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Supercritical carbon dioxide extraction of oil sand enhanced by water and alcohols as Co-solvents

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ABSTRACT

Oil upgrading due to the decrease of metal, asphaltene and sulfur content improves the quality and value of oil. The three-step sequential extraction from Nigerian oil sand samples by supercritical carbon dioxide (SC-CO_2) was carried out by the addition of ethanol, isopropanol, fresh water and salty water as co-solvents at (50, 60 and 65) MPa and 110 °C. The objective of this work was to increase both the recovery and the quality of the extracted liquid oil product. The change in color of the oil samples from black to orange observed after extraction could be attributed to the reduction in coke and asphaltene contents of the oil. The total oil recovery varied from 27% by pure carbon dioxide to 73.3% with the addition of salty water. Addition of water in the amount three times more than of ethanol facilitated similar or higher liquid recovery. The composition of oil samples gets heavier after each subsequent step while pressure has a lower effect as observed from the changes of refractive indices. Total sulfur content in extracted oil samples was reduced significantly up to (0.6–1.1) % compared to its content in the crude bitumen of 1.95%.

1. Introduction

Intergovernmental Panel on Climate Change pleads for reducing CO_2 in atmosphere by sequestering in underground storages and carbon capture systems, or by transition to alternative sources and renewable energy [1]. In the global climate policy, developing countries are also assumed to take over greater responsibilities in climate mitigation action. The extent to which they will effectively implement their commitment will depend on financial resources and transfer of technology from developed to developing countries. The existing technologies should be adapted to the needs of developing countries rather than radical or breakthrough innovations in order to achieve emission reduction and at the same time meet national development priorities [2].

1.1. Extraction of hydrocarbons by supercritical carbon dioxide

Hydrocarbon extraction by supercritical carbon dioxide is the technology where the need for oil meets the need for reduction of green-house gas emission allowing utilization of large quantities of CO_2. Carbon dioxide of natural or industrial origin is injected in the oil reservoirs for the extraction of crude oil as a method of Enhanced Oil Recovery in many countries. For example, the Shengli Power Plant in China, whose annual carbon dioxide emissions is $570\bullet10^4$ t, has built a carbon dioxide capture system, from which CO_2 will be used for flooding of the Shengli Oilfield and heavy oil production with further sequestration [3,4].

CO_2 was also found suitable for the extraction of bitumen/bituminous oil from tar/oil sands to be used for the road construction and production of synthetic crude. The experience of Canada, the biggest oil sand producer, has shown the benefits from oil sand exploitation such as employment and job creation, and huge federal and provincial revenues through taxes. However, high intensity oil sand exploitation from open pit mines using Hot Water Method has caused several serious environmental problems, which require protection of potable water and land reclamation. The process water with the addition of alkali used for oil sand treatment is stored in on-site toxic tailings ponds in an area covering 530 km^2 where they take up approximately 20% of the area. Not least of these is the significant increase in greenhouse gases produced by extracting and processing the bitumen into a usable product. Construction of carbon capture storage (CCS) allowed to reduce carbon emissions in Canada to between 26 and 50% per barrel since 1990 [5]. The use of CO_2 from the CCS for oil sand treatment would increase the understanding of significance and necessity of CO_2 conservation as a valuable product.

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Many developing countries such as Venezuela, Madagascar, Trinidad, Colombia, Albania, Mongolia have oil sand deposits. On the African continent, some substantial amounts exist in the Democratic Republic of Congo and Nigeria in the Benin Belt [6].

The Nigerian oil sand reserves are estimated in excess of 43 billion barrels of oil-in-place within the entire oil sand belt of 120 by 4–6 km [7]. Shallow oil sand deposits and their outcrops which can be mined in Edo, Ondo, Ogun and Lagos States are under investigation for many years [8,9]. Compared to Canada most of other countries have no such vast resources of fresh water for oil extraction to apply Hot Water Method. The CO_2 can be a replacement of water regardless that the intensity of extraction process will be lower.

1.2. Bituminous oil upgrading by supercritical fluids

Various hybrid methods which include supercritical fluids modified with small amounts of liquid solvents (toluene, ethanol, isopropanol, acetone and others) have been introduced. Poska suggested that a major advantage of the supercritical fluid process is that there is minimum entrainment of fine solids from the oil sands with the extracted bitumen [10]. Subramanian and Hanson successfully extracted Canadian bituminous oil using supercritical propane without extracting metals and asphaltenes [11]. Al-Sabawi et al., however, found that the improvements in the bitumen extraction yield using alkane solvents are accompanied by increases in the contents of microcarbon residue, nitrogen, sulfur, and metals [12]. Increasing bitumen production achieved due to higher extraction of heavier components, which typically contain higher concentrations of these impurities, often compromises the quality of the extracts.

The necessity of processing bitumen to obtain more gasoline and other liquid fuels has resulted in an increased demand to develop options to desulfurize and upgrade the bitumen. Sulfur is poisonous for the catalysts used in the refinery while existing refinery processes are poorly optimized for increasingly heavy and sulfur-rich feeds produced of unconventional resources. The molecular weight and viscosity both increase as the sulfur content increases [13]. The role of sulfur as crosslinks (sulfides) in aromatic associations is the main reason for this effect. Therefore, treating petroleum liquids to remove even small amounts of sulfur can be effective in having dramatic reductions in molecular weight [14].

The quality of the oil can be determined by molecular weight and aromaticity. However, modern studies of the physiochemical properties of multicomponent hydrocarbon systems based on standard methods typically are labor-intensive, expensive, take a long time, and require big samples and complicated treatment of the results. Therefore, investigations of oil sand processing and upgrading, and development of complementary methods of control for the bitumen quality and sulfur content is in demand.

Khan has developed a number of empirical equations to correlate the refractive indices (RI) of the oils and bitumens with the liquid hydrogen content (H) (weight percent), H/C ratio, aromaticity (carbon and proton), molar mass (M), density (d), and Conradson Carbon Residue (C) [15]. Fan et al. combined the results of studies of 67 oils in empirical correlations and suggested the evaluation of SARA (saturates, aromatic, resins, asphaltenes) analysis results by refractive indices [16]. The equations are presented in Table 1.

Most of the studies on bitumen extraction or upgrading were carried out using supercritical fluids other than carbon dioxide. This study represents the characterization of oil fractions extracted by SC-CO_2 modified with water or alcohols at 110 °C and (50, 60 and 65) MPa by refractive indices and total sulfur content. The aim of this study is to assess a type of SC-CO_2/co-solvent combination that can enhance the quality of extracted oil (lighter composition and less sulfur) while maintaining higher recovery.

2. Experimental section

2.1. Materials

The samples of oil sand were taken from the outcrop of Ofoso oil sand field on the onshore areas of the Eastern Dahomey (Benin) Basin, Nigeria. The 99.9% pure carbon dioxide was supplied by Strandmollen A/S, Denmark. Pure ethanol and propanol (99.9% purity) were purchased at VWR Prolab and AppliChem, BioChemica GmbH, Germany, respectively. Salty water was prepared by the addition of 25 g of NaCl to 1 L of distilled water.

2.2. Sample preparation

A sample of oil sand was weighed, put in a closed container and placed into the Electro Helios oven for melting at 120 °C. To evaluate evaporation losses, the weight of the sample was measured before and after heating. The sample of 100 g weighed 99.73 g after heating, implying that 0.27% of the sample weight was lost. In all experiments, the melted samples of 50 g weight were placed in the extraction cell, which is a stainless steel tube of 100 mL volume with a wall thickness of 1 cm, and mashed by a wooden stick to fill in the inner space.

2.3. SC-CO_2 extraction

The high pressure extractor Spe-ed SFE with a maximum operating pressure of 69 MPa was used to conduct the extraction

Table 1
Characterization of various properties of bituminous oil fractions using Refractive Indices by empirical correlations as suggested by *(Khan [15]) and **(Fan et al. [16]).

Property	Definition	Equation
*H Content (%)	Percent of hydrogen in the liquid oil (%)	$H = 57.264 - 30.50RI$
*H/C Ratio	Hydrogen-to-carbon ratio of liquid oil (atomic)	$H/C = 6.876 - 3.50RI$
*C (aro)	Carbon aromaticity (aromatic carbon mass fraction in the liquid oil)	$C(aro) = 3.657RI - 5.228$
*H (aro)	Proton aromaticity (aromatic elemental hydrogen mass fraction in liquid oil)	$H(aro) = 2.102RI - 3.103$
*M (g/mol)	Molar mass	$M = 4383.2 - 2655RI$
*d (g/cm^3)	Density	$d = 1.977RI - 2.08$
*Conradson carbon residue (%)	A destructive-distillation method for estimation of carbon residues in fuels and lubricating oils.	$C(Conradson) = 37.75RI - 55.29$
**S, %	Saturates	$S = -319RI + 539$
**R, %	Resins	$R = 221RI - 316$
**RA, %	Resins +Asphaltenes	$RA = 317RI - 455$