ISSN No:-2456-2165

# A Review on the Geologic Occurrence, Development and Associated Environmental Problems of Unconventional Hydrocarbon Energy Resources

*Kalu, E. O., Okeke O. C., Amadi, C. C., Akudike, J. C., Dozie, O. T., Sunday, E. U. and Okonkwo, S. I.
Rock Mechanics, Mining and Mineral/Energy Research Group, Department of Geology
Federal University of Technology, Owerri, Nigeria.

**Abstract:- Unconventional hydrocarbon energy resources are non renewable energy resources whose major constituents are hydrogen and carbon. They have indistinct source rock- reservoir rocks-trap rocks characteristics/boundaries and unique exploitation technologies including mining and processing (surface and underground production using retorts for exploitation of oil shale and coking units for exploitation of bitumen; in-situ treatment and recovery (underground production using thermal treatment, chemical flooding and gas injection for exploitation of heavy oils in particular); and well production /underground production using vertical drilling, horizontal drilling and hydraulic fracturing. Only well production technology is applicable to conventional hydrocarbon energy resources, that is petroleum and natural gas exploitation. There are five classes of unconventional hydrocarbon energy resources including: coal bed methane (CBM), oil shale, shale gas/shale oil, heavy oil/bitumen, and natural gas hydrates. Worldwide, the recoverable methane from coal bed methane resources is about 2625 tcf. Similarly, the recoverable billions of barrels of oil from shale oil, heavy oil and bitumen, resources worldwide are 28626,443 and 651, respectively. Over 90% of these, that is, shale oil, heavy oil and bitumen are found in USA Venezuela and Canada respectively. The environmental problems associated with development of unconventional hydrocarbon energy resources include: surface/groundwater pollution; water depletion; air pollution and hazards of solid wastes from oil shale and bitumen mining/ processing. However, energy produced from unconventional hydrocarbon energy resources are similar to those produced from other (conventional) energy resources and can be equally used for various purposes including industrial, residential, transportation and commercial.**

***Keywords:-*** *Unconventional, Energy Resources, Shale Gas, Oil Shale, Bitumen and Water Pollution.*

## I. INTRODUCTION

Energy resources are naturally occurring materials from which energy can be extracted or developed economically. Energy resources are related to mineral resources because the naturally occurring materials are most often concentration of mineral substances. (Craig et al., 2011) defined mineral resources as "a concentration of naturally occurring solid, liquid or gaseous material in or on earth's crust in such forms and amount that economic extraction of a commodity is currently or potentially feasible". In other words, energy resource is an example of a commodity that can be extracted from mineral resources.

Energy resources may be classified into renewable and non-renewable energy resources. The renewable energy resources comprise those resources that are continuously replenished within short time scales of hours, days, months or years. Examples include: hydroelectric energy, tidal energy; geothermal energy, ocean energy; wind energy, solar energy, and biomass (organic material derived from plants and animals). The non-renewable energy resources are those resources that are not replenished by natural processes operating on short timescales. Examples are crude oil, natural gas, coal, oil shale and nuclear energy.

Crude oil, natural gas and coal are also referred to as fossil fuel or fossil energy resources. The renewable and non-renewable energy resources are summarized in Table 1.

| Renewable Energy Resources | Non-Renewable Energy Resources |
|---|---|
| i. Hydroelectric energy<br>ii. Geothermal energy<br>iii. Tidal energy<br>iv. Biomass energy<br>v. Wind energy<br>vi. Solar energy<br>vii. Ocean energy | i. Crude oil/petroleum,<br>ii. Natural gas,<br>iii. coal,<br>iv. Nuclear energy<br>v. Oil shale |

Table 1:- Summary of available energy resources (Henry and Heinke, 1990)

ISSN No:-2456-2165

Petroleum forms from marine organic matter that is trapped in sediments and transformed into petroleum as a result of increasing temperature and pressure. The primary constituents of petroleum are hydrogen and carbon.

Natural gas, composed primarily of methane (CH4) forms biogenically when bacteria decompose shallowly buried organic matter and thermogenically when the temperature and pressure of deep burial cause some decomposition and reconstitution of the organic matter. Natural gas like petroleum is composed primarily of hydrogen and carbon.

Coal is sedimentary rock that forms from land plant materials that has not completely decayed; it is primarily composed of carbon hydrogen and oxygen. It occurs in ranks of increasing carbon, content beginning as peat and may be transformed into lignite, sub-bituminous coal, bituminous coal, and anthracite (Compton, 1977; Craig et al, 2011; Carlson and Plummer, 2008). Table 2 shows different ranks or varieties of coal based on composition.

The concept of coal rank is used to indicate stage of alteration attained by a particular substance, the greater the alteration the higher the rank of the coal.

| Coal Type | Coal Rank | Colour | Water Content (%) | Other Volatile | Carbon (%) | Approximate heat value BTU of heat per pound of coal |
|---|---|---|---|---|---|---|
| Peat (soft coal) | Low | Brown | 75 | 10 | 10-29 | Varies |
| Lignite (soft coal) | Low | Brownish black | 45 | 25 | 30-49 | 7000 |
| Sub-bituminous coal (Soft coal) | Low | Black | 25 | 35 | 65-79 | 10,000 |
| Bituminous coal (soft coal) | Medium | Black | 5-15 | 20-30 | 45-86 | 10,500-15,000 |
| Anthracite (hard coal) | Hard | Black | 5-10 | 5 | 90-99 | 14000-15000 |

Table 2:- Ranks (Varieties) of coal (Okeke et al, 2004; Carlson and Plummer, 2008; Martin et al, 1983).

Some authors including Crag et al (2011) believe that peat is not truly a coal but “pre-coal”.

Petroleum is a dark vicious liquid fuel natural gas is a gaseous fuel; and coal is a solid fuel. Hydrocarbons are organic compound that are composed of two elements namely: hydrogen and carbon. All hydrocarbons have the molecular formulary of CxHy, where x and y are positive whole numbers. Some examples are methane (CH**4**), propane (C3H8), and benzene (C**6**H**6**). According to Levorsen (2003) hydrocarbons are energy resources whether solid, liquid or gas are therefore energy resources whose major constituents are carbon and hydrogen and are associated with petroleum, natural gas or coal. All these are non-renewable energy resources.

On the basis of geologic occurrence and method of recovery or extraction non-renewable hydrocarbon energy resources may further be classified as conventional and unconventional hydrocarbon energy resources. The conventional hydrocarbon energy resources have distinct source rock, reservoir rock and traps characteristics and boundaries and can be extracted using traditional methods or techniques such as drilling. Examples of conventional hydrocarbon energy resources are petroleum (crude oil), natural gas and coal. These are also collectively called fossil fuels. Unconventional hydrocarbon energy resources, on the other hand may be defined as a continuous or sub-continuous accumulation of hydrocarbons whereby source rock and reservoir rock boundaries are not distinct and traditional method of extraction such as vertical drilling is not always sufficient unless enhanced techniques are applied in order to improve the porosity and permeability of the reservoir or access the energy resources optimally. Geologically, the unconventional hydrocarbon energy resources are characterized by source-reservoir rock paragenesis, indistinct trap boundaries and limited hydrodynamic influence on their origin and occurrence. Horizontal drilling, hydraulic fracturing, mining and processing in retorts or coking units and in-situ treatment (including steam/gas injection and chemical flooding) are some of the special technologies that are used in the extraction of unconventional hydrocarbon energy resources (Lake, 1989). Table 3 is the summary of the differences between conventional and unconventional hydrocarbon energy resources (Zou et al, 2012 and 2014).

| Category/Item | Conventional hydrocarbon energy resources | Unconventional hydrocarbon energy resources |
|---|---|---|
| Accumulating unit | Distinct structural stratigraphic or combined traps | Continuous reservoir (No trap) |
| Reservoir | Conventional reservoir with high porosity and permeability | Unconventional resources with ultra-low porosity and permeability |
| Configuration of source rock and reservoir | Reservoir may be from source rock | As one or in contact with each other |
| Migration | Secondary migration over long distance | Primary or secondary migration over relatively short distance |
| Trap system | Obvious trap or close trap | Well production (vertical well, horizontal well, hydraulic facture, mining and processing) |
| Accumulation hydrodynamics | Buoyancy is the main driving force | Buoyancy is limited |
| Percolation | Darcian percolation | Mainly non Darcian percolation |
| Fluid relationship | There is uniform fluid contact | No uniform fluid contact or pressure system and hydrocarbon saturation varies greatly |
| Distribution | Discrete or clustered distribution | Wide spread, continuous or quasi continuous at basin center or slope. |
| Resource Exploitation Technology | **Well production** (vertical well, horizontal well and occasional hydraulic fracturing) | **Surface production** (mining and processing in retorts for oil shale and coking units for bitumen)<br>**Underground production** (in-situ treatment and recovery) |

Table 3:- Summary of differences between conventional and unconventional hydrocarbon energy resources (Zou et al, 2012 and 2014)

According to (Klett and Carpentar, 2003; Klett and Schmoker, 2004; Cook, 2004; Schmoker,1995, 2002 and 2005; and Pollastro et al., 2007) the major types of unconventional hydrocarbon energy resources are:

- Coal bed methane (CBM)
- Oil shale
- Shale oil and shale gas
- Heavy oil and Bitumen
- Natural gas hydrates

Their importance as energy resources are related to their uses as extracted /processed energy from the unconventional sources. These uses are the same as the uses of the energy resources extracted from the conventional energy resources. According to (Stoker et al, 1975), the areas of energy use include: industrial, transportation, residential and commercial, Activities or types of use in each area are given Table 4.

| | Areas of use | | | |
|---|---|---|---|---|
| | **Industrial** | **Transportation** | **Residential** | **Commercial** |
| Type of use/activities | i. Metals and stone industry (mining and quarrying)<br><br>ii. Chemical and allied products<br><br>iii. petroleum refining and allied products<br><br>iv Cement and concrete products<br><br>v. Paper and related products | Fuel for:<br>i. Automobile<br>ii. Trucks<br>iii. Trains<br>iv. Ships<br>v. Air craft | i. Space heating<br><br>ii. Water heating,<br>iii. Refrigeration<br>iv. Air conditioner<br>v. Lighting<br>vii. Television operation<br>viii. Washing machine operation<br>ix Disk washing | i. Space heating<br>ii. Air Condition<br>iii. Refrigerator<br>iv. water heating<br>v. Cooking<br>vii Others |

Table 4:- Summary of areas of energy uses and their types of uses/activities (Stocker et al, 1975)

ISSN No:-2456-2165

Activities represented by the industrial area are primarily those resulting in the production of consumer goods. In the transportation area, the activities are involved in moving people and materials from one place to another. In the residential area, the activities provide comfort and convenience for living quarters. The activities of the commercial area are activities and organizations that are not listed in the other areas and they include construction companies, insurance companies, finance companies, hotels, restaurants, schools, museums and government institutions.

## II. GEOLOGIC OCCURRENCE AND DEVELOPMENT OF UNCONVENTIONAL HYDROCARBON ENERGY RESOURCES

### *A. Coal Bed Methane (CBM)*

➢ *Geologic occurrence*

When coal forms water and natural gas in the form of methane are trapped in fine pores and fractures in the coal. Stearns (2005) defined coal bed methane as a gas that is formed during coal formation and stored within microspores of the coal or within its fractures. It is usually in an adsorbed state and stored within the confines of coal bed. The gas is similar to the conventional natural gas in terms of composition. Its main composition is methane ($CH_4$) and was formed as a result of later stage coalification. (Rice, 1993).

The genetic formation of CBM is in two ways and they are:

- Biogenic coal bed methane
- Thermal coal bed methane

There are four types of coal including; peat, lignite, bituminous (including subbituminous) and anthracite. Peat and lignite coal are the low-ranking coal and they are highly porous with high water content and they are equally responsible for the production of biogenic gas and other fluids in minute form under conditions of low temperature and pressure. As the maturity of coal increases, it expels more and more water which is attributed to increasing rate of compaction due to increase in the weight of the overburden layer High ranking coals, bituminous and anthracite are formed as a result of increased temperature and pressure resulting in less water content and more carbon content.

The porosity/pore space also reduces significantly and there is a significant increase in the temperature and pressure condition. The increase in temperature leads to a decrease in bacterial activities. The organic matter and carbon dioxide in methane are subjected to thermal action and thereby transformed to secondary methane gas known as thermal methane (Zou, 2013). CBM generally occurs in adsorbed state in the coal bed because of the attraction and bonding between the surface molecule within the coal matrix and the methane gas. Some of the countries with large resources of coal bed methane are; Russia, USA, China, Canada, United Kingdom, India, Ukraine, Kazakhstan and Turkey (Stearns et al, 2005); Mills 1971), estimated that the total coal bed methane resources worldwide to be as high as 7,500tcf. In the United State the overall resource is about 700tcf; only about 100tef is likely to be recoverable.

➢ *Development*

- *Pumping out water to reduce pressure in the coal bed.*

Boreholes are drilled to the bottom of the coal seam and these boreholes are filled with water. Submersible pumps are later installed to remove the water. Pumping out of the water automatically lowers the pressure and methane gas is subsequently released in huge quantities. The same pumps and pipes that are used to pump out the water are also used to pump out CBM from the borehole. (Carlson and Plummer, 2008) state that coal can store six to seven times more gas than an equivalent amount of rock in an ordinary natural gas field).

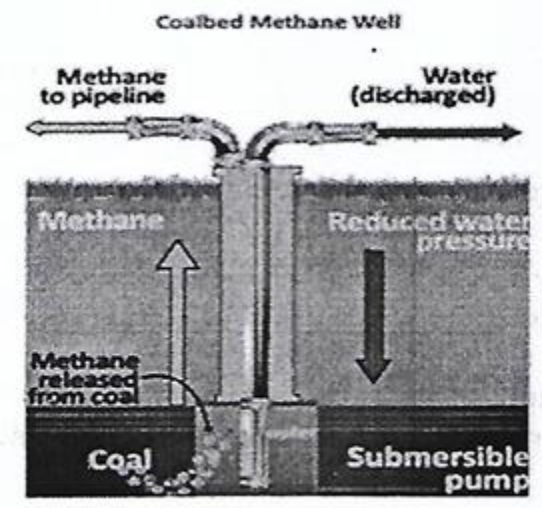


Fig 1:- Schematic to illustrate extraction of WBM using borehole and pumps. (Stearns et al, 2005).

- *Use of gas hydrate technology*

An alternative method for extracting CBM is the use of gas hydrate technology. Gas hydrates are classified as clathrates which are usually in solid or crystalline form whereby the host molecule is water and the enclosed or guest molecule is methane (Zou, 2013). These hydrates are known for consuming large amounts of gas under high pressure and low temperature and in so doing, solid crystalline (complexes) are formed. Using this method, the coal bed methane gas can be easily transported (Stearns, et al, 2005). The identification of the hydrate, its storage and transportation of the hydrate, its storage and transportation are the major challenges involved in applying this method. Some of the ways to promote the formation of the hydrate are use of surphactants, also called hydrate promoters (Kumar et al, 2015) use of copper nano particles in water (Li et at 2006), use of potato starch (Fakharia et al, 2012) and water spraying to increase surface areas between phases (Brown et at, 2010).

- *Use of hydraulic fracturing technology:*

Methane gas appeases in adsorbed phase within the coal bed. Hydraulic fracturing/ technology may be used to increase the fractures, the coal bed and thereby releasing the gas (Craig et al, 2011; Okeke 2015).

*B. Oil Shale*

➢ *Geologic occurrence*

Oil shale is a very fine-grained sedimentary rock that has a high proportion of insoluble organic matter (Kerogen) which can be converted to oil or gas by processing (Metz, 1974 Okeke and Okogbue, 2011). According to De Nervers (1965), the chemical difference between petroleum and kerogen is primarily of molecular geometry. Whereas petroleum molecules are particularly composed of linear chain with some attached rings and branches and very little linking between the chains, kerogen chains are cross tinked to a significant extent. When kerogen is heated to about 900F (480$^0$C) the links between the chains break and the solid is chemically transformed into crude oil (representing 60% of the kerogen weight), a fuel gas (9%) and coke like solid (25%). The composition of a typical high grade oil shale is given in Table 5.

| **Composition** | **Weight (%)** |
|---|---|
| Organic Matter | 13.8 |
| Carbon | (80.5) |
| Hydrogen | (10.5) |
| Nitrogen | (1.3) |
| Sulphur | (8.2) |
| | **(100)** |
| Mineral matter | 86.2 |
| Carbonates, mainly dolomites | 48 |
| Feldspars | 21 |
| Quartz | 13 |
| Clays, mainly illite | 13 |
| Analcite | 4 |
| Pyrite | 1 |
| | **(100)** |

Table 5:- Composition of typical high grade oil shale (25 gallons of oil per metric ton) (US Department of the Interior, 1973)

Oil shales form where there is simultaneous deposition of fine-grained mineral debris and organic materials in a nonoxidizing (reducing) environment). The fine grained nature of the sediments indicates that the deposition must have occurred in quiet lakes, swamps or marine basins that were rich in organic matter. Continued sedimentation of overlaying rocks provided the compaction and burial depth so that temperature probably rose to100$^o$C to 150$^o$C. This mild heating resulted in the loss of much of the most volatile fractions and left the heavier molecular weight and more refractory organic residue. Oil shale is the most abundant energy resources in the world. Table 6 shows some of the occurrences. The best-known oil shale in the United State is the Green River Formation which covers more than 40,000 square kilometers in Colorado, Wyoming and Utah with deposits of up to 650 meters thick. The oil shale which includes numerous fossils of fish skeleton, was formed from mud deposited on the bottom of large shallow Eocene lakes. The organic matter comes from algae and Other organisms that lived in the lakes. According to (Carlson and Plummer, 2008), the green River Formation includes more than 400 billion barrels of oil in rich beds that yield over 25 gallons of oil per metric ton of rock, and another 1,400 billion barrels of oil in lower grade beds that yield 10 to 25 gallons of oil per metric ton of rock. In green River Formation alone an estimated 400 to 600 billion barrels may be recoverable (Knutson and Dana, 1982).

| **Country** | **Billions of barrel (bbl) Recoverable** |
|---|---|
| United States | 2085 |
| Russia | 248 |
| Cango | 100 |
| Brazil | 82 |
| Italy | 73 |
| Morocco | 53 |
| Jordan | 34 |
| Australia | 32 |
| **World Total** | **2826** |

Table 6:- World oil shale resources in billions of barres of recoverable oil (World Energy Council, 2001)

➢ *Development*

Two methods of development or production are currently used for the recovery of hydrocarbons from oil shale. They are (a) surface mining and processing (b) In situ retorting.

- *Surface mining and processing methods*

The method involves open-pit mining or bulk underground mining of the shale, grinding it into fine particles and heating it to about 500$^0$C in a large coke-like kiln called retort. The volatilized hydrocarbons are condensed and can then be processed in the same manner as conventionally recovered oil and gas. To be viable, the refining process must yield more fuel than it consumes.
Fig 2 shows schematic diagram of surface mining and processing of oil shale (US. Department of Interior 1973; De Nevers, 1973).

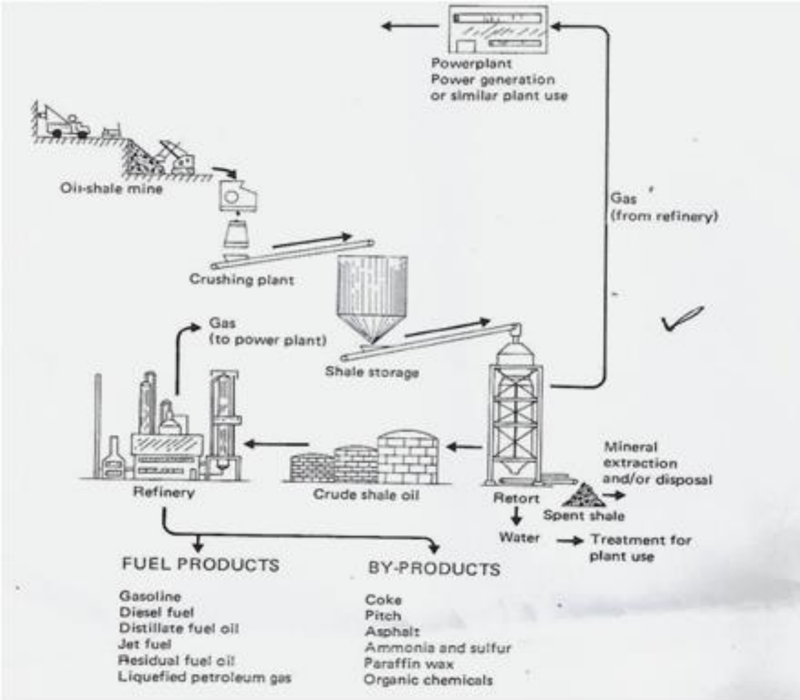


Fig 2:- Oil Shale Surface Processing (US Department of the Interior, 1973; De Nevers, 1973)

The environmental problems that are associated with surface mining and processing of oil shale may include:

- ✓ Economic problem: The mining and construction processing facilities are very expensive
- ✓ Environmental problems:

1. A great amount of water is needed during processing (Three barrels of water are needed to produce one barrel of oil using existing technology)
2. Disposal of mining waste (stripped shale) during mining and spent shale during operation/processing)
3. Leaching of the shale waste rock may lead to pollution of surface and groundwater resources.

- *In situ retorting method*

This method is similar to processes used for enhanced oil and tar sand recovery. It involves the development of underground tunnels, known as drifts, either above and below or on both sides of a block of oil shale as much as 10 meters (30ft) or more each side. After the tunnels are completed, the rock is broken by explosives. The broken rock is then ignited and the rate of combustion is controlled by a flow of air, diesels fuel and steams. As the fire burns downward in a vertical retort or from one side to the other in a horizontal retort, the rock ahead of the combustion zone is heated to approximately 500$^0$C; much of the kerogen is vaporized and driven to zone to be drawn out as oil and gas through wells or drains.

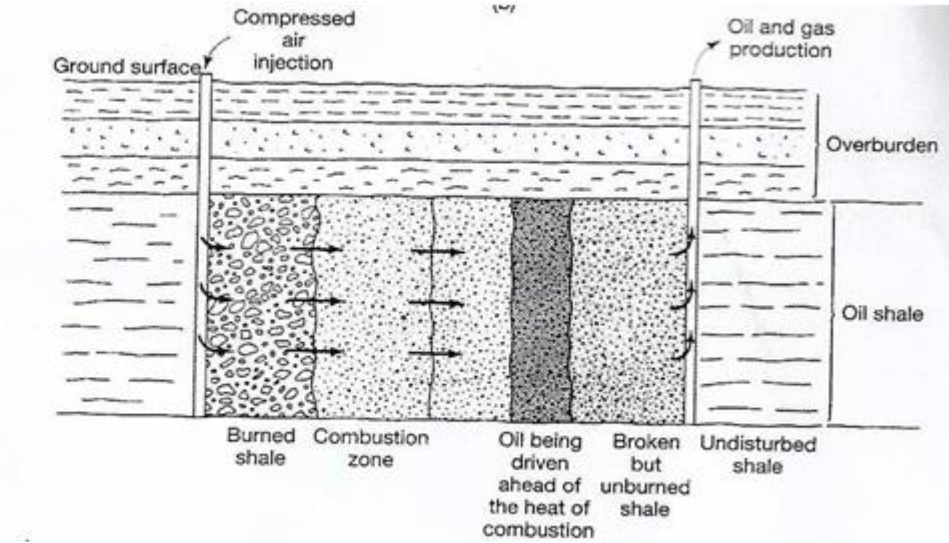


Fig 3:- illustrates the in-situ retorting process.
In-situ oil shale retorting (Craig et al, 2011).

*C. Shale oil and shale gas*

➢ *Occurrence*

**Shale oil** can be defined as already generated oil that is stored within the micro scale to nano scale reservoir spaces of organic rich shale formation. The shale acts as both the source rock and reservoir rock (Zou, 2013). This oil has not undergone migration but tends to accumulate in the source rock. Oil can be found and exploited from highly fractured shale such as the Rasron Basin in New Mexico (Mallory 1977, Woodward, 1984). This shale is usually found in mild slopes, depressions or basin margins where hydrocarbon content cannot be easily expelled. The distribution of such oil is not influenced by structures as it possesses no defined entrapment system. Examples of producing fractured shale oil reservoirs include oil fields of Santa Maria District California (Regan, 1953).

**Shale gas** can be defined as a natural gas that is produced from an organically rich shale (Curtis, 2002; Boyer, 2006). It can be said to be an accumulation of biogenic gas and thermogenic gas of mixed origin. Shale acts as both the source rock and the reservoir rock. Presence of carboniferous shale and black shale (Okeke and Okogbue 2011), increase the potentials for formation of shale gas. One of the predominant factors that influence the formation of shale gas is:

- High TOC (Total Organic carbon) which indicates high gas saturation and for shale gas to be generated, a TOC value of 0.58) is required (Obaje et al, 2004). Examples of naturally fractured shale gas reservoirs include the Devonian shale of the Appalachian Basin Michigan Basin and Illinois Basin all in the USA (USGS,1995, Loucks and Ruppel, 2007; Explorer, 2001 and 2002).

➢ *Development*

Shales generally have low permeability even when naturally fractured to constitute reservoir for shale oil or shale gas. Enhanced production/development must be applied to ensure their optimum exploitation. Such enhanced production techniques include hydraulic fracturing, and horizontal drilling of oil/gas wells. Okeke and Okogbue 2011; Okeke, 2015 and Boyer, 2006).

**Hydraulic fracturing** can be defined as type of induced instability whereby a section of the borehole is pressurized until failure occurs thereby initiating fractures and expanding fractures encountered in the area (Okeke 2015, Martinez et al 1992). Hydraulic fractioning is responsible for increasing North America's oil reserve by more than 8 billion barrel (bbl) ($1.3x10^9m^3$) (Girdley et at, 1984). There are records that indicate that hydraulic fracturing has effect of improving permeabilities of shale from values less than 0.1 and to as high of 910md (Okeke and Okogbue, 2011).

**Horizontal drilling** is an act of drilling wells whereby wells are drilled initially vertically to a certain/ target/depth deposits and then deviated mostly at $90^0$ from horizontal direction to a vertical direction within the rock formation. Because fractures in shale gas/oil reservoirs are generally vertical, horizontal wells are always drilled into the shale for better contact with the gas/oil pay zone. Examples of producing shale oil are shown Table 7 and 8 respectively.

| Name of oil field | Location | Reservoir Rocks |
|---|---|---|
| Santa Maria oil field | California | 75% fractured shale and 25% sands |
| Strawberry oil field | Western Texas | 100% fractured shale |
| Florence oil field | Colorado | 100% fractured shale |

Table 7:- Examples of oil production from naturally fractured shale reservoir (Hubert and Willis 1955, Levorsen, 2003)

| Formation | Basin | Basin Area (Sq.M) ($Km^2$) | Estimated shale gas in place (Tcf) | Estimated recoverable shale gas (Tcf) |
|---|---|---|---|---|
| Ohio Shale | Appalachian | 160000 (409600) | 225-258 | 14.5-27.5 |
| Antrim Shale | Michigan | 122000 (312320) | 35-76 | 11.0-18.9 |
| New Albany | Illinois | 33000 (135680) | 86-160 | 1.9-19.2 |
| Barnet shale | Fort Worth | 42000 (10,752) | 500-1000 | 42.0-76.0 |
| Lewis Shale | San Juan | 42000 (10752) | 96-101 | NA |

Table 8:- United States of America (USA) fractured shale gas (Gas bearing) resources (USGS,1995)

*D. Heavy Oil and Bitumen*

➢ *Occurrence*

Petroleum is a spectrum that ranges from the freely flowing crude that has a water like viscosity to heavy oil that is tarlike and will only flow if heated or altered by viscosity lowering additives to bitumen (tar sands) that cements sand grains together and which will not flow at all. The heavy oil and bitumen have these common characteristics.

- Dark characteristics.
- So vicious that they will neither flow naturally nor respond effectively to primary or secondary recovery techniques.
- High in Sulphur (3-6%) nickel and vanadium (up to 500 PPM).
- Rich in hydrocarbon known as asphaltenes (a primary constitute of asphalt). Heavy oils and bitumen either occur alone or are found with liquid petroleum. Heavy oils and bitumen owe their origin to those three processes that may be operated single or jointly on petroleum including.

ISSN No:-2456-2165

- ✓ **Oxidation** of liquid petroleum and the loss of lightweight volatile fractions, leaving behind the heavy organic molecules.
- ✓ **Thermal Maturation** in which the light fractions have been driven off or converted to gas due to natural heating
- ✓ **Biodegradation** in which bacteria consume the lighter fractions, leaving heavier components behind. Heavy coils have low API gravity (10-20 API) and high viscosity (20cp). Due to its viscosity, transportation of heavy oil through pipelines and porous media require extra energy and may sometimes require the addition of heat in order to effect better flow.

Heavy oils and bitumen occur in several parts of the world. The largest known deposits are in Northern Alberta, Canada and in the Orinococo Basin of Venezuela, but significant resources also exist in the United States of America. middle East oil fields and Russia, Table 9 shows regional distribution of recoverable heavy oils and bitumen.

| Region | Heavy Oil | Natural Bitumen |
|---|---|---|
| North America | 35.3 | 531.0 |
| South America | 266.0 | 0.1 |
| Africa | 7.2 | 43.0 |
| Europe | 49 | 0.2 |
| Middle East | 78.2 | 0 |
| Asia | 29.6 | 42.8 |
| Others | 22.0 | 34.0 |
| World Total | 443.2 | 651.1 |

Table 9:- Regional distribution of estimated recoverable heavy oil and bitumen (tar sand) in billions of barrels (Craig et al, 2011).

Some geologists believe that oil sands (tar sand represent oil that arose from source rocks but never became trapped and concentrated by structural trap, (Carlson and Plummer, 2008; Okeke and Okogbue, 2011), further explained that hydrocarbon migration along faults may leak to the surface or leak into porous media where it may not be trapped to form a pool.

In such a circumstance, oil sands (tar sand) may be found as in the case of South Western parts of Nigeria, Canada and Azerbaijan (Caspian Sea). The tar sands deposit of South Western Nigeria has been estimated to be over 30 billion barrels of oil equivalent (Nwachukwu, 2003). As at 2005 (The Leading Edge, 2005), oil production from Canadian tar sands was estimated at 140,000 barrels per day (b/d). Almost 20% of Canada's present oil production comes from those oil sands. Counting on this unconventional resource, this gives Canada the second-largest oil reserves in the world after Saudi Arabia.

➢ *Development*

Heavy oil and bitumen (also known as oil sands or tar sands) differ from the more conventional oil and gas reservoir by virtue of the high-viscosity and density hydrocarbons that they contain. They are generally solids (bitumen) and semi-solids. (Heavy oil) at ordinary temperatures and therefore are not recoverable by ordinary petroleum production methods.

Two methods of development are known including;

- Mining Extraction and Processing/Refining method: This method applies only to bitumen processing. Bitumen deposit consisting of hydrocarbons and sand are strip mined using large excavators or draglines. The bitumen deposit being solid and oil bearing is actually mineral (oil mining) rather than being drilled like in the conventional drilling of oil and gas wells in oil fields (oil drilling). (Rice, 1932; Shea, 1947; Hoffman and Ruehl, 1953). The petroleum is then extracted from the bitumen using hot water. Once separated, the petroleum (oil) is processed in special refineries to remove Sulphur and to produce a variety of petroleum products (Fig. 4).

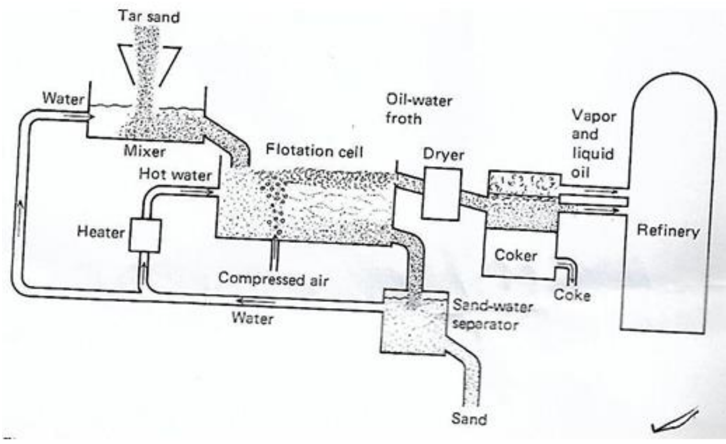


Fig 4: Extraction of hydrocarbon from bitumen (De Nevers, 1965)

- In-situ treatment, Recovery and Processing/Refining: This method applies to heavy all that are so dense and viscous that even if they flow into oil wells at very slow rate, may not be economic to be pumped and bitumen (tar sands) that are completely solid.

✓ Thermal Treatment Method:

1. **Steam injection**: This involves injection of high-pressure steam into the reservoir for a period of time which can be up to a month and after which injection is stopped.
2. **Use of Electrical/ Electromagnetic Devices**: Another aspect of thermal method is heating the reservoir with electrical/electrometric devices (electric electromagnetic a microwave technologies). The liquefied or light-weight oil may then be pumped out through appropriate oil wells.
3. **In situ combustion method**: This includes igniting some of the oil or bitumen underground and then letting heat generated by the fire melt or fractionate the lighter components so that they can be recovered from pumped wells. (Rodriguez et al, 2008; Das 2008; Alvarado and Manrique, 2010).

✓ Chemical flooding such as surfactant chemical additives: This involves injection of chemical into the reservoir (bitumen or heavy oil deposit). The injected fluid dissolve or mixes with the oil and reduces the viscosity improves inability of the oil to be pumped out from well (Shon et al, Gogarty, 1997; Lake 1989).

✓ Gas injection: This involves injection of natural gas (Mostly CH**4**) or Carbon dioxide, (C02) which will dissolve some of the heavy oil and allow it to flow so that it be pumped out (Jessen et al, 1998; Yelling and Metcalfe, 1980).

The best-known oil sand deposit in this world is the Athabasca Tar Sand in Northern Canada. Both mining/Extraction and in-situ treatment/ recovery techniques (Steam/gas injection) techniques are used in the exploitation of the tar sands deposit.

The environmental problems associated with development of heavy oil and bitumen energy resources are generally similar to that of development of oil shale energy resources, namely environmental impacts of mining/bitumen/tar sands (land degradations mine dusts/air pollution), water depletion/water pollution associated with bitumen extraction and in situ treatment practices (thermal treatment and flooding).

### *E. Natural Gas Hydrates*

➢ *Occurrences*

These are composed of unusual mixture of ice and gas in which methane (one of the gases in natural gas) is trapped in ice crystals (Atilhan et al, 2012). These hydrates are metastable in which the stability and properties are attributed to both temperature and pressure. Gas hydrates are formed when water comes in contact with molecule of gas (CH**4**) at low temperature and high pressure. The host molecule is the water while the guest molecule is the gas. They are held together by hydrogen bonds and stabilized by Vandar Waals Forces. They are found in extreme environments, notably permafrost in polar regions and in the deep ocean floor. The amount of gas hydrate in the ocean floor is staggering. According to (Collett, 2004), there may be at least twice the amount of potential fuel tied up in the gas hydrate as in all petroleum and nature gas combined.

Gas hydrates are important in industries where they may be used in the production and processing of nature gas and oil gas injection in experimental production of unconventional heavy oil energy resources.

Natural gas hydrate is very flammable, ignitable easily in air, when it comes in contact with oxygen, and gives water, carbon dioxide and energy.

i.e. $CH4+02 \longrightarrow CO2+H20+Energy$

The Carbondioxide produced though can be used in gas injection is also like methane a greenhouse gas and can contribute to global warming.

➢ *Development*

Natural gas hydrates are easily ignitable when in contact with oxygen. Commercial exploitation of gas hydrate deposit present formidable challenges. Mining of the deposit at the deep extreme ocean floor and permafrost required is an extreme technological problem.

Recent studies (Suess et al 1999 and Collett 2004) have proved the availability of high gas hydrate in the Canadian arctic region (River Mckenzie Delta). The cost of production and transportation to possible users is still enormous in today's petroleum economics (Lee et al 2011). This is why (Collett, 2004) described gas condensate as "a future energy resource".

## III. CASE HISTORIES OF ENVIRONMENTAL PROBLEM AND BENEFITS ASSOCIATED WITH DEVELOPMENT OF UNCONVENTIONAL HYDROCARBON ENERGY RESOURCES.

### *A. Overview*

Occurrence of most of the unconventional energy resources (coal bed methane, shale oil, heavy oil and shale oil, shale gas) are associated with the traditional/conventional fossil fuel energy resources, that is, coal, petroleum and natural gas. Some activities such as drilling and refining of petroleum, also apply to development of unconventional hydrocarbon resources. But some activities such as mining of oil shale or bitumen are peculiar to the unconventional hydrocarbon resources while activities such as hydraulic fracturing is practiced in the development of conventional and unconventional hydrocarbon resources (Okeke 2015, Girdley et al, 1989).

*B. Problems and benefits associated with oil shale development*

(Craig et at., 2011) and (Stoker et al., 1975) identified the environmental problems of land degradation/dust pollution associated with mining of shale, large quantity of water needed for the processing of the shale, management of solid waste produced during mining and burned shale produced after processing, and pollution of ground water where the burned shale is leached by rainfall and other source of surface water.

(Craig et at., 2011) also identified the benefit that are associated with d envelopment of oil shale energy resources to include;

- Production of ammonia and sulphur from processing of gas produced from oil shale processing.
- Production of chemicals including:
- Halite (HaCL)
- Darsonate (NaA(Co3)(0H2)
- Nahocolite (NaHC03)
- Production of aluminum (N2)3 and Sodium Carbonate (Na2C03)

C. Problems and benefits associated with use of hydraulic fracturing techniques in development of coal bed methane and shale gas/shale oil energy resources.

- *Preamble*

As earlier defined, Hydraulic fracturing is s technique of artificially fracturing of rocks at depth by injection of fluid under pressure (Martinez et al, 1992). The primary objective of hydraulic fracturing is to improve the porosity and permeability thereby enhance oil and gas production in conventional (sandstone and limestone) and unconventional (shale gas, shale oil and coal bed methane) reservoirs.

- *The major environmental problems associated with hydraulic fracturing practices include air, emission/pollution water depletion water pollution. These are discussed below;*
  Air Emission /Pollution

- Air Emission/Air pollution from hydraulic fracturing are related to methane leaks originating from wells and emission from diesel on natural gas-powered equipment such as compressors, drilling rigs, pumps etc. The components of the air emissions with healthy implications on humans if the threshold values are exceeded are sulphur dioxide, carbon monoxide and lead (Jain and Rao 2009; Schmidt, 2011). According to Khitoliya (2007), the health effects of these air pollutants on humans include irritation of eyes, cough and shortness of breath (sulphur dioxide), reduction in oxygen carrying capacity of blood (carbon monoxide), and risk of lead poison which may lead of impairment of central nervous system (lead). Methane emissions have potential of contributing to greenhouse gas (Howarth et al, 2011).
- Water depletion/water contamination Hydraulic fracturing uses between 4500 and 1.5 million US gallons (80-6000m$^3$) of water per well with large projects using up to 5 million US gallons (20,000m$^3$) (Abdala and Drohan, 2010). Additional water is used when wells are refractured several times. An average well requires 3 to 8 million US gallons over its life time Using the case of Marcellus Shale Gas Development as an example, as of 2008, hydraulic fracturing accounted for 650 million US gallons (2.500000m$^3$) per year which was about 8% water use in the area overlying Marcellus Shale (Abdala and Drohan, 2010). The large volumes of water required have raised concerns of hydraulic fracturing in arid area such as Karoo in South Africa (Less and Andersen, 1994).

During periods of low stream flow, it may affect water supplies for municipalities and industries such as power generation, recreation and aquatic life.

There are also concern about possible contamination of ground water by hydraulic fracturing fluid, both as it is injected under high pressure into the ground and as it returns to the surface. (Mooney, 2011). Chemical additives used in hydraulic fracturing fluids are the sources of contamination. Some of these chemicals are: polyacrylamide, ethylene glycol, borate salts guar gum, sodium chloride and citric acid. While some of the chemicals are common and generally harmless, some are known carcinogens at high enough doses (USHR, 2011).

- *Benefits*

In addition to use of hydraulic fracturing to improve production of oil/gas in both conventional and unconventional reservoirs, hydraulic fracturing has other engineering applications including;

- Measurement of in-situ stress of rocks at great depths. The stress measured major principal stress and minor principal stress are relevant in earthquake control studies, oil/gas drilling, underground mining of solid minerals and tunnel construction (Fairhust, 1964 and 1968, Hamson 1974; Canon and Graze 1938).
- Estimation of upper limit of grouting pressure in dam construction (Penman and Charles 1981 Morgenstern and Vaughan, 1963).
- Estimation of upper limit to be applied in-situ measurement of soil rock permeability by constant head/pumping-in test (Kennard, 1970; Jaegar, 1979; Goodman, 1980).

## IV. CONCLUSION

Energy resources are naturally occurring materials from which energy can be extracted economically. Energy resources may further be classified into renewable and non-renewable energy resources. The renewable energy resources comprise those resources that are replenishable within hours, days, months or years. Examples include; hydroelectric energy, tidal energy, geothermal energy, wind energy, solar energy, ocean energy and biomass (organic materials derived from plants and animals). The non-renewable energy resources are those resources that are not replenishable in natural processes operating on short time scales. Examples include: petroleum (crude oil) natural gas and coal. Petroleum, natural gas and coal are also called

ISSN No:-2456-2165

fossil fuel or fossil energy resources. They are also called hydrocarbon energy resources because their major constituents are hydrogen and carbon)

These non-renewable hydrocarbon energy resources, petroleum, natural gas and coal are further classified into conventional hydrocarbon energy resources and unconventional hydrocarbon energy resources. The conventional hydrocarbon energy resources have distinct source-rock, reservoir-rock and trap characteristics and boundaries; and traditional production wells (vertical and horizontal drilling operation) are used for their extraction or exploitation.

The unconventional hydrocarbon energy resources, reservoir rock paragenesis and trap boundaries. Unique or enhanced oil/gas recovery techniques in addition to the traditional production wells are often used for their extraction or exploitation. Such unique techniques include hydraulic fracturing of reservoir rocks, mining and processing of oil shale and bitumen in retorts and coking, units respectively and in-situ combustion such as gas injection to extract heavy oil. Five types of unconventional hydrocarbon energy resources are recognized and they include

- Coal bed methane (CBMS)
- Oil shale
- Shale oil and shale gas
- Heavy oil and bitumen
- Nature gas hydrate

Each type of the unconventional hydrocarbon energy resources has unique source rock-reservoir rock characteristics and extraction techniques. Generally, coal bed methane is extracted by use of vertical production wells drilled into coal bed and oil shale is processed with retorts after mining. Similarly, bitumen is processed with coking units after mining. Shale oil and shale gas are exploited by drilling of horizontal wells and hydraulic fracturing of the reservoir rock. Heavy oils are processed in-situ using steam injection or chemical flooding. Natural gas hydrates are also exploited using vertical production wells drilled into permafrost regions of the world.

The environmental problems of development/exploitation of unconventional hydrocarbon energy resources include; land degradation caused by mining of oil shale and bitumen), air pollution (caused by dusts from mining of oil shale and air emissions from hydraulic fracturing operations and water depletion/pollution caused by activities associated with exploitation of coal bed methane, oil shale/bitumen and shale gas/shale oil).

## REFERENCES


[1]. Abdalla, C.W. and Drohan, J.R., (2010). Water withdrawals for development of Marcellus Shale Gas in Pennsylvania, In: Introduction to Pennsylvania Water Resources (Report). The Pennsylvania State University.

[2]. Atilhan, M., Aparico, S., Benyahia, F., Beniz, E., (2012). Natural gas hydrates. Advances in Natural Gas Technology, 10:194-212.

[3]. Batruna, M. and Daggez, A. (2010). Drilling and completion of horizontal wells. SPE Publication Houston Texas, USA.

[4]. Boyer, C. (2006). Producing gas from its source. Oil Field Review,18(3):36-49

[5]. Brown, T. O., Taylor, C.E and Bernardo M.P. (2010). Rapid gas hydrate formation processes. Will they work? Energies 3(6): 1154-1125.

[6]. Canon, G.E. and Craze, R.C (1938). Excessive pressure and pressure variation with depth of petroleum reservoir in the Gulf Region of Texas and Louisiana, Trans, America Institution Min &Met. Engr, 127:31-38.

[7]. Carlson, D.H. and Plummer C. C (2008). Physical Geology: Earth Revealed, 8th Edition McGraw's-Hili Book Company, New York.

[8]. Cook, T. (2004). Calculation of estimated ultimate recovery (EUR) for wells in assessment units of continuous hydrocarbon accumulations: USGS Powder River Basin Province Assessment Team. Total Petroleum System and Coalbed Gas, Wyoming and Montana. USGS Digital Data Service DOS -69-C, l-6

[9]. Collett, T. S. (2004). Gas hydrates as a future energy resource. Geotimes (November 2004):24-27

[10]. Craig, J. R., Vaughan, DJ and Skinner, B. J. (2011). Earth Resources and the Environment. Prentice Hace, New York.

[11]. Compton, R.R. (1977), interpreting the earth. Harcourt Brace Jovaovich, Inc. New York.

[12]. Curtis, J. B. (2002). Fractured shale-gas systems. AAPG Bull. 88 11): 1921-1938

[13]. Dar, S. (2008) Electromagnetic heisting in viscous oil reservoir (SPE-117693). Proc. International Symposium on thermal Operation in Heavy Oil recovery (20-23 Oct. 2008), Calgary, Canada.

[14]. De Nevers, N. (1965). The Secondary recovery of petroleum. Scientific American (July1965):35-42

[15]. De Nevers, N. (1973). Final Environmental statement for the Prototype Oil Shale Leasing Program, Government printing Office, Washing com D.C.

[16]. Explorer, (2001) Shale gas exciting again ANG. Explorer, website:http//wwwaapg.org/explorer/2001.

[17]. Explorer, (2002). Barnett Shale living up to potential Explorer (July, 2002), 23(7):18-27.

[18]. Fairhurst, C. (1964). Measurement of in-situ rock stresses with particular reference to hydraulic fracturing. Rock Mechanics and Engineering Geology, 2:129-147.
[19]. Fairhurst, C. (1968). Methods of determining in-situ rock stresses at great depths, US Corps of Engineers, Nebraska. Technical Report No, 1068.
[20]. Fakharian, H., Garji, H., Naderi, N.A. and Kamele M. (2012). Potato Starch as methane hydrate promoter, fuel, 94:356-360.
[21]. Girdley, J. C., Hold Itch, S. A., Nerode, D. E. and Veatch, R. W. (1989). Recent Advances in Hydraulic Fracturing. Society of Petroleum Engineers (SPE) Manograph Series, No. l2, Richardson, Texas.
[22]. Gogarty, W. B. (1997}. Oil recovery with surfactants: history and current analysis. In: Improved oil recovery by surfactants and polymer flooding [Shan, D.O. and Schechter (eds.)], Academic Press, U.K.
[23]. Goodman, R. E. (1980), Introduction to rock mechanics. John Wiley and Sons, New York.
[24]. Green, D. W. and Willhite, G. A. (1981) Enhanced oil recovery. SPC textbook Serial Society of Petroleum Engineer, Housetem USA).
[25]. Hamson, B. C. (1974). Determination of stresses in deep holes and around tunnels by hydraulic fracturing. Proc. US Rapid excavation and tunneling Conf., 2:1539-1560.
[26]. Henry, J. G. and Heinki, G. W. (1990). Environmental Science and Engineering, 2nd Edition. Prentice Hall of India Private Limited. New Delhi, India.
[27]. Howarth, R. W., Santoro, R. and Ingraffes, A. (2011). Methane and greenhouse-gas as footprint of natural gas from shale formations. Climatic Change (Springer) 106(4):679-690.
[28]. Hoffman, F. and Ruehl W. (1953). One mining in Germany Monthly (July 1953): 20-23, and (August 1953):25-33.
[29]. Hubert, M. K. and Willis D. G. (1955). Important fractured reservoirs in the United States Proc.4th World Petroleum Congress (June, 1955), 57-84 Texas) section 1A.
[30]. Jaegar, J.C. (1979). Rock mechanics and Engineering.2nd Edition, Methuen &Co., London,
[31]. Jain, S. K and Rao S. S. (2009). Industrial Safety, Health and Environmental Management System. 2nd Edition. Khana Publishers, New Delhi, India
[32]. Kennard, R.M. (1970). The measurement of soil permeability in-situ by the Constant Head Test. Ph.D. Thesis, University of London.
[33]. Khitoliya, K. K. (2007). Environmental Pollution S. Chard & company Ltd New Delhi, India.
[34]. Kumar. A., BhaHacharhee, G., Kulkaine, B. D. and Kumer, R. (2015). Role of surfactants in promoting gas hydrate formation, industries and Engineering Chemistry Research, (54) 9: 12217-1222.
[35]. Klett, T. R. and Carpenter, R. R (2003). for span Model Users Guide USGS Open File Report, 03-354, 1-35.
[36]. Klett, T. R. and Schmoker, J. W. (2004). Geological forum input data form and operational procedures for the assessment of continuous petroleum accumulations. Unital- Piceance Province case study (Utah and Colorodo: DDS-69-B, 1-9.
[37]. Knutson, C. F. and Dana, G. F. (1982). Developments in oil shale in 1981. AAPG Bull. 66(11): 1210-1221.
[38]. Lake & L. W (1989). Enhanced oil recovery. Prentice Hall, Eaglewood.
[39]. Lee, J. Y., Yun, T. S., Ryu, B. J. and Cho, G. C. (2011). Review on the gas hydrate development and production as a new energy resource. Journal of Civil Engineering, 15(4): 689-696.
[40]. Less, C. and Anderson, N. (1994). hydro fracture: State of the art in South Africa. Applied Hydrogeology (Feb., 1994), 5E-53.
[41]. Li, J. Liang, D. Guo, K. Wang, R and fan S (2006). Formation and Association of HFC 1349 Gas Hydrate in Nano-Copper Suspension. Energy Conversion and Management, 47 (2): 201-210.
[42]. Loucks, R. G. and Ruppel, S. C. (2007). Mississippian Barnet shale: lithofacies and depositions selling of deep-seated shale water succession in the Fort Worth Basin, Texas AAPG Bull, 9(4): 579-661.
[43]. Levorsen, A. I. (2003). Geology of petroleum. 2nb Indian Edition. CBS Publishers and Distributors, New Delhi, India.
[44]. Li, J., Liang, D., Guo, k., Wang, R. and Fan, S. (2006). Formation and dissociation of HFC1349 Gas Hydrate in Nano Copper Suspension. Energy Conversion and Management, 42(2):201-210.
[45]. Mallory, W. W. (1977). Oil and gas from fractured shale reservoirs in Colorado and Northwest New Mexico. Rocky Mountain Association of Geologists Special Publication No.l, 38p.
[46]. Martin, M. G., John, W. I. and Wender, I. (1983). Coal science, Vol. 2. Academic Press, London.
[47]. Martinez, S.L. Steancon, R. E. and Couler, A.W. (1992). Formation fracturing. In: Petroleum Engineering Handbook (H.B, Bradley, Ed.) SPE Richardson TX. 55.1-55.12
[48]. Metz, W.D (1974). Oil Shale: A huge resource of low-grade fuel. Science, (June 1974): 1271-1275.
[49]. Mills, G.A. (1971). Gas from coal: Energy of the future Environmental Science and Technology (Dec 1971): 1178-1182.
[50]. Mooney, C. (2011). The truth about fracking. Scientific American 305(5): 80-85.
[51]. Morgenstern, N.R. and Vaughan, R, R. (1963). Some Observations in allowable grouting pressures. Proc. Conference on Grouts and Drilling Muds in Engineering Practice, Butterwords, London.
[52]. Nevarado, V. and Manrique E. (2010), Enhanced oil recovery: An update review Energies, 3:1529-1575.
[53]. Nwachukwu, J.O. (2003). The Bitumen Deposits of Nigeria. NAPE News, 3(2)11.
[54]. Obaje, N. G., Wehner, H., Scheeden, G., Abubakar, M. B. and Jauro, A. (2004). Hydrocarbon prospectively of Nigerians' inland basin from the viewpoint of organic geochemistry and organic petrology. AAP-G Bull. 88(3): 325-353.
[55]. Okeke, O. C. (2010). Influence of pressure gradients and fracturing in oil field rocks on hydrocarbon

accumulation and exploitation: A review. Global Journal of Geol. Sci. 8(l): 25-34.

[56]. Okeke, O. C. (2015). A review of the mechanism and engineering significance of hydraulic fracturing. FUTOs Journal Series, 1(1); 95-110.

[57]. Okeke, O. C. and Okogbue, C. O. (2011) Shales: A review of their classification, properties and importance to the petroleum industry. Global Journal of Geol. Sci. 9(l):55-73.

[58]. Okeke, O. C. Akalonu, A. N and Jonathan, A. E. (2004). Mineralogical composition and depositional environment of Enugu Coal, Southeastern Nigeria. Advances in Geosciences, 2:24-31.

[59]. Penman, A. D. and Charles, J. A. (1981). Assessing the risk of hydraulic fracturing in dam cores. Proc. 10th Int. Conf. in Soil Mech. & Foundation Engineering, Stockholm.

[60]. Pollastro, R. M., Emil D. A and Phillip M. S. (2007). Total petroleum system assessment of undiscovered resources in the giant Barnet Shade continuous (unconventional) gas accumulations. Fort Worth Basin, Taxas. AAPG Bull. 91(4): 551-578.

[61]. Regan, L. J. (1953) Fractured shale reservoir of California AAPG Bull.37 (Feb. 1953}:201:206.

[62]. Rice, D. D. (1993). Composition and origin of coalbed gas in hydrocarbons from coal. AAPG studies in Geology No. 3S (B.E. Law and D.D. Rice, eds.) Americans Association of Petroleum Geologists Tulsa, Oklahoma: 159-184.

[63]. Rice, G.S. (1932). Mining of petroleum by underground methods US Burean of Mines. Bull. 351-159p

[64]. Rodriquez, R., Bashbush J.L. and Rincon A. (2008). A feasibility of using electrical drainhole heated in Faja heavy oil reservoir (SPE-17687) Boc International Symposia on Thermal Operational in heavy oil recovery (20-23 Oct.2008), Calgary Canada.

[65]. Schmidt, C. (2011), Blind rush? Shale gas boom proceeds amidst human health questions. Environmental Health perspectives, 119(8):348-353.

[66]. Schmoker, J. W. (1995). Method for assessing continuous type (unconventional) hydrocarbon accumulations. In: O.L. Gautier, G.L. Dolton, K.I. Takashi, and K.L. Varnes (eds.) National assessment of United States and gas resources results, methodology and supporting data. USGS digital data series DDS-30:1-30.

[67]. Schmoker, J. W (2002). Resource assessment perspectives for unconditional gas systems AAPG Bull: 86(11): 1939-1945.

[68]. Schmoker, J. W (2005). USGS assessment concept for continuous petroleum accumulations -/USGS Special Report 1(2005): 1-9.

[69]. Shea, G.B. (1947). Mining for oil in Japan. Production Monthly (December 1947):- 1928.

[70]. Shen, A., Fishwick, R., Wood, J., Leek, G., Rigby, S. and Greaves, M. (2010) A review of novel techniques for heavy oil and bitumen extraction and upgrading. Energy and Environment Sci. 3:700-714.

[71]. Stearns, M., Tindala, J.A., Gronin, G., Friendel, M. J. and Bergquist, E. (2005). Effects of Coal bed methane discharge waters on vegetables and soil ecosystem in Powder River Basin. Water, Air & Soil Pollution, 168(4):33-57.

[72]. Stoker, H. S., Seager, S., Land Capener, R. L. (1975). Energy: From source to use. Scott, Foresman and company, Illinois, USA.

[73]. Suess, E., Bohrmann, G. Greinert, J. and Lausch, E. (1999). Flammable ice Scientific American (Novemberl999)76-83.

[74]. The Leading Edge, (2005). Review of HIS Energy Report on 10-year petroleum TRENDS (1994-2003) SEG Tulsa 24(1): 28-31.

[75]. US Department of the interior, (1973), Final Environmental Statement for the Prototype Oil shale Leasing Program. Government Printing Office Washington D.C.

[76]. US Geological Survey (USGS), 1995. National Assessment of United States oil and gas resources USGS Government Printing Office Washing D.C. 20p.

[77]. USHR (2011). Chemicals used in hydraulic fracturing. Report by Committee on energy and commerce. US House of Representatives

[78]. World Energy Council (WEC) (2001). Oil shale-world Energy Resources, http/www/world energy.org

[79]. Woodward, J. Meissner F. F. and Clayton, J. I. (1984). Hydrocarbon Source rocks of the Greater Rocky Mountain Region: Denver, Colorado Rocky Mountain Association of Geologists, 557P.

[80]. Yelling, W. F. and Metcalfe, R. S. (1980). Determination and prediction of CO minimum miscibility pressures, Journal of petroleum technology, 32:160-165.

[81]. Zou, C.N. (20013). Unconventional hydrocarbon geology. Beijing, China (in Chinese) Geological Publishing House, Beijing China (in Chinese)

[82]. Zou, C. N., Zhu, R. k. and WU, ST. (2012). Types, characteristics, genesis and prospects of conventional and unconventional hydrocarbon accumulations. Acta pet sin, 33(2):173-187

[83]. Zou, C.N., Yang, Z., and Zhang G.S. (2014). Conventional and unconventional petroleum accumulations: Concepts and practical significance. Petroleum exploration and development, 41(1):14-30.