ENHANCED OIL RECOVERY USING AIR INJECTION (CO_2)

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ABSTRACT

Air injection has traditionally been employed to extract heavy crude oil in the production field, however studies have shown that this practice is abandoned when light crude oil in the reservoir runs out. Therefore, in order to comprehend their potential for high-pressure air injection (HPAI) enhanced oil recovery (EOR), this work investigated the kinetics and combustion of light crude oil in-situ the reservoir. The approaches provided a precise description of the combustion and kinetics of three (3) light crude oils taken from the Canadian offshore of Newfoundland. The crude with the lowest API, 30.214, had the lowest enthalpy change, 10.9 J/g, and the highest onset oxidation temperature, 220 ^{o}C, while the crude with the highest API, 46.963, had the highest onset oxidation temperature. had the highest enthalpy (24.6 J/g), and its beginning oxidation temperature (140 ^{o}C) was the lowest. Studying the effects of 10% water saturation on one of the crude samples (Sample A), it was found that the onset oxidation temperature increased by 40 ^{o}C and the enthalpy change decreased by 9 J/g. These results showed that the flexible Differential Scanning Calorimetry thermograms may produce accurate oil recovery results with good correlation coefficients ($r > 0.9$) when combined with kinetic modeling technique. Then, accurate thermo-kinetic parameters might be provided using this trustworthy information, such as the onset, peak, and endset temperatures and their corresponding heat flow patterns. kinetic triplets like the reaction model, pre-exponential, and activation energy Accurate reservoir screening requirements for an air injection EOR process can also be determined.

Keyword: *Crude oil, oxidation, EOR, air injection, combustion, kinetics*

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1. INTRODUCTION

Enhanced Oil Recovery (EOR) is a tertiary recovery procedure that mobilizes oil trapped in pores by severe capillary forces after primary and secondary recovery. The most popular types of EOR processes are thermal, chemical, solvent, and gas. As a result of the decline of rising, oil production has depleted oil reserves, and there are calls for more environmentally friendly practices. Petroleum engineers are currently driving EOR projects towards more effective EOR processes techniques. One of such effective technique is the injection of air/flue gas, which is inspired by environmentally friendly carbon-dioxide (CO2) sequestration and a low-cost source of air because of its quantity and availability, air was chosen as an injectant in the EOR project, it's at a cheap price It may be delivered simply by using a compressor, and the total idea has a minimal starting cost and the cost of operation compared to other EOR method. The recovery efficiency of low permeability reservoir is from 20 to 25% in the oilfield, the proportion of low permeability reservoir in proving EOR flooding will lead to a large number of CO2 (about 40 to 60% of the injected gas) spilling out of the ground along with the gas produced during oil recovery (hereinafter refer to as extraction of gas). The flue gas (which contains nitrogen and carbon dioxide) created by the burning of oxygen in the air to sweep oil is an alternative to air injection. This EOR approach is known as light oil air injection when used in light oil reservoirs, and in-situ combustion when used in heavy oil reservoirs. Some studies carried out to describe criteria as well as performance of air injection projects gave positive results even though experimental condition could not mimic the adiabatic of the reservoir. Temperature regimes, heat energy content, pressure and temperature dependence during oil combustion were also studied using simple Arrhenius type model which assumes constant kinetic parameters throughout the reaction. There have been few researches which reports on the complexities of combustion reaction of crude oils where kinetic parameters fluctuate or the alteration of the oxidations zones.

2. LITERATURE REVIEW

Hydrocarbons in nature accumulate in geological traps underneath the earth surface called reservoirs; these reservoirs are porous and permeable and are usually trapped by water or an impermeable rock in its bank. These oil reservoirs are usually classified based on the mechanism of their production which are; water-drive, Gas cap drive and the dissolved gas drive reservoir. There are three major distinct stages in the life of an oil well; these are the primary, the secondary and the tertiary stage otherwise known as the enhanced oil recovery. The primary recovery has several mechanisms of oil production, but most importantly, production occurs at natural pressures of the reservoir i.e the reservoir energy is used to produce its hydrocarbon contents. Pump installations are necessary when the reservoir pressure drops and productions decline. This usually account for 12-15% recovery of original-oil-in-place (OOIP), this percentage is less for heavy oils but higher for lighter oils. The secondary stage is necessary after the primary stage, this is when the natural pressure has depleted and production has subsequently declined, most practices in the secondary stages include gas and water injections which were initially present in the reservoir. This technique allows the injectants to sweep the oil to the producer while still maintaining reservoir pressure. Thistype of recovery is due to energy given to the reservoir by the injection of water or gas. Water floodingis very attractive in a reservoir that has a large water aquifer and this type of recovery accounts for an additional 15-20% OOIP over primary. Tertiary recovery also known as Enhanced Oil Recovery (EOR) and historically comes after the secondary stage which requires the introduction of technique that improves reservoir oil flow to the producer. Thismay involve injection of fluids that are miscible/near miscible with oil (typically carbon dioxide), steam, air and other formulations polymers. This method recovers additional 10-15% over the secondary methods.

2.1 ENHANCED OIL RECOVERY (EOR) CONCEPT

The engineering activity applied to various oil reservoirs for the purpose of producing more hydrocarbons is termed enhanced oil recovery. This technique involves injection of material that was not initially present in the reservoir and the measure of the ability of such technique to recover more oil, other than the natural depletion of EOR efficiency. Shallow reservoirs have more viscous oil compared to deeper reservoirs and this has led to various thermal techniques to recover them. The economics of many EOR processes have so many uncertainties unfortunately, thereby requiring screening studies to be performed on each reservoir before arriving at a decision to proceed on a particular EOR technique. It should also be noted that no single EOR technique has been discovered to be applicable to all reservoirs as a unified method; therefore, techniques are usually developed to address reservoirs with particular/specific characteristics. Enhanced oil recovery (EOR) is a tertiary recovery process which is normally applied after primary and secondary recovery, applied to mobilize oil trapped in pores by vicious capillary forces. Thermal, chemical and solvent/gases are the most common form of various EOR process. Figure 2.2 shows a summary of EOR classifications as described by several authors. EOR is divided into two major parts; the thermal and the non-thermal. The thermal which is the major focus of this research involves oxidation which is instigated by oxygen present in air to produce flue gases which have been studied to be miscible with oil thereby increasing sweep efficiency of oil for incremental oil recovery.

2.2 AIR INJECTION FOR ENHANCED OIL RECOVERY (EOR)

This is another form of gas injection enhanced oil recovery (EOR) but the gas injected in this case is air. It shows a promising EOR technique for reservoir of various characteristics such as high temperature, low permeability and also light oils. The mechanism of oil recovery can be classified intotwo types; where the air injected into the reservoir, the oxygen in air combust with a small amount of oilto generate heat which in return reduce viscosity. It is called in-situ combustion but if injected air generates flue gas for the purpose of miscibility/sweeping gas in a light oil reservoir, it is called light oil air injection. The breakdown of thermal EOR method is illustrated in Figure below. The various light oil air injection are classified into air, oxygen enrichment and high pressure air injection depending on conditions set for the reservoir.

2.3 RESERVOIR FLUID STUDIES AND EXPERIMENTS

Crude oils are complex mixtures consisting basically of hydrocarbons and compounds of nitrogen, sulphur, oxygen, carbon dioxide and metals in lower concentrations (Tarek, 2007). The major and minor constituents affect the behaviour (physical and chemical properties) of the reservoir oils. Reservoir management requires reliable and accurate description of phase behaviour and volumetric data of crude oils (Danesh, 1998). The volumetric data of the oils which mimic reservoir conditions are determined experimentally as a function of Temperature and Pressure. The relationships of pressure, volume and temperature obtained from these experiments helps to optimize reservoir performances from the reservoir fields.

Generally, the laboratory tests used to characterise reservoir oil sample can be classified into three (3). They are Primary tests, Routine tests and the Special laboratory PVT tests.

2.3.1 PRIMARY TESTS

These are simple routine tests carried out on site. They include specific gravity tests and gas to oil (GOR) ratio of the produced hydrocarbons.

2.3.1.1 SPECIFIC GRAVITY (SG) TESTS

Density of oil is the ratio of mass of oil per unit volume. Crude oil density is pressure dependent due to presence of gas as its constituents and it is specified by the oil specific gravity (s.g) which is the densityof the oil relative to that of pure water both measure at standard conditions. However, it is common to use the API gravity which is related to the specific gravity given in Equation 2.39

given by;

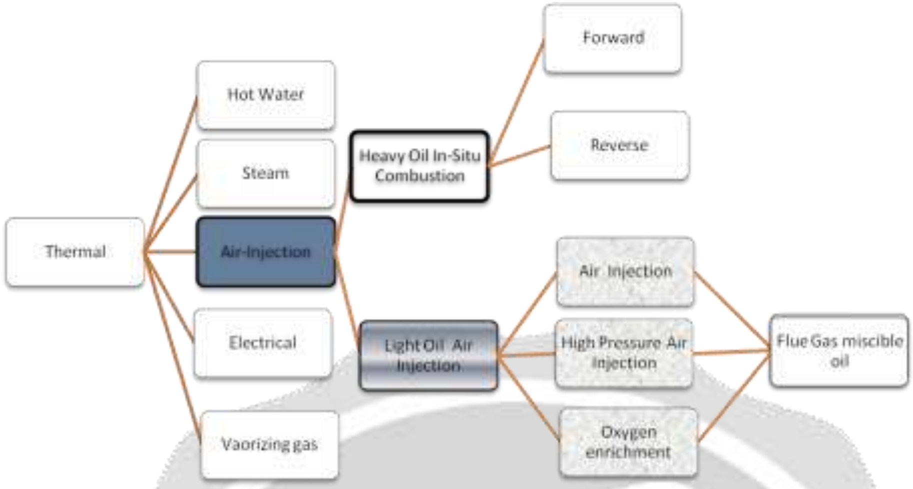


Figure 2.1: Air Injection Route in Thermal EOR Process.

Air injection process illustrated in Figure 2.5 shows where air is used to improve oil recovery. The air is injected is injected in zone A by the injector. The oxygen in air is consumed as shown in the oxygen profile at zone B where oxidation reaction occurs. In Zone C, oxidation of part of the oil with air generates heat as well as products of combustion and flue gases such as CO_2, CO and unreacted N_2 gases. Zone D shows the displacement of oil by oil viscosity reduction or flue gas sweeping as the cases may be depending on whether it is an in-situ combustion or low oil air injection. Finally, at zone E (producer section) where the displaced oil is collected and incremental production of original oil in place (OOIP) is recorded.

Proc

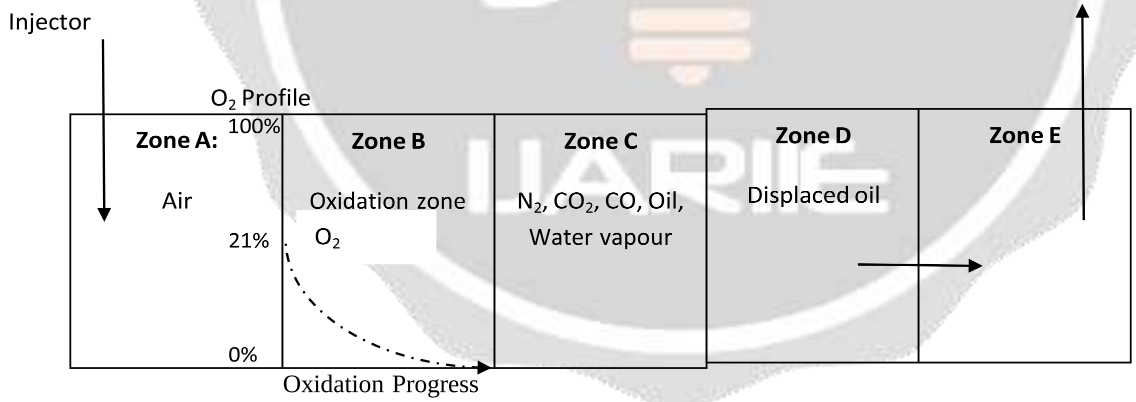


Figure 2.2: An air injection process diagram.

2.1.1 LIGHT OIL AIR INJECTION

Air injection for enhanced oil recovery is increasingly receiving considerable attention after secondary water flood process. This is due to the abundance and low cost of air. A high pressure air injection (HPAI) has also been applied to light oil reservoirs and study based on performance has led to several proposal or estimating recovery factors on such projects.

This method involves the injected air to combust a small fraction of oil to produce flue gases which is responsible for reservoir oil displacement. It also favours high recovery due to immiscible gas displacement, oil swelling, reservoir re-pressurization, flue gas stripping and sequestration.

2.2 KINETICS OF THERMAL EOR

Thermal characteristics of crude oils have been investigated over the years by the use of variousanalytical techniques. This is due to the fact that crude oil are mixtures of complex hydrocarbon fractions which tend to behave differently from reservoirs to reservoirs, so the need to fully understand its kinetics to help optimize recovery potentials.

2.2.1 COMBUSTION REACTION OF CRUDE OIL

In an air injection EOR, oxygen contained in air reacts with the hydrocarbon fuel (CH_x) at the combustionzone to generate heat, and bi-products of its combustion reaction given by the general stoichiometric equation as described by Mamora (1995).

$$CH_x + \left(1 - \frac{m}{2} + \frac{x}{4}\right) O_2 \rightarrow (1-m)CO_2 + mCO + \frac{x}{2} H_2O$$

x = atomic hydrogen-carbon (H/C) ratio of fuel, m = fraction of carbon oxidised to carbon monoxide.

2.2.2 OXIDATION OF SULFUR CONTAINING CRUDE OILS

Acidic crude oils are known to be sulphur bearing. Crude oils having sulphur contents greater than 0.15 wt% are known as sour crude while those with less than 0.15% are known as sweet crude. Sulfur contenthas been studied over the years and discovered to increase as boiling temperature of crude oil fraction increases. The sulfur containing hydrocarbons are known to have high molecular weight which is why upto 70 to 90% of all the sulfur hydrocarbons are concentrated in fuel oil and tar. Sulphur in hydrocarbons exists in many forms; as dissolved sulfur, colloidal state, dissolved H_2S, mercaptans, sulfides (thioesters), polysulfides (aliphatic), cyclic and thiophene derivatives. The cyclic and thiophene derivatives are usually found in the kerosene fraction and are extremely difficult to isolate. Thiophenes are thermally stable, and do not react with metals but they dissolve well in sulfuric acid. Resinous and asphaltene part also contain very complex compounds including sulfur, nitrogen and oxygen. Sulphur content is known to be responsible for naphthenic acid corrosion in crude oils by two (2) processes; the naphthenic attack and hydrogen sulfide attack are shown from equations 2.2 and 2.3 respectively.

$Fe + R\text{-}COOH \rightarrow Fe(RCOO)_2 + H_2$ (Naphthenic attack on Iron (carbon steel) (2.2)

$Fe + H_2S \rightarrow FeS + H_2$ (H_2S corrosion attack) (2.3)

Equation 2.4 shows the regeneration of naphthenic acid with the precipitation of iron sulfide which implies that naphthenic crude seems to be more corrosive with low sulfur at high temperature than the crude oil on high naphthenic value and with high sulfur content

$Fe(RCOO)_2 + H_2S \rightarrow FeS + 2RCOOH$ (2.4)

Nigerian crude oils are known to have very low sulfur between 0.04 to 0.15 wt% (Chevron Corporation, 2016; TOTSA, 2016). In Niger-delta region, aromatic sulphurs are common such as thiophenes. Dibenzothiophene (DBT), 1-methyl Dibenzothiophene, 4 methyl dibenzothiophene, and 2,3 dimethyl dibenzothiophene. Light crude oils are characteristic of Nigerian crude oils and C_2 - C_6 mercaptans have boiling fraction corresponding to 35-140 ^oC. Mercaptans have a characteristic unpleasant smell and can be used as an odorant in gas facilities to warn of gas leaks. Organic Sulfoxides, sulphate salts and complexes such as thiobenzophenones (TBP) $(C_6H_5)_2CS$ were found to be present in alphaltene fraction of some Nigerian crude oils. These crude oils are found in reservoirs from Belema, Imo and Eket oil fields in the Niger Delta area, Nigeria.

2.3 AIR INJECTION FOR RESERVOIR OXIDATION

Combustion or oxidation in-situ reservoir requires the oxidizing agent, heat and the fuel. Combustion of crude oil in the reservoir gives a double effect

1. Heat effects: which reduces viscosity of the oil (Kuhlman, 2000; Moore *et al.*, 1992) and
2. Fluegas sweeps: flue gas mixes with the oil, thereby increasing mobility ratio and eventually leading to enhance flow of oil to the producer. A typical crude oil combustion reaction is shown in equation 2.5

$C_xH_y + O_2 \rightarrow$ Energy + Flue gas (2.5)

Similar to aliphatic sulphides, disulphides combust to produce flue gases and water as shown in equation 2.6 and 2.7.

$C_3H_7SSC_3H_7 + O_2 \rightarrow 2C_3H_6 + H_2S + SO_2$ (2.6)

$C_3H_6 + 2O_2 \rightarrow CO_2 + CO + CH_4 + H_2O$ (2.7)

This equation can be used to determine volume of oxygen required for flue gas production using the simple mole concept. Equal amount of volume of oxygen will be required for production sulphur containing flue gas, while twice molar volume will be needed to produce the other flue gases from light crude oil.

2.4 AMOUNT OF AIR REQUIRED FOR ENHANCED OIL RECOVERY

The mole concept is based on ratio of reactants. In Equation 2.6 where the stoichiometry of the aliphatic sulphide and oxygen is 1:1, i.e 1 molar volume (22.4 dm^3) of $C_3H_7SSC_3H_7$ requires 1 molar volume of oxygen to produce 2 molar volume of propene (C_3H_6) and one molar volume each of hydrogen sulphide and sulphur dioxide.

This implies that 22.4 dm^3 of $C_3H_7SSC_3H_7$ will require 22.4 dm^3 of Oxygen for the reaction, which is equivalent to (22.4/21 *100) = 1.07 dm^3 amount of air to produce 44.8 dm^3 of propene and 22.4 dm^3 each of hydrogen sulphide and sulphur dioxide. Using a Basis of 1 dm^3 = 1000 cm^3 for simplicity, 1000 cm^3 of each reactants i.e sulphide hydrocarbon ($C_3H_7SSC_3H_7$) and oxygen (4761.90 cm^3 of Air) will produce 1000m^3 each of products as shown in equation, i.e 2000 cm^3 of C_3H_6, C_3H_6 and 1000 cm^3 each of H_2S, and SO_2 (2000 cm^3 hydrocarbons and 2000 cm^3 flue gas).

$C_3H_6 + 2O_2 \rightarrow CO_2 + CO + CH_4 + H_2O$ (2.7)

This equation can be used to determine volume of oxygen required for flue gas production using the simple mole concept. Equal amount of volume of oxygen will be required for production sulphur containing flue gas, while twice molar volume will be needed to produce the other flue gases from light crude oil.

2.4 KINETICS BY ISO-CONVERSIONAL METHODS

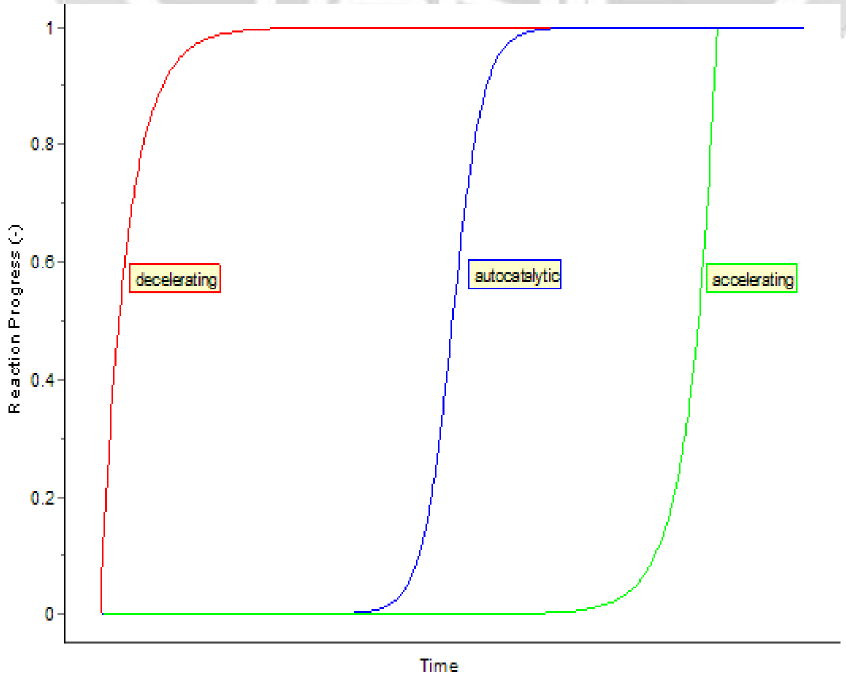
The iso-conversional method has found wide applications in reactions analysis where the decomposition reactions proceeds through multiple stages, where mechanisms are generally unknown or where description of simpler models gives poor results (Iliyas *et al*., 2010). This method is the principle in which reaction rate at constant reaction progress α is only a function of temperature (T). These methods allow for the determination of the kinetic parameter, activation energy (E) i.e dependence of E on α without assuming the explicit form of f(α) which implies E is not constant but vary as reaction progresses. E= E(α). There are three modifications of the iso-conversional method;

1. Differential (Friedman)
2. Integral (Flynn-Ozawa-Wall)
3. Advanced integral based on non-linear procedure (Vyazovkin)

2.6.1 DIFFERENTIAL (FRIED MAN)

The advanced thermo kinetic software (AKTS) applies this type of modification in its analysis employing the logarithm of reaction rate as a function of reciprocal of temperature. If decomposition follows a single mechanism, then a single pair of arrhenius parameters with simple model as in Equation 2.26 and 2.27. Thermal analysis where there is only one value for activation energy and one for pre-exponential factor, Equation 2.28 will be adequate.

There are various reaction models f(α) but they can be grouped to three (3) major classes (acceleration, decelerations and autocatalytic) when the dependence of reaction progress with time is put into consideration. They have unique characteristic reaction profiles as shown in Figure 2.3



2.5 ARRHENIUS STUDIES OF EOR KINETICS USING OXYGEN CONSUMPTION BASES

A fuel varying geometry is used in this case so that as reaction progresses, oxygen consumption is related to the Arrhenius equation as given by Mamora, (1995) and Greaves *et al* (1998).

3. MATERIALS AND METHODS

Table 3.1 List of materials and utilities used in the enhanced oil recovery study

S/no	Materials/Utilities	Details	Manufacturer/Source
1	Crude Oils	Offshore Newfoundland, Canada	Offshore Newfoundland, Canada
2	Mine tailings	Sulfide mineral tailings	Voisey Bay tailings site, Newfoundland and Labrador
3	High Pressure gold pansand lid	Pressure resistance Crucible, M20.081reu02.	Swiss Institute for the Promotion ofSafety and Security.
4	Spherical Bomb test cells	ARCTC-SS316L-L-C-E; thickness of 0.5 mm, stem 3.17 mm; burst pressure of 425 bar and mass of 8.6g.	Thermal Hazard Technology, UK
5	Epoxy Resin	Epoxy tooling resin	ARYA Chem, Canada
6	Nut and Ferrule sets	Nut and Ferrule (1/4, 1/8, 1/16) withadaptors.	Swagelok, Atlantic Valve & Fitting Co. New Brunswick, Canada.
7	Compressed medical air	CO2-103L-295-500; 6.32 m^3	Air Liquid, Canada Inc.
8	Distilled water	Distilled water	Chemistry Department. Memorial University of Newfoundland.
9	Nitrogen gas	SPG-NIT1AL44, Size 6.32 m^3	Air Liquide Canada Inc.

3.1 CONSTANT VOLUME DEPLETION TEST (CVD)

Constant volume depletion tests involve the simulation of reservoir depletion performance and compositional variation on gas condensates and volatile oils. Its secondary purpose is to generate information on volumetric changes taking place with the well stream when operated at standard conditions. The experiment is carried out by transferring the reservoir fluid into a PVT cell at a fixed temperature T, (often at reservoir temperature. The test is started at saturation pressure (P_{sat}) where a known composition Z_i and volume (V_{sat}) are recorded and the compressibility factor Z_{sat} is calculated using the real gas equation $Z_{sat} = PV_{sat}/n_iRT$. (n_i is initial no of moles of the gas). The volume is then reduced in a stepwise manner by opening a valve on the top of the cell which allows the gas deplete. At each volume depletion stage, the pressure and volume readings are taken and corresponding compressibility factor (Z) calculated (Tarek, 2006).

Table 3.2 List of Equipment used in the enhanced oil recovery study.

S/no	Equipment	Details	Manufacturer/Model
1	Viscometer	Digital viscometer	Brokfield Ultra viscometer, ModelDV-E
2	Differential Scanning calorimeter	With Gas controller GC 2000	Mettler Toledo, Model no 822e
3	Accelerating ratecalorimeter	Designed to Dow patents 1980 and 1984.	Thermal Hazard Technology, UK
4	Mineral liberationanalyzer	MLA software developed by Julius Kruttschnitt mineral research group	FEM MLA 650 F
5	Rotary micro riffler	Aluminum bowl, 120 cm^3 capacity Spinning riffler	Quantachrome Cooporation,Europe
6	PVTsim 19.0 software	Reservoir simulation software	Calsep PVTsim

3.2. EXPERIMENTAL PROCEDURE

This section details the series of methods employed to achieve desired results in the study of air injection for the enhancement of improved oil recovery.

Physical properties of the oils were first determined using a density bottle and a rheometer. Thermal properties were then studied using thermal instruments such as the differential scanning calorimetry (DSC) and the accelerating rate calorimeter (ARC), correlations were also used to determine the API gravity and the specific heat capacity of the oils. Minerals analysed using a Mineral Liberation Analyser (MLA) were used to study their effect on crude oil oxidation.

3.3 SLIM TUBE EXPERIMENT

This involves the injection of miscible gas in reservoir oil. Gases such as nitrogen, carbon dioxide or natural gas are often injected into the reservoir during enhanced oil recovery (EOR) of depleted oil wells. The miscibility of these gases in the oil favours EOR which implies that the gas and oil form one phase independent of mixing ratio. Miscibility in reservoir usually occurs at the gas-oil front or in between and allows for complete displacement of reservoir oil. In situations where gas is not completely soluble in the oil, gas break out occurs. This is when some of the insoluble gas forms the gas phase of a higher mobility compared to the oil. This then leads to the subsequent production of the injected gas also knows as gas cycling through the reservoir (Pederson and Christenson, 2007).

3.4 SEPARATOR TESTS

Separator tests otherwise known as flash separation tests are carried out to determine the changes in volumetric behaviours of reservoir fluids as it passes through the separator or series of separators. It is carried out on the original oil at bubble point conditions. These separators precedes the stock tank where the reservoir fluid is eventually collected at standard conditions. The behaviour of reservoir fluid behaviour is affected by the conditions (temperature and pressure) of the surface separators. Separator tests provide essential information about the optimum surface operation of the separators to maximise the oil production in the stock tank.

3.5 DIFFERENTIAL LIBERATION (VAPORIZATION) EXPERIMENT

The experiment is conducted by first transferring the oil into a cell fixed at reservoir temperature. The experiment is usually started at saturation pressure and pressure reduced in a stepwise manner to liberated the gas and flashed to standard conditions as illustrated in Figure 2.14. The procedure is repeated up to 10 - 15 times to end at standard conditions (Tarek, 2007). The primary data of each stage comprises of oil formation factor which is defined as the oil volume at actual pressure divided by residual oil volume at standard condition; the solution gas to oil ratio which is the standard gas volume liberated from oil in stages that follow divided by the residual oil volume; the gas formation factor defined as the volume of gas at actual condition divided by the molecular weight of atmospheric air (Pederson & Christenson, 2007).

3.1.VISCOSITY DETERMINATION

The Brookfield Ultra Viscometers / Rheometers was used to determine the viscosity of the crude oils. It was turned on, leveled and auto-zeroed. The level was adjusted using the three feet on the bottom of the base and confirmed using the bubble on the top of the head. The crude oil sample to be measured was poured into the cylindrical holding container. The standard spindles supplied with the viscometer was then used with a 600 ml low form Griffin beaker. The water bath was then connected and maintained at 25^{o}C and viscosity reading taken for all the samples. Viscosity was calculated from the plot of shear stress (dynes/cm^{2}) vs shear rate (1/s), where the slope of the proportional line is the viscosity.

3.2 SPECIFIC HEAT CAPACITY DETERMINATION

Heat capacity of the crude oils were determined using the correlation from Manning and Thompson (Manning, 1995). Equation 3.1 expresses the Manning and Thompson correlation.

$$C_p = \left(2 * 10^{-3} * T - 1.429\right) * SG + \left(2.678 * 10^{-3}\right) * T + 3.049$$

where; Cp = specific heat capacity (kJ/ kg. ^{o}C)T = Temperature (^{o}C)
SG = Specific gravity of oil at 15^{o}C.

3.2.1 DIFFERENTIAL SCANNING CALORIMETRY (DSC) TESTS

Mettler Toledo with gas controller GC2000 as shown in plate 3.1 was used to carry out Dynamic DSC on eight (8) crude oil samples. Nitrogen gas flow rate of 200 ml/min was used for the tests. An amount of 5 ± 0.5 mg of oil sample was enclosed in a high pressure gold pan and ramped at 10, 8, 4 and 2 K/min after pre-calibration of the instrument. Each test was conducted at least twice to ascertain good experimental reproducibility. It was ensured that the atmosphere was dry and flow of nitrogen gas was maintained to eliminate air.

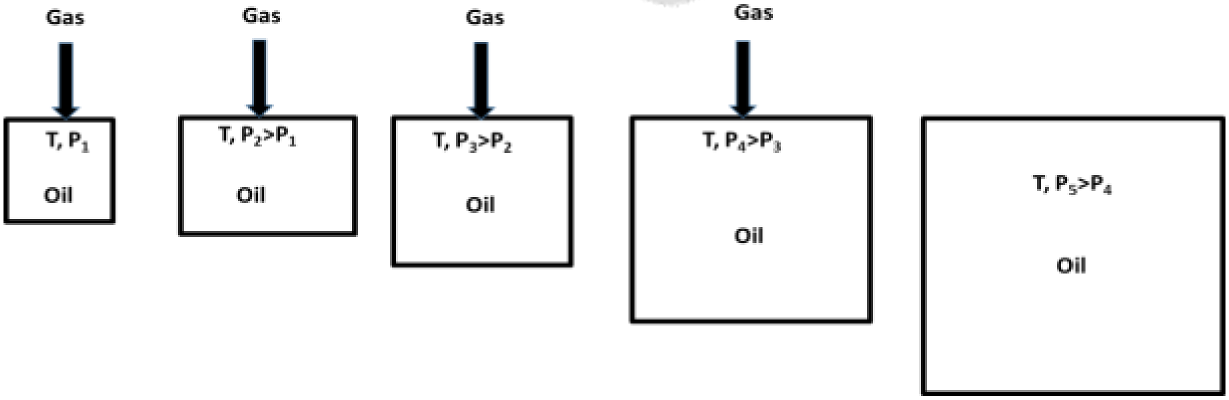
3.2.2 ACCELERATING RATE CALORIMETER (ARC) TESTS

Samples of crude oil (5 $\pm$ 0.5 g) with mine tailings were examined using an ARC. The sample was loaded in an ARC stainless steel test cell. The cell containing the sample was fixed to the top heater before being connected to the temperature thermocouple and the pneumatic pressure line. The setup was now lowered into the cylindrical heater and balanced to a stable position before the ARC door was locked. The ARC was then powered on, with sample and test cell information imputed and the calibration file uploaded to a “Heat-wait-seek” algorithm which is the main operational mode of the ARC system as shown in Figure 3.1. The sample’s temperature was raised (heat) to a set temperature (T) before proceeding to the (wait) period (time t = 15 minutes) where thermal equilibrium was attained (i.e. the difference between temperature of the test cell (bomb) and its surrounding tends to zero). The ARC then proceeded to the seek mode where if the self-heat value exceeds a set threshold (dT/dt = 0.02 ^{o}C/min) an exotherm mode is activated until the self-heat falls below the threshold. If the self- heat falls below the threshold (Tonset), the sequence of “heat-wait-seek” is re-started for the next heat step, If not, the test goes to cool mode when the end temperature reaches the final experiment temperature (T_f). After the cool mode, the test goes idle and stops. The test data was then exported for analysis when the end temperature was reached

3.2.3 SWELLING TESTS

Swelling tests are usually conducted on reservoirs that are to be depleted by gas injection or dry gas cycling scheme. This is started on a reservoir oil, at saturation pressure in a PVT cell operated at reservoir temperature. A known amount of gas is injected into the cell containing the oil. The pressure is then increase at constant temperature until all the injected gas is dissolved in the reservoir oil. The pressure and the swollen volume of the dissolved gas in oil are then recorded. Moregas is injected and pressure increased until all the gas goes into solution with the oil

Figure 2.18: Schematic Representation of Swelling Test (Tarek, 2007)



4. RESULTS AND DISCUSSION

Properties of the Crude oils
Table 4.1 shows the viscosity, API and specific heat capacity properties of the analysed crude oil samples

Crude Sample	**OilViscosity(cP)**	**API gravity**	**Specific Heat Capacity (kJ/kg.K)**
A	5.44	46.96	1.888
B	7.90	44.06	1.926
C	4.99	30.21	1.910
D	25.70	40.02	1.833
E	11.90	41.91	1.898
F	8.18	38.98	1.882
G	24.90	32.46	1.846
H	10.11	46.91	1.889

4.2 Thermal Behaviours of Crude Oils using DSC

Thermal behaviour of all the reservoir crude oils was first carried out in the DSC ramped at 10 K/min and the obtained DSC thermograms are depicted in Figure 4.1. Three (3) samples (A, B, and C) showed clear peaks of oxidation between 130^{o}C and 300^{o}C, which is an indication that they have measurable exothermic signals. The temperature range between the onset and the end set falls in the low temperature oxidation zone and makes them a probable candidate for high pressure air Injection.

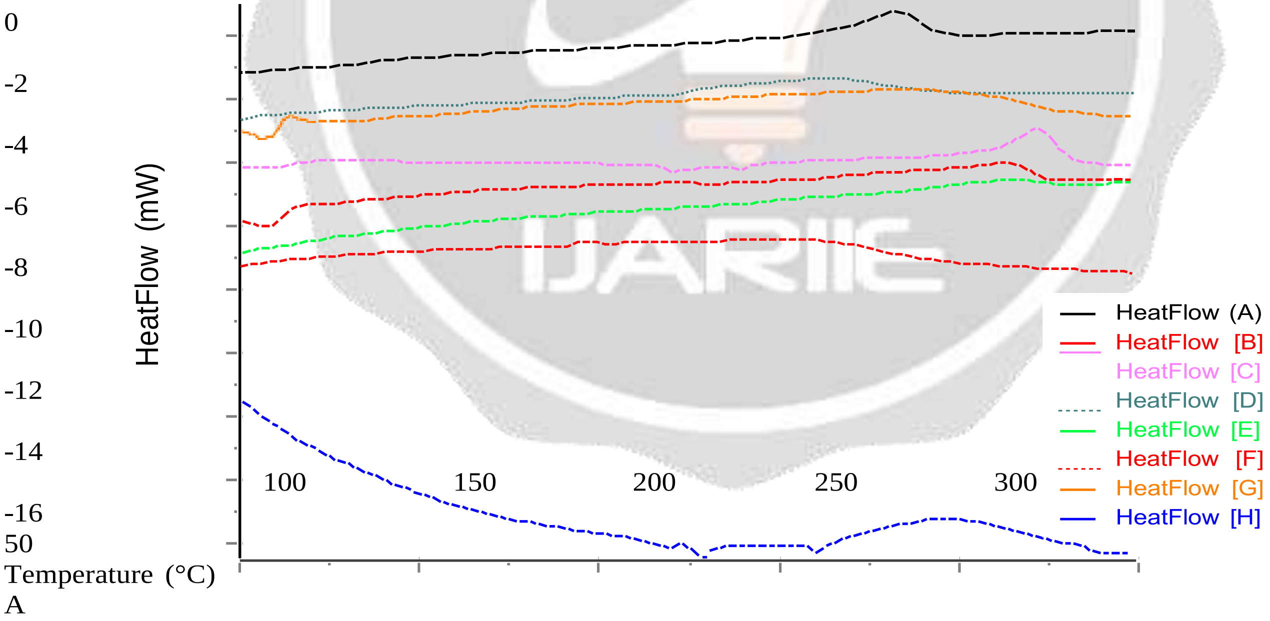


Figure 4.1: DSC thermograms of crude oil samples at 10K/min (Refer to Table 4.1 for propertiesof samples A-H).

Therefore, the DSC thermograms of the samples that had measurable exothermic signals were then further ramped at 8, 4 and 2 K/min and at least three (3) best thermograms were saved and exported to the AKTS and NETZSCH software. These were then used for iso-conversional and model based kinetics simulations as presented in the next Section.

The use of Mine Tailings as catalysts in crude oil oxidation reactions

This section presents the study of how the oxidation behaviours of crude oil was enhanced by the use of mine tailings as catalysts. These findings will encourage further study on how to optimize the catalyst obtained in the tailings for enhanced oil recovery as well as screening studies for candidate reservoirs. The backscattered image of tailings obtained from Newfoundland Labrador , Canada as well as the color code corresponding to its constituents are shown in Appendix A. Pyrrhotite mineral was observed to be the most abundant mineral in the tailings analysed with an amount of 83.51 wt%. The summary of the constituents obtained in the mineral liberation analysis are presented in Table 4.3.

Table 4.2: MINERAL AND CHEMICAL CONSTITUENTS OF THE TAILINGS

Mineral Constituents	**Amount (wt%)**	**Chemical Elements**	**Amount (wt%)**
Pyrrhotite	83.51	Iron	61.08
Magnetite	10.29	Sulphur	30.06
Plagioclase	2.06	Silicon	1.16
Amphibole	0.68	Aluminum	0.46
Orthopyroxene	0.37	Calcium	0.31
Olivine	0.31	Magnesium	0.31
Pentlandite	0.32	Oxygen	5.35
Others	2.46	Others	1.27
Total	100	Total	100

Several studies on mine sites in Nigeria have been conducted over the years. Some mine sites aroundthe north to the east of Nigeria have been noted to contain tailings rich in sulphide associated minerals. The Arufu mining district below the river Pii tributaries in Benue State Nigeria have been found to be rich in lead, zinc and cadmium. It has also been recorded to contain minerals such as biotite, diotite, sandstone, limestone and shale. Most importantly, studies reveal it contained sulphide associated with the Pb-Zn minerals.

Figure 4.2: Sulphide Associated Mineral sites in Nigeria

In Itakpe, Kogi State, an iron ore processing site has access to rich minerals of haematite, quartz and other several metallic minerals such as iron (III) oxide (Fe_2O_3), iron (II, III) oxide (Fe_3O_4), silicon oxide (SiO_2), alumina (Al_2O_3), calcium oxide (CaO), magnesium oxide (MgO), pottasium and sulphur (Ajaka, 2006). Quartz-gold-sulphide minerals also exist at the Birnin Gwari artisanal gold mining area of the north-western part of Nigeria which is known to have high lead content (Waziri, 2014). Several mines are yet to be explored while around Kaduna, there is a new discovery of mineral rich in high grade Nickel (Ali, 2016; Ezeamalu, 2016; Nwakalor 2016). These associated sulphide minerals are in most cases responsible for the oxidation or self-heating behaviour of the minerals. This is a potential for oxidation instigation for crude oil for the purpose of enhanced oil recovery which could be beneficial for Nigerian crude oil production in the future. The future when Nigeria will turn to its deplete oil wells for economic and environment friendly method of production

This section discusses the effect of reservoir temperature, reservoir pressure and reservoir sulphur content on improved oil recovery prospect in Nigeria. The crude oil data obtained from Jaubert *et al* (2002) was regressed with the given isothermal expansion data and Isothermal differential vaporization data using the Soave-Redlich-Kwong (SRK). The lumping method of similar molecular weight was adopted in PVTsim 19. The saturation pressure calculated deviated by 21.26% when calculated using the SRK equation of state. Lumping method to 3 pseudo component was used for tuning which yielded a lower deviation of -9.43 %. The tuned oil properties are presented in Appendix. An Anova analysis on experimental runs generated from the design of experiment is presented in Appendix H. An optimum desirability of one (1) was chosen from the design of experiment analysis and a final equation based on coded factors generated as presented in Appendix H.

4.3. EFFECT OF RESERVOIR CONDITIONS ON OIL RECOVERY ON NIGERIAN CRUDE OIL

This section discusses the effect of reservoir temperature, reservoir pressure and reservoir sulphur content on improved oil recovery prospect in Nigeria. The crude oil data obtained from Jaubert *et al* (2002) was regressed with the given isothermal expansion data and Isothermal differential vaporization data using the Soave-Redlich-Kwong (SRK). The lumping method of similar molecular weight was adopted in PVTsim 19. The saturation pressure calculated deviated by 21.26% when calculated using the SRK equation of state. Lumping method to 3 pseudo component was used for tuning which yielded a lower deviation of -9.43 %. The tuned oil properties are presented in Appendix. An Anova analysis on experimental runs generated from the design of experiment is presented in Appendix H. An optimum desirability of one (1) was chosen from the design of experiment analysis and a final equation based on coded factors generated as presented in Appendix H.

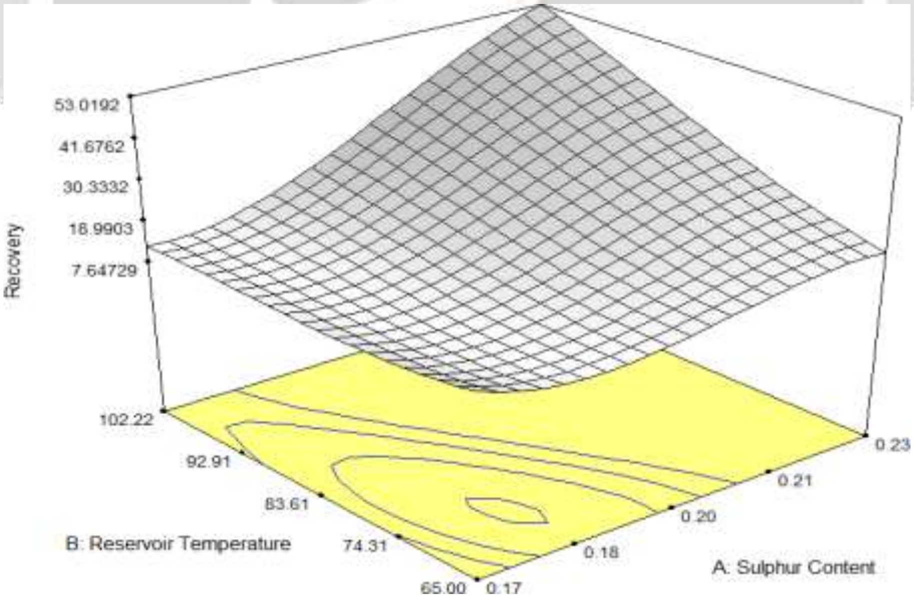


Figure 4.2: Effect of reservoir temperature and sulphur content on oil recovery

Figure 4.2 shows the effect of sulphur content and reservoir temperature on recovery. Although sulphur is not desirable in high amount in the reservoir, an improved recovery of oil as reservoir temperature and sulphur content increased in the reservoir. This can be attributed to the effect of SO_2as a constituent of flue gas known to influence combustion (Dong and Huang, 2002; Abu-Khamsin, 2003; Niu *et al.*, 2011).

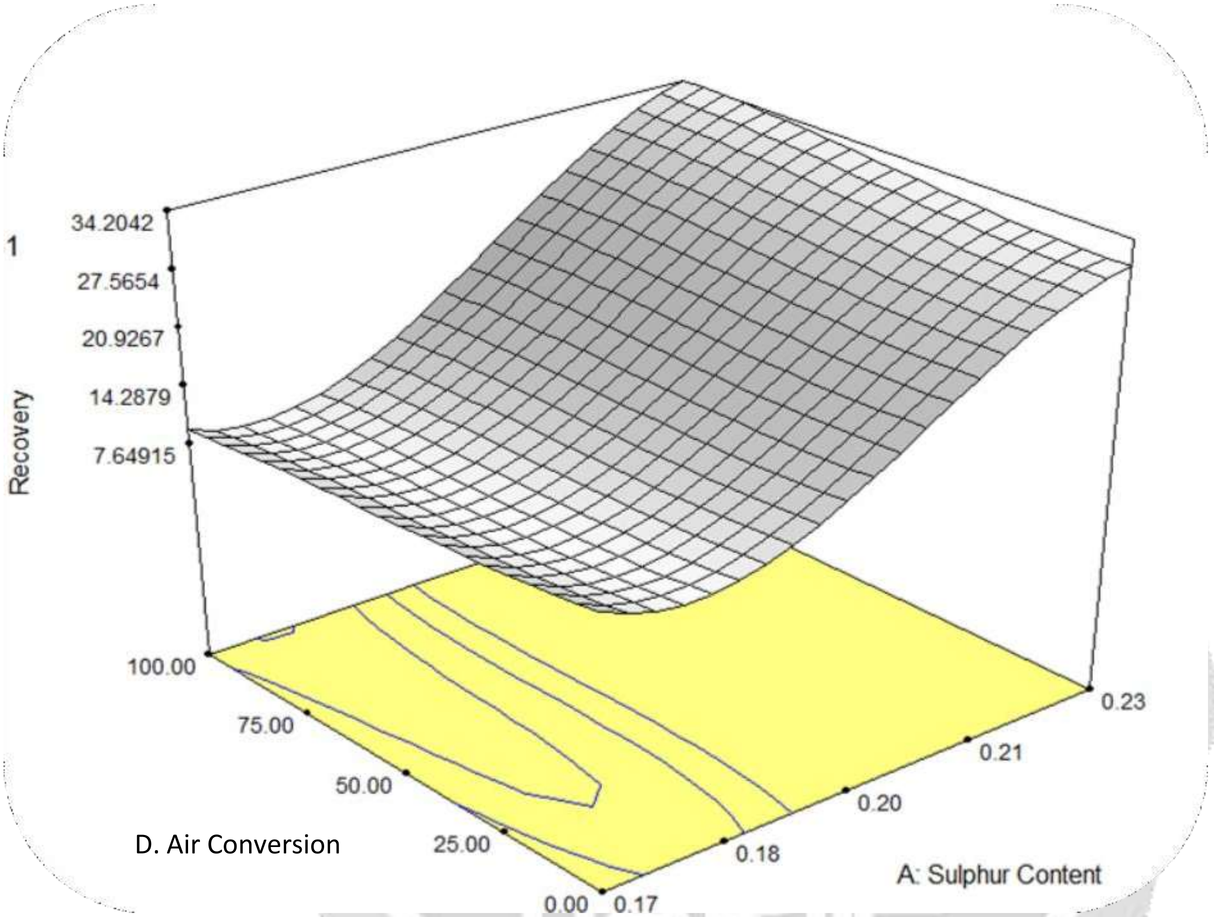


Figure 4.3: Effect of extent of air oxidation and sulphur content on oil recovery

Figure 4.3 shows the effect of the extent of air oxidation and sulphur content on oil recovery.

5. CONCLUSIONS

1. The superiority of the iso conversional studies can easily be observed based on the activation energy determination. Sample A when analysed using the iso-conversional method, had a non- constant activation energy between 50 - 235 kJ/mol as the reaction progressed to completion while with the simple Arrhenius model analysis, a constant activation energy of 133.6 kJ/mol was determined for the reaction. This is evident in the other samples analysed.

2. The detected onset oxidation temperatures of the reactions for sample A was in the low temperature oxidation zones (140 ^{o}C) while samples B (215 ^{o}C) and C (220 ^{o}C) recorded their onset oxidation temperature in the medium temperature oxidation zones respectively.

3. The estimated activation energies using the ASTM E-698 method were observed to be higher forthe lower API gravity crude samples. Sample A which high API gravity of 46.963 had a low activation of 133.6 kj/mol while sample C with low API gravity of 30.214 recorded the highest activation energy of 176.5 kj/mol.

4. The apparent activation energy using the iso-conversional method increased as the reaction progressed with sample A recording a peak at $\alpha = 0.58$ due to production of flue gases which hampers oxidation reaction hence the larger activation barrier.

5.1. Recommendations

Future work should investigate the risk analysis of Air injection projects operating on catalytic enhancements.
A comparison of historical data vs simulated data should be carried out for future reliability analysis.
A study of Coking problem during air injection projects should be carried out to see effect on overall oil recovery.
Although 20% tailings showed the highest temperature lowering of the onset temperature, screening different crude oils for their response to specific tailings is highly recommended before field project.

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