

The Bitumen Extraction from Nigerian Tar Sand Using Dense Carbon Dioxide

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The need for alternative sources of energy has become even more acute in light of the recognition of the dwindling conventional world oil reserves. The interest in exploring other avenues of complimenting and/or eventually replacing this resource is growing quite rapidly. A ready alternative to conventional crude oil is oil sands which are abundant and vastly unexplored. The huge deposits of tar sand found in South-Western Nigeria remain untapped due to concerns about the environmental impact. The consequences of the methods in processing tar sand, ranging from water pollution to emission of greenhouse gases, especially in Canada bring in to sharp focus the urgent need for an alternative means of extracting oil from tar sand. A more effective and less environmentally damaging procedure could be the break through needed to open a new chapter in the exploitation of oil sands.

The alternative recovery procedure is supercritical carbon dioxide extraction. 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 CO₂ 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. Nigerian tar sand is known to be composed of 84 % sand, 17 % bitumen, 4 % water and 2 % mineral clay. Using this data, 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.

1. Introduction

1.1 Tar sands

World energy demand is increasing and the current crude oil is being produced from the light oil deposits which are only one third of all world oil reserves. The other two thirds belong to heavy and extra heavy crude oil group and only one per cent is being exploited. With the increasing prices of crude oil, the production from the heavy and extra heavy oils will become more economically profitable and the scale of their exploitation will increase.

The petroleum formation process exists due to thermal transformation of soluble bitumen and insoluble kerogen dispersed in organic substances. Like most typical thermal transformation reactions, the petroleum generation rate increases with increasing burial depth and consequently with increasing temperature. In shallow oil deposits located near the surface where oil deposits have access to surface waters containing oxygen, biodegradation takes place. Tar sands are the product of biodegradation and chemical changes due to bacteria degradation and water washing.

The tar sand is a sedimentary rock that contains bitumen or other heavy petroleum that, in natural state, cannot be recovered by conventional petroleum-recovery methods. This condition usually applies to oils having a gravity less than 12 °API. The largest world deposits are in Canada, Venezuela, Madagascar, USA, and Russia (Chilingar and Yen, 1978). The recovery of bitumen from tar sand is a difficult process due to its high viscosity. Viscosity reduction is achieved mainly by injecting steam (300-340 °C) and solvents into the sands. These processes use more water and require larger amounts of energy than conventional oil extraction. The most efficient method in use currently is surface mining, where tar sand is excavated, washed with hot water and NaOH is added to the sand to improve bitumen separation from the sands. Wetting agents such as caustic sodium and sodium silicate can be used as processing aids during the hot water digestion of tar sands (Miller and Misra, 1982).

The quartzose tar sands are of fluvial and lacustrine origins with the highest contents of tar being present in the clean, well sorted fluvial sands. The maximum tar-oil content is 18-20 % by weight of saturated sand. In spite of the high energy consumption required in extraction of bitumen from tar sand, it is an economically viable enterprise and it is being undertaken in vast tar sand deposits in Canada. The degree of oil saturation in a formation which is generally measured in weight per cent varies from 0 to as high as 18 %. The Athabasca tar sands, the biggest tar sand deposits in the world have an average degree of saturation between 11-12 % (Chilingar and Yen, 1978).

With the expected increase in crude oil prices in the foreseeable future, interest in tar sand will spread to other countries as well. The current mining technologies use mainly open pit mining and the in situ operations where hot steam is used. This processing procedure leads to environmental problems with the improper disposing of toxic water and the releasing of CO₂ into the atmosphere. The main problem with the present extraction methods arise from the contamination of water bodies. There are already lagoons contaminated with the toxic waste from tar sand mining. Another problem is the transport of bitumen through pipelines; due to their high viscosity it is impossible to transport them like conventional crude oil. In order to transport bitumen, it is mixed with conventional crude or chemicals to decrease viscosity which enhances flow. Transported bitumen also contains impurities like sand and other waste which need to be removed at great cost. The problems of impurities in the bitumen and the operational problems from the mentioned methods can be decreased by application of the supercritical carbon dioxide method.

1.2 Bitumen

Organic matter in bituminous substances has been regarded as the residue of organic life that occurs as viscous impregnations in sandstones, siltstones, shales, and carbonates. These deposits were probably derived from a saline-lacustrine sapropel and owe their variable properties to differences in the environment of deposition. A variety of naturally occurring bituminous materials are present in the organic constituents of oil shales. These substances range from liquid petroleum through heavy, viscous asphalts to solid asphaltites and asphaltic pyrobitumens. Bitumens are classified into following groups: Mineral waxes, Asphalts, Asphaltites and Oil-shale bitumen.

Bitumens are solid or semisolid hydrocarbons which are sticky, black and highly viscous. They are naturally occurring substances that are considered to be complex mixtures of high-molecular-weight hydrocarbons and non-hydrocarbons which can be separated into fractions consisting of oily material, resins, asphaltenes, and carbenes. These fractions merge into one another and their atomic C/H ratio increases with each succeeding member, except for the carbenes which differ mainly in having more oxygen than the asphaltenes. Three types of hydrocarbons are present in bitumens: paraffinic, naphthenic, and aromatic hydrocarbons. Non-hydrocarbons in bitumen have heterocyclic atoms consisting of sulphur, nitrogen, and oxygen. The asphaltenes usually contain more aromatic compounds than the resins and the oily fractions. The resins contain aromatic or naphthenic hydrocarbons and the components of oily fraction may have naphthenic or paraffinic structure. The naphthenic plus paraffinic contents in bitumen increase with decreasing content of aromatic hydrocarbons, the oily fraction having the lowest aromatic content. The molecular weights of various bitumen fractions vary from about 300 to 1500 for the oily fraction and resins, and from about 600 to 10 000 for the asphaltenes, and to probably higher values for the carbenes.

1.3 Supercritical extraction of tar sands as an alternative

Supercritical Fluid Extraction (SFE) is attracting a great deal of interest because the technique can considerably reduce sample preparation time and can provide bitumen recovery from solid and semisolid samples that is equal to or better than that of the classical extraction techniques. In addition, supercritical fluids have both gas- and liquid-like properties. They possess gas-like mass-transfer properties and the

solvation characteristics of liquids. Their high diffusivity allows them to penetrate solid materials, and their liquid-like densities enable them to dissolve bitumen from a solid matrix. Supercritical fluids are compressible, and small pressure changes produce significant changes in their density and in their ability to solubilize compounds. Also, supercritical fluids have almost no surface tension and thus can penetrate low-porosity materials. In addition, their very low viscosity provides favourable flow characteristics. These properties enable supercritical fluids to provide excellent extraction efficiency and speed.

If the CO₂ is employed for recovery in addition to the upgrade of present CO₂ systems where 90 % of CO₂ is recycled, the contribution of CO₂ to greenhouse effect will be greatly reduced. Also the pollution of a valuable resource such as with chemicals from washing methods will be prevented.

The supercritical extraction seems a cost effective and environmentally friendly method in comparison with the present industrial methods. This study deals with the extraction of Nigerian tar sand by liquid carbon dioxide and its improvement.

2. Materials and methods

2.1 Reactor

The process of extraction was carried out using a commercial high pressure extractor Spe-ed SFE. Prior to the insertion of the sample into system, the extractor together with extraction cell was preheated to 110 °C. The sample of tar sand itself was preheated to 120 °C in a heating oven for two hours purposely to melt the sample; it was then inserted into already heated extraction cell. The extraction cell, which has the shape of a 30 cm long steel tube with a wall thickness of 1 cm and closed from each side by cap ends, was connected with the inlet and outlet CO₂ tubes. The door of the extractor was closed to minimize temperature losses. Before beginning the experiments, the CO₂ inlet and outlet valves were closed. The experiment was made in three runs consecutively. To initiate the experiment, the inlet valve of the system was opened, and CO₂ was fed into the system from storage tank continuously by a pump with a maximum capacity of 69.0 MPa to attain the required pressure.

After 30 min in static mode for the first run, the outlet valve was opened to collect the extracted bitumen into a test tube with the top plugged with cotton in to trap the hydrocarbons in gas phase. The test tube was also cooled with cold water at 18 °C to improve the condensation of the gas phase. The empty test tubes were weighed before the collection. The bitumen was collected into a test tube during 10 min of collection time. Afterwards, the outlet valve was closed for another 30 min during which period the CO₂ was interacting with the tar sand in order to make the second run. The same procedure as described for the first run was repeated for the second and third runs. When the collection time for the third run was finished, the pressure was decreased to the possible minimum by the manual reactor control unit, the inlet CO₂ valve was closed and the outlet valve was opened until CO₂ from the system dissipated completely. Later, the extraction cell was dismantled from the system, carefully opened and the remaining tar sand was taken out from the extraction cell. The unit was cleaned to make it ready for the next experiment. The remaining tar sand and the test tubes with collected bitumen were weighed by using a balance. In further analysis of the recovery, the samples from first, second and third runs would be compared. The remains after the extraction would be compared to the initial sample and the collected samples in order to calculate the losses due to outgassing. The reactor is described in more detail in work of other authors (Rudyk et al., 2013, Spirov and Rudyk, 2013).

2.2 Sample preparation

The tar sand sample was taken from the Ofoso tar sand field located in the Nigerian tar sand belt which lies on the onshore areas of the Eastern Dahomey (Benin) Basin. The tar sand is located on or near the surface and thus is suitable for surface mining as in Alberta, Canada.

The obtained tar sand was in a solid compact form, with slight bitumen odour. As it was not possible to work with the sample at this stage, it was manually broken down by hammer into smaller pieces and 100 g was inserted into the oven Electro Helios, and heated up to 120 °C for the period of two hours. Two hours was adequate for the sand part turn very soft and the bitumen part to have a strong odour. After this period of time it was possible to mash the sample and insert into the extractor. The sample after preheating was measured to ascertain if anything had evaporated. Generally the initial amount going into the oven was 100 g and after heating was 99.73 g. The calculated sample loss is equal to 0.27 %.

Two different extractor fillings were investigated in this work. In order to check the effect of tar sand volume and consequently carbon dioxide volume on extraction, the reactor was filled up to 75 % in the first

case and 50 % in second case by tar sand. The bitumen content according to the measurement from the experiments in AAU laboratory is equal to 12 % and it was used to calculate the recovery.

3. Results and discussions

3.1 Reactor volume filled to 75 % capacity

The extraction for the batch where the reactor is 75 % occupied with sand was made at two extractor operating temperatures (80 °C and 110 °C) with constant pressure of 65 MPa. In both cases the extraction was made in three runs consecutively.

The extraction at the temperature of 80 °C for the first run was 8.18 %, for the second run 2.75 %. The plugging of the reactor occurred for the third run and lead to the rupture of the rubber O-ring which seals the cap end for emergency reasons. The third run was repeated several times, but it always led to the plugging of the extractor outlet and due to this reason, the extraction process was discontinued. The reason may be that previously heated sample of tar sand cooled from 120 °C down to 80 °C and the bitumen is too viscous to flow or the reactor pipes got plugged by the same reason as the cap ends. The total recovery was 10.94 %. Outgassing losses were 8 %.

There is also an interesting observation that the extracted bitumen in the test tube from the first run had black colour, but the colour of bitumen from the second run had light brown colour. When the contents of both test tubes (run one and run two) are compared the black content looks less viscous and flows better than the content from the second run. The light brown content sticks to the wall and moves very slowly.

The results for extraction at 110 °C are very promising. The recovery for the first run was 1.67 %, second 17.05 % and third run 0.75 %. The total recovery is 19.47 %. The outgassing value was calculated from the reactor residues and is equal to 8.77 %.

The experiment results can be seen in figure 1 where the results for all three runs are plotted. The reactor temperature of 110 °C has better recovery, because the sample is not cooling down as quickly as it is in the case of 80 °C.

The relatively small recovery values for the first run and third run compared to the second is attributable to the following reasons. The interaction time of carbon dioxide and the bitumen part is inadequate for the first run and the lighter hydrocarbons necessary for the extraction of the heavier fractions were extracted in second run hindering extraction in the third run. Due to this reason two runs will give efficient recovery in case of reactor filling of 75 % in operating temperature of 110 °C.

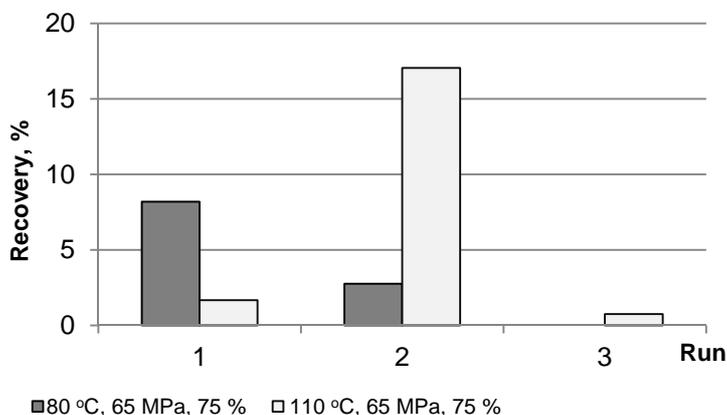


Figure 1: Recovery of the reactor filled with 75 %, the operating pressure is 65 MPa. For the dark grey region the temperature was 80 °C and for the light grey the temperature was 110 °C

3.2 Reactor volume filled in 50 %

For the extractor filled to 50 % of its volume with sand the temperature was kept constant at 110 °C. Two series of test were made at the pressure of 50 MPa for the first case and 65 MPa for the second one. Only one run was made at 50 MPa where the recovery was 2.16 % and the losses due to outgassing 1.66 %. The recovery for the 65 MPa was made in three runs, where the recovery for first run was 5 %, second 6.33 % and third 3.66 %. The total recovery was 15 % and the outgassing loss was 11.66 %.

In the figure 2a is compared first run for the 50 MPa and for 65 MPa. The comparison shows that increase of the pressure from 50 MPa by 15 MPa increases the efficiency of the recovery two times. Also the colours of the extracts collected from the first runs for 50 MPa and 60 MPa differ. The collected bitumen from the 50 MPa has the brown colour, but the sample from the 60 MPa is the dark brown with black tone. In the figure 2b is shown the recovery for the three runs at 65 MPa operation pressure. As observed from the experiment, the losses due to outgassing are minimal for the first run. The outgassing occurs on the second and third runs.

3.3 Comparison

As can be seen from figure 3, the recovery is higher for the second run in the case where the extractor is filled up to 75 %. The recovery for the 50 % filling is more equally distributed among all three runs, but for the 75 % the recovery mainly takes place during second run. The total recovery for all three runs in case of 75 % filling was equal to 19.47 % and the recovery for the 50 % was equal 15 %.

This can be explained by the volume occupied in the reactor by CO₂. The gas oil ratio for the 50 % filled is higher than 75 %, but the extraction is lower meaning not all of the CO₂ reacts with the sample. In the case of 75 %, the gas oil ratio is smaller and the gas reacts more efficiently and it leads to 4.47 % higher recovery than for 50 %.

All the results show that recovery of bitumen from tar sand by application of high pressure at the temperature range of 80 °C and 110 °C is possible. This observation compares favourably with the results of other authors who used high temperature (300 °C) and low pressure (Pang and McLaughlin, 1985, Demirbas, 2000). There was the usage of various co-solvents to improve recovery by the mentioned authors but their recoveries are relatively low compared to those in this work. Using of co-solvents will be the next step of this work.

Supercritical carbon dioxide technology could be applied directly in tar sand processing plants instead of the application of NaOH and vast amounts of water to achieve separation of bitumen from the tar sand. The generation of tailing ponds containing toxic water would be decreased which is the big environmental issue.

With many of the big oil companies already invested in the development of mines, the productions of oil from tar sand will increase rapidly over a short period of time. The introduction of new technology which will improve recovery and is more environmentally friendly would be a great asset for the future of tar sand mining.

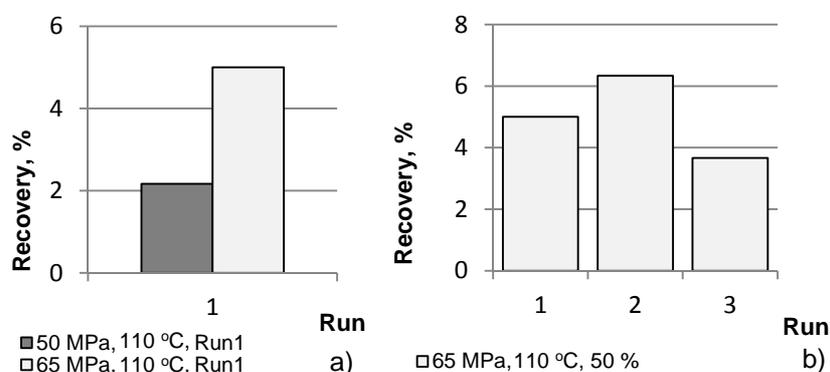


Figure 2: a) The Run1 for 110 °C in both cases, where the pressure differs. The recovery for 65 MPa is almost twice bigger than for 50 MPa. Figure b) The recovery for three runs for 65 MPa, 110 °C, reactor filled by 50 %.

The source of CO₂ needed for the supercritical extraction could be solved through construction of new CO₂ capture and storage plants. In literature are several works on investigating CO₂ transportation and its problems as described in (Vianello et al., 2012).

The filling of the designed vessel in which the extraction occurs plays an important role on the extraction process itself. As has been previous explained an optimum reactor filling is required to maximize the process and to minimize the operational costs.

4. Conclusions

In this study the supercritical carbon dioxide extraction was tested on Nigerian tar sands. In the experiment where the reactor space is occupied by 75 % gives the recovery of 10.94 % for the operating temperature 80 °C and recovery of 19.47 % for 110 °C. The recovery for the extraction occupied volume by 50 % is 15 % for 110 °C which is 4.47 % lower than for the 75 % at the same conditions. The collected sample in the first run is darker or is black in colour and less viscous than the second and third runs. The colour of the second is brown and third is bright brown. The samples from the second and third extraction stick to the wall. This observation shows that lighter hydrocarbons were extracted during the first run and the heavier during second and third. Losses due to outgassing are happening between second and third runs, because measurement for the first run shows minimal losses. The experiment shows that the filling of the reactor is an important factor affecting recovery.

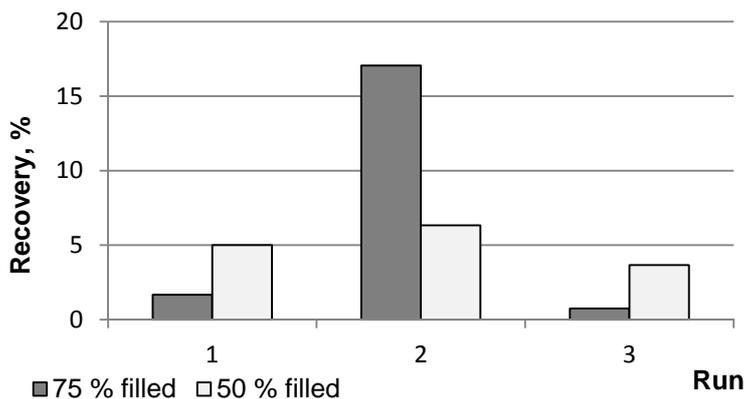


Figure 3: The tar sand recovery for the samples filled in 75 % in first case and for the reactor filled by 50 % in second case.

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