Hydrocyclone (*Source: Dahm and Chapman, 2014*)

3.6.1.4 Dissolved Air Floatation (DAF):

Dissolved air floatation technique uses gas bubbles to lift lighter suspended particles to the surface of a tank for removal. The dissolved air comes out of solution: micro-bubbles rise and capture small, light particles (e.g., grease, oils, and organic material), bringing them to the surface as foam to effectively filter out lightweight particles. The foam is scraped off the surface. Heavier solids are collected from the bottom of the tank. Since the dissolved air generally provides significant aeration, oxidizable compounds may form complexes that will also be readily removed. The dissolved air floatation equipment exists in mobile unit and does not require pre-treatment of produced water to effectively remove low density particles. Operations of DAF at higher temperatures could be more difficult as the viscosity of water is less and oils and greases could become dissolved.

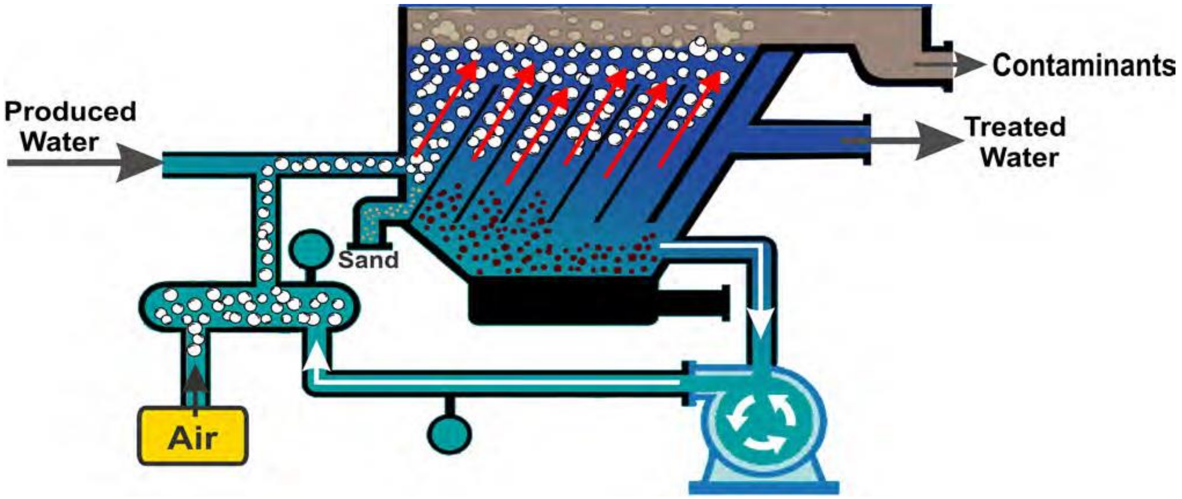


Figure 3.7: Dissolved Air Floatation Method (*Source: Dahm and Chapman, 2014*)

3.6.1.5 Chemical Oxidation:

This is a well-established and reliable technology for the removal of COD, BOD, organic and some inorganic compounds present in produced water *(Barratt et* *al., 1997)*. It is applicable to all types of produced water irrespective of TDS and salt concentration. Chemical oxidation treatment depends on oxidation / reduction reactions occurring together in produced water because free electrons cannot exist in solution *(ALL, 2003)*. Oxidants commonly used include ozone, peroxide, permanganate, oxygen and chlorine. The oxidant mixes with contaminants and causes them to break down. The oxidation rate of this technology depends on chemical dose, type of the oxidant used, raw water quality and contact time between oxidants and water *(Colorado, 2009)*. Chemical cost during this process may be high *(AWWA and ASCE, 2012)*. Energy consumption accounts for about 18% of the total cost of operations and maintenance *(Colorado, 2009)*. It requires minimal equipment and has a life expectancy of 10 years or greater and solid separation post-treatment may be employed to remove oxidized particles *(Colorado, 2009)*.

3.6.1.6 Ion Exchange Technology:

Ion exchange is a widely applied technology in industrial operations for various purposes, including utilization for the treatment of CBM produced water. It is especially useful in the removal of monovalent and divalent ions and metals by resins from produced water *(Clifford, 1999)*. *Nadav,1999* suggested that ion exchange has the potential to remove boron from RO permeate of produced water. Ion exchange technology has a lifespan of about 8 years and will require pre-treatment options for solid removal. It also requires the use of chemicals for resin regeneration and disinfection. The operating cost accounts for more than 70% of the overall cost of this technology *(Colorado, 2009)*.

3.6.1.7 Biological Treatment:

In the biological treatment method, aerobic and anaerobic microorganisms are used to treat produced water. Activated sludge, trickling filters, sequencing batch reactors (SBRs), chemostate reactors, biological aerated filters (BAF), and lagoons are typical employed during aerobic produced water treatment. The micro-organisms used for biological produced water treatment could be sourced from naturally occurring micro-organisms, commercial microorganisms, specific groups of microorganisms or acclimated sewage sludge.

Activated sludge is the usual method for treating produced water. In a continuous-flow pilot plant, an oil skimmer is used to remove oil before treatment in an activated sludge system. Naturally occurring microbial growth is employed in an aeration tank. The activated sludge treatment unit could maintain a total petroleum hydrocarbon (TPH) removal efficiency of 98–99% at a solids retention time (SRT) of 20 days *(Tellez et al., 2002)*. *Freire et al., 2002* studied COD removal efficiency of acclimated sewage sludge in SBR with different percentages of produced water and sewage. In 45% and 35% (v/v) mixtures of wastewater, COD removal efficiencies varied from 30% to 50%. Salinity of the produced water sample does not have significant effect on COD removal in biological treatment since the inhibitory effect of high salinity on the microbial culture will be negligible *(Dfaz et al., 2000)*.

Table 3.3: Technologies used for produced water treatment and their capabilities (*Source: Nasri and Jafari, 2017*)

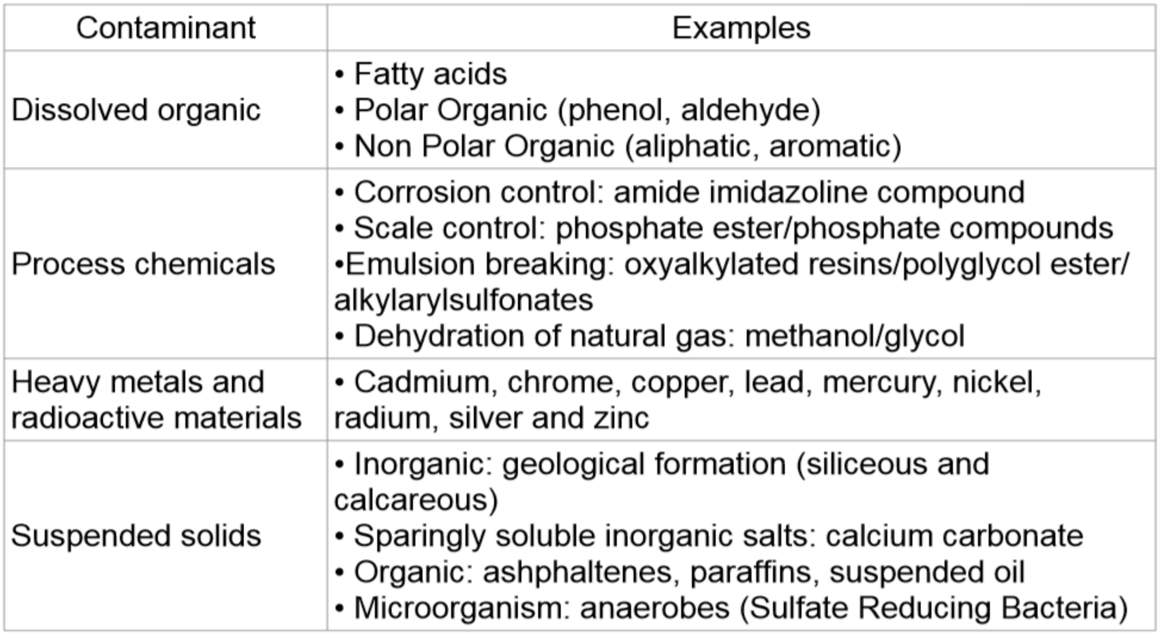
Treatment method	De-oiling	Suspended particles removal	Iron removal	Softening (Ca and Mg removal)	Soluble/trace organics removal	Desalting
API separator	■	■				
Deep bed filter	■	■				
Hydrocyclone	■	■				
Aeration and sedimentation		■				
Precipitation		■	■			
Ion exchange			■	■		
Biological treatment					■	
Thermal desalination		■		■		■
Activated carbon	■		■	■	■	
Chemical treatment	■				■	
Ultrafiltration	■	■			■	
Nanofiltration	■	■	■	■	■	■
Reverse osmosis	■	■	■	■	■	■
Electrodialysis			■	■		■

There are several other methods employed in the treatment of produced water. The choice of the technology to use is dependent on several conditions; they include regulatory acceptance, site location, technical feasibility, costs, as well as availability of infrastructure and equipment. The thermal separation process, reverse osmosis technology, microfiltration, nanofiltration, ultrafiltration, electrodialysis are some of the technologies that are currently being used to treat produced water from crude oil production to regulatory specifications.

3.6.2 Characteristics of Produced Water

Produced water is a mixture of organic and inorganic materials. Some factors such as geological location of the field, its geological formation, lifetime of its reservoirs, and type of hydrocarbon product being produced affect the physical and chemical properties of produced water *(Veil et al., 2004)*. Produced waters characteristics depend on the nature of the producing / storage formation from which they are withdrawn, the operational conditions, and chemicals used in process facilities. The composition of produced water from different sources can vary by order of magnitude. However, produced water composition is qualitatively like oil and / or gas production *(Fillo et al., 1992)*. The major compounds of produced water include dissolved and dispersed oil compounds, dissolved formation minerals, production chemical compounds, production solids (including formation solids, corrosion and scale products, bacteria, waxes, and asphaltenes), and dissolved gases *(Hansen and Davies, 1994)*.

Table 3.4: Major Characteristics of Produced Water (*Source: Igwe et al; 2013*)



Contaminant	Examples
Dissolved organic	• Fatty acids • Polar Organic (phenol, aldehyde) • Non Polar Organic (aliphatic, aromatic)
Process chemicals	• Corrosion control: amide imidazoline compound • Scale control: phosphate ester/phosphate compounds •Emulsion breaking: oxyalkylated resins/polyglycol ester/ alkylarylsulfonates • Dehydration of natural gas: methanol/glycol
Heavy metals and radioactive materials	• Cadmium, chrome, copper, lead, mercury, nickel, radium, silver and zinc
Suspended solids	• Inorganic: geological formation (siliceous and calcareous) • Sparingly soluble inorganic salts: calcium carbonate • Organic: ashphaltenes, paraffins, suspended oil • Microorganism: anaerobes (Sulfate Reducing Bacteria)

3.6.2.1 Dissolved and Dispersed Oil Compounds:

Oil is a mixture of hydrocarbons including benzene, toluene, ethylbenzene, and xylenes (BTEX), naphthalene, phenantherene, dibenzothiophene (NPD), polyaromatic hydrocarbons (PAHs) and phenols. Water cannot dissolve all hydrocarbons, so most of the oil is dispersed in water *(Ekins et al., 2007)*. The amounts of dissolved and suspended oil present in produced water (prior to treatment) are related to the oil composition, pH, salinity, TDS (total dissolved solids), temperature, oil/water ratio, type and quantity of oilfield chemicals, type and quantity of various stability compounds (waxes, asphaltenes, fine solids) *(Hansen and Davies, 1994)* .

3.6.2.2 Dissolved Formation Minerals:

Inorganic dissolved compounds in produced water include anions and cations, heavy metals, and naturally occurring radioactive materials (NORM). Produced water contains a wide range of both cations and anions. All of them have similar patterns of concentration for different metals *(Faksness et al., 2004)*.

3.6.2.3 Production Chemical Components:

During oil and gas production process, some chemicals are added to treat or prevent operational problems. Treatment chemicals (production treating, gas processing, and stimulation) and production treating chemicals (scale and corrosion inhibitors, biocides, emulsion breakers, antifoam and water treatment chemicals) are used in these processes *(Stephenson, 1992)*.

3.6.2.4 Production Solids:

Production solids are a wide range of materials including formation solids, corrosion and scale products, bacteria, waxes, and asphaltenes. Sulphides (polysulphides and hydrogen sulphide) are also generated in produced water by bacterial reduction of sulphate. Inorganic crystalline substances such as SiO2, Fe2O3, Fe3O4, and BaSO4 are also found in the suspended solids in produced water *(Shubo et al., 2000)*.

3.6.2.5 Dissolved Gases:

CO_2, O_2, and H_2S are common gases included in produced water.

3.6.3 Cost of Produced Water Treatment

Considering that produced water constituents and volume generated vary from one facility to another, the costs expended on treatment are also varied. In the produced water / wastewater management lifecycle, the main cost components are sourcing, storage, transportation, treatment and disposal costs *(Slutz et al., 2012)*. The cost of treatment is also specific to the time of evaluation and therefore the need to use recent publication / literature for referencing costs. The costs components of produced water treatment also vary by and are influenced by the position of the market. Some of the key components of produced water treatment are discussed below.

3.6.3.1 Transportation:

At the end of produced water treatment, the treated produced water is transported to point where it is used or disposed. The transportation of treated produced water could be either by trucks or through pipeline network *(Eaton, 2014)*. In cases where the produced water treatment plant is located away from the production facility especially when the operator has contracted another company to handle the produced water treatment, the cost of transporting the produced water to the treating facility is included.

Transportation is a function of distance between the production / treatment facility and the reuse / disposal location. For truck transportation, the cost is a function of distance, the truck volume and overall time. *Slutz et al., 2012* presented a general range of $0.02-0.04 per bbl per mile. *Dunkel, 2016* used $1.50 per bbl for 10 miles ($0.15 per bbl per mile). *McCurdy, 2011* estimates an average of $1.00 per bbl per hour.

Pipeline transportation of produced water provides potential cost savings and social benefits *(Collins, 2016; Dunkel, 2016; Jacobs, 2016; Schilling, 2016)*. Primary social benefits of pipelines include reducing traffic, road damage and exhaust pollution from trucks in areas with high oil and gas activity. As material and construction costs vary significantly, pipeline costs range considerably and are reported as a simple dollar per bbl per mile. *Slutz et al., 2012* reports a range of $0.02-0.40 per bbl per mile, ranging from lowest fast line to highest HDPE pipe cost. *Dunkel, 2016* reports $3-4 million for a 12 inch, buried HDPE pipe with 35,000 bbl per day capacity spanning 10 miles and operating at $0.03 per bbl. Assuming full capacity operating at a year, this equates to an overall estimate $0.03 per bbl per mile. Wolfcamp Water Partners has a pipeline cost of less than $0.02 per bbl per mile (*Partners, 2011*).

3.6.3.2 Disposal

Produced water disposal wells are commonly used for disposal of treated produced water at onshore locations but at offshore locations, treated produced water could be dumped overboard into the water body if they meet discharge limits set by the regulatory body. The cost of injection is varied by regional geology, which influences the capacity and cost to drill the injection well. (*Slutz et al., 2012*) documents a range of injection costs of \$0.75-3.00 per bbl. The closeness of the injection well to the water treatment facility also affects the cost of injection. *McCurdy, 2011* reported commercial SWD disposal costs of \$0.50-2.50 per bbl. Injection costs in the Bakken were estimated to be between \$0.50 and \$1.75 per bbl *(Center, 2010; Ruyle, 2015)*.

3.6.3.3 Treatment

The real cost of treating the produced water is widely varied and dependent upon many factors, including constituents in the produced water, desired effluent criteria, power source availability and treatment technology used. The ultimate cost per bbl will be a factor of treatment unit capital, operation and maintenance, profit margin and personnel required. Depending on the amount of supervision, personnel alone could cost \$1.00 per bbl or more *(Dunkel, 2016)*. For produced water requiring minimal treatment, such as suspended solids and oil removal, the treatment cost could range from \$1.00-2.00 per bbl. For extensive treatment and cleaner effluent, such as desalination, treatment cost could range from \$3.50-6.25 per bbl *(Slutz et al., 2012)*. In 2016, Approach Resources reported an overall cost of \$1.50 per bbl at one of their PW treatment systems, while Apache reported a cost of only \$0.29 per bbl *(Collins, 2016)*.

3.6.3.4 Source Water:

Source water cost for crude oil production operations is variable depending on type of water (i.e. ground water, surface water, treated PW, municipal effluent) and drought conditions of the region. *Slutz et al., 2012* observed surface water costs as low as $0.01-0.02 per bbl in the Marcellus. Ground and surface water ranged from $0.25-0.35 per bbl in the Barnett, Eagle Ford and Haynesville. In the Bakken and Denver-Julesburg, source water ranged from $0.50-1.00 per bbl (*Slutz et al. 2012*). *Sharr, 2014* reports freshwater sourcing costs ranging from $0.30-0.80 per bbl in the Eagle Ford. *Arnett et al., 2014* proposed an average cost of $0.50 per bbl for ground water in the Eagle Ford. In the Permian, ground water prices range from $0.16-0.50 per bbl, with an average and extreme of $0.37 and $0.80 per bbl (*Cook et al., 2015*). *Collins, 2016* reported Permian freshwater costs in the range of $0.40-0.50 per bbl, Santa Rosa brackish water as $0.35-45 per bbl and Odessa municipal effluent as $0.27 per bbl.

3.6.4 Energy Expenditure in Produced Water Treatment:

The energy consumed for treatment of produced water accounts for 15 to 40% of the operating cost in conventional produced treatment systems. The conventional treatment system requires between 0.3 and 0.6 KWh/m^3 *(Soares et al., 2017)* but when there are limitations of area or high qualities are required for the effluent, alternative technologies with higher power consumption may be adopted *(Garrido et al., 2011)*. *Wang et al., 2016* explains that electricity is the common source of energy in the oil field and it is used to power pumps, valves, compressors and other equipment for the treatment of produced water as well as the entire production process. Traditional water and wastewater treatment systems are costly, and often inefficient and great energy users (*Mahgoub et al., 2010*). Notwithstanding the associated cost, energy consumption is still considered one of the greatest anthropogenic sources of greenhouse gases and it causes some of the most relevant impacts on the warming of the earth *(Vilanova et al., 2015)*. A conventional produced water treatment system, for example, has a potential to produce up to 1,400 ton of CO2 per annum during its operation *(Muga and Mihelcic, 2008)*.

Produced water quality, especially its salinity (TDS), varies widely across basins and will determine its potential for reuse and the degree of treatment required for reuse and disposal options. *Racoviceanu et al., 2007* estimates that the conventional chemical coagulation will consume between 0.68 and 0.72 $kWhm^{-3}$ but *Xu et al., 2016* believes that 39–100 $kWhm^{-3}$ are required for electrocoagulation based on the electrical conductivity (EC) of the water. The total energy (thermal and electric combined) requirement for Thermal Desalination processes is higher than other processes (40 -120 kWh/m^3) while 3.5-4.5 kWh/m^3 is required for Reverse Osmosis or Nanofiltration (NF) (*Graham et al., 2015*). Energy is expended in various operations in treatment of produced water; in backwashing in Media Filtration, in dissolution of gas in Gas Floatation and in all pumping operations in Hydrocyclones, Evaporation ponds, Ion exchange processes etc. Approximately 1 – 4 $KWhm^{-3}$ is required for the operation of Biological Aerated Filters, about 18% of the total energy consumption of the production facility is required for chemical oxidation process, and 0.14 – 0.20 KWh/Ib NaCl equivalent is used to treat produced water in Electrodialysis /Electrodialysis Reversal (*Igunnu and Chen, 2014*).

In a conventional produced water management, if the final effluent is to be used for enhanced oil recovery or pressure maintenance, then total energy requirement includes:

$E_{EOR} = E_P + E_T + E_I$ ………………….…….…………………….Equation (3.1)

Where E_P = Energy required to pump produced water to the treatment facility.

E_T = Energy required for treatment of the produced water; E_P = Energy required to pump the treated water through the treatment facility and to disposal location; E_I = Energy requirements for injection of treated water into the disposal well.

On the other hand, if the final effluent is required for disposal to a location, the total energy requirement is expressed as:

$E_{DSP} = E_P + E_T + E_D$ …….…….………………….…………….……….. Equation (3.2)

Where E_P = Energy required to pump produced water to the treatment facility; E_T = Energy required for treatment of the produced water; E_D = Energy required to pump the treated water to disposal location.

The energy consumption in the pumping of produced water to the produced water treatment plant depends on the pump capacity, the pump efficiency, the pump type and the differential pressure between the suction and the discharge of the pump. *Singh and Kansal, 2016* estimated consumption at 0.09 kWh/m3 in India, or 45.3% of the total used for the produced water treatment operation. In the USA, the expenditure at this stage is 0.04 kWh/m^3, in New Zealand it varies between 0.04 and 0.19 kWh / m^3, in Canada it is around 0.02 and 0.1 kWh/m^3 *(Matos et al., 2014)*, in Hungary it is between 0.045 and 0.14 kWh/m^3, and in Australia it is estimated to be between 0.1 and 0.37 kWh/m^3. *Bodik and Kubaska, 2013; Longo et al., 2016* had suggested a global consumption average of 5 to 18% for pumping.

The energy consumption for produced water treatment will depend on the flow, effluent quality, types of processes adopted and quality of the effluent *(Fitzosimons et al., 2016)*. At the end of the produced water treatment, it is still necessary to expend energy on the final disposal of the effluent, which is usually done in saltwater disposal well, enhanced oil recovery wells or into water bodies in offshore locations. About 0.02 kWh/m^3 is required to dispose the final effluent in Australia (*Wakeel et al., 2016*) it could take up to 0.24 kWh/m^3 (*Brasil, 2016*).

3.7 ENERGY DYNAMICS IN CRUDE OIL PRODUCTION

Energy efficient industry, buildings and transportation could reduce the world's projected energy needs in 2050 by one-third (*Rokke, 2015*). According to the Global Carbon Capture and Storage Institute, oil and gas industry is regarded as the most energy-intensive of all industrial processes. It is believed to consume about 20% of its output for its own process needs. The existing energy efficiency processes for exploration and production is considered low by any standards, as it hardly reaches 20%. Compared to the state-of-the-art power generation technology reaching over 60% efficiency, it is obvious that there is a huge potential for the reduction of power demand for the exploration and production business (*The Global CCS Institute, 2018*).

Extraction of crude oil and natural gas from the reservoir involves expenditure of huge amount of energy. Crude oil and natural gas are trapped under pressure; the pressure is responsible for flow of the fluids to the surface during production. In many cases, the trapped pressure is usually not enough to cause flow to the surface naturally thus the need for energy. Moreover, it has been observed that as the field is being produced, the reservoir continues to lose pressure therefore demanding more and more energy to lift the fluid to the surface. The energy required to produce crude oil and natural gas continues to increase as the field age. The equipment involved in crude oil and natural gas production use a lot of energy as well. These include heat exchangers, pumps, and compressors etc.

Deep water production of crude oil and natural gas required more energy to produce a barrel or cubic foot of crude oil and natural gas respectively. Most sub-sea systems are remotely operated and therefore fed by energy from above the water or from onshore power sources that are capable of supplying and controlling fully autonomous production systems with electricity at depths of 2,000 meters and below (*The Global CCS Institute, 2018*). In colder regions, more energy, mostly in the form of heat, may also be required. The figure below represents the energy consumption by key events in the life of a typical oil field.

The improvement of the energy efficiency of a production process in an oil and gas field would require a thorough understanding of the energy utilization concepts, the integration concepts, the proper energy mix and the evolution of production process on the use of minimum energy to achieve same production with no additional effect to the environment.

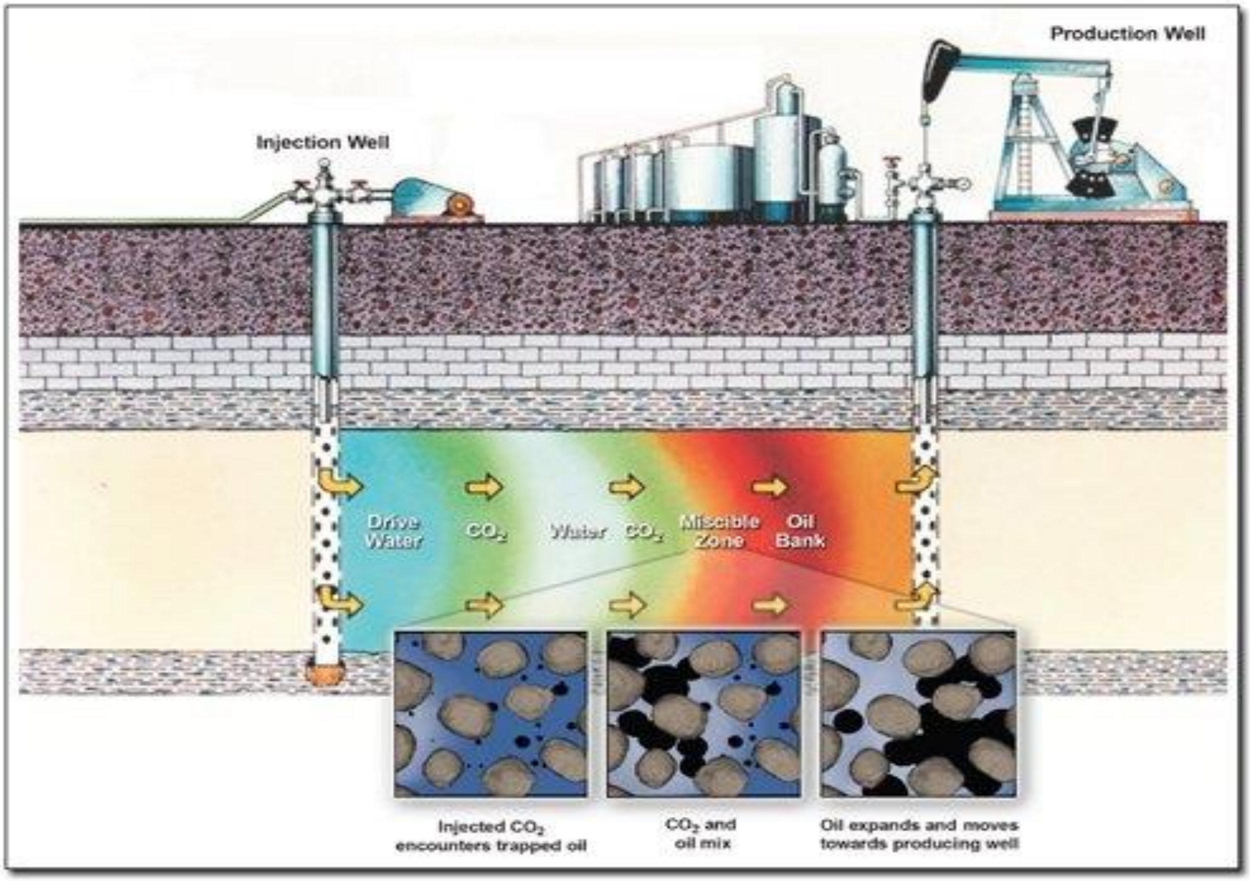


Figure 3.8: Enhanced oil recovery using CO_2 and Water (Source: *Paschoa, 2014*)

Oil and gas companies have a strong financial incentive to save energy, because of the large share of energy in the overall cost of operating their facilities. Efficient energy use reduces costs along the whole supply chain and makes energy more affordable to consumers. In practice, the oil and gas industry has also put up some strategies to improve the efficiency of oil and gas processes, combat associated waste and reduce emissions. Some of these efforts include energy systems management, involving the use of information technology to analyse and control energy consumption in production and refining processes; application of more efficient exploration, through improved drilling success rates thanks to advances in seismic surveying and analysis, and drilling techniques; co-generation of heat and power and the recovery of waste heat from production units using heat exchangers; reduced flaring and venting of associated gas, through investment in gas processing and distribution; improved process operations and equipment, such as more efficient pumps and compressor turbines, and high-pressure pipelines, which require less energy input per unit of oil or gas transported per kilometre (*Accenture, 2012*).

3.7.1 The Energy Efficiency Concept:

Energy efficiency is the use technology that requires less energy to perform the same function. The other way, it is the use of the same amount of energy to deliver more services. It is a way of managing the growth in energy consumption. It is a process that saves money on energy bill and reduces the amount of greenhouse gases going into the atmosphere. Energy efficiency is not energy conservation although both are energy reduction techniques. Energy conservation is any behaviour that results in the use of less energy and may entail going without some services in order to save energy. The habit of turning the lights off when leaving the room and recycling aluminium cans are both ways of conserving energy whereas replacing an incandescent lamp with a compact fluorescent lamp (which uses much less energy to produce the same amount of light) is energy efficiency.

Anywhere energy is used, including oil and gas production process, there are opportunities to increase efficiency. In most cases, energy efficiency measures will pay for themselves over time in the form of lower energy bills. Economic analysis of the cost of various energy efficiency measures, compared with that of building various types of energy sources that emit less GHG than fossil-powered plants, shows that most energy efficiency measures are cheaper, and therefore pay for themselves faster, than most kinds of energy generation (*Arthur, 2015*). Energy efficiency is considered the most abundant, cheapest, fastest approach to reducing emissions of greenhouse gases into the atmosphere (*Sorrell, 2015*). The route for making an existing process energy efficient may involve improving existing processes, commercializing new processes, recycling waste, energy and materials, investing in renewable raw materials and creating products that enable energy savings (*Patt and Banholzer, 2009*).

Optimisation of energy use in an industrial process like the oil and gas production process often leads to positive environmental impacts and cost savings. In these plants, the owners would want to ensure that their investments are delivering optimal functionality, efficiency and good profits. The areas where better energy efficiency and savings can be achieved are process piping (especially high temperature ones), heat exchangers, pressure vessels, compressors, pumps, boilers, filters, flue ducts, valve boxes, flanges, the flare stack, tank walls and roofs.

A simple way of increasing the efficiency of an industrial process is to ensure that it is properly insulated; minimising energy consumption and maximising the effective lifetime of the plant are highly valuable benefits of a well-insulated process. The process of insulation saves energy and thereby cost and reduces the emission of CO_2 and other greenhouse gases.

3.7.2 Energy Consumption and Energy Loss:

In industrial processes, when a quantity of energy is put into a machine or device for conversion into another form of energy, the output energy in the desired form is only a part of the input energy. The balance is the energy loss. It therefore means that conversion of energy from one form to the other is not 100% efficient. This principle applies to all industrial processes in which energy is used in any form for the manufacture of products. The energy is lost along the flow process, through leaks from facilities, rubbing of surfaces, release of heat to the atmosphere etc. This leads to the concept of efficiency.

The efficiency of an energy converter is now defined as the quantity of energy in the desired form (the output energy) divided by the quantity of energy put in for conversion (the input energy). Efficiency is usually denoted by the Greek letter, η.

$$\eta = \frac{\text{Output Energy}}{\text{Input Energy}} \quad \text{……………………Equation (3.3)}$$

The terminologies "energy utilization" and "energy generation" also refer to the conversion of energy from one form to another and therefore involves energy loss in one way or the other. For instance, in space heating, energy is utilized by conversion of the chemical energy of the wood into heat. Moreover, the generation of energy by a diesel engine means that the engine can convert chemical energy of oil into mechanical energy.

The production of crude oil and natural gas involves conversion of energy from one form to another during which some energy losses are incurred until the crude oil and natural gas are good for export. The sum of all the energy used during this process including the energy losses is referred to as the consumed energy. The cost of the energy consumed in the manufacture of products determines to a great extent the cost of a unit of that product.

3.8 SUMMARY

Crude oil and natural gas are usually trapped under pressure in the reservoir. The pressure, in most cases, are enough to push the crude out from the oil well to the surface of the earth. This natural flow of crude oil to the surface of the earth will continue if the pressure in the reservoir is high enough. The crude oil and natural gas that flows from the reservoir to surface of the earth come with impurities that need to be removed to meet sale specifications. The basic sediments (salt, mud and sand) and water in the crude oil is removed while the associated crude oil, water, H_2S, CO_2 and N_2 are removed in the case of natural gas. The process of extracting hydrocarbons from the reservoir and separating the mixture of liquid hydrocarbon (crude oil), natural gas, water and solids; removing the constituents that are non-saleable and preparing the crude oil and natural gas for sale is called Production.

Oil and gas reservoirs are found in both onshore and offshore location hence production could be either onshore or offshore. In onshore locations, production is done at the flowstations whereas it is done on platforms offshores. Floating Production Storage and Offloading (FPSO) or Floating Storage and Offloading (FSO) vessels could be used in offshore locations. The role of these vessels in crude oil and natural gas production is reflected in their description above.

The oil and gas process is an assemblage of process equipment that takes the reservoir fluids from the wellhead manifolds and delivers stabilized marketable products, in the form of crude oil, condensate or natural gas to the required specifications. The production facility could be made up of the process, fuel gas treatment system, the flare system, water injection system, produced water treatment system, gas treatment / re-injection system. The major equipment in the production facility are the manifold, heat exchangers / steam heaters, separators, pumps, compressors, and metering systems.

The production, handling and transportation of crude oil require the use of various types of chemicals. These chemicals may be added at all stages of the production process, from the water injection phase in which the hydrocarbon resources are being extracted, through the oil-water separation phase, and including the transport phase where the recovered oil is sent to pipelines. Some of the commonly used oilfield chemicals are scale inhibitors, corrosion inhibitors, biocides, oxygen scavengers, emulsion breakers, antifoam agents, drag reducing agents, hydrate inhibitors, hydrogen sulphide scavengers, paraffin control agents, pour point depressants and asphaltene control agents.

The production and consumption of petroleum come with unavoidable environmental impacts that may be regional or global in scale, including air pollution, climate change, land and water pollution due to oil spills. Production of petroleum has caused local detrimental impacts to soils, surface and ground waters and the ecosystems. Some of the key pollutants generated from the production of crude oil and natural gas are produced water, chemicals, crude oil, naturally occurring radioactive materials (NORM), air pollutants, heat, light, noise, pipelines and installations.

Produced water is the main source of pollutants in crude oil production and contain various compounds at levels considered toxic to plant and animal life.

In order to dispose produced water, it must be treated to reduce the concentrations of these compounds to acceptable limits. Some of the technologies employed for the treatment of produced water include adsorption, media filtration, hydrocyclones, dissolved air floatation, chemical oxidation, ion exchange, membrane treatment and biological treatment.

Production of crude oil and natural gas from the reservoir also involves expenditure of huge amount of energy. Although petroleum is trapped in the reservoir under pressure, in many cases, the pressure may not be enough to cause the flow of the fluid to the surface naturally thus the need for energy. As the field is produced, the reservoir continues to lose pressure therefore demanding more and more energy to lift the fluid to the surface. The heat exchangers, pumps and compressors use a lot of energy and are used in the production of crude oil and natural gas. Energy is also expended during the treatment of produced water for disposal or use. The energy expended is dependent on the final use of the treated produced water. It is suggested after review of existing literature that system integration and optimization of process variables could be applied to save energy in crude oil production process.

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CHAPTER FOUR

ENVIRONMENTAL AND ECONOMIC EFFECTS OF CRUDE OIL PRODUCTION

4.1 INTRODUCTION

The growth of the oil industry over the past few years has been dramatic. Although in Nigeria recent attacks on oil and gas installations by militant groups have led to a decline in the total production, the recorded production increase in some other countries especially the United States has been huge. Across the United States, total annual crude oil production increased from 2.4 billion barrels in 2012 to over 5.7 billion barrels in 2018 *(US EIA, 2019)*. At the same time, production of crude oil in Nigeria declined from 860 million barrels to 698 million barrels *(DPR Report, 2018)*. The primary reasons for the growth have ranged from advancement in technology, which has helped to unlock previously unrecoverable reserves in shales and deep offshore locations to the discovery of new reserves *(IEA, 2018 Outlook)*. The economic benefits of crude oil production activities (including multiplier effects) are estimated to include almost US $1.2 trillion in gross product each year as well as more than 9.3 million permanent jobs in the United States *(Perryman, 2014)*.

The rise in global demand for crude oil has led to the increased global production in attempt to meet the world energy demand. From estimation, it has been found that to meet the projected increase in world oil demand, the total petroleum supply in 2030 is required to reach 118 million barrels per day from 80 million barrels per day as at 2003 *(Berdzenadze, 2015)*. New oil and gas reserves have been discovered in Kenya, Uganda, Mauritania, Tanzania and Ghana in the last few years. In some of these countries, production has already started. Oil and gas deposits in deep offshore locations in many developing countries are being produced today. The production of non-conventional oil and gas deposits by fracking in shales has also been vigorous as more studies are focused on reducing the cost of production of oil and gas in shales.

Solids, liquids and gaseous forms of wastes and pollutants are generated from crude oil production. The management of these wastes and pollutants is difficult except there is a concise laid down plan for the expected wastes and pollutants prior to crude oil production. Since the cost of management of waste and pollutants from crude oil production is normally high, producing companies tend to avoid this cost. Production has emitted greenhouse gases to the atmosphere, released produced water into water bodies and spilled crude oil on the soil. These have posed challenges to the existence of plants and animals in oil producing communities.

Infrastructural development is about the greatest challenge of most developing countries as government struggle to provide good access roads and public transportation, schools and quality education, hospitals and medicines to the citizens. The discovery of crude oil and natural gas in these countries comes to the rescue as foreign exchange, taxes and royalties are earned from the production of crude oil. Apart from the benefits to the state, citizens are provided with employment and sometimes scholarships, electricity, pipe-borne water and access roads by the producing companies.

In view of the dearth of infrastructure in most developing countries, the economic advantage of crude oil production has always been the focus in these countries leaving the environmental impacts to the background. This is the reason for the volume of environmental degradation from crude oil production in the Niger Delta region of Nigeria where crude oil production activities have been on-going for over sixty years. The air, land and water in this region has been polluted by crude oil production through release of natural gas, spill of crude oil and improper disposal of wastes including produced water.

4.2 ENVIRONMENTAL COSTS ASSOCIATED WITH CRUDE OIL PRODUCTION

In most cases, crude oil exists in the reservoir with natural gas. In the evaluation of the environmental costs, the effect of production of natural gas would be considered as they are produced alongside when they exist together. The impacts on the environment as a result of production of crude oil and natural gas results from long-term habitat change within the oil and gas field, production activities, waste management, noise, the presence of workers and potential spills. These activities could potentially impact on the environment as detailed below:

4.2.1 Noise:

The main sources of noise during the production of crude oil and natural gas include compressor and pumping stations, producing wells (including occasional flaring), and vehicle traffic. Compressor stations produce noise levels between 64 and 86 dBA at the station to between 58 and 75 dBA at about 1 mile (1.6 kilometers) from the station *(Davorin, 2013)*. The primary impacts from noise is localized disturbance to wildlife, recreationists, and residents. Noise associated with cavitation is a major concern for landowners, livestock, and wildlife *(Spellman, 2014)*.

4.2.2 Air Quality:

The primary emission sources during the production of crude oil and natural gas include compressor and pumping station operations, vehicle traffic, production well operations, separation of oil and gas phases, and on-site storage of crude oil. Emissions include volatile organic compound (VOCs), nitrogen oxides, sulphur dioxide, carbon monoxide, benzene, toluene, ethylbenzene, xylenes, polycyclic aromatic hydrocarbons (PAHs), hydrogen sulphide, particulates, ozone, and methane. Venting or flaring of natural gas (methane) may occur during oil production, well testing, oil and gas processing, cavitation, well leaks, and pipeline maintenance operations. Methane is a major greenhouse gas. Air pollution during oil and gas production may cause health effects and reduce visibility.

4.2.3 Cultural Resources:

Production of crude oil and natural gas could also impact on the cultural resources by unauthorized collection of artefacts and the alteration of visual image *(Rodas, 2010)*. The presence of the aboveground structures alters the associated landscape component of the cultural resources. Damage to localities caused through off-highway vehicle (OHV) and the potential for indirect impacts (e.g., vandalism and unauthorized collecting) also exist.

4.2.4 Ecological Resources:

The adverse impacts to ecological resources during production of crude oil and natural gas could occur from disturbance of wildlife from noise and human activity, exposure of biota to contaminants, and mortality of biota from colliding with aboveground facilities or vehicles *(Ouren et al., 2007)*. The presence of production wells, ancillary facilities and access road reduces the habitat quality, disturbs the biota and thus affects ecological resources *(Macdonald et al., 2007)*. The presence of an oil or gas field could also interfere with migratory and other behaviours of some wildlife. Discharge of produced water inappropriately onto soil or into surface water bodies can result in salinity levels too high to sustain plant growth. Wildlife is always prone to contact with petroleum-based products and other contaminants in reserve pits and water management facilities *(Jones et al., 2015)*. They can become entrapped in the oil and drown, ingest toxic quantities of oil by preening (birds) or licking their fur (mammals); or succumb to cold stress if the oil damages the insulation provided by feathers or fur. In locations where naturally occurring radioactive material (NORM)-bearing produced water and solid wastes are generated, mismanagement of these wastes can result in radiological contamination of soils or surface water bodies *(Burton et al., 2014)*.

4.2.5 Hazardous Materials and Waste Management:

Industrial wastes are generated during routine operations (lubricating oils, hydraulic fluids, coolants, solvents, and cleaning agents). These wastes are typically characterized, placed in containers and labelled before being transported to an appropriate permitted off-site disposal facility as a standard practice. Impacts could result if these wastes were not properly handled and were released to the environment. Environmental contamination could occur from accidental spills of herbicides or, more significantly, oil. Chemicals in open pits used to store wastes may pose a threat to wildlife and livestock. "Fracking" fluids can contain potentially toxic substances such as diesel fuel (which contains benzene, ethylbenzene, toluene, xylenes, naphthalene, and other chemicals), PAHs, methanol, formaldehyde, ethylene glycol, glycol ethers, hydrochloric acid, and sodium hydroxide. Sand separated from produced water must be properly disposed as it is often contaminated with oil, trace amounts of metals, or other naturally occurring constituents. Production could also cause accumulation of large volumes of scale and sludge wastes inside pipelines and storage vessels *(Attalah et al., 2012)*. These wastes may be transported to offsite disposal facilities. Produced water can become a significant waste stream during the production of crude oil and natural gas. Regulations govern the disposal of this waste stream; the majority of it is disposed by underground injection either in disposal wells or, in mature producing fields, in enhanced oil recovery wells (i.e., wells through which produced water and other materials are injected into a producing formation in order to increase formation pressure and production). In some locations, produced water may carry NORM to the surface.

4.2.6 Health and Safety:

Possible impacts to public health and safety during production include accidental injury or death to workers and, to a lesser extent, the public. Health impacts could result from water contamination, dust and other air emissions, noise, soil contamination, and stress (e.g., associated with living near an industrial zone). Potential fires and explosions would cause safety hazards. Cavitation could ignite grass fires. Increased or reckless driving by oil or gas workers would also create safety hazards. In addition, health and safety issues include working in potential weather extremes and possible contact with natural hazards, such as uneven terrain and dangerous plants, animals, or insects *(McMichael et al., 2003)*.

4.2.7 Land Use:

Land use impacts during the production of crude oil and natural gas would be an extension of those that occurred during the drilling/development phase. Although it is possible for farmers or fisher men to carry out activities around the well locations, restrictions would always exist.

4.2.8 Paleontological Resources:

The existence of access roads creates a threat to paleontological resources during oil and gas production by allowing for unauthorized collection of fossils.

4.2.9 Socioeconomics:

Although new jobs and businesses would be created and royalties and taxes paid to landowners and government, there is a potential negative impact on the value of properties located in the proximity of oil and gas field *(Bennett, 2013)*. This effect increases as the number of wells increase.

4.2.10 Soils and Geological Resources:

The main impact from production would be the depletion of recoverable oil and gas reserves. Possible geological hazards (earthquakes, landslides, and subsidence) could be activated by oil and gas extraction activities *(Morton, 2003)*. Although it is rare, the injection of produced water in disposal wells could trigger localized seismic activity *(Buchanan et al., 2014)*.

4.2.11 Transportation:

The impact of crude oil and natural gas production to transportation would be basically due to the daily vehicular movement of light trucks and cars used for surveillance and movement of materials. Heavy truck traffic would be limited to periodic visits to a well site for workovers and formation treatment.

4.2.12 Water Resources:

During the life of a production well, the integrity of the well casing and cement will determine the potential for adverse impacts to groundwater *(Ingraffea et al., 2014)*. If subsurface formations are not sealed off by the well casing and cement, aquifers can be impacted by other non-potable formation waters. Hydraulic fracturing fluids have the potential to contaminate groundwater drinking reservoirs *(Osborn et al., 2011)*.

Stimulation fluids may penetrate away from the fracture and into surrounding formation. When stimulation ceases and production resumes, these chemicals may not be completely recovered and pumped back into the wellbore, and, if mobile, may be available to migrate through an aquifer. Most produced water is unfit for domestic or agricultural purposes (e.g., it is extremely salty or contains NORM or toxic compounds). If it is disposed of by release to the surface without treatment, it can cause soil and surface water contamination. Most of the produced water is disposed via injection in disposal wells or enhanced recovery wells *(Rubinstein and Mahani, 2015)*.

4.3 ECONOMIC IMPACTS OF CRUDE OIL PRODUCTION

Oil and gas have remained the lifeblood of the world economy for over one hundred years accounting for over half of mankind's primary energy supply *(Rahman, 2004)*. These high energy density and easily available fossil fuels have played important roles in some of the biggest industries like chemicals, transport, power, petrochemicals etc *(Farris, 2012)*. The availability of cheap, abundant energy lifts nations out of poverty therefore energy security has become national priority for most nations. Crude oil supply has become very important especially in the face of rising demand for energy for comfort and technological development.

The total measure of economic effects of crude oil production on the host nation or community especially for developing countries could be best described by the impacts: direct, indirect and induced. The direct impacts are measured as the jobs, labour income and value added to the oil and gas industry whereas indirect impacts are measured with the same yardstick but occurring across the supply chain due to crude oil and natural gas production activities. Induced impacts are measured as jobs labour income, and value addition resulting from household spending of labour and proprietor's income earned either directly or indirectly from crude oil and natural gas production activities *(Kleinhenz and Smith, 2011)*.

Crude oil and natural gas production activities have been found to make enormous economic contributions that benefit both the host nations and the citizenry. Some of the ways through which crude oil and natural gas production contribute to the economy include:

4.3.1 Taxes:

Oil and gas companies, involved in crude oil and natural gas production, pay billions of dollars in taxes to the government of their host countries every year. These funds are used for important social services, such as education, health care and provision of infrastructure that benefit the citizens of the country.

4.3.2 Oil and Gas Royalties:

Royalty is the share the government receives from companies producing crude oil and natural gas from the nation's reserves. The amount is a percentage of the money realized from sale of the produced crude oil and natural gas and therefore dependent on the volume of crude oil or natural gas produced.

4.3.3 Employment and Job creation:

The oil industry employs millions of people all over the world. These are usually high-paying jobs that make a great percentage of them live above the average income, spend within the community and pay taxes to the governments.

4.3.4 Gross Regional Product (GRP):

The total change in value addition generated by direct spending. GRP is conceptually the same type of measure as gross domestic product (GDP), which is also a measure of value addition and indicates the market value of goods and services, at purchaser prices, produced by all economic resources located in the country. Crude oil production has been found to increase the GRP of the states and in turn the GDP of the country.

4.3.5 Local Expenditure on Goods and Services:

The periodic injection of purchasing power through its local expenditure on goods and services by the oil and gas production industry is another way of contributing to the economy of the host country. Payments to local contractors for goods and services and for direct purchases has the capacity to stimulate the economy and exert secondary influences, through multiplier process on the level of output and employment in other related sections of the economy.

4.3.6 Provision of Foreign Exchange Reserves:

Since crude oil and natural gas are sold in international markets, producing countries has the potential to earn and save foreign exchange in reserves. This puts the country's economy in healthy position and gives her the capacity to finance the foreign exchange cost of any development program.

4.3.7 Contribution to Power Supply and Public Utilities:

Natural gas could be used to power turbines for the generation of electricity. Associated gas is still being flared today in many oil fields in developing countries: this could be turned to power and used for industrialization of the producing community. In some cases, producing companies have supplied electricity to the host communities to aid development.

4.3.8 Investment:

Most oil and gas companies are quoted at the various stock exchange markets. This makes it possible for citizens to invest in these stocks and enjoy the privilege of the innovation, growth and dividends associated with such investment.

Crude oil and natural gas production is done either on land on water. The area occupied for this purpose would have been used for the purpose of farming and fishing respectively. In most communities where oil and gas production activities are being carried out, the traditional occupations of the people prior to oil and gas discovery are being abandoned. The country, in some cases, may even resort to total reliance on the production of oil and natural gas for economic growth leading to a mono product economy. For example, Nigeria is currently in this dilemma as over 70% of the country's earning is crude oil and natural gas dependent *(PWC, 2015)*.

Although a great deal of the expertise required to produce crude oil and natural gas is sourced from locations far from the field; in some cases, overseas, the industry most of the times provides the host and surrounding communities with employment for unskilled and low skilled labour. There are opportunities to learn from the best hands in the industry and get exposed to the most recent technologies on the various operations. In cases where the production of crude oil and natural gas is done in onshore locations, sub-contractors from the host and adjoining communities are usually given priority after pre-qualification. In all, the communities benefit from employment, provision of infrastructure (in the form of corporate social responsibility from the companies), award of scholarships, shopping from employees of the company etc.

4.4 GAS FLARING AND VENTING IN CRUDE OIL PRODUCTION

Emissions from fossil fuel and biomass burning account for most energy-related air pollution in most parts of the world *(Reddy and Boucher, 2007)*. Energy-related emissions are released through the entire spectrum of oil and gas activities, from upstream emissions during crude oil and natural gas extraction and production to end-use emissions from petroleum burned for transport, heating, cooking and the like. Production of crude oil and natural gas is a major operation of the petroleum industry which involves nearly 100 countries around the world *(Cholakov and Nath, 2009)*. The process of production of crude oil and natural gas leads to the emission of some gaseous compounds into the air. Combustion of oil and gas, release from leaking equipment, intentional releases, release due to operational failures and poor handling are some of the sources of these air emissions.

Figure 4.1: Gas flaring in the Niger Delta, Nigeria (Source: Bassey, 2016)

The option to release gases to the atmosphere by flaring and venting is an essential practice in crude oil and natural gas production, primarily for safety reasons *(Kearns et al., 2000)*. Flaring is the controlled burning of natural gas produced in association with crude oil in the course of routine crude oil and natural gas production operations whereas venting is the controlled release of unburned gases directly into the atmosphere *(Abdulkadir et al., 2013)*. In conventional oil and gas production practices, the availability of a flare or a vent ensures that associated natural gas can be safely disposed of in emergency and shut-down situations. When crude oil is the primary target of production and the associated natural gas can neither be safely stored nor used commercially, it is advisable to either flare or vent the gas in order to reduce the risk of fire and explosion.

Flaring and venting of natural gas represent loss in the total value of produced hydrocarbon and therefore the need to optimize the operation of crude oil and natural gas production *(Eboh, 2015)*. Although there are varieties of mechanisms that may potentially be used to reduce flaring, it may not be feasible to sell some or all the gas for reasons that are often a combination of geography, availability of customers, and government energy policies *(Ishisone, 2004)*. Similarly, it may also not be technically or economically feasible to re-inject all the gas into underground reservoirs. Therefore, gas may have to be flared as a waste product. In some cases, venting may be preferable to flaring, depending on considerations such as local noise impacts, toxicity of gases being produced, and hydrocarbon content of the gas *(Ite and Ebok, 2013)*.

Environmental and resource conservation considerations are among critical reasons why flaring and venting should always be minimised as much as reasonably practicable and consistent with international safety considerations. The selection, design, specification, operation and maintenance of most flares and vent stack in oil and gas industry is governed by the provisions of ANSI/API STD 537 (the same provisions as ISO 25457) and ANSI/API STD 521. Apart from the ability to diversely affect the local environment, flaring and venting produce emissions which have had the potential as a main contributor to global warming and continue to do so *(Amaechi and Biose, 2016)*. In developing African countries, like in most other oil and gas producing nations, there are stipulated penalties for flaring associated natural gas aimed at discouraging unnecessary burning of natural gas to conserve the hydrocarbon energy resource. This regulation coupled with other strategies are responsible for the decline in the percentage of the natural gas flared in Nigeria over the years as shown in the table below:

Table 4.1: Volume of gas produced, utilised and flared in Nigeria ($\times 10^6$ standard m^3)

Year	Production	Utilisation	Flared	% Flared
2005	60,466.0	37,656.5	22,809.7	37.72
2006	64,842.5	41,610.5	23,232.0	35.83
2007	73,818.2	50,693.4	23,124.8	31.33
2008	73,687.0	54,692.4	18,994.6	25.78
2009	63,093.2	47,904.9	15,188.3	24.07
2010	79,844.5	64,419.5	15,425.0	19.32
2011	84,006.3	69,736.2	14,270.1	16.99
2012	84,838.3	71,663.7	13,174.6	15.53
2013	79,626.5	67,507.7	12,118.8	15.22
2014	86,325.2	75,172.9	11,152.3	12.92
2015	85,232.2	75,535.9	9,687.3	11.37
2016	76,789.7	68,076.4	8,181.2	10.65
2017	83,193.1	73,417.7	9,180.1	11.05

Source: Adapted from *DPR, 2018*.

It has been shown that production of crude oil and natural gas without flaring and venting is neither technically nor economically feasible. In the face of this challenge, it becomes pertinent to understand the criticality of the technical, economic, environmental, and social effect of flaring and venting in the production of crude oil and natural gas. A review of these concerns of flaring and venting of natural gas from oil and gas production will help explain the need for the search for ways through which flaring and venting of natural gas could be optimized or their impacts reduced.

4.4.1 Flaring and Flare Systems:

Flaring is the controlled burning of natural gas in the course of routine oil and gas production operations *(Ismail and Umukoro, 2012)*. This burning occurs at the tip of a flare stack or boom. A complete flare system consists of the flare stack or boom and pipes which collect the gases to be flared. The flare tip at the end of the stack or boom is designed to assist entrainment of air into the flare to improve burn efficiency *(David, 1996)*. Seals installed in the stack prevent flashback of the flame, and a vessel at the base of the stack removes and conserves any liquids from the gas passing to the flare *(Emam, 2015)*. A flare is normally visible and generates both noise and heat *(Cheremisinoff, 2013)*. During flaring, the burned gas generates mainly water vapour and carbon dioxide *(Bott, 2007)*. Efficient combustion in the flame depends on achieving good mixing between the fuel gas and air, and on the absence of liquids. Low pressure pipe flares are not intended to handle liquids and do not perform efficiently when hydrocarbon liquids are released into the flare system. The percentage combustion efficiency of a well-designed and operated flares is often higher than 98% *(McDaniel, 1983)*.

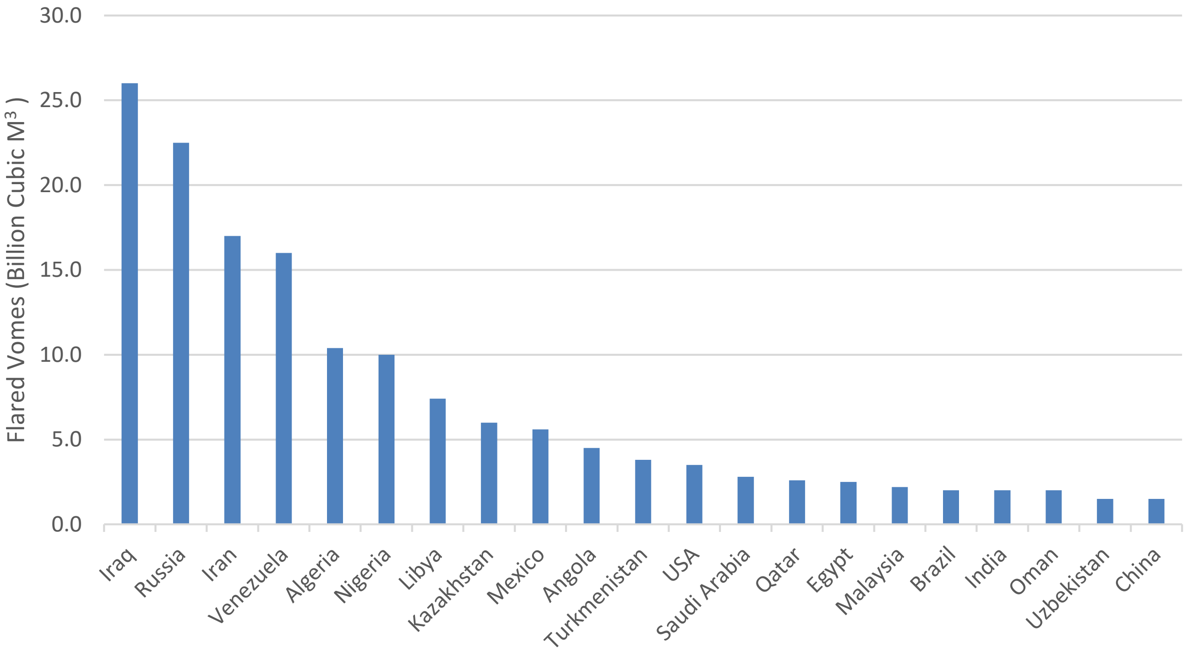


Figure 4.2: Top 20 Flaring Countries in the World *(Source: Pieprzyk and Hilje, 2015)*

The gas to be flared at the flare stack in oil and gas production process may come from a variety of sources. It may be the excess gas not used for power generation, unburned process gas from the process facilities, gas from process upsets, equipment changeover or maintenance *(Abuhesa, 2010)*. Occasionally, production shutdowns may require the temporary flaring of all the gas stored on or arriving at a facility to release high pressure and avoid a catastrophic situation occurring *(Upadhyay et al., 2013)*.

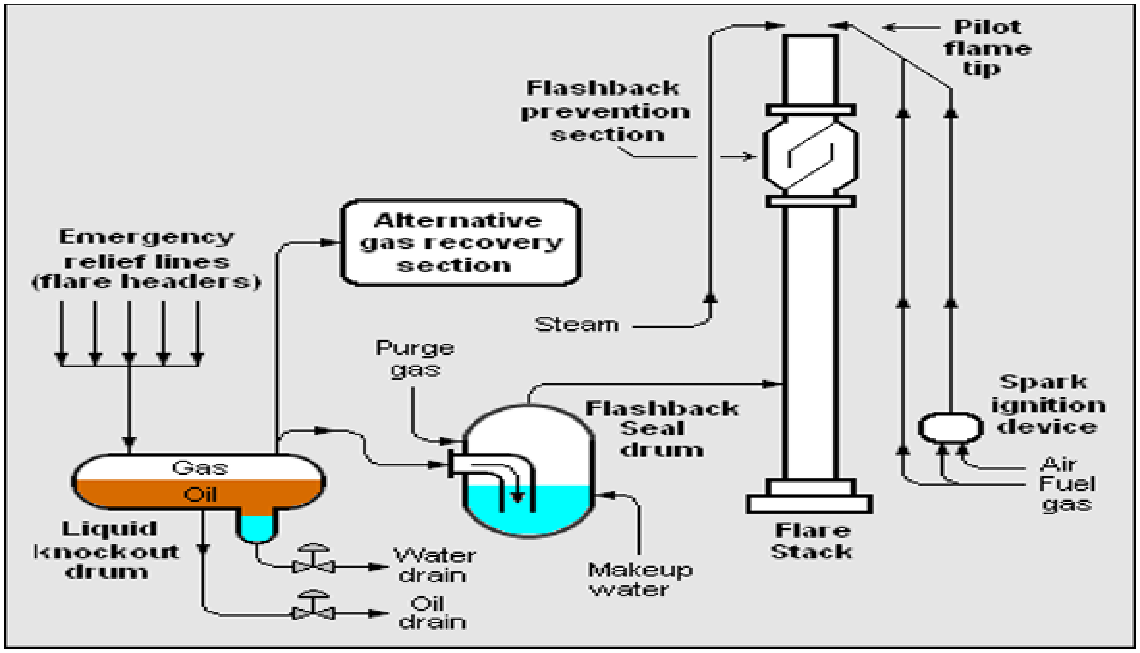


Figure 4.3: Sketch of a typical Flare System *(Source: Ngene et al., 2016)*

4.4.2 Venting:

Venting is the controlled release of gases into the atmosphere in the course of oil and gas production operations *(Frills, 2012)*. These gases might be natural gas or other hydrocarbon vapours, water vapour, and other gases, such as carbon dioxide, separated in the processing of oil or natural gas *(Miirima, 2008)*. In venting, the natural gases associated with the oil and gas production are released directly into the atmosphere and not burned. Safe venting is assured when the gas is released at high pressure and is lighter than air such that the strong mixing potential of high-pressure jets ensures proper mix of the discharged hydrocarbon gases with the air down to safe concentrations at which there is no risk of explosion *(Sha, 2016)*. Venting is normally not a visible process. However, it can generate noise, depending on the pressure and flow rate of the vented gases. In some cases, venting is the best option for disposal of the associated gas. For example, in some cases, a high concentration of inert gas may be present in the associated gas. Without sufficiently high hydrocarbon content, the gas will not burn, hence flaring is not a viable option. The purging of process systems with inert gas may justify venting as the safest means of disposal.

4.4.3 Environmental Concerns of Flaring and Venting:

i. Technical (Safety): The availability of a flare or a vent is necessary in oil and gas production operations. It ensures that safe disposal of the hydrocarbon gas inventory in the process installation is possible in emergency and shut-down situations. Where gas cannot be stored or used commercially, it is essential that the risk of fire and explosion be reduced by either flaring or venting. Even where associated gas is being sold or reinjected, small amounts of gas will still need to be flared or vented for safety reasons. Oil and gas processing and storage equipment is often operated at high pressures and temperatures. When abnormal conditions occur, the control and safety systems must release gas to the emergency flare or vent to prevent hazards to the employees or public. Good maintenance and operating strategies are the main mechanisms used to keep this already small volume as low as practicable. Emergency flares are normally fitted with pilot systems maintaining a small flame as the ignition source in case the full-size flare is activated. Recent technology has designed and installed flare system to operate without pilot flame and hence without emission when not active *(Mashour et al., 2009)*. The toxicity of the gases being disposed is another safety issue in the application of flaring and venting *(Nolan, 2010)*. In some situations, the toxicity of the gas relative to the toxicity of its combustion products may need to be considered when choosing between flaring and venting as a means of disposal. An example would be where gas containing hydrogen sulphide is being produced. Hydrogen sulphide gas can be fatal if inhaled; even at low concentrations but if burned the resulting sulphur dioxide is relatively less toxic *(Vallero, 2014)*.

ii. Environmental Effects and Consequences: Environmental agencies, independent to the oil and gas industry, sometimes express concerns about the environmental impacts of flaring and venting. One such concern relates to the potential for global climate change. Both carbon dioxide and methane (the major component of natural gas) are known as greenhouse gases associated with concerns about global warming *(Stoker, 2015)*. Flaring produces predominantly carbon dioxide emissions, while venting produces predominantly methane emissions. The two gases have different effects, however. The global warming potential of a kilogram of methane is estimated to be twenty-one times that of a kilogram of carbon dioxide when the effects are considered over one hundred years *(Dutch, 2009)*. When considered in this context, flaring will generally be preferred over venting in the design of new facilities where enough amounts of gas will be produced to run a flare. While there are still many uncertainties in our understanding of the complex issue of climate change, it makes sense to avoid the unnecessary release of carbon dioxide or methane into the atmosphere, where practicable. Apart from the concern of global climate change, flaring and venting also have the potential to contribute to local environmental impacts such as local air quality *(Ajugwo, 2013)*; and thus, need to be properly managed. Although the global warming potential of methane when compared to carbon dioxide usually suggests that flaring is a more environmentally attractive option than venting, onshore oil and gas developments sometimes prefer venting because it is less visible and produces less noise *(Hendry, 2014)*. In all cases, the company has the responsibility to make parties involved aware of all aspects of the issue to ensure reasoned decisions are taken and supported.

iii. Resource Conservation: The natural gas burned in a flare or vented to the atmosphere is a natural resource which could be effectively used as a source of energy or for production of beneficial chemicals and petrochemicals. This is another valid concern being expressed about flaring and venting. The need to obtain as much value as practicably possible from the production of hydrocarbon has kept the oil and gas industry in continuous search for ways to minimize flaring and venting without violating safety considerations. Many oilfields currently still in production were started several decades ago, when there was less concern about conservation of resources than there is today. The issue of global warming was not identified but oil and gas companies were constantly seeking methods to reduce wastage of natural gas and maximise the financial returns from the resources being developed. In 1950, the Indonesian oil industry flared 95% of the total volumes of associated gas that it produced but this volume declined to approximately 28% by 1985 *(Barns and Edmonds, 1990)*. The rate of improvement of the extent to which natural gas resources were conserved in mature oil producing regions were dependent on some factors among which were the availability of local markets for the gas and governments incentives to consumers and suppliers / investors *(Marland et al., 1998)*.

4.5 GREENHOUSE GASES AND CLIMATE CHANGE

Greenhouse gases are those gases in the atmosphere which allow direct passage of sunlight with its relatively shortwave energy to the earth's surface unimpeded. The shortwave energy in the visible and ultraviolet portion of the spectra heats the earth’s surface resulting in the longer-wave infrared energy in the form of heat being reradiated to the atmosphere. These greenhouse gases in the lower atmosphere absorb this energy thereby allowing less heat to escape back to space and trapping part of the re-radiated heat in the atmosphere. This is referred to as greenhouse effect. Many greenhouse gases occur naturally in the atmosphere, such as carbon dioxide, methane, water vapor, and nitrous oxide. Some greenhouse gases are however synthetic; and these include the chlorofluorocarbons (CFCs), the hydrofluorocarbons (HFCs), the perfluorocarbons (PFCs) and sulphur hexafluoride (SF_6).

Although the major greenhouse gas in the atmosphere is water vapour (H_2O), it has a short lifetime in the atmosphere as part of the natural water cycle. Notwithstanding the human emissions of water vapour, it is considered that its effects has not been altered and therefore it is not regarded as an anthropogenic greenhouse gas. The six major anthropogenic greenhouse gases as recognised by the Kyoto Protocol are: carbon dioxide (CO_2); methane (CH_4); nitrous oxide (N_2O); hydrofluorocarbon (HFCs); perfluorocarbons (PFCs) and sulphur hexafluoride (SF_6).

In 2017, carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O) contributed 73%, 18% and 6%, respectively to the anthropogenic greenhouse effect in the world *(Olivier and Peters, 2018)*. CO_2, CH_4 and N_2O in the atmosphere are currently increasing by 1.2%, 1.2% and 1.4% per year respectively *(Olivier and Peters, 2018)*. The rise in the atmospheric concentrations of both the natural and man-made gases over the last few centuries has been attributed to the industrial revolution. The global population has increased and so has the reliance of the world on fossil fuels such as coal, crude oil and natural gas. The production of these fossil fuels as well as their combustion to deliver energy account for the release of a great volume of these greenhouse gases into the atmosphere. Methane (CH_4) and nitrous oxide (N_2O) are also emitted from rice paddy fields.

The amount of infra-red radiation (heat) that could be absorbed and how long this heat could be trapped in the atmosphere differ from one greenhouse gas to another. This is referred to as the global warming potential (GWP). The GWP relates the amount of heat trapped by a certain mass of the gas in question to the amount of heat trapped by a similar mass of carbon dioxide. It is usually calculated over a 100-year time interval. For example, GWP of methane over a 100-year period is 25, which means if the same mass of methane and carbon dioxide were emitted into the atmosphere, methane will trap 25 times more heat than carbon dioxide. Table 4. 2 compares the global warming potential (GWP) of common greenhouse gases.

Table 4.2: GWP and Atmospheric Lifetime for Various Greenhouse Gases (Source: *Smith, 2014*)

Greenhouse Gases	**Chemical Formula**	**GWP for a 100-year Time-Horizon**	**Lifetime (years)**
Carbon Dioxide	CO_2	1	Variable
Methane	CH_4	25	12
Nitrous Oxide	N_2O	289	114
HCFC-12	$CHClF_2$	1,810	12
Tetrafluoroethane	CF_4	7,390	50,000
CFC-12	$CClF_2$	10,900	100
Hexafluoroethane	C_2F_6	12,200	10,000
Nitrogen trifluoride	NF_3	17,200	740
Sulphur Hexafluoride	SF_6	22,800	3,200

4.5.1 Greenhouse Gases from Crude Oil Production

Methane (CH_4):

Methane (CH_4) constitutes the major component of natural gas; attaining up to 85% of the overall gas composition. It is an extremely effective absorber of radiation, but its atmospheric concentration is less than that of carbon dioxide (CO_2) and its lifetime in the atmosphere is brief (10-12 years) compared to some other greenhouse gases (such as CO_2, N_2O, CFCs). Methane is released into the atmosphere through both natural and anthropogenic sources. It is released as part of the biological processes in low oxygen environments, such as in swamplands or in rice production and cattle ranches.

Carbon Dioxide (CO_2):

Naturally, the production and absorption of carbon dioxide (CO_2) cancels each other by the interaction between living organisms in the ecosystem. This balance has however been altered by the activities of man: production of crude oil and natural gas and combustion of coal, crude oil, natural gas and wood for energy since the advent of the industrial revolution. Carbon dioxide was the first greenhouse gas demonstrated to be increasing in atmospheric concentration at the last half of the 20th century and is measured to have an average global concentration of 370 ppm in the atmosphere today.

Water Vapour (H_2O):

Water vapor is the most abundant greenhouse gas in the atmosphere. Increase in temperature of the atmosphere leads to evaporation of more water from the rivers, oceans, reservoirs and even the soil. Since the air is lighter due to increased temperature, it is warmer and therefore capable of holding more water vapour in the atmosphere. The water vapour high concentration in the atmosphere and its greenhouse characteristics allows for absorption of a great deal of the infra-red radiation energy radiated from the earth thus further warming the atmosphere and making room for more water vapour. This is referred to as a “positive feedback loop”. As water vapour concentration increases in the atmosphere, more of the vapour will eventually condense into clouds. This is the interesting part as clouds can reflect incoming solar radiation allowing less energy to reach earth's surface.

Ozone (O_3):

This is a molecule made up of three oxygen atoms which is formed in the stratosphere as result of the interaction of ultraviolet radiation and oxygen. Action of sunlight on the exhaust emissions from automobiles, pollution from factories and emissions from burning vegetation. Consequently, ozone has higher concentrations in and around cities than in sparsely populated areas, though there is some transport of ozone downwind of major urban areas. Ozone is an important contributor to photochemical smog. Though the lifetime of ozone is short and is therefore not well-mixed through the atmosphere, concentrations of ozone in the atmosphere have risen since the pre-industrial era, and it is now considered to be the third most important greenhouse gas after carbon dioxide and methane. An additional complication of ozone is that it also interacts with and is modulated by concentrations of methane.

Nitrous Oxide (N_2O):

Although nitrous oxide could be produced naturally by actions of microbes in soil and water, addition of fertilizers rich in nitrogen to soils could serve as a man-made source for the greenhouse gas. The increasing use of fertilizers over the last century is believed to be responsible for the rise in the global concentration of nitrous oxide. Some industrial processes like fossil fuel-fired power plants, nylon production, nitric acid production and vehicle emissions also contribute to the atmospheric load of nitrous oxide.

Chlorofluorocarbons (CFCs):

Chlorofluorocarbons (CFCs) have no natural source but were entirely synthesized for such diverse uses as refrigerants, aerosol propellants and cleaning solvents. The production of these stratospheric ozone destroyers has been halted globally and as such their concentration in the atmosphere has ceased to increase. The CFCs have long atmospheric lifetimes and therefore some concentrations of the compound will remain in the atmosphere for over one hundred years. Other long-lived synthesized greenhouse gases of concern are CF_4 (carbon tetrafluoride), SF_6 (sulphur hexafluoride) and the HFCs (hydrofluorocarbons). The HFCs (hydrofluorocarbons) are however less stable in the atmosphere, have a shorter lifetime and comparably less impact as a greenhouse gas.

Others:

Although carbon monoxide (CO) is not considered a direct greenhouse gas, because it does not have strong absorbing capacity for thermal infra-red energy from the earth surface, it is however able to modulate the production of methane and tropospheric ozone. CO is predominantly generated from activities; it is a product of incomplete combustion. Vehicle emissions remained a great source of CO until the use of catalytic converters came into play.

Volatile Organic Compounds (VOCs) also have a small direct impact as greenhouse gases, as well being involved in chemical processes which modulate ozone production. VOCs include non-methane hydrocarbons (NMHC), and oxygenated NMHCs (eg. alcohols and organic acids), and their largest source is natural emissions from vegetation. However, there are some anthropogenic sources such as crude oil and natural gas production, vehicle emissions, fuel production and biomass burning.

4.5.2 Analysis of Climate Change:

Climate is defined as long-term averages and variations in weather measured over a period of several decades. The Earth's climate system includes the land surface, atmosphere, oceans, and ice. The global climate is changing rapidly in many aspects and the primary cause of these changes are traceable to human activities. There are several evidences for changes in the climate system abounds; some of these indicators are shown in Figure 4.1 below.

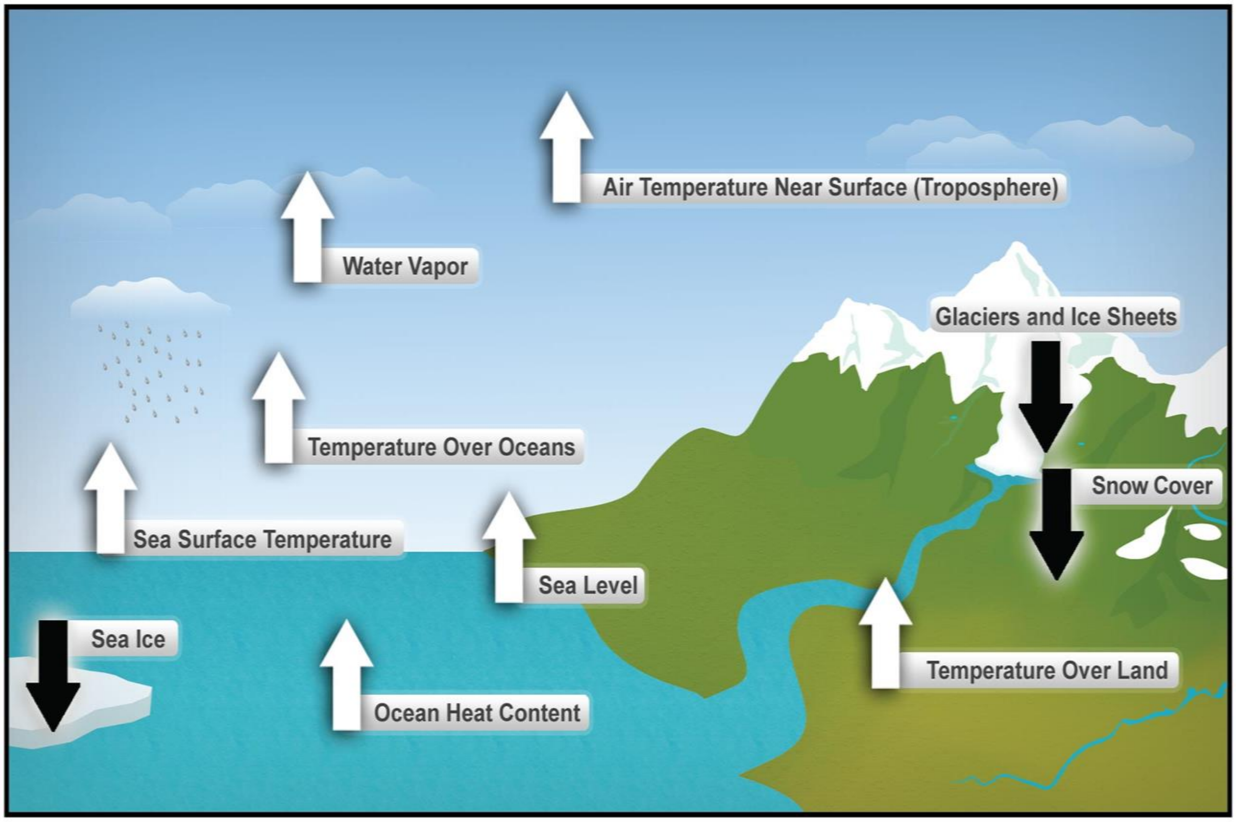


Figure 4.4: Indicators of warming of the world (Source: *Kennedy et al., 2010*)

The temperatures at the surface, in the troposphere (the active weather layer extending up to about 5 to 10 miles above the ground), and in the oceans have all increased over recent decades as shown in Figure 4.4. This is consistent with scientific theories and the largest temperature changes are occurring around the poles especially in the Arctic region. Snow and ice cover have decreased in most areas. Atmospheric water vapor is increasing in the lower atmosphere, because a warmer atmosphere can hold more water. Sea levels are also increasing. Changes in other climate-relevant indicators such as growing season length have been observed in many areas. Worldwide, the observed changes in average conditions have been accompanied by increasing trends in extremes of heat and heavy precipitation events and decreases in extreme cold *(Alexander et al., 2006)*.

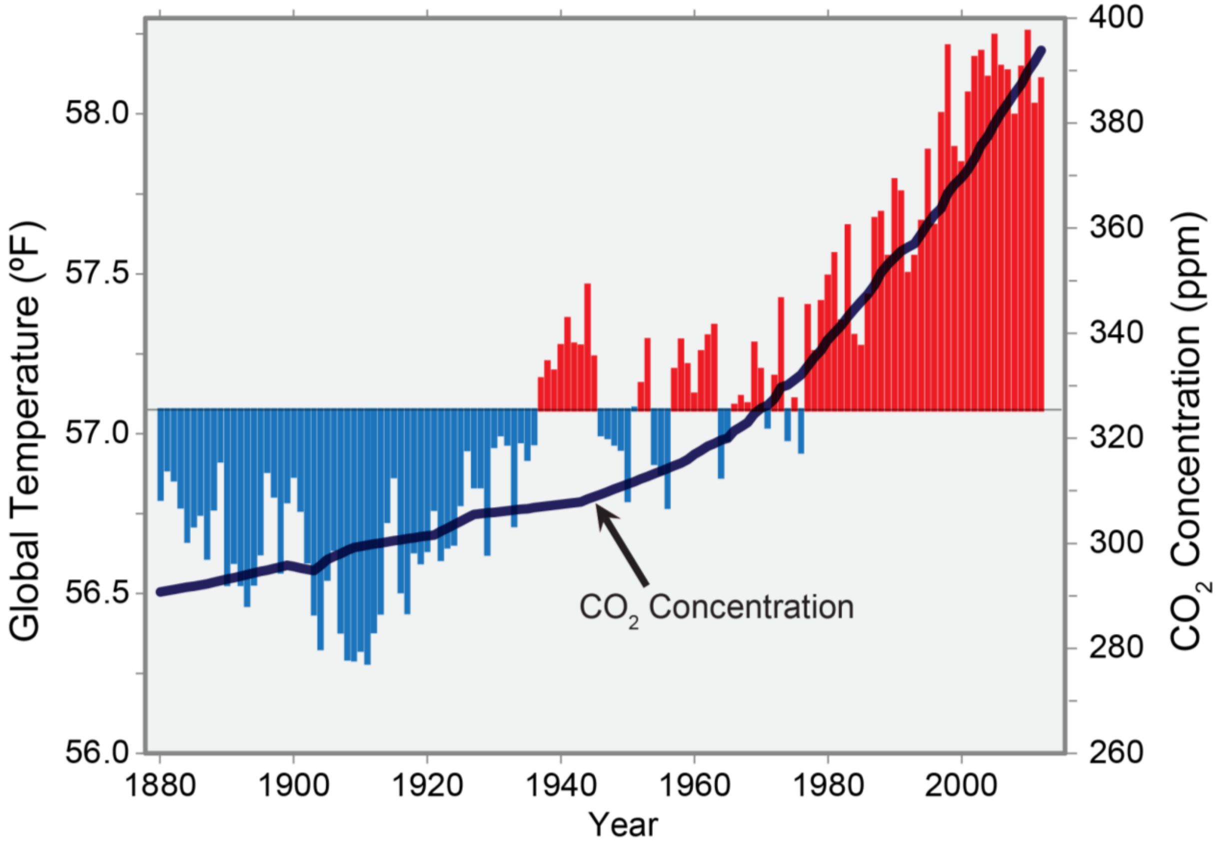


Figure 4.5: Global temperature and Carbon dioxide (Source: *Karl et al., 2009*)

The recent warming of the climate has been shown to be beyond the domain of natural drivers of climate change. It is a fact that over the last five decades, natural factors (solar forces and volcanoes) alone would have led to a slight cooling *(Gillett et al., 2012)*. Most of the warming at the global scale over the past fifty years can only be explained by the effects of human activities *(Santer et al., 2013; Stott et al., 2010)*, especially the emissions from production of crude oil and natural gas, burning fossil fuels (coal, oil, and natural gas) and from deforestation. The emissions from human influences that are affecting climate include heat-trapping gases form crude oil and natural gas production such as carbon dioxide (CO_2), methane, and nitrous oxide, and particles such as black carbon (soot), which has a warming influence, and sulphates, which have an overall cooling influence *(IPCC, 2007; Wigley and Santer, 2013)*.

The conclusion that human activities are responsible for the recent change in climate is drawn from multiple lines of independent evidence. Some of these are:

1. Our understanding of the scientific explanation of how certain gases trap heat, how the climate system responds to increases in these gases, and how other human and natural factors influence climate.
2. The reconstructions of past climates using evidence such as tree rings, ice cores, and corals to show that global surface temperatures over the last several decades are clearly unusual, with the last decade (2000-2009) warmer than any time in at least the last 1300 years and perhaps much longer *(Mann et al., 2008)*.
3. The use of climate models to simulate the climate of the past century, separating the human and natural factors that influence climate. When the human factors are removed, these models show that solar and volcanic activities would have slightly cooled the earth, and other natural variations are too small to explain the amount of warming. When human

influences are included, the models reproduce the warming observed over the past fifty years as shown in Figure 4.6.

4. The "fingerprint" studies which have attributed the observed climate changes to some causes. For example, the fact that the stratosphere (the layer above the troposphere) is cooling while the earth's surface and lower atmosphere is warming is an indication that the warming is due to increases in heat-trapping gases. In contrast, if the observed warming had been due to increases in solar output, earth's atmosphere would have warmed throughout its entire extent, including the stratosphere *(Santer et al., 2013)*. In addition to such temperature analyses, scientific attribution of observed changes to human influence extends to many other aspects of climate, such as changing patterns in precipitation (*Min et al., 2011)*, increasing humidity *(Willet et al., 2007)*, changes in pressure, and increasing ocean heat content.

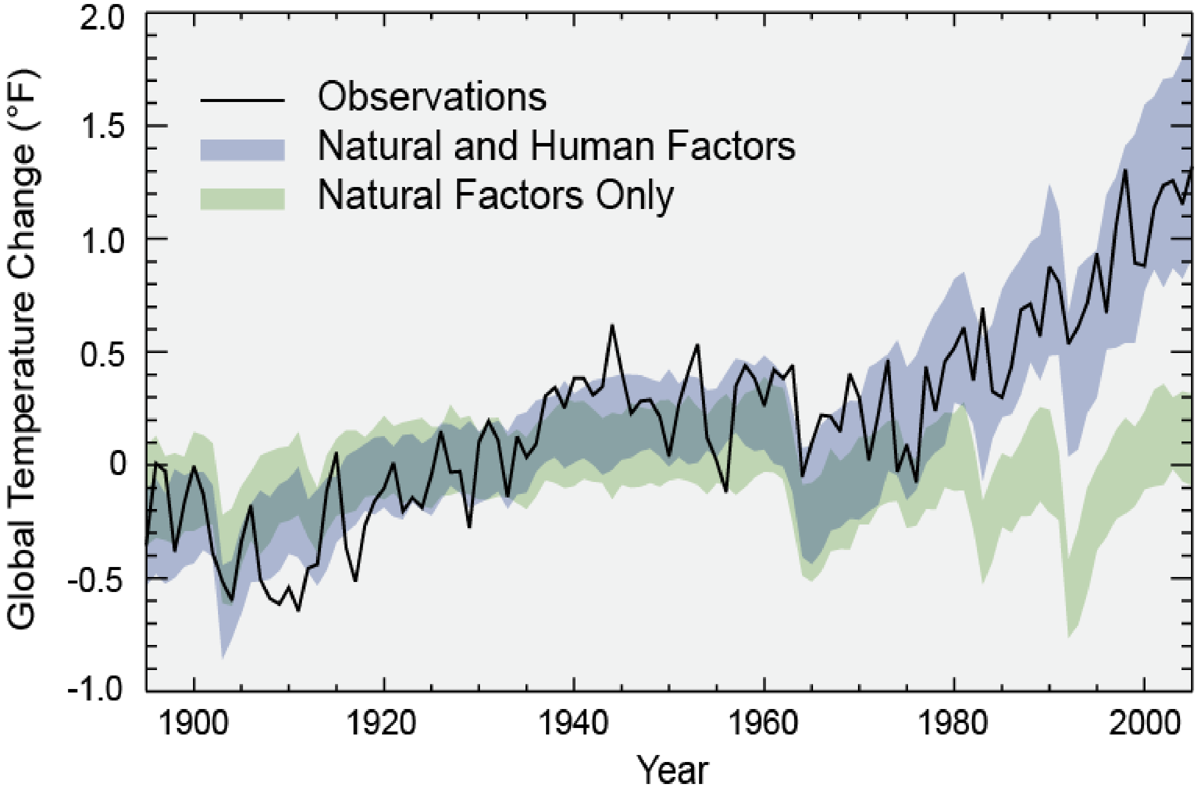


Figure 4.6: Separating human and natural influences on climate (Source: Adapted from *Huber and Knutti, 2010)*.

4.5.3 Mitigation of Greenhouse Effects:

Records show that the annual global greenhouse gas (GHG) emissions have continued to grow since the industrial revolution. The driving force for the anthropogenic GHGs emissions include production of crude oil and natural gas, population growth, economic growth, fossil fuel consumption and land use change. Since the beginning of industrial revolution to date, the cumulative anthropogenic carbon dioxide (CO_2) emission released into the atmosphere has continued to increase. The atmospheric concentrations of methane (CH_4) and nitrous oxide (N_2O) have also increased significantly. As a result, changes in climate has caused impacts on natural and human systems across the globe, and continued GHGs emission will cause further climate change impacts.

In order to prevent this further climate change impact, mitigations policies that can substantially reduce the risks associated with human-induced global warming is currently being suggested globally. Climate change mitigation consists of actions to limit the magnitude or rate of long-term global warming and its related effects. It generally involves reductions in anthropogenic (human) emissions of greenhouse gases (GHGs). The mitigation options available could be grouped under the following headings:

1. Demand Side Management: This option is centred on the lifestyle and behaviour, dietary change, energy efficiency and conservation, demand side switching sources and demand side grid management.
2. Alternative Energy Sources: implementation of renewable energy, nuclear power, coal to gas fuel switching, heat pump and fossil fuel phase out strategies fall under this option.
3. Sinks and Negative Emissions: Reforestation and afforestation, avoided desertification, carbon capture and storage and enhanced weathering are options under this heading.
4. Geoengineering: Carbon dioxide removal methods (CRM) and solar radiation management (SRM) are considered under this group.
5. Non-CO_2 GHGs: Control of methane production from plants and animals; and release of other non-CO_2 GHGs are considered here.

4.6 SUMMARY

Global production of crude oil has been on the increase as the world population rise continuously; people are also demanding for more comfort due to raised standard of life; industrial revolution has led to proliferation of manufacturing plants and more people, goods and services are moved from one place to another. The energy required to support these activities are mainly provided by crude oil and natural gas. The quest to produce more crude oil to meet these demands have brought about technological advancements, discovery and production of crude oil and natural gas in deep offshore locations and shale.

Crude oil exists with natural gas in most cases in the reservoir and therefore associated natural gas is usually produced alongside when crude oil is produced. The impact of crude oil production on the environment also considers that of the produced associated natural gas. Some of the key impacts of the production process on the environment includes the disturbance created by noise, the impact on air quality, cultural resources and ecological resources, the effect of hazardous materials and waste management, the health and safety effects etc.

The production of crude oil also impacts on the economy of the host nation directly or indirectly. The crude oil production activities have been found to make enormous contribution to the economy of the host nation and its citizenry through various ways which include payment of taxes and royalties, creation of jobs and employment opportunities, contribution to gross regional product (GRP), enhancement of local expenditures on goods and services, provision of foreign exchange reserves, contribution to the provision of power, public utilities and infrastructure etc.

Crude oil production is believed to be neither technically nor economically feasible without venting or flaring of associated natural gas. Flaring and venting of natural gas have adverse effect on both the environment and the total recoverable income from the production process as the burned or lost natural gas which represent lost source of energy could have been used to produced chemicals or petrochemicals. Natural gas could contain up to 85% methane (CH4) in its composition when burned releases carbon dioxide to the atmosphere. Methane and carbon dioxide are the key greenhouse gases responsible for greenhouse effect and subsequently climate change.

CHAPTER FIVE

POLLUTION REDUCTION AND ENERGY SAVING IN CRUDE OIL PRODUCTION

5.1 INTRODUCTION

As the population of the world is growing, more energy is needed to meet transportation, residential, commercial and industrial demands. Crude oil is a primary energy source and thus production activities have been on the increase to meet the increasing energy demand. These activities have generated pollutants which are managed at the downstream end of the production process. With stricter regulations and production of crude oil from difficult terrain, it becomes necessary to avoid the extra costs involved in post-production treatment of pollutants and the likely penalties for failing to meet regulatory limits. This has led to the idea of applying process integration techniques on the production process with targets set on energy savings and pollution reduction.

Pollution control strategies currently applied to crude oil production processes are formulated without recourse to the process that generates the pollutants; focus is beamed on the terminal streams and environmental goals thereby providing solutions that deals only with the pollution at hand rather than making sure that the process generates little or no pollutant. The realisation that dealing with the root cause of the pollution problem at the core of the production process is a better option and has led to the adoption of in-plant pollution prevention strategies.

Process integration as a holistic approach to process design and operation provides a unique framework for integrating environmental issues with other process objectives such as profitability, yield enhancement, debottlenecking and energy savings. It could be categorised into three main components: synthesis, analysis and optimisation.

5.2 THE POLLUTANT REDUCTION ALGORITHM:

The potential environmental impact of a production process is usually caused by the energy and material that the process takes from or emits to the environment (*Cabezas et al., 1998*). Although the potential environmental impact cannot be directly measured, it is possible to calculate it from related measurable quantities using the relationship between them. The conservation equation could be applied to define potential environmental impact as thus:

$$\frac{\mathrm{d}\,Isyst}{\mathrm{d}t} = \dot{I}in - \dot{I}out + \dot{I}gen \qquad \text{………………………………… (Equation 5.1)}$$

Where $Isys$ is the potential environmental impact content inside a process, $\dot{I}in$ is the input rate of impact, $\dot{I}out$ is the output rate of impact and $\dot{I}gen$ is the rate at which impact is generated from the system by chemical reactions and other sources. If the process consumes potential environmental impact, then $\dot{I}gen$ becomes negative. For steady state processes, the conservation equation becomes:

$$0 = \dot{I}in - \dot{I}out + \dot{I}gen \qquad \text{………………………………………… (Equation 5.2)}$$

Equation 5.2 implies that there is no accumulation of potential impact in the system. For steady state processes, due to chemical transformation and changes in the state parameters of temperature and pressure, $\dot{I}gen$ is never exactly equal to zero since $\dot{I}out$ is never equal $\dot{I}in$.

For a crude oil production process, application of equations (5.1) and (5.2) requires an expression that relates to the conceptual potential environmental impact to measurable quantities. If we consider, in the first instant, that only inflow of material to be responsible for the for the impact, then the expression relating potential chemical environment impact to measurables is:

$$\dot{I}i = \sum_j \dot{I}_j^{(i)} = \sum_j \dot{M}_j^{(i)} \sum_k x_{kj} \psi_{j+\cdots} \qquad \text{………………………… (Equation 5.3)}$$

where the sum over *j* is taken over the streams of input *i* or output *i*, the sum over *k* is taken over all chemicals *k;* $\dot{I}i$ is the rate of potential environmental impact either in (*i*=in) or out of the process (*i*=out); $\dot{I}_j^{(i)}$ is the rate of potential environmental impact for stream *j* which x_{kj} may be an input or an output; $\dot{M}_j^{(i)}$ is the mass flow rate of stream *j* which may again be either an input or an output; x_{kj} is the mass fraction of chemical *k* in stream *j*, and ψ_j is the overall potential environmental impact of chemical, *j*. Equation (5.3) is a first order approximation that does not include the synergistic effects that can occur when multiple chemicals are present.

For steady state processes, using equation (5.2), we can define two categories of indexes for the environmental impact of crude oil production. All non-products are considered pollutants and the potential environmental impact of product is zero (*Hillaly and Sikdar, 1994*). Thus, $\psi_j = 0$ for all products, *j*. The first of the indexes (impact generation) could be obtained by adding the superscript NP for non-product to equation (5.2) and solving:

$$\dot{I}_{gen}^{NP} = \dot{I}_{out}^{NP} - \dot{I}_{in}^{NP} \qquad \text{.. (Equation 5.4)}$$

Where $\dot{I}_{out}^{NP}$ and $\dot{I}_{in}^{NP}$ are the potential environmental impacts due to the pollutants in the output and input respectively. The index, $\dot{I}_{gen}^{NP}$ measures the total rate at which the process generates potential environmental impact due to non-products. However, by dividing equation (5.4) by the rate at which process generates product, we will obtain a specific impact generation:

$$\hat{\dot{I}}^{NP}_{gen} = \frac{\dot{I}^{NP}_{gen}}{\sum_p \dot{P}_p} = \frac{\dot{I}^{NP}_{out} - \dot{I}^{NP}_{in}}{\sum_p \dot{P}_p} \quad \text{.. (Equation 5.5)}$$

where the sum over *p* is taken over all the products *p*, and $\dot{P}_p$ is the mass flowrate of product *p*. $\hat{\dot{I}}^{NP}_{gen}$ measures the potential impact created by all non-products in producing a unit mass of all the products *p*. If we set the potential environmental impact ψ_j of one in equation (5.5), we will obtain another index that has the effect of assigning the same potential environmental impact to all non-products. The index, $\acute{\dot{M}}^{NP}_{gen}$ is a measure of the mass inefficiency of the process, i.e. it gives the ratio of mass converted to an undesirable form to mass converted to a desirable form.

$$\acute{\dot{M}}^{NP}_{gen} = \frac{\sum_j \dot{M}^{(out)}_j \sum_k x^{NP}_{kj} - \sum_j \dot{M}^{(in)}_j \sum_k x^{NP}_{kj}}{\sum_p \dot{P}_p} \quad \text{...................... (Equation 5.6)}$$

where the summation over $\dot{M}^{(out)}_j$ is taken only over output streams, the summation over $\dot{M}^{(in)}_j$ is taken only over input streams, and the summation over x^{NP}_{kj} is taken only over all non-products *k* in stream *j*. The units of $\acute{\dot{M}}^{NP}_{gen}$ are mass of non-products per mass of products.

The first index of the second category of indexes (impact emission) $\dot{I}^{NP}_{out}$ is simply the total rate of potential environmental impact output due to non-products. $\dot{I}^{NP}_{out}$ is calculated from equation (5.3) subject to $\psi_j = 0$ for all products *j*. The index, $\dot{I}^{NP}_{out}$ is a measure of the rate at which the process emits potential environmental impact, and it has units of potential environmental impact per time. The second index of the second category $\hat{I}^{NP}_{out}$ is obtained by dividing the rate of potential environmental impact output due to non-products by the output rate of products to give:

$$\hat{I}^{NP}_{out} = \frac{\dot{I}^{NP}_{out}}{\sum_p \dot{P}_p} \quad \text{.......................................} \text{ (Equation 5.7)}$$

The index, $\hat{I}^{NP}_{out}$ has units of potential environmental impact per mass of products. This expression measures the potential environmental impact emitted in production of a unit mass of product – the pollution index, ɸ of *Mallick et al., 1996.*

However, if we set the potential environmental impact ψ_j of all products to zero and that of non-products to one, we obtain from equation (5.7) another index expressed as:

$$\acute{M}^{NP}_{out} = \frac{\sum_j \dot{M}^{(out)}_j \sum_k x^{NP}_{kj}}{\sum_p \dot{P}_p} \quad \text{.......................................} \text{ (Equation 5.8)}$$

This expression is related to the pollution index, ϕ_n, of *Hilaly and Sikdar, (1994)* by:

$$\acute{M}^{NP}_{out} = \sum_n \phi_n \quad \text{.......................................} \text{ (Equation 5.9)}$$

where the summation is taken over all products, *n*. $\acute{M}^{NP}_{out}$ measures the amount of non-product or pollutant mass emitted in manufacturing a unit mass of products, and it has units of non-product mass per mass of products. It is also a mass inefficiency measure.

The first categories of indices, $\dot{\mathrm{I}}^{NP}_{gen}$, $\hat{\mathrm{I}}^{NP}_{gen}$ and $\acute{\mathrm{M}}^{NP}_{gen}$ characterize some aspects of generation of potential environmental impacts within a production process. They describe the ability of the process to produce desired products while creating a minimum of new undesired and potentially environmental impact. The smaller the value of these indices, the more environmentally friendly the process. The second category, $\dot{\mathrm{I}}^{NP}_{out}$, $\hat{\mathrm{I}}^{NP}_{out}$ and $\acute{\mathrm{M}}^{NP}_{out}$ also characterize some aspects of the emission of potentially environmental impact from the production processes. It addresses the ability of the process to produce desired products while inflicting on the environment a minimum of undesired potential environmental impact.

In order to apply the methodology so far discussed, estimation of the potential environmental impact of chemical is required. A relative impact number, ψ_j will be given to each chemical *j*. To apply ψ_j to the methodology, we adapt the methodology developed by Mallick et al., 1996:

$$\psi_j = \sum_l \alpha_l \psi^{s}_{j,l} \qquad \text{………………………………………... (Equation 5.10)}$$

where the sum is taken over categories of potential chemical environmental impacts, e.g. ozone depletion potential, human health, etc. α_l is a relative weighting factor for impact of type *l* independent of chemical *j*, and $\psi_{j,l}^{s}$ is the specific potential environmental impact of chemical *j* for an impact of type *l*. α_l has units of potential environmental impact per mass. The values for the $\psi_{j,l}^{s}$ are obtained from the relative rankings or scores for chemicals and normalizing according to,

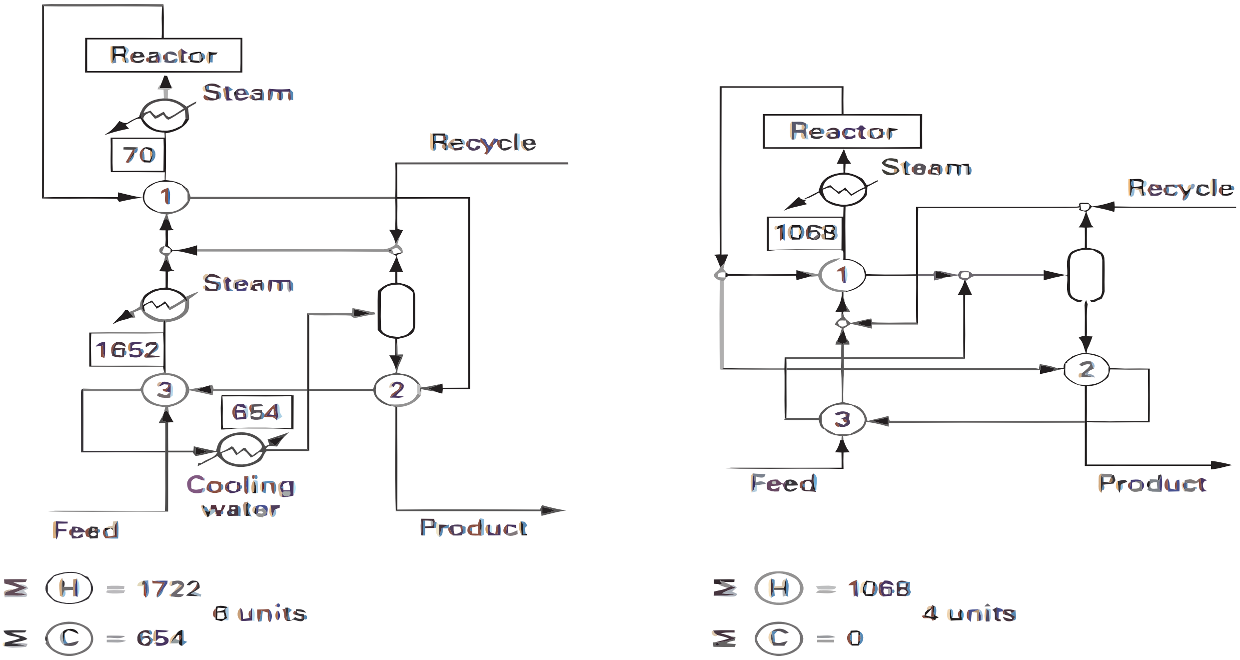
$$\psi_{j,l}^{s} = \frac{(Score)_{i,j}}{[(Score)_i]_j + 2\sigma_j} \quad \text{……………………………………… (Equation 5.11)}$$

where $(Score)_{i,j}$ is the relative score of chemical *i* on some arbitrary scale within impact category j, $[(Score)_i]_j$ is the arithmetic average of the scores of all chemicals *i* within impact category *j*, and σ_j is the standard deviation of all the chemical scores in impact category *j*. The normalizing factor $[(Score)_i]_j + 2\sigma_j$ assures that about 75% of the normalized chemical score numbers $\psi_{j,l}^{s}$ will be between 0 and 1 irrespective of the statistical distribution of the initial scores as expected from Chebyshev's theorem (*Lapin, 1975*). If the chemical scores happen to follow a normal distribution, then the normalization range extends to approximately 95% of the scores.

5.3 PROCESS INTEGRATION

Process integration is a holistic approach to process design and optimisation which exploits the interaction between different units to employ resources effectively and minimise costs. It is also referred to as an integrated process design or process synthesis *(El-Halwagi, 2006; Smith, 2005)*. One of the most common process integration technique, the pinch analysis technique, is used to minimise energy consumption and thereby maximise heat recovery. Pinch analysis technique is also referred to as heat integration or an energy integration technique. Although the earliest application of the pinch analysis technique was for energy integration *(Linnhoff et al.,1982; Shenoy, 1995)*, the technology has also found application in mass-exchange networks *(El-Halwagi and Manousiouthakis, 1989)*, water minimization *(Wang and Smith, 1994)*, material recycle *(El-Halwagi et al., 2003)* and other areas where resources optimisation or pollution reduction is required.

Process integration is not limited to new process plants; it is also applied in process plant modification in retrofit and debottlenecking as well as in the operation of existing processes *(Hallale, 2001)*. The process considers the interaction of the whole system in its analysis unlike the analytical approach which would attempt to optimise process units independently missing the opportunity that would have resulted from potential interactions among them. In process integration, heat rejected by one unit in the process plant could be fed into another unit where energy is required thereby reducing the overall energy consumption.



(a) Design as usual (b) Design with targets

Figure 5.1: Flowsheets for the front end of a specialty chemical process (*Source: Kemp, 2007*)

In the flowsheets above, application of process integration to the traditional design (a) led to decrease in the number of heat transfer units required and reduction of the utility heating load by about 40%.

The earliest form of process integration, pinch analysis techniques, were originally developed from the 1970s onwards at the ETH Zurich and Leeds University, United Kingdom (*Linnhoff and Flower, 1978; Linnhoff, 1979*). Around the time, Imperial Chemical Industries (ICI) Plc set up research and application teams to explore and develop these techniques and later used the pinch analysis techniques to solve the energy requirement restriction on the expansion of a crude distillation unit of an oil refinery.

Following the success recorded, ICI expanded the use of pinch analysis throughout the company identifying, on the average, about 30% energy savings on processes previously considered to be optimised (*Linnhoff and Turner, 1981*). Within a few years, seminar papers describing many of the key techniques had been published (*Linnhoff and Hindmarsh, 1983; Linnhoff et al., 1983; Townsend and Linnhoff, 1983*). Pinch-type analysis has also been extended to situations beyond energy usage, notably to wastewater minimisation (*Wang and Smith, 1994, 1995; Smith, 2005*) and the "hydrogen pinch" (*Alves, 1999; Hallale and Liu, 2001*).

Process synthesis is a component of process integration which deals with combining and integrating process units and streams to meet set objectives. It guides the designer in generation and screening of various process technologies, alternatives, configurations, and operating conditions (*El-Halwagi, 1997; Nishida et al., 1981*). While synthesis is aimed at combining the process elements into a coherent whole, analysis involves the decomposition of the whole into its constituent elements for individual study of performance. Hence, once a process is synthesized, its detailed characteristics (e.g., flowrates, compositions, temperature, and pressure) are predicted using analysis techniques. These techniques include mathematical models, empirical correlations, and computer-aided process simulation tools (e.g., ASPEN Plus, ChemCAD III, PRO II, HYSIM, EnviroPro).

5.4 PROCESS SIMULATION

The analysis of the detailed characteristics of a synthesized process is very important in process integration. The use of computer aided process simulation tool is one way to carry out this analysis and it is the most commonly used technique for complex processes. Process simulation is the representative modelling of systems to establish a safe virtual environment in which the process attributes could be tested and refined across a full range of production levels. It could also be described as a systemic description of material and energy streams in a process plant by means of computer simulation with the scope of designing the plant or understanding its operation.

In order to achieve best results during process design, the engineer normally consider alternatives and various sequences. The testing of these alternatives and sequences could be geared towards cost optimisation, yield enhancement, energy savings, pollution reduction etc. In many complex processes, the process design engineer may not be able to keep track of all the alternatives considering the volume of calculations and iterations involved; he will resort to simulation to do this. The formulation of the simulation model is usually based on the basis upon which chemical process design is done; mass and energy balances, reaction engineering, thermodynamics and economics.

5.5 SIMULATION OPTIMISATION

Optimisation is the process which ensures that full potential of a production process is tapped through the choice of the best design parameters, calibration and evaluation of the chosen simulation parameters (*Yusup et al., 2012; Chandramohan and Baskaran, 2012*). In a simulation environment, it can be defined as the process of finding the best input variable values from among all possibilities without explicitly evaluating each possibility (*Carson and Maria, 1997*). The objective of simulation optimization is to minimize the resources spent while maximizing the information obtained in a simulation environment. This process when applied to production processes, component designs and simulation models could be very complex and time-consuming especially if the optimization problems are of high dimensionality and nonlinear nature (Simpson *et al.,* 2001; Huang *et al.,* 2006).

For a general simulation model comprising of *n* input variables (x_1, x_2, x_3,…,x_n) and *m* output variables (y_1, y_2, y_3,…,y_m), simulation optimisation means finding optimal settings of the input variables which yields the best possible result for the output variables.

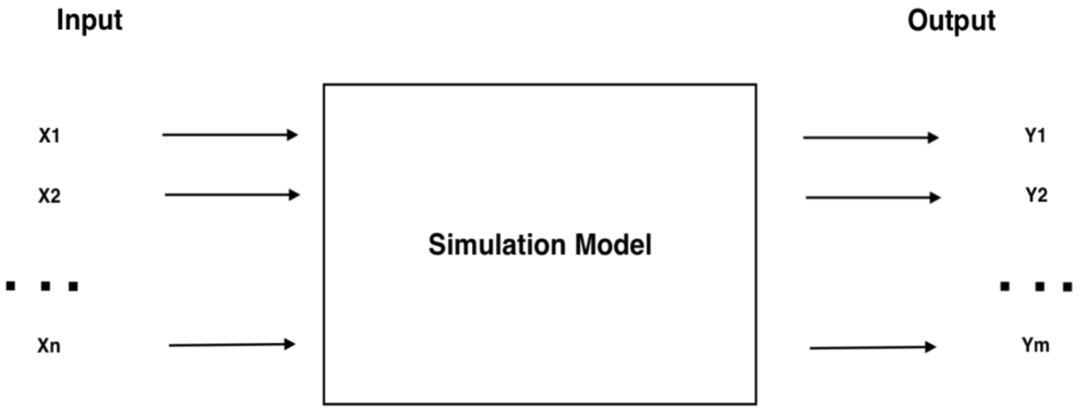


Figure 5.2: Representation of generalised simulation model

The output of a simulation model is used to provide feedback on progress of the research for optimal solution. This is also used to determine further inputs to the simulation model.

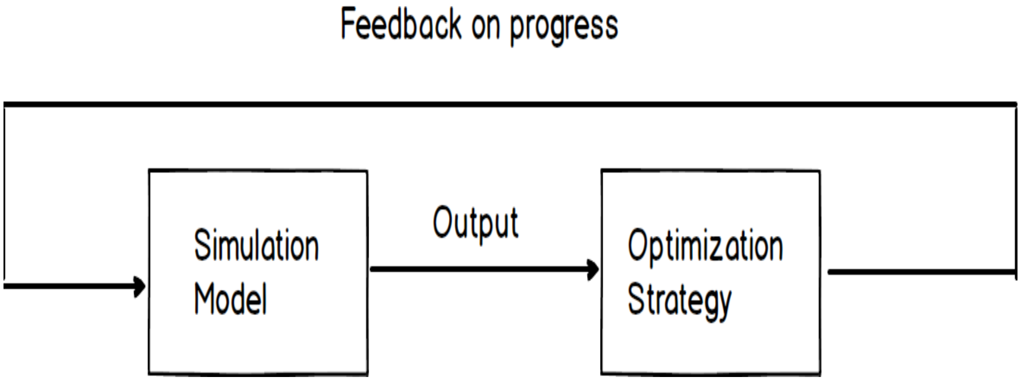


Figure 5.3: A simulation optimisation model (*Carson and Maria, 1997*)

Simulation optimisation methods can be categorised into six as:

5.5.1 Gradient Based Search Methods: These methods estimate the response function gradient (∇f) to assess the shape of the objective function and employ deterministic mathematical programming techniques. The commonly employed gradient estimation methods are:

a. ***Finite Differences*** where partial derivatives of the output variable f(x) are estimated as;

$$\frac{\partial f}{\partial x_i} = \frac{f(x_1,\ldots x_i+\Delta_i,\ldots x_n)-f(x_1,\ldots,x_i,\ldots x_n)}{\Delta_i} \quad \ldots\ldots\ldots\ldots\ldots\ldots \text{(Equation 5.12)}$$

To estimate the gradient at a specific value of x, at least n+1 configurations of the simulation model must be run. To obtain a more reliable estimate of ∇f using finite difference, there may be need for multiple observation for each partial derivative thereby increasing the already high computational cost (*Carson and Maria, 1997*). Finite difference is the crudest method of estimating gradient (*Azadivar, 1992*).

b. ***Likelihood Ratios (LR)***, also called score function where the gradient of the *expected value* of the output variable with respect to an input variable is expressed as the expected value of a function of input and simulation parameters. For a Poisson process with rate λ, if N_T is the number of events in time interval (0, T), and y is an output variable, then;

$$\frac{\partial}{\partial \lambda} E(y) = E[\left(\frac{N_T}{\lambda} - T\right) y] \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(Equation 5.13)}$$

This method is suitable for transient and regenerative simulation optimization problems.

c. **Perturbation Analysis (PA):** In this method, all partial gradients of an objective function are estimated from a single simulation run. This represents a significant advantage in terms of computational efficiency. When infinitesimal perturbation analysis (IPA) and likelihood ratios (LR) methods are applied to a given problem, the IPA gradient estimator is more efficient (*Glynn, 1989b*).

d. **Frequency Domain Method (FDM):** In this experiment, selected input parameters are oscillated sinusoidally at different frequencies during one long simulation run. Frequency domain methods have been studied in Schruben and Cogliano (1987) and Jacobson and Schruben (1988).

5.5.2 Stochastic Optimization: This involves the finding of a local optimum for and objective function whose values are not known analytically but can be estimated to or measured. This method which was proposed in the early 1950s has Robbins-Monro and Keifer-Wolfowitz as the two most commonly used algorithms for stochastic optimisation.

5.5.3 Response Surface Methodology (RSM): This is a procedure for fitting a series of regression models to the output variable of a simulation model (by evaluating it at several input variable values) and optimising the resulting regression function. The process starts with a first order regression function and the steepest ascent or descent search method. In general, RSM requires a smaller number of simulation experiments relative to many gradient based methods.

5.5.4 Heuristic Methods: These are the latest developments in the field of direct search methods that are frequently used for simulation optimization; and they include:

a. ***Genetic Algorithms (GA):*** It is a search strategy that employs random choice to guide a highly exploitative search, striking a balance between exploration of the feasible domain and exploitation of the optimum solutions (*Holland, 1992*).

b. **Evolutionary Strategies (ES):** These algorithms are like GA and imitate the principles of natural evolution as a method to solve parameter optimisation problems.

c. **Simulated Annealing (SA):** It is a stochastic search method analogous to the physical annealing process where an alloy is cooled gradually so that a minimal energy state is achieved.

d. **Tabu Search (TS):** Tabu search was developed by Fred Glover and is used for solving combinatorial optimization problems ranging from graph theory to pure and mixed integer programming problems.

e. **Nelder and Mead's Simplex Search:** The search starts with points in a simplex consisting of p+1 vertex (not all in the same plane in the feasible region. It proceeds by continuously dropping the worst point in the simplex and adding a new point determined by the reflection of the worst point through the centroid of the remaining vertices. The disadvantages of this method include the assumption of convex feasible region and implementation of problem involving the handling of feasibility of constraints.

5.5.5 A-Teams: An asynchronous team is a process that involves combining various problem-solving strategies so that they can interact synergistically. De Souza and Talukdar (1991) viewed an A-team as a process that is both fast and robust. They have demonstrated that A-teams consisting of GA and conventional algorithms, such as Newton's Method and Levenberg-Marquardt algorithms, for solving sets of non-linear algebraic equations results in considerable savings in the amount of computational effort necessary for finding solutions.

5.5.6 Statistical Methods: Some of the key statistical method are the Importance Sampling Methods, Ranking and Selection and Multiple Comparisons with the Best. While the importance sampling method has been used to achieve significant speed ups in simulations involving rare events, such as failure in a reliable computer system, ranking and selection method is used in finding the best combination to maximize either productivity or cost. Multiple comparison with the best is used to select the best of a finite number of system designs.

Simulation software like Aspen Hysys could be used to solve classic optimisation problems. However, when complex optimisation is involved, simulation optimisation software that has special search procedure to guide a series of simulation towards revealing optimal or near optimal scenarios may be required. Some of the software include ProModel, AutoMod, Micro Saint, LayOPT and FactoryOPT. It is also possible to link any of the optimisation software with Aspen Hysys.

5.6 SUMMARY

Crude oil production process generates pollutants which have potential environmental impacts. These pollutants are generated by the energy and materials that the process take from or emit to the environment. On this basis, the conservation of energy equation could be applied to define the potential environmental impact of the pollutants generated by the crude oil production process. In modelling the process, it is considered that the desired product (crude oil) has a potential environmental impact of zero. All other non-desired products generated from the production process are considered pollutants and their potential environmental impact estimated.

The concept of process integration is employed for both new and existing process plants to optimize product production and reduce pollutant generation. This process exploits the interaction between different units of the production process to employ resources effectively and minimize cost. Pinch analysis technique is the most commonly used process integration technique. It was earlier used for heat integration but has now found application in mass exchange network, water minimization, material recycle, pollution reduction and other areas where resource optimization is desired.

Process simulation and optimization processes are required for optimum performance of production process and their application would maximize production of desired product and minimize generation or undesired products (or pollutants). There are various methods through which simulation optimization could be performed but the process used is determined by the required number of runs, the number of variables and the nature of the problem.

Aspen Hysys and some other process simulation software could be used to solve classic optimization problems during process simulation. However, when complex optimization problems are encountered the software are linked with optimization software or the optimized solution are fed into the simulation software as input.

CHAPTER SIX

METHODOLOGY – MATERIALS AND METHODS

6.1 INTRODUCTION

In the oil and gas industry, produced water management has been of critical environmental concern over the years. The concern has continued to increase in magnitude with increase in demand for petroleum and more volumes of produced water being released to the environment due to crude oil production. The laws of most countries stipulate that produced water from crude oil production be treated to certain conditions before release to the environment. This post-production treatment could cost a lot of money.

The basis of the methodology of this research is an understanding of pollution reduction or in-plant pollution prevention strategies by process integration with energy savings and pollutant reduction targets. The synthesis of the process is aimed to bring about the prediction of detailed thermodynamic characteristics of the process (e.g flowrates, compositions, pressure, temperature) using process simulation as analysis data tool. The methodology which could be grouped into four categories: sampling and laboratory analysis, process flow sheeting and simulation, optimisation and analysis of results have been achieved following some known standards, procedures, guidelines, codes and legislations.

The case study facilities (offshore and onshore) have been fully described. The results of laboratory analysis and the temperature / pressure measurements from the process plant were used as inputs for the process simulation. The sampling points on the case study facilities were identified and reasons for location provided. The materials (including equipment and reagents) and the procedures for each of the four steps in the methodology has been explicitly described in this chapter.

6.2 CASE STUDY FACILITIES

6.2.1 IZOMBE FLOWSTATION, NIGERIA

The Izombe Flowstation (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.

Izombe Flowstation 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 well fluids 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.

Figure 6.1: The Izombe Flowstation Manifold

6.2.2 FPSO PRINCESS AWENI (FORMERLY ARMADA PERKASA)

This crude oil production facility is a Floating Production Storage and Offloading (FPSO) vessel which is currently located in Okoro field. Okoro field, located in Oil Mining Lease (OML) 112, is situated 12 kilometres offshore Nigeria in an average water depth of 14 metres in the eastern Niger Delta. The field which was discovered in 1975 and started production of crude oil in June 2008 is operated by Amni International Petroleum Development Company Limited (AMNI).

The FPSO Princess Aweni, 201.2m long with a breadth of 32.2m, has a 27,000 barrel of oil per day production process and storage capacity for 360,000 barrels of crude oil. is located 1km south of the field at 13m of water. It features an eight-point mooring system and is connected to the Okoro wellhead platform through flowlines and risers. The FPSO currently produces 16,000 barrels of oil per day.

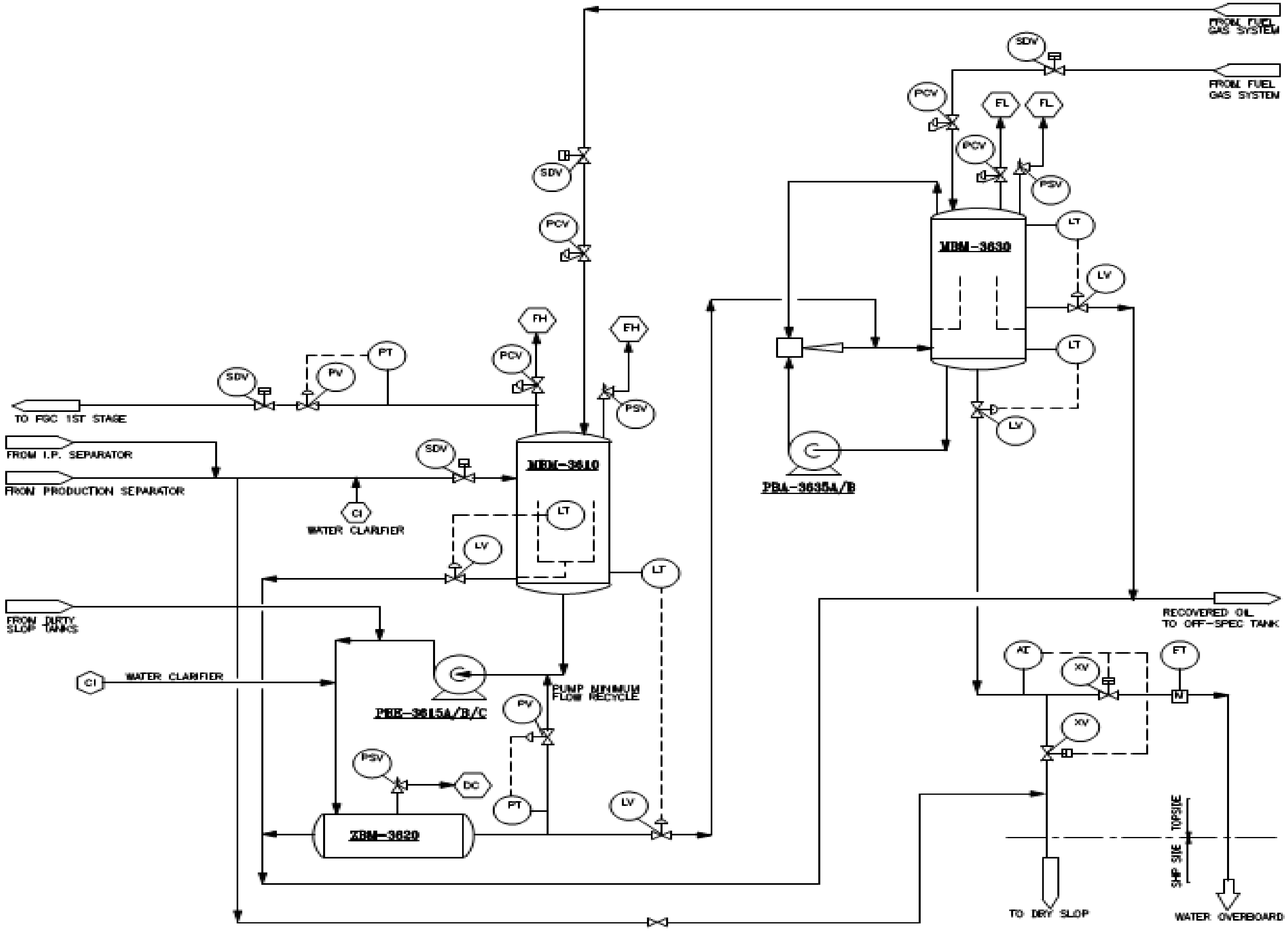


Figure 6.2 Process and Instrument Diagram of FPSO Princess Aweni Produced Water System

6.3 STRATEGY

6.3.1 SAMPLING AND DATA COLLECTION

In crude oil production, there are standard sampling requirements and procedure for produced water in offshore and onshore oil and gas installations which are set by the regulator. Since this sampling process is for research and requires more accurate results than the one from normal production process, more stringent processes were followed.

Sampling Points:

Sampling points were identified and marked on the production processes in line with the criteria for choice of sampling points. These sampling points were chosen at the entrance of the reservoir fluid (crude oil, produced water and natural gas), at the middle of the production process and at the end of the production process after the produced water had undergone some form of treatment. The selection of sampling points on these case study facilities has been done with the objective of monitoring and recording any change in concentration / toxicity of the selected pollutants as produced water passes through the production process. The sampling points for the case study facilities are shown in the table below:

Table 6.1: Produced water sampling points for case study facilities

Case Study Facility	Point 1	Point 2	Point 3	Point 4	Point 5
Izombe Flowstation	Manifold	Line Heater Exit	WIJ Pump Inlet	N/A	N/A
FPSO Princess Aweni	Manifold	PW Surge Drum Exit	Hydrocyclone Inlet	PW Degasser	PW Analyser Exit

Materials:

Some of the materials used for sample collection and transportation to laboratory include 1000ml Amber glass bottles, 2-litre plastic containers, 300ml plastic bottles, sulphuric acid, nitric acid, labels and marker pen.

Method:

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. These samples are put in a container that shields them from direct sunlight and transported to the laboratory. The collection of samples from Izombe Flowstation was done between November 17, 2017 and April 28, 2018 while sampling at the FPSO Princess Aweni happened between March 9, 2018 and August 10, 2018. Samples were collected and analysed weekly throughout this period.

Observation / Challenges:

The first set of samples collected from Izombe Flowstation on September 20, 2017 did not give the expected results at the laboratory because the prescribed sampling, preservation and transportation procedures for produced water were not followed. It was a learning curve in the project. The logistics to access the facilities was also another challenge but the Department of Petroleum Resources, Nigeria's oil and gas industry regulator, helped the researcher.

Conclusion:

Produced water samples were the source for the base data for this research work. The sampling process was thorough and extensive. Collection of samples over a period of six months in each location was enough to get the quality of data required for the research.

6.3.2 LABORATORY ANALYSIS

Objective:

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. 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) and Recommended Practice for Analysis of Oilfield Waters (API RP – 45).

The selected pollutants are grouped into six following the method for the determination of their concentrations in the produced water samples. The groups are as shown below:

Table 6.2 Pollutant Groups and Concentration Determination Methods

S/N	**Pollutant Group**	**Method /Equipment**
1.	BTEX (Benzene, Toluene)	Gas Chromatography with Ionisation Detector (GC-FID)
2.	Phenols, Phosphates, Ammonia, Nitrates	HACH DR 3900

3.	Metals (Lead, Chromium)	Flame Atomic Absorption Spectrometry (Flame AAS).
4.	Chlorides and Salinity	Titrimetry
5.	PH / Total Dissolved Solid (TDS)	PH Meter / TDS Meter
6.	Oil in Water Content	Triple Peak Method

BTEX Analysis

Materials and Reagents:

Some of the materials required for BTEX analysis are auto sampler vials, 150 µL vial inserts, crimp seals, vial crimper, de-crimper, 10 µL autosampler syringe, non-polar capillary column. Some of the reagents are acetone, carbon disulphide, petroleum ether, air and nitrogen

Methods and Procedures:

The analysis was carried out by Gas Chromatography with Flame Ionisation Detector (GC-FID) method using Agilent 6890 Gas Chromatograph.

In order to ensure good performance, performance check was first performed prior to casework using petroleum ether blank or Carbon disulphide adsorption elution blank. The samples were then re-examined to ensure that the resulting chromatographs are within the limits before using the instrument for casework.

The samples were prepared and analysed using ARSON.M GC-FID program: The carrier gas was hydrogen. After the autosampler with a 10µL syringe injection was used to perform solvent washes from the wash bottle, a 5.0µL sample was injected with a fast plunger speed, no sample washes, and three sample pumps. The set-up was run in split mode at 240^{0}C with a 50:1 split ratio. In the oven, a temperature program starting at 80^{0}C was ramped at 20^{0}C per minute until 280^{0}C. It was held at 280^{0}C for 2 minutes. HP-5MS or DB-5MS column 0.25 mm in diameter, about 30 m long with a 0.25 µm film thickness was used. The column was kept at a constant flow of 1.6 mL/min. The detector temperature was set at 300^{0}C. The flow rate for hydrogen was 30.0 mL/min, for air was 400.0 mL/min, and the makeup flow of nitrogen was 25.0 mL/min.

After the data has been collected, the resulting data file was loaded in the data analysis program for examination. The resulting chromatograph was then included in the case record.

Phenols, Phosphates, Ammonia and Nitrates Analysis

Materials, Methods and Reagents:

HACH DR 3900 used for this analysis is a laboratory spectrophotometer that has the capacity to determine the concentration of selected pollutants in the sample produced water. This device applied different methods for every pollutant whose concentration in the sample produced water was being determined.

Metals (Pb, Cr) Analysis

Materials and Reagents:

Some of the materials required for Metals analysis are 1 litre acid washed polyethylene bottles for samples, beakers, measuring cylinders. Some of the reagents are hydrochloric acid, Nitric acid, fuel (acetylene), oxidants (air for lead, nitrous oxide for chromium)

Methods and Procedures:

Analysis was carried out by Flame Atomic Absorption Spectrophotometry (FAAS). Preliminary treatment of produced water by filtration was done. The produced water samples were first acidified; Hydrochloric acid for Chromium concentration detection and Nitric acid for Lead concentration detection. Hollow Cathode Lamp was chosen for analysis and allowed to warm up for fifteen minutes. The instrument was properly aligned, the monochromator positioned at the correct wavelength and slit width, and the current was adjusted according to the manufacturer's recommendation. The flame was lighted, flow of fuel and oxidant regulated as the burner and nebulizer were used to adjusted flow rate for maximum percent absorption and stability. The photometer was balanced. A calibration curve was constructed by plotting the concentrations of the standards against absorbances. The proper concentration was read out.

To determine the concentration of chromium concentration, the use of optimum flame condition is encouraged to avoid interference by high levels of iron, cobalt and chlorides.

Oil in Water Analysis

Materials and Reagents:

Some of the materials required for Oil in Water analysis are measuring cylinders, infra-red spectrophotometer, silica cells, conical flasks, volumetric flasks, 50 ml burette, graduated pipettes and analytical balance. The reagents include Hydrochloric acid (concentrated), Sodium chloride, Magnesium sulphate (dried at 500oC for 4 hours), Tetrachloroethylene (TTCE) stabilized with alkylphenol and Florisil. Calibration reagents are toluene, hexadecane, and 2,6,10,14-tetramethylpentadecane.

Methods and Procedures:

The analysis was carried out by Gas Chromatography with Flame Ionisation Detector (GC-FID) method using Agilent 6890 Gas Chromatograph. About 2.5 ml of hydrochloric acid was first added to acidify the sample and 100 ml of TTCE to the effluent in the sample container. The sample was placed onto the magnetic stirrer and stirred for 30 min±1 min at approximately 1500 rev/min. Approximately 50 ml of fresh TTCE was eluted through the column and collected in a stoppered conical flask for use as a blank. The TTCE was drained from the column until it was approximately 2 mm above the column packing. The content of the sample container was decanted into a 500 ml separating funnel and allowed to settle. The TTCE extract layer was ran-off into a clean glass beaker. The water was drained off into a 500 ml measure cylinder and the volume read to the nearest 2.5 ml. One of the 10 mm silica cells was filled with TTCE blank, the cell placed in the beam of the spectrometer and scanned to cover the range 3400cm^{-1} to 2600cm^{-1}. The cell was removed, emptied and dried with clean dry air. It was filled gain with the TTCE extract from above, placed in the beam of the spectrometer and scan over the range 3400cm^{-1} to 2600cm^{-1}. These absorbance values are used to calculate the oil content of the produced water sample.

Chlorides and Salinity Analysis

Materials and Reagents:

Some of the materials required for chlorides and Salinity analysis are measuring cylinders, burette and stand, conical flask and pipette. The reagents include potassium chromate indicator solution, standard silver nitrate titrant.

Methods and Procedures:

The analysis was carried out by Titrimetry (chlorinity titration) to determine chloride ions concentration in the produced water sample. This method determines the chloride ion concentration of a solution by titration with silver nitrate. Silver nitrate solution was slowly added to the sample till it led to the formation of a precipitate of silver chloride.

$Ag^{+}_{(aq)} + Cl^{-}_{(aq)} \rightarrow AgCl_{(s)}$ ……………………………. Equation 6.1

The nitrate solution was added until the end point of the titration occurs when all the chloride ions have been precipitated. A little more silver ions reacted with the chromate ions of the indicator, potassium chromate, to form a red-brown precipitate of silver chromate.

$2Ag^{+}_{(aq)} + CrO_4{}^{2-}_{(aq)} \rightarrow Ag_2CrO_{4(s)}$ ……………………… Equation 6.2

Equation 6.1 was used to determine the moles of chloride ions reacting and thereby the concentration in the produced water sample.

pH and TDS Measurements

Materials and Reagents:

Some of the materials required for pH and TDS measurement are the HANNA Edge PH meter and TDS meter respectively. The reagent for pH measurement is the buffer solution of disodium tetraborate solution.

Methods

The pH meter was calibrated by dipping the probe into the buffer solution. Calibration was done with three buffer solutions at pH of 4.0, 7.0

and 10.0 to ensure more precise measurements. The probe was dipped into the produced water sample and the pH is read out and recorded.

6.3.3 BOUNDARY CONDITIONS

Table 6.3: Onshore Crude Oil Production Facility Parameters

S/N	**Major Equipment**	**Design Considerations**		**Operating Parameters**	
		Temperature (°C)	**Pressure (psig)**	**Temperature (°C)**	**Pressure (psig)**
1.	Production Manifold	93.3	230	37.78 – 43.33	115 - 120
2.	Production Separator	93.3	230	37.78 – 43.33	115 - 120
3.	Line Heater	93.3	50	50 – 55	30 - 40
4.	Free Water Knock Out Vessel	93.3	50	37.78 – 43.33	30 – 40
5.	WIJ Pump Inlet	93.3	50	30 -32	14.7

Table 6.4: Offshore Crude Oil Production Facility Parameters

S/N	**Major Equipment**	**Design Considerations**		**Operating Parameters**	
		Temperature (°C)	**Pressure (psig)**	**Temperature (°C)**	**Pressure (psig)**
1.	Production Manifold	93	350	60	296
2.	Produced Water Surge Drum	93	75.42	60	4.35
3.	Produced Water Hydrocyclone	93	149.39	60	85.57
4.	Produced Water Degasser	93	75.42	60	4.35

5.	Produced Water Analyser Exit	93	14.7	28 -32	14.7

6.3.4 PROCESS SIMULATION AND OPTIMISATION

Process simulation and optimization are generally required for optimum performance of production process and their application could be used to maximize production of desired product and minimize generation or undesired products. In the case of this research, the process simulation and optimization are aimed at minimizing pollutant generation from the crude oil production process.

The Process Simulator:

Aspen *Hysys* process simulator has been used for the research work. *Hysys* is a software for steady-state and dynamic process simulation originally created by Hyprotech, a Canadian company but presently developed and marketed by Aspentech, an American company based in Massachusetts, United States. The software includes tools for the estimation of physical properties and liquid–vapour phase equilibrium; heat and material balances, design, optimisation of oil and gas processes and process equipment. *Hysys* has been acquired and modified by Aspen. It comprises a library of the physical properties of a large number of chemical species; a set of subroutines to estimate the behaviour of many types of plant equipment (heat exchangers, reactors, etc.) and a graphical user interface to accept specifications for the case and display results. The user can describe the process in terms of unit operations interconnected by process streams, and the programme solves all the mass/energy/equilibrium equations, taking into consideration the specified design parameters. Aspen Hysys is an interactive and flexible process modelling software that allows the engineers to design, monitor, troubleshoot; perform process operational improvement and asset management. This provided an enhanced productivity, reliability, decision-making and profitability of the plant life cycle. All necessary information pertaining to pure components flash and physical properties calculations is contained in the fluid package. Proper selection of thermodynamic models during process simulation is necessary as a starting point for accurate process modelling. A process that is otherwise fully optimised in terms of equipment selection, configuration and operation can be rendered worthless if the process simulation is based on inaccurate fluid package and thermodynamics models. Hysys requires minimal input data from the user. The most important input parameters needed for streams are the temperature, pressure and flow rate of the stream. Hysys offers a variety of utilities that can be attached to process stream and unit operations. The tools interact with the process and provide additional information. The flowsheet within the Hysys simulation environment can be manipulated by the user to estimate desired output.

Simulation Procedure:

The simulation for this research project has been carried out using Aspen *HYSYS 8.8*. The basic procedure are as follows:

- The light end components are selected, and the properties of the fluid is then entered to adequately characterize it.
- The thermodynamic model (fluid package) befitting the process is selected using the information in Figure 6.3 and Table 6.3.
- Peng Robinson (PR) is selected as the fluid package for this simulation as the produced water is considered electrolytic.
- Enter the *Simulation Environment* and develop the process flowsheet by adding all the unit operations involved in the process.
- Link the unit operations to create a process flow diagram; o model of the crude oil production facility.
- Complete the flowsheet by adding the required data to the case study flowsheet. Data have been measured from field or determined by laboratory analysis. This is done for both case study production facilities (Onshore and Offshore)
- The various sample points are clearly marked on the flowsheet for both case study facilities (three points for onshore facility and five points for offshore facility).

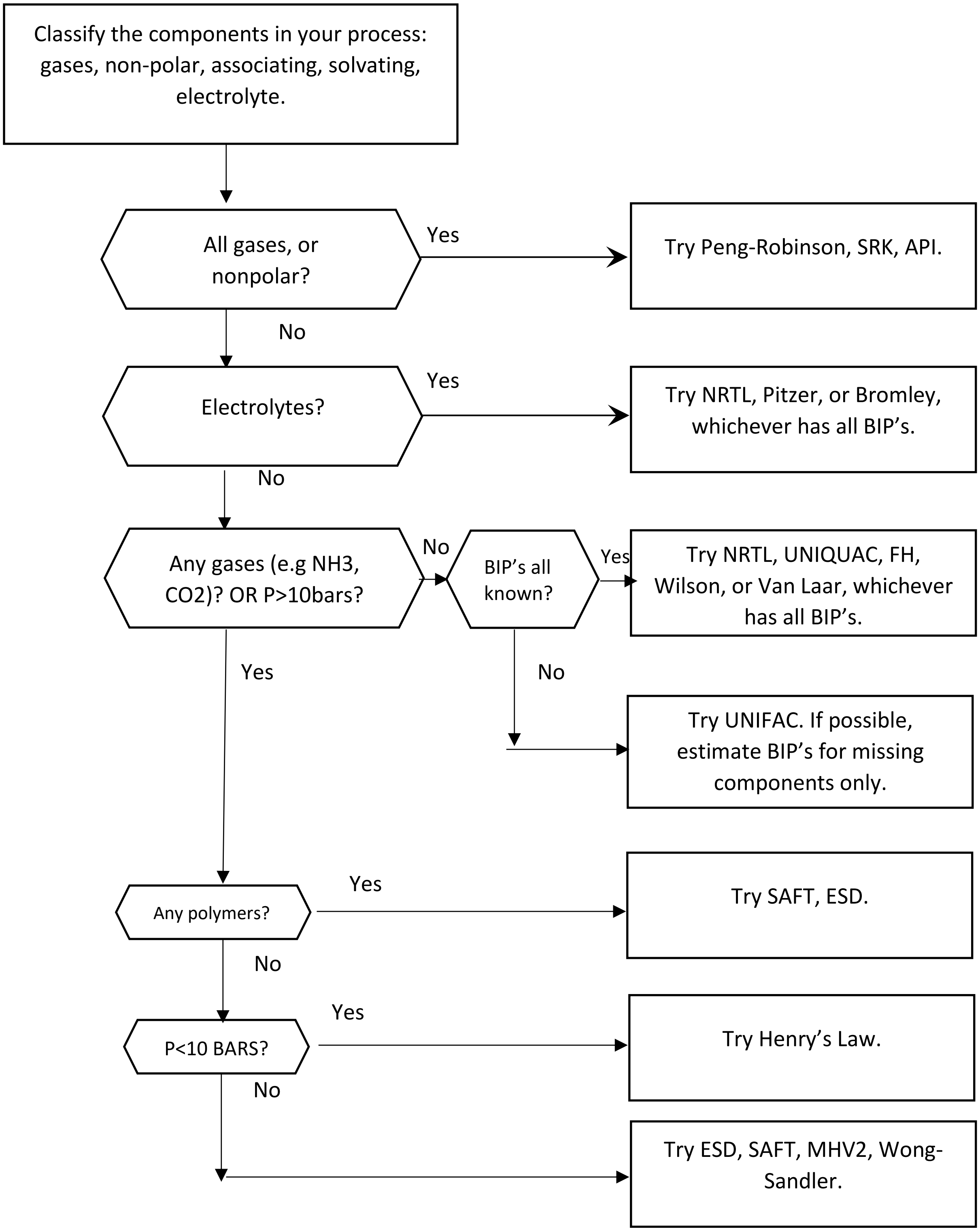


Figure 6.3 Thermodynamic model selection basis flowchart (Aspentech, 2004)

Thermodynamic Assessment:

The objective of the simulation for this research work is to reduce the concentration of the identified pollutants in the produced water. The identified pollutants are metals (chromium and lead), BTEX (benzene and toluene), phenols, phosphates, ammonia, nitrates and chlorides. It is believed that thermodynamic variables affect the concentration of these pollutants in produced water. The research is set to show if the postulation is true and the procedure are:

- Confirm that the data input on the base case flowsheet are those measured from the plant and extracted from the laboratory analysis of the produced water sample.
- Disconnect the flowsheet at point immediately after second sample point (Line Heater for Izombe Flowstation, PW Surge Drum for FPSO Princess Aweni).
- Alter the thermodynamic variables (temperature and pressure) at the Line Heater or the PW Surge Drum)
- Run the simulation and record the results obtained.
- Repeat the runs for various temperature and pressure combinations until the lowest concentration are obtained for the selected pollutants at downstream "Sample Point 2".
- Connect "Sample Point 2" to the rest of the flowsheet and run the simulation.

- Repeat the runs for various temperature and pressure combinations at the separators downstream "Sample Point 2" until the lowest concentrations are obtained for the selected pollutants at downstream "Sample Point 3".
- Record all results obtained at "Sample Point 2", "Sample Point 3", "Sample Point 4"and "Sample Point 5" (sample points 4 and 5 apply to the offshore facility only).

6.3.5 ESTIMATION OF ENERGY SAVINGS IN CASE STUDY FACILITIES

The case study facilities are existing crude oil production facilities. These facilities are in onshore and offshore locations. While the onshore facility relies on chemical treatment to reduce the volume of pollutants in the produced water to meet regulatory limits prior to re-injection into the reservoir, the offshore facility has a produced water treatment (PWT) facility. The results from the samples at the end of each facility prior to discharge or injection into the water disposal wells show that while the offshore facility met the Nigerian regulatory authorities limits for discharge of produced water for the selected pollutants, the onshore production facility at the water injection pump did not meet the regulatory requirements. The result of the research has been applied to ensure that the produced water at the end of the onshore production process met the regulatory limit without installation of a produced water treatment unit. It was also applied on the offshore production facility and the concentrations obtained at the various point along the production process indicated reduction in pollutants concentration. Process simulation indicates that if the research result is applied in the absence of the produced water treatment (PWT) unit, the final effluent will meet regulatory limits.

In order to estimate the energy savings obtained due to application of the research result on the case study crude oil production facilities, the following steps should be taken:

i. Identify the type of produced water treatment process that suits the production facility.
ii. Obtain the estimate energy requirement for the chosen produced water treatment unit from literature. This value is usually given in per unit volume of produced water treated.
iii. Calculate the volume produced water generated from the case study production facilities.
iv. Calculated the total energy that would have been expended to treat the produced water using ii and iii above.
v. The value obtained in v above represents the total energy saving at the case study facility due to application of the research result.

6.3.6 VALIDATION OF MODEL AND DATA

Data collection process for the simulation exercise considered several factors with the view of ensuring high quality data were used for the modelling process. In other to test the effect of the research environment on data quality and results, onshore and offshore crude oil production facilities were selected and data collection in both facilities was carried out over a cumulative period of twelve months; a time considered long enough to capture any variation that would have resulted over the research period. The case study facilities were selected such that while one has a conventional produced water treatment facility, the other does not. The absence of produced water treatment facility in the onshore facility enabled the research to evaluate the full capability of the research results while the presence of produced water treatment facility in the offshore facility provided the research opportunity to evaluate the effect of the research result on the concentration of pollutants along the produced water treatment process. Moreover, the sample collection process, preservation procedure and the timing between sample collection and laboratory analysis ensured that the produce water samples were not degraded prior to extraction of data from laboratory tests.

In the evaluation of the performance of the model at data analysis and evaluation of research results using the case study facilities, the data from the simulation process is validated using real life data obtained from the case study process plants.

6.3.7 ANALYSIS OF RESULTS

Process simulation and optimization are generally required for optimum performance of production process and their application would maximize production of desired product and minimize generation or undesired product. In the research the overall essence of simulation and optimization is the reduction of pollutants concentration in the produced water from the crude oil production process and the ensuing energy savings following such pollutant reduction.

The results from simulation and optimization are benchmarked against regulatory limits of the pollutants to ensure that the objective of the resulting produced water not passed through cost prohibitive secondary treatment is achieved. This comparison was conducted for the simulations results from the offshore and onshore case study facilities.

6.4 SUMMARY

The methodology of the research is based a combination of laboratory experimentation and testing, system modelling using flow sheeting tools, system analysis and optimization.

Laboratory analyses are conducted on various samples of produced water collected under varying conditions to measure the amount of specific pollutants contained in the samples. The produced water samples are collected at different points along the crude oil production process. The temperatures and pressures of these sample points are measured and recorded. The result of these tests and the measured thermodynamic variables of temperature and pressure would serve as input data for the process simulation.

Process simulation using data produced by laboratory analyses and thermodynamic variable of temperature and pressure obtained directly from the process plant. Other sources of data for the simulation may include the component data sheets, the process flow diagrams, the piping and instrumentation diagrams, engineering assumptions and reference textbooks. Aspen Hysys 8.8 has been used for this simulation exercise. The boundary conditions for the simulation process is the upper limit of the design conditions of the various equipment in the crude oil production process.

The results obtained from the process simulation exercise are compared with the engineering design details of the process plant. This is to ensure that the adjusted variables are within the design range for the process plant. The resulting thermodynamic condition due to the manipulation of the thermodynamic variables are also matched with the design conditions. The model is validated by comparison with real data obtained from production process.

The optimisation of the process in the research was obtained by the cumbersome repeated alteration of temperature and pressure values on key equipment until best result which does not violate the design condition is obtained. The energy savings due to application of this process is computed by using the average energy consumption of the applicable conventional treatment method (obtained from literature) for the offshore and onshore crude oil production facilities.

CHAPTER SEVEN

RESULTS, ANALYSIS AND DISCUSSION

7.1 INTRODUCTION

The results from the research work could be classified into processed and unprocessed information and have been gathered from various sources including measurements from process plants, drawings and engineering documents, laboratory analyses, and process simulations. Each result has been used to answer some questions and, in some cases, used to further the research work by serving as input for the next stage of work. The unprocessed results like measurements from process plants and data from engineering documents have been used as inputs for process simulation. They are regarded as primary data. The results from laboratory analyses are regarded as secondary data while process simulation results are considered tertiary data. The tertiary data from process simulation represents the highest value with regards to the aim of the research work.

The results from the entire research work have been gathered in tables and in groups in relation to their need along the research. Since the research work spanned over a period of more than thirty-six months, the average of the results obtained for each of the month has been used. The analysis of the results has been focused on the ability of the obtained results to answer the research questions and the fulfilment of the key research objectives. The analysis of the results also tried to note the deviations of the results from research expectations and the areas that may require further work to ensure appropriate values are obtained from the research work.

7.2 DATA AND RESULTS

7.2.1 MEASUREMENTS AND DESIGN DATA

Onshore:

Sampling and field data measurement at the onshore location, Izombe Flowstation (IFS), were done between November 17, 2017 and April 28, 2018. Thermodynamic variables of pressure and temperature were measure directly from the pressure gauges and thermometers respectively while the production from the data was obtained from the available data at the production engineering department. The measurements are contained in Table 7.1 below:

Table 7.1: Average monthly field measurements and production data at Izombe Flowstation

S/N	Measurement Dates	Sampling Points	Thermodynamic Parameters		
			Total Production (bbls/day)	Operating Pressure (psi)	Operating Temperature (°C)
1	November 2017	Production Manifold	3,260	116	41
		Line Heater Exit		38	51.7
		WIJ Pump Inlet		14.7	30
2.	December 2017	Production Manifold	3,320	118	42
		Line Heater Exit		39	52.2
		WIJ Pump Inlet		14.7	31
3.	January 2018	Production Manifold	3,280	116	41
		Line Heater Exit		38	52
		WIJ Pump Inlet		14.7	30
4.	February 2018	Production Manifold	3,300	118	41
		Line Heater Exit		39	52
		WIJ Pump Inlet		14.7	31
5.	March 2018	Production Manifold	3,320	116	41
		Line Heater Exit		38	52.2
		WIJ Pump Inlet		14.7	31
6.	April 2018	Production Manifold	3,300	118	41
		Line Heater Exit		39	52
		WIJ Pump Inlet		14.7	31

Note: WIJ – Water Injection

Offshore:

Sampling and field data measurement at the offshore location, FPSO Princess Aweni, were done between March 9, 2019 and August 10, 2018. Thermodynamic variables of pressure and temperature were measure directly from the pressure gauges and thermometers respectively while the production from the data was obtained from the available data at the production engineering department. The measurements are contained in Table 7.2 below:

Table 7.2: Average monthly field measurements and production data at FPSO Princess Aweni.

Measurement Period		**March 2018**			**April 2018**			**May 2018**			**June 2018**			**July 2018**			**August 2018**		
Thermodynamic Variables		**Operating Temperature (ºC)**	**Operating Pressure (psi)**	**Total Production (bbls/day)**	**Operating Temperature (ºC)**	**Operating Pressure (psi)**	**Total Production (bbls/day)**	**Operating Temperature (ºC)**	**Operating Pressure (psi)**	**Total Production (bbls/day)**	**Operating Temperature (ºC)**	**Operating Pressure (psi)**	**Total Production (bbls/day)**	**Operating Temperature (ºC)**	**Operating Pressure (psi)**	**Total Production (bbls/day)**	**Operating Temperature (ºC)**	**Operating Pressure (psi)**	**Total Production (bbls/day)**
Sampling Points	**Production Manifold**	61	296	16,200	60	294	16,000	61	296	16,100	60	294	15,900	59	294	15,800	60	294	16,000
	PW Surge Drum Inlet	60	29.1		59	29.0		60	29.0		59	29.0		59	29.1		60	29.0	
	Hydrocyclone Inlet	60	98		59	97		60	98		60	99		60	98		60	98	
	PW Degasser	60	98		59	97		60	98		60	99		60	98		60	98	
	PW Analyser Exit	31	14.7		30	14.7		30	14.7		28	14.7		28	14.7		30	14.7	

Note: PW – Produced Water

7.2.2 LABORATORY ANALYSIS RESULTS

Onshore:

The samples collected weekly at the onshore location, Izombe Flowstation (IFS) over the period between November 17, 2017 and April 28, 2018 were subjected to laboratory analysis. The presence and quantity of some selected pollutants in the produced water samples were determined. A summary of the monthly average laboratory results is contained in Table 7.3.

Table 7.3 Average of the results of laboratory tests of samples collected at Izombe Flowstation during the period of study (November 2017 – April 2018)

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 (No Unit)	pH Meter	7.11	6.95	6.65
2	Benzene	GC (FID)	0.52	0.20	0.03
3	Toluene	GC (FID)	0.51	0.16	0.07
4	Phenol	HACH DR 3900	0.75	0.24	0.15
5	Lead	AAS (FLAME)	1.37	0.99	0.37
6	Chromium	AAS (FLAME)	0.90	0.79	0.66
7	Copper	AAS (FLAME)	0.05	0.04	0.01
8	Iron	AAS (FLAME)	4.99	3.07	0.40
9	Zinc	AAS (FLAME)	0.23	0.21	0.19
10	Phosphate	HACH DR 3900	0.05	0.17	0.20
11	Ammonia	HACH DR 3900	11.20	8.27	5.61
12	Nitrates	HACH DR 3900	20.46	22.50	18.42
13	TDS	TDS Meter	17433	16483	12666
14	Chlorides	Titrimetry	6200	5516	5158
15	Salinity	Titrimetry	9683	8506	7123

Note: TDS – Total Dissolved Solids

Offshore:

The samples collected weekly at the offshore location, FPSO Princess Aweni over the period between March 9, 2018 and August 10, 2018 were subjected to laboratory analysis. The presence and quantity of some selected pollutants in the produced water samples were determined (See Table 7.4).

Table 7.4 Average of the results of laboratory tests of samples collected at FPSO Princess Aweni during the period of study (March – August 2018)

S/N	Sample Parameter	Analytical Method	Conc. at P1 (mg/l)	Conc. at P2 (mg/l)	Conc. at P3 (mg/l)	Conc. at P4 (mg/l)	Conc. at P5 (mg/l)
1	pH (no unit)	pH Meter	7.48	7.46	7.46	7.42	7.42
2	Benzene	GC (FID)	0.64	0.60	0.54	0.03	0.01
3	Toluene	GC (FID)	0.84	0.66	0.58	0.23	0.12
4	Phenol	HACH DR 3900	0.64	0.52	0.43	0.18	0.14
5	Lead	AAS (FLAME)	0.84	0.64	0.43	0.13	0.01
6	Chromium	AAS (FLAME)	0.92	0.81	0.63	0.23	0.01
7	Copper	AAS (FLAME)	0.05	0.04	0.03	0.02	0.01
8	Iron	AAS (FLAME)	4.93	3.73	1.54	0.22	0.19
9	Zinc	AAS (FLAME)	0.23	0.20	0.18	0.04	0.02
10	Phosphate	HACH DR 3900	0.69	0.49	0.41	0.23	0.14
11	Ammonia	HACH DR 3900	12.82	10.18	2.94	0.37	0.32
12	Nitrates	HACH DR 3900	27.03	21.14	18.10	8.73	8.19
13	TDS	TDS Meter	6808	6283	6021	5741	5155
14	Chlorides	Titrimetry	8764	8166	7866	6184	5768
15	Salinity	Titrimetry	6583	6225	5166	2816	2458

Note: PW – Produced Water; TDS – Total Dissolved Solids; P1-Production Manifold; P2-PW Surge Drum Inlet; P3-Hydrocyclone Inlet; P4-PW Degasser Inlet; P5-PW Analyser Exit.

7.2.3 PROCESS SIMULATION RESULTS

Onshore:

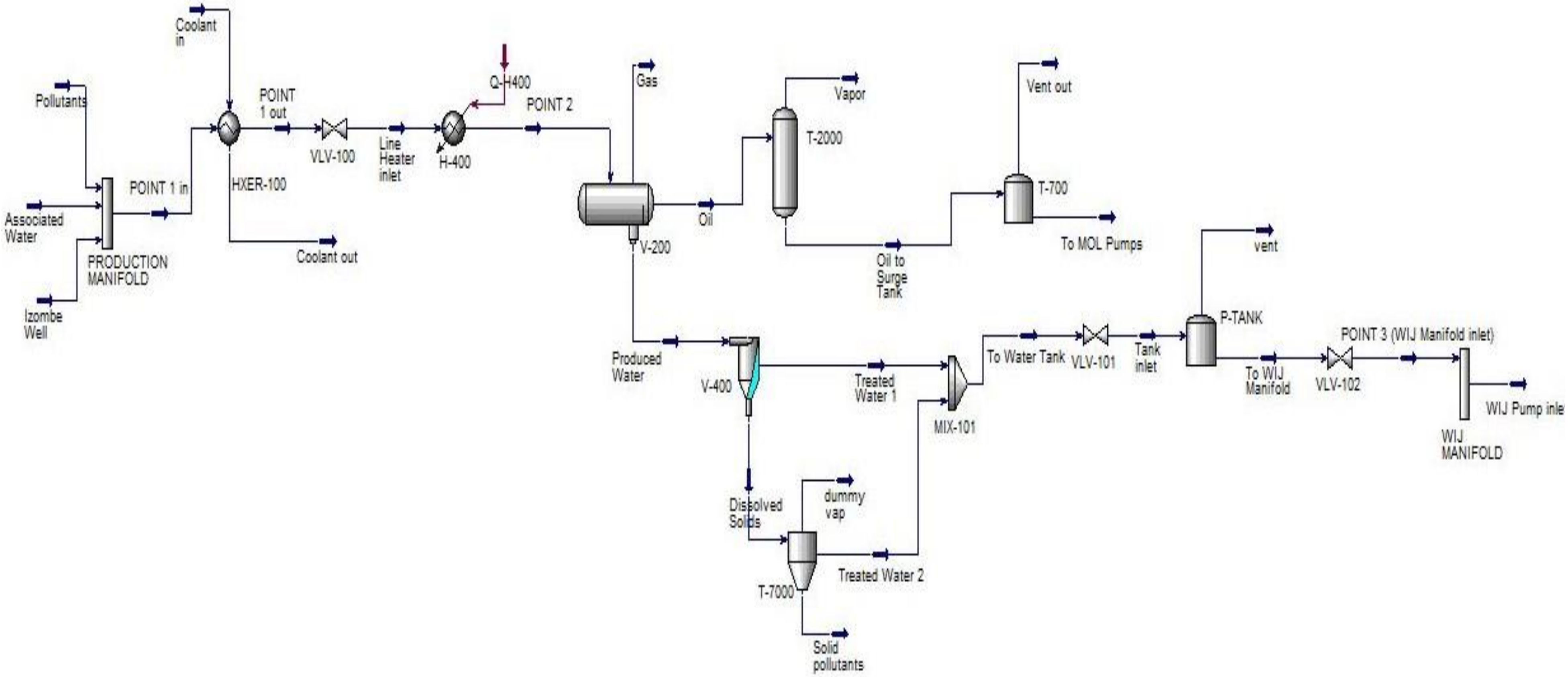


Figure 7.1 Simulation Flowsheet of the Izombe Flowstation indicating the points of sample collection

Produced water has been represented in the Hysys 8.8 environment as water with the presence of crude oil and dissolved pollutants. The pollutants exist in solution and therefore modelled using Electrolytes NRTL fluid package. The best results for the various simulation runs are the ones with least concentrations of key pollutants and within design range of the case study facility. The results obtained from the laboratory analysis over the six-month period remained relatively stable with negligible deviations thus average thermodynamic values were used for the simulations. The results are recorded in Tables 7.5 and 7.6.

Table 7.5: Simulation Results of Pollutant Concentrations at different Temperatures around Selected Sampling Points at Izombe Flowstation (mg/litre)

Sample Parameter	Production Manifold						Line Heater Exit						Water Injection Pump					
	25°C	30°C	35°C	45°C	50°C	55°C	35°C	40°C	45°C	50°C	55°C	60°C	15°C	20°C	25°C	35°C	40°C	45°C
Benzene	0.6043	0.6225	0.6236	0.3163	0.2105	0.1503	0.2524	0.2407	0.2342	0.2231	0.1052	0.0287	0.04268	0.0398	0.03616	0.0211	0.01194	0.006
Toluene	0.5018	0.5055	0.5081	0.5105	0.5104	0.5094	0.1983	0.1942	0.1827	0.1708	0.1058	0.0531	0.07157	0.0712	0.07076	0.0654	0.05840	0.047
Phenol	0.7237	0.7326	0.7408	0.7560	0.7635	0.7711	0.2307	0.2330	0.2356	0.2386	0.2422	0.2516	0.14589	0.1469	0.14823	0.1514	0.15347	0.1552
Lead	1.3210	1.3374	1.3527	1.3814	1.3958	1.4108	0.9480	0.9581	0.9699	0.9837	1.0003	1.0447	0.35930	0.3621	0.36534	0.3737	0.37929	0.38615
Chromium	0.8680	0.8788	0.8887	0.9074	0.9166	0.9263	0.7574	0.7653	0.7745	0.7852	0.7979	0.8319	0.64130	0.6462	0.65189	0.6665	0.67610	0.68792
Copper	0.0493	0.0497	0.0499	0.0500	0.0459	0.0397	0.0419	0.0414	0.0409	0.0403	0.0219	0.0087	0.01033	0.0103	0.01016	0.0099	0.00969	0.00924
Iron	4.8182	4.8767	4.9301	5.0286	5.0768	5.1259	2.9574	2.9853	3.0169	3.0536	3.0967	3.2094	0.38971	0.3925	0.39559	0.4035	0.40860	0.41482
Zinc	0.2293	0.2302	0.2305	0.2292	0.2177	0.1856	0.2269	0.2228	0.2180	0.2124	0.1916	0.1854	0.20147	0.1987	0.19515	0.1660	0.13029	0.06738
Phosphate	0.0497	0.0499	0.0500	0.0458	0.0326	0.0163	0.1816	0.1788	0.1755	0.1717	0.1673	0.1569	2.1502	2.1362	2.0756	1.6639	1.31213	0.95313
Ammonia	13.780	12.849	12.041	10.204	9.144	8.1416	9.8923	9.3602	8.8772	8.4361	5.8308	5.3073	6.84758	6.4140	6.02584	4.5584	2.96840	0.16017
Nitrates	20.487	20.546	20.542	20.359	20.183	19.951	24.636	24.109	23.497	19.801	18.026	17.265	1.97517	1.9418	1.90102	1.7966	1.73306	1.66254
Salinity	13362	12010	10857	9004.8	8254.2	7594.9	11505	10485	9589.5	8798.1	8094.9	6902.3	9946.6	8918.7	8032.9	6593.4	6003.8	5482.5

Table 7.6: Simulation Results of Pollutant Concentrations at different Pressures around Selected Sampling Points at Izombe Flowstation (mg/litre)

Sample Parameter	Production Manifold						Line Heater Exit						Water Injection Pump					
	90psi	100psi	110psi	125psi	135psi	145psi	25psi	30psi	35psi	45psi	50psi	55psi	5psi	10psi	20psi	25psi	30psi	35psi
Benzene	0.4183	0.4619	0.5099	0.3918	0.2915	0.1952	0.1905	0.1959	0.1973	0.2046	0.2075	0.2099	0.02779	0.0291	0.03072	0.0312	0.03159	0.03188
Toluene	0.7815	0.7133	0.6115	0.4083	0.2805	0.1505	0.1580	0.1593	0.1594	0.1609	0.1614	0.1618	0.06864	0.0695	0.07033	0.0705	0.07060	0.07063
Phenol	0.9844	0.9389	0.8736	0.5597	0.3809	0.2359	0.2646	0.2592	0.2513	0.2137	0.1876	0.1543	0.15371	0.1515	0.14267	0.1336	0.11672	0.0812
Lead	1.3967	1.3865	1.3767	0.1263	0.1135	0.0944	1.0101	0.9986	0.9958	0.7799	0.5733	0.3675	0.37958	0.3739	0.32659	0.2394	0.12816	0.02842
Chromium	0.9174	0.9108	0.9044	0.8591	0.8090	0.7830	0.8057	0.7968	0.7946	0.7521	0.6870	0.6424	0.67677	0.6668	0.54010	0.3293	0.14529	0.02056
Copper	0.0504	0.0503	0.0501	0.0459	0.0427	0.0394	0.0392	0.0397	0.0398	0.0404	0.0406	0.2023	0.00971	0.0099	0.01008	0.0101	0.01016	0.01018
Iron	5.0842	5.0485	5.0138	0.4596	0.3730	0.3021	4.9255	4.7446	4.0859	2.0421	1.0240	0.0303	0.40925	0.4038	0.39664	0.3540	0.29168	0.23585
Zinc	0.2306	0.2305	0.2303	0.2266	0.2129	0.2083	0.2029	0.2071	0.2080	0.2134	0.2155	0.2355	0.18022	0.1862	0.19299	0.1950	0.19643	0.19747
Phosphate	0.0502	0.0502	0.0501	0.0499	0.0497	0.0496	0.1652	0.1681	0.1686	0.1723	0.1737	0.1749	19.1335	19.667	20.2571	20.425	20.5430	20.6256
Ammonia	8.7189	9.6262	10.547	11.955	12.911	13.883	6.2143	7.0360	7.7073	9.3430	10.168	10.997	3.70476	4.6829	6.66462	7.6685	8.68124	9.70295
Nitrates	20.461	20.478	20.474	20.435	20.393	20.340	21.607	22.132	22.244	22.935	23.201	23.426	17.3032	17.982	18.7709	19.010	19.1865	19.3184
Salinity	7618.4	8378.5	9144.0	10302	11081	11866	6515.0	7363.8	7942.5	9596.5	10426	11259	4727.2	5959.7	8440.4	968.62	10942	12201

Offshore:

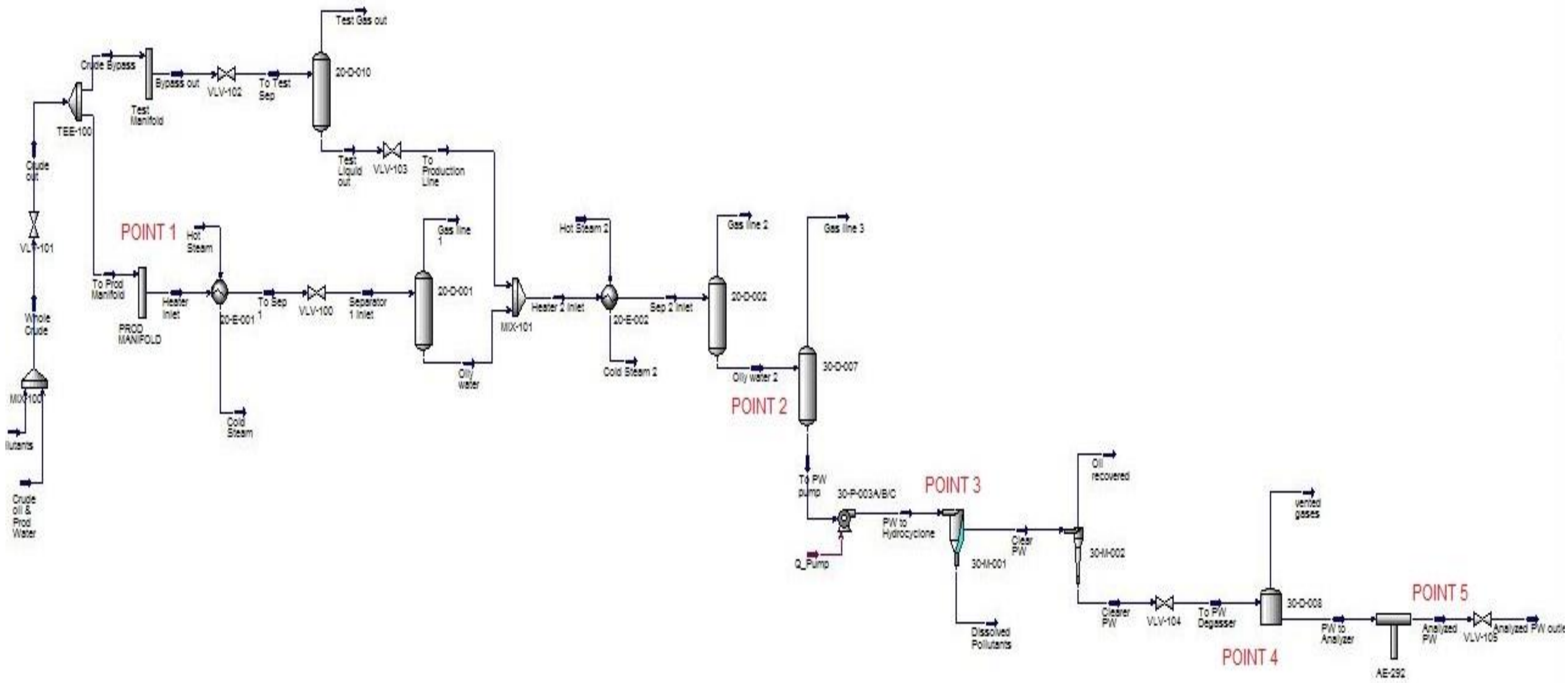


Figure 7.2 Simulation Flowsheet of the FPSO Princess Aweni indicating the points of sample collection

The case study offshore production facility is a more advanced treatment unit and has more heat exchangers in comparison with the onshore case study facility. The produced water has also been modelled in the Hysys 8.8 environment as electrolyte with the presence of crude oil. The pollutants exist in solution and therefore modelled using Electrolytes NRTL fluid package. The best results for the various simulation runs are the ones with least concentrations of key pollutants and within design range of the case study facility. The results are tabulated below:

Table 7.7: Simulation Results of Pollutant Concentrations at different Temperatures around Selected Sampling Points at FPSO Princess Aweni

Sample Parameter	Production Manifold						Hydrocyclone Inlet						Produced Water Analyser Exit					
	45°C (mg/l)	50°C (mg/l)	55°C (mg/l)	65°C (mg/l)	70°C (mg/l)	75°C (mg/l)	45°C (mg/l)	50°C (mg/l)	55°C (mg/l)	65°C (mg/l)	70°C (mg/l)	75°C (mg/l)	15°C (mg/l)	20°C (mg/l)	25°C (mg/l)	35°C (mg/l)	40°C (mg/l)	45°C (mg/l)
Benzene	0.6217	0.6299	0.6362	0.6441	0.6460	0.6467	0.5994	0.5973	0.5741	0.4349	0.2828	0.0252	0.0102	0.0102	0.0101	0.0054	0.0051	0.005
Toluene	0.8081	0.8208	0.8314	0.8473	0.8532	0.8579	0.5803	0.5814	0.5818	0.4809	0.3579	0.2157	0.1246	0.1218	0.1196	0.1135	0.1082	0.1022
Phenol	0.6095	0.6204	0.6299	0.6461	0.6531	0.6596	0.4249	0.4277	0.4305	0.4362	0.4392	0.4424	0.1283	0.1304	0.1346	0.1426	0.1428	0.1434
Lead	0.7980	0.8124	0.8250	0.8464	0.8559	0.8648	0.4196	0.4225	0.4254	0.4314	0.4347	0.4382	0.0075	0.0082	0.0088	0.0116	0.0128	0.0138
Chromium	0.8791	0.8948	0.9087	0.9322	0.9425	0.9522	0.6173	0.6216	0.6258	0.6344	0.6391	0.6441	0.0078	0.0079	0.0084	0.0113	0.0118	0.0122
Copper	0.0513	0.0520	0.0527	0.0537	0.0540	0.0543	0.0334	0.0334	0.0334	0.02832	0.0233	0.0173	0.013	0.0124	0.0115	0.0068	0.0062	0.0061
Iron	4.6948	4.7783	4.8513	4.9747	5.0282	5.0780	1.5108	1.5207	1.5303	1.5499	1.5602	1.5712	0.0126	0.0151	0.0178	0.0191	0.0192	0.0193
Zinc	0.2235	0.2267	0.2293	0.2329	0.2340	0.2347	0.1850	0.1847	0.1842	0.1422	0.0881	0.0279	0.0219	0.0219	0.0218	0.0182	0.0143	0.0112
Phosphate	0.6630	0.6729	0.6809	0.6922	0.6959	0.6985	0.4124	0.4122	0.4114	0.3081	0.2405	0.2022	0.1594	0.1508	0.1485	0.1238	0.1004	0.0902
Ammonia	16.300	14.984	13.899	11.825	10.752	10.083	3.451	3.2608	3.091	2.3001	1.3742	0.3558	0.3842	0.3636	0.3442	0.2515	0.1712	0.1004
Nitrates	26.112	26.480	26.770	27.153	27.261	27.319	19.325	19.280	18.9033	15.9551	12.7831	7.9757	0.9123	0.8992	0.8647	0.6811	0.5017	0.2906
Salinity	8760.1	7965.0	7282.9	6176.2	5722.7	5321.3	6626.6	6077.7	5594.5	3785.9	2945.3	2413.9	2665.3	1217.7	871.2	438.4	402.1	385.8

Table 7.8: Simulation Results of Pollutant Concentrations at different Pressures around Selected Sampling Points at FPSO Princess Aweni

	Production Manifold						Hydrocyclone Inlet						Produced Water Analyser Exit					
Sample Parameter	**270psi (mg/l)**	**280psi (mg/l)**	**290psi (mg/l)**	**300psi (mg/l)**	**310psi (mg/l)**	**320psi (mg/l)**	**85psi (mg/l)**	**90psi (mg/l)**	**95psi (mg/l)**	**105psi (mg/l)**	**110psi (mg/l)**	**115psi (mg/l)**	**5psi (mg/l)**	**10psi (mg/l)**	**20psi (mg/l)**	**25psi (mg/l)**	**30psi (mg/l)**	**35psi (mg/l)**
Benzene	0.6474	0.6453	0.643	0.6317	0.6138	0.5935	0.5386	0.5388	0.5396	0.5408	0.5412	0.5414	0.0098	0.0099	0.0101	0.0101	0.0101	0.0101
Toluene	0.8721	0.8644	0.8548	0.7842	0.7236	0.6327	0.6841	0.6725	0.6421	0.4808	0.3801	0.2274	0.1181	0.1183	0.1162	0.1141	0.1108	0.1076
Phenol	0.6481	0.645	0.6418	0.6138	0.5836	0.5124	0.4736	0.4652	0.4534	0.3317	0.2306	0.1429	0.1416	0.1407	0.1293	0.1093	0.1011	0.1001
Lead	0.8490	0.8449	0.8408	0.7866	0.7233	0.6283	0.4316	0.4303	0.4291	0.3467	0.2255	0.1244	0.0101	0.0101	0.0084	0.0056	0.0053	0.0051
Chromium	0.9351	0.9305	0.9260	0.8921	0.8469	0.8012	0.6347	0.6328	0.6311	0.5576	0.4225	0.2246	0.0101	0.0101	0.0089	0.0054	0.0052	0.0047
Copper	0.0539	0.0537	0.0535	0.0482	0.0441	0.0385	0.0334	0.0334	0.0333	0.0283	0.0234	0.0182	0.0099	0.01	0.01	0.01	0.01	0.01
Iron	4.9906	4.9665	4.9425	4.6184	4.0943	3.487	1.5510	1.5467	1.5425	1.3534	0.8304	0.2165	0.0222	0.0211	0.0159	0.0105	0.0086	0.0082
Zinc	0.2340	0.2331	0.2322	0.2123	0.1544	0.0184	0.1831	0.1832	0.1833	0.1834	0.1834	0.1833	0.0174	0.0196	0.0223	0.0225	0.0226	0.0228
Phosphate	0.6954	0.6927	0.6900	0.6572	0.5844	0.4681	0.4098	0.4099	0.4100	0.3099	0.2098	0.1896	0.1402	0.1412	0.1412	0.1417	0.1419	0.142
Ammonia	11.478	11.989	12.510	13.0399	13.5807	14.1322	2.5681	2.7096	2.8522	3.1410	3.2871	3.4345	0.2116	0.2687	0.3250	0.3463	0.3607	0.3702
Nitrates	27.285	27.188	27.088	25.986	23.8818	21.0755	18.046	18.069	18.087	18.109	18.114	18.116	0.7443	0.7837	0.8196	0.8198	0.8217	0.8241
Salinity	5995.4	6221.7	6449.2	6677.7	6907.4	7138.2	4549.2	4786.2	5023.8	5500.7	5739.91	5979.7	1628.5	2055.3	2915.0	3347.9	3783.0	4220.2

7.2.4 ENERGY SAVINGS IN CASE STUDY FACILITIES

Onshore:

Recommended produced water treatment facility – Gas Floatation

Estimate energy requirement from literature – 0.036 – 0.072 KWh/bbl (Soares, 2017)

Average daily volume of produced water – 3,297 barrels

Energy that would be expended by PWT – 0.054 KWh/bbl x 3,297 bbls (0.054 KWh/bbl is at the middle of the range from Soares, 2017) = 178.038 KWh

The energy saved daily for used of the research result to run the crude oil production facility other than installation of produced water treatment (PWT) unit is 178.038 KWh

The tariff for electricity from Eko Electricity Distribution Company in Nigeria on industrial consumers – N36.00 / KWh

The cost of energy saved daily by application of the result of the research to the onshore case study (Izombe Flowstation) = 178.038 x 36.00 = N6,409.37

Cost of energy saved over one year of operation at the Izombe Flowstation if the research result is employed = 365 x 6,409.37 = N2,339,420.05

Offshore:

Recommended produced water treatment facility – Hydrocyclone

Estimate energy requirement from literature – 0.036 – 0.072 KWh/bbl (Soares, 2017)

Average daily volume of produced water – 16,000 barrels

Energy that would be expended by PWT – 0.065 KWh/bbl x 16,000 bbls (0.065 KWh/bbl is at the middle of the range from Soares, 2017) = 1,040 KWh

The energy saved daily for used of the research result to run the crude oil production facility other than installation of produced water treatment (PWT) unit is 1,040 KWh

The tariff for electricity from Eko Electricity Distribution Company in Nigeria on industrial consumers – N36.00 / KWh

The cost of energy saved daily by application of the result of the research to the offshore case study (FPSO Princess Aweni) = 1,040 x 36.00 = N37,440

Cost of energy saved over one year of operation at the FPSO Princess Aweni if the research result is employed = 365 x 37,440 = N13,665,600

7.3 ANALYSIS / DISCUSSION OF RESULTS

The results from the simulation using the thermodynamic variables of temperature and pressure on the onshore and offshore case study facilities have been gathered and subjected to analysis. The analyses are found below:

7.3.1 ONSHORE FACILITY CASE STUDY:

7.3.1.1 The effect of temperature on the concentrations of pollutants:

Figures 7.3 to 7.20 represent the behaviour of the various group of pollutants in the produced water sample when subjected to temperature variations at various points along the crude oil production process.

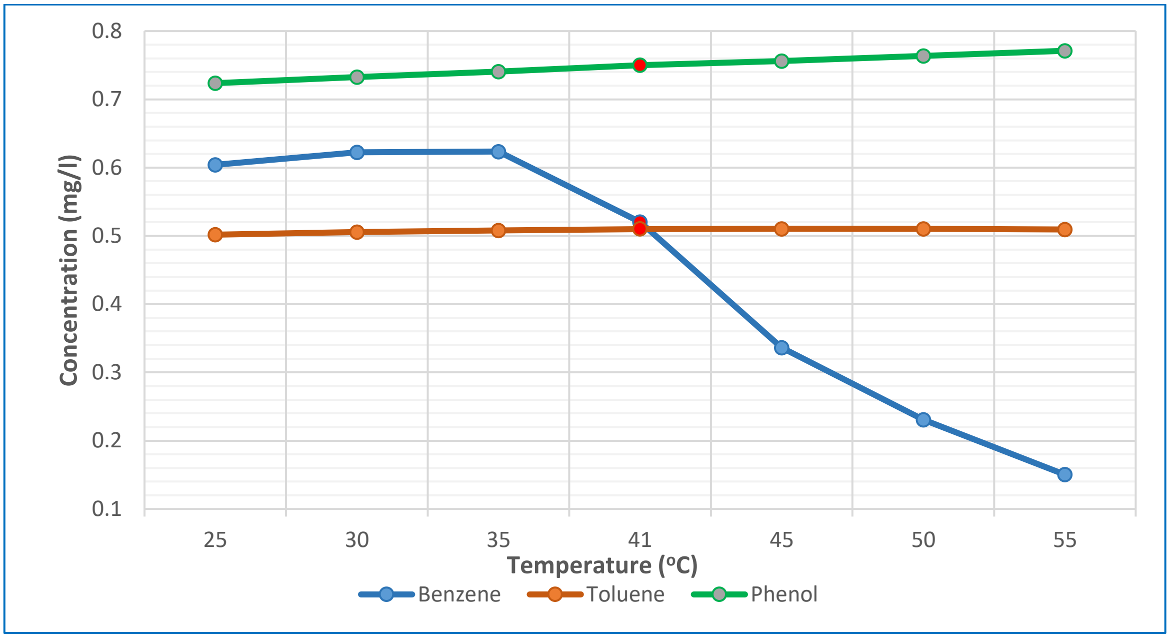


Figure 7.3 Concentrations of Benzene-Toluene-Phenol pollutants at different temperatures at the Manifold

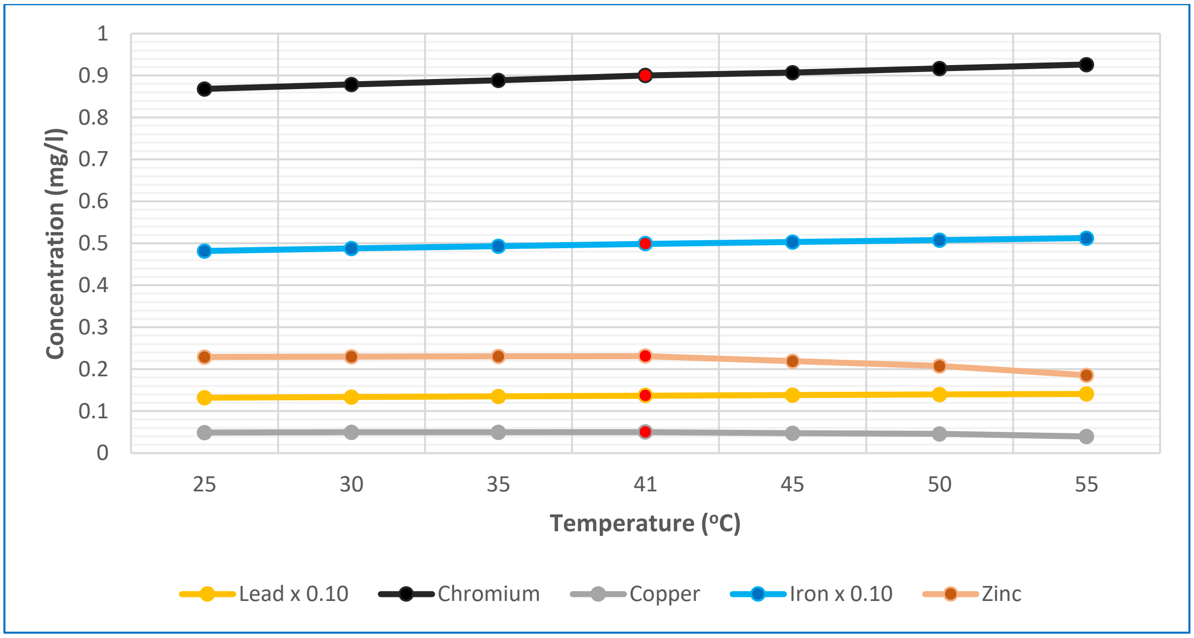


Figure 7.4 Concentrations of metal pollutants at different temperatures at the Manifold

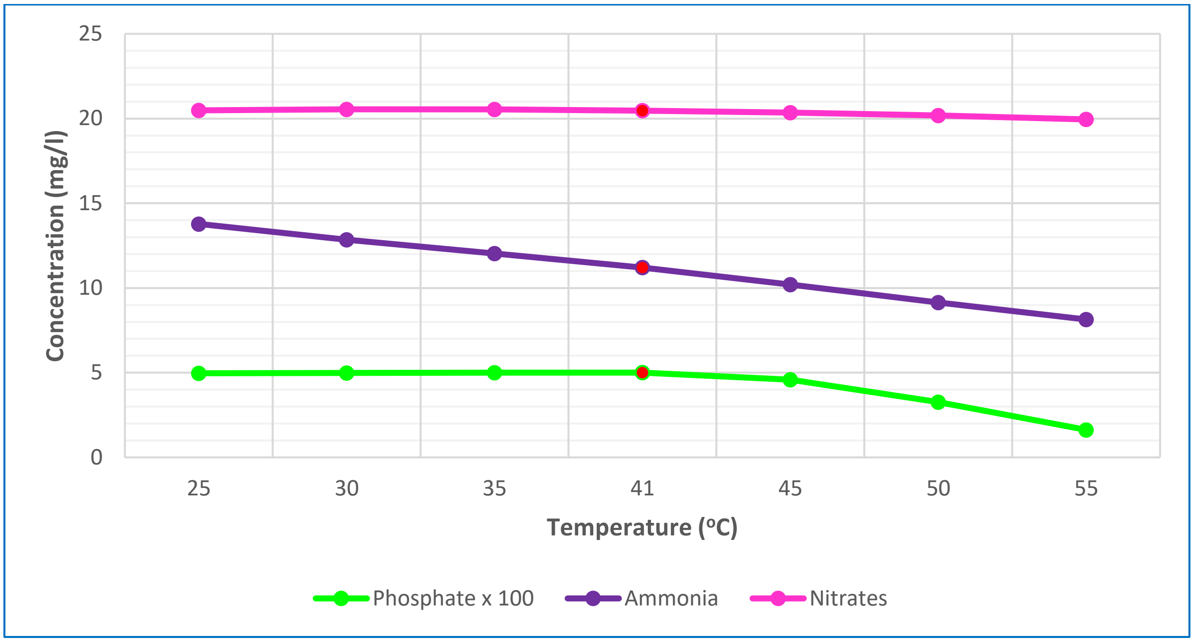


Figure 7.5 Concentrations of non-metal pollutants at different temperatures at the Manifold

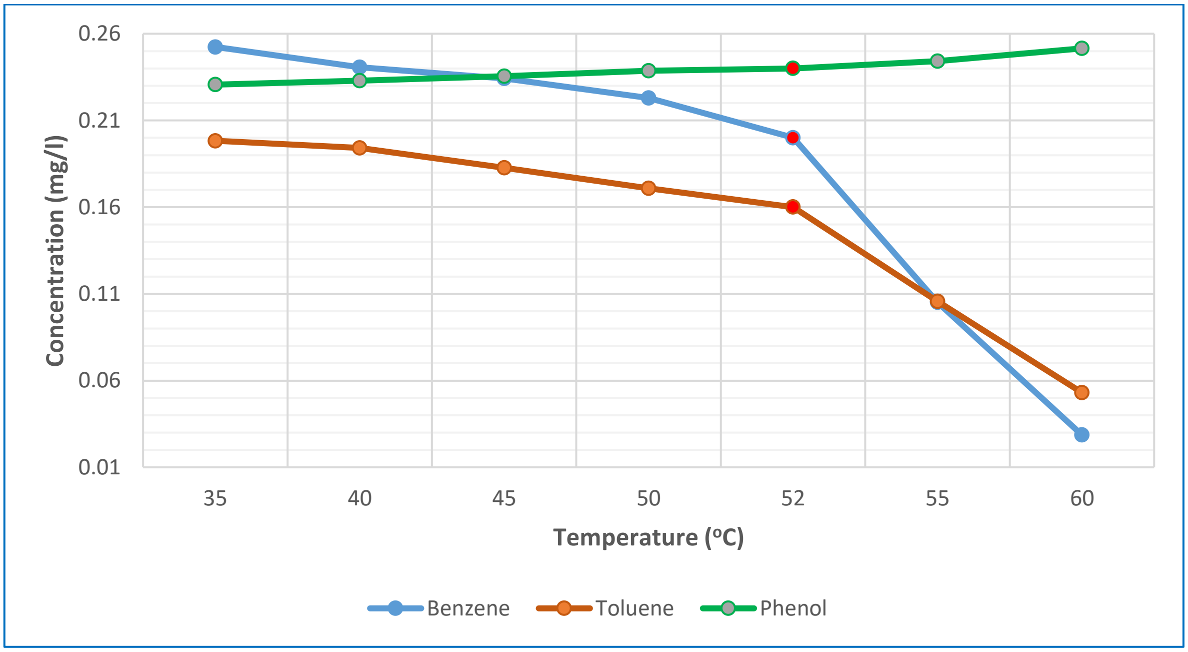


Figure 7.6 Concentrations of Benzene-Toluene-Phenol pollutants at different temperatures at the Line Heater exit

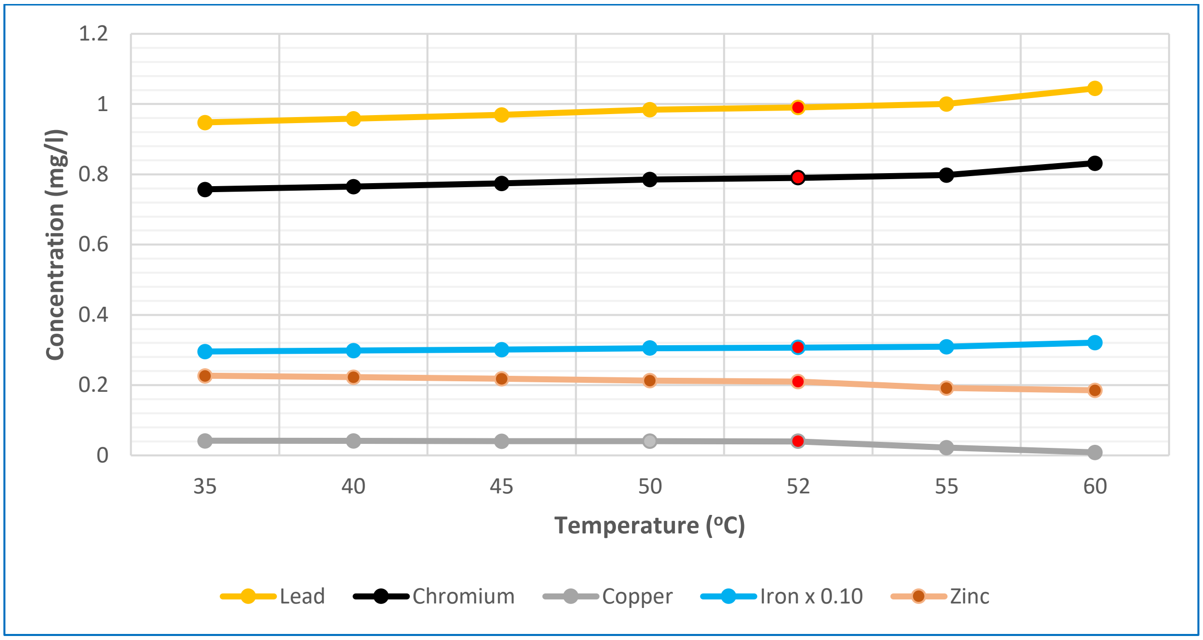


Figure 7.7 Concentrations of metal pollutants at different temperatures at the Line Heater exit

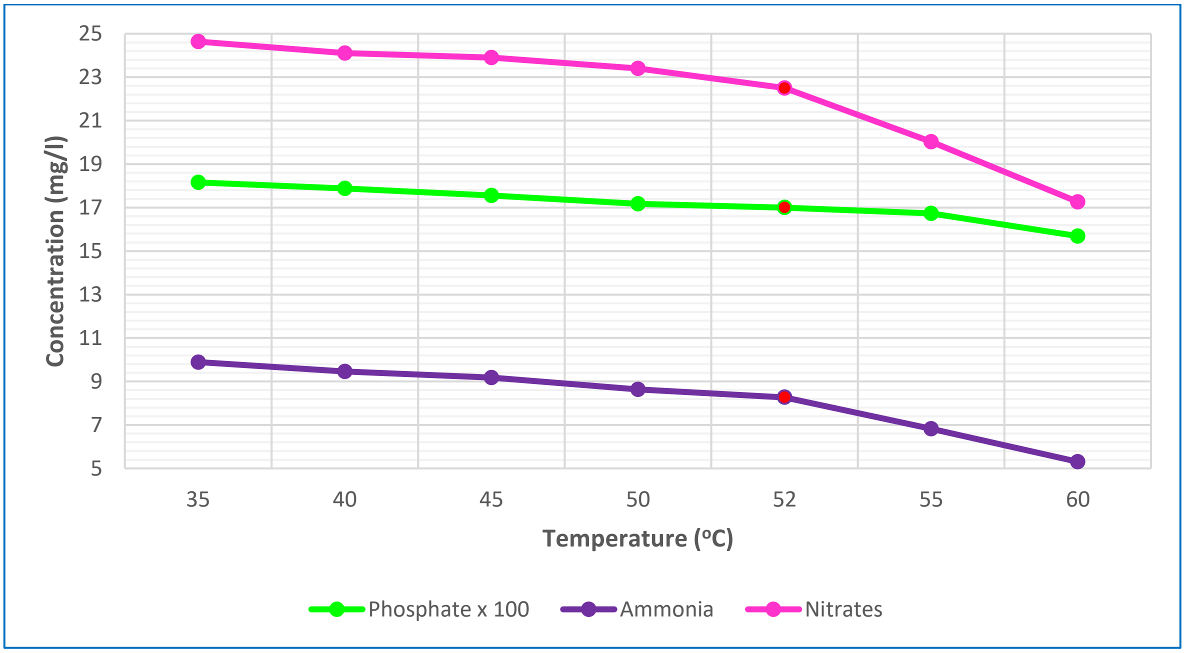


Figure 7.8 Concentrations of non-metal pollutants at different temperatures at the Line Heater exit

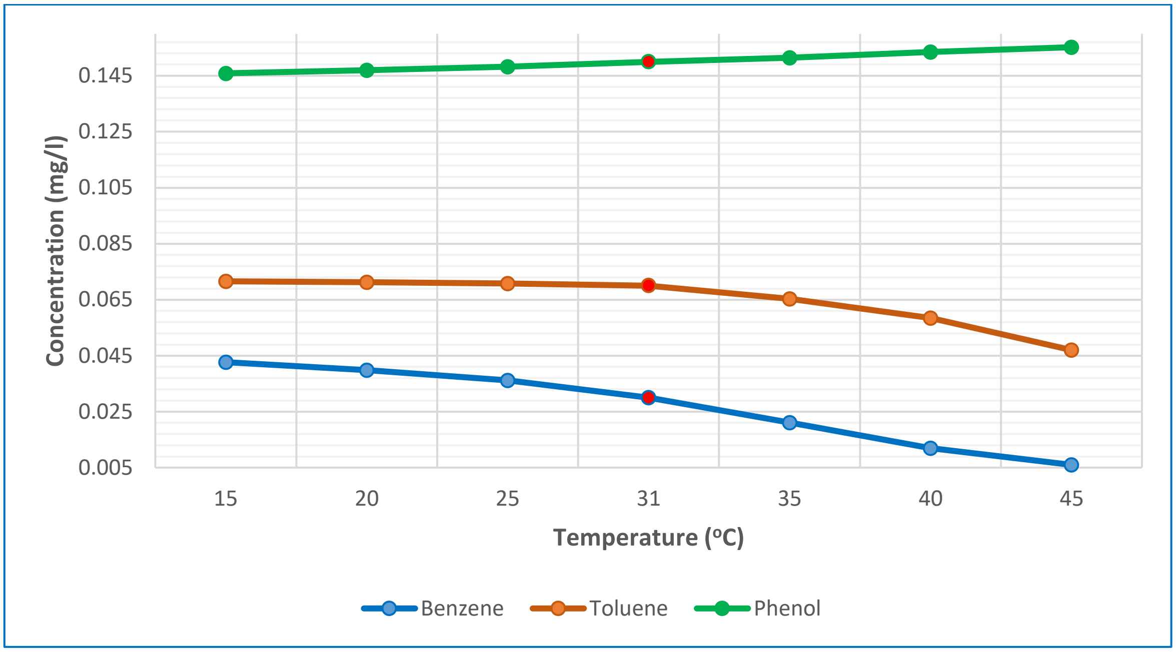


Figure 7.9 Concentrations of Benzene-Toluene-Phenol pollutants at different temperatures at the water Injection Pump

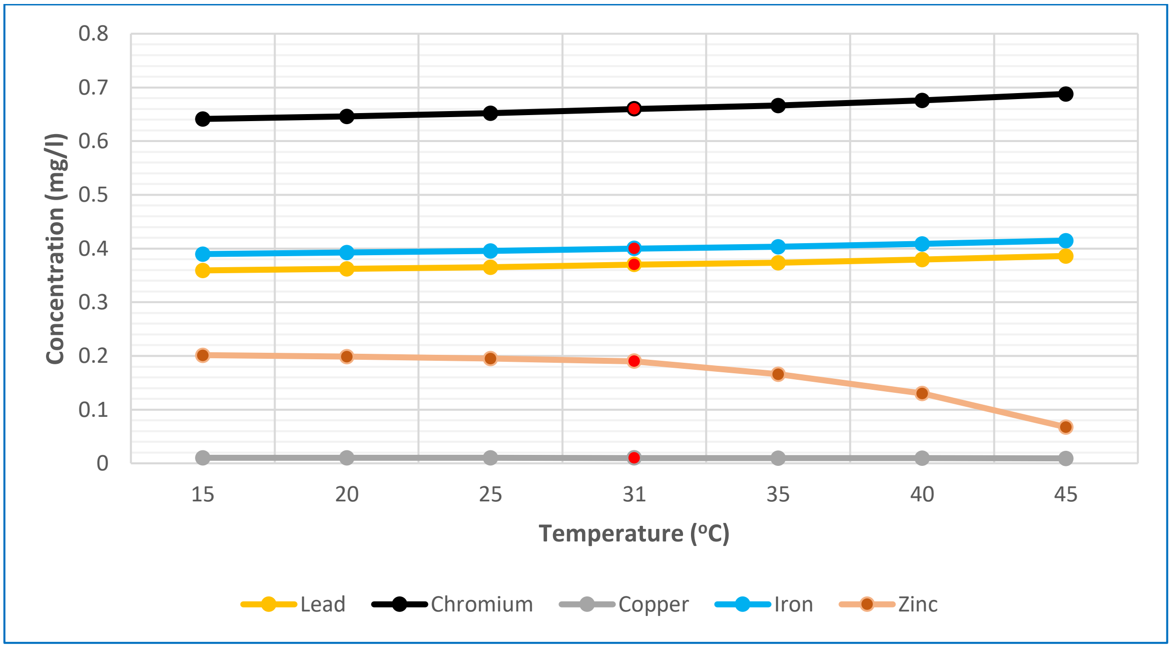


Figure 7.10 Concentrations of metal pollutants at different temperatures at the Water Injection Pump

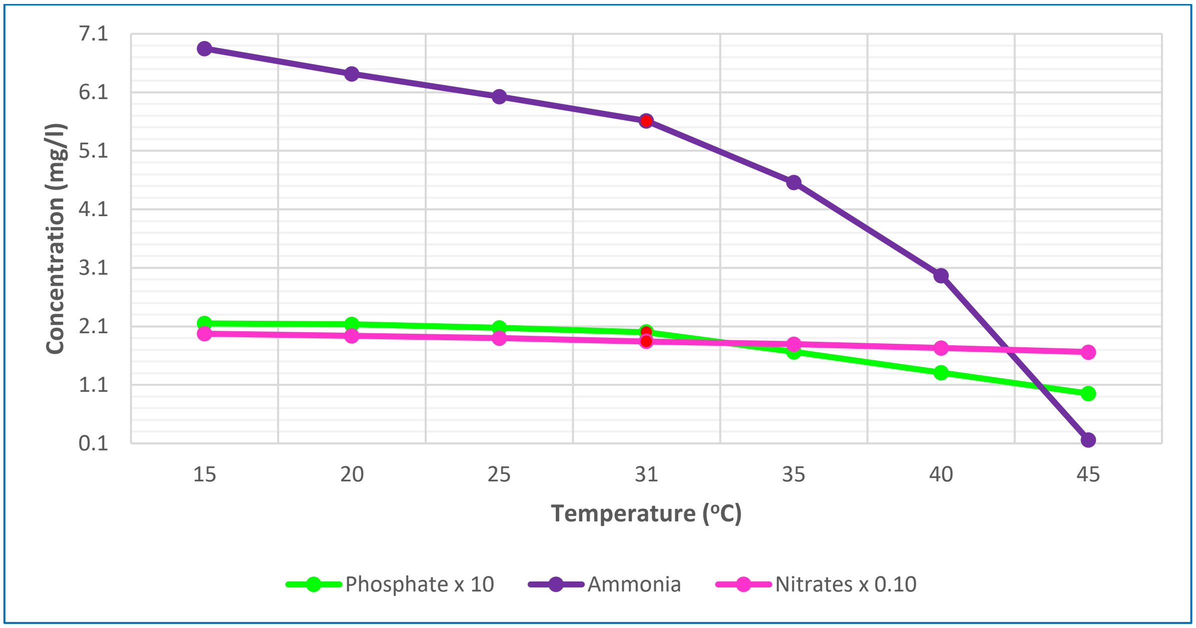


Figure 7.11 Concentration of non-metal pollutants at different temperatures at the Water Injection Pump

7.3.1.2 The effect of pressure on the concentrations of pollutants:

Figures 7.12 to 7.20 represent the behaviour of the various group of pollutants in the produced water sample when subjected to pressure variations at various points along the crude oil production process.

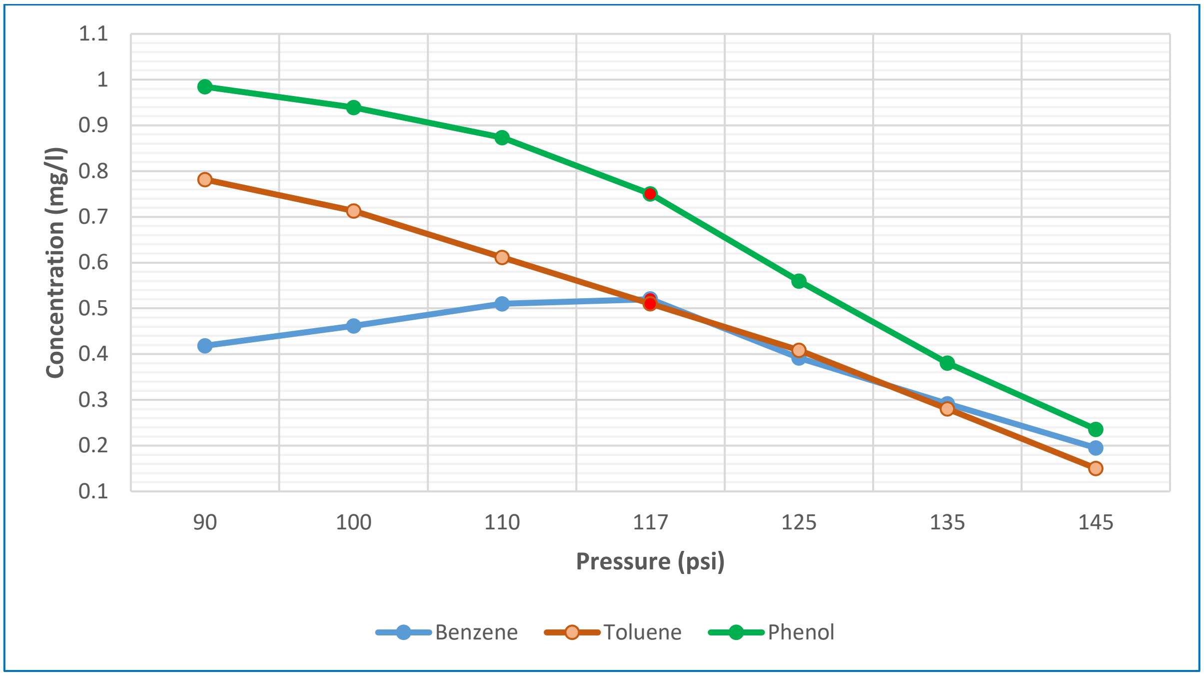


Figure 7.12 Concentrations of Benzene-Toluene-Phenol pollutants at different pressures at the Manifold

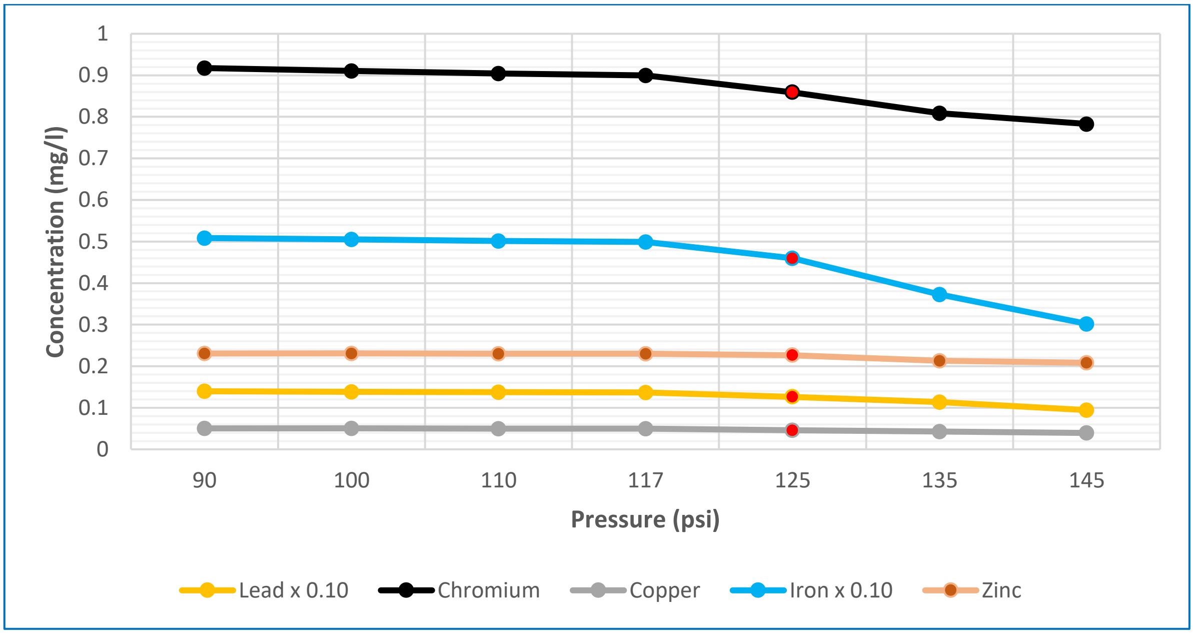


Figure 7.13 Concentrations of metal pollutants at different pressures at the Manifold

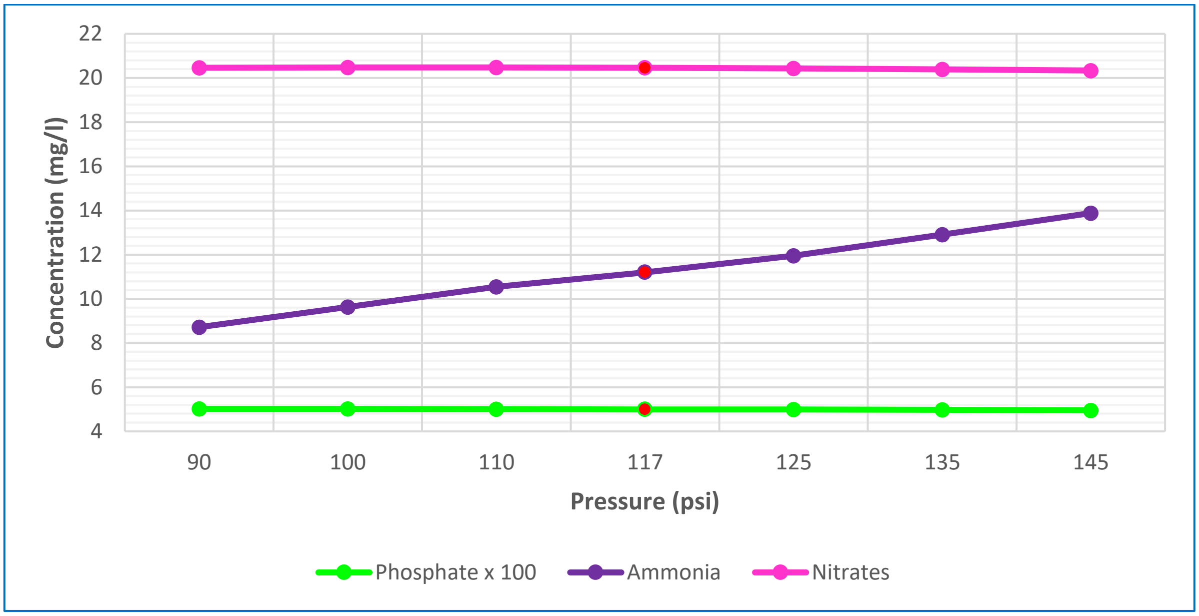


Figure 7.14 Concentrations of non-metal pollutants at different pressures at the Manifold

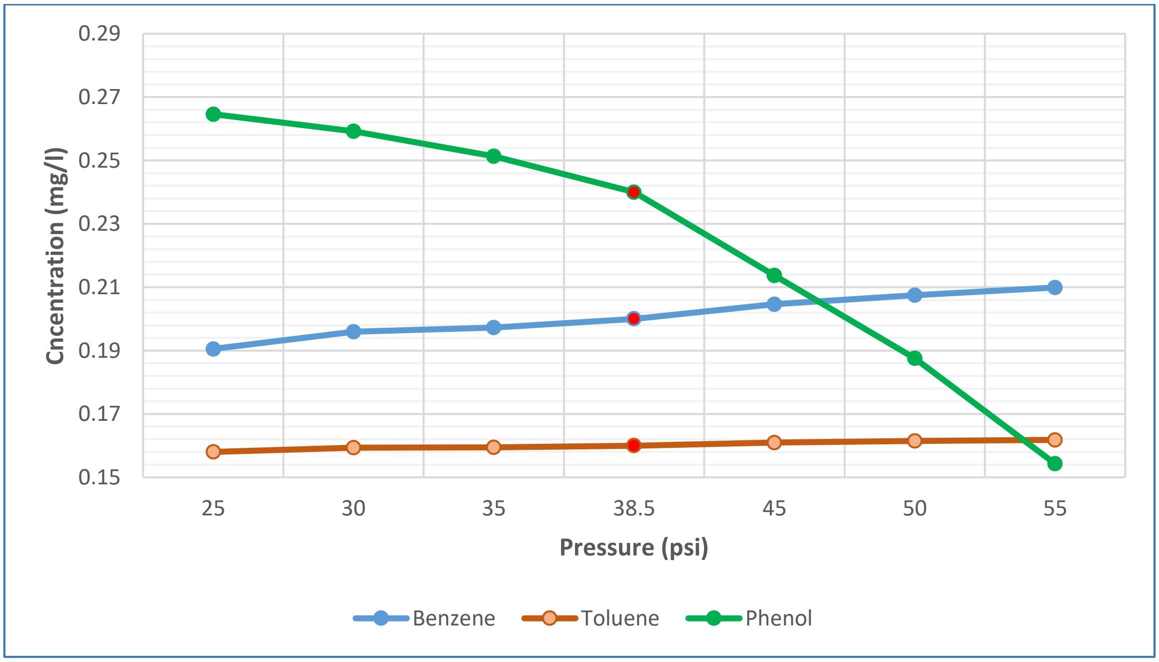


Figure 7.15 Concentrations of Benzene-Toluene-Phenol pollutants at different pressures at the Line Heater exit

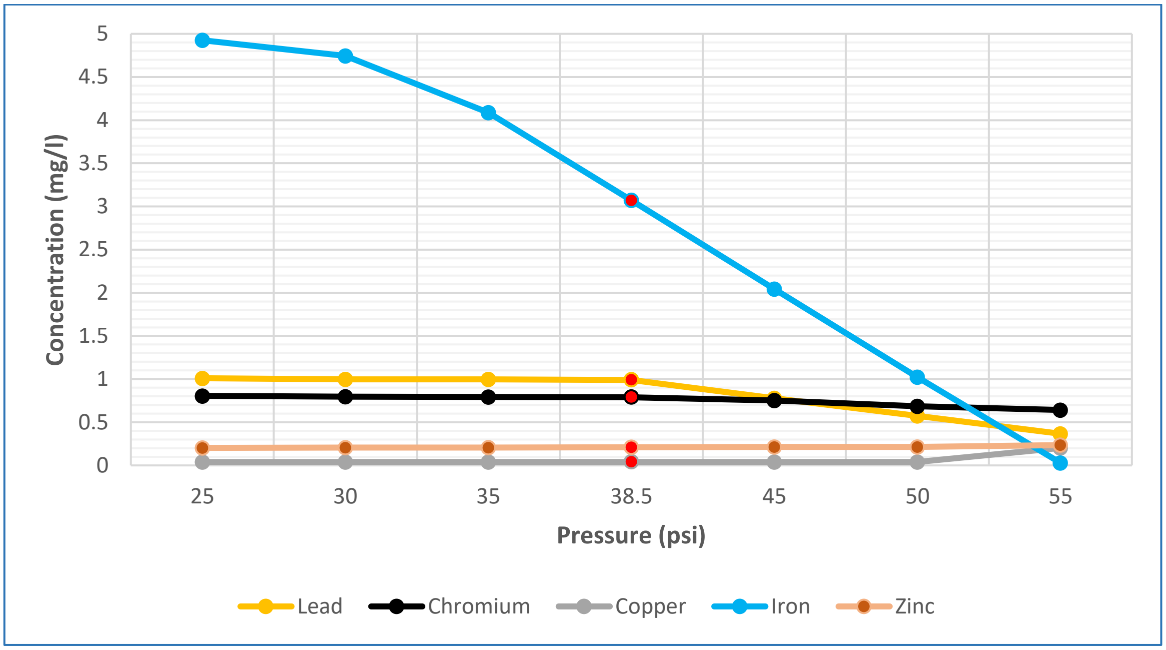


Figure 7.16 Concentrations of metal pollutants at different pressures at the Line Heater exit

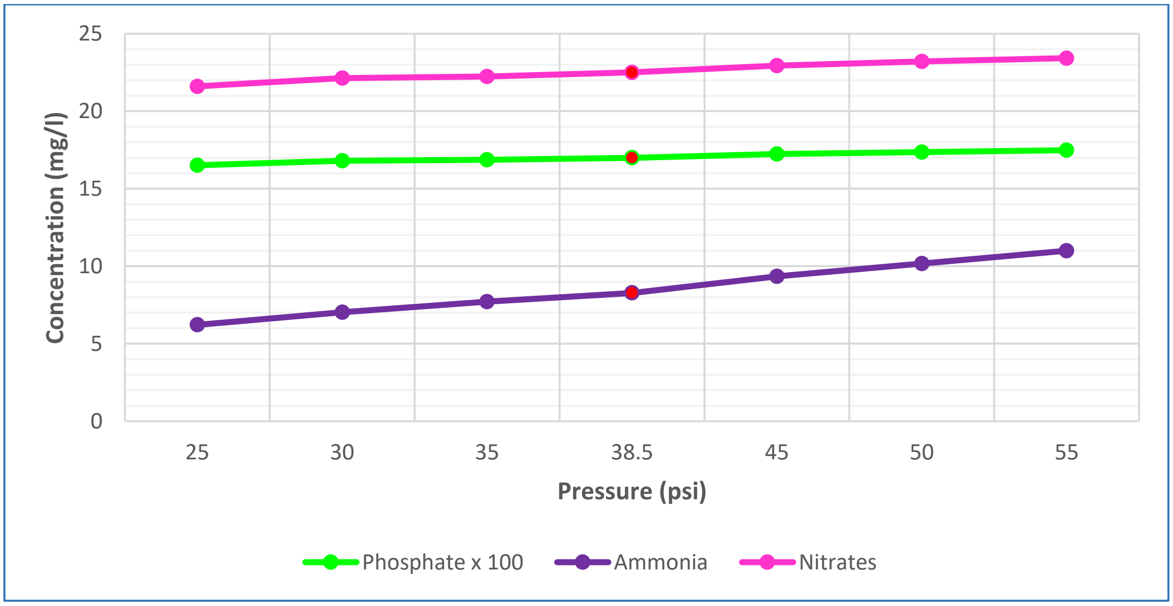


Figure 7.17 Concentrations of non-metal pollutants at different pressures at the Line Heater exit

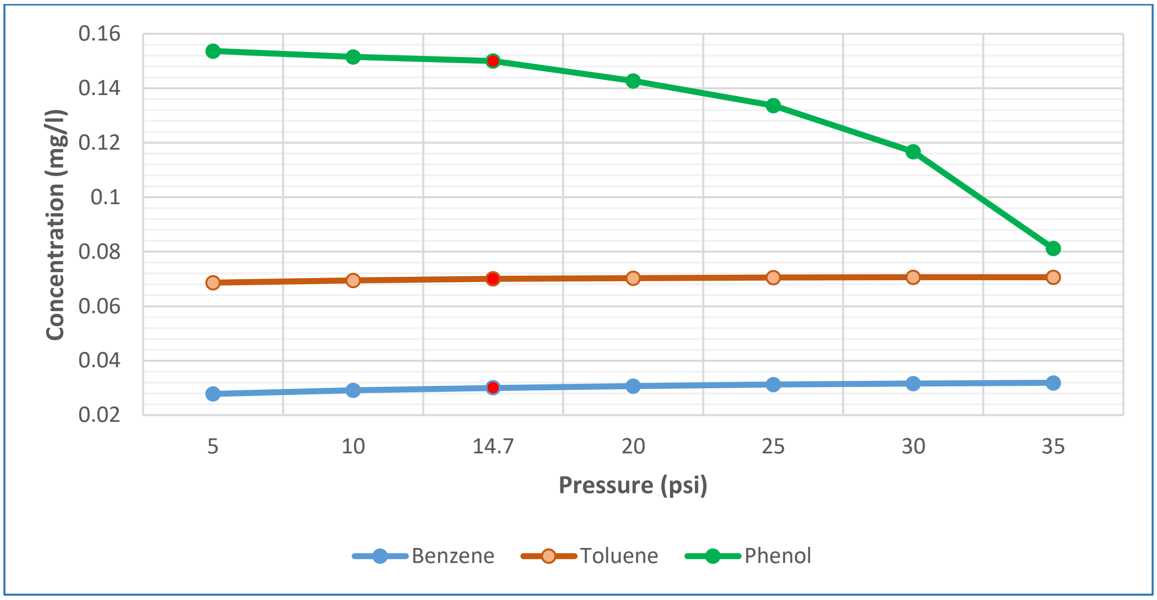


Figure 7.18 Concentrations of Benzene-Toluene-Phenol pollutants at different pressures at the Water Injection Pump

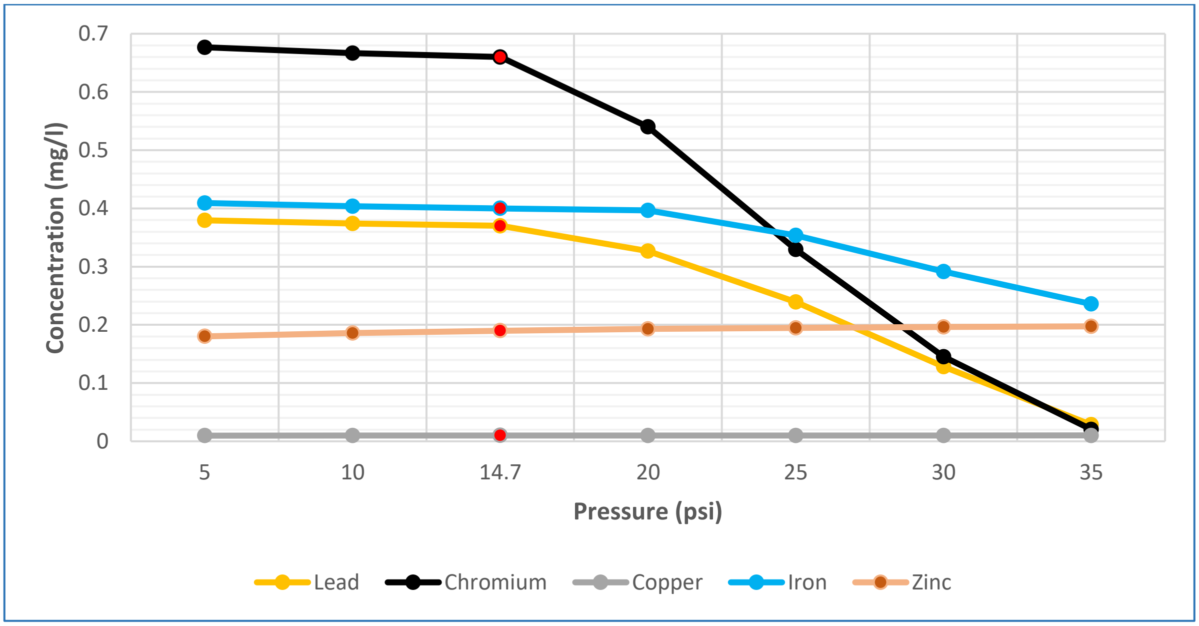


Figure 7.19 Concentrations of metal pollutants at different pressures at the Water Injection Pump

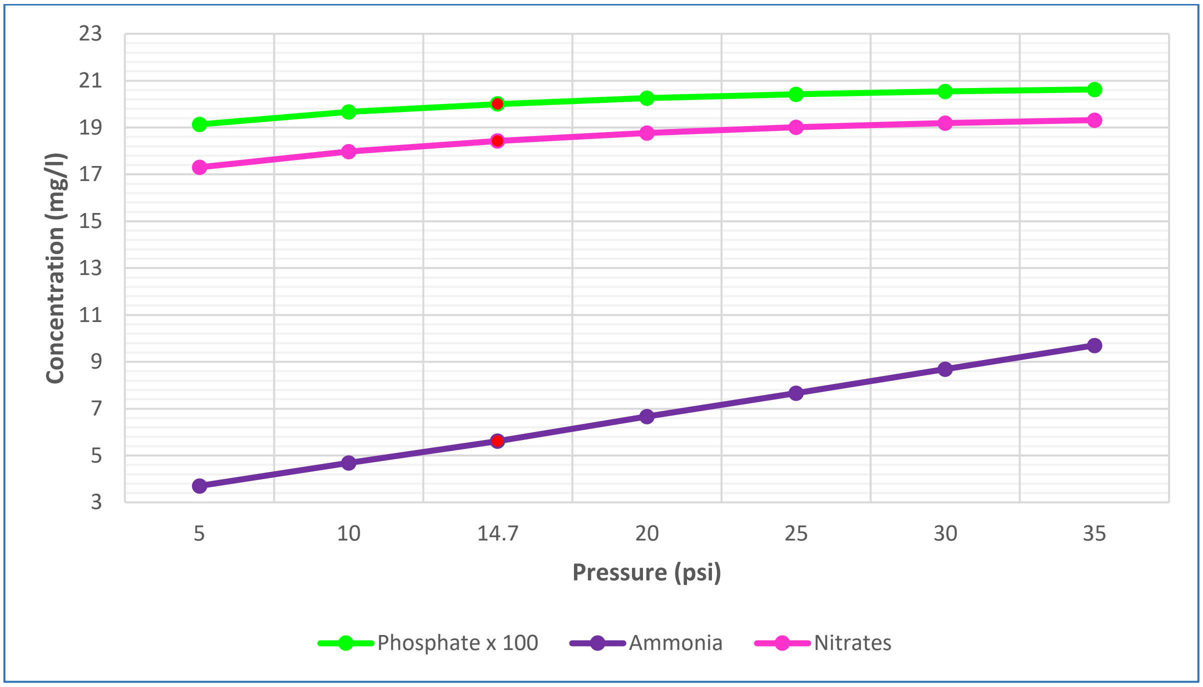


Figure 7.20 Concentrations of non-metal pollutants at different pressures at the Water Injection Pump

At the production manifold, Figures 7.3 – 7.5 show that from simulation the concentration of benzene increased with temperature until 35°C after which the concentration of the benzene started to decrease. The implication of this result is that in order to reduce the concentration of benzene in the produced water leaving the sample point at the production manifold, the temperature of the fluid at the production manifold must be kept higher than 35°C. The results also show that to minimize the concentration of copper leaving the manifold in produced water, the manifold temperature should be above 45°C. Zinc and phosphates concentrations according to the result could also be reduced by maintaining temperature of the production manifold at not less than 41°C. Toluene, phenol, lead, chromium, iron and chlorides showed continuous increase in concentration with temperature in the resulting produced water. The implication of this result is that in order to reduce the concentration of any of these pollutants in the produced water leaving the manifold, the process should be subjected to the minimum allowable operating temperature.

Figures 7.12 -7.14 indicate that pressure increase across the production manifold reduces the concentration of most of the pollutants in the resulting produced water leaving the manifold except ammonia and salinity where continuous increase in concentration were recorded in the resulting produced water. Benzene and nitrates concentrations were observed to initially increase but start to decrease at pressures of 125 psi and 110 psi respectively.

As contained in Tables G1 and G4 at Appendix G, simulations show that at temperature range of 41°C – 45°C and operating pressure, the process will generate the best decrease in benzene concentration of 5.09×10^{-2} mg l^{-1} $^{o}C^{-1}$ but at 50°C – 55°C and operating pressure, it will give the best decrease in phosphates concentration of 3.3×10^{-1} mg l^{-1} $^{o}C^{-1}$ at the production manifold. This gives opportunity to increase the temperature of the fluid at manifold if the target is to reduce the concentrations of benzene and phosphate to as low as possible. However, if the fluid is subjected to a pressure in the range of 117 -125 psi at operating temperature, the concentrations of benzene, phenol and chromium will decrease by 1.60 x 10^{-2} mg l^{-1} psi^{-1}, 2.38 x 10^{-2} mg l^{-1} psi^{-1} and 5.11 x 10^{-3} mg l^{-1} psi^{-1} respectively. The design temperature and pressure of the production separators where the fluid will flow into from the manifold are 93^{o}C and 230 psig respectively; they should not be exceeded.

Figures 7.6 – 7.8 indicate that at the exit of the line heater, increase in the temperature of the produced water leaving the line heater decreases the concentration of benzene, toluene, copper, zinc, phosphate, ammonia, nitrates and salinity but increases the concentrations of phenol, lead, chromium and iron in the resulting produced water at the line heater exit. In this case, the regulatory limits of the pollutants are of great importance in determining the temperature at which to operate the line heater in order to achieve reduction in the concentration of target pollutants.

Pressure increase across the line heater, as shown in Figures 7.15 – 7.17, yields opposite effect to that of temperature thereby resulting in increase in the concentrations of benzene, toluene, copper, zinc, phosphate, ammonia, and nitrates but decrease in the concentrations of phenol, lead, chromium and iron. An optimum pressure with the guide of the regulatory limits will be required for the operation of the line heater to achieve reduction in concentrations of target pollutants in the resulting produced water at the exit of the line heater.

Simulation results at the line heater exit contained at Tables G2 and G5 in Appendix G also show that at temperature range of $52^{o}C$ – $55^{o}C$ and operating pressure, the process will generate the best decrease in benzene, toluene, ammonia and nitrates concentrations of 3.16×10^{-2} mg l^{-1} $^{o}C^{-1}$, 1.81 $\times 10^{-2}$ mg l^{-1} $^{o}C^{-1}$,8.13×10^{-1} mg l^{-1} $^{o}C^{-1}$ and 1.49 mg l^{-1} $^{o}C^{-1}$ respectively. Pressure of 50 – 55 psi will decrease the concentrations of phenol by 6.66×10^{-3} mg l^{-1} psi^{-1} while 45 – 50psi will decrease the concentrations of lead, and chromium by 4.13×10^{-2} mg l^{-1} psi^{-1} and 1.30×10^{-2} mg l^{-1} psi^{-1} respectively. The fluid flows into the Free Water Knock Out drum afterwards and must not exceed its design temperature and pressure of $93^{o}C$ and 75psig respectively.

Figures 7.9 – 7.11 indicate that at the water injection pump inlet, the pattern observed at the exit of the line heater subsists as temperature increase leads to decrease in the concentrations of benzene, toluene, copper, zinc, phosphate, ammonia, nitrates and salinity but increase in the concentrations of phenol, lead, chromium and iron in the resulting produced water. Increasing the pressure of the system gradually at the same point gives a reverse result as the concentrations of benzene, toluene, copper, zinc, phosphate, ammonium, nitrate and salinity were found to increase with pressure in the resulting produced water while the concentrations of phenol, lead, chromium and iron decreased along the same path.

According to Tables G3 and G6 in Appendix G, ensuring that a temperature range of $40^oC– 45^oC$ is achieved at the Water Injection Pump will decrease the concentrations of toluene, ammonia and nitrates by 2.28×10^{-3} mg l^{-1} $^oC^{-1}$, 5.62×10^{-1} mg l^{-1} $^oC^{-1}$ and 1.41×10^{-2} mg l^{-1} $^oC^{-1}$ respectively. Figures 7.18 and 7.19 indicate that at a pressure range of 20 – 35 psi, concentration of phenol, lead and chromium could be reduced.

7.3.2 OFFSHORE FACILITY CASE STUDY:

7.3.2.1 The effect of temperature on the concentrations of pollutants:

Figures 7.21 to 7.35 represent the behaviour of the various group of pollutants in the produced water sample form the offshore facility when subjected to temperature variations at various points along the crude oil production process.

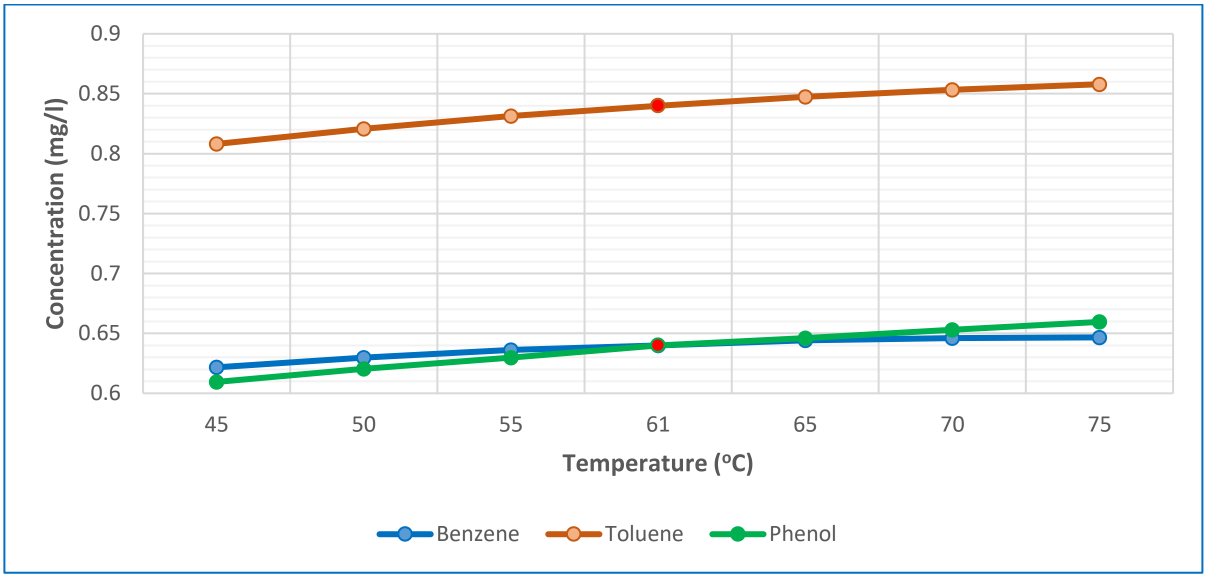


Figure 7.21 Concentrations of Benzene-Toluene-Phenol pollutants at different temperatures at the Production Manifold

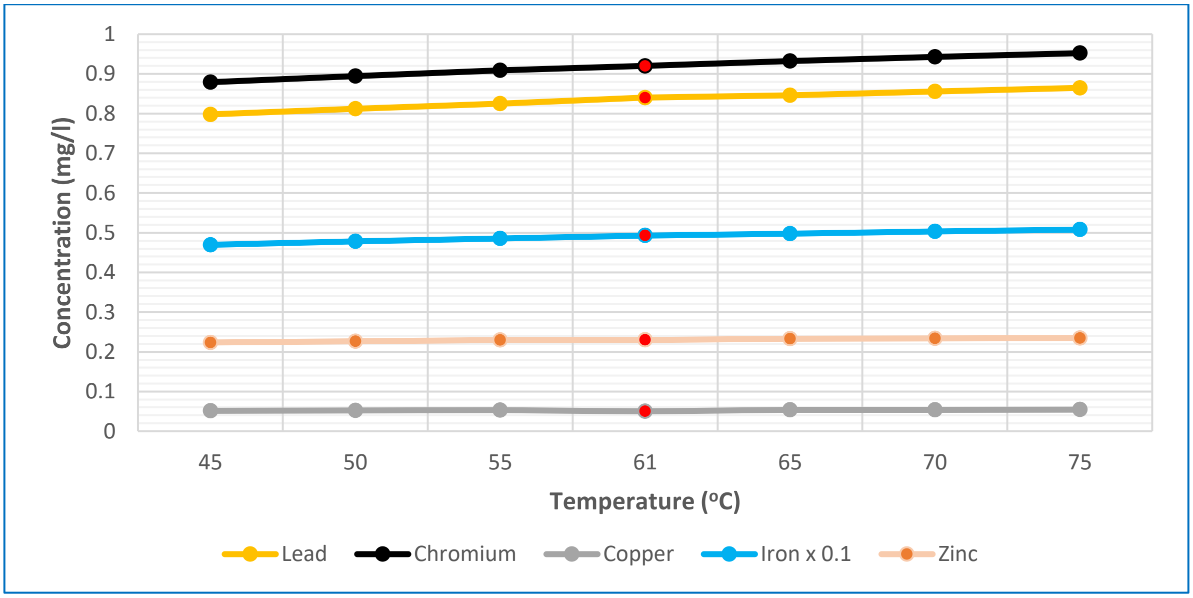


Figure 7.22 Concentrations of metal pollutants at different temperatures at the Production Manifold

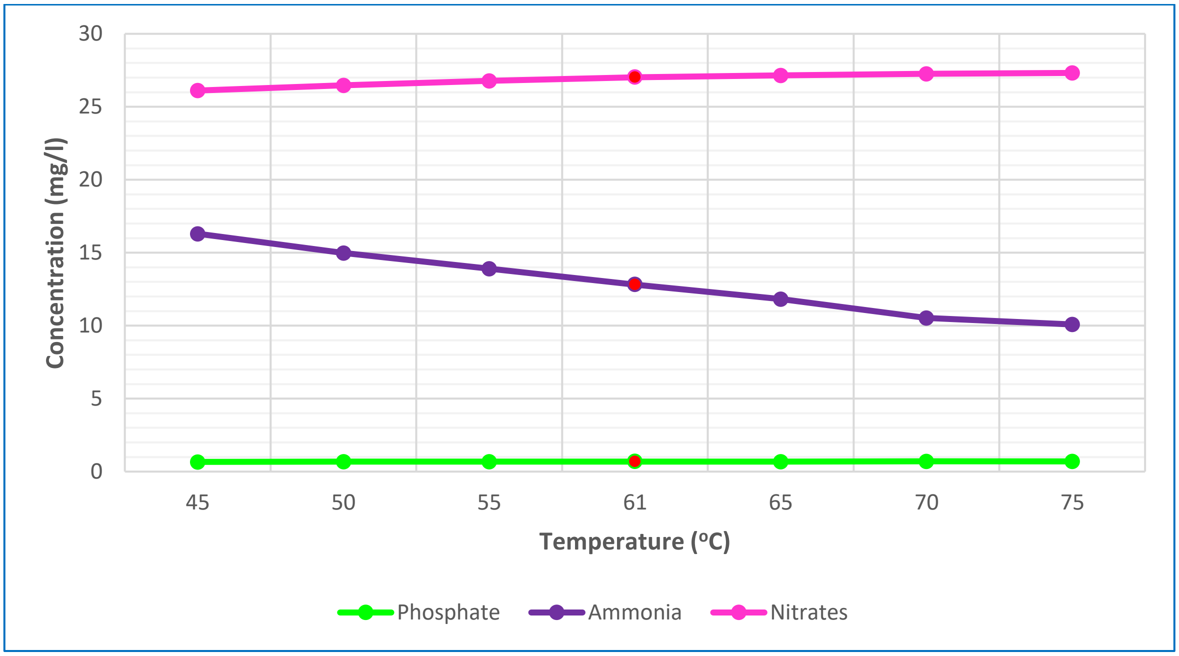


Figure 7.23 Concentrations of non-metal pollutants at different temperatures at the Production Manifold

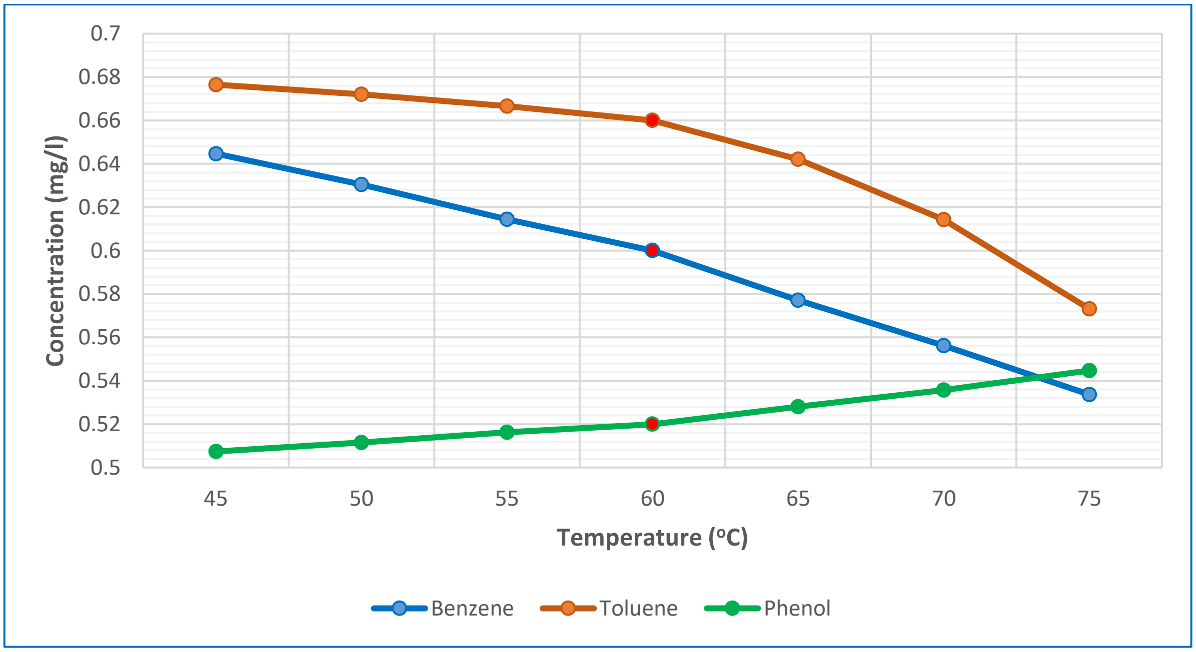


Figure 7.24 Concentrations of Benzene-Toluene-Phenol pollutants at different temperatures at the PW Surge Drum Inlet

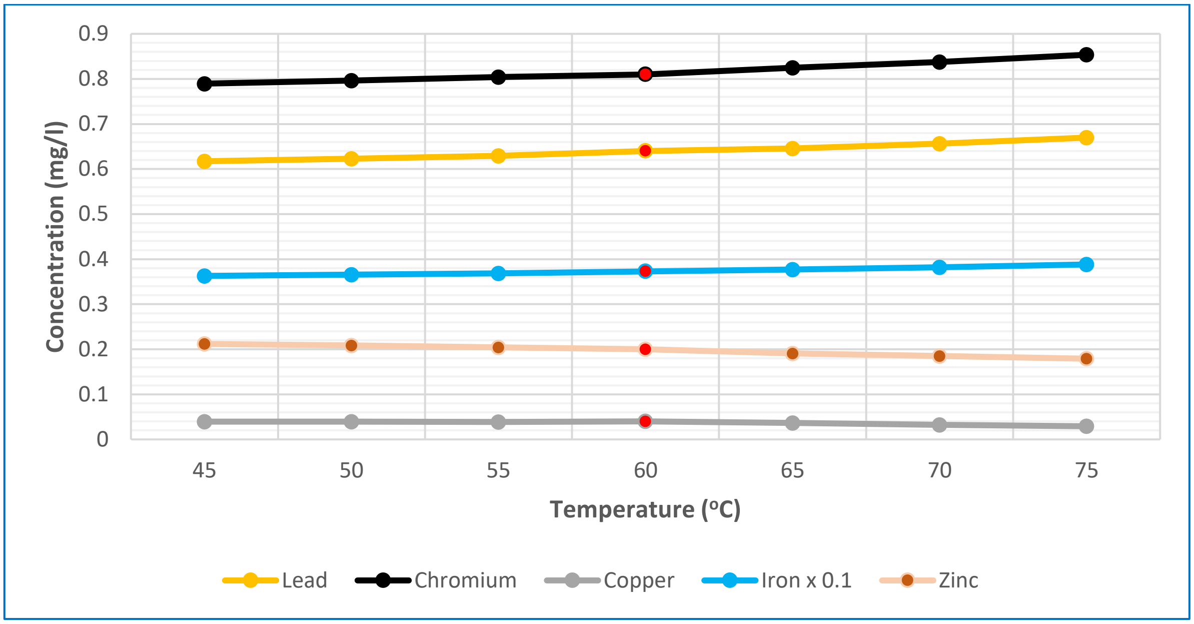


Figure 7.25 Concentrations of metal pollutants at different temperatures at the PW Surge Drum Inlet

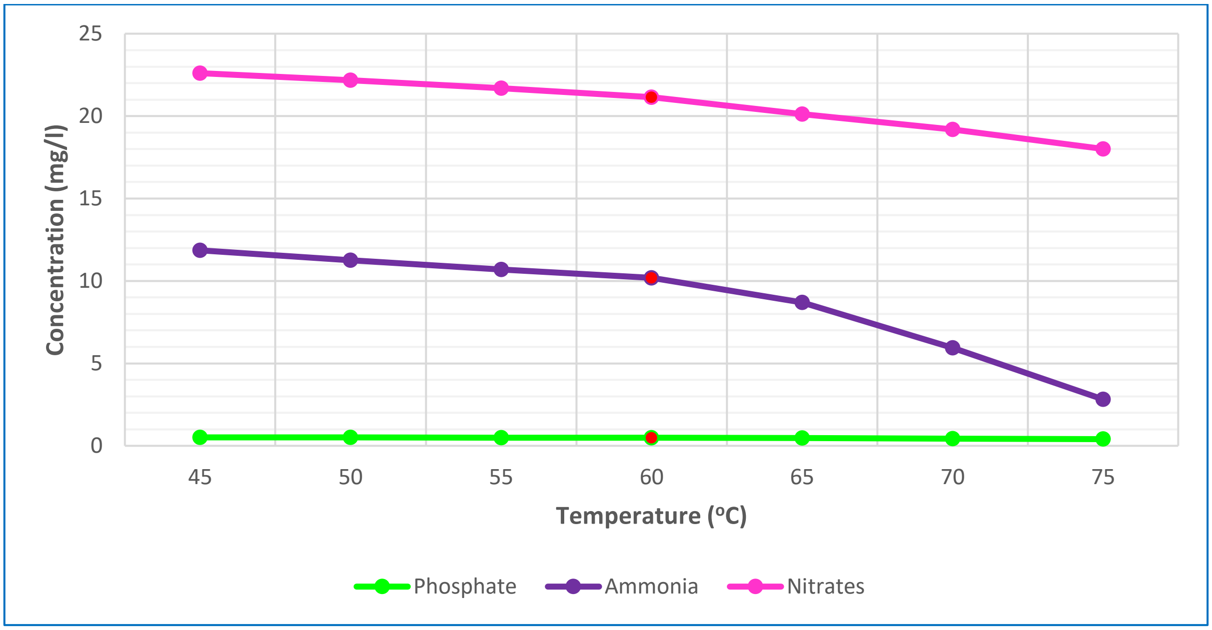


Figure 7.26 Concentrations of non-metal pollutants at different temperatures at the PW Surge Drum Inlet

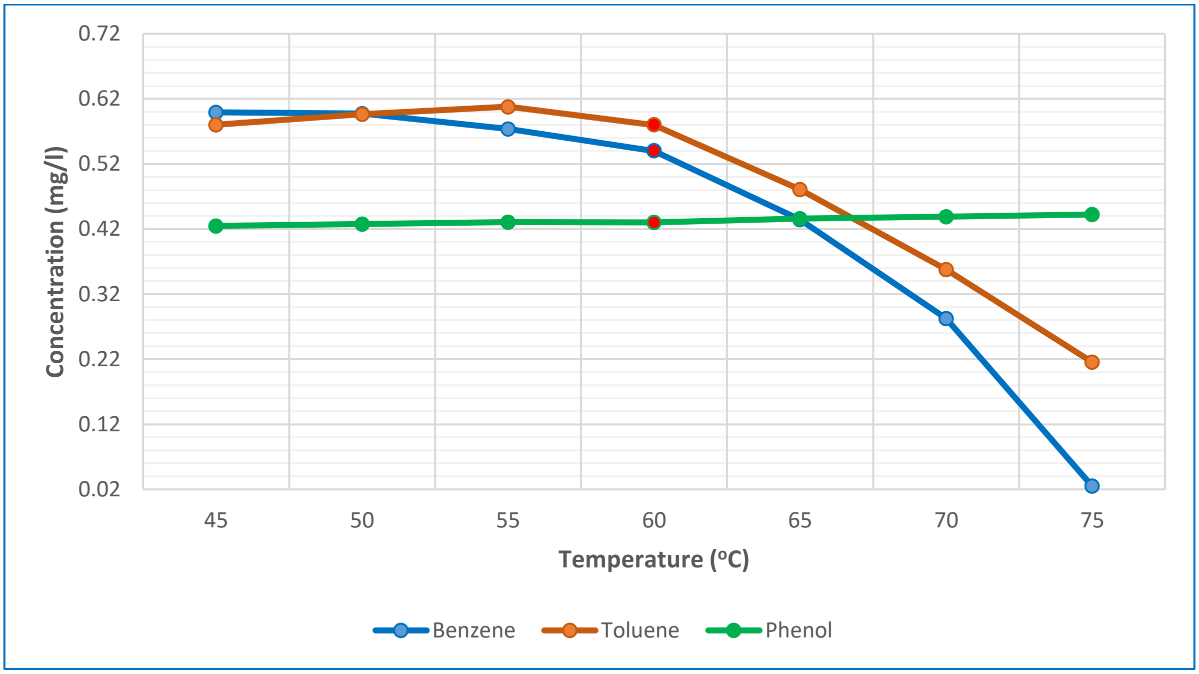


Figure 7.27 Concentrations of Benzene-Toluene-Phenol pollutants at different temperatures at the Hydrocyclone Inlet

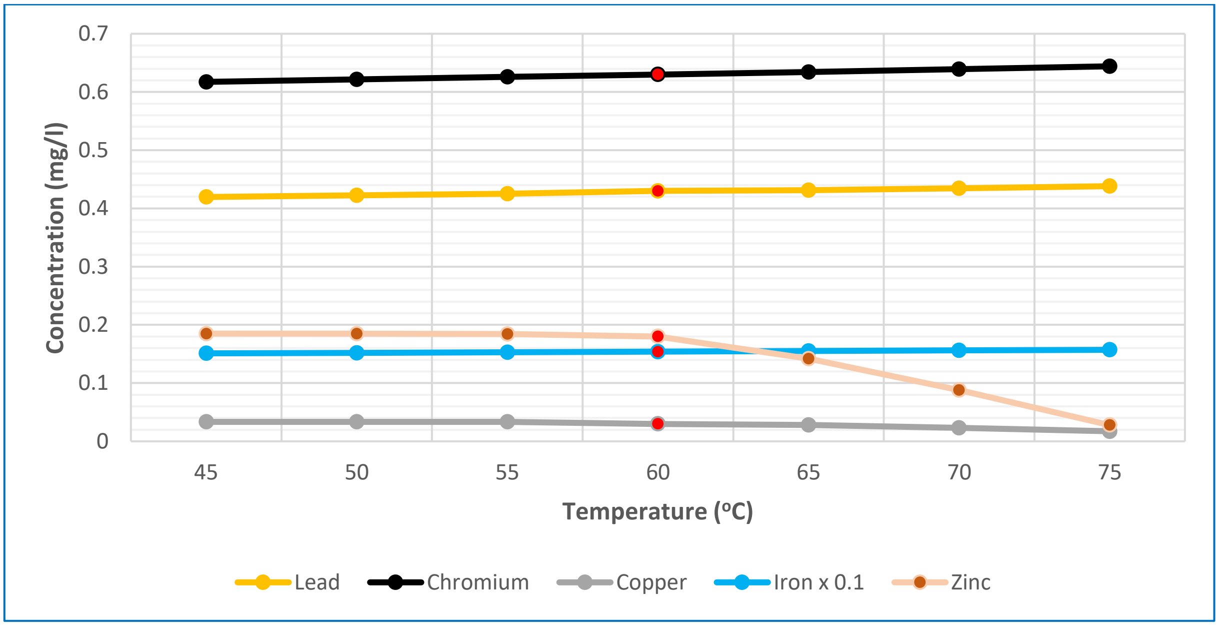


Figure 7.28 Concentrations of metal pollutants at different temperatures at the Hydrocyclone Inlet

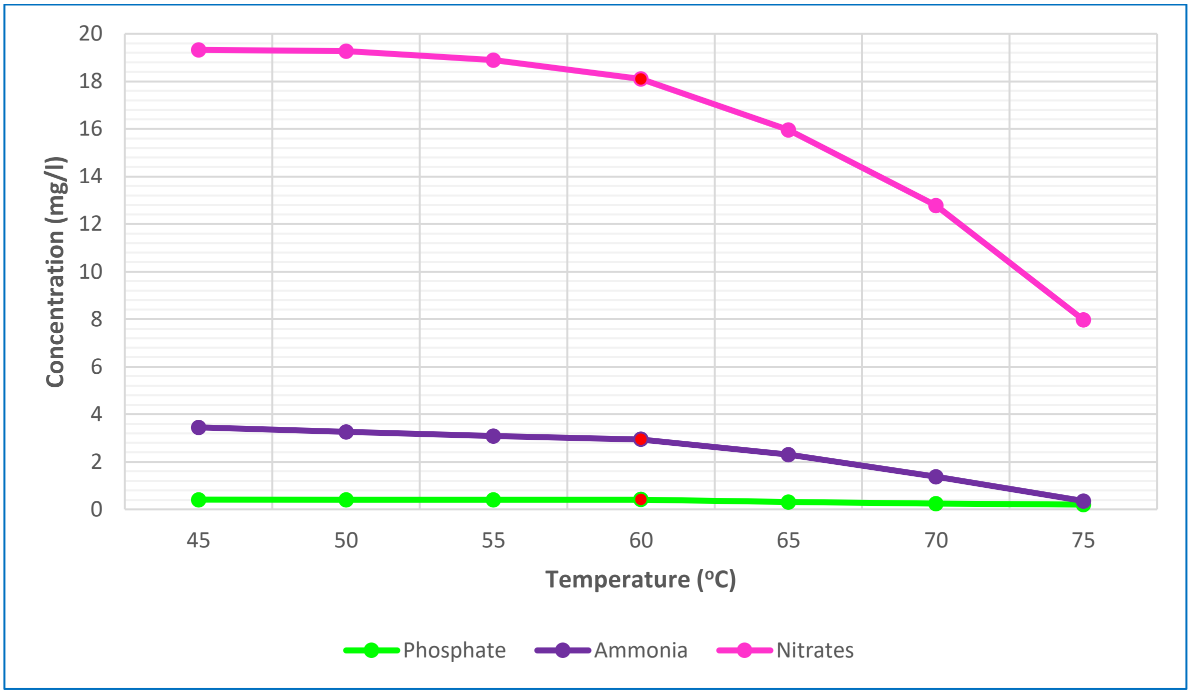


Figure 7.29 Concentrations of non-metal pollutants at different temperatures at the Hydrocyclone Inlet

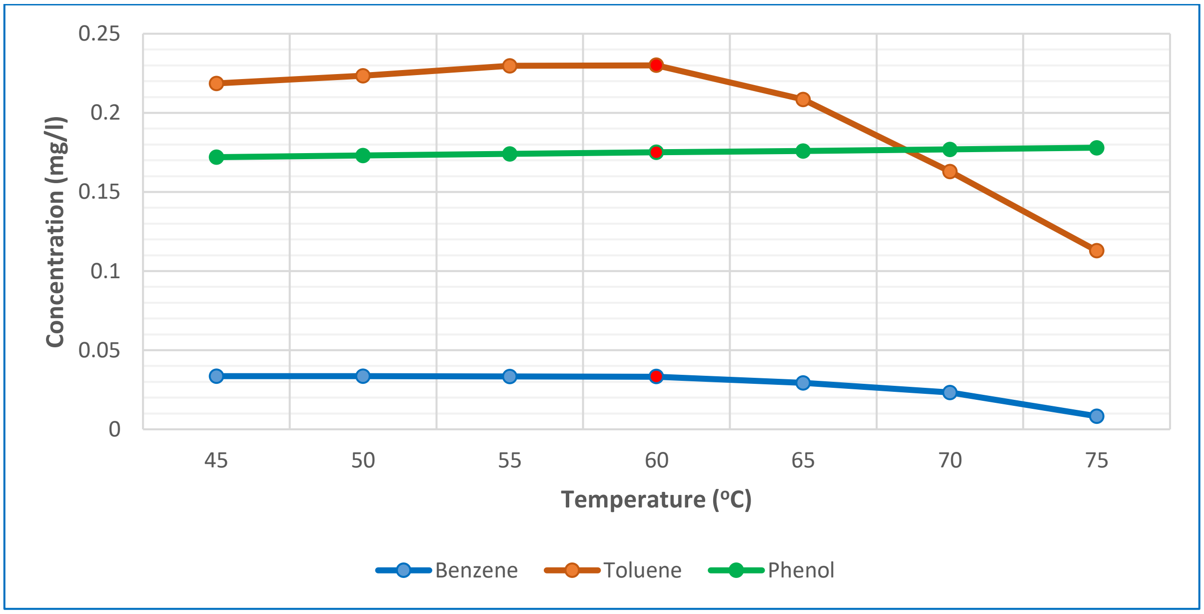


Figure 7.30 Concentrations of Benzene-Toluene-Phenol pollutants at different temperatures at the Produced Water Degasser Inlet

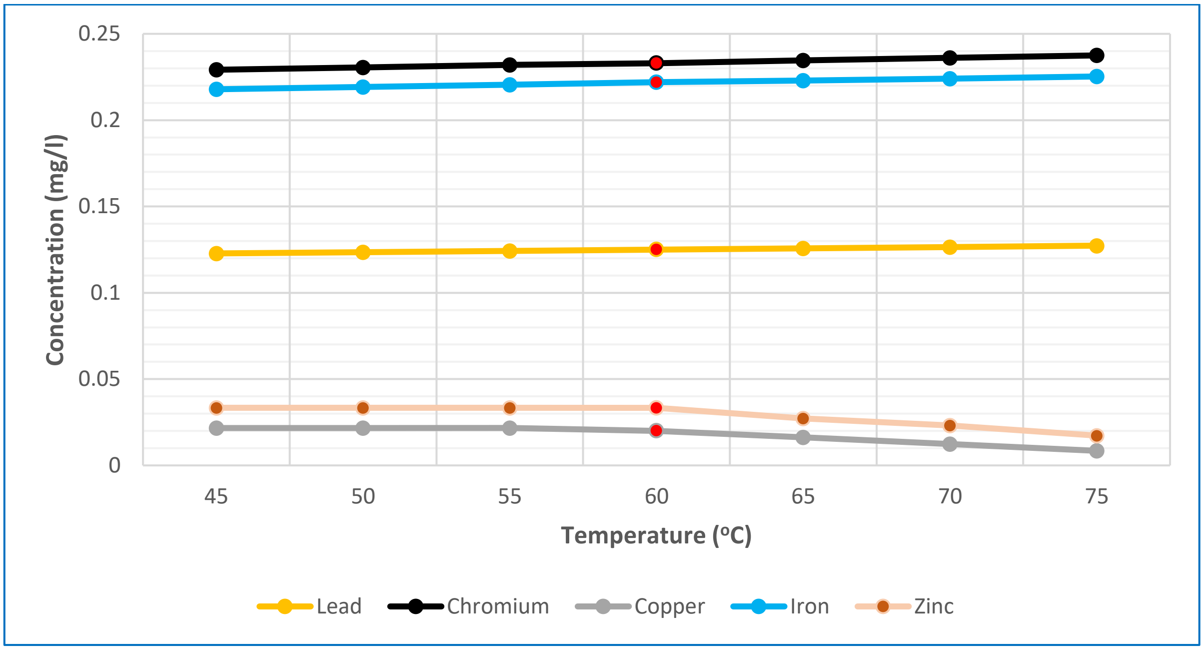


Figure 7.31 Concentrations of metal pollutants at different temperatures at the Produced Water Degasser Inlet

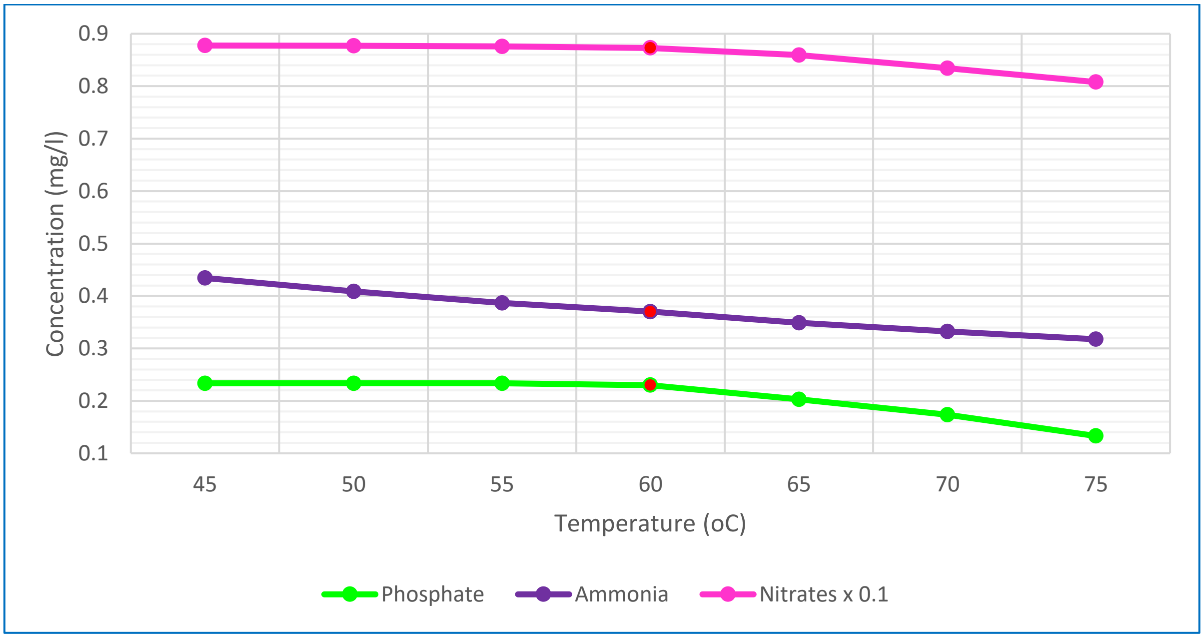


Figure 7.32 Concentrations of non-metal pollutants at different temperatures at the Produced Water Degasser Inlet

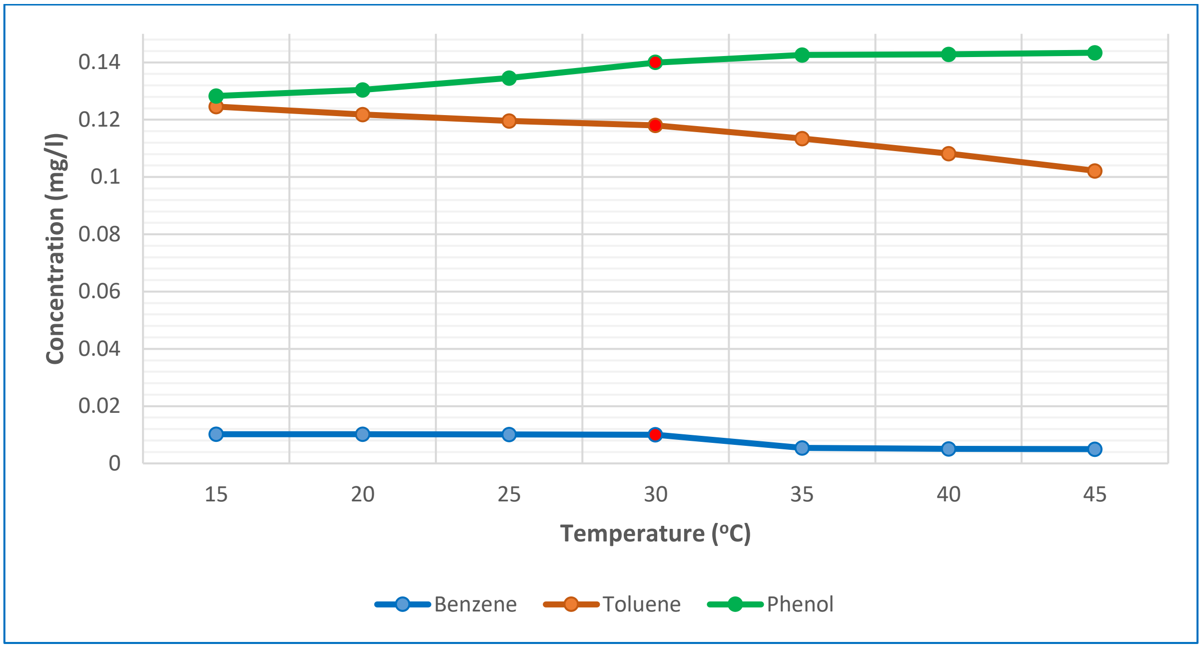


Figure 7.33 Concentrations of Benzene-Toluene-Phenol pollutants at different temperatures at the Produced Water Analyser Exit

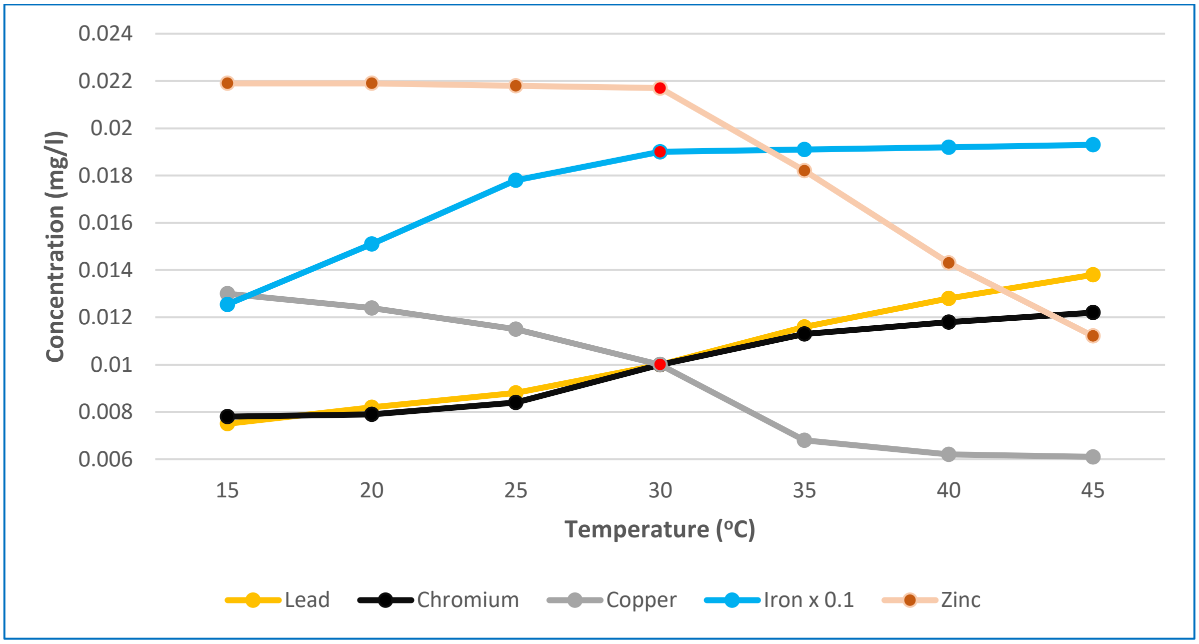


Figure 7.34 Concentrations of metal pollutants at different temperatures at the Produced Water Analyser Exit

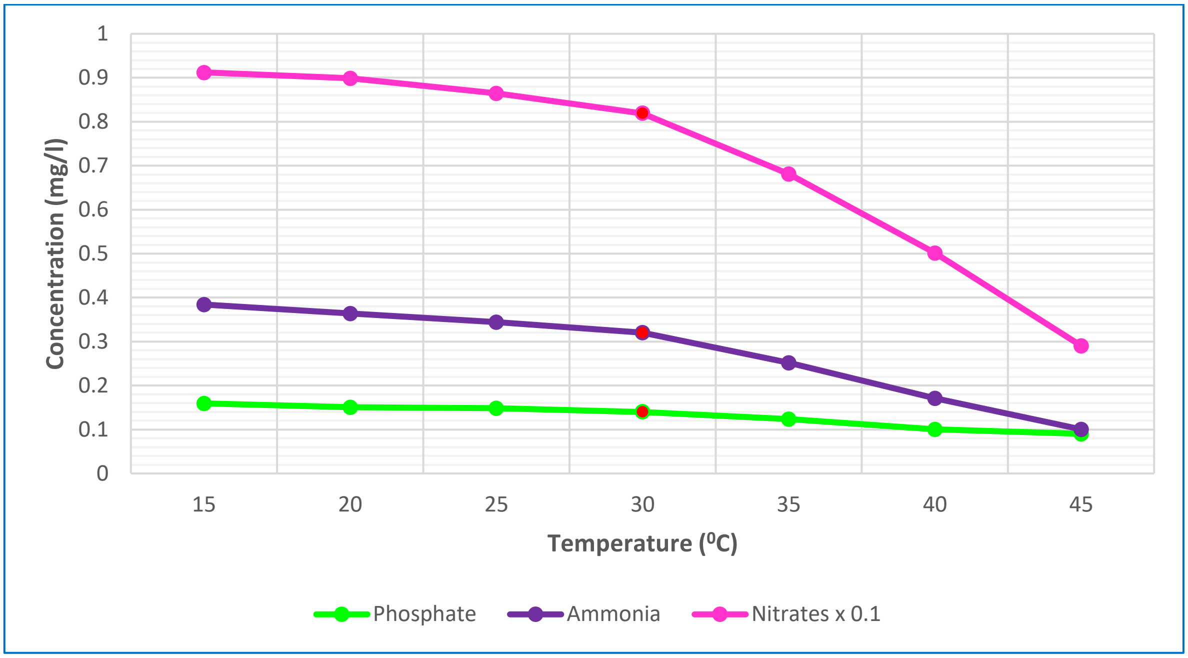


Figure 7.35 Concentrations of non-metal pollutants at different temperatures at the Produced Water Analyser Exit

7.3.2.2 The effect of pressure on the concentrations of pollutants:

Figures 7.36 to 7.50 represent the behaviour of the various group of pollutants in the produced water sample when subjected to pressure variations at various points along the crude oil production process.

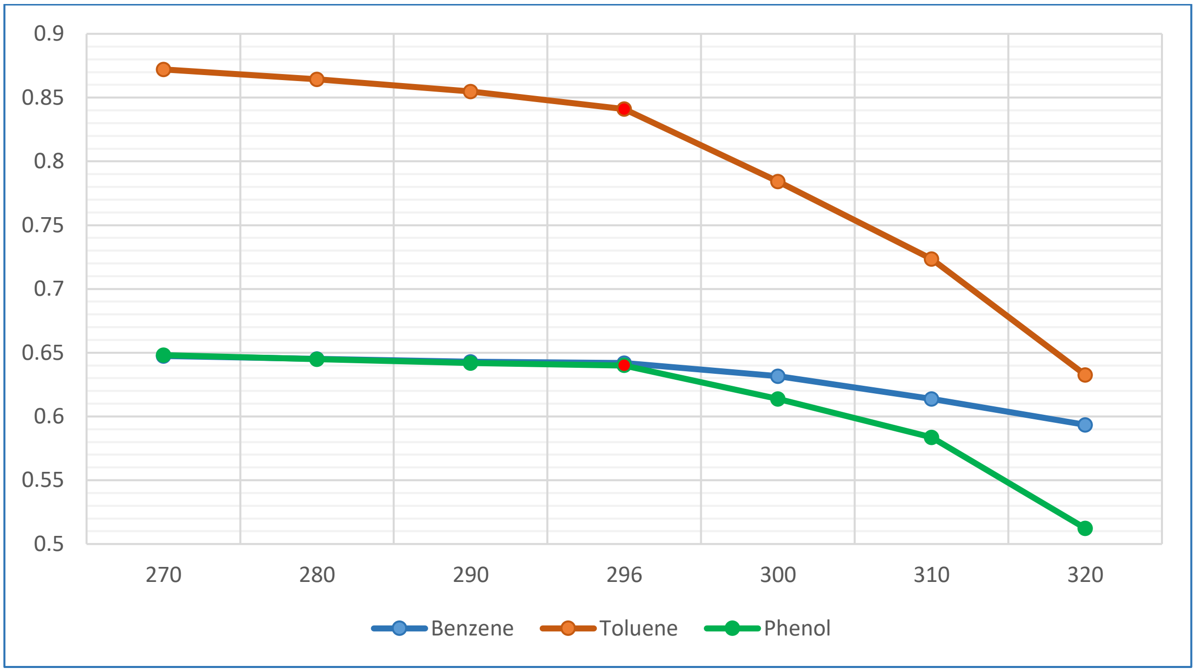


Figure 7.36 Concentrations of Benzene-Toluene-Phenol pollutants at different pressures at the Production Manifold

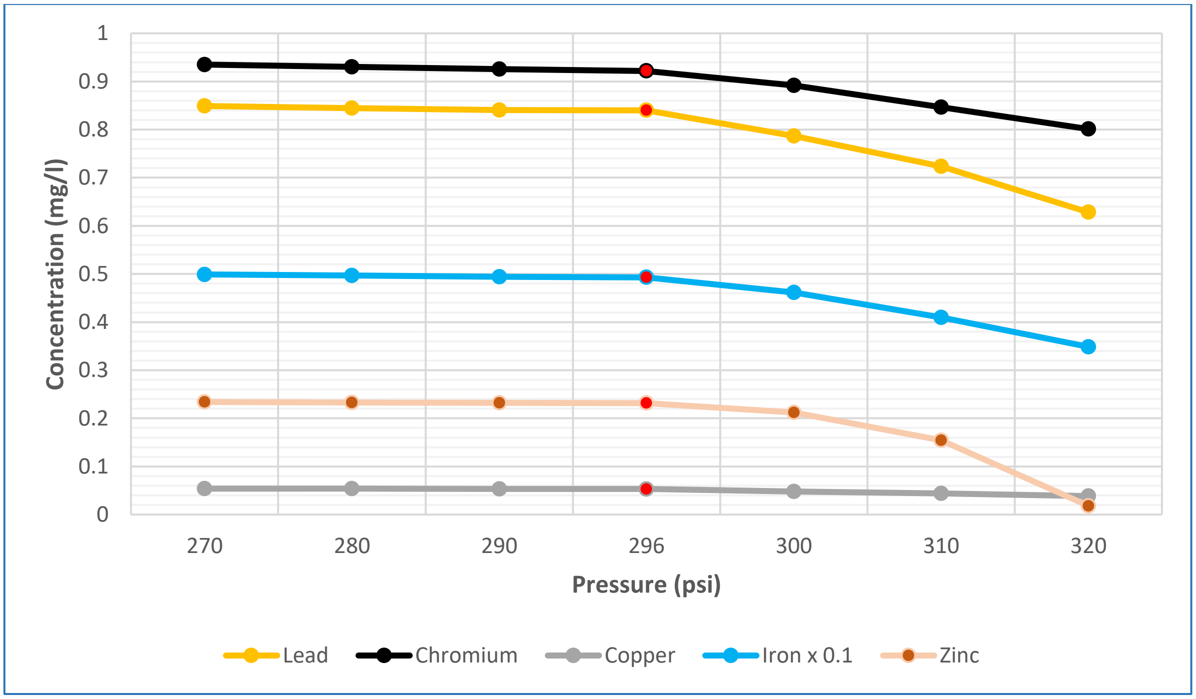


Figure 7.37 Concentrations of metal pollutants at different pressures at the Production Manifold

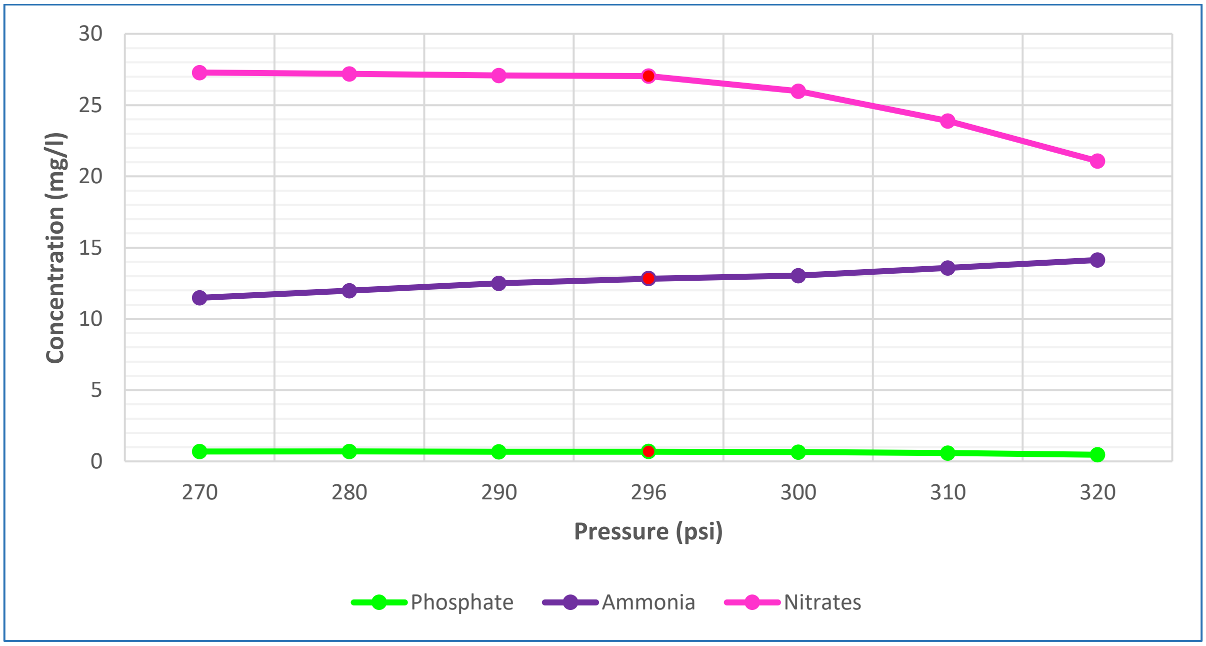


Figure 7.38 Concentrations of non-metal pollutants at different pressures at the Production Manifold

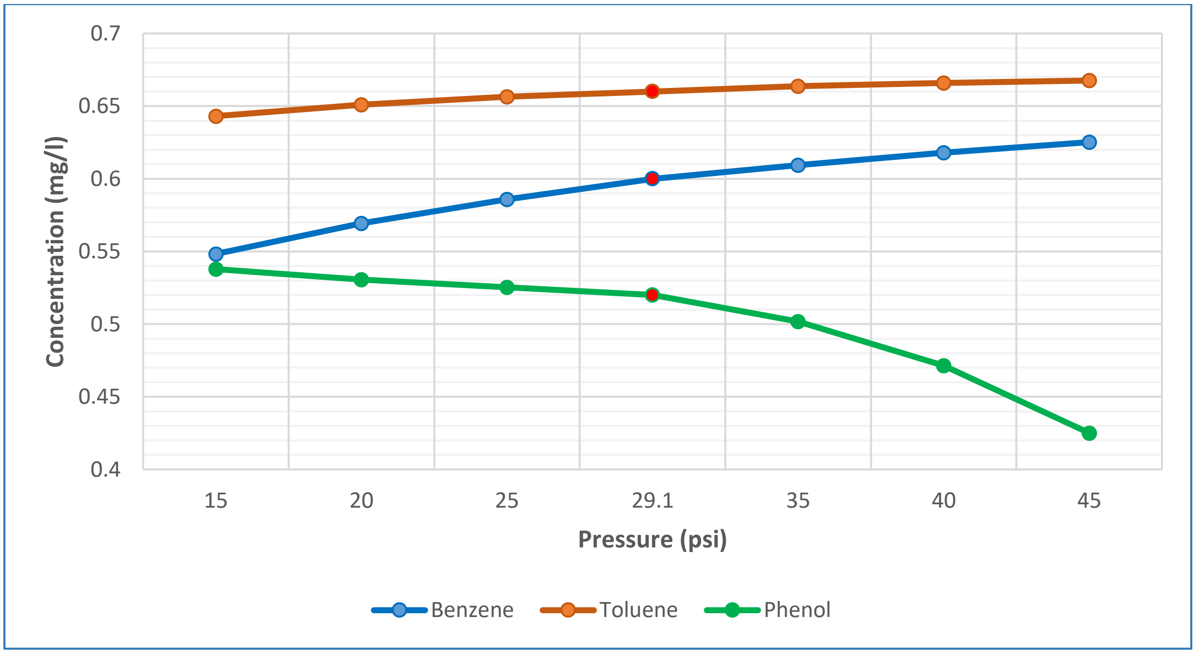


Figure 7.39 Concentrations of Benzene-Toluene-Phenol pollutants at different pressures at the PW Surge Drum Inlet

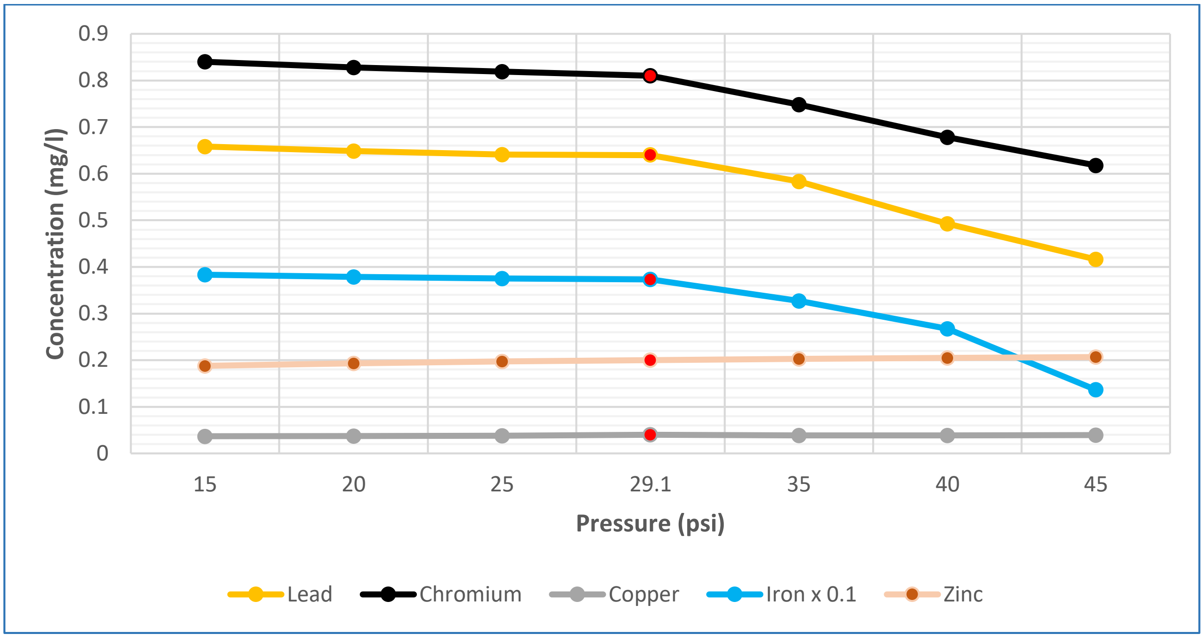


Figure 7.40 Concentrations of metal pollutants at different pressures at the PW Surge Drum Inlet

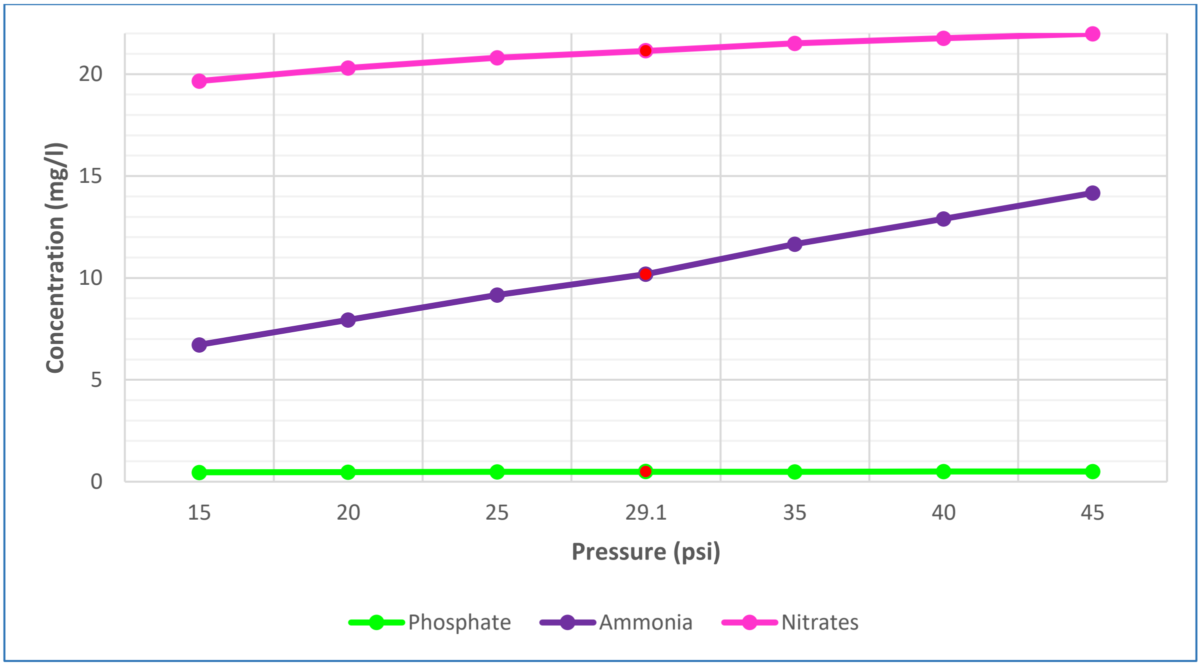


Figure 7.41 Concentrations of non-metal pollutants at different pressures at the PW Surge Drum Inlet

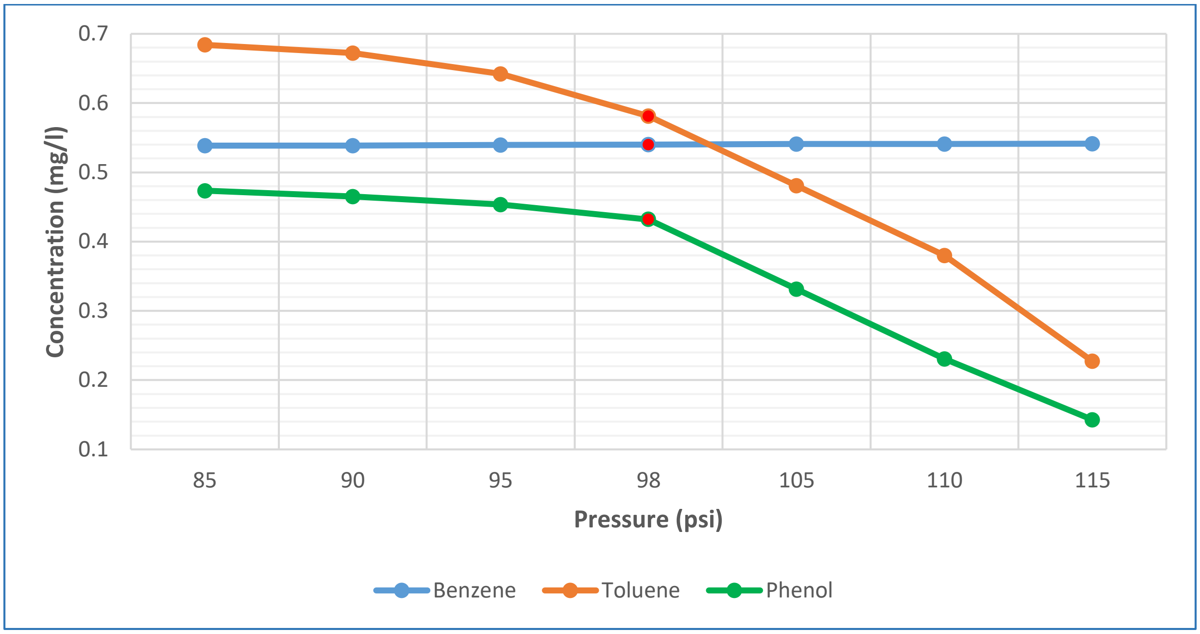


Figure 7.42 Concentrations of Benzene-Toluene-Phenol pollutants at different pressures at the Hydrocyclone Inlet

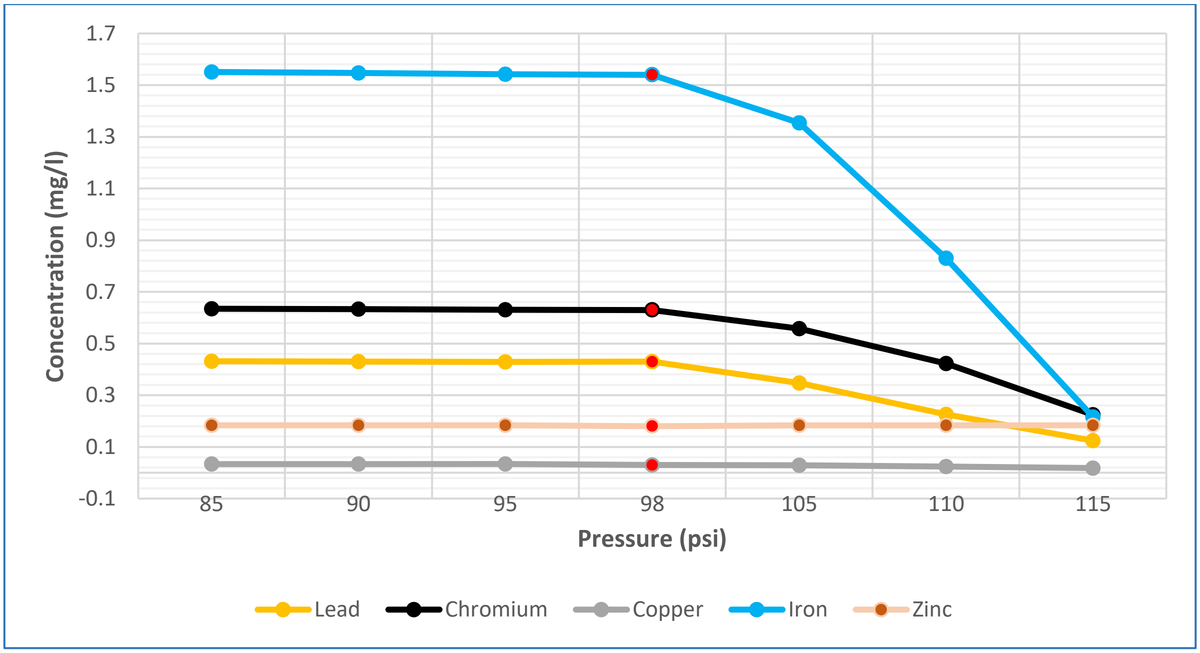


Figure 7.43 Concentrations of metal pollutants at different pressures at the Hydrocyclone Inlet

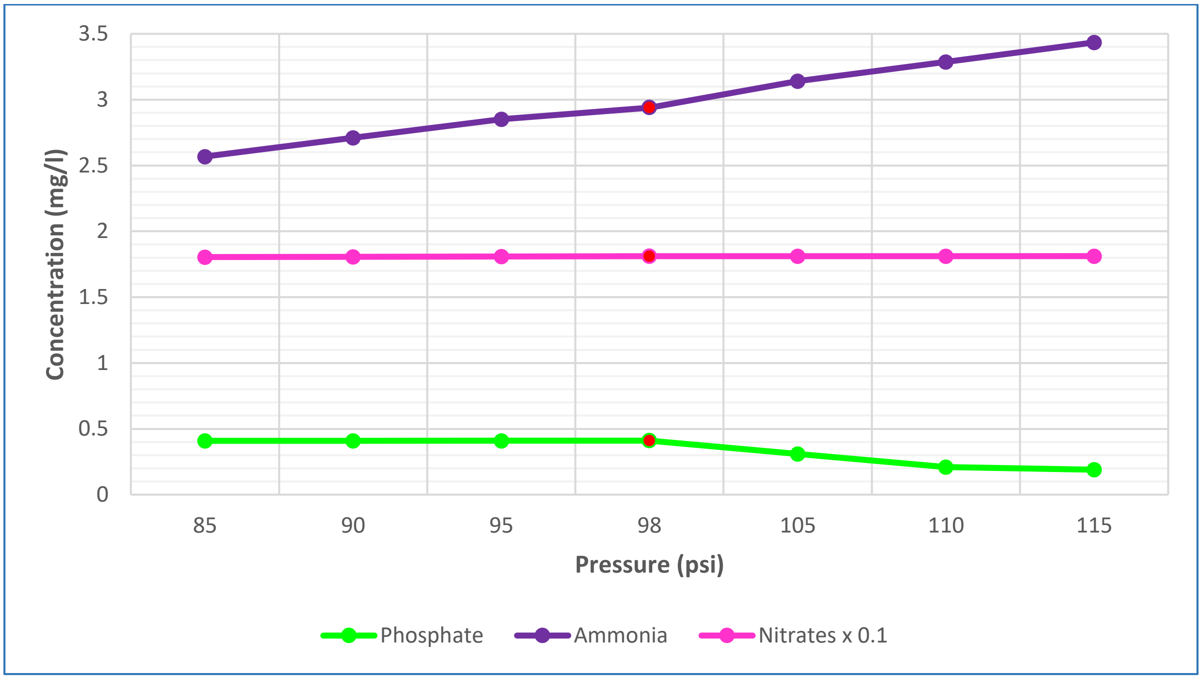


Figure 7.44 Concentrations of non-metal pollutants at different pressures at the Hydrocyclone Inlet

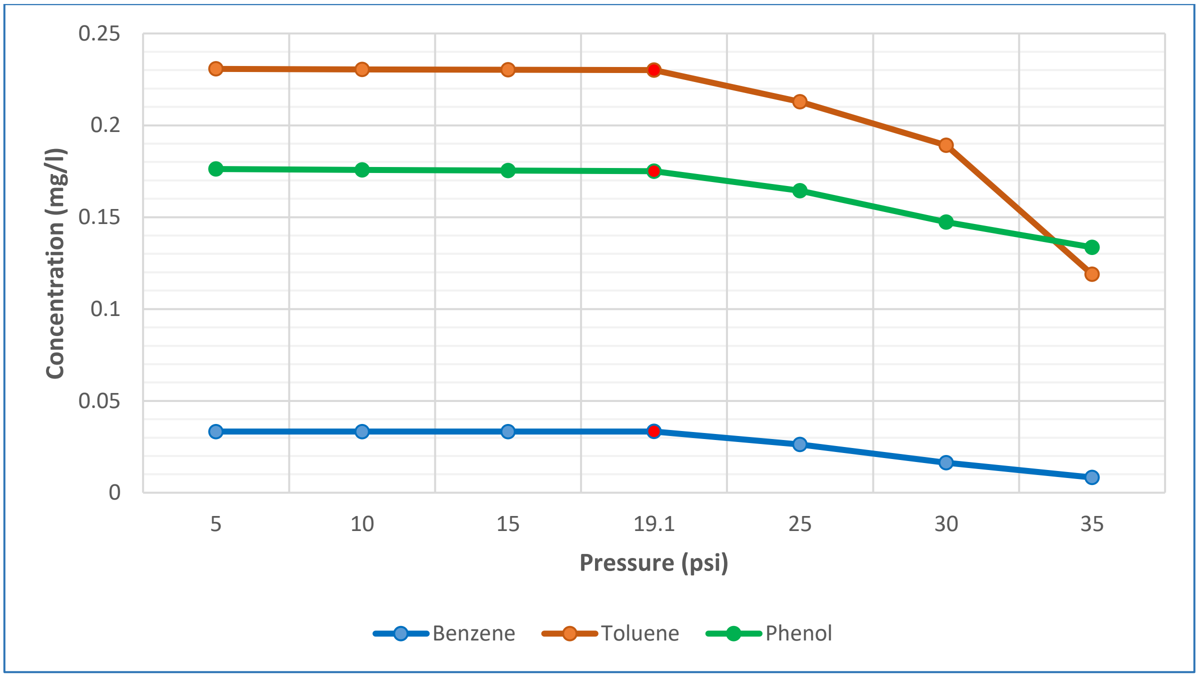


Figure 7.45 Concentrations of Benzene-Toluene-Phenol pollutants at different pressures at the Produced Water Degasser Inlet

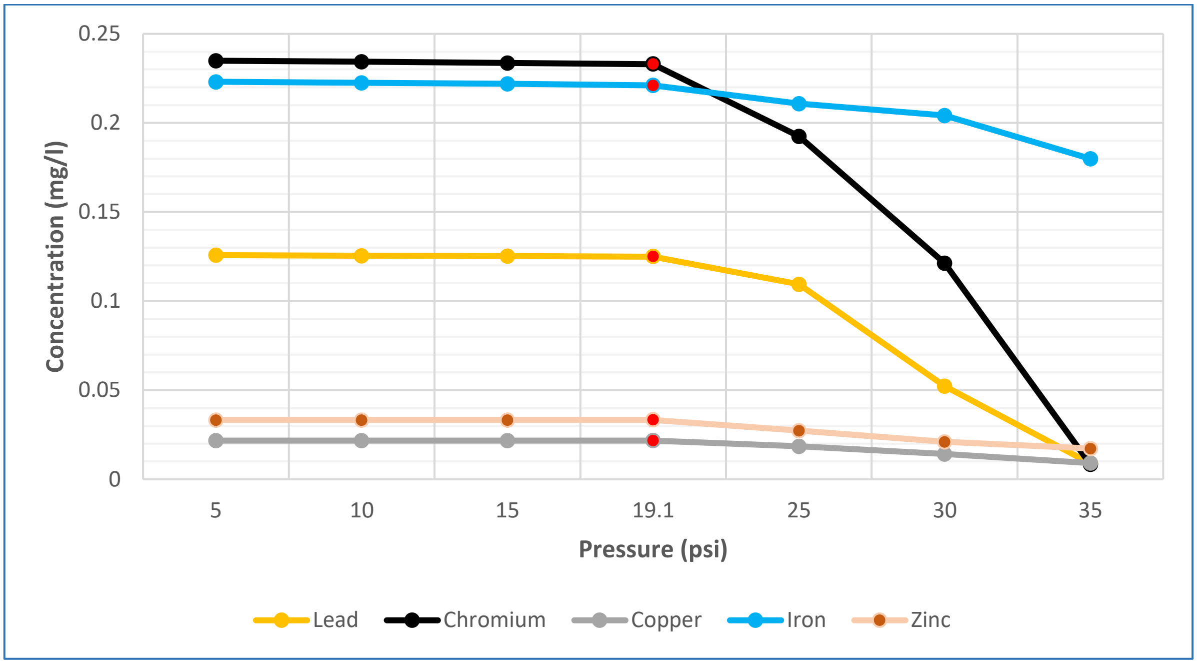


Figure 7.46 Concentrations of metal pollutants at different pressures at the Produced Water Degasser Inlet

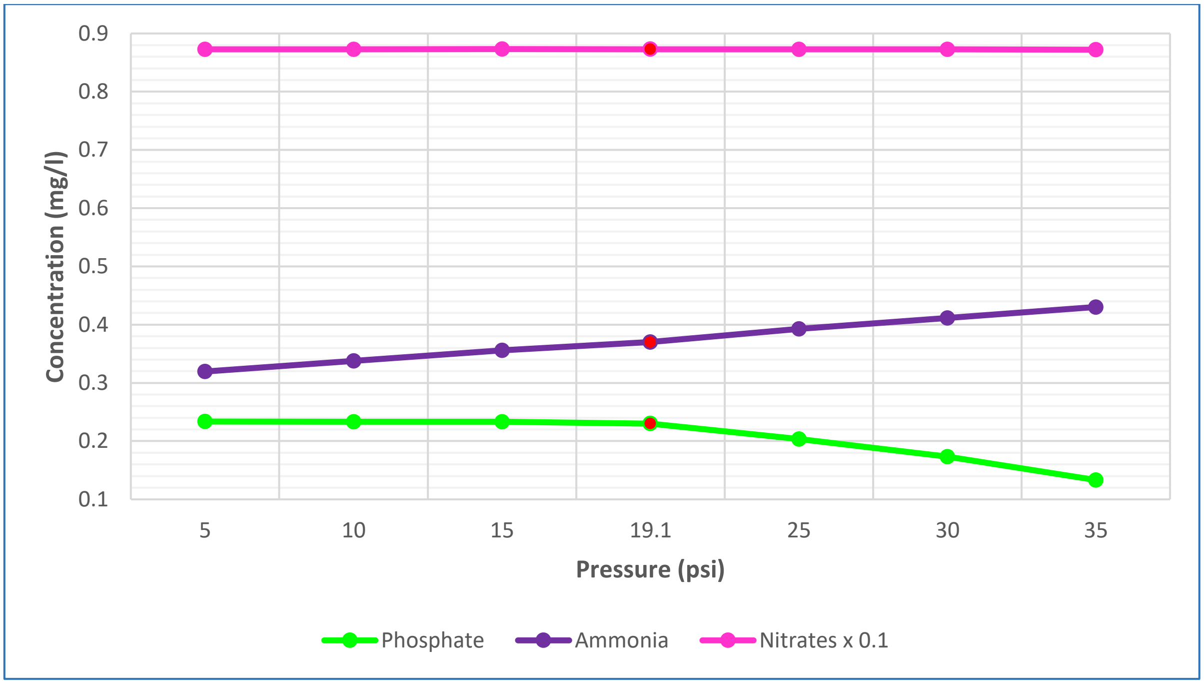


Figure 7.47 Concentrations of non-metal pollutants at different pressures at the Produced Water Degasser Inlet

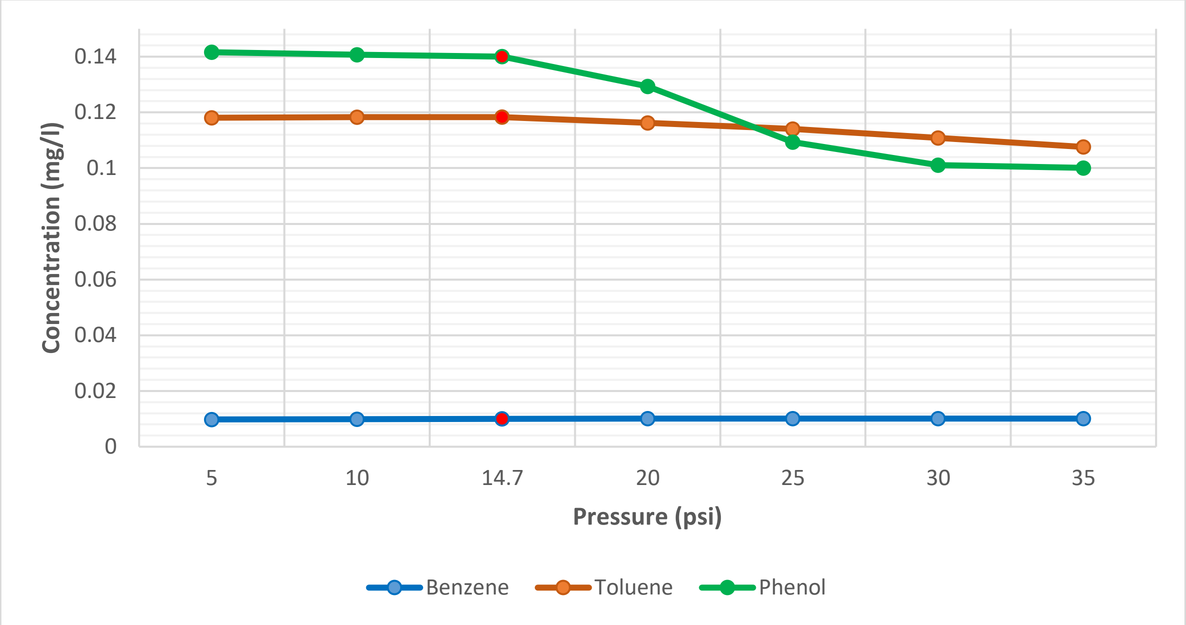


Figure 7.48 Concentrations of Benzene-Toluene-Phenol pollutants at different pressures at the Produced Water Analyzer Exit

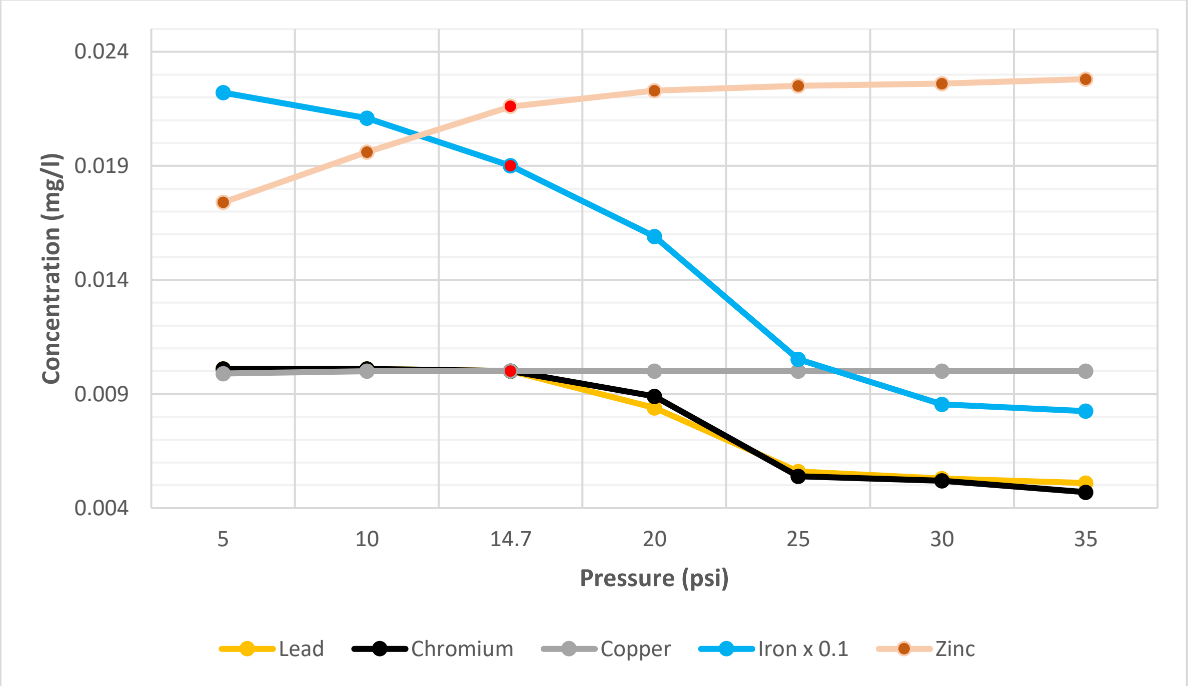


Figure 7.49 Concentrations of metal pollutants at different pressures at the Produced Water Analyzer Exit

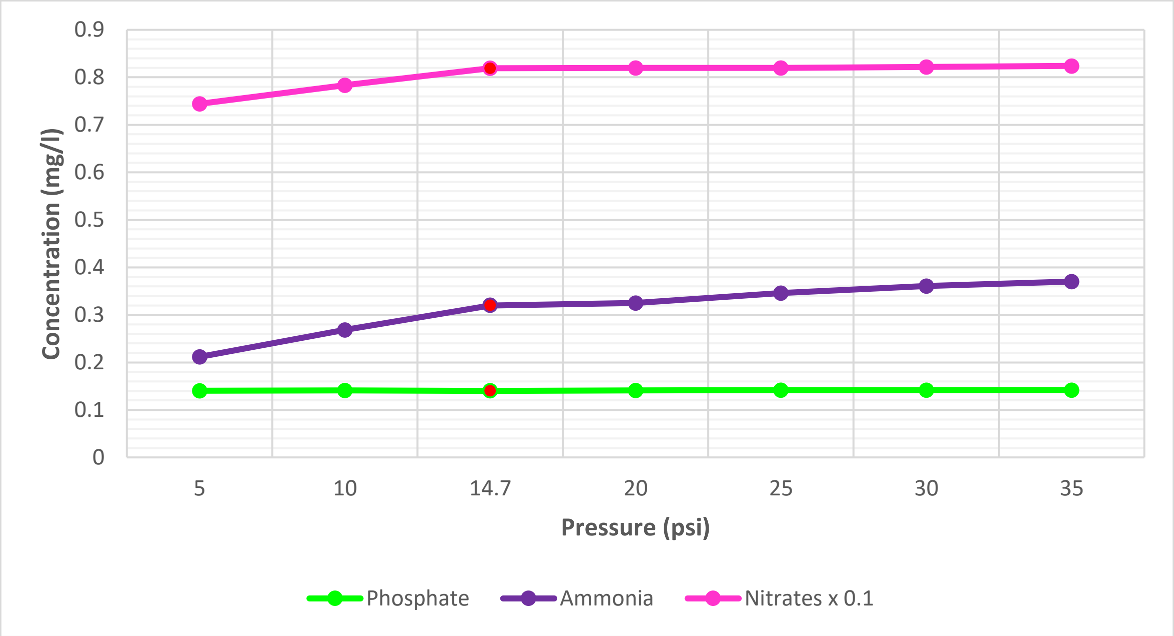


Figure 7.50 Concentrations of non-metal pollutants at different pressures at the Produced Water Analyzer Exit

The simulations using the data from the offshore production facility, as indicated in Figures 7.21 – 7.23, show that at the production manifold, the concentration of all the pollutants under consideration except ammonia increased with temperature increase. However, Figures 7.36 – 7.38 show that pressure increase across the production manifold produced reduction in concentration of these pollutants across the manifold except for ammonia. The implication is that an optimum condition of temperature and pressure combination which must produce pollutant concentration lower than regulatory limit is required to operate the crude oil production process.

Tables H1 and H6 in Appendix H show that at temperature range of 45^0C – 50^0C and operating pressure at the production manifold, ammonia concentration will show a decrease of 2.63×10^{-1} mg l^{-1} $^0C^{-1}$. The steepest decrease caused by pressure variation is recorded at 310 – 320 psi and operating temperature. At these conditions, the concentrations of benzene, toluene, phenol, lead, chromium and phosphates decreased by 2.03×10^{-3} mg l^{-1} psi^{-1}, 9.09×10^{-3} mg l^{-1} psi^{-1}, 7.12×10^{-3} mg l^{-1} psi^{-1}, 9.50×10^{-3} mg l^{-1} psi^{-1} , 4.57×10^{-3} mg l^{-1} psi^{-1} and 1.16×10^{-2} mg l^{-1} psi^{-1} respectively. Although higher pressure will show steeper decrease, the design temperature and pressure of the first stage separator where the fluid will flow into are 93^0C and 676 psig; and must not be exceeded.

The concentrations of benzene, toluene, copper, zinc, phosphate, ammonia and nitrates decreased with temperature at the produced water surge drum inlet as shown in Figures 7.24 – 7.26. The concentrations of phenol, lead, iron and iron conversely increased under the same conditions. However, Figures 7.39 – 7.41 show that application of varying pressures across the same area when other operating parameters are unchanged produced increased concentrations at the produced water surge drum inlet for benzene, toluene, copper, zinc, phosphate, ammonia and nitrates but decrease in the concentrations of phenol, lead, chromium and iron. Based on available results, a combination of optimum pressure and temperature conditions will also be required to reduce the concentrations of selected pollutants to acceptable limits.

At the inlet of the produced water surge drum, Tables H2 and H7 in Appendix H show that if a temperature of 60^0C– 75 ^0C is achieved at the operating pressure, simulations show that the concentrations of benzene, toluene, phosphate and ammonia will decrease by 4.56 x 10^{-3} mg l^{-1} $^0C^{-1}$, 8.22 x10^{-3} mg l^{-1} $^0C^{-1}$,7.94 x 10^{-3} mg l^{-1} $^0C^{-1}$ and 6.26 x10^{-1} mg l^{-1} $^0C^{-1}$ respectively. Under operating temperature, the steepest concentration decrease is recorded at 35 – 45 psi for phenol, lead and chromium corresponding to 9.26 x 10^{-3} mg l^{-1} psi^{-1}, 1.81 x 10^{-2} mg l^{-1} psi^{-1} and 1.40 x 10^{-2} mg l^{-1} psi^{-1} respectively. The fluid from this sample point flows into the produced water surge drum whose design temperature and pressure are 93^0C and 75.4psig respectively.

At the hydrocyclone inlet, Figures 7.27 – 7.29 indicate that temperature increase led to decrease in the concentrations of benzene, copper, zinc, phosphates, ammonia and nitrates but increase in the phenol, lead, chromium and iron. The concentration of toluene in the produced water increased with temperature until the temperature of 55^0C beyond which the concentration of toluene in the sample starts to decrease with increase in temperature. Figures 7.42 – 7.44 show that the same effect is observed on the concentration of phosphates when process is subjected to pressure variation upstream the hydrocyclone inlet; the concentration of phosphates starts to decrease after 98 psi. The concentrations of the pollutants at the inlet of the hydrocyclone are also affected as those whose concentrations increased due to temperature increase had their concentrations decreased due to pressure increase.

Tables H3 and H8 in Appendix H show that temperature range of 70^0C – 75^0C and operating pressure at the hydrocyclone inlet will decrease the concentrations of benzene, toluene and ammonia by 5.15 x 10^{-2} mg l^{-1} $^0C^{-1}$, 2.84 x10^{-2} mg l^{-1} $^0C^{-1}$ and 2.04 x10^{-1} mg l^{-1} $^0C^{-1}$ respectively. Conversely, pressure of 105 – 115 psi will reduce the concentrations of toluene, phenol, lead, and chromium by 3.05 x 10^{-2} mg l^{-1} psi^{-1}, 2.02 x 10^{-2} mg l^{-1} psi^{-1}, 2.42 x 10^{-2} mg l^{-1} psi^{-1} and 3.96 x 10^{-2} mg l^{-1} psi^{-1} respectively. The design temperature and pressure of the hydrocyclone are 93^0C and 149.4psi respectively.

Although the concentrations of the pollutants have been comparatively reduced at the inlet of the produced water degasser, Figures 7.30 – 7.32 show that the effect of temperature is still observed as reduction in the concentrations of benzene, zinc, ammonia and nitrates. Toluene concentration decreases with temperature after the 65^0C mark while copper and phosphates show similar behaviour at temperature of 55^0C. Phenol, lead, chromium and iron concentrations increased with temperature. Figures 7.45 -7.47 show that pressure increase at the produced water degasser inlet results to decrease in the concentrations of all pollutants except ammonia and nitrates.

At the produced water degasser inlet, Tables H4 and H9 in Appendix H show that temperature of 70^0C– 75^0C and operating pressure will yield 3.0 x10^{-3} mg l^{-1} $^0C^{-1}$, 1.0 x10^{-2} mg l^{-1} $^0C^{-1}$, 8.16 x10^{-3} mg l^{-1} $^0C^{-1}$ and 5.28 x10^{-3} mg l^{-1} $^0C^{-1}$ decrease in benzene, toluene, phosphates and nitrates concentrations. Pressure range of

25 – 35 psi at operating temperature will lead to reduction in the concentrations of benzene, toluene, phenol, lead, chromium and phosphates by 2.0 x 10^{-3} mg l^{-1} psi^{-1}, 1.41 x 10^{-2} mg l^{-1} psi^{-1}, 3.40 x 10^{-3} mg l^{-1} psi^{-1}, 1.14 x 10^{-2} mg l^{-1} psi^{-1}, 2.26 x 10^{-2} mg l^{-1} psi^{-1} and 8.0 x 10^{-3} mg l^{-1} psi^{-1} respectively. The design temperature and pressure of the produced water degasser are 93^{0}C and 75.4psi respectively.

The results from the exit of the produced water analyser as contained in Figures 7.33 – 7.35 show that subjecting the system to varying temperatures also led to decrease in the concentrations of benzene, copper, zinc, phosphates, ammonia, and nitrates while those of toluene, phenol, lead, chromium, iron and chlorides increased as the temperature increased. However, Figures 7.48 – 7.50 show that pressure increase resulted to decrease in concentration of phenol, lead, chromium and iron but increase in others.

At the analyser exit, Tables H5 and H10 in Appendix H show that an elevated temperature between 35^{0}C and 45^{0}C will lead to reduction of the concentrations of benzene, toluene, phosphates, ammonia and nitrates by 9.2 x10^{-4} mg l^{-1} $^{0}C^{-1}$, 1.2 x10^{-3} mg l^{-1} $^{0}C^{-1}$, 4.68 x10^{-3} mg l^{-1} $^{0}C^{-1}$, 1.61 x10^{-2} mg l^{-1} $^{0}C^{-1}$ and 4.22 x10^{-3} mg l^{-1} $^{0}C^{-1}$ respectively. At pressure of 20 – 30 psi, the concentrations of toluene, phenol, lead, and chromium reduced by 6.6 x 10^{-4} mg l^{-1} psi^{-1}, 2.86 x 10^{-3} mg l^{-1} psi^{-1}, 4.0 x 10^{-4} mg l^{-1} psi^{-1} and 5.0 x 10^{-4} mg l^{-1} psi^{-1} respectively. Pressure decrease at this point is only a theoretical expression and not practicable since the system operates at atmospheric pressure as a minimum at the analyser exit.

The concentrations of most of the pollutants under incremental temperature and pressure variation followed a regular behavioural pattern. In most cases, the resultant effect of temperature and pressure at the same sample point reciprocate each other; the pollutants whose concentrations decreased with temperature increase are observed to show increase in concentration when incremental pressures were applied. There were also cases where temperature and pressure limits were reached for pollutants; these points are vital since they determine temperatures and pressures beyond which the behaviour of the concentrations of the pollutants with respect to the application of these thermodynamic variables are reversed. In the selection of the operating conditions for the reduction of pollutant concentration in the produced water, the knowledge of these points is very important and must be put into application.

7.3.2.3 The combined effect of varied temperatures and pressures on the concentrations of pollutants:

In order to optimize the effect of temperature and pressure on the concentrations of the pollutants further, the results from the studies of the various sample points were used to select the most critical sample points. The most critical sample point is the point at which the highest degree of concentration change was observed. The Line Heater Exit and the Hydrocyclone Inlet were chosen for the onshore and offshore facilities respectively. The results of these simulations are tabulated below:

Table 7.9: Concentrations of pollutants at combined different temperatures and pressures at the Line Heater Exit at the IFS.

	25psi, 50^{0}C (mg/l)	**30psi, 50^{0}C (mg/l)**	**35psi, 52^{0}C (mg/l)**	**38.5psi, 52^{0}C (mg/l)**	**25psi, 55^{0}C (mg/l)**	**30psi, 55^{0}C (mg/l)**	**35psi, 60^{0}C (mg/l)**	**38.5psi, 60^{0}C (mg/l)**	**35psi, 70^{0}C (mg/l)**	**40psi, 70^{0}C (mg/l)**
Benzene	0.190	0.196	0.197	**0.200**	0.058	0.069	0.025	0.029	0.018	0.022
Toluene	0.158	0.159	0.159	**0.160**	0.125	0.087	0.055	0.053	0.048	0.050
Phenol	0.235	0.232	0.204	**0.240**	0.232	0.224	0.218	0.243	0.226	0.231
Lead	1.011	0.899	0.796	**0.990**	0.863	0.821	0.812	0.879	0.854	0.894
Chromium	0.806	0.797	0.752	**0.790**	0.782	0.771	0.760	0.792	0.775	0.783
Copper	0.039	0.040	0.040	**0.040**	0.038	0.023	0.018	0.009	0.008	0.011
Iron x 0.10	3.127	3.096	3.087	**3.070**	2.851	2.473	2.170	2.042	2.012	2.271
Zinc	0.203	0.207	0.208	**0.210**	0.195	0.200	0.196	0.185	0.180	0.185
Phosphate x 100	0.165	0.168	0.169	**0.170**	0.159	0.163	0.160	0.157	0.148	0.152
Ammonia	6.204	7.027	7.699	**8.270**	5.901	6.686	7.125	5.307	6.492	7.191
Nitrates	21.577	22.110	22.226	**22.500**	20.627	21.231	20.840	17.265	16.885	19.459

Table 7.10: Concentrations of pollutants at combined different temperatures and pressures at the Hydrocyclone Inlet at the FPSO Princess Aweni.

	95psi, 55^{0}C (mg/l)	**100psi, 55^{0}C (mg/l)**	**105psi, 60^{0}C (mg/l)**	**98psi, 60^{0}C (mg/l)**	**98.5psi, 60^{0}C (mg/l)**	**95psi, 70^{0}C (mg/l)**	**100psi, 70^{0}C (mg/l)**	**105psi, 75^{0}C (mg/l)**	**110psi, 75^{0}C (mg/l)**	**110psi, 80^{0}C (mg/l)**
Benzene	0.544	0.548	0.542	0.532	**0.540**	0.128	0.329	0.025	0.022	0.018
Toluene	0.581	0.580	0.579	0.580	**0.580**	0.347	0.478	0.216	0.225	0.204
Phenol	0.348	0.327	0.369	0.414	**0.430**	0.337	0.335	0.332	0.348	0.339
Lead	0.388	0.346	0.362	0.413	**0.430**	0.427	0.416	0.412	0.407	0.421
Chromium	0.467	0.452	0.483	0.530	**0.630**	0.563	0.543	0.525	0.512	0.534

Copper	0.030	0.030	0.030	0.030	**0.030**	0.023	0.028	0.018	0.023	0.014
Iron x 0.10	1.533	1.529	1.535	1.540	**1.540**	1.163	1.359	1.053	1.156	1.031
Zinc	0.181	0.181	0.180	0.180	**0.180**	0.077	0.128	0.028	0.067	0.023
Phosphate x 100	0.412	0.411	0.410	0.410	**0.410**	0.275	0.386	0.202	0.243	0.200
Ammonia	2.987	3.138	3.127	2.926	**2.940**	2.385	2.514	2.006	2.347	2.001
Nitrates	18.205	18.207	18.112	18.099	**18.100**	15.764	16.801	14.956	14.680	14.472

The results show that at the Line Heater exit of the onshore facility, the best results in concentrations reductions for benzene, toluene, phosphates and nitrates are obtained at 35psi,70^{0}C while 35psi,52^{0}C rendered the best concentration reductions for phenol, lead and chromium. At the Hydrocyclone inlet of the offshore facility, 110psi,80^{0}C produced the best concentration reduction for benzene, toluene, phosphates and nitrates whereas phenol, lead and chromium concentrations are best reduced at 100psi,55^{0}C. The results show that for the purpose of reduction of the concentrations, the selected pollutants could be grouped into two bands with each band's concentration affected by a combined temperature and pressure conditions. In order to optimally reduce the concentrations of all the involved pollutants, it is reasonable to select thermodynamic conditions that fall within the range for these two bands.

7.3.3 EVALUATION OF RESEARCH WORK:

7.3.3.1 Efficiency of the research work on pollutant reduction:

The concentration of the pollutants in the produced water sample selected for the study (benzene, toluene, phenol, lead, chromium, phosphate and ammonia) were reduced by the research work. The case study onshore facility (Izombe Flowstation) relied on chemical treatment for reduction of pollutants ‘concentration to meet regulatory limits whereas the offshore facility (FPSO Princess Aweni) has a produced water treatment system incorporated into the production process.

The results from the samples at the end of each facility prior to discharge or injection into the water disposal wells show that while the offshore facility met the Nigerian regulatory authorities limits for discharge of produced water for the selected pollutants, the onshore production facility at the water injection pump did not meet the regulatory requirements for benzene, chromium, lead and ammonia.

Table 7.11: Pollutants reduction by research at onshore and offshore facilities

S/N	Pollutants	IFS Sample at WIJ 14.7psi, 31°C (mg/l)	Simulation Results at WIJ Pump 14.7psi 45°C (mg/l)	Pollutants Reduction at IFS (mg/l)	FPSO Aweni Sample at PW Analyser Exit 14.7psi, 30°C (mg/l)	Simulation Results at PW Analyser Exit 25psi 35°C (mg/l)	Pollutants Reduction at FPSO Aweni (mg/l)
1	Benzene	0.030	0.008	0.022	0.010	0.006	0.004
2	Toluene	0.070	0.067	0.003	0.118	0.108	0.01
3	Phenol	0.150	0.105	0.045	0.140	0.113	0.027
4	Lead	0.370	0.036	0.334	0.010	0.006	0.004
5	Chromium	0.660	0.024	0.636	0.010	0.006	0.004
6	Copper	0.010	0.009	0.001	0.010	0.008	0.002
7	Iron	0.400	0.239	0.161	0.190	0.108	0.082
8	Zinc	0.190	0.085	0.105	0.0217	0.012	0.0097
9	Phosphate	0.200	0.108	0.092	0.1417	0.104	0.0377
10	Ammonia	5.610	0.182	5.428	0.3233	0.102	0.2213
11	Nitrates	18.42	6.625	11.795	8.1867	3.825	4.3617

The result above shows that the research tried to seek the appropriate thermodynamic conditions of temperature and pressure necessary to reduce the concentrations of these pollutants to meet and exceed regulatory requirements. The concentration of the pollutants in the produced water was reduced by simulations along the production process line by temperature and pressure variations; therefore a lower concentration of pollutants obtained at the production manifold is used as feed to the production separator resulting to further reduction in the concentration of the pollutants since the temperature – pressure variations are continuously used in the simulation process to achieve the best possible pollutant concentration reduction along the process at the end of the production process.

7.3.3.2 Comparison with regulatory limits:

The final concentrations of the pollutants at the water injection pump inlet and the produced water analyser exit for the onshore and offshore facilities respectively were compared to regulatory limits. The results of the comparisons indicate that at the beginning of the process, the concentrations of benzene, chromium, lead and ammonia at the onshore production facility were higher than the regulator limits of Nigerian authorities but met these limits after simulation process; the resulting concentrations are lower than the regulatory limits.

Table 7.12: The final concentration of pollutants against Nigeria's regulatory limits

S/N	Pollutants	IFS Sample at WIJ 14.7psi, 31°C (mg/l)	Simulation Results at WIJ Pump 14.7psi 45°C (mg/l)	DPR Limits for Pollutants (mg/l)	FPSO Aweni Sample at PW Analyser Exit 14.7psi, 30°C (mg/l)	Simulation Results at PW Analyser Exit 25psi 35°C (mg/l)	DPR Limits for Pollutants (mg/l)
1	Benzene	0.030	0.008	0.010	0.010	0.006	0.010
2	Toluene	0.070	0.067	0.700	0.118	0.108	0.700
3	Phenol	0.150	0.105	0.500	0.140	0.113	0.500
4	Lead	0.370	0.036	0.050	0.010	0.006	0.050
5	Chromium	0.660	0.024	0.030	0.010	0.006	0.030
6	Copper	0.010	0.009	1.500	0.010	0.008	1.500
7	Iron	0.400	0.239	1.000	0.190	0.108	1.000
8	Zinc	0.190	0.085	1.000	0.0217	0.012	1.000
9	Phosphate	0.200	0.108	5.000	0.1417	0.104	5.000
10	Ammonia	5.610	0.182	0.200	0.3233	0.102	0.200
11	Nitrates	18.42	6.625	20.00	8.1867	3.825	20.00

For the offshore production facility whose concentrations met regulatory limits from the beginning, the research shows that it is possible to reduce the concentration of pollutants in the produced water by adjusting the thermodynamics parameters of temperature and pressure.

Table 7.13: The final concentration of pollutants against regulatory limits for the USA, European Union and World Health Organisation (Source: US EPA (2018); EU (2017) and WHO (2011))

S/N	Sample Parameter	IFS Sample at WIJ 14.7psi, 31°C (mg/l)	Simulation Results at WIJ Pump 14.7psi 45°C (mg/l)	FPSO Aweni Sample at PW Analyzer Exit 14.7psi, 30°C (mg/l)	Simulation Results at PW Analyzer Exit 25psi 35°C (mg/l)	DPR Limits (mg/l)	USA Limits (mg/l)	EU Limits (mg/l)	WHO Limits (mg/l)

1	Benzene	0.030	0.008	0.010	0.006	0.010	0.005	0.001	0.001
2	Toluene	0.070	0.067	0.118	0.108	0.700	1.000	0.700	0.700
3	Phenol	0.150	0.105	0.140	0.113	0.500	2.000	0.500	2.000
4	Lead	0.370	0.036	0.010	0.006	0.050	0.015	0.010	0.010
5	Chromium	0.660	0.024	0.010	0.006	0.030	0.100	0.050	0.050
6	Copper	0.010	0.009	0.010	0.008	1.500	1.300	2.000	2.000
7	Iron	0.400	0.239	0.190	0.108	1.000	0.300	0.200	0.500
8	Zinc	0.190	0.085	0.0217	0.012	1.000	5.000	3.000	3.000
9	Phosphate	0.200	0.108	0.1417	0.104	5.000	1.300	0.100	0.100
10	Ammonia	5.610	0.182	0.3233	0.102	0.200	0.400	0.300	0.200
11	Nitrates	18.42	6.625	8.1867	3.825	20.00	10.00	50.00	50.00

The regulatory limits of the United States of America and European Union for most of the pollutants were also met by the final concentrations at the water injection pump inlet and the produced water analyzer inlet. This shows that where stricter regulations are in place, the application of temperature and pressure dynamics on the production facility could be used to meet requirements without resorting to the installation of the cost prohibitive produced water treatment system.

7.3.4 VALIDATION OF RESEARCH RESULTS

Table 7.14 Validation of Results from Onshore Facility**:**

S/N	**Pollutants**	**Line Heater Exit**		**WIJ Pump Inlet**	
		Real life Sample Conc. (mg/l)	**Best Simulation Result (mg/l)**	**Real life Sample Conc. (mg/l)**	**Best Simulation Result (mg/l)**
1	Benzene	0.200	0.018	0.030	0.008
2	Toluene	0.160	0.048	0.070	0.067
3	Phenol	0.240	0.204	0.150	0.105
4	Lead	0.990	0.796	0.370	0.036
5	Chromium	0.790	0.752	0.660	0.024

6	Copper	0.040	0.008	0.010	0.009
7	Iron	3.070	2.012	0.400	0.239
8	Zinc	0.210	0.180	0.190	0.085
9	Phosphate	0.170	0.142	0.200	0.108
10	Ammonia	8.270	5.307	5.610	0.182
11	Nitrates	22.50	16.885	18.420	6.625

Table 7.15: Validation of Results from Offshore Facility:

S/N	Pollutants	PW Hydrocyclone Inlet		PW Analyser Exit	
		Real life Sample Conc. (mg/l)	Best Simulation Result (mg/l)	Real life Sample Conc. (mg/l)	Best Simulation Result (mg/l)
1	Benzene	0.540	0.018	0.010	0.006
2	Toluene	0.580	0.204	0.120	0.108
3	Phenol	0.430	0.327	0.140	0.113
4	Lead	0.430	0.346	0.010	0.006
5	Chromium	0.630	0.452	0.010	0.006
6	Copper	0.030	0.014	0.010	0.008
7	Iron	1.540	1.031	0.190	0.108
8	Zinc	0.180	0.023	0.020	0.012
9	Phosphate	0.410	0.200	0.140	0.104
10	Ammonia	2.940	2.001	0.320	0.102
11	Nitrates	18.10	14.472	8.190	3.825

7.4 SUMMARY

The research has used unprocessed data gathered from the field and various engineering documentations for the onshore and offshore case study facilities to generate processed information from simulation. The results from the process simulations have been analysed to obtain the best possible outcomes believing that the facility will yield exactly as indicated from simulation.

The ‘classical’ simulation results would naturally transfer the outcomes from point 1 to become input for point 2. Under ‘regular’ simulation, this may be true or false and depends on the ability of the facility to adjust to the theoretical thermodynamic conditions. In the ‘regular’ simulation approach employed, the results obtained from laboratory tests on the samples collected at the various sample points were used as inputs for simulations at the points. Although the approach eliminated the doubts of the ability of the facility to achieve the same results obtained through simulation, it was not as efficient as expected as the results of the concentrations of the pollutants which were expectedly lower were not used as input for the next stage. Notwithstanding, the final concentrations obtained by simulations using pressure and temperature variations for both regular and classical simulations were below regulatory limits for the Nigeria oil and gas industry.

The trend in the reduction of the concentrations of each pollutant per degree of change in temperature or per psi of pressure gave guide to the range of temperature and pressure required for a certain degree of reduction in concentration for any of the selected pollutants in the produced water sample. It was observed against the outcomes of preliminary investigations that concentrations of these pollutants do not continue to decrease or increase along straight line with temperature or pressure increase. This discovery made the research more interesting and the choice of optimum thermodynamic conditions for each of the pollutants somewhat specific.

Considering the results of the samples from the laboratories, the simulation yielded concentration of pollutants that are lower than that produced by the production process for both case studies and met the regulatory limits of Nigeria and to a great extent the United States and the European Union. The limits for the European Union and World Health Organisation applied in the comparative study are drinking water limits since discharge into water especially offshore is prohibited in the European Union. The efficiency of the research is higher with the onshore facility considering that the offshore facility has a produced water treatment facility that could treat the produced water to meet Nigeria's regulatory limits.

CHAPTER EIGHT

CONCLUSIONS, OUTLOOK AND RECOMMENDATIONS

8.1 INTRODUCTION

The summary of the research study contains a definition of the problem in a simple language and the frame under which the research work has been formed covering the local regulatory requirements and the alternatives to this research study. The aim of the study, the various methods of data collection, simulation, optimisation and analysis are also contained in the summary of the study. The key findings of the research gave details of the extent to which the specific objectives have been attained in order to justify that the research overall aim was achieved. There are some significant implications of the research especially for engineers and designers in the design and operation of crude oil production facilities. These key implications have been shared. About four key limitations of the research findings have also been highlighted. This well researched study has covered a great deal but there are still areas that could not be covered due to time, resources and scope; some of these areas for futuristic research study have been listed.

8.2 SUMMARY OF THE STUDY

Crude oil production consumes a great deal of energy and generates various kinds of pollutants which have potential environmental impacts. Produced water which co-exists with crude oil and natural gas in the reservoir is the main pollutant of the crude oil production process. Produced water is seven to eight times greater by volume than oil produced at any oilfield (*Igwe et al., 2013*) and may contain a wide variety of organic and inorganic pollutants, suspended solids, salt water used for water flooding, production chemicals, and low concentrations of hazardous substances that occur naturally in the reservoir, such as heavy metals, aromatic hydrocarbons, alkyl phenols and radioactive substances (*OSPAR Commission, 2009; Hansen et al., 1994*).

The local regulations require that produced water is managed in such a way that it is not released into the environment in its toxic nature. The common option is usually to treat the fluid to an acceptable condition before it is disposed. This process involves the design and installation of produced water treatment system which could involve high capital and recurrent costs and the expenditure of huge amount of energy. High cost of installation and operation of produced water treatment facility and the likely sanctions from the regulatory bodies in the case of failure to meet the required limits reduces the profitability of crude oil production. In attempt to reduce the pollution and energy expenditure associated with management of produced water from crude oil production, this research investigates the use of thermodynamic variables of temperature and pressure for the reduction of pollutants generated from crude oil production operations.

In order to achieve the aim of the study, various methods of data collection and analyses were employed in the study. The study combined qualitative and quantitative approaches. At early stage of the research study, data were collected through testing of representative produced water samples in the laboratory, extraction of information from engineering design documentation and direct reading of values from gauges and meters in the field and through production records. The process of primary data collection at the onshore and offshore production facilities happened over a cumulative period of twelve months. Models of the case study crude oil production facilities were designed and created on process simulation environment to test the research objective of pollution reduction and energy savings in the crude oil production process. Several runs were made with different thermodynamic conditions and the guides being the design parameters, the operational parameters and the results of the laboratory results. The results from the simulations were recorded. The result of the simulations was analysed to determine the temperature-pressure values across key equipment / sample points which will result to the minimum pollution / concentration of key pollutants in the produced water sample resulting from the production process.

The study found that application of process integration techniques on crude oil production process with set targets by the manipulation of thermodynamic variables of temperature and pressure could be used for pollutant reduction (reduction of the concentration of pollutants in produced water) and energy savings on the production process. This research could be used to meet regulatory limits on produced water disposal without installation of produced water treatment units. The research study has provided new knowledge on crude oil production process which will be helpful in the design of new or modification of existing crude oil production process where minimum environmental impacts and energy savings are desired.

8.3 KEY FINDINGS OF THE STUDY

The findings of the study are discussed in line with the overall aim and the specific objectives that the study has been designed to achieve. The objectives have been restated in this section and the extent to which they have been met are summarized.

Objective 1: *Apply a systematic framework for simulating, analysing and optimising existing and future crude oil production process plants*;

The work in chapter five provides details of the meaning of simulation, optimisation and analysis while chapter six enumerated the tools, techniques, procedures used for process simulation, optimisation and analysis for the research project. Chapter seven contains the results of simulation, optimisation and analysis in tables, graphs and charts.

Objective 2: *Evaluate the efficiency of the combination of optimisation and process simulation techniques on waste / pollutants generation in crude oil production process;*

In chapter seven, simulation models for the case studies have been used to show the effect of optimisation of variables on the concentrations of the pollutant in produced water resulting from crude oil production.

Objective 3: *Investigate the relationship, if any, between the improvement in energy efficiency of crude oil production process and the volume of wastes / pollutants generated from the process*;

The ability of the research work to show that pollutant concentration in produced water could be reduced to acceptable regulatory limits in chapter seven has been considered as an energy saving achievement since the energy consumed for produced water treatment optimisation will not be required. The determination of the amount of energy saved due to reduction and achievement of regulatory limit will be a subject for future research work.

Objective 4: *Generate generic and specific models that describe adequately the crude oil production processes;*

The description of crude oil production process in process flow diagrams and process and instrumentation diagrams is contained in chapter three. However, the models used for the simulation and optimisation of the onshore and offshore case study facilities are found in chapter seven.

Objective 5: *Investigate the thermodynamic, economic and environmental trade-off for a model crude oil and natural gas production process;*

Chapter four presents the detailed economic and environmental cost for crude oil production. The thermodynamic trade-off required to achieve environmentally friendly crude oil production is demonstrated in chapter seven.

Objective 6: *Determine the energy savings due to the application of the research results on production facilities.*

The energy savings that could be made from deployment of the result of the study on the case study facilities have been calculated in Section 7.2.4. The energy that could be saved annually due to application of the research results at the offshore and onshore facilities are 379,600 KWh and 64,983.87 KWh respectively.

8.4 IMPLICATIONS FOR INDUSTRIAL PRACTICE

The findings of the research study have significant implication for practice in crude oil and natural gas production in the oil and gas industry. The study shows that thermodynamic parameters of temperature and pressure which are hitherto used in design to ensure that reservoir fluid conditions accommodated while maximizing crude oil and natural gas production could also be used to regulate the concentration of pollutants in the produced water produced alongside crude oil and natural gas. The application of the findings of the research could be found in practice in process equipment and facilities design, crude oil and natural gas production optimization, production cost reduction and regulatory compliance.

There is need to consider pollution reduction during the design process for green projects (new facilities). In order to achieve this, there may be need for inter-professional collaborative competency upgrade especially for design engineers and managers. In practice, when engineers design for pollution reductions, the focus should be on optimization of the design in line with international industry practices.

In order to achieve regulatory limits in produced water disposal, it is necessary to pay attention to the individual constituents of the produce water and the concentration of each pollutant in the produced water sample. The process of pollutant reduction in produce water has been shown to follow pollutant targets and therefore could be defined to be somewhat specific. To drive down the concentrations of the chosen pollutant targets require a certain direction of variation for the temperature and pressure variables along the production process.

Process integration may also be required to prepare existing crude oil production facilities for pollutants reduction and subsequently energy savings. There may be need to install heat exchangers, heaters and pumps or change their positions or that of other existing equipment to achieve desired conditions. Engineers may therefore require more training of system integration to prepare for the abundant benefits of the findings of the research. The achievement of results using the recommendations of the research requires skill, patience and complete knowledge of the design and operating conditions for existing facilities.

Research shows that pollutant reduction using variation of thermodynamic parameters of temperature and pressure could be employed in both onshore and offshore facilities. It could also be used on green or brown projects for the design and construction of new plants or upgrade of existing ones respectively.

8.5 LIMITATIONS OF THE STUDY

The methodological approach has tried to make this research as universal as possible but notwithstanding these efforts some limitations have been identified and they include:

a. **Source of samples:** The produced water samples were collected from crude oil production facilities at the Izombe Flowstation (onshore) and FPSO Pincess Aweni (offshore) in Nigeria. Oil and gas reservoir structure determines the nature of crude oil as well as the accompanying produced water. It is therefore true that even though the produced water and crude oil from other reservoir may behave along similar lines, it may be difficult to conclude that exact results would be achieved.

b. **Constituent equipment of the production facility:** In the production of crude oil, several considerations are made in the selection of the type of separation and stabilizing equipment required. This will to a great degree determine the level of separation and the quality of produced water that results from the process. The constitution of the equipment required for the facility is therefore a limiting factor especially for existing facilities in the application of this research technique for pollutants reduction and energy saving in crude oil production processes.

c. **Arrangement of equipment in the production facility:** The arrangement of the heaters, heat exchangers, separators, pumps and tanks are also important in the removal of pollutants and subsequently energy savings in crude oil production. Therefore, the result obtained may vary with the variation of the positioning of the equipment.

d. **The polluting constituents of the produced water sample:** The concentrations of the polluting constituents of the produced water sample from the crude oil production process are usually the main target when using this research technique to reduce pollutants and subsequently save energy. Since the polluting constituents and their concentration vary with the source of the produced water, it is therefore a limitation to the application of the research result.

8.6 RECOMMENDATIONS FOR FUTURE RESEARCH

The reduction of pollutants and saving of energy from crude oil production processes has focused primarily on produced water because it constitutes to a great extent the major source of pollution for crude oil production process. The findings have made possible an environmentally friendly and highly profitable crude oil production process. As much as the research tried to cover as much scope as possible, there are still areas that could be considered for further investigations. The following areas of investigations are therefore recommended for future research:

- The effect of other thermodynamic variables like residence time and volumetric flow rates on pollutants reduction in crude oil production processes.
- The material balance requirement for achievement of regulatory limits for the concentration of pollutants in the produced water from crude oil production process.
- Determination of the energy savings from the pollutants' reduction process in crude oil production process.

- Energy requirements for the achievement of regulatory limits of pollutants in the absence of produced water treatment system in crude oil production.
- Facility improvement and upgrade requirements for environmentally friendly crude oil production process.
- Economic evaluation of the pollution reduction process in crude oil production process.
- Mathematical modelling for pollutant reduction and energy savings in crude oil production process.

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APPENDICES

APPENDIX A: MONTHLY LABORATORY RESULTS FROM IZOMBE FLOWSTATION

Table A1: Average of the results of laboratory analysis of samples collected at Izombe Flowstation in 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 (no unit)	6.97(no unit)	6.68(no unit)
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	Copper	AAS (FLAME)	0.05	0.04	0.01
8	Iron	AAS (FLAME)	4.97	2.76	0.38
9	Zinc	AAS (FLAME)	0.22	0.20	0.18
10	Phosphate	HACH DR 3900	0.03	0.12	0.14
11	Ammonia	HACH DR 3900	10.65	7.90	5.50
12	Nitrates	HACH DR 3900	20	22.89	16.94
13	TDS	TDS Meter	17,100	16,600	12,400
14	Chlorides	Titrimetry	6,000	5,500	5,200
15	Salinity	Titrimetry	9,900	8,665	7,175

Note: TDS – Total Dissolved Solids

Table A2 Average of the results of laboratory analysis of samples collected at Izombe Flowstation in December 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	7.14(no unit)	6.96(no unit)	6.62(no unit)
2	Benzene	GC (FID)	0.52	0.21	0.04
3	Toluene	GC (FID)	0.54	0.18	0.10
4	Phenol	HACH DR 3900	0.74	0.22	0.14
5	Lead	AAS (FLAME)	1.28	0.94	0.42
6	Chromium	AAS (FLAME)	0.92	0.84	0.69
7	Copper	AAS (FLAME)	0.06	0.04	0.01
8	Iron	AAS (FLAME)	4.98	2.66	0.36
9	Zinc	AAS (FLAME)	0.24	0.22	0.19
10	Phosphate	HACH DR 3900	0.05	0.15	0.16
11	Ammonia	HACH DR 3900	10.64	7.92	5.52
12	Nitrates	HACH DR 3900	22.24	21.89	16.86
13	TDS	TDS Meter	18,200	16,500	12,800
14	Chlorides	Titrimetry	6,000	5,400	5,100
15	Salinity	Titrimetry	9,800	8,500	7,400

Note: TDS – Total Dissolved Solids

Table A3 Average of the results of laboratory analysis of samples collected at Izombe Flowstation in January 2018

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	6.98(no unit)	6.86(no unit)	6.65(no unit)
2	Benzene	GC (FID)	0.48	0.17	0.02
3	Toluene	GC (FID)	0.47	0.14	0.06
4	Phenol	HACH DR 3900	0.65	0.18	0.10
5	Lead	AAS (FLAME)	1.22	0.96	0.37
6	Chromium	AAS (FLAME)	0.88	0.78	0.66
7	Copper	AAS (FLAME)	0.05	0.03	0.01
8	Iron	AAS (FLAME)	5.06	3.56	0.49
9	Zinc	AAS (FLAME)	0.24	0.21	0.20
10	Phosphate	HACH DR 3900	0.02	0.10	0.12
11	Ammonia	HACH DR 3900	10.40	7.60	4.64
12	Nitrates	HACH DR 3900	19.88	20.76	16.82
13	TDS	TDS Meter	17,000	16,400	12,200
14	Chlorides	Titrimetry	6,000	5,200	5,100
15	Salinity	Titrimetry	9,600	8,600	7,100

Note: TDS – Total Dissolved Solids

Table A4 Average of the results of laboratory analysis of samples collected at Izombe Flowstation in February 2018

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(no unit)	6.97(no unit)	6.66(no unit)
2	Benzene	GC (FID)	0.52	0.20	0.03
3	Toluene	GC (FID)	0.50	0.14	0.06
4	Phenol	HACH DR 3900	0.75	0.26	0.20
5	Lead	AAS (FLAME)	1.45	0.90	0.34
6	Chromium	AAS (FLAME)	0.92	0.85	0.70
7	Copper	AAS (FLAME)	0.06	0.04	0.01
8	Iron	AAS (FLAME)	4.98	2.88	0.39
9	Zinc	AAS (FLAME)	0.22	0.21	0.17
10	Phosphate	HACH DR 3900	0.04	0.15	0.16
11	Ammonia	HACH DR 3900	10.42	8.80	5.80
12	Nitrates	HACH DR 3900	18.68	21.68	20.04
13	TDS	TDS Meter	18,100	17,300	14,200
14	Chlorides	Titrimetry	6,200	5,600	5,050
15	Salinity	Titrimetry	9,200	8,425	7,050

Note: TDS – Total Dissolved Solids

Table A5 Average of the results of laboratory analysis of samples collected at Izombe Flowstation in March 2018

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	7.15(no unit)	6.95(no unit)	6.65(no unit)
2	Benzene	GC (FID)	0.52	0.22	0.04
3	Toluene	GC (FID)	0.50	0.20	0.06
4	Phenol	HACH DR 3900	0.84	0.26	0.18
5	Lead	AAS (FLAME)	1.34	1.20	0.35
6	Chromium	AAS (FLAME)	0.94	0.83	0.70
7	Copper	AAS (FLAME)	0.05	0.03	0.001
8	Iron	AAS (FLAME)	4.90	2.60	0.34
9	Zinc	AAS (FLAME)	0.22	0.21	0.18
10	Phosphate	HACH DR 3900	0.08	0.20	0.26
11	Ammonia	HACH DR 3900	12.45	8.60	5.80
12	Nitrates	HACH DR 3900	21.85	24.86	20.42
13	TDS	TDS Meter	17,400	16,800	12,600
14	Chlorides	Titrimetry	6,400	5,600	5,100
15	Salinity	Titrimetry	9,800	8,450	7,010

Note: TDS – Total Dissolved Solids

Table A6 Average of the results of laboratory analysis of samples collected at Izombe Flowstation in April 2018

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	7.20(no unit)	6.98(no unit)	6.62(no unit)
2	Benzene	GC (FID)	0.55	0.22	0.04
3	Toluene	GC (FID)	0.50	0.14	0.07
4	Phenol	HACH DR 3900	0.82	0.32	0.14
5	Lead	AAS (FLAME)	1.65	0.94	0.31
6	Chromium	AAS (FLAME)	0.86	0.64	0.55
7	Copper	AAS (FLAME)	0.05	0.04	0.01
8	Iron	AAS (FLAME)	5.04	3.93	0.41
9	Zinc	AAS (FLAME)	0.23	0.22	0.20
10	Phosphate	HACH DR 3900	0.06	0.27	0.34
11	Ammonia	HACH DR 3900	12.65	8.80	6.40
12	Nitrates	HACH DR 3900	20.08	22.92	19.42
13	TDS	TDS Meter	16,800	15,300	11,800
14	Chlorides	Titrimetry	6,600	5,800	5,400
15	Salinity	Titrimetry	9,800	8,400	7,005

Note: TDS – Total Dissolved Solids

APPENDIX B: MONTHLY LABORATORY RESULTS FROM FPSO PRINCESS AWENI

Table B1 Average of the results of laboratory analysis of samples collected at FPSO Princess Aweni in March 2018

S/N	Sample Parameter	Analytical Method	Conc. at P1 (mg/l)	Conc. at P2 (mg/l)	Conc. at P3 (mg/l)	Conc. at P4 (mg/l)	Conc. at P5 (mg/l)
1	pH (no unit)	pH Meter	7.48	7.46	7.46	7.42	7.42
2	Benzene	GC (FID)	0.62	0.58	0.54	0.03	0.01
3	Toluene	GC (FID)	0.84	0.65	0.58	0.23	0.12
4	Phenol	HACH DR 3900	0.64	0.52	0.44	0.18	0.14
5	Lead	AAS (FLAME)	0.84	0.64	0.43	0.12	0.01
6	Chromium	AAS (FLAME)	0.92	0.81	0.62	0.23	0.01
7	Copper	AAS (FLAME)	0.05	0.04	0.03	0.02	0.01
8	Iron	AAS (FLAME)	4.97	3.76	1.20	0.23	0.20
9	Zinc	AAS (FLAME)	0.22	0.20	0.18	0,03	0.02
10	Phosphate	HACH DR 3900	0.68	0.48	0.41	0.24	0.14
11	Ammonia	HACH DR 3900	12.80	10.20	2.24	0.36	0.32
12	Nitrates	HACH DR 3900	26.82	21.46	18.12	8.82	8.20
13	TDS	TDS Meter	7,150	6,250	6,020	5,800	5,150
14	Chlorides	Titrimetry	9,000	8,500	8,200	6,215	5,850
15	Salinity	Titrimetry	6,600	6,250	5,200	2,900	2,600

Note: PW – Produced Water; TDS – Total Dissolved Solids; P1-Production Manifold; P2-PW Surge Drum Inlet; P3-Hydrocyclone Inlet; P4-PW Degasser Inlet; P5-PW Analyser Exit.

Table B2 Average of the results of laboratory analysis of samples collected at FPSO Princess Aweni in April 2018

S/N	Sample Parameter	Analytical Method	Conc. at P1 (mg/l)	Conc. at P2 (mg/l)	Conc. at P3 (mg/l)	Conc. at P4 (mg/l)	Conc. at P5 (mg/l)
1	pH(no unit)	pH Meter	7.49	7.48	7.46	7.44	7.42
2	Benzene	GC (FID)	0.66	0.60	0.55	0.04	0.01
3	Toluene	GC (FID)	0.84	0.68	0.59	0.24	0.12
4	Phenol	HACH DR 3900	0.66	0.52	0.44	0.16	0.13
5	Lead	AAS (FLAME)	0.86	0.64	0.43	0.14	0.01
6	Chromium	AAS (FLAME)	0.94	0.82	0.64	0.23	0.01
7	Copper	AAS (FLAME)	0.06	0.04	0.04	0.03	0.01
8	Iron	AAS (FLAME)	4.99	3.85	2.40	0.20	0.18
9	Zinc	AAS (FLAME)	0.24	0.20	0.19	0.04	0.02
10	Phosphate	HACH DR 3900	0.72	0.52	0.42	0.21	0.15
11	Ammonia	HACH DR 3900	12.90	10.50	4.24	0.38	0.33
12	Nitrates	HACH DR 3900	26.86	20.45	18.14	8.80	8.30
13	TDS	TDS Meter	7,100	6,250	6,020	5,950	5,180
14	Chlorides	Titrimetry	9,000	8,600	8,200	6,205	5,860
15	Salinity	Titrimetry	6,700	6,250	5,300	2,950	2,550

Note: PW – Produced Water; TDS – Total Dissolved Solids; P1-Production Manifold; P2-PW Surge Drum Inlet; P3-Hydrocyclone Inlet; P4-PW Degasser Inlet; P5-PW Analyser Exit.

Table B3 Average of the results of laboratory analysis of samples collected at FPSO Princess Aweni in May 2018

S/N	Sample Parameter	Analytical Method	Conc. at P1 (mg/l)	Conc. at P2 (mg/l)	Conc. at P3 (mg/l)	Conc. at P4 (mg/l)	Conc. at P5 (mg/l)
1	pH(no unit)	pH Meter	7.48	7.46	7.46	7.42	7.42
2	Benzene	GC (FID)	0.61	0.56	0.50	0.03	0.01
3	Toluene	GC (FID)	0.84	0.66	0.57	0.21	0.11
4	Phenol	HACH DR 3900	0.67	0.55	0.42	0.18	0.16
5	Lead	AAS (FLAME)	0.84	0.63	0.41	0.12	0.01
6	Chromium	AAS (FLAME)	0.96	0.82	0.68	0.27	0.01
7	Copper	AAS (FLAME)	0.05	0.03	0.03	0.02	0.01
8	Iron	AAS (FLAME)	4.98	3.76	1.20	0.23	0.18
9	Zinc	AAS (FLAME)	0.25	0.20	0.18	0.04	0.03
10	Phosphate	HACH DR 3900	0.73	0.48	0.41	0.24	0.15
11	Ammonia	HACH DR 3900	13.60	10.20	2.24	0.36	0.33
12	Nitrates	HACH DR 3900	27.65	21.46	18.12	8.43	8.20
13	TDS	TDS Meter	5,150	6,250	6,020	5,800	5,150
14	Chlorides	Titrimetry	9,200	8,400	8,200	6,205	5,800
15	Salinity	Titrimetry	6,500	6,200	5,100	2,750	2,500

Note: PW – Produced Water; TDS – Total Dissolved Solids; P1-Production Manifold; P2-PW Surge Drum Inlet; P3-Hydrocyclone Inlet; P4-PW Degasser Inlet; P5-PW Analyser Exit.

Table B4 Average of the results of laboratory analysis of samples collected at FPSO Princess Aweni in June 2018

S/N	Sample Parameter	Analytical Method	Conc. at P1 (mg/l)	Conc. at P2 (mg/l)	Conc. at P3 (mg/l)	Conc. at P4 (mg/l)	Conc. at P5 (mg/l)
1	pH(no unit)	pH Meter	7.47	7.46	7.44	7.42	7.40
2	Benzene	GC (FID)	0.72	0.68	0.57	0.04	0.01
3	Toluene	GC (FID)	0.86	0.67	0.59	0.24	0.12
4	Phenol	HACH DR 3900	0.60	0.50	0.42	0.17	0.13
5	Lead	AAS (FLAME)	0.85	0.63	0.44	0.13	0.01
6	Chromium	AAS (FLAME)	0.90	0.81	0.60	0.21	0.01
7	Copper	AAS (FLAME)	0.06	0.04	0.04	0.02	0.01
8	Iron	AAS (FLAME)	4.88	3.46	2.04	0.21	0.18
9	Zinc	AAS (FLAME)	0.23	0.20	0.19	0.03	0.02
10	Phosphate	HACH DR 3900	0.66	0.48	0.40	0.23	0.13
11	Ammonia	HACH DR 3900	11.90	9.80	4.46	0.38	0.34
12	Nitrates	HACH DR 3900	26.80	20.55	17.85	8.70	8.06
13	TDS	TDS Meter	7,050	6,450	6,010	5,400	5,150
14	Chlorides	Titrimetry	8,180	7,500	7,200	6,215	5,500
15	Salinity	Titrimetry	6,400	6,150	5,100	2,800	2,100

Note: PW – Produced Water; TDS – Total Dissolved Solids; P1-Production Manifold; P2-PW Surge Drum Inlet; P3-Hydrocyclone Inlet; P4-PW Degasser Inlet; P5-PW Analyser Exit.

Table B5 Average of the results of laboratory analysis of samples collected at FPSO Princess Aweni in July 2018

S/N	Sample Parameter	Analytical Method	Conc. at P1 (mg/l)	Conc. at P2 (mg/l)	Conc. at P3 (mg/l)	Conc. at P4 (mg/l)	Conc. at P5 (mg/l)
1	pH(no unit)	pH Meter	7.46	7.46	7.45	7.42	7.41
2	Benzene	GC (FID)	0.62	0.58	0.54	0.03	0.01
3	Toluene	GC (FID)	0.83	0.65	0.58	0.23	0.12
4	Phenol	HACH DR 3900	0.63	0.52	0.44	0.18	0.14
5	Lead	AAS (FLAME)	0.80	0.64	0.43	0.12	0.01
6	Chromium	AAS (FLAME)	0.90	0.81	0.62	0.23	0.01
7	Copper	AAS (FLAME)	0.05	0.04	0.03	0.02	0.01
8	Iron	AAS (FLAME)	4.78	3.76	1.20	0.23	0.20
9	Zinc	AAS (FLAME)	0.23	0.20	0.18	0,03	0.02
10	Phosphate	HACH DR 3900	0.66	0.48	0.41	0.24	0.14
11	Ammonia	HACH DR 3900	12.90	10.20	2.25	0.36	0.32
12	Nitrates	HACH DR 3900	27.22	21.46	18.20	8.82	8.20
13	TDS	TDS Meter	7,250	6,250	6,040	5,700	5,150
14	Chlorides	Titrimetry	9,205	8,500	8,200	6,115	5,650
15	Salinity	Titrimetry	6,700	6,250	5,200	2,700	2,500

Note: PW – Produced Water; TDS – Total Dissolved Solids; P1-Production Manifold; P2-PW Surge Drum Inlet; P3-Hydrocyclone Inlet; P4-PW Degasser Inlet; P5-PW Analyser Exit.

Table B6 Average of the results of laboratory analysis of samples collected at FPSO Princess Aweni in August 2018

S/N	Sample Parameter	Analytical Method	Conc. at P1 (mg/l)	Conc. at P2 (mg/l)	Conc. at P3 (mg/l)	Conc. at P4 (mg/l)	Conc. at P5 (mg/l)
1	pH(no unit)	pH Meter	7.48	7.46	7.46	7.42	7.42
2	Benzene	GC (FID)	0.62	0.58	0.54	0.03	0.01
3	Toluene	GC (FID)	0.84	0.65	0.58	0.23	0.12
4	Phenol	HACH DR 3900	0.64	0.52	0.44	0.18	0.14
5	Lead	AAS (FLAME)	0.84	0.64	0.43	0.12	0.01
6	Chromium	AAS (FLAME)	0.92	0.81	0.62	0.23	0.01
7	Copper	AAS (FLAME)	0.05	0.04	0.03	0.02	0.01
8	Iron	AAS (FLAME)	4.97	3.76	1.20	0.23	0.20
9	Zinc	AAS (FLAME)	0.22	0.20	0.18	0,03	0.02
10	Phosphate	HACH DR 3900	0.68	0.48	0.41	0.24	0.14
11	Ammonia	HACH DR 3900	12.82	10.20	2.20	0.36	0.30
12	Nitrates	HACH DR 3900	26.82	21.46	18.14	8.82	8.16
13	TDS	TDS Meter	7,150	6,250	6,020	5,800	5,150
14	Chlorides	Titrimetry	8,000	7,500	7,200	6,150	5,950
15	Salinity	Titrimetry	6,600	6,250	5,100	2,800	2,500

Note: PW – Produced Water; TDS – Total Dissolved Solids; P1-Production Manifold; P2-PW Surge Drum Inlet; P3-Hydrocyclone Inlet; P4-PW Degasser Inlet; P5-PW Analyser Exit.

APPENDIX C: POLLUTANT CONCENTRATIONS AT DIFFERENT TEMPERATURE AND PRESSURE AT THE SELECTED SAMPLING POINTS IN IZOMBE FLOWSTATION

Table C1: Pollutants concentrations at different temperatures and pressures at the Production Manifold

Concentrations at varying Temperatures at the Production Manifold								
S/N	**Sample Parameter**	**117psi, 41°C (mg/l)**	**25°C (mg/l)**	**30°C (mg/l)**	**35°C (mg/l)**	**45°C (mg/l)**	**50°C (mg/l)**	**55°C (mg/l)**
1	Benzene	0.52	0.6743	0.6525	0.6236	0.3163	0.2105	0.1503
2	Toluene	0.51	0.5018	0.5055	0.5081	0.5105	0.5104	0.5094
3	Phenol	0.75	0.7237	0.7326	0.7408	0.7560	0.7635	0.7711
4	Lead	1.37	1.3210	1.3374	1.3527	1.3814	1.3958	1.4108
5	Chromium	0.90	0.8680	0.8788	0.8887	0.9074	0.9166	0.9263
6	Copper	0.05	0.0493	0.0497	0.0499	0.0500	0.0459	0.0397
7	Iron	4.99	4.8182	4.8767	4.9301	5.0286	5.0768	5.1259
8	Zinc	0.23	0.2293	0.2302	0.2305	0.2292	0.2177	0.1856
9	Phosphate	0.05	0.0497	0.0499	0.0500	0.0458	0.0326	0.0163
10	Ammonia	11.20	13.780	12.849	12.041	10.204	9.144	8.1416
11	Nitrates	20.46	20.487	20.546	20.542	20.359	20.183	19.951
12	Chlorides	6,200	6029.6	6092.2	6145.6	6231.5	6266.4	6297.1
13	Salinity	9,683	13362	12010	10857	9004.8	8254.2	7594.9
Concentrations at varying Pressures at the Production Manifold								
S/N	**Sample Parameter**	**117psi, 41°C (mg/l)**	**90psi (mg/l)**	**100psi (mg/l)**	**110psi (mg/l)**	**125psi (mg/l)**	**135psi (mg/l)**	**145psi (mg/l)**
1	Benzene	0.52	0.4183	0.4619	0.5099	0.3918	0.2915	0.1952
2	Toluene	0.51	0.7815	0.7133	0.6115	0.4083	0.2805	0.1505
3	Phenol	0.75	0.9844	0.9389	0.8736	0.5597	0.3809	0.2359
4	Lead	1.37	1.3967	1.3865	1.3767	0.1263	0.1135	0.0944
5	Chromium	0.90	0.9174	0.9108	0.9044	0.8591	0.8090	0.7830

6	Copper	0.05	0.0504	0.0503	0.0501	0.0459	0.0427	0.0394
7	Iron	4.99	5.0842	5.0485	5.0138	0.4596	0.3730	0.3021
8	Zinc	0.23	0.2306	0.2305	0.2303	0.2266	0.2129	0.2083
9	Phosphate	0.05	0.0502	0.0502	0.0501	0.0499	0.0497	0.0496
10	Ammonia	11.20	8.7189	9.6262	10.547	11.955	12.911	13.883
11	Nitrates	20.46	20.461	20.478	20.474	20.435	20.393	20.340
12	Salinity	9,683	7618.4	8378.5	9144.0	10302	11081	11866

Table C 2: Pollutants concentrations at different temperatures and pressures at the Line Heater Exit

Concentrations at varying Temperatures at the Line Heater Exit								
S/N	**Sample Parameter**	**38.5psi, 52°C (mg/l)**	**35°C (mg/l)**	**40°C (mg/l)**	**45°C (mg/l)**	**50°C (mg/l)**	**55°C (mg/l)**	**60°C (mg/l)**
1	Benzene	0.20	0.2524	0.2407	0.2342	0.2231	0.1052	0.0287
2	Toluene	0.16	0.1983	0.1942	0.1827	0.1708	0.1058	0.0531
3	Phenol	0.24	0.2307	0.2330	0.2356	0.2386	0.2422	0.2516
4	Lead	0.99	0.9480	0.9581	0.9699	0.9837	1.0003	1.0447
5	Chromium	0.79	0.7574	0.7653	0.7745	0.7852	0.7979	0.8319
6	Copper	0.04	0.0419	0.0414	0.0409	0.0403	0.0219	0.0087
7	Iron	3.07	2.9574	2.9853	3.0169	3.0536	3.0967	3.2094
8	Zinc	0.21	0.2269	0.2228	0.2180	0.2124	0.1916	0.1854
9	Phosphate	0.17	0.1816	0.1788	0.1755	0.1717	0.1673	0.1569
10	Ammonia	8.27	9.8923	9.3602	8.8772	8.4361	5.8308	5.3073
11	Nitrates	22.50	24.636	24.109	23.497	19.801	18.026	17.265
12	Salinity	8,507	11505	10485	9589.5	8798.1	8094.9	6902.3
Concentrations at varying Pressures at the Line Heater Exit								
S/N	**Sample Parameter**	**38.5psi, 52°C (mg/l)**	**25psi (mg/l)**	**30psi (mg/l)**	**35psi (mg/l)**	**45psi (mg/l)**	**50psi (mg/l)**	**55psi (mg/l)**
1	Benzene	0.20	0.1905	0.1959	0.1973	0.2046	0.2075	0.2099

2	Toluene	0.16	0.1580	0.1593	0.1594	0.1609	0.1614	0.1618
3	Phenol	0.24	0.2646	0.2592	0.2513	0.2137	0.1876	0.1543
4	Lead	0.99	1.0101	0.9986	0.9958	0.7799	0.5733	0.3675
5	Chromium	0.79	0.8057	0.7968	0.7946	0.7521	0.6870	0.6424
6	Copper	0.04	0.0392	0.0397	0.0398	0.0404	0.0406	0.2023
7	Iron	3.07	4.9255	4.7446	4.0859	2.0421	1.0240	0.0303
8	Zinc	0.21	0.2029	0.2071	0.2080	0.2134	0.2155	0.2355
9	Phosphate	0.17	0.1652	0.1681	0.1686	0.1723	0.1737	0.1749
10	Ammonia	8.27	6.2143	7.0360	7.7073	9.3430	10.168	10.997
11	Nitrates	22.50	21.607	22.132	22.244	22.935	23.201	23.426
12	Salinity	8,507	6515.0	7363.8	7942.5	9596.5	10426	11259

Table C 3: Pollutants concentrations at different temperatures and pressures at the Water Injection (WIJ) Pump

Concentrations at varying Temperatures at the WIJ Pump								
S/N	**Sample Parameter**	**14.7psi, 31°C (mg/l)**	**15°C (mg/l)**	**20°C (mg/l)**	**25°C (mg/l)**	**35°C (mg/l)**	**40°C (mg/l)**	**45°C (mg/l)**
1	Benzene	0.03	0.04268	0.0398	0.03616	0.0211	0.01194	0.006
2	Toluene	0.07	0.07157	0.0712	0.07076	0.0654	0.05840	0.047
3	Phenol	0.15	0.14589	0.1469	0.14823	0.1514	0.15347	0.1552
4	Lead	0.37	0.35930	0.3621	0.36534	0.3737	0.37929	0.38615
5	Chromium	0.66	0.64130	0.6462	0.65189	0.6665	0.67610	0.68792
6	Copper	0.01	0.01033	0.0103	0.01016	0.0099	0.00969	0.00924
7	Iron	0.40	0.38971	0.3925	0.39559	0.4035	0.40860	0.41482
8	Zinc	0.19	0.20147	0.1987	0.19515	0.1660	0.13029	0.06738
9	Phosphate	0.20	2.1502	2.1362	2.0756	1.6639	1.31213	0.95313
10	Ammonia	5.61	6.84758	6.4140	6.02584	4.5584	2.96840	0.16017
11	Nitrates	18.42	1.97517	1.9418	1.90102	1.7966	1.73306	1.66254
12	Salinity	7,123	9946.6	8918.7	8032.9	6593.4	6003.8	5482.5
Concentrations at varying Pressures at the WIJ Pump								

S/N	Sample Parameter	14.7psi, 31°C (mg/l)	5psi (mg/l)	10psi (mg/l)	20psi (mg/l)	25psi (mg/l)	30psi (mg/l)	35psi (mg/l)
1	Benzene	0.03	0.02779	0.0291	0.03072	0.0312	0.03159	0.03188
2	Toluene	0.07	0.06864	0.0695	0.07033	0.0705	0.07060	0.07063
3	Phenol	0.15	0.15371	0.1515	0.14267	0.1336	0.11672	0.0812
4	Lead	0.37	0.37958	0.3739	0.32659	0.2394	0.12816	0.02842
5	Chromium	0.66	0.67677	0.6668	0.54010	0.3293	0.14529	0.02056
6	Copper	0.01	0.00971	0.0099	0.01008	0.0101	0.01016	0.01018
7	Iron	0.40	0.40925	0.4038	0.39664	0.3540	0.29168	0.23585
8	Zinc	0.19	0.18022	0.1862	0.19299	0.1950	0.19643	0.19747
9	Phosphate	0.20	19.1335	19.667	20.2571	20.425	20.5430	20.6256
10	Ammonia	5.61	3.70476	4.6829	6.66462	7.6685	8.68124	9.70295
11	Nitrates	18.42	17.3032	17.982	18.7709	19.010	19.1865	19.3184
12	Salinity	7,123	4727.2	5959.7	8440.4	968.62	10942	12201

APPENDIX D: POLLUTANT CONCENTRATIONS AT DIFFERENT TEMPERATURE AND PRESSURE AT THE SELECTED SAMPLING POINTS IN FPSO PRINCESS AWENI

Table D 1: Pollutants concentrations at different temperatures and pressures at the Production Manifold

Concentrations at varying Temperatures at the Production Manifold								
S/N	**Sample Parameter**	**296psi, 61°C (mg/l)**	**45°C (mg/l)**	**50°C (mg/l)**	**55°C (mg/l)**	**65°C (mg/l)**	**70°C (mg/l)**	**75°C (mg/l)**
1	Benzene	0.64	0.6217	0.6299	0.6362	0.6441	0.6460	0.6467
2	Toluene	0.84	0.8081	0.8208	0.8314	0.8473	0.8532	0.8579
3	Phenol	0.64	0.6095	0.6204	0.6299	0.6461	0.6531	0.6596
4	Lead	0.84	0.7980	0.8124	0.8250	0.8464	0.8559	0.8648
5	Chromium	0.92	0.8791	0.8948	0.9087	0.9322	0.9425	0.9522
6	Copper	0.05	0.0513	0.0520	0.0527	0.0537	0.0540	0.0543
7	Iron	4.93	4.6948	4.7783	4.8513	4.9747	5.0282	5.0780
8	Zinc	0.23	0.2235	0.2267	0.2293	0.2329	0.2340	0.2347
9	Phosphate	0.69	0.6630	0.6729	0.6809	0.6922	0.6959	0.6985
10	Ammonia	12.82	16.300	14.984	13.899	11.825	10.752	10.083
11	Nitrates	27.03	26.112	26.480	26.770	27.153	27.261	27.319
12	Salinity	6,583	8760.1	7965.0	7282.9	6176.2	5722.7	5321.3
Concentrations at varying Pressures at the Production Manifold								
S/N	**Sample Parameter**	**296psi, 61°C (mg/l)**	**270psi (mg/l)**	**280psi (mg/l)**	**290psi (mg/l)**	**300psi (mg/l)**	**310psi (mg/l)**	**320psi (mg/l)**
1	Benzene	0.64	0.6474	0.6453	0.643	0.6317	0.6138	0.5935
2	Toluene	0.84	0.8721	0.8644	0.8548	0.7842	0.7236	0.6327
3	Phenol	0.64	0.6481	0.645	0.6418	0.6138	0.5836	0.5124
4	Lead	0.84	0.8490	0.8449	0.8408	0.7866	0.7233	0.6283
5	Chromium	0.92	0.9351	0.9305	0.9260	0.8921	0.8469	0.8012
6	Copper	0.05	0.0539	0.0537	0.0535	0.0482	0.0441	0.0385

7	Iron	4.93	4.9906	4.9665	4.9425	4.6184	4.0943	3.487
8	Zinc	0.23	0.2340	0.2331	0.2322	0.2123	0.1544	0.0184
9	Phosphate	0.69	0.6954	0.6927	0.6900	0.6572	0.5844	0.4681
10	Ammonia	12.82	11.478	11.989	12.510	13.0399	13.5807	14.1322
11	Nitrates	27.03	27.285	27.188	27.088	25.986	23.8818	21.0755
12	Salinity	6,583	5995.4	6221.7	6449.2	6677.7	6907.4	7138.2

Table D 2: Pollutants concentrations at different temperatures and pressures at the Produced Water (PW) Surge Drum Inlet

Concentrations at varying Temperatures at the PW Surge Drum Inlet								
S/N	**Sample Parameter**	**29.1psi, 60°C (mg/l)**	**45°C (mg/l)**	**50°C (mg/l)**	**55°C (mg/l)**	**65°C (mg/l)**	**70°C (mg/l)**	**75°C (mg/l)**
1	Benzene	0.60	0.6447	0.6305	0.6144	0.5772	0.5562	0.5337
2	Toluene	0.66	0.6765	0.6721	0.6666	0.6422	0.6143	0.5732
3	Phenol	0.52	0.5074	0.5115	0.5162	0.5281	0.5357	0.5447
4	Lead	0.64	0.6173	0.6228	0.6291	0.6457	0.6565	0.6697
5	Chromium	0.81	0.7895	0.7962	0.8041	0.8244	0.8376	0.8536
6	Copper	0.04	0.0397	0.0393	0.0389	0.0367	0.0321	0.0292
7	Iron	3.73	3.6288	3.6563	3.6880	3.7685	3.8202	3.8822
8	Zinc	0.20	0.2118	0.2084	0.2045	0.1909	0.1853	0.1791
9	Phosphate	0.49	0.5111	0.5042	0.4960	0.4661	0.4264	0.4051
10	Ammonia	10.18	11.858	11.254	10.699	8.7024	5.9501	2.8215
11	Nitrates	21.14	22.604	22.180	21.692	20.1253	19.1849	18.0115
12	Salinity	6,225	8010.9	7346.5	6754.9	5747.7	5315.2	4921.1
Concentrations at varying Pressures at the PW Surge Drum Inlet								
S/N	**Sample Parameter**	**29.1psi, 60°C (mg/l)**	**15psi (mg/l)**	**20psi (mg/l)**	**25psi (mg/l)**	**35psi (mg/l)**	**40psi (mg/l)**	**45psi (mg/l)**
1	Benzene	0.60	0.5483	0.5694	0.5858	0.6094	0.6180	0.6252

2	Toluene	0.66	0.6431	0.6509	0.6565	0.6637	0.6659	0.6676
3	Phenol	0.52	0.5378	0.5307	0.5253	0.5017	0.4714	0.4251
4	Lead	0.64	0.6582	0.6487	0.6414	0.5831	0.4927	0.4162
5	Chromium	0.81	0.8400	0.8282	0.8193	0.748	0.678	0.6179
6	Copper	0.04	0.0369	0.0376	0.0380	0.0387	0.0389	0.0391
7	Iron	3.73	3.8332	3.7857	3.7493	3.269	2.675	1.366
8	Zinc	0.20	0.1879	0.1933	0.1974	0.203	0.205	0.2067
9	Phosphate	0.49	0.4615	0.4728	0.4812	0.4928	0.4969	0.5001
10	Ammonia	10.18	6.7211	7.9412	9.1697	11.652	12.906	14.169
11	Nitrates	21.14	19.664	20.313	20.812	21.518	21.773	21.982
12	Salinity	6,225	4135.2	4874.8	5615.0	7103.3	7849.5	8597.2

Table D 3: Pollutants concentrations at different temperatures and pressures at the Hydrocyclone Inlet

Concentrations at varying Temperatures at the Hydrocyclone Inlet								
S/N	**Sample Parameter**	**98psi, 60^{o}C (mg/l)**	**45^{o}C (mg/l)**	**50^{o}C (mg/l)**	**55^{o}C (mg/l)**	**65^{o}C (mg/l)**	**70^{o}C (mg/l)**	**75^{o}C (mg/l)**
1	Benzene	0.54	0.5994	0.5973	0.5741	0.4349	0.2828	0.0252
2	Toluene	0.58	0.5803	0.5814	0.5818	0.4809	0.3579	0.2157
3	Phenol	0.43	0.4249	0.4277	0.4305	0.4362	0.4392	0.4424
4	Lead	0.43	0.4196	0.4225	0.4254	0.4314	0.4347	0.4382
5	Chromium	0.63	0.6173	0.6216	0.6258	0.6344	0.6391	0.6441
6	Copper	0.03	0.0334	0.0334	0.0334	0.02832	0.0233	0.0173
7	Iron	1.54	1.5108	1.5207	1.5303	1.5499	1.5602	1.5712
8	Zinc	0.18	0.1850	0.1847	0.1842	0.1422	0.0881	0.0279
9	Phosphate	0.41	0.4124	0.4122	0.4114	0.3081	0.2405	0.2022
10	Ammonia	2.94	3.451	3.2608	3.091	2.3001	1.3742	0.3558
11	Nitrates	18.10	19.325	19.280	18.9033	15.9551	12.7831	7.9757

12	Salinity	5,167	6626.6	6077.7	5594.5	3785.9	2945.3	2413.9

Concentrations at varying Pressures at the Hydrocyclone Inlet

S/N	Sample Parameter	98psi, 60°C (mg/l)	85psi (mg/l)	90psi (mg/l)	95psi (mg/l)	105psi (mg/l)	110psi (mg/l)	115psi (mg/l)
1	Benzene	0.54	0.5386	0.5388	0.5396	0.5408	0.5412	0.5414
2	Toluene	0.58	0.6841	0.6725	0.6421	0.4808	0.3801	0.2274
3	Phenol	0.43	0.4736	0.4652	0.4534	0.3317	0.2306	0.1429
4	Lead	0.43	0.4316	0.4303	0.4291	0.3467	0.2255	0.1244
5	Chromium	0.63	0.6347	0.6328	0.6311	0.5576	0.4225	0.2246
6	Copper	0.03	0.0334	0.0334	0.0333	0.0283	0.0234	0.0182
7	Iron	1.54	1.5510	1.5467	1.5425	1.3534	0.8304	0.2165
8	Zinc	0.18	0.1831	0.1832	0.1833	0.1834	0.1834	0.1833
9	Phosphate	0.41	0.4098	0.4099	0.4100	0.3099	0.2098	0.1896
10	Ammonia	2.94	2.5681	2.7096	2.8522	3.1410	3.2871	3.4345
11	Nitrates	18.10	18.046	18.069	18.087	18.109	18.114	18.116
12	Salinity	5,167	4549.2	4786.2	5023.8	5500.7	5739.91	5979.7

Table D 4: Pollutants concentrations at different temperatures and pressures at the Produced Water (PW) Degasser Inlet

Concentrations at varying Temperatures at the PW Degasser Inlet

S/N	Sample Parameter	19.1psi, 60°C (mg/l)	45°C (mg/l)	50°C (mg/l)	55°C (mg/l)	65°C (mg/l)	70°C (mg/l)	75°C (mg/l)
1	Benzene	0.03	0.0336	0.0336	0.0335	0.02931	0.02329	0.0083
2	Toluene	0.23	0.2187	0.2234	0.2298	0.2084	0.1629	0.1129
3	Phenol	0.18	0.1720	0.1730	0.1740	0.1760	0.1769	0.1780
4	Lead	0.13	0.1228	0.1235	0.1243	0.1257	0.1265	0.1273
5	Chromium	0.23	0.2292	0.2306	0.2320	0.2347	0.2361	0.2375
6	Copper	0.02	0.0216	0.0216	0.0217	0.0162	0.0124	0.0085
7	Iron	0.22	0.2179	0.2192	0.2205	0.2229	0.2241	0.2253

8	Zinc	0.03	0.0334	0.0334	0.0334	0.0272	0.0231	0.0173
9	Phosphate	0.23	0.2334	0.2336	0.2336	0.2032	0.1739	0.1331
10	Ammonia	0.37	0.4343	0.4090	0.3867	0.3487	0.3324	0.3175
11	Nitrates	8.73	8.7752	8.7729	8.7583	8.593	8.342	8.078
12	Salinity	2,817	3612.4	3313.2	3049.9	2609.1	2423.5	2256.6

Concentrations at varying Pressures at the PW Degasser Inlet

S/N	Sample Parameter	19.1psi, 60°C (mg/l)	5psi (mg/l)	10psi (mg/l)	15psi (mg/l)	25psi (mg/l)	30psi (mg/l)	35psi (mg/l)
1	Benzene	0.03	0.0333	0.0333	0.0333	0.0263	0.0163	0.0083
2	Toluene	0.23	0.2307	0.2305	0.2302	0.2129	0.1892	0.1189
3	Phenol	0.18	0.1862	0.1857	0.1843	0.1644	0.1474	0.1336
4	Lead	0.13	0.1358	0.1335	0.1315	0.1094	0.0523	0.0089
5	Chromium	0.23	0.2349	0.2343	0.2337	0.1925	0.1213	0.0084
6	Copper	0.02	0.0217	0.0217	0.0217	0.0186	0.0142	0.0091
7	Iron	0.22	0.2231	0.2225	0.2220	0.2109	0.2042	0.1799
8	Zinc	0.03	0.0333	0.0333	0.0333	0.0273	0.0211	0.0173
9	Phosphate	0.23	0.2336	0.2335	0.2334	0.2033	0.1732	0.1332
10	Ammonia	0.37	0.3195	0.3375	0.3557	0.3926	0.4114	0.4303
11	Nitrates	8.73	8.7279	8.7308	8.7318	8.7292	8.7258	8.7213
12	Salinity	2,817	2480.1	2609.3	2738.8	2998.7	3129.2	3259.9

Table D 5: Pollutants concentrations at different temperatures and pressures at the Produced Water (PW) Analyser Exit

Concentrations at varying Temperatures at the PW Analyser Exit

S/N	Sample Parameter	14.7psi, 30°C (mg/l)	15°C (mg/l)	20°C (mg/l)	25°C (mg/l)	35°C (mg/l)	40°C (mg/l)	45°C (mg/l)
1	Benzene	0.01	0.0102	0.0102	0.0101	0.0054	0.0051	0.005
2	Toluene	0.12	0.1246	0.1218	0.1196	0.1135	0.1082	0.1022

3	Phenol	0.14	0.1283	0.1304	0.1346	0.1426	0.1428	0.1434
4	Lead	0.01	0.0075	0.0082	0.0088	0.0116	0.0128	0.0138
5	Chromium	0.01	0.0078	0.0079	0.0084	0.0113	0.0118	0.0122
6	Copper	0.01	0.013	0.0124	0.0115	0.0068	0.0062	0.0061
7	Iron	0.19	0.0126	0.0151	0.0178	0.0191	0.0192	0.0193
8	Zinc	0.02	0.0219	0.0219	0.0218	0.0182	0.0143	0.01121
9	Phosphate	0.14	0.1594	0.1508	0.1485	0.1238	0.1004	0.0902
10	Ammonia	0.32	0.3842	0.3636	0.3442	0.2515	0.1712	0.1004
11	Nitrates	8.19	0.9123	0.8992	0.8647	0.6811	0.5017	0.2906
12	Salinity	2,458	2665.3	1217.7	871.2	438.4	402.1	385.8

Concentrations at varying Pressures at the PW Analyser Exit

S/N	**Sample Parameter**	**14.7psi, 30°C (mg/l)**	**5psi (mg/l)**	**10psi (mg/l)**	**20psi (mg/l)**	**25psi (mg/l)**	**30psi (mg/l)**	**35psi (mg/l)**
1	Benzene	0.01	0.0098	0.0099	0.0101	0.0101	0.0101	0.0101
2	Toluene	0.12	0.1181	0.1183	0.1162	0.1141	0.1108	0.1076
3	Phenol	0.14	0.1416	0.1407	0.1293	0.1093	0.1011	0.1001
4	Lead	0.01	0.0101	0.0101	0.0084	0.0056	0.0053	0.0051
5	Chromium	0.01	0.0101	0.0101	0.0089	0.0054	0.0052	0.0047
6	Copper	0.01	0.0099	0.01	0.01	0.01	0.01	0.01
7	Iron	0.19	0.0222	0.0211	0.01591	0.01052	0.00855	0.00825
8	Zinc	0.02	0.0174	0.0196	0.0223	0.0225	0.0226	0.0228
9	Phosphate	0.14	0.1402	0.1412	0.1412	0.1417	0.1419	0.142
10	Ammonia	0.32	0.2116	0.2687	0.3250	0.3463	0.3607	0.3702
11	Nitrates	8.19	0.7443	0.7837	0.8196	0.8198	0.8217	0.82414
12	Salinity	2,458	1628.5	2055.3	2915.0	3347.9	3783.0	4220.2

APPENDIX E: PICTURES OF ACTIVITIES AT FIELD AND IN THE LABORATORY

Pic E1: Sample collection bottles for analysis

Pic E 2: Sample Collection at Different Sampling Points in Crude Oil Production Facilities in Nigeria

Pic E 3: Sessions in the laboratory including:

(i) Top Left: Extracting Produced Water Sample from the Sampling Container for Analysis

(ii) Top right: Determining the Concentrations of Benzene and Toluene Pollutants at the Gas Chromatograph with Flame Ionisation Detector (GC-FID).

(iii) Bottom left: Measuring the pH of Produced Water Samples

(iv) Bottom right: Reading of the Basic Sediment and Water (BSW) value from Crude Oil Sample from a Centrifuge Machine.

APPENDIX F: SAMPLE LABORATORY RAW RESULTS

```
Date File C: /CHEM32/1/DATA/IESL OB 90/IESL2  2017-11-30  11-21-
05/141F0301.D

Sample Name: POINT 2
=====================================================
Acq. Operator         : IESL                      Seq. Line :  3
Acq. Instrument       : Instrument  1       Location  :  Vial 141
Injection Date        : 20/12/2017  11:53:07 AM     Inj:    I
Acq. Method           : C:/CHEM32/1/DATA/IESL OB 90/IESL2 2017-11-30
11-21-05/BTEX.M
Last changed          : 5/26/2016 6:44:51 PM by IESL
Analysis Method       :C:/CHEM32/1/METHODs/BTEX.M
Last changed          :12/21/2017 3:42:57 PM by IESL
                      (Modified after loading)
Method Info           : BTEX METOD
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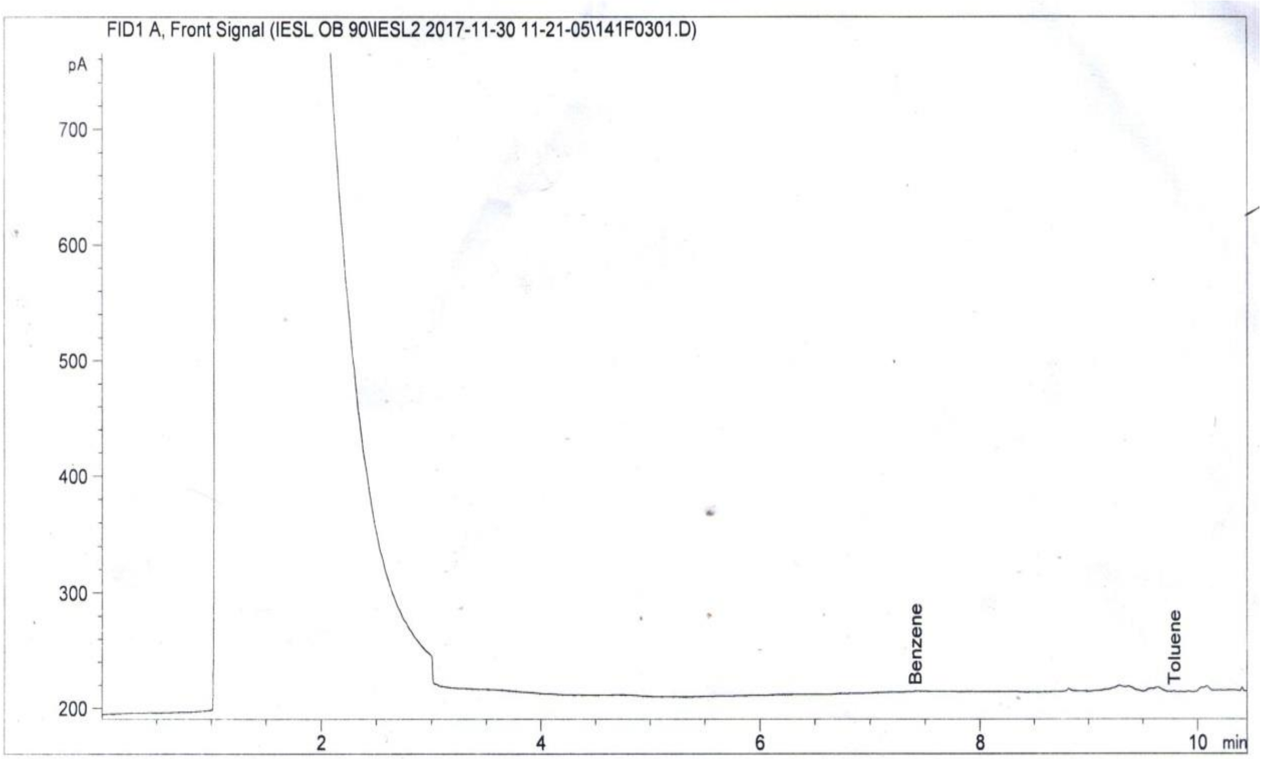

```
==================================================
                  External Standard Report
==================================================
Sorted by              :        Signal
Calib. Data Modified   :        12/21/2017 3:42:52 PM
Multiplier             :        6.000e-3
Dilution               :        1.0000
Do not Multiplier & Dilution Factor with ISTDs
```

```
Signal 1:  FID1 A, Front Signal

RetTime    Type        Area      Amt/Area   Amount     Grp   Name
(min)       (pA*s)                          (mg/L)
--------|-------|--------|--------|-------|--|----------------------------
-
7.410      VV         1.68856    18.63933   1.88842e-1    Benzene
9.786      VV         1.27588    18.90717   1.44740e-1    Toluene
Totals:                                     3.33582e-1

============================================================

Instrument 1 12/21/2017 3:43:03 PM IESL


Date File C: /CHEM32/1/DATA/IESL OB 90/IESL2  2017-11-30  11-21-
05/141F0401.D
Sample Name: POINT 3
==============================================================
Acq. Operator    : IESL                      Seq. Line :  4

Acq. Instrument  : Instrument  1             Location  :  Vial 141
Injection Date   : 20/12/2017  11:53:07 AM             Inj:     I
                                              Inj Volume: 1 Ul

Acq. Method      : C:/CHEM32/1/DATA/IESL OB 90/IESL2 2017-11-30 11-
21-05/BTEX.M
Last changed     : 5/26/2016 6:44:51 PM by IESL
Analysis Method  : C:/CHEM32/1/METHODS/BTEX.M
Last changed     : 12/21/2017 3:54:34 PM by IESL
                      (Modified after loading)
Method Info      : BTEX METOD
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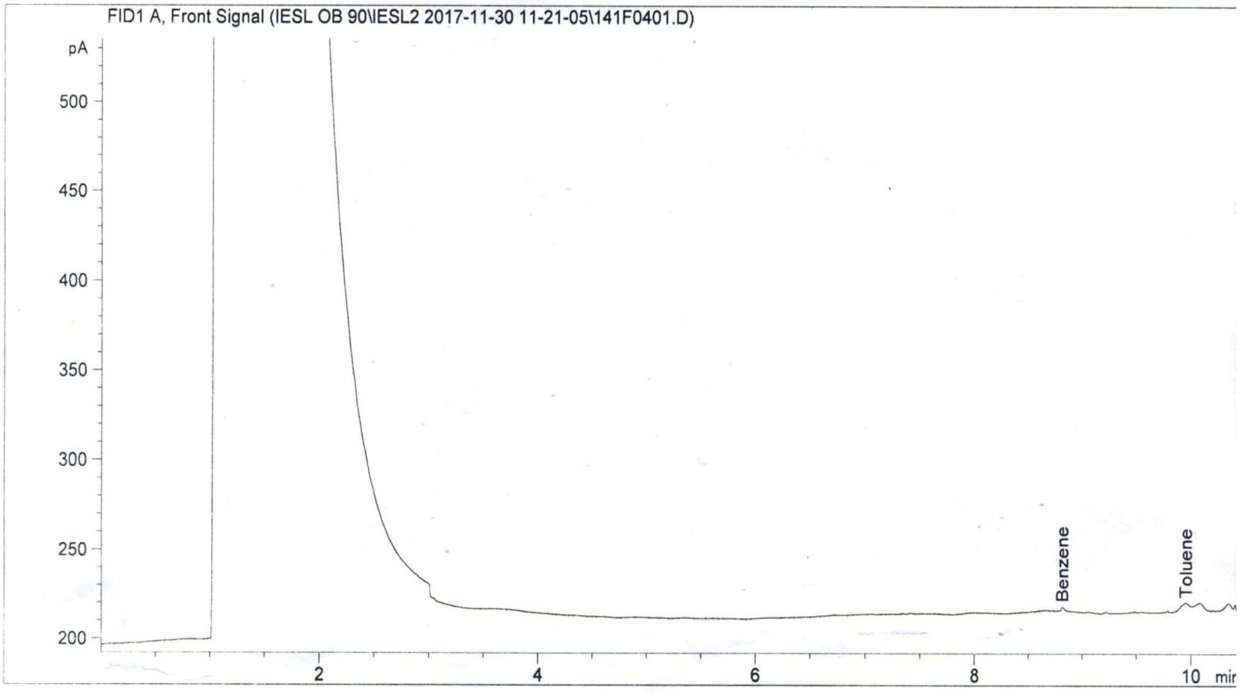
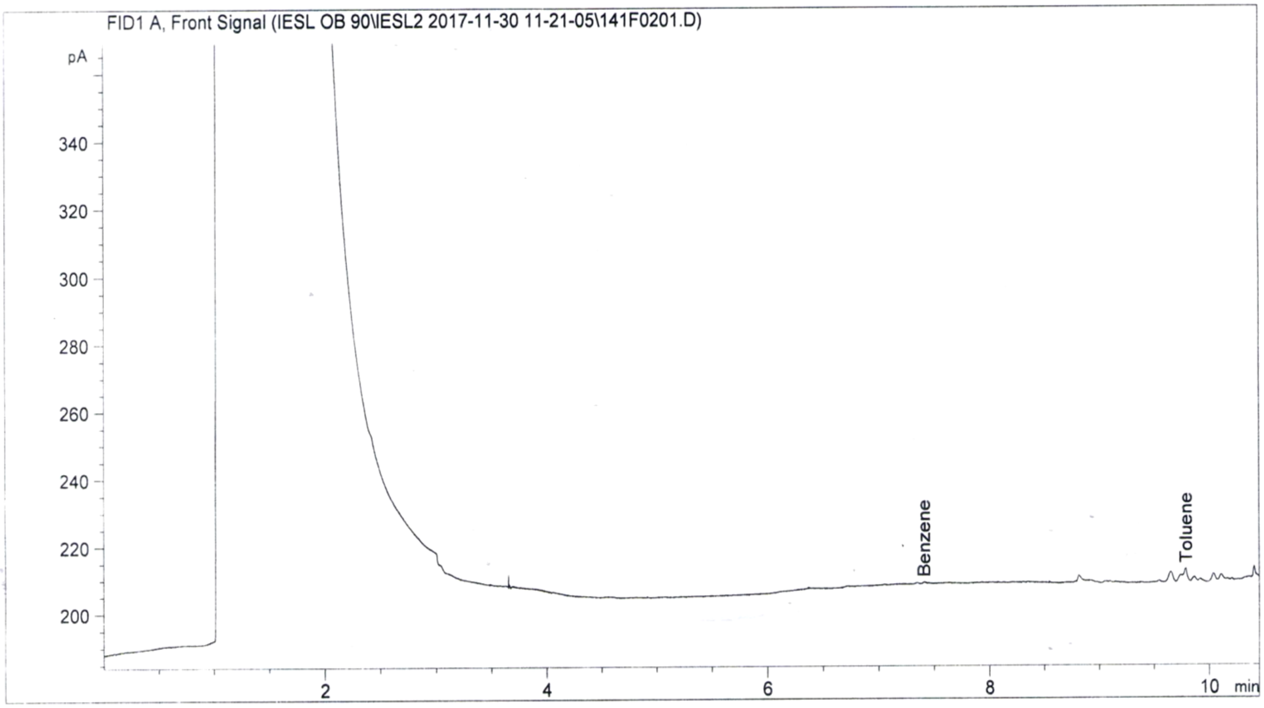


```
Calib. Data Modified   :        12/21/2017 3:54:34 PM
Multiplier             :        6.000e-3
Dilution               :        1.0000
Do not use Multiplier & Dilution Factor with ISTDs
Signal 1:  FID1 A, Front Signal

RetTime    Type      Area      Amt/Area     Amount     Grp Name
(min)       (pA*s)                          (mg/L)
--------|-------|--------|--------|-------|--|-----------------------------
---
8.814      BB        4.83532    6.48361e-1 1.88102e-2      Benzene

9.953      BV        27.30191   5.03406e-1 8.24636e-2      Toluene

Totals:                                   1.01274e-1

============================================================
Instrument 1 12/21/2017 3:54:40 PM IESL
```

```
Date File C: /CHEM32/1/DATA/IESL OB 90/IESL2  2017-11-30  11-21-
05/141F0201.D

Sample Name: POINT 1
============================================================
Acq. Operator    : IESL                             Seq. Line :  2
Acq. Instrument  : Instrument  1                    Location  :  Vial
141
Injection Date   : 20/12/2017  11:37:58 AM                   Inj:  I
                                                     Inj Volume: 1 UI


Acq. Method      : C:/CHEM32/1/DATA/IESL OB 90/IESL2 2017-11-30 11-
21-05/BTEX.M
Last changed     : 5/26/2016 6:44:51 PM by IESL
Analysis Method  :C:/CHEM32/1/METHODS/BTEX.M
Last changed     :12/21/2017 3:40:53 PM by IESL
                     (Modified after loading)
Method Info      : BTEX METOD
```



```
Sorted by              :          Signal

Calib. Data Modified :          12/21/2017 3:40:16 PM

Multiplier             :          6.000e-3

Dilution               :          1.0000

Do not use Multiplier & Dilution Factor with ISTDs

============================================================
                 External Standard Report
 ============================================================
Signal 1:  FID1 A, Front Signal

Calib. Data Modified   :          12/21/2017 3:40:16 PM
Multiplier              :          6.000e-3
Dilution                :          1.0000
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1:  FID1 A, Front Signal

RitTime    Type   Area        Amt/Area   Amount   Grp   Name
(min)             (pA*s)                 (mg/L)
--------|-------|--------|-----|----------------|--|-----------------------
-
7.405      VV    9.98394e-1  8.34516   4.99905e-1     Benzene
9.786      VV    9.48418     9.06454   5.15818e-1     Toluene
Totals:                               5.65809e-1

============================================================
Instrument 1 12/21/2017 3:41:25 PM IESL
```

APPENDIX G: CHANGES IN CONCENTRATIONS OF POLLUTANTS AT THE IZOMBE FLOWSTATION FROM SIMULATIONS

TABLE G1: EFFECT CHANGES IN TEMPERATURE ON CONCENTRATION AT THE MANIFOLD

	25^{0}C		**30^{0}C**		**35^{0}C**		**41^{0}C**		**45^{0}C**		**50^{0}C**		**55^{0}C**
Benzene	0.6043	0.0036	0.6225	0.0002	0.6236	-0.0173	0.5200	**-0.0509**	0.3163	-0.0212	0.2105	-0.0120	0.1503
Toluene	0.5018	**0.0007**	0.5055	0.0005	0.5081	0.0003	0.5100	0.0001	0.5105	0.0000	0.5104	-0.0002	0.5094
Phenol	0.7237	**0.0018**	0.7326	0.0016	0.7408	0.0015	0.7500	0.0015	0.7560	0.0015	0.7635	0.0015	0.7711
Lead x 0.10	1.3210	**0.0033**	1.3374	0.0031	1.3527	0.0029	1.3700	0.0028	1.3814	0.0029	1.3958	0.0030	1.4108
Chromium	0.8680	**0.0022**	0.8788	0.0020	0.8887	0.0019	0.9000	0.0018	0.9074	0.0018	0.9166	0.0019	0.9263
Copper	0.0493	0.0001	0.0497	0.0000	0.0499	0.0000	0.0500	0.0000	0.0500	-0.0008	0.0459	**-0.0012**	0.0397
Iron x 0.10	4.8182	**0.0117**	4.8767	0.0107	4.9301	0.0100	4.9900	0.0096	5.0286	0.0096	5.0768	0.0098	5.1259
Zinc	0.2293	0.0002	0.2302	0.0001	0.2305	0.0001	0.2310	-0.0005	0.2292	-0.0023	0.2177	**-0.0064**	0.1856
Phosphate x 100	0.0497	0.0000	0.0499	0.0000	0.0500	0.0000	0.0500	-0.0011	0.0458	-0.0026	0.0326	**-0.0033**	0.0163
Ammonia	13.7800	-0.1862	12.8490	-0.1616	12.0410	-0.1402	11.2000	**-0.2490**	10.2040	-0.2120	9.1440	-0.2005	8.1416
Nitrates	20.4870	0.0118	20.5460	-0.0008	20.5420	-0.0137	20.4600	-0.0252	20.3590	-0.0352	20.1830	**-0.0464**	19.9510

TABLE G2: EFFECT CHANGES IN TEMPERATURE ON CONCENTRATION AT THE LINE HEATER EXIT

	35^{0}C		**40^{0}C**		**45^{0}C**		**50^{0}C**		**52^{0}C**		**55^{0}C**		**60^{0}C**
Benzene	0.2524	-0.0023	0.2407	-0.0013	0.2342	-0.0022	0.2231	-0.0116	0.2000	**-0.0316**	0.1052	-0.0153	0.0287
Toluene	0.1983	-0.0008	0.1942	-0.0023	0.1827	-0.0024	0.1708	-0.0054	0.1600	**-0.0181**	0.1058	-0.0105	0.0531
Phenol	0.2307	0.0005	0.2330	0.0005	0.2356	0.0006	0.2386	0.0007	0.2400	0.0007	0.2422	**0.0019**	0.2516
Lead	0.9480	0.0020	0.9581	0.0024	0.9699	0.0028	0.9837	0.0031	0.9900	0.0034	1.0003	**0.0089**	1.0447
Chromium	0.7574	0.0016	0.7653	0.0018	0.7745	0.0021	0.7852	0.0024	0.7900	0.0026	0.7979	**0.0068**	0.8319
Copper	0.0419	-0.0001	0.0414	-0.0001	0.0409	-0.0001	0.0403	-0.0002	0.0400	**-0.0060**	0.0219	-0.0026	0.0087
Iron x 0.10	2.9574	0.0056	2.9853	0.0063	3.0169	0.0073	3.0536	0.0082	3.0700	0.0089	3.0967	**0.0225**	3.2094
Zinc	0.2269	-0.0008	0.2228	-0.0010	0.2180	-0.0011	0.2124	-0.0012	0.2100	-0.0061	0.1916	**-0.0012**	0.1854
Phosphate x 100	0.1816	-0.0006	0.1788	-0.0007	0.1755	-0.0008	0.1717	-0.0008	0.1700	-0.0009	0.1673	**-0.0021**	0.1569
Ammonia	9.8923	-0.1064	9.3602	-0.0966	8.8772	-0.0882	8.4361	-0.0831	8.2700	**-0.8131**	5.8308	-0.1047	5.3073
Nitrates	24.6360	-0.1054	24.1090	-0.1224	23.4970	-0.7392	19.8010	1.3495	22.5000	**-1.4913**	18.0260	-0.1522	17.2650

TABLE G3: EFFECT CHANGES IN TEMPERATURE ON CONCENTRATIONS AT THE WATER INJECTION PUMP

	15^{0}C		**20^{0}C**		**25^{0}C**		**31^{0}C**		**35^{0}C**		**40^{0}C**		**45^{0}C**
Benzene	0.0427	-0.0006	0.0398	-0.0007	0.0362	-0.0010	0.0300	**-0.0022**	0.0211	-0.0018	0.0119	-0.0012	0.0060
Toluene	0.0716	-0.0001	0.0712	-0.0001	0.0708	-0.0001	0.0700	-0.0012	0.0654	-0.0014	0.0584	**-0.0023**	0.0470
Phenol	0.1459	0.0002	0.1469	0.0003	0.1482	0.0003	0.1500	0.0004	0.1514	**0.0004**	0.1535	0.0003	0.1552
Lead	0.3593	0.0006	0.3621	0.0006	0.3653	0.0008	0.3700	**0.0009**	0.3737	0.0011	0.3793	0.0014	0.3862
Chromium	0.6413	0.0010	0.6462	0.0011	0.6519	0.0014	0.6600	0.0016	0.6665	0.0019	0.6761	**0.0024**	0.6879
Copper	0.0103	0.0000	0.0103	0.0000	0.0102	0.0000	0.0100	0.0000	0.0099	0.0000	0.0097	**-0.0001**	0.0092
Iron	0.3897	0.0006	0.3925	0.0006	0.3956	0.0007	0.4000	0.0009	0.4035	0.0010	0.4086	**0.0012**	0.4148
Zinc	0.2015	-0.0006	0.1987	-0.0007	0.1952	-0.0009	0.1900	-0.0060	0.1660	-0.0071	0.1303	**-0.0126**	0.0674
Phosphate x 100	2.1502	-0.0028	2.1362	-0.0121	2.0756	-0.0126	2.0000	**-0.0840**	1.6639	-0.0704	1.3121	-0.0718	0.9531
Ammonia	6.8476	-0.0867	6.4140	-0.0776	6.0258	-0.0693	5.6100	-0.2629	4.5584	-0.3180	2.9684	**-0.5616**	0.1602
Nitrates	1.9752	-0.0067	1.9418	-0.0082	1.9010	-0.0098	1.8420	-0.0114	1.7966	-0.0127	1.7331	**-0.0141**	1.6625

TABLE G4: EFFECT CHANGES IN PRESSURE ON CONCENTRATION AT THE MANIFOLD

	90psi		**100psi**		**110psi**		**117psi**		**125psi**		**135psi**		**145psi**
Benzene	0.4183	0.0044	0.4619	0.0048	0.5099	0.0014	0.5200	**-0.0160**	0.3918	-0.0100	0.2915	-0.0096	0.1952
Toluene	0.7815	-0.0068	0.7133	-0.0102	0.6115	-0.0145	0.5100	-0.0127	0.4083	-0.0128	0.2805	**-0.0130**	0.1505
Phenol	0.9844	**-0.0046**	0.9389	-0.0065	0.8736	-0.0177	0.7500	**-0.0238**	0.5597	-0.0179	0.3809	-0.0145	0.2359
Lead x 0.10	0.1397	-0.0001	0.1387	-0.0001	0.1377	-0.0001	0.1370	-0.0013	0.1263	-0.0013	0.1135	**-0.0019**	0.0944
Chromium	0.9174	-0.0007	0.9108	-0.0006	0.9044	-0.0006	0.9000	**-0.0051**	0.8591	-0.0050	0.8090	-0.0026	0.7830
Copper	0.0504	0.0000	0.0503	0.0000	0.0501	0.0000	0.0500	**-0.0005**	0.0459	-0.0003	0.0427	-0.0003	0.0394
Iron x 0.10	0.5084	-0.0004	0.5049	-0.0003	0.5014	-0.0003	0.4990	-0.0049	0.4596	**-0.0087**	0.3730	-0.0071	0.3021
Zinc	0.2306	0.0000	0.2305	0.0000	0.2303	0.0000	0.2300	-0.0004	0.2266	-0.0014	0.2129	**-0.0005**	0.2083
Phosphate x 100	0.0502	0.0000	0.0502	0.0000	0.0501	0.0000	0.0500	0.0000	0.0499	**0.0000**	0.0497	0.0000	0.0496
Ammonia	8.7189	0.0907	9.6262	0.0921	10.5470	0.0933	11.2000	0.0944	11.9550	0.0956	12.9110	**0.0972**	13.8830
Nitrates	20.4610	0.0017	20.4780	-0.0004	20.4740	-0.0020	20.4600	-0.0031	20.4350	-0.0042	20.3930	**-0.0053**	20.3400

TABLE G5: EFFECT CHANGES IN PRESSURE ON CONCENTRATION AT THE LINE HEATER EXIT

	25psi		**30psi**		**35psi**		**38.5psi**		**45psi**		**50psi**		**55psi**
Benzene	0.1905	**0.0011**	0.1959	0.0003	0.1973	0.0008	0.2000	0.0007	0.2046	0.0006	0.2075	0.0005	0.2099
Toluene	0.1580	**0.0003**	0.1593	0.0000	0.1594	0.0002	0.1600	0.0001	0.1609	0.0001	0.1614	0.0001	0.1618
Phenol	0.2646	-0.0011	0.2592	-0.0016	0.2513	-0.0032	0.2400	-0.0040	0.2137	-0.0052	0.1876	**-0.0067**	0.1543
Lead	1.0101	-0.0023	0.9986	-0.0006	0.9958	-0.0017	0.9900	-0.0323	0.7799	**-0.0413**	0.5733	-0.0412	0.3675
Chromium	0.8057	-0.0018	0.7968	-0.0004	0.7946	-0.0013	0.7900	-0.0058	0.7521	**-0.0130**	0.6870	-0.0089	0.6424
Copper	0.0392	0.0001	0.0397	0.0000	0.0398	0.0001	0.0400	0.0001	0.0404	0.0000	0.0406	**0.0323**	0.2023
Iron	4.9255	**-0.0362**	4.7446	-0.1317	4.0859	-0.2903	3.0700	-0.1581	2.0421	-0.2036	1.0240	-0.1987	0.0303
Zinc	0.2029	0.0008	0.2071	0.0002	0.2080	0.0006	0.2100	0.0005	0.2134	0.0004	0.2155	**0.0040**	0.2355
Phosphate x 100	0.1652	**0.0006**	0.1681	0.0001	0.1686	0.0004	0.1700	0.0004	0.1723	0.0003	0.1737	0.0002	0.1749
Ammonia	6.2143	0.1643	7.0360	0.1343	7.7073	0.1608	8.2700	0.1651	9.3430	0.1650	10.1680	**0.1658**	10.9970
Nitrates	21.6070	**0.1050**	22.1320	0.0224	22.2440	0.0731	22.5000	0.0669	22.9350	0.0532	23.2010	0.0450	23.4260

TABLE G6: EFFECT CHANGES IN PRESSURE ON CONCENTRATIONS AT THE WATER INJECTION PUMP

	5psi		**10psi**		**14.7psi**		**20psi**		**25psi**		**30psi**		**35psi**
Benzene	0.0278	**0.0003**	0.0291	0.0002	0.0300	0.0001	0.0307	0.0001	0.0312	0.0001	0.0316	0.0001	0.0319
Toluene	0.0686	**0.0002**	0.0695	0.0001	0.0700	0.0001	0.0703	0.0000	0.0705	0.0000	0.0706	0.0000	0.0706
Phenol	0.1537	-0.0004	0.1515	-0.0003	0.1500	-0.0014	0.1427	-0.0018	0.1336	-0.0034	0.1167	**-0.0071**	0.0812
Lead	0.3796	-0.0011	0.3739	-0.0008	0.3700	-0.0082	0.3266	-0.0174	0.2394	**-0.0222**	0.1282	-0.0199	0.0284
Chromium	0.6768	-0.0020	0.6668	-0.0014	0.6600	-0.0226	0.5401	**-0.0422**	0.3293	-0.0368	0.1453	-0.0249	0.0206
Copper	0.0097	**0.0000**	0.0099	0.0000	0.0100	0.0000	0.0101	0.0000	0.0101	0.0000	0.0102	0.0000	0.0102
Iron	0.4093	-0.0011	0.4038	-0.0008	0.4000	-0.0006	0.3966	-0.0085	0.3540	**-0.0125**	0.2917	-0.0112	0.2359
Zinc	0.1802	**0.0012**	0.1862	0.0008	0.1900	0.0006	0.1930	0.0004	0.1950	0.0003	0.1964	0.0002	0.1975
Phosphate x 100	19.1335	**0.1067**	19.6670	0.0709	20.0000	0.0485	20.2571	0.0336	20.4250	0.0236	20.5430	0.0165	20.6256
Ammonia	3.7048	0.1956	4.6829	0.1973	5.6100	0.1990	6.6646	0.2008	7.6685	0.2025	8.6812	**0.2043**	9.7030
Nitrates	17.3032	**0.1358**	17.9820	0.0932	18.4200	0.0662	18.7709	0.0478	19.0100	0.0353	19.1865	0.0264	19.3184

APPENDIX H: CHANGES IN CONCENTRATIONS OF POLLUTANTS AT THE FPSO PRINCESS AWENI FROM SIMULATIONS

TABLE H1: EFFECT CHANGES IN TEMPERATURE ON CONCENTRATION AT THE MANIFOLD

	45^{0}C		**50^{0}C**		**55^{0}C**		**61^{0}C**		**65^{0}C**		**70^{0}C**		**75^{0}C**
Benzene	0.6217	**0.0016**	0.6299	0.0013	0.6362	0.0006	0.6400	0.0010	0.6441	0.0004	0.6460	0.0001	0.6467
Toluene	0.8081	**0.0025**	0.8208	0.0021	0.8314	0.0014	0.8400	0.0018	0.8473	0.0012	0.8532	0.0009	0.8579
Phenol	0.6095	**0.0022**	0.6204	0.0019	0.6299	0.0017	0.6400	0.0015	0.6461	0.0014	0.6531	0.0013	0.6596
Lead	0.7980	**0.0029**	0.8124	0.0025	0.8250	0.0025	0.8400	0.0016	0.8464	0.0019	0.8559	0.0018	0.8648
Chromium	0.8791	**0.0031**	0.8948	0.0028	0.9087	0.0019	0.9200	0.0031	0.9322	0.0021	0.9425	0.0019	0.9522
Copper	0.0513	0.0001	0.0520	0.0001	0.0527	0.0001	0.0530	**0.0002**	0.0537	0.0001	0.0540	0.0001	0.0543
Iron x 0.1	0.4695	**0.0017**	0.4778	0.0015	0.4851	0.0013	0.4930	0.0011	0.4975	0.0011	0.5028	0.0010	0.5078
Zinc	0.2235	0.0006	0.2267	0.0005	0.2293	0.0001	0.2300	**0.0007**	0.2329	0.0002	0.2340	0.0001	0.2347
Phosphate	0.6630	**0.0020**	0.6729	0.0016	0.6809	0.0015	0.6900	0.0006	0.6922	0.0007	0.6959	0.0005	0.6985
Ammonia	16.3000	**-0.2632**	14.9840	-0.2170	13.8990	-0.1798	12.8200	-0.2488	11.8250	-0.2146	10.7520	-0.1338	10.0830
Nitrates	26.1120	**0.0736**	26.4800	0.0580	26.7700	0.0433	27.0300	0.0307	27.1530	0.0216	27.2610	0.0116	27.3190

TABLE H2: EFFECT CHANGES IN TEMPERATURE ON CONCENTRATION AT THE PW SURGE DRUM INLET

	45^{0}C		**50^{0}C**		**55^{0}C**		**60^{0}C**		**65^{0}C**		**70^{0}C**		**75^{0}C**
Benzene	0.6447	-0.0028	0.6305	-0.00322	0.6144	-0.00288	0.6	**-0.00456**	0.5772	-0.0042	0.5562	-0.0045	0.5337
Toluene	0.6765	-0.0009	0.6721	-0.0011	0.6666	-0.00132	0.66	-0.00356	0.6422	-0.00558	0.6143	**-0.00822**	0.5732
Phenol	0.5074	0.00082	0.5115	0.00094	0.5162	0.00076	0.52	0.00162	0.5281	0.00152	0.5357	**0.0018**	0.5447
Lead	0.6173	0.0011	0.6228	0.00126	0.6291	0.00218	0.64	0.00114	0.6457	0.00216	0.6565	**0.00264**	0.6697
Chromium	0.7895	0.00134	0.7962	0.00158	0.8041	0.00118	0.81	0.00288	0.8244	0.00264	0.8376	**0.0032**	0.8536
Copper	0.0397	-8E-05	0.0393	-8E-05	0.0389	0.00022	0.04	**-0.00066**	0.0367	-0.00092	0.0321	-0.00058	0.0292
Iron x 0.1	0.3629	0.00055	0.3656	0.000634	0.3688	0.00084	0.373	0.00077	0.3769	0.001034	0.382	**0.00124**	0.38822
Zinc	0.2118	-0.0007	0.2084	-0.00078	0.2045	-0.0009	0.2	-0.00182	0.1909	-0.00112	0.1853	**-0.00124**	0.1791
Phosphate	0.5111	-0.0014	0.5042	-0.00164	0.496	-0.0012	0.49	-0.00478	0.4661	**-0.00794**	0.4264	-0.00426	0.4051
Ammonia	11.858	-0.1208	11.254	-0.111	10.699	-0.1038	10.18	-0.29552	8.7024	-0.55046	5.9501	**-0.62572**	2.8215
Nitrates	22.604	-0.0848	22.18	-0.0976	21.692	-0.1104	21.14	-0.20294	20.125	-0.18808	19.185	**-0.23468**	18.0115

TABLE H3: EFFECT CHANGES IN TEMPERATURE ON CONCENTRATION AT THE HYDORCYCLONE

	45^{0}C		**50^{0}C**		**55^{0}C**		**60^{0}C**		**65^{0}C**		**70^{0}C**		**75^{0}C**
Benzene	0.5994	-0.0004	0.5973	-0.0046	0.5741	-0.0068	0.5400	-0.0210	0.4349	-0.0304	0.2828	**-0.0515**	0.0252
Toluene	0.5803	0.0002	0.5814	0.0001	0.5818	-0.0004	0.5800	-0.0198	0.4809	-0.0246	0.3579	**-0.0284**	0.2157
Phenol	0.4249	0.0006	0.4277	0.0006	0.4305	-0.0001	0.4300	**0.0012**	0.4362	0.0006	0.4392	0.0006	0.4424
Lead	0.4196	0.0006	0.4225	0.0006	0.4254	**0.0009**	0.4300	0.0003	0.4314	0.0007	0.4347	0.0007	0.4382
Chromium	0.6173	0.0009	0.6216	0.0008	0.6258	0.0008	0.6300	0.0009	0.6344	0.0009	0.6391	**0.0010**	0.6441
Copper	0.0334	0.0000	0.0334	0.0000	0.0334	-0.0007	0.0300	-0.0003	0.0283	-0.0010	0.0233	**-0.0012**	0.0173
Iron x 0.1	0.1511	0.0002	0.1521	0.0002	0.1530	0.0002	0.1540	0.0002	0.1550	0.0002	0.1560	**0.0002**	0.1571
Zinc	0.1850	-0.0001	0.1847	-0.0001	0.1842	-0.0008	0.1800	-0.0076	0.1422	-0.0108	0.0881	**-0.0120**	0.0279
Phosphate	0.4124	0.0000	0.4122	-0.0002	0.4114	-0.0003	0.4100	**-0.0204**	0.3081	-0.0135	0.2405	-0.0077	0.2022
Ammonia	3.4510	-0.0380	3.2608	-0.0340	3.0910	-0.0302	2.9400	-0.1280	2.3001	-0.1852	1.3742	**-0.2037**	0.3558
Nitrates	19.3250	-0.0090	19.2800	-0.0753	18.9033	-0.1607	18.1000	-0.4290	15.9551	-0.6344	12.7831	**-0.9615**	7.9757

TABLE H4: EFFECT CHANGES IN TEMPERATURE ON CONCENTRATION AT THE DEGASSER INLET

	45^{0}C		**50^{0}C**		**55^{0}C**		**60^{0}C**		**65^{0}C**		**70^{0}C**		**75^{0}C**
Benzene	0.0336	0.0000	0.0336	0.0000	0.0335	0.0000	0.0333	-0.0008	0.0293	-0.0012	0.0233	**-0.0030**	0.0083
Toluene	0.2187	0.0009	0.2234	0.0013	0.2298	0.0000	0.2300	-0.0043	0.2084	-0.0091	0.1629	**-0.0100**	0.1129
Phenol	0.1720	0.0002	0.1730	0.0002	0.1740	0.0002	0.1750	0.0002	0.1760	0.0002	0.1769	**0.0002**	0.1780
Lead	0.1228	0.0001	0.1235	0.0002	0.1243	0.0001	0.1250	0.0001	0.1257	0.0002	0.1265	**0.0002**	0.1273
Chromium	0.2292	0.0003	0.2306	0.0003	0.2320	0.0002	0.2330	0.0003	0.2347	0.0003	0.2361	**0.0003**	0.2375
Copper	0.0216	0.0000	0.0216	0.0000	0.0217	-0.0003	0.0200	-0.0008	0.0162	-0.0008	0.0124	**-0.0008**	0.0085
Iron	0.2179	0.0003	0.2192	0.0003	0.2205	**0.0003**	0.2220	0.0002	0.2229	0.0002	0.2241	0.0002	0.2253
Zinc	0.0334	0.0000	0.0334	0.0000	0.0334	0.0000	0.0333	**-0.0012**	0.0272	-0.0008	0.0231	-0.0012	0.0173
Phosphate	0.2334	0.0000	0.2336	0.0000	0.2336	-0.0007	0.2300	-0.0054	0.2032	-0.0059	0.1739	**-0.0082**	0.1331
Ammonia	0.4343	**-0.0051**	0.4090	-0.0045	0.3867	-0.0033	0.3700	-0.0043	0.3487	-0.0033	0.3324	-0.0030	0.3175
Nitrates x 0.1	0.8775	0.0000	0.8773	-0.0003	0.8758	-0.0006	0.8730	-0.0027	0.8593	-0.0050	0.8342	**-0.0053**	0.8078

TABLE H5: EFFECT CHANGES IN TEMPERATURE ON CONCENTRATION AT THE MANIFOLD

	15^{0}C		**20^{0}C**		**25^{0}C**		**30^{0}C**		**35^{0}C**		**40^{0}C**		**45^{0}C**
Benzene	0.0102	0.0000	0.0102	0.0000	0.0101	0.0000	0.0100	**-0.0009**	0.0054	-0.0001	0.0051	0.0000	0.0050
Toluene	0.1246	-0.0006	0.1218	-0.0004	0.1196	-0.0003	0.1180	-0.0009	0.1135	-0.0011	0.1082	**-0.0012**	0.1022
Phenol	0.1283	0.0004	0.1304	0.0008	0.1346	**0.0011**	0.1400	0.0005	0.1426	0.0000	0.1428	0.0001	0.1434
Lead	0.0075	0.0001	0.0082	0.0001	0.0088	0.0002	0.0100	**0.0003**	0.0116	0.0002	0.0128	0.0002	0.0138
Chromium	0.0078	0.0000	0.0079	0.0001	0.0084	**0.0003**	0.0100	0.0003	0.0113	0.0001	0.0118	0.0001	0.0122
Copper	0.0130	-0.0001	0.0124	-0.0002	0.0115	-0.0003	0.0100	**-0.0006**	0.0068	-0.0001	0.0062	0.0000	0.0061
Iron x 0.1	0.0126	0.0005	0.0151	**0.0005**	0.0178	0.0002	0.0190	0.0000	0.0191	0.0000	0.0192	0.0000	0.0193
Zinc	0.0219	0.0000	0.0219	0.0000	0.0218	0.0000	0.0217	-0.0007	0.0182	**-0.0008**	0.0143	-0.0006	0.0112
Phosphate	0.1594	-0.0017	0.1508	-0.0005	0.1485	-0.0017	0.1400	-0.0032	0.1238	**-0.0047**	0.1004	-0.0020	0.0902
Ammonia	0.3842	-0.0041	0.3636	-0.0039	0.3442	-0.0048	0.3200	-0.0137	0.2515	**-0.0161**	0.1712	-0.0142	0.1004
Nitrates x 0.1	0.9123	-0.0026	0.8992	-0.0069	0.8647	-0.0091	0.8190	-0.0276	0.6811	-0.0359	0.5017	**-0.0422**	0.2906

TABLE H6: EFFECT CHANGES IN PRESSURE ON CONCENTRATION AT THE PRODUCTION MANIFOLD

	270psi		**280psi**		**290psi**		**296psi**		**300psi**		**310psi**		**320psi**
Benzene	0.6474	-0.0002	0.6453	-0.0002	0.6430	-0.0001	0.6420	-0.0010	0.6317	-0.0018	0.6138	**-0.0020**	0.5935
Toluene	0.8510	0.0013	0.8644	-0.0010	0.8548	-0.0014	0.8410	-0.0057	0.7842	-0.0061	0.7236	**-0.0091**	0.6327
Phenol	0.6481	-0.0003	0.6450	-0.0003	0.6418	-0.0002	0.6400	-0.0026	0.6138	-0.0030	0.5836	**-0.0071**	0.5124
Lead	0.8490	-0.0004	0.8449	-0.0004	0.8408	-0.0001	0.8400	-0.0053	0.7866	-0.0063	0.7233	**-0.0095**	0.6283
Chromium	0.9351	-0.0005	0.9305	-0.0004	0.9260	-0.0004	0.9220	-0.0030	0.8921	-0.0045	0.8469	**-0.0046**	0.8012
Copper	0.0539	0.0000	0.0537	0.0000	0.0535	0.0000	0.0533	-0.0005	0.0482	-0.0004	0.0441	**-0.0006**	0.0385
Iron x 0.1	0.4991	-0.0002	0.4967	-0.0002	0.4943	-0.0001	0.4930	-0.0031	0.4618	-0.0052	0.4094	**-0.0061**	0.3487
Zinc	0.2340	-0.0001	0.2331	-0.0001	0.2322	0.0000	0.2318	-0.0020	0.2123	-0.0058	0.1544	**-0.0136**	0.0184
Phosphate	0.6954	-0.0003	0.6927	-0.0003	0.6900	0.0000	0.6900	-0.0033	0.6572	-0.0073	0.5844	**-0.0116**	0.4681
Ammonia	11.4782	0.0511	11.9890	0.0521	12.5100	0.0310	12.8200	0.0220	13.0399	0.0541	13.5807	**0.0551**	14.1322
Nitrates	27.2848	-0.0097	27.1880	-0.0100	27.0880	-0.0058	27.0300	-0.1044	25.9860	-0.2104	23.8818	**-0.2806**	21.0755

TABLE H7: EFFECT CHANGES IN PRESSURE ON CONCENTRATION AT THE PRODUCED WATER SURGE DRUM INLET

	15psi		**20psi**		**25psi**		**29.1psi**		**35psi**		**40psi**		**45psi**
Benzene	0.5483	**0.0042**	0.5694	0.0033	0.5858	0.0028	0.6000	0.0019	0.6094	0.0017	0.6180	0.0014	0.6252
Toluene	0.6431	**0.0016**	0.6509	0.0011	0.6565	0.0007	0.6600	0.0007	0.6637	0.0004	0.6659	0.0003	0.6676
Phenol	0.5378	-0.0014	0.5307	-0.0011	0.5253	-0.0011	0.5200	-0.0037	0.5017	-0.0061	0.4714	**-0.0093**	0.4251
Lead	0.6582	-0.0019	0.6487	-0.0015	0.6414	-0.0003	0.6400	-0.0114	0.5831	**-0.0181**	0.4927	-0.0153	0.4162
Chromium	0.8400	-0.0024	0.8282	-0.0018	0.8193	-0.0019	0.8100	-0.0124	0.7480	**-0.0140**	0.6780	-0.0120	0.6179
Copper	0.0369	0.0001	0.0376	0.0001	0.0380	**0.0004**	0.0400	-0.0003	0.0387	0.0000	0.0389	0.0000	0.0391
Iron x 0.1	0.3833	-0.0009	0.3786	-0.0007	0.3749	-0.0004	0.3730	-0.0092	0.3269	-0.0119	0.2675	**-0.0262**	0.1366
Zinc	0.1879	**0.0011**	0.1933	0.0008	0.1974	0.0005	0.2000	0.0006	0.2030	0.0004	0.2050	0.0003	0.2067
Phosphate	0.4615	**0.0023**	0.4728	0.0017	0.4812	0.0018	0.4900	0.0006	0.4928	0.0008	0.4969	0.0006	0.5001
Ammonia	6.7211	0.2440	7.9412	0.2457	9.1697	0.2021	10.1800	**0.2944**	11.6520	0.2508	12.9060	0.2526	14.1690
Nitrates	19.6640	**0.1298**	20.3130	0.0998	20.8120	0.0656	21.1400	0.0756	21.5180	0.0510	21.7730	0.0418	21.9820

TABLE H8: EFFECT CHANGES IN PRESSURE ON CONCENTRATION AT THE HYDROCYCLONE INLET

	85psi		**90psi**		**95psi**		**98psi**		**105psi**		**110psi**		**115psi**
Benzene	0.5386	0.0000	0.5388	**0.0002**	0.5396	0.0001	0.5400	0.0001	0.5408	0.0001	0.5412	0.0000	0.5414
Toluene	0.6841	-0.0023	0.6725	-0.0061	0.6421	-0.0204	0.5810	-0.0143	0.4808	-0.0201	0.3801	**-0.0305**	0.2274
Phenol	0.4736	-0.0017	0.4652	-0.0024	0.4534	-0.0071	0.4320	-0.0143	0.3317	**-0.0202**	0.2306	-0.0175	0.1429
Lead	0.4316	-0.0003	0.4303	-0.0002	0.4291	0.0003	0.4300	-0.0119	0.3467	**-0.0242**	0.2255	-0.0202	0.1244
Chromium	0.6347	-0.0004	0.6328	-0.0003	0.6311	-0.0004	0.6300	-0.0103	0.5576	-0.0270	0.4225	**-0.0396**	0.2246
Copper	0.0334	0.0000	0.0334	0.0000	0.0333	**-0.0011**	0.0300	-0.0002	0.0283	-0.0010	0.0234	-0.0010	0.0182
Iron	1.5510	-0.0009	1.5467	-0.0008	1.5425	-0.0008	1.5400	-0.0267	1.3534	-0.1046	0.8304	**-0.1228**	0.2165
Zinc	0.1831	0.0000	0.1832	0.0000	0.1833	**-0.0011**	0.1800	0.0005	0.1834	0.0000	0.1834	0.0000	0.1833
Phosphate	0.4098	0.0000	0.4099	0.0000	0.4100	0.0000	0.4100	-0.0143	0.3099	**-0.0200**	0.2098	-0.0040	0.1896
Ammonia	2.5681	0.0283	2.7096	0.0285	2.8522	0.0293	2.9400	0.0287	3.1410	0.0292	3.2871	**0.0295**	3.4345
Nitrates x 0.1	1.8046	**0.0005**	1.8069	0.0004	1.8087	0.0004	1.8100	0.0001	1.8109	0.0001	1.8114	0.0000	1.8116

TABLE H9: EFFECT CHANGES IN PRESSURE ON CONCENTRATION AT THE PRODUCED WATER DEGASSER INLET

	5psi		**10psi**		**15psi**		**19.1psi**		**25psi**		**30psi**		**35psi**
Benzene	0.0333	0.0000	0.0333	0.0000	0.0333	0.0000	0.0333	-0.0010	0.0263	**-0.0020**	0.0163	-0.0016	0.0083
Toluene	0.2307	0.0000	0.2305	-0.0001	0.2302	-0.0001	0.2300	-0.0024	0.2129	-0.0047	0.1892	**-0.0141**	0.1189
Phenol	0.1862	-0.0001	0.1857	-0.0003	0.1843	-0.0031	0.1750	-0.0015	0.1644	**-0.0034**	0.1474	-0.0028	0.1336
Lead	0.1358	-0.0005	0.1335	-0.0004	0.1315	-0.0022	0.1250	-0.0022	0.1094	**-0.0114**	0.0523	-0.0087	0.0089
Chromium	0.2349	-0.0001	0.2343	-0.0001	0.2337	-0.0002	0.2330	-0.0058	0.1925	-0.0142	0.1213	**-0.0226**	0.0084
Copper	0.0217	0.0000	0.0217	0.0000	0.0217	0.0000	0.0217	-0.0004	0.0186	-0.0009	0.0142	**-0.0010**	0.0091
Iron	0.2231	-0.0001	0.2225	-0.0001	0.2220	**-0.0003**	0.2210	-0.0014	0.2109	-0.0013	0.2042	**-0.0049**	0.1799
Zinc	0.0333	0.0000	0.0333	0.0000	0.0333	0.0000	0.0333	-0.0009	0.0273	**-0.0012**	0.0211	-0.0008	0.0173
Phosphate	0.2336	0.0000	0.2335	0.0000	0.2334	-0.0011	0.2300	-0.0038	0.2033	-0.0060	0.1732	**-0.0080**	0.1332
Ammonia	0.3195	0.0036	0.3375	0.0036	0.3557	**0.0048**	0.3700	0.0032	0.3926	0.0038	0.4114	0.0038	0.4303
Nitrates x 0.1	0.8728	0.0001	0.8731	0.0000	0.8732	-0.0001	0.8730	0.0000	0.8729	-0.0001	0.8726	**-0.0001**	0.8721

TABLE H10: EFFECT CHANGES IN PRESSURE ON CONCENTRATION AT THE PRODUCED WATER ANALYSER EXIT

	5psi		10psi		14.7psi		20psi		25psi		30psi		35psi
Benzene	0.0098	0.0000	0.0099	**0.0000**	0.0100	0.0000	0.0101	0.0000	0.0101	0.0000	0.0101	0.0000	0.0101
Toluene	0.1181	0.0000	0.1183	0.0000	0.1183	-0.0004	0.1162	-0.0003	0.1141	**-0.0007**	0.1108	-0.0006	0.1076
Phenol	0.1416	-0.0002	0.1407	-0.0001	0.1400	-0.0020	0.1293	**-0.0029**	0.1093	-0.0016	0.1011	-0.0002	0.1001
Lead	0.0101	0.0000	0.0101	0.0000	0.0100	-0.0003	0.0084	**-0.0004**	0.0056	-0.0001	0.0053	0.0000	0.0051
Chromium	0.0101	0.0000	0.0101	0.0000	0.0100	-0.0002	0.0089	**-0.0005**	0.0054	0.0000	0.0052	-0.0001	0.0047
Copper	0.0099	**0.0000**	0.0100	0.0000	0.0100	0.0000	0.0100	0.0000	0.0100	0.0000	0.0100	0.0000	0.0100
Iron x 0.1	0.0222	-0.0002	0.0211	-0.0004	0.0190	-0.0006	0.0159	**-0.0008**	0.0105	-0.0004	0.0086	-0.0001	0.0083
Zinc	0.0174	**0.0004**	0.0196	0.0004	0.0216	0.0001	0.0223	0.0000	0.0225	0.0000	0.0226	0.0000	0.0228
Phosphate	0.1402	0.0002	0.1412	**-0.0003**	0.1400	0.0002	0.1412	0.0001	0.1417	0.0000	0.1419	0.0000	0.1420
Ammonia	0.2116	**0.0114**	0.2687	0.0109	0.3200	0.0009	0.3250	0.0030	0.3463	0.0029	0.3607	0.0019	0.3702
Nitrates x 0.1	0.7443	**0.0079**	0.7837	0.0075	0.8190	0.0001	0.8196	0.0000	0.8198	0.0004	0.8217	0.0005	0.8241