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Supercritical water treatment of oil sludge, a viable route to valorize waste oil materials

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HIGHLIGHTS

- Valorization of waste oil sludge using SCW treatment.
- Produced valuable gas and liquid fuels.
- Parametric study of the SCW reaction.
- Confirmed the solvation and dispersant properties of SCW in the reaction.
- Hydrogen is not being supplied by water in such reactions.

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ABSTRACT

Treatment of oil sludge generated from a pilot-scale upgrading process plant using supercritical water (SCW) was studied in detail to ascertain alternate ways of valorizing. SCW is a highly active agent, providing a suitable medium for converting heavy residues into lighter fuel compounds. Various operating conditions such as temperature and reaction time were investigated in this study; the results showed that a considerable amount of valuable oil and gas compounds can be recovered from the waste feedstock (up to ~18.6 wt% recovery). The gas produced was a hydrogen and methane-rich stream, which potentially can be utilized as fuel. In addition, the quantity of oil produced was significant considering the source feed, and rich in valuable saturate and aromatic hydrocarbons. Simulated distillation showed the oil contained mainly naphtha and light gasoil. It was concluded that a high reaction temperature and severity accelerated the product recovery yields, although the amount of coke generated increased. To address the current literature debate regarding the role of water and whether or not hydrogen is supplied from water, a detailed oxygen element balance was performed. The results proved that hydrogen is mainly supplied from hydrocarbon materials and not from water. Moreover, water acted as an excellent dispersant and solvent in the recovery of light compounds from heavy molecules through various radical reactions.

1. Introduction

A global trend of dwindling resources of conventional petroleum has put a spotlight on searching for new hydrocarbon energy resources such as oil sand, and oil shale. Canada's oil sands are the third-largest proven crude oil reserves in the world (about 168 billion barrels), after Saudi Arabia and Venezuela [1]. Oil produced from oil sands is often referred to as unconventional oil or bitumen; it is highly viscous in its natural state, which means it does not readily flow. Therefore, oil sands bitumen requires either the addition of diluent, or upgrading to meet pipeline specifications, before transporting to downstream refining facilities. CanmetENERGY is the Canadian leader in technology development for upgrading of oil sands crude and other heavy and extra heavy oil resources. As considerable amounts of oil sludge are produced from the processing of such crude oils, CanmetENERGY has undertaken research to mitigate the serious environmental issues regarding the waste products of processing heavy and extra heavy crudes. As these waste materials inherently contain valuable carbonaceous compounds, CanmetENERGY has also focused research efforts on new ways not only to dispose of such materials in the landfills, but also on the valorization of these heavy hydrocarbon waste products as a critical sludge management strategy.

Incineration is the traditional pathway to dispose the oil sludge with combustion at a temperature over 800 °C. However, the

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operation results in generation of large flue gases which must be scrubbed due to the air pollution regulations [2,3]. Thermal processing of oil sludge by pyrolysis is another conventional hydrogen-free method to convert these waste materials to the reusable fuels products [2–4]. Application of additives or catalyst in order to enhance the rate of pyrolysis conversion was also investigated in some works [5,6]. Generally, most pyrolysis studies were focused on the use of oil storage tank sludge, which seldom contains significant amount of the extra heavy fractions and impurities, for example, asphaltene. These extra heavy aromatic compounds tend to polymerize and form nuclei of the coke in the severe thermal operations [7–9]. One can say that the common problem with thermal processing of extra heavy fossil residue is lower liquid product yield and larger quantities of cokes, which may cause operational problems or decrease the value of the process [10,11].

Supercritical water (SCW) treatment has been introduced as a catalyst-free technology in order to convert a wide range of carbonaceous materials, such as sludge, tar and biomass into lighter and valuable substances, mainly through radical reactions [11–16]. The process is performed above supercritical condition of water (374 °C and 220 bar), where water becomes highly active. Beyond the critical point, water acts as both liquid-like and gas-like phases, where physical properties vary in response to the density change. The properties of SCW are very different from ambient water. For example, in contrast to ambient water, SCW is a poor solvent for electrolytes. In addition, it is a unique solvent for non-polar molecules, like heavy hydrocarbons, due to its low dielectric constant and poor hydrogen bonding; hence many hydrocarbons are miscible in SCW [11,17,18]. Density and viscosity both decrease in the supercritical state, subsequently enhancing dispersion and mass transfer of non-polar substances within the reaction environment [19]. The recent applications of SCW in thermal treatment of extra heavy oil and residues have shown promising results, where the coke formation was considerably suppressed and the liquid product yields were accordingly increased [20,21].

The purpose of this study was to explore the possibility of valorization of Canadian oil sands derived sludges produced through pilot-plant processes at CanmetENERGY-Devon. These sludges were treated using an in-house developed SCW process to explore the possibility of producing valuable products. To the best of our knowledge, this is the first work that deals with SCW treatment of oil sludge gathered from a bitumen upgrader in pilot-scale operation. The oil sludge feedstock was treated with SCW at various operating conditions, time and temperature, in an autoclave pilot-scale batch reactor. Detailed analytical analyses were made in order to characterize the products, and to clarify the role of water in the mechanisms of the radical reactions.

2. Experimental

2.1. Materials and analytical methods

Oil sludge was obtained from upgrading experiments of oil sands bitumen, conducted at the CanmetENERGY-Devon research center. Several analytical standards and instruments were used to analyse the feedstock and products, as listed in Table 1. The feed (sludge) analysis data is presented in Table 2. The feed sample was a solid-phase, cake-like compound, with a small H/C atomic ratio. The asphaltene contents of the feed and products were estimated from the difference of pentene and toluene insoluble fractions (PI and TI). The pentene and toluene insoluble fractions were respectively determined according to the procedures ASTM D4055 and D4072.

2.2. Experimental method

A high-pressure pilot-scale autoclave, able to operate up to 450 °C and a pressure over 277 bar was used for the experiments. A diagram of the setup is provided in Fig. 1. The autoclave internal diameter (ID) and height were 8.9 cm and 33 cm, respectively. In addition, an insert (ID 8.1 cm and length 26.7 cm) was used during experiments to facilitate collection of the solid and liquid products. The cooling rate of autoclave was improved by means of a cooling water coil installed inside the reactor (with cooling water on, and the furnace partially removed, the temperature of the reactor contents dropped to below 300 °C in about 10 min). A turbo fan type mixer with three blades and a diameter of 7.6 cm was used to stir the feed materials within the reactor chamber. The reactor was loaded with given amounts of feed (sludge and water) and then sealed. The system was checked for leaks at a pressure of 277 bar, flushed with nitrogen, and then evacuated. Reactor skins and liquid temperature and pressure were monitored continuously. If the reactor pressure did not increase to 242.3 bar within the planned timeframe, distilled water was pumped at 5 mL/min to achieve the target pressure. Operating temperature was maintained for the desired run time. At the end of the run, to make easier the product collection and the separation from the residual feed, the product and the water were collected in the supercritical condition at KO drum located downstream of the reactor. It happened by opening of the relevant isolating valve for a couple of seconds. Then, the heater was shut off, and the furnace was removed. The next day, gases, from the main reactor and KO drum, were first collected in the gas sampling bag and submitted for refinery gas analysis. Most product and water were collected from the KO drum. Next, the main reactor, mostly containing residue solids, was opened, the materials were collected, and the reactor was

Table 1
Analyses conducted for the materials.

Feedstock and solid analysis	Liquid product analysis	Gas product analysis
Micro carbon residue (MCR) (Alcor MCRT-130, ASTM D4530)	Micro carbon residue (MCR) (Alcor MCRT-130, ASTM D 4530)	Gas Analysis (Agilent 3000 Fast MicroGC)
Proximate Analysis (Moisture, Ash, Vol. Matter, Fixed carbon) (TGA Q500, ASTM D5142)	Simulated Distillation (Agilent 6890N, ASTM D7169)	
Insolubles, Pentane (PI) (ASTM D4055)	SARA (Asphaltene + Saturates + Aromatics + Polars) (ASTM D2007M)	
Insolubles, Toluene (TI) (ASTM D4072)	Insolubles, Pentane (PI) (ASTM D4055)	
CHN (Carbon, Hydrogen, Nitrogen) (Elementar Vario Micro Cube, ASTM D5373)	CHN (Carbon, Hydrogen, Nitrogen) (Elementar Vario Micro Cube, ASTM D5291)	
Elemental Sulfur (Combustion IR, Leco SC632, ASTM D1552)	Elemental Sulfur (XRF) (Oxford Inst. X-Supreme8000, ASTM D4294),	
Metals by Inductively Coupled Plasma Mass Spectrometry (ICP-MS, Agilent 7700)	Oxygen (Pyrolysis method) (Elementar Vario Micro Cube)	
Oxygen (Pyrolysis method) (Elementar Vario Micro Cube)	Kinematic viscosity (Anton Paar SVM3000, ASTM D7042)	