

Nanoparticle technology for heavy oil in-situ upgrading and recovery enhancement: Opportunities and challenges



Rohallah Hashemi, Nashaat N. Nassar*, Pedro Pereira Almao

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

HIGHLIGHTS

- Overview the recent application of nanoparticles in oil upgrading and recovery.
- Overview the oil quality enhancement by using nanoparticles.
- Overview the challenges facing nanoparticle applications.
- Overview the available recovery mechanism of nanoparticles.
- Proposal of the possible applications of nanoparticles in wettability alteration.

ARTICLE INFO

Article history:

Received 5 May 2014

Received in revised form 14 July 2014

Accepted 18 July 2014

Keywords:

Nanotechnology

Nanoparticles

Heavy oil

Upgrading

Recovery

In-situ

ABSTRACT

With more than 170 billion barrels of estimated oil sands reserves in Canada, Canada has the third largest oil reserves in the world. However, more than 80% of oil sand's reserves are located deep underground and could not be accessed by surface mining. Nonetheless, a number of in-situ recovery methods have been developed to extract heavy oil and bitumen from deep reservoirs. Once produced, bitumen is transferred to upgraders converting low quality oil to synthetic crude oil. However, in the present context, heavy oil and bitumen exploitation process is not just high-energy and water intensive, but also it has significant environmental footprints as it produces significant amount of gaseous emissions and wastewater. In addition, the level of contaminants in bitumen requires special equipment, and has also environmental repercussions.

Recently, nanotechnology has emerged as an alternative technology for in-situ heavy oil upgrading and recovery enhancement. Nanoparticle catalysts (nanocatalysts) are one of the important examples on nanotechnology applications. Nanocatalysts portray unique catalytic and sorption properties due to their exceptionally high surface area-to-volume ratio and active surface sites. In-situ catalytic conversion or upgrading of heavy oil with the aid of multi-metallic nanocatalysts is a promising cost effective and environmentally friendly technology for production of high quality oils that meet pipeline and refinery specifications. Further, nanoparticles could be employed as inhibitors for preventing or delaying asphaltene precipitation and subsequently enhance oil recovery. Nevertheless, as with any new technologies, there are a number of challenges facing the employment of nanoparticles for in-situ catalytic upgrading and recovery enhancement. The main goal of this article is to provide an overview of nanoparticle technology usage for enhancing the in-situ catalytic upgrading and recovery processes of crude oil. Furthermore, the article sheds lights on the advantages of employment of nanoparticles in heavy oil industry and addresses some of the limitations and challenges facing this new technology.

© 2014 Elsevier Ltd. All rights reserved.

Contents

1. Introduction	375
2. In-situ prepared ultradispersed nanoparticles	375
3. Synthesis of nanocatalysts	377

* Corresponding author. Tel.: +1 (403) 210 9772; fax: +1 (403) 282 3945.

E-mail address: nassar@ucalgary.ca (N.N. Nassar).

4. Required facilities for nanocatalysts application in heavy oil upgrading and recovery	377
5. Nanocatalysts transport behavior inside the porous media	378
6. Modeling of reaction kinetics	378
7. Recovery enhancement	380
8. Quality enhancement	380
8.1. H/C atomic ratio	380
8.2. Viscosity reduction and API increment	381
8.3. Coke reduction	381
8.4. Sulfur removal	382
8.5. Coke formation mitigation	382
9. Gas emission reduction	383
10. Nanocatalysts recycling	383
11. Hydrogen consumption	384
12. Inhibition of formation damage	384
13. Environmental effect of nanoparticles	384
14. Conclusions	385
Acknowledgments	385
References	385

1. Introduction

There is no doubt that the world is facing formidable challenges in meeting energy demands as the available conventional energy supplies are decreasing due to several factors [1], such as enormous growth of world population, competing demands from a variety of users, increasing industrialization and motorization of the world, and increasing technical development and living standard. Therefore, it is necessary to look for alternative energy supplies that can be produced from natural resources.

Various natural energy resources have been explored; including biomass, vegetable oils, biodiesel, etc. [2]. These resources are believed to be environment-friendly fuels [3], but they are costly and insufficient in meeting energy demands. Further, usually these types of fuels need to be formulated to meet the relevant properties of conventional fuels [3]. Most importantly, they require advanced attention to evaluate their advantages, disadvantages and specific applications. These facts have led to an increased demand on the upgrading and recovery of unconventional oil in order to meet current and future energy needs

Accordingly, due to an increase interest in alternative energy resources and utilization of fossil fuels, like unconventional crude oil, Alberta oil sands have now become an important source of alternative energy resources [4]. Actually, the International Energy Agency (IEA) has predicted that, by the year 2030, about 60% of the total worldwide energy growth will be met by fossil fuel sources such as heavy oil, coal, and natural gas [5]. Nonetheless, due to its high viscosity, low hydrogen to carbon ratio and high sulfur and nitrogen content, there are a number of challenges associated with bitumen recovery and upgrading in the present context. These challenges need to be surmounted to make it a sustainable and economically feasible alternative [6–10].

Among the challenges to be solved are the reduction in costs associated with the production and transportation of oil sands and the improvement of synthetic crude quality to meet stringent market specifications with less environmental footprints [11]. Nanotechnology is a rapidly growing technology with considerable potential applications and benefits [12]. It provides unprecedented opportunities to develop more cost effective and environmentally friendly heavy oil upgrading and recovery processes. Interest in using nanotechnology in heavy oil processing is driven from the unique physical and chemical properties of the nano-scale particles [13]. In the world of nanotechnology, a nanoparticle acts as a whole unit in terms of its transport behavior and properties, and its diameter is sized between 1 and 100 nm. In other words, as the size of a particle reduces to nanoscale (i.e., 1–100 nm) the

properties begin to change dramatically as the percentage of atoms at the surface of a material becomes significant, a phenomena which is attributed to the large surface area to volume ratio [14]. Quantum confinement, surface plasmon resonance, high adsorption affinity, enhanced catalytic activity, good dispersion ability and intrinsic reactivity are just some of the unique properties associated with nanoparticles [15].

Nowadays, because of these properties nanoparticles are used in vast areas of engineering applications, such as heavy oil upgrading [16–18], fuel cell technology [19,20], polymer nanocomposites [21–23], catalysis [24–26], and wastewater treatment [27–29], to name only a few. However, there are uncertainties associated with nanoparticles applications, which should be deeply explored.

Among the potential applications enumerated for nanoparticles are in oil and gas industry, specially upgrading and recovery enhancement of heavy feedstocks by nanoparticle catalysts [30]. In addition to its high surface area, these catalysts should maintain ultra-dispersion ability and high catalytic activity. The ability to engineer desired surface functionalities of nanoparticles by tuning its characteristics as well as the possibility of its in-situ preparation makes nanotechnology an attractive unique option for heavy oil upgrading and recovery. In addition, owing to their small size and transport behavior, nanoparticles can be employed in-situ within the reservoir environment where upgrading and recovery are needed [11,31].

Extensive research was performed ranging from synthesis of nanocatalysts to pilot plant application for ex-situ and in-situ upgrading processes at the University of Calgary. However, there is still long way to investigate all aspects of these nanocatalysts properties and performances. Here, we briefly review what are known about nanoparticles and their behavior as adsorbent/catalysts for heavy oil upgrading and recovery as well as possible challenges for future implementations. We also discuss state-of-the-science knowledge and instrumentations related to nanocatalysts implementation for upgrading and recovery of Athabasca bitumen. It should be noted here that a comprehensive discussion of the applications of nanotechnology to heavy oil upgrading and recovery is beyond the scope of this article. The main objectives here are to discuss the opportunities and challenges of using nanoparticles as adsorbent/catalysts in the upgrading and recovery of heavy oil.

2. In-situ prepared ultradispersed nanoparticles

Placement of catalysts inside the porous media is one of the important steps to apply the idea of “underground refinery” for

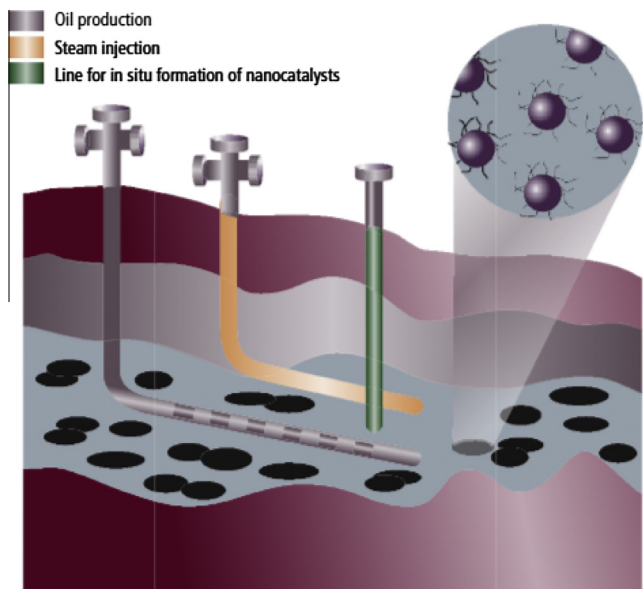


Fig. 1. Cartoon representation of in-situ heavy oil upgrading and recovery coupling ultradispersed nanocatalysts and the SAGD process, whereupon light oil is produced at the surface and heavy molecules, solids and minerals stay sub-surface. Obtained from Ref. [31] with permission.

bitumen upgrading and recovery enhancement [32]. Supported catalysts could be placed only inside the production well to perform in-situ upgrading. Due to coke deposition and metal poisoning occurring in three phases, supported catalysts system deactivates [33]. The three phases are constant deactivation rate of catalyst caused by metal deposition and blocking active catalysts sites, coke deposition on the fresh catalyst network and rapid deactivation of catalyst caused by metal deposition which results in constriction of pore mouth [34]. Therefore, upgrading of heavy feeds with desired efficiency requires large pore volumes as well as tolerance to the feedstock constituents.

Good catalytic properties, such as high porosity and resistance to pore plugging are favorable properties for processing of heavy

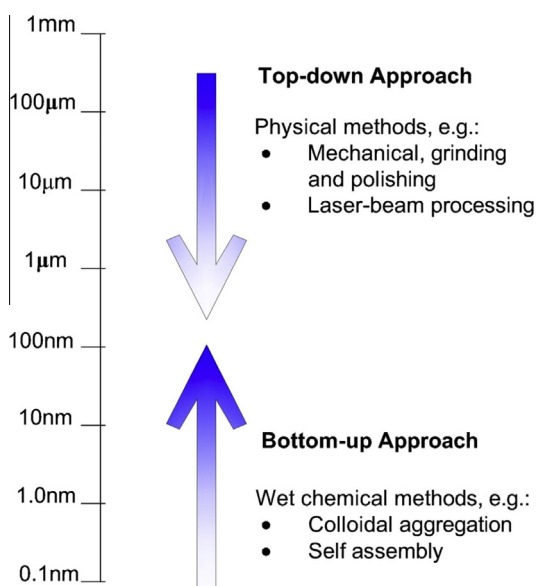


Fig. 2. Schematic representation illustrating the top-down and bottom-up approaches for nanocatalysts preparation. Obtained from Ref. [47] with permission.

feedstocks [35]. In order to overcome mainly the pore plugging problem ultra-dispersed nanocatalysts were developed for industrial applications [34]. In addition, dispersion is a very important concept in catalyst industry [36]. Experts in commercial catalysis research are looking to find the ultra dispersed (UD) catalysts to achieve higher conversion at the applied pressure and temperature conditions [37,38]. This is the reason for using dispersed catalysts for hydrocracking of heavy feedstocks.

There exist several advantages with the usage of nanocatalysts; including: (a) small size of nanocatalysts offer large surface area to volume ratio which results in improved catalytic performance for processing purposes, (b) the probability of contacts between reactants is increased because of nanocatalysts mobilization inside the reactor which ultimately increases the economics of the upgrading process, (c) absence of any fixed bed catalysts because of nanocatalysts implementation inside the medium make possible longer run times for conversion as there is no need of catalyst replacement, (d) in absence of any pores in UD nanocatalysts, loss of activity will not be presented compared to supported catalysts [39], (e) propagation of nanocatalysts inside the porous media and reacting in-situ cause bitumen dissolution as well as viscosity reduction of produced liquid, and (f) successful in situ processing reduces the operating costs as well as environmental concerns associated with bitumen production such as greenhouse gas (GHG) emissions, SO_x and NO_x production, solid waste by-products and even fresh water consumption [11].

Nanocatalysts were introduced into the porous media to perform upgrading inside the reservoir to convert bitumen to lighter products. A cartoon representation shown in Fig. 1 shows the potential mechanism of nanocatalysts application for bitumen upgrading and recovery during the steam assisted gravity drainage (SAGD) process [31]. Since SAGD is the dominant recovery process for bitumen production, then the final goal for the nanocatalysts usage is to couple both the benefits of nanocatalysts presence inside the porous media as well as thermal drive mechanism simultaneously. However, there is a long way and extensive work to commercialize and test the proposed method for in situ processes inside the porous media.

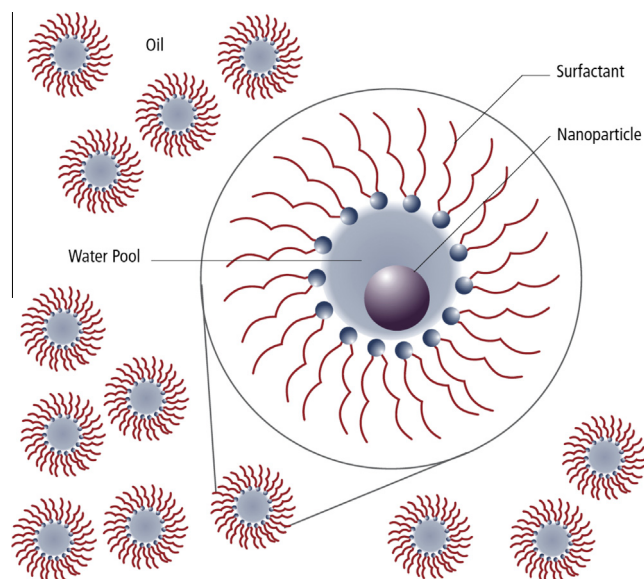


Fig. 3. Schematic representation of water-in-oil microemulsions. The water pools solubilise the precursors and accommodate the resultant nanoparticles. The size of the water pool can be manipulated by controlling the ratio of mole water/mole surfactant. Obtained from Ref. [31] with permission.

3. Synthesis of nanocatalysts

A number of preparation techniques have been reported for nanoparticles manufacturing [40–48]. These methods can be grouped into top-down and bottom-up methods as seen in Fig. 2 [47]. Top-down methods are defined as those by which nanoparticles are directly prepared from bulk materials via the generation of isolated atoms by using various distribution techniques that involve physical methods, such as milling or grinding, laser beam processing, repeated quenching and photolithography [48]. Bottom-up approaches involve molecular components as starting materials linked with chemical reactions, nucleation and growth processes to promote the formation of nanoparticles [49–57].

There are various bottom-up methods for preparation of nanocatalysts, such as water-in-oil microemulsions or reversed micelles [43,46,49], chemical reduction [50], hot-soap [51,52], sol-gel [53], pyrolysis [54], and spray pyrolysis [55]. Water-in-oil microemulsion method is commonly used for in-situ formation of nanoparticles in heavy oil matrix. Emulsion preparation is obtained by mixing oil, water and a stabilizing agent such as surfactant [56]. Preparation procedure and conditions are selected in such a way to have microemulsion in the media. Microemulsion hold specific properties such as very low interfacial tension, small microstructure, thermodynamic stability and translucence that can be used in variety of applications [57]. Water-in-oil (w/o) microemulsion preparation technique was described in literatures [43,46,49,56]. In brief, aqueous solution of corresponding metals were added to a w/o emulsion and then mixed for certain time. After that, a base aqueous solution is added to initiate nucleation and growth of the nanoparticles, which remain stable in suspension. Fig. 3 shows a simple cartoon representation illustrates the structure of reverse-micelle “nano-reactor” used for in-situ formation of nanoparticle [31].

Preparation of nanocatalysts could be obtained by mixing two reacting systems (one containing the precursor salt and the other a reducing agent) in form of microemulsions [58]. Capek [58] has reported a comprehensive study on the preparation of nanoparticles in w/o microemulsions with formulations for Fe, Pt, Ni, Au, Cd, Pd, Ag and Cu. Thus, microemulsions are considered as a breakthrough for nanocatalysts preparation, especially for in-situ applications such as upgrading and recovery of bitumen. For heavy oil conversion, an emulsion was developed in presence of water claiming steam cracking of vacuum gas oil (VGO) catalyzed by catalytic emulsion [59]. Furthermore, a catalytic nanoparticle solution prepared by decomposition of w/o emulsion was successfully implemented to catalyze hydroprocessing reaction [60]. Thompson et al. [34] performed a work on Mo nanoparticle reaction performance for Athabasca bitumen upgrading [34]. A lab scale reactor packed with sand particles were used to explore the formation of mixed oxy-carbides composed by MoO_2 , MoO_3 and MoC as well as agglomeration of nanocatalysts promoted by surfactant-media interactions. Using the microemulsion method, Ni, Mo and Ni-Mo nanoparticles (approximately 10 nm) were prepared for hydrodesulfurization with the potential of using for in situ upgrading as well as on surface [61]. It can be concluded that synthesis and preparation of nanocatalysts were performed successfully based on literature. However, stability of nanoparticles inside the prepared/reaction media and control over particle size as well as particle recovery and regeneration are still an important issue for nanoparticle implementation.

Mechanical separation and deposition of UD nanocatalysts based on their motion inside the viscous fluid media has been investigated in a cylindrical geometry [62]. 2D and 3D convective-dispersive models were developed and validated based on experimental tests [62]. In addition, concentration profiles for particles (ranging from micro to the nano scale) movement through

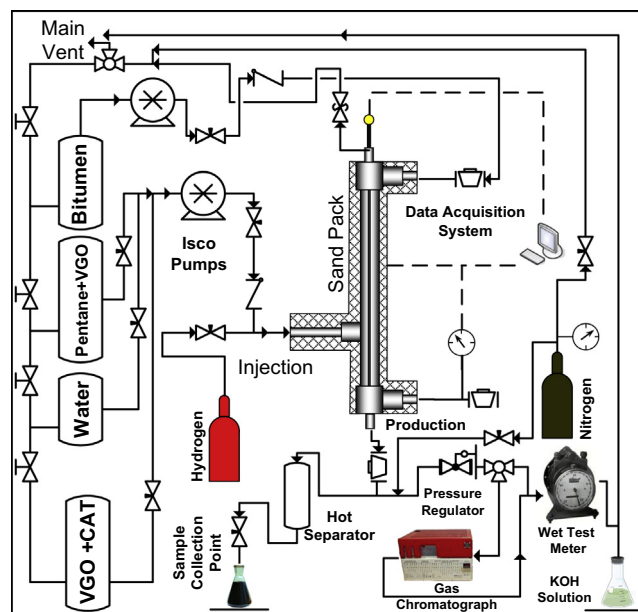


Fig. 4. Schematic representation of the experimental setup for in-situ upgrading and recovery enhancement of Athabasca bitumen. Obtained from Ref. [63] with permission.

fluid media as a function of their position and time were successfully predicted. Published results showed that dispersion coefficient is a function of fluid medium properties (density, viscosity and volumetric flux) and a large number for dispersion coefficient in the medium shows particles tendency for sedimentation [62]. In addition, deposition tendency of particles were related to a factor namely “critical particle diameter” [62]. For different scenarios (i.e., initial particle concentration, velocity change and medium viscosity change), change in medium properties caused that sedimentation of UD particles to occur in lower or higher critical particle diameter. It is worth mentioning that agglomeration of UD nanoparticles inside the medium plays an important role in sedimentation of nanoparticles as well as efficiency of produced nanoparticles from desired metal precursors.

As a part of commercial application for the nanocatalysts in heavy oil industry, it should be noted that there exists another challenge, which is the mass production of nanocatalysts in the field scale applications. It is worth mentioning that production of nanocatalysts for the batch reactor experiments as well as pilot plant tests (continuous mode) have been performed successfully [63,64]. However, for the field scale applications, there should be availability of surface facilities or suppliers that can provide large quantities of required nanoparticles with the economically viable prices.

4. Required facilities for nanocatalysts application in heavy oil upgrading and recovery

Implementation of new advanced technologies is directly associated with the usage of hi-tech systems for industrial developments [65]. Due to the nature of UD nanocatalysts upgrading difficulties, it is essential to acquire control systems to avoid or mitigate any associated risks. Presence of hydrogen as well as high pressure and temperature conditions will introduce risk of plugging and even explosion which enforce need for high level of control systems.

Fig. 4 shows a schematic representation of the experimental set-up which was used to mimic nanocatalysts injection inside

the porous media at a high pressure and temperature [63]. As seen, it is required to use many monitoring tools as well as sophisticated control systems to ensure the process is meeting the required desired product while taking the safety into consideration. Further, to the best of our knowledge, the cost of nanocatalysts for in-situ upgrading and recovery of bitumen is never mentioned in the literature. The cost of nanocatalysts depends primarily on the local availability of their precursors, types, preparation techniques and method of application. Because the nanocatalysts could be prepared in-situ, within the reservoir environment, the materials costs could be reduced. Nevertheless, more investigations on the cost effectiveness of the nanocatalysts application as an alternate technology for bitumen upgrading and recovery enhancement are needed to evaluate the economic of these processes with higher precision.

5. Nanocatalysts transport behavior inside the porous media

After preparation and synthesis of nanocatalysts in a micro-emulsion system, an important issue regarding the usage of nanocatalysts for bitumen upgrading is the feasibility of nanocatalysts transport inside the porous media. To conduct successful upgrading process underground, placement of nanocatalysts in appropriate zone inside the oil sand medium is necessary. It should be noted that there exists a huge area of research for the transport behavior of nanoparticles in porous media [66]. However, most of the studies are focused on the transport behavior of the nanoparticles in deep bed filtration for wastewater treatment, and the obtained results could not be applied for reaction conditions in the oil sand based matrix. Accordingly, very little information is available on the flow behavior of UD nanocatalysts in oil sand packed bed.

Recently, our research group reported on the transport behavior of metallic and multimetallic UD nanocatalysts, suspended in vacuum gas oil, inside an oil sand porous media at different experimental and operational conditions [66–68]. Results demonstrated that the propagation of UD nanocatalysts in an oil sands packed bed column at typical pressure and temperature of SAGD recovery process is feasible, as neither major permeability reduction nor pore plugging were observed.

It should be noted that the experiments conducted by Zamani et al. [68] were performed at low temperatures and in the absence of cracking reaction which showed that nanocatalysts were able to propagate through the sand medium, but larger agglomerated particles were filtered out and remained inside the porous media [68]. However, the authors reported that the retention of nanocatalysts had a negligible effect on the pressure drop and caused no permeability damage inside the experimental medium. Further, retention mechanism on the surface was mainly attributed to adsorption, and analysis showed that adsorption is not reversible. In addition, specific deposit profile along the sand pack showed that nanocatalysts continued to be filtered out deep inside the porous medium, but higher retention occurred in the entrance of the sand pack. Moreover, Zamani et al. [68] reported that the sand media retained 14–18% of injected UD nanocatalysts, mainly at the bed entrance [68].

Hashemi et al. [67] investigated the transport behavior of nanocatalysts in an oil sands porous media at high pressure and temperature of typical SAGD conditions (i.e., presence of reaction) [67]. In their study, the authors reported on the effects of temperatures and permeability on the transport behavior of ultradispersed multimetallic (Ni–Mo–W) nanocatalysts inside an Athabasca oil sands packed bed column. Experiment results showed that aggregation of nanocatalysts was observed in all cases (i.e., low and high temperatures and different sand permeability).

The authors showed that the deposition tendency for nanocatalysts is strongly affected by the type of metal, temperature, and sand permeability. Increasing the temperature favored the aggregation, this was attributed to the increase in frequency of particle collision because of heavy oil viscosity reduction and subsequently, higher aggregation rate. Further, a high-permeability-oil-sands-packed bed has a lower amount of deposited nanocatalysts compared to the low-permeability medium. Again, deposition of nanocatalysts mainly occurred at the entrance of the injection zone and rapidly decreased across the reaction zone. However, same as low temperature experiments, deposition of nanocatalysts inside the porous media has a meager influence on medium permeability. Again, pressure drop analysis showed no major permeability damage across the reaction zone [67].

One of the most important aspects of nanocatalysts transport inside the porous media is the control over the particle size during the injection and reaction times. In addition to pressure drop via permeability reduction, particle size would impact on dispersion ability, adsorption affinity and catalytic activity of nanoparticles inside the medium [67]. It should be noted that most of these studies are at the initial steps for fulfilling the idea of in-situ upgrading with the promising results to future enhancement in the area of heavy oil technologies.

In addition to numerous experimental studies, robust mathematical modeling of nanocatalysts transport behavior inside the porous media would provide valuable information on the concept of particle mass transfer. Modeling of mass transfer and deposition behavior of fine particles in cylindrical channels were studied by several researchers [34,62,69–72]. It should be noted that mathematical modeling of such processes are very complex and sometimes require incorporating empirical correlation as well. Furthermore, presence of viscous fluid in the medium enforces even more complexity to the equations; nonetheless, importance of UD nanocatalysts in the heavy oil and bitumen industries justifies the necessity of conducting scrutinizing study in this area.

In one of the novel studies [62], our research group has developed a mathematical model for nanocatalysts transport and deposition that takes into account the geometry of the channel, fluid medium properties and characteristics, particle diameter and concentration, and the effects of the temperature on the particle agglomeration and deposition of nanocatalysts. 2-D and 3-D convective–dispersive model, which delivers the concentration profile of particles immersed in fluid media enclosed in a circular cross section, were validated by experiments performed in an injection rig [62]. Despite the very large effort, by changing the physical properties of media and geometry, it is required to conduct new experiments to estimate the coefficient existed in the mathematical model equations [62].

In conclusion, propagation of nanocatalysts inside the porous media is feasible and ultradispersed multimetallic nanocatalysts could be controllably delivered through oil sands porous media into a targeted heavy oil reservoir, where they could work as adsorbents/catalysts for heavy oil upgrading. However, some portion of injected particles could be retained inside the porous media. Nonetheless, the deposited particles inside the medium can potentially increase the activity of the medium [63] and could be predicted by mathematical modeling [62].

6. Modeling of reaction kinetics

Hydrocracking kinetics of heavy oil was investigated in many aspects considering various kinetics models based on the proposed cracking reaction schemes [73–79]. Presence of many parallel reactions in hydrocracking at the same time would suggest proposing network of reactions for kinetics modeling [73,74]. Fig. 5 shows a

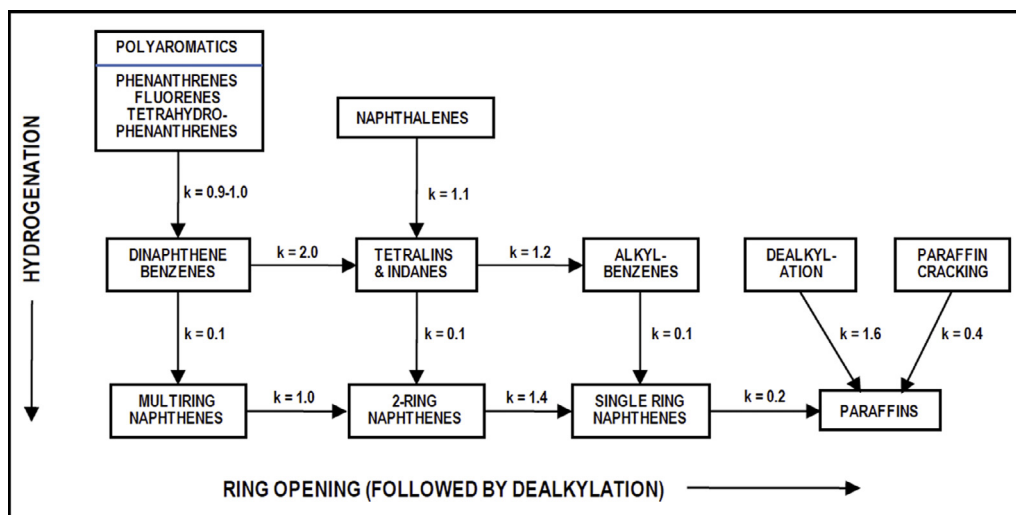


Fig. 5. Sets of reactions with relative velocities occurring during hydrocracking process. Obtained from Ref. [75] with permission.

schematic representation of a generic family of hydrocracking reactions and approximate velocity constant for a conventional oil [75]. As seen, some reactions are faster than others depending on the nature of the reaction process.

For the case of unconventional oil, the presence of large molecules such as resins and asphaltenes in the heavy oil and bitumen matrixes makes the kinetics process very complex. However, using the traditional grouped lumping concept along with pseudo components definition representing the heavy feedstock are common methods for bitumen kinetic study [80–82]. It should be noted that group selection is a very crucial step in this approach and consequently determines the amount of required experimental study to estimate the kinetic parameters. Generally, first order rate equation with respect to bitumen is considered for the kinetic study of bitumen [77,83,84]. In addition, incorporating higher number of lumped groups was considered in literature, which resulted in more complex equations as well as higher precision in kinetic modeling [83,85,86]. Fig. 6 shows a schematic representation of a proposed lumped kinetic model which contains series of reactions with certain velocity constants [77].

Kinetics modeling of Athabasca bitumen reaction at various conditions has been reported in literature [87–90]. In particular, performance of catalytic and non-catalytic hydrocracking of Athabasca bitumen was evaluated using the lump kinetic method which includes combination of separated functions [85,86].

It is believed that the introduction of the nanocatalysts into bitumen or heavy oil matrix causes a considerable change in the

reaction mechanisms as nanocatalysts open new pathways for the reaction. Galarraga et al. [64] performed a preliminary hydro-processing reaction kinetic in the presence of UD nanocatalysts for Athabasca bitumen proposing two different kinetics models to fit their experimental data. The first model was based on a simple power law of first order reactions and the second one was similar to the kinetics model which was proposed by Sanchez et al. [77]. This model was using a lumping method with series of reactions connected as a network scheme. Loria et al. [91] proposed a modified kinetics model using the same reaction scheme for the UD nanocatalysts. Fig. 7a and b shows both models. The five lumped pseudo components incorporate: residue (R), vacuum gas oil (VGO), distillates (D), naphtha (N), and gases (G). As can be observed, there exists quite a difference between the kinetic rate constants corresponding to the reactions.

Results of predicted product compositions were in good agreement with the lab data with the absolute error value of less than 7% [91]. In addition, predicted viscosity of produced liquids shows great reduction depending on temperature and residence time [91]. More importantly, it reveals that correct modeling scheme as well as accurate solution conditions would provide successful product prediction. Along with other studies, our group published series of articles on the kinetics decomposition of Athabasca bitumen and asphaltenes in the presence of nanocatalysts as well [9,11,92–96]. Despite all of the studies that have been performed in this field, there exists many area of research to fully understand the kinetics decomposition of heavy oil and bitumen.

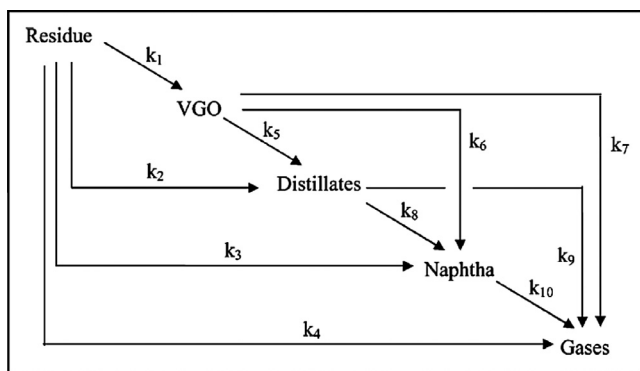


Fig. 6. Proposed schemes for lumped-kinetic modeling of HCK reactions. Obtained from Refs. [75,77] with permission.

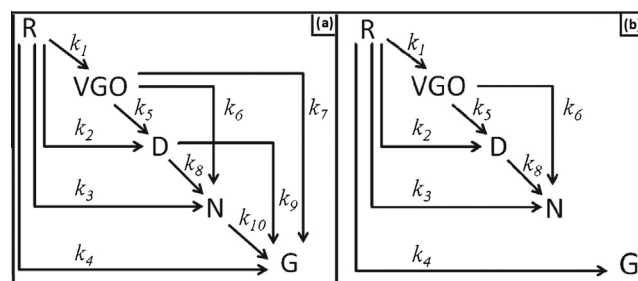


Fig. 7. Proposed kinetic models (a) hydroprocessing of bitumen in presence of UD catalysts. Obtained from Ref. [77] with permission; (b) Modified model for the UD catalyst. Obtained from Ref. [91] with permission.

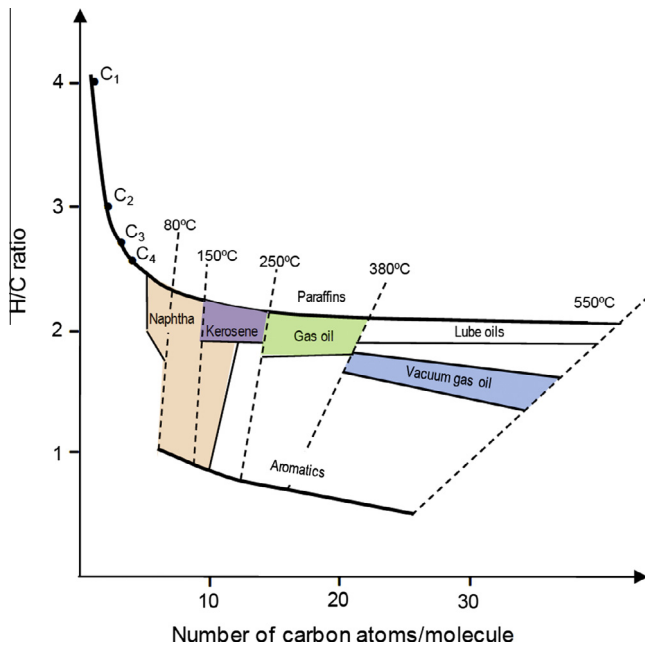


Fig. 8. Hydrogen to carbon ratio for the various petroleum cuts. Obtained from Ref. [98] with permission.

7. Recovery enhancement

Presence of nanoparticles inside the porous media enhanced the crude oil recovery by at least two main mechanisms. First, the production of lighter components via catalytic hydrocracking of heavy oil in presence of hydrogen and heat source [62,97–99], and second is wettability alteration of medium surface by coating with nanoparticles [100,101]. Hydrocracking of heavy oil and bitumen and the subsequent viscosity reduction in the oil pool as a result of bitumen contact with emitted hydrocarbon hot gases caused enhancement in heavy oil production [62]. Hashemi et al. [62] showed that there exists a recovery enhancement via injection of nanocatalysts inside the oil sand medium [62]. However, recovery process would be more efficient by coupling another thermal method (e.g., electrical heating or in-situ combustion) with the injection of nanocatalysts since the individual nanocatalysts recovery enhancement is not very significant. It is worth mentioning

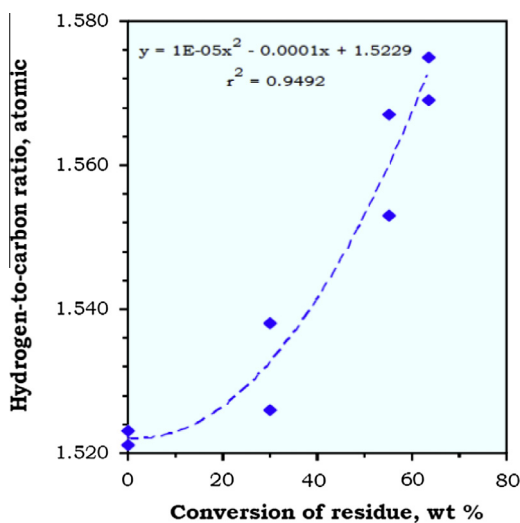


Fig. 9. Hydrogen-to-carbon ratio (H/C) of Athabasca bitumen at different conversion of residue for reaction performed at 380 °C. Obtained from Ref. [9] with permission.

here that by selecting higher quality catalyst carrier (e.g., crude oil with a high concentration of light ends) into the porous media higher recovery enhancement is expected. Wettability alteration of porous media by incorporating nanoparticles to enhance the oil production has been the focus of several experimental and theoretical studies [100–105]. In addition to small size, large surface area of nanoparticles can help to alter the properties of solid surface of porous media by in-situ coating process. Nanoparticles with tuned properties significantly alter the whole system wettability [106,107]. It should be noted that most of the reported works on this matter are experimental studies and no real field application has been reported. Further, one of the key challenges for the nanocatalysts usage in upgrading and recovery enhancement is the method of incorporating the nanocatalysts for hydrocracking processes. In heavy oil in-situ upgrading and SAGD recovery processes, there exist numerous factors that still have not been fully explored, such as impact of barriers and well testing methods. Hence, adding another upgrading and/or recovery mechanism coupled with the existing methods will add much higher complexity to the process of thermal recoveries. In the subsequent sections we are highlighting some of the potential opportunities and challenges on bitumen upgrading and recovery enhancement.

8. Quality enhancement

Evaluation of product quality is very important in any upgrading processes to determine the extent of increased value of heavy feedstocks. In addition to process cost-effectiveness, transportation pipe designs as well as processing facility specifications depend upon the quality of products [97]. Therefore, the quality of produced liquid streams generated from upgrading and recovery should be characterized on the basis of hydrogen to carbon ratio (H/C), API gravity, viscosity, micro carbon residue (MCR) content, sulfur and nitrogen content.

8.1. H/C atomic ratio

One of the main characteristic properties of heavy oil and bitumen is low value for H/C ratio. Fig. 8 shows H/C ratio for the various petroleum cuts [98]. Any enhancement to H/C ratio can be used as an indication for extent of heavy feedstock upgrading. Any thermal upgrading process involves simultaneous cracking and hydrogenation of heavy molecules to produce lighter components with smaller molecules as well as higher H/C ratios [99]. Galarraga and Pereira-Almao [9] successfully tested the catalytic hydroprocessing reactions of Athabasca bitumen in a batch mode.

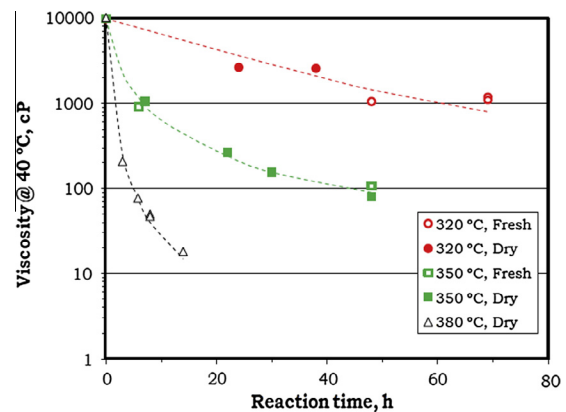


Fig. 10. Viscosity of liquid products from reaction at constant pressure of 3.45 MPa, temperatures of 320, 350 and 380 °C at reaction times from 3 up to 70 h. Obtained from Ref. [57] with permission.

The authors employed nanocatalysts suspension in-situ by using heavy oil emulsion and subsequently tested in a batch reactor using marginal levels of hydrogen and sand for bitumen upgrading.

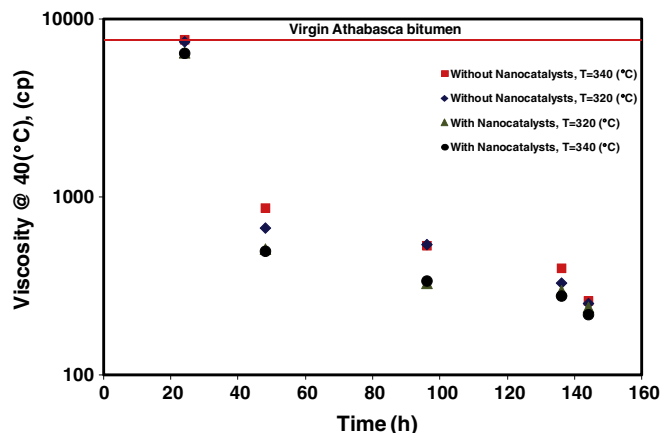


Fig. 11. Viscosity of produced liquid samples from oil sand porous media measured at 40 °C. Sample was produced at different times in the absence and presence of tri-metallic UD nanocatalysts at pressure of 3.5 MPa, hydrogen flow rate of 1 cm³/min, and temperatures of 320 and 340 °C. Obtained from Ref. [18] with permission.

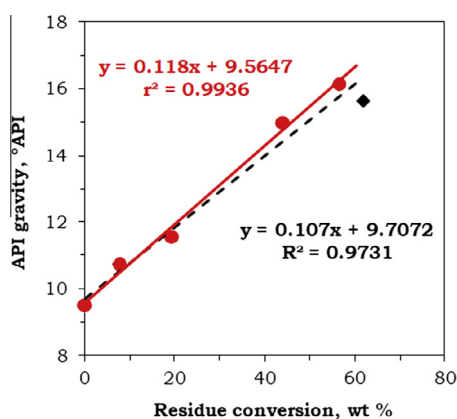


Fig. 12. API gravity of liquid products as a function of conversion for dry emulsion of UD nanocatalysts in batch reactor. Obtained from Ref. [57] with permission.

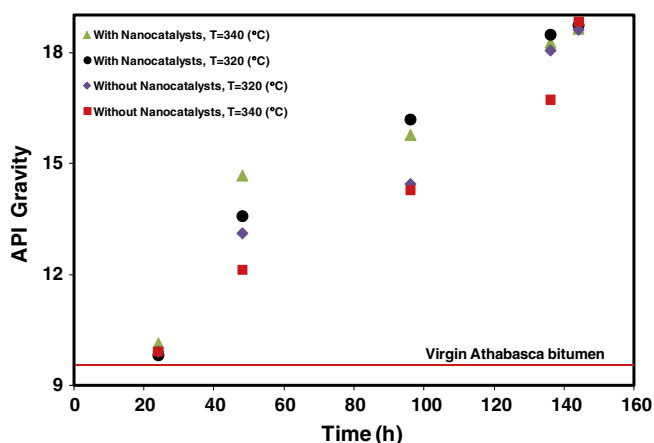


Fig. 13. API gravity of produced liquid samples from porous media at different times in the absence and presence of tri-metallic UD nanocatalysts at pressure of 3.5 MPa, hydrogen flow rate of 1 cm³/min, and temperatures of 320 and 340 °C. Obtained from Ref. [18] with permission.

Experimental results showed that nanocatalysts enhanced the upgrading of Athabasca bitumen by significantly increasing the H/C atomic ratio and reducing both viscosity and coke formation [9]. In addition, a significant reduction of sulfur and micro carbon residue was observed. Fig. 9 illustrates the H/C ratio enhancement for products obtained at 380 °C and 3.45 MPa as a function of residue conversion. It can be seen that there exists a polynomial trend for H/C ratio enhancement, which clearly provides enough evidence for effectiveness of nanocatalysts presence inside the porous media and effective incorporation of hydrogen within the liquid products. Based on produced results, nanocatalysts can enhance the H/C ratio via hydrocracking followed by hydrogenation process. In addition, higher H/C ratio occurs in higher conversion values.

8.2. Viscosity reduction and API increment

Reported results on nanocatalysts effectiveness for viscosity reduction showed successful records in batch and pilot tests [57,62]. Viscosity is considered as one of the most important factors for bitumen transportation via pipelines. For commercial transportation, bitumen API gravity is increased to a number of 19–21° API and viscosity of bitumen is decreased to approximately (250 cP at 10 °C) [108]. In the current context, most of mobility enhancement is performed on surface using surface upgrading facilities or appropriate diluent is used to meet refinery feedstock specifications [109]. UD nanocatalysts experiments using hydrogen performed in batch and packed bed reactors showed that in-situ upgrading and recovery processes can be implemented to enhance the quality of Athabasca bitumen that can meet pipeline transportation criteria without any diluent addition. Figs. 10 [57] and 11 [18] are examples of produced liquid viscosities from a batch reactor and packed bed reactor, respectively. As seen, presence of nanocatalysts inside the medium has dramatic effect on viscosity reduction of Athabasca bitumen.

Clearly, in both processes (i.e., batch and pilot tests), viscosity of products reduced against the time of the reaction. In addition, higher viscosity reduction occurred at higher temperatures. In both of the experimental series VGO was used as nanocatalysts carrier into the medium, and certainly by using lighter carrier, higher viscosity reduction can be observed since dilution was coupled with the thermal catalytic process during upgrading experiments. In addition to viscosity reduction, API gravity of products can be employed as a sign of quality enhancement.

As a result of heavy feedstocks upgrading, product density decreases and API gravity increases. Both experiments, batch and pilot plant, for Athabasca bitumen upgrading using UD nanocatalysts showed higher API gravity of the produced liquid. Fig. 12 shows the API gravity against conversion percentages in batch reactor [57]. It can be observed that API of 16 was achieved for higher conversion percentages. Furthermore, in pilot plant tests for different reaction times, API enhancement was measured in presence and absence of UD nanocatalysts and considerable improvement was detected for the experiment conducted in the presence of UD nanocatalysts [18]. Fig. 13 presents the API gravity measurements at different conditions. Clearly, nanocatalysts improved the API gravity significantly in both series of the tests, which again supports the potentials application of UD nanocatalysts for enhancing upgrading of heavy feedstocks.

8.3. Coke reduction

Micro carbon residue (MCR) contents of produced liquid samples were measured as another indication for quality enhancement by using a standard method [110]. MCR content measurement refers to amount of carbon residue which is left behind after the

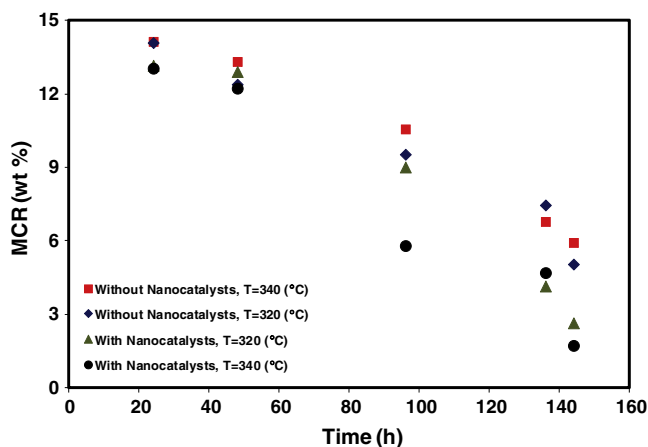


Fig. 14. MCR content of produced liquid samples from porous media as a function of reaction time in the absence and presence of tri-metallic UD nanocatalysts at pressure of 3.5 MPa, hydrogen flow rate of 1 cm³/min, and temperatures of 320 and 340 °C. Obtained from Ref. [18] with permission.

thermal treatment of the heavy feedstocks. High value of MCR content for a sample is interpreted as low quality product. Again, published results showed potential of UD nanocatalysts application for reducing the MCR content of heavy feedstocks [18,57]. In batch reactor test for Athabasca bitumen catalytic hydrocracking, MCR content was improved by including the UD nanocatalysts. Implementing the UD nanocatalysts changed the MCR from 16 wt% in the blank experiment up to about 11 wt% for selected experimental conditions [57]. For the continuous mode experiments, same observations were published regarding MCR reduction in produced samples [18]. Fig. 14 shows MCR reduction for the produced samples in presence and absence of UD nanocatalysts. It can be seen that, at higher temperature and in presence of nanocatalysts, lowest amount of MCR was measured which proves the effectiveness of nanocatalysts for hydrocracking reaction as well as quality enhancement confirming that UD nanocatalysts are improving the hydrogenation reactions and consequently reducing the potential for coke formation.

8.4. Sulfur removal

Environmental considerations enforce very stringent regulations on the sulfur content of fossil combustibles [111]. In hydro-treating processes, hydrodesulfurization is considered as one of the most important reactions which involves removing the sulfur from petroleum compounds to produce hydrogen sulfide as well as desulfurized compounds [99]. Generally, dispersed catalysts show higher percentages of sulfur removal compared with supported catalysts; owing to their effective accessibility [112–115].

Figs. 15 [57] and 16 [18] show the extent of sulfur removal for Athabasca bitumen in batch reactor and pilot plant tests at different temperatures, respectively. For batch reactor, at 380 °C up to 50% of sulfur content was removed at low reaction time (about 14 h).

In continuous mode experiments, the sulfur concentration decreased with both time and temperature (Fig. 16). It can be observed that presence of UD nanocatalysts enhanced the sulfur removal quite significantly, especially at lower temperature. This again confirms the effectiveness of UD nanocatalysts for enhancing the hydrodesulfurization reactions. However, sulfur removal is associated with hydrogen sulfide production, which can cause some negative aspects for the nanocatalysts implementation inside the porous media.

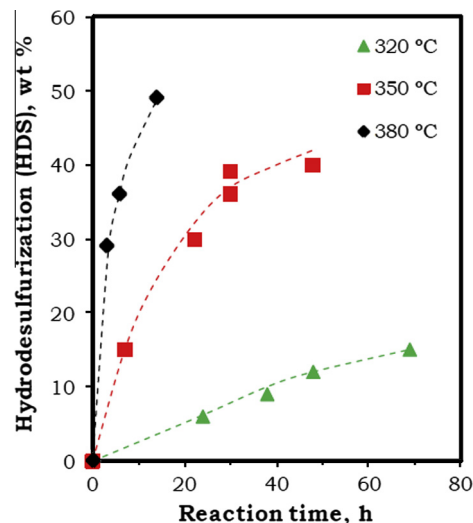


Fig. 15. Hydrodesulfurization of Athabasca bitumen as a function of reaction time evaluated at 3.45 MPa of hydrogen pressure and at temperatures of 320, 350, 380 °C using UD NiWMo nanocatalysts. Obtained from Ref. [57] with permission.

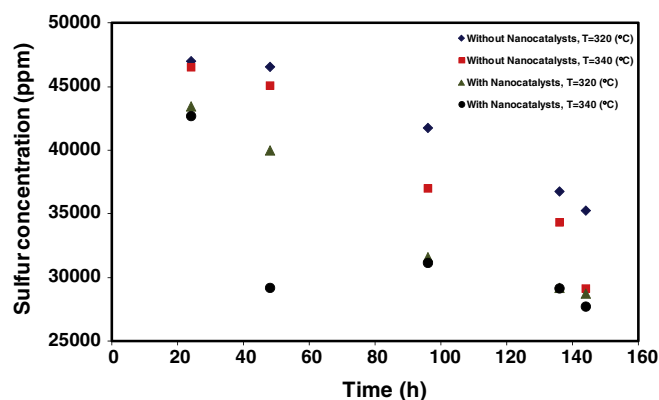


Fig. 16. Sulfur content of produced liquid samples from porous media at different times in the absence and presence of tri-metallic UD nanocatalysts at pressure of 3.5 MPa, hydrogen flow rate of 1 cm³/min, and temperatures of 320 and 340 °C. Obtained from Ref. [18] with permission.

8.5. Coke formation mitigation

During a typical thermal upgrading process, decomposition of heavy feedstocks is occurred in the presence of hydrogen to saturate the free radicals, and subsequently produce lighter components as well as huge amount of coke and considerable amount of light gas such as methane, ethane, and CO₂ [115,116]. It is expected that presence of catalysts inside the reaction medium would result in less amount of coke as catalysts can create new pathways in the reaction schemes [35].

Heavy oil and bitumen usually contain about 50 wt% of residue fraction with the normal boiling point higher than 545 °C [117]. For the purpose of heavy feedstocks upgrading, hydroprocessing catalysts should be resistant to deactivation caused by metal deposition and coke formation [118]. In this sense, there exists extensive research work to improve the catalysts activity by introducing UD nanocatalysts which navigate along with the heavy feedstocks as well as catalyzing the upgrading processes [119]. Furthermore, deactivation of UD nanocatalysts is less likely to occur than the conventional supported catalysts [120].

Published results on the nanocatalysts usage for Athabasca bitumen upgrading showed successful outcome, which again confirms the potential application of UD nanocatalysts for upgrading purposes. In batch reactor tests for Athabasca bitumen upgrading, coke formation was significantly reduced by using tri-metallic nanocatalysts emulsion with no detriment in residue conversion [57]. However, by increasing the severity of conditions coke formation increased dramatically.

For the continuous mode experiments, Fig. 17 depicts the coke contents (wt%) of produced samples against the reaction time at different temperatures in the presence and absence of UD tri-metallic nanocatalysts. Clearly, presence of nanocatalysts inside the porous medium significantly improved the quality of produced samples regarding coke content [17]. It is worth noting that temperature has a very drastic and sensitive effect on the coke formation during thermal processes [121]. Increasing the temperature speeds up the rate of thermal cracking reactions, which outperform the hydrogenating reactions that are thermodynamically hindered with temperature. Therefore, a higher proportion of free radicals will form and subsequently lead to the formation of a higher amount of coke [122].

It is beneficial to mention that Kennepohl and Sanford showed that the dispersed catalyst helped to reduce the coke formation much better than the supported catalyst during the upgrading of Athabasca bitumen at typical upgrading conditions. However, as dispersed concentration increases this benefit was reversed because the catalytic particles acted as coke seeds [115].

9. Gas emission reduction

There is no doubt that upgrading of heavy oil and bitumen with the current technologies produces considerable amounts of greenhouse gas (GHG) emissions. Due to this reason, the province of Alberta was the first in North America to legislate the GHG emission reduction for large industrial facilities [123]. Furthermore, increasingly stringent legislation limits on the level of fuel contaminants has enforced the industry to invest on the exploration of cost-effective and environmentally acceptable new technologies, integration with or enhancing the currently available technologies for heavy feedstocks processing [124].

One possible promising new technology is the in-situ upgrading, aims to improve the quality of crude oil and decrease the level of its contaminants, such as sulfur and nitrogen to a good extent [125] as well as the GHG emissions. However, not much is known about the produced gases emitted during the in-situ upgrading

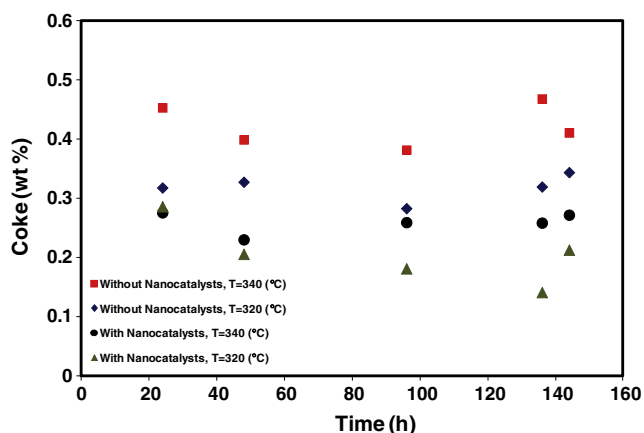


Fig. 17. Coke content of produced samples from porous media as a function of reaction time in the absence and presence of tri-metallic UD nanocatalysts at pressure of 3.5 MPa, hydrogen flow rate of 1 cm³/min, and temperatures of 320 and 340 °C [17] with permission.

process by using nanocatalysts. In a recent study, Hashemi et al. [17] investigated the effectiveness of nanocatalysts on gaseous emission reductions [17]. Results showed that the presence of tri-metallic nanocatalysts enhanced the hydrogenation reactions and consequently led to significant reduction in CO₂ emission. In the best case, at a high pressure and temperature conditions, CO₂ emission was reduced up to 50% compared with the case without the presence of nanocatalysts in the medium. Furthermore, UD nanocatalysts enhanced the production of hydrocarbon gases as results of hydrocracking that, consequently, works as diffusing solvent for enhancing heavy oil production. It is worth noting that gas emissions would remain as one of the most important challenges of the nanocatalysts upgrading process. Therefore, more laboratory investigations and pilot scale testing will be needed to investigate this issue with more details.

10. Nanocatalysts recycling

Presence of nanocatalysts inside the medium along with hydrogen incorporation aims to improve the quality of produced liquid via catalytic hydrocracking. As previously mentioned, fast deactivation of conventional supported catalysts is one of the major disadvantages compared to UD nanocatalysts. Presence of large molecules in the heavy feedstock has limited accessibility into the porous network of the conventional catalysts. This is the reason that hydroprocessing catalysts should be resistant to deactivation caused by metal deposition and coke formation [118]. UD nanocatalysts could provide desirable level of reaction activity as well as option to perform in the well level [126]. A key bottleneck to the in-situ applications will be the recyclability of the spent nanocatalysts that can provide cost-effectiveness for the process as well as reduction in the environmental footprints. Our research group developed a promising alternative for downhole upgrading process. Fig. 18 shows a schematic representation of this process. As seen, nanocatalysts are injected through injector well inside the porous media and upgraded oil is produced via recovery well. Produced liquid from the reservoir contains some active nanocatalysts inside the non-distillable residue which can be recycled and re-injected to the porous reservoir [127].

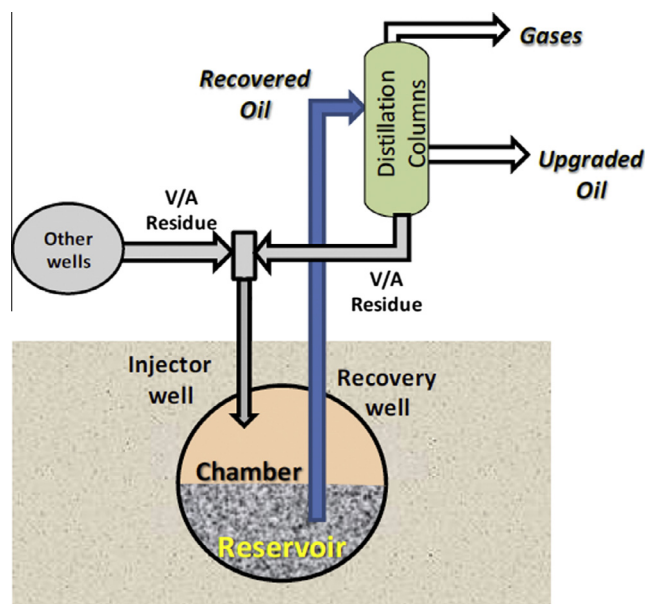


Fig. 18. Schematic representation of in-situ upgrading (ISU) process for non-conventional oil in the presence of UD catalysts. Obtained from Ref. [127] with permission.

It is absolutely crucial to understand the nanocatalysts behavior in many aspects such as the stability and the potential recycling methods of these particles. It will be in favor of the process economics if the UD nanocatalysts could be used several times before losing stability and catalytic activity. Reviewing the literatures showed that lack of extensive study in this area is quite tangible. As one important piece of work, Peluso [127] showed that it is feasible to recycle the UD nanocatalysts particles. However, there is the possibility of particle agglomeration, which is a slow and reversible process. To have a clear understanding of recycling potential and challenges, more laboratory investigations and pilot scale testing will be needed to implement this economically beneficial technique into the existing heavy oil industry.

11. Hydrogen consumption

In a typical hydroconversion process, heavy molecules of petroleum feedstocks with the high boiling point are split and saturated with hydrogen, forming lighter components with lower boiling point as well as less impurities [128]. High investment is required to conduct these types of processes since hydrogen consumption is an important issue. Presence of hydrogen promotes bond cleavage reactions which results in mitigating the coke formation as well as removing heteroatoms by controlling the polymerization process [128,129].

For a surface upgrading process at severe conditions (350–430 °C and 8.5–20 MPa), the required hydrogen is typically in the range of 200–590 nm³/m³ which is related to the H₂ to oil ratio of 505 and 1685 nm³/m³ [75]. It should be noted that current in-situ thermal recovery techniques rely mostly on natural-gas-fired steam boilers for steam generation. These processes require a large amount of hydrogen for bitumen upgrading. It is estimated that required hydrogen consumption for Canadian energy industry would exceed about 2.3 million tonnes by 2020 with the currently increasing bitumen production [130].

In a same sense for UD nanocatalysts application subsurface, hydrogen is required to interact with the heavy feedstocks in presence of nanocatalysts to improve the quality of reactions. As an initial guess, the required amount of hydrogen could be estimated on the basis of its solubility in crude oil. However, to perform the upgrading processes, much higher amount of hydrogen is needed. Further, as the reaction severity increased the hydrogen consumption would increase. It should be noted that the extent of hydrogen usage during the reactions depends on the quality of upgrading processes. Finally, we would like to point out that working with hydrogen at high pressure and temperature conditions also exhibit a high risk of safety issues. Therefore, a key challenge will be to maintain and enforce a high level of safety consideration upon the conduction of in-situ hydrocracking process.

It is very important to mention that processes related to the hydrogen usage are very sensitive in the industry due to hazards related to this gas. In addition, to conduct a field scale application, it is crucial to provide required sources of hydrogen for the subsurface upgrading processes. Furthermore, there are some challenges in the operational side such as method of introducing hydrogen to the porous media. For in-situ upgrading in the SAGD operations, one possible approach is to inject hydrogen from the injectors. Finally, in the presence of high temperature and pressure as well as the catalyst, risk of coking and plugging of porous media and consequently reduction of permeability should be considered as one of the possible risk of in-situ upgrading reactions.

12. Inhibition of formation damage

An important challenge during crude oil production and transportation is deposition of unstable polar heavy hydrocarbons like asphaltenes inside the medium [131,132]. This challenge is more

significant in heavy oil and bitumen since there exist higher percentages of heavy molecules in their chemical structure. One of the nanomaterial's applications that have been studied by researchers is inhibition of asphaltene deposition to avoid formation damage within the porous media [133–136]. Precipitation of asphaltene via mechanical or chemical processes in oil reservoirs can reduce the producing phase effective permeability and consequently decrease the productivity index [133,136]. Therefore, removing the unstable polar heavy hydrocarbons or finding an inhibitor to prevent or delay their precipitation is of paramount importance. Nanoparticles prevent asphaltene deposition by avoiding flocculation and precipitation simultaneously due to stabilization the asphaltenes content within the oil medium [133]. For subsurface application, for the purpose of recovery enhancement, in-situ adsorption of asphaltenes within the well by nanoparticles have been demonstrated as a way to upgrade oils to enhance liquid yields while reducing clogging of rock pores, viscosity, and well damage [133]. Nanoparticles can adsorb the asphaltenes from crude oil and subsequently get adsorb onto porous media surfaces, hence, delaying the asphaltenes precipitation behavior with changes in pressure, temperature, and composition and altering the surface wettability according to the wetting preference of the nanoparticles [133]. The ability of these nanoparticles to disperse and stabilize asphaltene aggregates through adsorption coupled with their small size has given rise to the concept of using them to prevent well damage. Nanoparticles can adsorb asphaltenes quickly, which prevents asphaltene deposition by avoiding flocculation and precipitation simultaneously due to stabilization the asphaltenes content within the oil medium, and lead to better recovery. The typical pore diameters in normal oil reservoirs are generally in the order of micrometers; hence, nanoparticles can flow through porous media without any pore plugging problems. Owing to their low size and consequent large surface, high proportion of atoms on the surface of the nanoparticle is expected to appear. This results in an increase in surface energy of nanoparticles and, hence, the adsorption of active and energetic unstable polar heavy hydrocarbons on a their surface can significantly alter the surface energy and wettability of the system. Accordingly, by tuning and manipulating nanoparticle surface properties, it is possible to design nanofluids or “smart fluids” that are typically synthesized by adding small volumetric fractions of nanoparticles to a liquid phase to enhance or improve some of the fluid properties [102]. Furthermore, most of metal oxide nanoparticles are of hydrophilic nature and, hence, their adsorption onto a surface can change the wettability toward water wetting [100]. It should be noted here that most of the reported works on this matter are limited to laboratory investigations and pilot scale testing. Nevertheless, a recent real practical oilfield test utilizing alumina-based nanofluids as wettability modifiers for altering the wettability of oil reservoir and inhibit asphaltene deposition was demonstrated by Zabala et al. [135], who proven that alumina-based nanofluids could be employed successfully for enhancing oil recovery and preventing formation damage. The authors conducted their field test on the use of nanofluid for asphaltene inhibition in the volatile Cupiagua Sur oil field in Colombia. They reported 14,900 barrels of additional cumulative production after 213 days of application. The authors concluded that well stabilized alumina-based nanofluids have good performance into the reservoir even at very low permeability conditions and it portray good retention in the formation for longer than six months.

13. Environmental effect of nanoparticles

Nanotechnology is the science and technology of controlling matters at nanoscale [137], promising to enhance the economics

in areas ranging from transportation to agriculture to health [138]. Over the last decade many nanomaterials have moved into the marketplace [139] with the direct and indirect application in the society. However, there are only minimal data on the nanomaterials exposure effect on the human health and environment. Moreover, results of the primitive studies showed some concerns about the effect of these nanomaterials [140].

From the environmental perspective, associated benefits of nanoparticles are combined with the potential challenges that may be difficult to predict. In addition, there exists a little information about the manufacturing, usage and disposal of the nanomaterials and any associated risks from the exposure of nanomaterials [141]. Furthermore, detection methods, measurement, analyzing and tracing the nanomaterials are in the process of development [142].

The process of heavy oil upgrading and recovery using nanoparticles as adsorbent/catalysts is quite new and challenging chemical process, and it is likewise the other area of nanotechnologies with the opportunities and challenges. To the best of our knowledge, some of the challenges have been presented in this study. However, there exist many challenges that should be scrutinized to cover the all aspect of the nanoparticles application. As an example, percentages of injected nanoparticles into the formation are deposited inside the medium [67] and will remain in-situ for many years which no study was performed on the long term environmental effect of these nanocatalysts. In the other side, some portion of the injected nanoparticles is produced by the upgraded or recovered oil, which all aspects of nanomaterial usage should be fully evaluated by experimental and modeling analysis. Furthermore, in the operational side, the possibility of groundwater contamination by the synthesized nanocatalysts should be considered as an operational failure risk. Produced sustainable nanocatalysts aim to show higher activity, higher selectivity, efficient recovery as well as durability and recyclability in a cost-effective process. Currently, our group is working on developing and implementing naturally occurring nanoparticles, which could have much less environmental impact compared to the synthesized or commercially available nanoparticles.

14. Conclusions

Owing to their unique properties, which are different from their bulk counterparts, nanoparticles have considerable potential applications as adsorbent and catalysts for enhancing heavy oil upgrading and recovery. However, employment of nanoparticle technology in oil industry is facing a number of limitation and challenges. This study sheds some lights on the potential application and challenges for implementing nanoparticle technology in heavy oil upgrading and recovery.

Synthesis of nanoparticles could be performed via various techniques. However, mass production of required nanoparticles and availability of surface facilities, stability of produced volume and control over the size of the particles are some of the important issues that should be addressed in any industrial applications. In addition, cost is very important parameter in any projects since it is essential to acquire hi-tech control systems to avoid or mitigate any associated risks due to the nature of high pressure and temperature reaction conditions.

For in-situ application and since the reaction media is porous, transport behavior of nanoparticles inside the porous media, deposition tendency on the surface and consequent permeability damage as well as pressure drop across the medium are quite important factors. Along with experimental studies, mathematical modeling of nanoparticles penetration as well as reaction kinetics of in-situ heavy oil inside the target mediums in reaction conditions

provides useful information. So far the results are very promising and there is still very long way to understand all aspects of nanoparticle behavior inside the porous media.

Presence of nanoparticles inside the porous media and providing appropriate reaction conditions with required elements including hydrogen would result recovery improvement as well as considerable quality enhancement in all 3-phases of liquid, gas and solid. Enhancement of viscosity, API gravity, carbon residue (MCR) content, sulfur and nitrogen content in liquid phase were significant. Higher quality of produced gases in terms of hydrocarbon gases as well as less carbon dioxide emission in gas phase and less amount of coke content in solid phase show very promising future for the nanoparticles in-situ implementation. Furthermore, nanoparticle based fluid could be employed successfully for changing reservoir wettability from an oil-wet to a water-wet condition. Injection of nanofluids into porous media caused an inhibition in the agglomeration, precipitation, and deposition of asphaltenes on the rock surfaces and hence led to improvements in oil recovery. However, environmental challenges should be scrutinized in a very good depth to mitigate any associated risks regarding the mass usage of nanoparticles. In this regards, recovery and re-using the nanoparticles could be very beneficial in terms of process economics as well as reduction of environmental footprints.

Acknowledgments

The authors acknowledge the Department of Chemical and Petroleum Engineering at the University of Calgary and the Alberta Ingenuity Centre for In Situ Energy, AICISE, for generously funding the project.

References

- [1] Gill SS, Tsolakis A, Dearn KD, Rodríguez-Fernández J. Combustion characteristics and emissions of Fischer–Tropsch diesel fuels in IC engines. *Prog Energy Combust Sci* 2011;37:503–23.
- [2] Perman R. *Natural resources and environmental economics*. Pearson Education; 2003.
- [3] Agarwal AK. Biofuels (alcohols and biodiesel) applications as fuels for internal combustion engines. *Prog Energy Combust Sci* 2007;33:233–71.
- [4] Berkowitz N, Speight JG. The oil sands of Alberta. *Fuel* 1975;54:138–49.
- [5] Kobayashi K. Forecasting supply and demand up to 2030. In: *The international energy agency*; 2005.
- [6] Pereira P, Romero T, Velasquez J, Tusa A, Rojas I, Camejo W, et al. Combined steam conversion process for treating vacuum gas oil; 2000.
- [7] Pereira P, Marzin R, Zacarias L, Cordova J, Carrazza J, Marino M. Steam conversion process and catalyst. United State Patent; 1999.
- [8] Carrazza J, Pereira P, Martinez N. Process and catalyst for upgrading heavy hydrocarbon. United State Patent; 1997.
- [9] Galarraga CE, Pereira-Almao P. Hydrocracking of Athabasca bitumen using submicronic multimetallic catalysts at near in-reservoir conditions. *Energy Fuels* 2010;24:2383–9.
- [10] Sosa-Stull C, Trujillo-Ferrer G, Lopez-Linares F, Pereira-Almao P. Athabasca bitumen upgrading using different species of the same ultra dispersed catalyst formulation. San Francisco, California, USA: American Chemical Society; 2010.
- [11] Pereira-Almao P. In situ upgrading of bitumen and heavy oils via nanocatalysis. *Can J Chem Eng* 2012;90:320–9.
- [12] Foster LE. *Nanotechnology: science, innovation, and opportunity*. Prentice Hall PTR; 2005.
- [13] Xiangling K, Ohadi M. Applications of micro and nano technologies in the oil and gas industry—overview of the recent progress. In: *Abu Dhabi international petroleum exhibition and conference*; 2010.
- [14] Bell AT. The impact of nanoscience on heterogeneous catalysis. *Science* 2003;299:1688–91.
- [15] Perez JM. Iron oxide nanoparticles: hidden talent. *Nat Nanotechnol* 2007;2:535–6.
- [16] Zarkesh J, Hashemi R, Ghaedian M, Khakhdaman HR, Ahmadpanah SJ, Khadzhiev S, et al. HRH: nano catalytic process to upgrade extra heavy crude/residual oils. In: *19th world petroleum congress*; 2008.
- [17] Hashemi R, Nassar NN, Pereira Almao P. In situ upgrading of athabasca bitumen using multimetallic ultradispersed nanocatalysts in an oil sands packed-bed column: Part 2. Solid analysis and gaseous product distribution. *Energy Fuels* 2014;28:1351–61.
- [18] Hashemi R, Nassar NN, Pereira Almao P. In situ upgrading of athabasca bitumen using multimetallic ultradispersed nanocatalysts in an oil sands

- packed-bed column: Part 1. Produced liquid quality enhancement. *Energy Fuels* 2014;28:1338–50.
- [19] Alatrakchi FA, Zhang Y, Angelidaki I. Nanomodification of the electrodes in microbial fuel cell: impact of nanoparticle density on electricity production and microbial community. *Appl Energy* 2014;116:216–22.
- [20] Zhu B, Fan L, Lund P. Breakthrough fuel cell technology using ceria-based multi-functional nanocomposites. *Appl Energy* 2013;106:163–75.
- [21] Winey KI, Vaia RA. Polymer nanocomposites. *MRS Bull* 2007;32:314–22.
- [22] Roy M, Nelson J, MacCrone R, Schadler L, Reed C, Keefe R. Polymer nanocomposite dielectrics the role of the interface. *IEEE Trans Dielect Electr Insul* 2005;12:629–43.
- [23] Tanaka T, Kozako M, Fuse N, Ohki Y. Proposal of a multi-core model for polymer nanocomposite dielectrics. *IEEE Trans Dielect Electr Insul* 2005;12:669–81.
- [24] Thomas JM, Johnson BF, Raja R, Sankar G, Midgley PA. High-performance nanocatalysts for single-step hydrogenations. *Acc Chem Res* 2003;36:20–30.
- [25] Joo SH, Park JY, Tsung C-K, Yamada Y, Yang P, Somorjai GA. Thermally stable Pt/mesoporous silica core-shell nanocatalysts for high-temperature reactions. *Nat Mater* 2008;8:126–31.
- [26] Jaramillo TF, Jørgensen KP, Bonde J, Nielsen JH, Hørch S, Chorkendorff I. Identification of active edge sites for electrochemical H₂ evolution from MoS₂ nanocatalysts. *Science* 2007;317:100–2.
- [27] Han F, Kambala VSR, Srinivasan M, Rajarathnam D, Naidu R. Tailored titanium dioxide photocatalysts for the degradation of organic dyes in wastewater treatment: a review. *Appl Catal A* 2009;359:25–40.
- [28] Hildebrand H, Mackenzie K, Kopinke F-D. Pd/Fe₃O₄ nano-catalysts for selective dehalogenation in wastewater treatment processes—influence of water constituents. *Appl Catal B* 2009;91:389–96.
- [29] Kaegi R, Voegelin A, Sinnet B, Zuleeg S, Hagendorfer H, Burkhardt M, et al. Behavior of metallic silver nanoparticles in a pilot wastewater treatment plant. *Environ Sci Technol* 2011;45:3902–8.
- [30] Krishnamoorti R. Extracting the benefits of nanotechnology for the oil industry. *J Petrol Technol* 2006;58.
- [31] Nassar NN, Husein MM, Pereira-Almao P. In-situ prepared nanoparticles in support of oil sands industry meeting future environmental challenges. *Expl Prod: Oil Gas Rev* 2011;9:46–8.
- [32] Weissman JG, Kessler RV. Downhole heavy crude oil hydroprocessing. *Appl Catal A* 1996;140:1–16.
- [33] Bartholomew CH. Mechanisms of catalyst deactivation. *Appl Catal A* 2001;212:17–60.
- [34] Thompson J, Vasquez A, Hill JM, Pereira-Almao P. The synthesis and evaluation of up-scalable molybdenum based ultra dispersed catalysts: effect of temperature on particle size. *Catal Lett* 2008;123:16–23.
- [35] Newson E. Catalyst deactivation due to pore-plugging by reaction products. *Ind Eng Chem Proc Des Dev* 1975;14:27–33.
- [36] Lemaitre J, Menon PG, Delannay F. The measurement of catalyst dispersion. In: *Characterization of heterogeneous catalysts*. New York: Marcel Dekker; 1984. p. 325–7.
- [37] Okamoto Y, Odawara M, Onimatsu H, Imanaka T. Preparation and catalytic properties of highly dispersed molybdenum and cobalt-molybdenum sulfide catalysts supported on alumina. *Ind Eng Chem Res* 1995;34:3703–12.
- [38] Velu S, Gangwal SK. Synthesis of alumina supported nickel nanoparticle catalysts and evaluation of nickel metal dispersions by temperature programmed desorption. *Solid State Ionics* 2006;177:803–11.
- [39] Yoosuk B, Kim JH, Song C, Ngamcharussrivichai C, Prasassarakich P. Highly active MoS₂, CoMoS₂ and NiMoS₂ unsupported catalysts prepared by hydrothermal synthesis for hydrosulfurization of 4,6-dimethylbenzothiophene. *Catal Today* 2008;130:14–23.
- [40] Wang D, Xie T, Li Y. Nanocrystals: solution-based synthesis and applications as nanocatalysts. *Nano Res* 2009;2:30–46.
- [41] Khoudiakov M, Gupta MC, Deevi S. Au/Fe₂O₃ nanocatalysts for CO oxidation: a comparative study of deposition-precipitation and coprecipitation techniques. *Appl Catal A* 2005;291:151–61.
- [42] Somorjai GA, Tao F, Park JY. The nanoscience revolution: merging of colloid science, catalysis and nanoelectronics. *Top Catal* 2008;47:1–14.
- [43] Husein MM, Nassar NN. Nanoparticle preparation using the single microemulsions scheme. *Current Nanosci* 2008;4:370–80.
- [44] Jung HM, Price KE, McQuade DT. Synthesis and characterization of cross-linked reverse micelles. *J Am Chem Soc* 2003;125:5351–5.
- [45] Husein MM, Nassar NN. Nanoparticle uptake by (w/o) microemulsions. In: *Fanun M, editor. Microemulsions: properties and applications*. Boca Raton, FL, USA: CRC Press, Taylor & Francis Group LLC; 2009. p. 465–79.
- [46] Nassar NN, Husein MM. Study and modeling of iron hydroxide nanoparticle uptake by AOT (w/o) microemulsions. *Langmuir* 2007;23:13093–103.
- [47] Nassar NN. Iron oxide nano-adsorbents for removal of various pollutants from wastewater: an overview. In: *Bhatnagar A, editor. Application of adsorbents for water pollution control*. Bentham Science Publishers; 2012. p. 81–118.
- [48] Niemeyer CM. Nanoparticles, proteins, and nucleic acids: biotechnology meets materials science. *Angew Chem Int Ed* 2001;40:4128–58.
- [49] Gobe M, Kon-No K, Kandori K, Kitahara A. Preparation and characterization of monodisperse magnetite sols in WO microemulsion. *J Colloid Interface Sci* 1983;93:293–5.
- [50] Bock C, Paquet C, Couillard M, Botton GA, MacDougall BR. Size-selected synthesis of PtRu nano-catalysts: reaction and size control mechanism. *J Am Chem Soc* 2004;126:8028–37.
- [51] Murray C, Norris D, Bawendi MG. Synthesis and characterization of nearly monodisperse CdE (E = sulfur, selenium, tellurium) semiconductor nanocrystallites. *J Am Chem Soc* 1993;115:8706–15.
- [52] Alivisatos AP, Johnsson KP, Peng X, Wilson TE, Loweth CJ, Bruchez MP, et al. Organization of nanocrystal molecules' using DNA; 1996.
- [53] Shen S, Hidajat K, Yu LE, Kawi S. Simple hydrothermal synthesis of nanostructured and nanorod Zn–Al complex oxides as novel nanocatalysts. *Adv Mater* 2004;16:541–5.
- [54] Yao Y-I, Ding Y, Ye L-s, Xia X-H. Two-step pyrolysis process to synthesize highly dispersed Pt–Ru/carbon nanotube catalysts for methanol electrooxidation. *Carbon* 2006;44:61–6.
- [55] Pluym T, Powell Q, Gurav A, Ward T, Kodas T, Wang L, et al. Solid silver particle production by spray pyrolysis. *J Aerosol Sci* 1993;24:383–92.
- [56] Hellweg T. Phase structures of microemulsions. *Curr Opin Colloid Interface Sci* 2002;7:50–6.
- [57] Galarraga CE. Upgrading Athabasca bitumen using submicronic NiWMo catalysts at conditions near to in-reservoir operation. Calgary: University of Calgary; 2011.
- [58] Capek I. Preparation of metal nanoparticles in water-in-oil (w/o) microemulsions. *Adv Colloid Interface Sci* 2004;110:49–74.
- [59] Pereira P, Marzin R, Zacarias L, Cordova J, Carrazza J, Marino M. Steam conversion process and catalyst. *Google Patents*; 1999.
- [60] Vasquez A. Synthesis, characterization and model reactivity of ultra dispersed catalysts for hydroprocessing. University of Calgary; 2009.
- [61] Lapeira CC. Development of a new methodology for preparing nanometric Ni, Mo and NiMo catalytic particles using transient emulsions. Calgary: University of Calgary; 2009.
- [62] Molina HJL. Transport of catalytic particles immersed in fluid media through cylindrical geometries under heavy oil upgrading conditions. Calgary: University of Calgary; 2009.
- [63] Hashemi R, Nassar NN, Pereira-Almao P, Pereira-Almao P. Enhanced heavy oil recovery by in situ prepared ultradispersed multimetallic nanoparticles: a study of hot fluid flooding for athabasca bitumen recovery. *Energy Fuels* 2013;27:2194–201.
- [64] Galarraga CE, Scott C, Loria H, Pereira-Almao P. Kinetic models for upgrading athabasca bitumen using unsupported NiWMo catalysts at low severity conditions. *Ind Eng Chem Res* 2011;51:140–6.
- [65] Cassiolato JE, Schmitz H. Hi-tech for industrial development: lessons from the Brazilian experience in electronics and automation. Psychology Press; 2002.
- [66] Zamani A, Maini B. Flow of dispersed particles through porous media—deep bed filtration. *J Petrol Sci Eng* 2009;69:71–88.
- [67] Hashemi R, Nassar NN, Pereira-Almao P. Transport behavior of multimetallic ultradispersed nanoparticles in an oil-sands-packed bed column at a high temperature and pressure. *Energy Fuels* 2012;26:1645–55.
- [68] Zamani A, Maini B, Pereira-Almao P. Experimental study on transport of ultra-dispersed catalyst particles in porous media. *Energy Fuels* 2010;24:4980–8.
- [69] Adamczyk Z, Van de Ven T. Deposition of particles under external forces in laminar flow through parallel-plate and cylindrical channels. *J Colloid Interface Sci* 1981;80:340–56.
- [70] Brady JF. The long-time self-diffusivity in concentrated colloidal dispersions. *J Fluid Mech* 1994;272:109–34.
- [71] Sarimeseli A, Kelbaliyev G. Modeling of the break-up of deformable particles in developed turbulent flow. *Chem Eng Sci* 2004;59:1233–40.
- [72] Yoshioka N, Karaoka C, Emi H. On the deposition of aerosol particles to the horizontal pipe wall from turbulent stream. *Kagaku Kagaku* 1972;36:1010–6.
- [73] Alhumaizi K, Akhmedov V, Al-Zahrani S, Al-Khowaiter S. Low temperature hydrocracking of *n*-heptane over Ni-supported catalysts: study of global kinetics. *Appl Catal A* 2001;219:131–40.
- [74] Krishna R, Saxena AK. Use of an axial-dispersion model for kinetic description of hydrocracking. *Chem Eng Sci* 1989;44:703–12.
- [75] Scherzer J, Gruia AJ. Hydrocracking science and technology. CRC Press; 1996.
- [76] Ancheyta J, Sánchez S, Rodríguez MA. Kinetic modeling of hydrocracking of heavy oil fractions: a review. *Catal Today* 2005;109:76–92.
- [77] Sánchez S, Rodríguez MA, Ancheyta J. Kinetic model for moderate hydrocracking of heavy oils. *Ind Eng Chem Res* 2005;44:9409–13.
- [78] Ayasse AR, Nagaiishi H, Chan EW, Gray MR. Lumped kinetics of hydrocracking of bitumen. *Fuel* 1997;76:1025–33.
- [79] Aoyagi K, McCaffrey WC, Gray MR. Kinetics of hydrocracking and hydrotreating of coker and oil sands gas oils. *Pet Sci Technol* 2003;21:997–1015.
- [80] Singh J, Kumar M, Saxena AK, Kumar S. Reaction pathways and product yields in mild thermal cracking of vacuum residues: a multi-lump kinetic model. *Chem Eng J* 2005;108:239–48.
- [81] Gray MR. Lumped kinetics of structural groups: hydrotreating of heavy distillate. *Ind Eng Chem Res* 1990;29:505–12.
- [82] Martens G, Marin G. Kinetics for hydrocracking based on structural classes: model development and application. *AIChE J* 2001;47:1607–22.
- [83] Köseoglu RÖ, Phillips CR. Kinetics of non-catalytic hydrocracking of Athabasca bitumen. *Fuel* 1987;66:741–8.
- [84] Köseoglu RÖ, Phillips CR. Kinetic models for the non-catalytic hydrocracking of Athabasca bitumen. *Fuel* 1988;67:906–15.
- [85] Köseoglu RÖ, Phillips CR. Effect of reaction variables on the catalytic hydrocracking of Athabasca bitumen. *Fuel* 1988;67:1201–4.
- [86] Köseoglu RÖ, Phillips CR. Kinetics and product yield distributions in the CoO-MoO₃Al₂O₃ catalysed hydrocracking of Athabasca bitumen. *Fuel* 1988;67:1411–6.

- [87] Phillips CR, Hsieh I-C. Oxidation reaction kinetics of Athabasca bitumen. *Fuel* 1985;64:985–9.
- [88] Phillips CR, Haidar NI, Poon YC. Kinetic models for the thermal cracking of athabasca bitumen: the effect of the sand matrix. *Fuel* 1985;64:678–91.
- [89] Gray MR, Ayasse AR, Chan EW, Veljkovic M. Kinetics of hydrodesulfurization of thiophenic and sulfide sulfur in Athabasca bitumen. *Energy Fuels* 1995;9:500–6.
- [90] Owusu-Boakye A, Dalai AK, Ferdous D, Adjaye J. Experimental and kinetic studies of aromatic hydrogenation, hydrodesulfurization, and hydrodenitrogenation of light gas oils derived from athabasca bitumen. *Ind Eng Chem Res* 2005;44:7935–44.
- [91] Loria H, Trujillo-Ferrer G, Sosa-Stull C, Pereira-Almao P. Kinetic modeling of bitumen hydroprocessing at in-reservoir conditions employing ultradispersed catalysts. *Energy Fuels* 2011;25:1364–72.
- [92] Nassar NN, Hassan A, Luna G, Pereira-Almao P. Kinetics of the catalytic thermo-oxidation of asphaltenes at isothermal conditions on different metal oxide nanoparticle surfaces. *Catal Today* 2013;207:127–32.
- [93] Nassar NN, Hassan A, Pereira-Almao P. Application of nanotechnology for heavy oil upgrading: catalytic steam gasification/cracking of asphaltenes. *Energy Fuels* 2011;25:1566–70.
- [94] Nassar N, Hassan A, Pereira-Almao P. Thermogravimetric studies on catalytic effect of metal oxide nanoparticles on asphaltene pyrolysis under inert conditions. *J Therm Anal Calorim* 2012;110:1327–32.
- [95] Nassar N, Hassan A, Luna G, Pereira-Almao P. Comparative study on thermal cracking of Athabasca bitumen. *J Therm Anal Calorim* 2013;114:465–72.
- [96] Nashaat NN, Hassan A, Vitale G. Comparing kinetics and mechanism of adsorption and thermo-oxidative decomposition of Athabasca asphaltenes onto TiO₂, ZrO₂, and CeO₂ nanoparticles. *Applied Catalysis A: General* 2014;484:161–71.
- [97] Martínez-Palou R, Mosqueira MdL, Zapata-Rendón B, Mar-Juárez E, Bernal-Huicochea C, de la Cruz Clavel-López J, et al. Transportation of heavy and extra-heavy crude oil by pipeline: a review. *J Petrol Sci Eng* 2011;75:274–82.
- [98] Billon A, Bigeard P. Hydrocracking. *Petrol Refining, Convers Processes*. 2001;3:331–64 [Chapter 10].
- [99] Gates BC, Katzer JR, Schuit GCA. *Chemistry of catalytic processes*. New York: McGraw-Hill; 1979.
- [100] Karimi A, Fakhrouieian Z, Bahramian A, Pour Khiabani N, Darabad JB, Azin R, et al. Wettability alteration in carbonates using zirconium oxide nanofluids: EOR implications. *Energy Fuel* 2012;26:1028–36.
- [101] Maghzi A, Mohammadi S, Ghazanfari MH, Kharrat R, Masihi M. Monitoring wettability alteration by silica nanoparticles during water flooding to heavy oils in five-spot systems: a pore-level investigation. *Exp Therm Fluid Sci* 2012;40:168–76.
- [102] Giraldo J, Benjumea P, Lopera S, Cortés FB, Ruiz MA. Wettability alteration of sandstone cores by alumina-based nanofluids. *Energy Fuels* 2013;27:3659–65.
- [103] Onyekonwu MO, Ogolo NA. Investigating the use of nanoparticles in enhancing oil recovery. In: Nigeria annual international conference and exhibition. Tinapa – Calabar, Nigeria: Society of Petroleum Engineers; 2010.
- [104] Ju B, Dai S, Luan Z, Zhu T, Su X, Qiu X. A study of wettability and permeability change caused by adsorption of nanometer structured polysilicon on the surface of porous media. *SPE Asia Pacific Oil and Gas Conference and Exhibition: Society of Petroleum Engineers*; 2002.
- [105] Ju B, Fan T. Experimental study and mathematical model of nanoparticle transport in porous media. *Powder Technol* 2009;192:195–202.
- [106] Zitha P. Smart fluids in the oilfield. *Exploration & Production: The Oil & Gas Review* 2005:66–8.
- [107] Mokhatab S, Araujo Fresky M, Rafiqul Islam M. Applications of nanotechnology in oil and gas E&P. *Journal of petroleum technology*. 2006; 58.
- [108] Syncrude_Canada. FAQs; 1996.
- [109] Anderson B, Chambers J, McMurray D. Market outlook for Athabasca bitumen—the economics of location; 1995.
- [110] Hassan A, Carbognani L, Pereira-Almao P. Development of an alternative setup for the estimation of microcarbon residue for heavy oil and fractions: effects derived from air presence. *Fuel* 2008;87:3631–9.
- [111] Breysse M, Djega-Mariadassou G, Pessayre S, Geantet C, Vrinat M, Pérot G, et al. Deep desulfurization: reactions, catalysts and technological challenges. *Catal Today* 2003;84:129–38.
- [112] de Agudelo MMR, Galarraga C. Catalyst for the simultaneous hydrodemetallization and hydroconversion of heavy hydrocarbon feedstocks. Google Patents; 1989.
- [113] Ramirez de Agudelo M, Galarraga C. A stable catalyst for heavy oil processing: III. Activity and selectivity. *Chem Eng J* 1991;46:61–8.
- [114] Chen K, Leung PC, Reynolds BE, Chabot J. Process for upgrading heavy oil using a highly active slurry catalyst composition. Google Patents; 2007.
- [115] Kennepohl D, Sanford E. Conversion of Athabasca bitumen with dispersed and supported Mo-based catalysts as a function of dispersed catalyst concentration. *Energy Fuels* 1996;10:229–34.
- [116] Sanford EC. Conradson carbon residue conversion during hydrocracking of Athabasca bitumen: catalyst mechanism and deactivation. *Energy Fuels* 1995;9:549–59.
- [117] Altgelt KH, Boduszynski MM. *Composition and analysis of heavy petroleum fractions*. New York: M. Dekker; 1994.
- [118] Ancheyta J, Rana MS, Furimsky E. Hydroprocessing of heavy petroleum feeds: tutorial. *Catal Today* 2005;109:3–15.
- [119] Pereira-Almao P. Fine tuning conventional hydrocarbon characterization to highlight catalytic upgrading pathways. Variability of the oil sands resource workshop. Lake Louise, AB; 2007.
- [120] Lee DK, Koon PS, Yoon WL, Lee IC, Woo SI. Residual oil hydrodesulfurization using dispersed catalysts in a carbon-packed trickle bed flow reactor. *Energy Fuels* 1995;9:2–9.
- [121] Wang Z, Guo A, Que G. Coke formation and characterization during thermal treatment and hydrocracking of Liaohe vacuum residuum. *Preprints Div Petrol Chem* 1998;43:530–3.
- [122] Demirel B, Wisner WH. Thermodynamic probability of the conversion of multiring aromatics to isoparaffins and cycloparaffins. *Fuel Process Technol* 1998;55:83–91.
- [123] Alberta Government. Alberta's oil sands; resourceful, responsible; 2008.
- [124] Gosselin P. Environmental and health impacts of Canada's oil sands industry. ON: Royal Society of Canada Ottawa; 2010.
- [125] McEachern P. Environmental management of Alberta's oil sands. 2009.
- [126] Nares HR, Schachat P, Ramirez-Garnica M, Cabrera M, Noe-Valencia L. Heavy-crude-oil upgrading with transition metals. In: Latin American & caribbean petroleum engineering conference; 2007.
- [127] Peluso E. Hydroprocessing full-range of heavy oils and bitumen using ultradispersed catalysts at low severity. Calgary: University of Calgary; 2011.
- [128] Rana MS, Sámano V, Ancheyta J, Diaz J. A review of recent advances on process technologies for upgrading of heavy oils and residua. *Fuel* 2007;86:1216–31.
- [129] Del Bianco A, Panariti N, Di Carlo S, Elmouchnino J, Fixari B, Le Perchec P. Thermocatalytic hydroconversion of heavy petroleum cuts with dispersed catalyst. *Appl Catal A* 1993;94:1–16.
- [130] Argonne_National_Laboratory. Assessing current, near-term, and long-term U.S. hydrogen markets. Decision and information sciences; 1995.
- [131] Adams JJ. Asphaltene adsorption, a literature review. *Energy Fuels* 2014;28:2831–56.
- [132] Akbarzadeh K, Hammami A, Kharrat A, Zhang D, Allenson S, Creek J, et al. Asphaltenes—problematic but rich in potential. *Oilfield Rev* 2007:22–43.
- [133] Franco CA, Nassar NN, Ruiz MA, Pereira-Almao PR, Cortés FB. Nanoparticles for inhibition of asphaltenes damage: adsorption study and displacement test on porous media. *Energy Fuels* 2013;27:2899–907.
- [134] Mohammadi M, Akbari M, Fakhrouieian Z, Bahramian A, Azin R, Arya S. Inhibition of Asphaltene precipitation by TiO₂, SiO₂, and ZrO₂ nanofluids. *Energy Fuels* 2011;25:3150–6.
- [135] Zabala R, Mora E, Botero O, Cespedes C, Guarín L, Franco C, et al. Nanotechnology for asphaltenes inhibition in cupiagua south wells. IPTC 2014: international petroleum technology conference; 2014.
- [136] Leontaritis K, Amaefule J, Charles R. A systematic approach for the prevention and treatment of formation damage caused by asphaltene deposition. *SPE Prod Facil* 1994;9:157–64.
- [137] Bergeson LL, Auerbach B. Reading the small print. *Environmental forum. The Environmental Law Institute*; 2004. p. 30–2.
- [138] Morris J, Willis J, Gallagher K. Nanotechnology white paper. US environmental protection agency. Washington, DC. <<http://www.epagov/osa/pdfs/nanotech/epa-nanotechnology-whitepaper-0207.pdf>> [Feb 2007]; 2007.
- [139] Kahan DM, Rejeski D. PProject on emeRging nanotechnologies; 2009.
- [140] Nel A, Xia T, Mädler L, Li N. Toxic potential of materials at the nanolevel. *Science* 2006;311:622–7.
- [141] Thomas T, Thomas K, Sadrieh N, Savage N, Adair P, Bronaugh R. Research strategies for safety evaluation of nanomaterials. Part VII: Evaluating consumer exposure to nanoscale materials. *Toxicol Sci* 2006;91:14–9.
- [142] Breggin LK, Carothers L. Governing uncertainty: the nanotechnology environmental, health, and safety challenge. *Columbia J Environ Law* 2006;31:285.