Bitumen Extraction from Tar Sands Using Solvent Techniques

Funsho Afolabi Taiwo Ojo Stephen Udeagbara Afeez Gbadamosi

Abstract - There is a vast deposit of tar sand containing bitumen in the South-Western part of Nigeria along the Ondo-Edo-Ogun-Lagos belt. These deposits in the shallow subsurface of this region are grossly untapped due to environmental risks and concerns, economic reasons and lack of technical know-how. While subsurface exploration and in situ recovery and upgrading have been embraced in countries like Canada and Venezuela, Nigeria has not yet exploit these recovery options in order to increase its total fossil energy reserves. The aim of this study is to evaluate solvent technique of subsurface extraction of bitumen from Nigerian tar sands which is cost-effective and operational-efficient. This work covers the use of an already established solvent as a pivot and two other new solvents, and comparing their results in terms of efficiency. The results obtained after the experimental work shows that *Ethyl Acetate* gave the highest rate of extraction while *Acetone* gave the lowest extraction rate. In terms of the recovered solvent, *Acetone* gave the highest solvent recovery while *Ethyl Acetate* gave the lowest. The result of this research work shows promises for the technique but it is not yet established via core/pilot scale. Thus it serves as a source of sensitization for government in the context of generation of revenue and increment of the fossil energy reserve.

Index Terms – Bitumen, Extraction, Nigerian tar sands, Solvents, Solvent technique, Recovery, Tar sands

1 INTRODUCTION

Nigeria has a considerable large deposit of natural bituminous tar sand also known as oil sand or oil impregnated sand. The Nigerian tar sand deposits can be found within the confine of the eastern margin of Dahomey basin which lies within a depot belt cutting across three major provinces/States which include: Ogun, Ondo, Edo states in the South-western and South-southern Nigeria respectively. Tar sand is composed mainly of heavy oil and clays that are rich in mineral and water. This heavy oil content of tar Sand is commonly called bitumen. In the raw state tar sand is strictly a black viscous substance. The total reserve of heavy oil is estimated to exceed 30 billion barrel [1]. Bituminous sand is wide spread in the South-western part of Nigeria in minable, economical quantity. These tar sands outcrops in a 29km by 6km belt, running from Okitipupa Ridge further down the edge of the tertiary Niger-Delta to the far west of Ijebu-Ode in Ogun State. Significant work has been carried out by various authors on the geology, origin, occurrence, processing and utility of the tar sands [1], [2], [3] & [4].

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1.1 Bitumen as an Extra Source of Energy Reserve in Nigeria

The Nigerian tar sand has an immense potential as an additional hydrocarbon based energy resource in Nigeria. Tar sand produces synthetic crude oil which if combined with Nigeria conventional crude oil will prolong the life span of the latter. This vast, extensive deposit of tar sands which stretches to parts of Lagos State of Nigeria covers a belt of about 120km with consistently high oil saturation.

Nigeria's bitumen is documented to rank fifth in the world, Canada having the world's largest deposit of this essential natural resource. Interestingly, too, this solid mineral is said to be about twice the existing oil reserve in the country and the largest chunk of it is reportedly located in Agbabu in Ondo State Discovered in 1900 [3]. However, two factors often described as disincentives to bitumen exploration/exploitation are the lack of technical expertise and the high cost of tapping the resource, in general terms. These, coupled with government's obvious non-seriousness because of oil money, have stalled even the feeble effort to exploit the country's bitumen resource.

Adegoke et al[3] put the recoverable bitumen in Nigeria exploitable by open-cast mining techniques at 1.079billion barrels. The heavy oil in-place for an area of 550 x 10^6m^2 south of the outcrop area with overburden in excess of 100m was put at 32.58 billion barrels. *Coker*[7] reported the recoverable reserves for areas designated as suitable exploitation by surface mining to be 3.6 x 10^6bbl bitumen. The total possible area covered by bitumen is estimated at about 189 sq.km, with an estimate of average thickness of pay at about 20m.

1.2 Tar Sand Chemical Composition

Bitumen is a semisolid hydrocarbon that is sticky, black and highly viscous. It's a naturally occurring substances that is considered to be a complex mixture of high-molecular-weight hydrocarbons and non-hydrocarbons which can be separated into fractions consisting of oily material, resins, asphaltenes, and carbenes. The tar sand is a sedimentary rock that contains bitumen and other heavy petroleum that, in natural state, cannot be recovered by conventional petroleum-recovery methods. Tar sand is composed of a mixture of about 10-20% bitumen and about 80-85% mineral matter including sands, clays and 4-6% water. They are believed to have been formed from biodegradation and water-washing of light crude due to lack of cap rock. The Nigerian Tar sand is believed to have been formed in a similar process. Tar sands are impregnated sands that yield mixtures of liquid hydrocarbons, which require further processing other than mechanical blending before becoming finished petroleum products. Until recently, Nigerian bitumen deposits were called tar sands, but are now known as oil sands. The viscous oil must be vigorously treated in order to convert it into upgraded oil before it can be used in refineries to produce gasoline, kerosene and other fuels, thus Oil sands must be mined or recovered In situ. Bituminous tar sand deposit of South-western Nigeria represents the product of in-reservoir transformation of convectional crude oil by microorganisms. The biotransformation of the heavy oil has led to the alteration of both the chemical and physical characteristics of this oil. The change in the chemical composition has posed a great problem to the refineries as feedstock tends to react with refineries components thereby destroying refining plant. Hence the commercial production of these resources has not been encouraged.

1.3 Aim of Study

The aim of the study is to evaluate solvent techniques of extraction of bitumen from Nigerian tar sands which are cost-effective, environmentally friendly and operational-effective while the following objectives assisted in attaining this aim:

1. To evaluate the potency of esters as compared to previously expensive solvents in use like acetone and toluene.

2. To evaluate the upgrading capability of these esters.

Basically, this study intends to promote the exploration and exploitation of bitumen from Nigerian tar sands which can aid in further revenue generation for the government and increment in the total fossil energy reserve of the country. The justification for this study is that Easy-to-find conventional reserves are far offshore in deepwaters and thus expensive and highly risky to exploit, while tar sands are at shallow depths in huge and commercial quantity onshore.

2 LITERATURE REVIEW

2.1 Methods of Extraction of Bitumen

Traditionally, the production of heavy oils and bitumen has been dominated by cold production from reservoirs that are either relatively close to the surface (as is in the case of Canadian oil sands) or easy to flow (as in the case of the lighter Venezuelan heavy oils) [5]. Since they are generally well understood techniques, they are seen as low-risk, primary or secondary production methods which may be followed up by alternative techniques to achieve higher recoveries. Enhanced Oil Recovery is usually considered as the third stage of production where the oil left behind by the low risk primary and secondary methods is extracted using more complex techniques. These techniques improve oil displacement efficiency in the reservoir by reducing the viscosity of the oil to ease flow or by literally pushing it through the reservoir. A second objective is to improve sweep efficiency: The volume of reservoir that is contacted during extraction.

2.2 Past Studies on Bitumen Extraction in Nigeria

A study on Solvent extraction of bitumen from Nigerian tar sands using toluene was investigated [5]. Pulverization of the tar sands followed by agglomeration in a mechanical shaker resulted in spherical agglomerates having higher bitumen contents than the mined tar sand. The extent of beneficiation was 4% and 19% for the high grade and low grade sands, respectively. Temperature, agitation, and tar sand/solvent (S/L) ratios were found to be significant variables affecting the dissolution of bitumen from the sand. S/L ratio has the greatest effect on extraction efficiency. The rate of bitumen extraction, expressed as extractability, showed great dependence on agitation. About 16-fold and 15-fold increases in extractability were obtained for S/L ratios of 1/20 and 1/5 respectively for a 2.8 fold increase in agitation.

A work by another author on Nigerian tar sands involving Steam injection and in-situ combustion methods of mining Agbabu bitumen deposit were studied [10]. Laboratory experiments were carried out on the bitumen deposit. The steam injection analysis was used to deduce values for key performance indicators such as water-oil ratio, oil-steam ratio, thermal ratio, heat loss to formation and energy requirements while the in situ combustion Laboratory analysis was used to obtain information on combustion characteristics of the formation, Air requirements and fuel consumption, etc. The results of the investigation indicate high susceptibility of Agbabu bitumen formation to the two mining methods. In addition, the comparative results of the two mining methods showed that the in situ combustion method was more efficient and economical than the steam injection method in the mining of the Agbabu bitumen deposit.

An alternative recovery technique known as supercritical carbon dioxide extraction was investigated [13]. Recent supercritical extractions use high temperatures and pressures. The upgrade in this research involves using high pressures and lower temperatures which saves energy and improves the process. The experimental study of the bitumen extraction from Nigerian tar sand by dense CO_2 was carried out by high pressure extractor. The samples of tar sand were first heated in an oven at 120 °C to melt. A 50 g sample of melted tar sand with addition of 3 g of ethanol was placed into an extractor and heated to 80 °C to initiate the experiment. Carbon dioxide was injected in to the extractor to create 50 MPa of pressure in static mode for 20 min after which the extract was collected. In the presence of ethanol, the extract had a lighter colour than the usual black. An extract of 19.47 % was calculated which makes the recovery achieved very encouraging. The experiment shows that recovery of bitumen from tar sand is possible under relatively low temperatures and can be possibly economically profitable.

3 METHODOLOGY

The purpose of this experiment was to evaluate solvent technique of extraction of bitumen from Nigerian tar sands using a laboratory means of extraction. The experimental work focuses on the bitumen extraction of a given sample of tar sand using three solvents (i.e. acetone, ethyl acetate and 3-methoxy butyl acetate). The extraction would indicate if the proposed solvents are more efficient as compared to already established solvent techniques.

3.1 Materials Used and Their Descriptions

Tar sands were collected from Agbabu (Figures 3.1) Ondo State. The solvents employed are the following:

Acetone – Also known as propanone with the chemical formula $(CH_3)_2CO$. It is a colourless, volatile, flammable liquid, and is the simplest ketone. Acetone is miscible with water and serves as an important solvent in its own right

***Ethyl Acetate* –** or ethyl ethanoate (EtOAc) is the organic compound with the formula CH_3-COO-CH_2-CH_3, simplified to $C_4H_8O_2$. This colourless liquid has a characteristic sweet smell (similar to pear drops). Ethyl acetate is the ester of ethanol and acetic acid

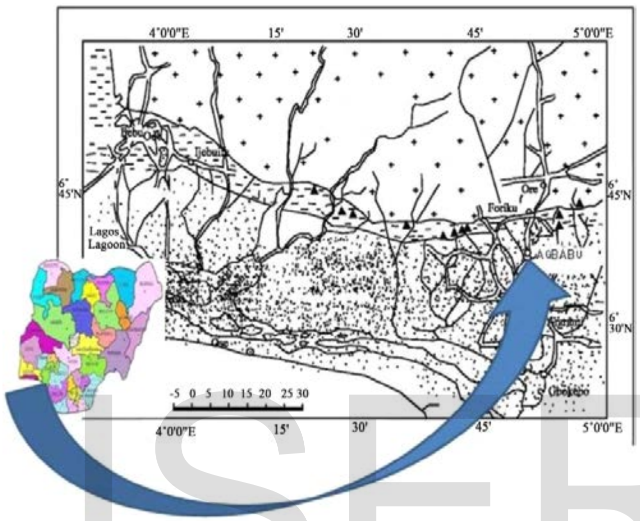

Fig. 3.1: Location of Sample Collection.

Fig. 3.2: Oil Sands Outcrop at Agbabu, Ondo State.

***3-MethoxyButyl Acetate* -** A liquid with an acrid odour. Flash point near 140°F. Slightly less dense than water. Vapors much heavier than air. Flammable and slightly soluble in water. When heated to decomposition, emits acrid smoke and irritating fumes.

3.2 Equipment

***Soxhlet Apparatus* -** An extractor that has three main sections: A percolator (boiler and reflux) which circulates the solvent, a thimble (usually made of thick filter paper) which retains the solid to be laved, and a siphon mechanism, which periodically empties the thimble. The assembly is typically made up of a source material containing the compound to be extracted which is placed inside the thimble that is loaded into the main chamber of the Soxhlet extractor. The extraction solvent is placed in a distillation flask which is placed on a heating element while a reflux condenser is placed atop the extractor.

Fig. 3.3: A Soxhlet Apparatus.

3.3 Experimental Procedure

A simple procedure was employed in this research work. The average weight of tar sand used in all three solvent extractions (i.e. *acetone, ethyl acetate* and *3-methoxy butyl acetate*) was 40g. The procedure is as follows for each of the solvents used:

- The tar sand samples were heated using the magnetic heated stirrer for 20-30mins and weighed 40g of the heated sample.
- Samples were placed in the thimble which was placed in the main chamber (extraction tube) of the Soxhlet apparatus.
- Solvent is poured from the top of the condenser into the distillation flask until there is a reflux giving an average volume of 250ml of solvent.
- The temperature of the heating element of the apparatus was raised to a level above the boiling point of the solvents. About 60^{o}C for *Acetone*, 80^{o}C for *Ethyl Acetate* and 175^{o}C for *3-Methoxy Butyl Acetate*.
- Weights of bitumen extracted were measured at time intervals of 0, 4, 12 and 24 hours during the extraction with a weighing balance.
- The weights of solvent recovered were also measured after each extraction with a weighing balance.
- The percentage recovery of bitumen extracted and the solvent recovered were determined.
- The weights of the remaining tar sand after each experiment were measured with a weighing balance.

4 RESULTS AND DISCUSSION

After a successful laboratory work using the three solvents and 40g of tar sand for each solvent at time intervals of 0, 4, 12 and 24 hours, the results obtained are summarized in tables, graphs and histogram below

Table 4.1: Weight of Extracted Bitumen versus Time for Different Solvents.

Time (Hours)	Acetone (g)	Ethyl Acetate (g)	3-Methoxy Butyl Acetate (g)
0	0.00	0.00	0.00
4	0.93	2.20	2.07
12	2.55	6.67	5.27
24	5.23	6.88	6.75

Table 4.2: Percentage of Extracted Bitumen versus Time for Different Solvents.

Time (Hours)	Acetone (%)	Ethyl Acetate (%)	3-Methoxy Butyl Acetate (%)
0	0.00	0.00	0.00
4	2.33	5.50	5.18
12	6.41	17.33	13.62
24	13.45	17.96	17.88

The results show that *Ethyl Acetate* gave the highest rate of extraction while *Acetone* gave the lowest extraction rate. *3-Methoxy Butyl Acetate* gave the second best extraction rate. Both esters used gave higher extraction rate than the pivot solvent acetone. These results are best described in tables and charts above, where they show the weights and percentages of bitumen extracted.

Fig. 4.1: A Graph Showing the Weight of Extracted Bitumen versus Time for Different Solvents.

Fig. 4.2: A Histogram Showing the Percentage of Extracted Bitumen versus Time for Different Solvents.

In terms of the recovered solvent, *Acetone* gave the highest solvent recovery while *Ethyl Acetate* gave the lowest. The solvent recovery of *3-Methoxy Butyl Acetate* is rather low as compared to *Acetone*. For the remaining tar sand, as shown in fig. 4.3, *Acetone* gave the highest weight of tar sand after the extraction. This is simply because the solvent did not extract the whole bitumen in the tar sand. This was not so for *Ethyl Acetate* and *3-Methoxy Butyl Acetate* which came very close to extracting all the bitumen in the tar sand.

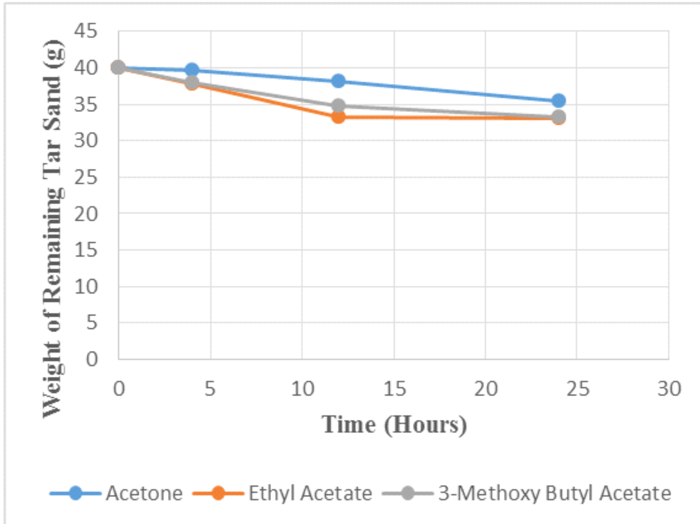

Fig. 4.3: A Graph Showing the Weight of Remaining Tar Sand versus Time for Different Solvents.

All in all, in terms of the weight and percentage of bitumen extracted and weight of remaining tar sand, *Ethyl Acetate* gave the best, followed by *3-Methoxy Butyl Acetate* and then *Acetone*. Furthermore, in terms of weight and percentage of solvent recovered, *Acetone* gave the best, followed by *3-Methoxy Butyl Acetate* and then *Ethyl Acetate*. During the course of the laboratory work, the following observations were made:

- The bitumen extracted with *Acetone* at different time intervals were in a small volume and highly viscous while The bitumen extracted with *Ethyl Acetate* and *3-Methoxy Butyl Acetate* at different time intervals were in a large volume and very light implying that esters had possibly upgraded the extracted bitumen.
- The time taken for the extraction of all the bitumen in a given tar sand sample using *Ethyl Acetate* and *3-Methoxy Butyl Acetate* were shorter compared to *Acetone* which took a longer time. Most of the bitumen was recovered after 12 hours using *Ethyl Acetate*, Most of the bitumen was recovered after 24 hours using *3-Methoxy Butyl Acetate* and Not all the bitumen in the tar sand sample were recovered after 24 hours using *Acetone*.

In terms of cost, *Acetone* remains the cheapest compared to the other two solvents costing around $25 per litre While *Ethyl Acetate* and *3-Methoxy Butyl Acetate* cost $32 and $51 per litre respectively. In terms of payback time for the rate of recovery of bitumen, *Ethyl Acetate* will give the most favourable payback time while *Acetone* will give the least favourable payback time, however, in terms of solvent regeneration, *Acetone* will be preferred to other solvents. These factors are very important in the choice of solvent. In all, ethyl acetate remains the best solvent with regards to operational efficiency and cost. This being that its use will generate enough revenue within a short period of time that would have outweighed the cost of solvent generation at the long run.

5 CONCLUSION

Ethyl Acetate gave the best result in terms of weight and percentage of bitumen extracted while *Acetone*, as the pivot solvent, gave the lowest result in terms of weight and percentage of bitumen extracted although solvent regeneration could be an encouraging factor to be considered during selection coupled with the fact that it is cheaper. *Ethyl Acetate* and *3-Methoxy Butyl Acetate* reduced the viscosity of the extracted bitumen meaning the bitumen extracted with the solvents are upgraded bitumen, While those extracted with *Acetone* remained highly viscous. Thus, employing the use of *Ethyl Acetate* and *3-Methoxy Butyl Acetate* for extraction of bitumen will save cost of injecting steam or hot water

In other to improve this research work it is recommended that a laboratory coreflooding technique for solvent extraction of bitumen should be investigated which should be coupled with a more detailed and in-depth cost analysis in order to validate the choice of solvent. The novel solvent technique shows promise so a pilot scale study would serve as a ground work which can be built upon. Also, the research should incorporate environmental impact assessment to evaluate the possible risk on the immediate communities where these tar sands are found. In all, this research study should sensitize the government in the context of generation of revenue, employment creation and increment of the energy reserve.

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