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Enhanced Heavy Oil Recovery by in Situ Prepared Ultradispersed Multimetallic Nanoparticles: A Study of Hot Fluid Flooding for Athabasca Bitumen Recovery

Rohallah Hashemi, Nashaat N. Nassar,* and Pedro Pereira Almaso

Department of Chemical and Petroleum Engineering, University of Calgary, 2500 University Drive N.W., Calgary, Alberta, Canada T2N 1N4

ABSTRACT: Many in situ recovery methods have been developed to extract heavy oil and bitumen from deep reservoirs. The “underground refinery” approach using a nanosize ultradispersed (UD) catalyst is one of the alternatives to surface upgrading that may become the “next generation” of oil sands industry improvement. Water-in-vacuum gas oil microemulsions containing trimetallic (W, Ni, and Mo) ultradispersed colloidal nanoparticles could penetrate inside the porous medium and react with the bitumen. This study is aimed at developing a catalytic-enhanced oil recovery method for Athabasca bitumen recovery through the viscosity reduction mechanism with the aid of trimetallic nanoparticles. In this study, series of experiments were conducted at a pressure of 3.5 MPa, residence time of 36 h, and temperatures from 320 to 340 °C in an oil sands packed bed column. Results of three consecutive categories of hot fluid injection (in the presence or absence of trimetallic nanoparticles) are presented. For the first category, the obtained experimental results showed that the recovery curve for vacuum gas oil injection without nanocatalysts was at a plateau. In the second series of tests, observations proved that adding a certain percentage of pentane enhanced the recovery performance of injection tests. The third phase of experiments was conducted in the presence of trimetallic nanocatalysts in emulsion with vacuum gas oil. Results showed the effectiveness of nanocatalysts for enhancing the recovery performance compared with the cases of no nanoparticle implementation.

■ INTRODUCTION

Heavy oil and bitumen are important hydrocarbon resources that play increasingly important roles in the global economy.¹ At commercial scales, many in situ thermal recovery methods have been proposed and developed to extract heavy oil and bitumen from deep reservoirs.^{2–8} These in situ thermal recovery methods can be divided into two main categories, steam injection and in situ combustion.⁹

In situ thermal recovery methods resemble the recovery of conventional oil, whereby bitumen extraction is accomplished by drilling horizontal wells and subsequently injecting steam or generating heat, which reduces bitumen viscosity and allows it to flow to the surface. In the steam injection process, known as steam-assisted gravity drainage (SAGD), steam is used as the heat carrier to reduce the viscosity of bitumen and, consequently, reduce the flow resistance of bitumen through porous media, which increases the cumulative recovery and production rate.^{10,11}

For in situ combustion, or “fire flood”, the heat is generated and propagated along the reservoir by igniting a part of the original heavy oil-in-place and subsequently reduces the viscosity of the unburnt bitumen, thereby improving its flow.^{9,12} The high energy intensity and huge amount of water consumption, especially for the SAGD process, as well as the low quality of the produced bitumen through the in situ thermal recovery processes pose challenges for future deployment of the current technologies. Therefore, it is necessary to search for new ideas or alternatives in the field of in situ recovery to improve current technologies and make them environmentally sound and cost-effective.

In situ upgrading of bitumen or heavy oil is an innovative environmentally friendly approach and recently is attracting considerable attention.^{13–15} This approach uses the reservoir as a high-temperature reactor, and it is based on integrating the catalytic hydrogenation reaction with thermal recovery methods.^{5,16,17} The idea of the underground refinery project is to use porous media as a chemical reactor with a series of chemical reactions (i.e., hydrocracking, hydrotreating, etc.) to improve the quality of produced heavy oil and bitumen.^{5,18} This requires placement of the catalyst deep into the heavy oil plume by transporting a catalyst suspension through the sand medium.^{15,19,20}

To conduct a successful underground upgrading process, several steps are considered to improve the quality of products,⁵ namely: (1) presence of catalyst in formation or an appropriate zone near production well; (2) mobilization of reactants including heavy oil and coreactants such as steam or hydrogen; and (3) creation of necessary processing conditions to achieve reasonable degree of upgrading (i.e., sufficient temperature and pressure). It should be noted here that several important underground heavy oil recovery and upgrading processes have been reported, which are implemented at the pilot plant and field scales. These include steam distillation and in situ upgrading processes,³ conventional fireflood field projects and dry combustion,⁴ solvent-based in situ processes and propane deasphalting,^{21–23} thermal upgrading and visbreaking of heavy oil,^{24–26} in situ hydrogenation and hydroprocessing,^{27–29} toe-

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Table 1. Properties of Athabasca Bitumen and Nexen VGO Used for Experiments

property	bitumen	property	VGO
viscosity at 40 °C (cP)	7550	viscosity at 40 °C (cP)	122.314
API gravity (°API)	9.5	API gravity (°API)	19.1
microcarbon residue (wt %)	12	microcarbon residue (wt %)	NA
H/C (atomic ratio)	1.52 ± 0.001	H/C (atomic ratio)	NA
sulfur (wt %)	4.25	sulfur (wt %)	2.73
distillation cuts (wt %)		distillation cuts (wt %)	
naphtha: IBP–213 °C	2.76 ± 0.29	IBP–235 °C	10.92
distillates: 213–343 °C	14.89 ± 0.81	235–280 °C	7.97
VGO: 343–545 °C	34.68 ± 1.81	280–343 °C	16.60
residue: >545 °C	47.95 ± 1.57	residue: >343 °C	64.51

to-heel air injection (THAI) process,^{6,30} aquathermolysis,^{7,31} and in situ combustion (ISC).^{2,32,33}

The main mechanism of the in situ recovery and upgrading processes is to decrease bitumen viscosity and enhance the liquid quality, which subsequently improve the productivity index of the producer well. In recent years, there has been extensive effort to create an economically efficient underground in situ upgrading and recovery process for unconventional oils, such as heavy oil and bitumen. There are several advantages for underground upgrading processes such as (1) capital cost reduction of lifting operation and transportation from down-hole to refinery center, (2) production of higher value energy by viscosity reduction, and (3) extremely low to zero environmental footprints due to reduction in contaminant levels such as metals, sulfur content, and waste hydrocarbons.

In situ upgrading using ultradispersed (UD) nanocatalyst is one of the promising options from both environmental and economical aspects, which may become the “next generation” of oil sands industry improvement.¹⁴ In this process, a suspension of ultradispersed nanosized particles is injected into the reservoir to upgrade heavy oil and bitumen. Nanosized particles were chosen due to their unique properties, such as high surface area to volume ratio, high degree of dispersion in porous media, excellent adsorption affinity, and high catalytic activity.^{34–39} It should be noted here that the subject of down-hole upgrading by UD nanocatalysts is relatively new, and consequently the available published literature data are limited.

UD nanocatalysts for hydroprocessing reactions were successfully developed in heavy oil matrix and subsequently tested in a batch reactor for Athabasca bitumen upgrading by our research group at the University of Calgary.^{40,41} Experimental results showed that UD nanocatalysts enhanced the upgrading of Athabasca bitumen by significantly increasing the hydrogen/carbon atomic ratio and reducing both viscosity and coke formation.⁴² In addition, a significant reduction of sulfur and micro carbon residue was observed. However, before any field test or industrial application of these in situ prepared UD nanocatalysts, it is deemed necessary to test their performance in a continuous flow mode. To better mimic the SAGD process conditions, a pilot plant setup is designed and constructed to simulate the major elements of the SAGD reservoir, such as injection and production lines, oil pool (i.e., in SAGD the injector well is typically surrounded by steam and the producer well is surrounded by liquid oil and water; this liquid oil and water zone is frequently referred to as the “oil pool”), and reservoir top.

The UD nanocatalysts were injected into the oil pool by hot fluid nanocatalyst carrier. The transport behavior of these multimetallic UD nanocatalysts in an oil sands packed bed

column at a typical SAGD temperature and pressure was investigated in our previous study.⁴³ It has been found that propagation of multimetallic UD nanocatalysts in oil sands media is feasible under a typical pressure and temperature of SAGD process, as neither major permeability reduction nor pore plugging was observed. This work is a continuation of our previous studies,^{42,43} and it aims at experimentally investigating the effect of UD nanocatalysts on the recovery enhancement of Athabasca bitumen in a one-dimensional (1D) continuous flow oil sands packed bed column. The present work holds great promise for in situ heavy oil upgrading and recovery. It should be noted here that the effect of nanocatalyst content in the porous media and temperature on the extent of Athabasca bitumen upgrading and subsequent liquid quality improvement shall be communicated in another study.

■ EXPERIMENTAL SECTION

Fluids and Chemicals. Silica sand was purchased from AGSCO (99% of SiO₂, AGSCO, Hasbrouck Heights, NJ, USA) and used as a sand source for porous media fillup. Absolute permeability of about 250 darcy was measured by using the sand size of 12–20 mesh (U.S. sieves) for packing the reactor. Porous medium was saturated with Athabasca bitumen (JACOS, Alberta, Canada). For pentane experiments, pentane (C₅H₁₂, 99%, Sigma-Aldrich) was used as diluent and vaporizing component.

Vacuum gas oil (VGO) obtained from Nexen, Alberta, Canada, which is a heavy petroleum distillate cut produced as a lateral product in a vacuum distillation column, was used as nanocatalyst carrier into the porous media. Properties of the utilized Athabasca bitumen and VGO were reported in our previous study¹⁵ and are presented in Table 1 as a reference. The following precursors were used to prepare trimetallic nanocatalysts, namely, nickel acetate tetrahydrate (99%, Sigma-Aldrich), ammonium metatungstate (99%, Sigma-Aldrich), and ammonium molybdate tetrahydrate (99%, Sigma-Aldrich). Carbon disulfide (99%, Sigma-Aldrich) was used to prepare the produced liquid samples for simulated distillation analysis. Utilized gases for experiments including nitrogen, helium, hydrogen, air, and argon were provided by Praxair Specialty Gases & Equipment (Calgary, AB, Canada).

Preparation of Nanocatalyst Suspension. A water-in-vacuum gas oil microemulsion method was employed for preparing nanocatalyst suspension.^{44–50} Details on the preparation procedure of colloidal trimetallic nanocatalysts in VGO have been described in our previous studies.^{40,51,52} Figure 1 shows a schematic of the nanocatalyst preparation algorithm. In brief, preparation of nanocatalyst suspension was started by mixing 99.57 wt % VGO and 0.43 wt % HLB-8 surfactant at 700 rpm and 60 °C, and then the mixture was stirred for about 30 min to reach stability. Aqueous solutions of the corresponding metallic precursors were added to the mixture and then agitated for about 30 min at 60 °C. The mixture of metallic precursors, surfactant, and VGO was kept for 8 h at a temperature of 40 °C under low stirring (200 rpm) to evaporate the water (down to at least 0.5 wt %) and subsequently initiate nucleation and growth of

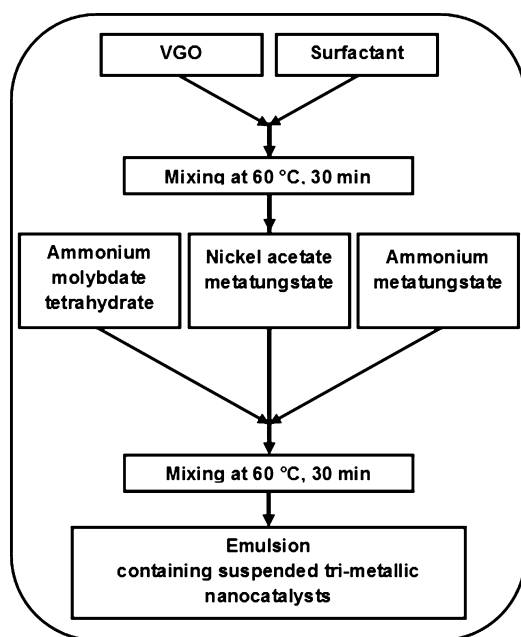


Figure 1. Schematic representation of colloidal trimetallic nanocatalysts preparation algorithm.

Table 2. Concentration of Colloidal Trimetallic Nanocatalysts in the Feed

component	ppm	additives	
		component	percentage (with respect to oil)
Ni	72		
Mo	240	water (wt%)	2.11
W	408	surfactant (HLB-8)	0.43

trimetallic nanoparticles, which remained stable in suspension.^{40,51,52} Table 2 shows the concentration of trimetallic nanocatalysts used in this study as well as percentages of water and surfactant. The atomic metallic ratios (metal/total metal) were as follows: Mo = 0.6267, Ni = 0.1808, and W = 0.1924.

Experimental Setup. A schematic of the experimental setup can be seen in Figure 2, which mainly consists of the following elements: reserve tanks; vertical stainless steel reactor covered by insulators; Isco pumps (Teledyne Isco, Lincoln, NE, USA) for injection of hot fluid into the medium as well as saturating the porous media with Athabasca bitumen; nitrogen and hydrogen gas cylinders for pressurizing and saturating the free radicals; gas analysis instruments; and produced sample collectors.

The reactor column is made of stainless steel and has a 90 cm height and a 2.16 cm inner diameter. Reserve tanks were used to maintain all injecting fluids before injection inside the medium. To help fill the pumps, all liquids except water were maintained under low nitrogen pressure. Hot fluids (VGO containing nanocatalysts, steam, and mixed VGO) were injected individually inside the porous media via a hot fluid generator into the top section of the oil pool (lower part of the sand pack column).

All fluids were heated to the test temperature by covering the hot fluid generator with heating tapes. Hot fluids were injected from the injection point and, after entering inside the medium, affect the contained fluids of porous media and subsequently enhance the production of heavy liquids from the production point. To monitor the temperature inside the reactor, a specially designed 10-point thermocouple was placed in the middle of the packed bed reactor and fixed by two mesh rings at the top and bottom of the reactor. Isco pumps were used to inject liquids at the desired rates inside the medium. Produced liquids from porous media were collected inside a

hot separator (500 cm³) and at certain time intervals were transferred to sampling containers for post-mortem analysis.

Hydrogen was used during the injection process to saturate the free radicals (from thermal cracking of heavy oil) and to reduce the possibility of coke formation as well as plugging of the reactor. Nitrogen as an inert gas was used to purge and pressurize the lines at the start of experiments. All produced gases from porous media were passed through the wet test meter and gas chromatography to measure rates and compositions.

Experimental Procedure. Preparation of porous media for experiments was started by washing the silica sands with deionized water to remove dust, cement, tiny particles, and any kind of impurities that may exist within the sands provided by the vendor. Washed sands were kept inside a vacuum oven for 24 h at 60 °C to be dried. About 452 g of dried and cleaned sands was used to fill the stainless steel column reactor for one experiment.

To avoid sand production, three mesh rings were used in the top, bottom, and entrance of the injection point. Test temperature was provided by using special types of heating tapes installed at the outside body of the reactor. At the same time, the reactor body was covered by a fiberglass casing to reduce heat loss. Nitrogen was also used for purging the system until oxygen disappeared completely, as confirmed by the gas chromatograph (GC).

To ensure the integrity of the system for the experiments, a leak test was performed by pressurizing the packed bed reactor with nitrogen to 5.5 MPa. A 1% change in pressure per hour was considered to be the maximum allowable pressure reduction during the leak test. After that, the reactor pressure was reduced to 3.5 MPa, and then the column was heated to the desired temperature while the pressure was maintained at 3.5 MPa. When the reactor column working pressure and temperature were attained, approximately 5 pore volumes of Athabasca bitumen was first injected through the column in the down-flow mode to displace the water and saturate the bed with bitumen to simulate the oil sands conditions.

The actual experiment started by switching of the inlet gas from pure nitrogen to a hydrogen feed and introducing the injecting fluid (VGO containing nanocatalysts). At this point, the zero reaction time for recovery and upgrading experiment was considered. The run was conducted until approximately 100 cm³ of VGO containing nanocatalysts was injected into the porous media. Some runs were repeated twice to confirm the reproducibility of the experiment, which was achieved successfully. For those runs the standard deviations were calculated and are presented in the figures as error bars.

During the tests and at different time intervals, the produced liquid sample was taken for analysis and the produced gas was taken from the bottom of the reactor column to be analyzed by the GC. At the end of the run, the reactor column was vented and cooled to room temperature, and the solid products (packed media) were carefully discharged from the reactor column for analysis. After that, the column and assembly were washed with toluene, soap, and hot water; therefore, the apparatus could be ready for another cycle of experiments.

Analytical Methods. To confirm the extent of recovery enhancement, different characterization techniques were implemented to analyze the produced liquid streams. In this part of the study, the produced liquid samples were analyzed using standard characterization techniques as follows: (a) water content in produced liquid was measured by the Karl Fischer titration method using a Mettler-Toledo model DL-32 (A. Daigger & Co., Vernon Hill, IL, USA); (b) residue content (545 °C⁺) was estimated following an ASTM procedure (D7169-2005) by using high-temperature simulated distillation (HTSD) that was carried out in an Agilent GC (Mississauga, ON, Canada) following the method developed by Carbognani et al.⁵³

In the case of the steam injection test, water content of the produced stream was quantified using a Dean–Stark distillation method. Figure 3 shows a schematic representation of the Dean–Stark distillation unit, which is used for water–bitumen separation.⁵⁴ In this method, produced liquid samples (water + bitumen) were mixed with excess toluene and then the mixture was transferred into a boiling flask. To avoid any bubble bumping, a small amount of boiling chips

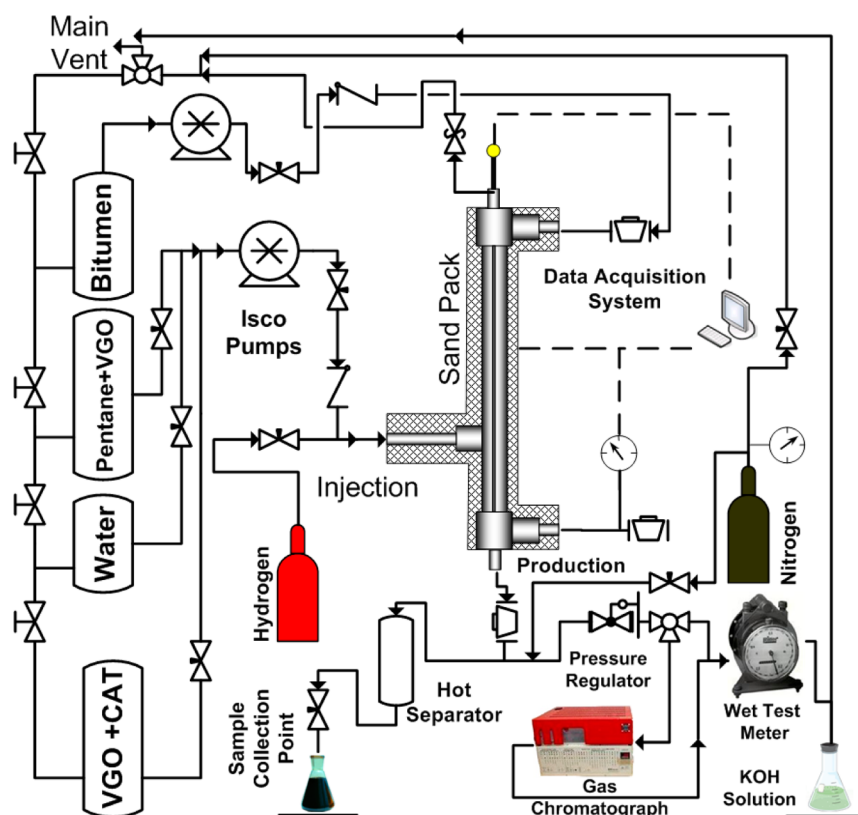


Figure 2. Schematic representation of the experimental setup.

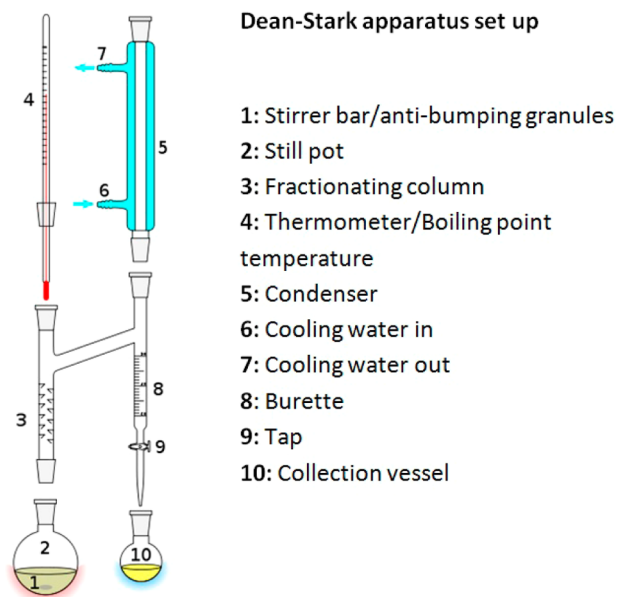


Figure 3. Schematic representation of the Dean–Stark distillation unit setup.⁵⁴

was added into the mixture and then the boiling flask was heated by an electrical mantle.

Vapors of water and toluene passed through the fractionating column and, after cooling, condensed on the condenser wall. All condensates dripped into the graduated buret with a distinct phase level between organic and aqueous phases. Continuous heating of the flask was caused to fill the buret and overflow the piled up condensates. Because the top phase of the buret column was toluene, it was recycled into the flask and the cycle of extraction continues until no water could be seen inside the column.

RESULTS AND DISCUSSION

The main goal of this study was to investigate the effectiveness of ultradispersed nanocatalysts for enhancing the recovery of Athabasca bitumen in an oil sands packed bed column. The experiments were conducted in a consecutive order to apply a systematic approach for the flow of study. Results of eight experiments were presented in this paper.

Table 3 shows the specifications of the tests considered in this study. It should be noted that reactor pressure, hydrogen flow rate, initial hot fluid injection rates, and medium permeability were kept fixed for all tests. The first test was conducted by steam injection into the porous media to ensure that the selected sands can represent a typical SAGD reservoir. The next two tests were considered as control tests, without trimetallic nanocatalysts, to evaluate the recovery performance in the absence of the trimetallic nanocatalysts. After that, tests 4, 5, and 6 were conducted to evaluate the presence of a light solvent at different mass fractions in VGO matrix as injecting fluid. The last two tests were performed at different temperatures in the presence of trimetallic nanocatalysts to study the effect of temperature on the recovery enhancement.

The results of these tests were presented as recovery curves to evaluate the effectiveness of different types of hot fluid on recovery enhancement. It is worth noting that steam injection test was performed in a low permeability sand pack (absolute permeability about 10 darcy) as well. However, in the low permeability media steam chamber growth was very weak and the presented recovery curve was not matched with a typical SAGD reservoir performance. This was the reason that high-permeability sands were selected in the current study.

Flood of Saturated Porous Media by Steam. To evaluate the porous media, a steam injection test was carried

Table 3. Specifications of the Experimental Tests Considered in This Study

	test							
	1	2	3	4	5	6	7	8
injecting liquid	steam	VGO	VGO	pentane (5 wt %)	pentane (10 wt %)	pentane (15 wt %)	VGO + n-cats	VGO + n-cats
temperature (°C)	243.5	320	340	340	340	340	320	340
pressure (MPa)	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5
porosity (%)	33	33.1	33.2	33.1	33	33.4	32.9	33.2
absolute permeability (darcy)	243.9	246	245.3	240.7	242.5	244.5	244	244.7
nominal particle concentration (ppm)	0	0	0	0	0	0	720	720
residence time (h)	NA	36	36	36	36	36	36	36
hot fluid injection rate (cm ³ /min)	NA	0.01	0.01	0.01	0.01	0.01	0.01	0.01
hydrogen flow rate (cm ³ /min)	NA	1	1	1	1	1	1	1

out by using the same sand as for the nanocatalyst experiments. Before steam injection, porous medium was saturated by Athabasca bitumen. The main reason was to ensure that this model has the same recovery performance as a typical SAGD process. An experimental temperature of 245 °C was used, as it corresponds to the steam saturation temperature at 3.5 MPa. Figure 4 shows the steam oil ratio (SOR) and percentage of

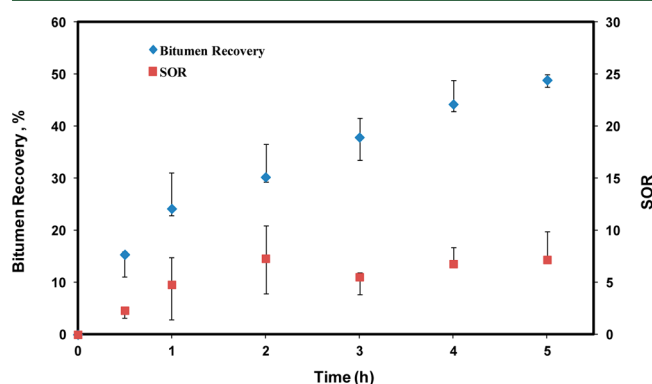


Figure 4. Recovery performance and SOR of steam injection into the high permeability sand packed bed at pressure of 3.5 MPa, steam injection rate of 1 cm³/min, and temperature of 243.5 °C.

Athabasca bitumen recovery at different times. As seen, the SAGD performance is quite reasonable based on cumulative recovery (about 50% of IOIP) and steam oil ratio. However, SOR is higher than a typical SAGD process, which is expected because of compensation for the high amount of heat loss that occurred from the reactor wall.

The findings of this experiment show that by using the sand size of 12–20 mesh (U.S. sieves) and designed reactor height, a typical SAGD reservoir could be simulated. Higher permeability of the medium is a compensation for the lower height of the reactor compared with a real bitumen reservoir.

Hot Fluid Flood Study. To evaluate the effectiveness of nanocatalysts on enhancement of the Athabasca bitumen recovery, series of experiments were conducted in the sand pack. With these tests, the incremental oil recovery of different injection scenarios was obtained, and in each test the effect of one parameter on the recovery curve was studied. The first series of tests were conducted in the absence of nanocatalysts, whereas the last two tests were performed in the presence of nanocatalysts. Produced fluids were analyzed by standard

techniques to determine the bitumen content and to demonstrate the recovery curves.

Hot VGO Injection. As a blank or control experiment (i.e., in the absence of nanocatalysts), Nexen VGO was injected inside the medium saturated with Athabasca bitumen at 3.5 MPa and different temperatures of 320 and 340 °C. Figure 5 shows the

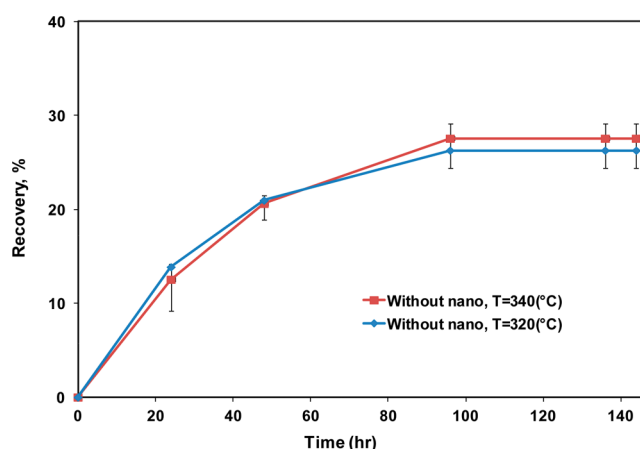


Figure 5. Recovery performance of VGO injection into the high permeability sand packed bed at different times in the absence of trimetallic UD nanocatalysts at pressure of 3.5 MPa, VGO injection rate of 0.01 cm³/min, hydrogen flow rate of 1 cm³/min, and temperatures of 320 and 340 °C.

production percentage of IOIP against the injection time. As seen, the cumulative bitumen production curve increased with time and leveled off after approximately 95 h. Analysis of produced liquid showed no trace of bitumen in the sample collected after 95 h. This indicates that, after depletion of the oil pool region, all produced liquid was mainly VGO, and injection of hot stream was not effective on the recovery enhancement. Moreover, temperature shows a slightly significant effect on the bitumen production from porous media.

Effect of Light Pentane Injection. The presence of light hydrocarbon in the injection stream enhances the production of heavy hydrocarbon deposit. To evaluate the effect of light hydrocarbon component (light solvent) on recovery of bitumen, three sand pack flood tests were carried out at 3.5 MPa, temperature of 340 °C, and different mass percentages of pentane (5, 10, and 15%). Figure 6 shows the recovery curves for this set of experiments. Clearly, oil recovery increased with increasing solvent concentration.

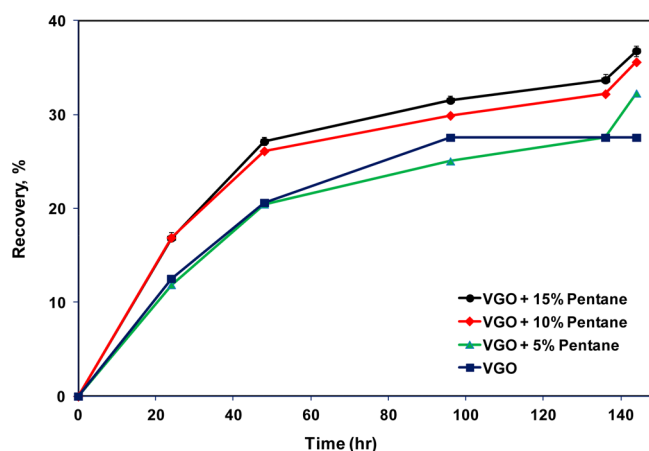


Figure 6. Recovery performance of mixed VGO and pentane (0, 5, 10, and 15 wt %) injection into the high permeability sand packed bed at different times in the absence of trimetallic UD nanocatalysts at pressure of 3.5 MPa, hot fluid injection rate of 0.01 cm³/min, hydrogen flow rate of 1 cm³/min, and temperature of 340 °C.

The lowest recovery was attained for the experiment conducted with 5 wt % pentane in the injection fluid, and the highest recovery was attained for 15 wt % pentane test. This is expected as pentane acts as a diluent for bitumen as well as a vaporizing component, so increasing pentane concentration will favor the reduction of bitumen viscosity and subsequently enhance its mobility, which, in turn, results in higher recovery. More importantly, in comparison with the control experiments, Figure 6 shows that the recovery is increased and shifted up from the level off stage. Furthermore, with careful observations on the trend recovery curves, it was concluded that after depletion of oil pool, production of bitumen continues from the upper section of the oil pool.

The mechanism of enhancement could be related to expansion of solvent and consequent viscosity reduction of Athabasca bitumen. Nevertheless, it should be noted here that the high cost of the solvent-based process makes it challenging for future application, as solvent price is an important factor to select the percentages of the mixture.⁵⁵

Effect of Nanocatalysts. The bitumen recovery was enhanced by light hydrocarbon injection, and our previous study for a batch experiment mode showed that UD nanocatalysts enhanced the upgrading of Athabasca bitumen by significantly increasing the hydrogen/carbon atomic ratio and reducing both viscosity and coke formation.⁴² This phenomenon was used to implement the nanocatalyst injection concept inside the porous media, as it is anticipated that the produced light liquid as well as emitted gases during the upgrading will contribute to bitumen viscosity reduction and subsequently enhance its recovery as well as upgrade from the oil pool. Therefore, to evaluate the effectiveness of nanocatalysts present inside the porous media, two set of experiments were conducted at the same conditions as the control experiments except a certain concentration of nanocatalysts was added to the injecting fluid.

Details of nanocatalyst concentration are demonstrated in Table 2. Tests were performed at a pressure of 3.5 MPa and temperatures of 320 and 340 °C. Figure 7 shows the bitumen recovery as a function of the injection time. As seen, recovery of bitumen increased with time and continues until the end of the experiments. It should be noted that the observed trends were

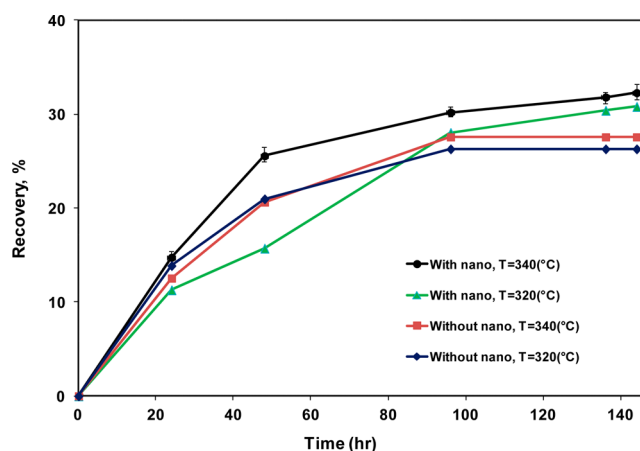


Figure 7. Recovery performance of hot VGO injection into the high permeability sand packed bed at different times in the presence of trimetallic UD nanocatalysts at pressure of 3.5 MPa, hot fluid injection rate of 0.01 cm³/min, hydrogen flow rate of 1 cm³/min, and temperatures of 320 and 340 °C.

similar to the experiments conducted with percent pentane injection. It can be interpreted that the presence of nanocatalysts inside the medium was the cause of the production of lighter components via catalytic hydrocracking, which were confirmed with the analysis of produced gas from porous media. In addition, higher temperature experiments showed higher ultimate recovery.

Results of the recovery curves clearly show the significant effect of nanocatalyst presence inside the porous media. It should be noted that recovery enhancement was proved by closing the total material balance of the nanocatalyst tests. Figure 8 shows the graphs for total injected hot fluid and total produced liquid for the nanocatalyst experiments at temperatures of 320 and 340 °C.

As seen, the differences between the injected and produced liquid interpreted as the total amount of produced bitumen. This graph clearly shows the enhancement of bitumen production via injection of the nanocatalysts. As mentioned, the presence of nanocatalysts inside the medium enhanced the

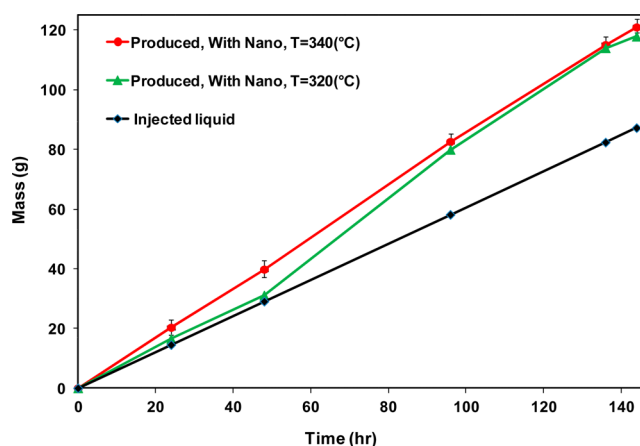


Figure 8. Material balance for the hot VGO injection into the high permeability sand packed bed at different times in the presence of trimetallic UD nanocatalysts at pressure of 3.5 MPa, hot fluid injection rate of 0.01 cm³/min, hydrogen flow rate of 1 cm³/min, and temperatures of 320 and 340 °C.

cracking of the heavy bitumen and produced lighter components and gaseous emission.

The penetration of the produced gases toward the top section of the oil pool as vaporizing components was considered as the main reason for the increase in the recovery of bitumen. In this process, the vaporized hydrocarbon mixture acts as solvent to diffuse and dissolve in bitumen to reduce the viscosity and make it mobile. Figure 9 shows the total volume

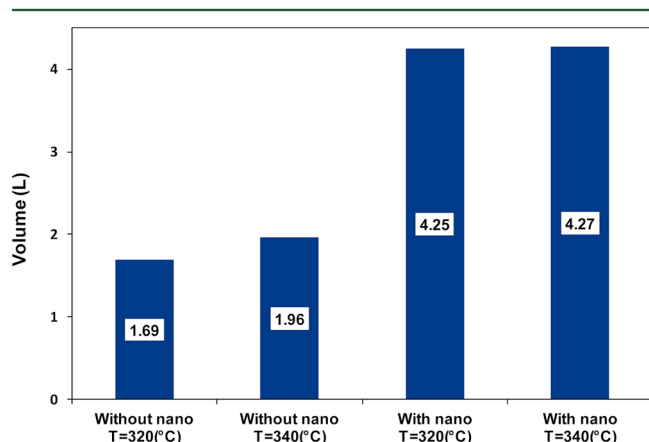


Figure 9. Total volume of produced gases at standard condition ($T = 25\text{ }^{\circ}\text{C}$, $P = 0.1\text{ MPa}$) for the hot VGO injection into the high permeability sand packed bed in the presence and absence of trimetallic UD nanocatalysts at pressure of 3.5 MPa, hot fluid injection rate of $0.01\text{ cm}^3/\text{min}$, hydrogen flow rate of $1\text{ cm}^3/\text{min}$, and temperatures of 320 and 340 $^{\circ}\text{C}$.

of produced gases for the experiments conducted in the presence and absence of nanocatalysts. It can be observed that the total volume of gas produced in the experiments with nanocatalysts is at least twice the volume of gases produced from experiments without nanocatalysts. In addition, a considerable percentage of gases in the experiment conducted without nanocatalysts was carbon dioxide, whereas in the experiments conducted in the presence of nanocatalysts the hydrocarbon gases were quite significant. Table 4 shows the

Table 4. Produced Liquid Quality Enhancement Percentages with the Use of Nanocatalysts at the Temperature of 340 $^{\circ}\text{C}$

reaction time (h)	API increment %	viscosity reduction %	MCR reduction %	residue 545 ⁺ reduction %
24	2.17	16.13	7.74	11.24
48	17.34	42.79	8.19	51.08
96	9.47	36.69	45.05	62.68
136	8.41	30.17	30.74	53.40
144	0	16.35	70.81	37.03

percentages of produced liquid quality enhancement for the experiments conducted in the presence of nanocatalysts at a temperature of 340 $^{\circ}\text{C}$. Clearly, in the presence of trimetallic nanocatalysts, significant reductions in viscosity, MCR, and carbon residue as well as API increment are observed. This supports that the in situ formed nanoparticles not only enhanced the recovery of bitumen but also acted as catalysts for enhancing the hydrocracking reaction.⁴² It is worth noting that detailed analysis of the produced liquid and gases as well as quality enhancement of produced liquids shall be communicated in another study.

CONCLUSIONS

In this study, the effect of different hot fluid injection scenarios on Athabasca bitumen recovery performance inside a continuous packed bed reactor was investigated. The amount of produced bitumen was depicted by recovery curves, at different times and temperatures for each scenario. The recovery curve behavior for the VGO injection, without nanocatalysts, increased with time and leveled off after 95 h. Adding different mass percentages of pentane to the VGO enhanced the recovery of bitumen from the oil pool due to expansion of solvent and consequent viscosity reduction of Athabasca bitumen. The presence of trimetallic nanocatalysts in the injecting hot fluid (VGO matrix) enhanced the Athabasca bitumen recovery. This may be due to the presence of nanocatalysts inside the medium leading to the production of lighter components via catalytic hydrocracking of bitumen and the subsequent viscosity reduction of bitumen presence in the oil pool as a result of contact with emitted hot gases.

AUTHOR INFORMATION

Corresponding Author

*Phone: (403) 210-9772. Fax: (403) 210-3973. E-mail: nassar@ucalgary.ca.

Notes

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