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Understanding the roles of switchable-hydrophilicity tertiary amines in recovering heavy hydrocarbons from oil sands

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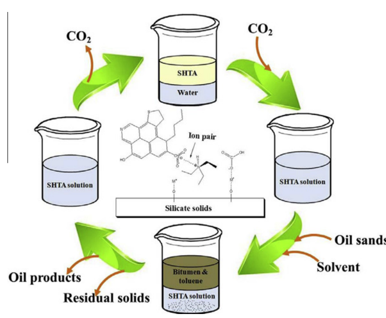
HIGHLIGHTS

- The SHTAs in their hydrophilic form facilitate bitumen recovery from oil sands.
- The SHTAs addition improves the quality of bitumen product and residual solids.
- The SHTAs ions could alter the bitumen–solid interfaces by forming ions pairs.
- The SHTAs could be recycled at least 5 times without sacrificing their efficiency.

GRAPHICAL ABSTRACT



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ABSTRACT

A kind of novel process aids, switchable-hydrophilicity tertiary amines (SHTAs, such as triethylamine, N, N-dimethylcyclohexylamine, N,N-dimethylbenzylamine) in their hydrophilic forms, have been synthesized and applied to enhancing heavy hydrocarbons recovery from oil sands ores in the solvent extraction. It is observed that the addition of SHTA solution increases the recovery of heavy hydrocarbons and improves the quality of bitumen product (less solids entrained) and residual solids (less solvents and chemicals attached). According to the surface characterizations by FT-IR, SEM–EDS, wettability test, zeta potential measurements and QCM-D (a surface material adsorption detection), it is found that the external addition of SHTAs solution plays an important role in modifying the bitumen and solids surfaces. The improved processability was mainly attributed to the absorption of cation ions (*e.g.*, $[Et_3NH]^+$) of SHTAs on bitumen surface, forming ions pairs. The formation of ions pairs reduces the interactions between bitumen components (*e.g.*, asphaltenes or other polar materials) and the solid surface, which significantly increases the wettability of solid surfaces. Consequently, the detachment of bitumen materials from the solid surfaces becomes much easier and more complete. In addition, the efficiency of the recycled SHTAs is found to be not influenced much even the SHTAs are recycled for 5 times, indicating a promising application of this kind of 'green chemicals' in unconventional petroleum production or soil remediation.

1. Introduction

Oil sands, an unconventional petroleum consisting of heavy oil (or bitumen), sand grains, clays and water, is an alternative of conventional crude oil [1,2]. It was reported that the total world

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unconventional petroleum was estimated to account for about 70% of the total world oil reserves. Take Canadian oil sand as an example, with more than 1.7 trillion barrels of bitumen *in situ*, the present commercial production of bitumen from oil sands is about 1.6 million barrels per day [3,4]. Although a series of technologies have been proposed for bitumen recovery from oil sands ores, the currently commercial process for the separation of minable ores is the hot water-based extraction (HWBE) process which has been working in Alberta, Canada for about 5 decades [5]. However, this HWBE process needs to be operated at high temperatures of 70–80 °C and consumed nearly 2 m^3 of water to produce one barrel of bitumen, resulting in high energy and water consumption [6]. To allow the bitumen production at lower cost and alleviate the environmental issues, some novel separation concepts have been largely proposed during the past decades, such as solvent extraction, aqueous-nonaqueous hybrid process, pyrolysis, or even bio-extraction, etc [2,7–11]. Due to the high bitumen recovery, mild operation conditions and good applicability for all kinds of oil sands ores, the solvent extraction process gained increasing attention from industrial and academic fields [12].

To enhance the liberation of bitumen and finally improve the bitumen recovery as much as possible, functional chemicals, such as sodium hydroxide, surfactants, ionic liquids etc., have been added as process aids during the extraction [4,11,13,14]. Using ionic liquids (ILs) instead of water solution to work together with solvent to extract bitumen from oil sands, Painter et al. [14] reported an enhanced bitumen recovery up to 90%. Similar results were obtained by Li et al. when using ionic liquids and composite solvents as extraction agents [11]. Unfortunately, the recycling of these externally added chemicals was found to be one of the most challenges which impeded the scaling-up of these hybrid processes. For example, ILs can be separated and reused by distillation method [14], however, the loss of ILs during the process and huge energy consumption of evaporating water limit this technology in the laboratory level. Therefore, searching for efficient and recyclable "green chemical additives" is an important research area related to the unconventional petroleum production.

Recently, a kind of recyclable "green chemical" has been synthesized and reported by Jessop et al. [15] which could be used as switchable solvents for extraction. The working principle of this kind of "solvent" is dependent on the switchability of tertiary amines by protonation and deprotonation in the presence and absence of CO_2 respectively (Eq. (1)) [16,17]. A water-soluble bicarbonate salt will be synthesized and dissolved in the water when CO_2 is injected into the water-tertiary amine system. However, if the above homogeneous system was heated (above 60 °C) to remove the CO_2 [16], the tertiary amines would be released from the water, forming two immiscible phases once again. This reversible route allows the recycling of the process aids, resulting in a potential reduction in operational cost and pollution.

$$NR_3 + H_2O + CO_2 \rightleftarrows NR_3H^+ + HCO_3^- \quad (1)$$

Although these switchable chemicals are mostly applied as solvents to purifying oil products, such as soybean oil [18], algae oil [19], bitumen [20], high density polystyrene powder [16] and phenolic compounds [21], the application of these switchable hydrophilicity chemicals as process aids in heavy hydrocarbon extraction from unconventional petroleum ores would be much more attractive due to its recoverability. Thereby, in this study, the switchable-hydrophilicity tertiary amines (SHTAs) will be used as novel process aids together with solvents in enhancing the heavy hydrocarbons recovery from oil sands ores. The aims of this study are to: (i) investigate the effect of SHTAs on bitumen recovery from oil sands ores; (ii) understand the exact mechanisms of SHTAs-assisted solvent extraction, and (iii) provide a potential method to screening more effective process aids for the enhancement of heavy hydrocarbons recovery from oil sands ores.

2. Materials and methods

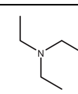
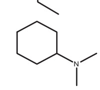
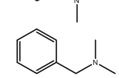
2.1. Materials

Chemicals, such as triethylamine, N,N-dimethylcyclohexylamine, N,N-dimethylbenzylamine, toluene, n-heptane and sodium hydroxide, at their analytical grade, were purchased from Tianjin Jiangtian Technology Co. Ltd., China. The physicochemical properties of tertiary amines were shown in Table 1. Gases, such as CO_2 and N_2 with the purity of 99.9%, were provided by Tianjin Liufang Technology Co. Ltd., China. The Athabasca oil sands ores used in this study contained 11.30 wt% bitumen, 0.64 wt% water and 88.06 wt% solids (fine solids content: 15 wt% of the total minerals). Fine solids were obtained by screening through a 44 μm sieve.

2.2. Synthesis of SHTA solution

SHTA solution (SHTA in its hydrophilic form) was synthesized based on Eq. (1) by reacting tertiary amines with CO_2 and water. Briefly, tertiary amines (20 mL) were added into a three-necked flask together with deionized (DI) water at the proportion of 1:1 by volume, which appeared as two immiscible phases, shown in Fig. 1a [16]. Subsequently, CO_2 was evenly injected into the liquids by a glass conduit (Φ 5 mm) at 500 mL/min to react with the

Table 1
Physicochemical properties of the tertiary amines used in this study.

Name	Structure	ρ[a] (g/cm^3)	B.P.[b] (°C)	pK_a
Triethylamine (Et_3N)		0.73	89	10.68
N,N-dimethyl-Cyclohexylamine ($CyNMe_2$)		0.85	159	10.48
N,N-dimethylbenzylamine ($BnNMe_2$)		0.89	183	9.03

[a] Density.
[b] Boiling point.

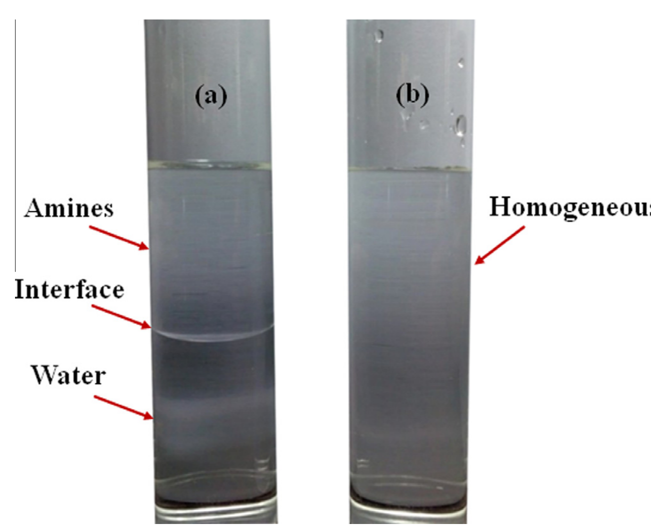


Fig. 1. Amines-water system: (a) appearing at two immiscible phases before CO_2 injection, and (b) forming homogeneous SHTA solution after CO_2 injection.