

Review

A Review of Laboratory-Scale Research on Upgrading Heavy Oil in Supercritical Water

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Abstract: With the growing demand for energy and the depletion of conventional crude oil, heavy oil in huge reserve has attracted extensive attention. However, heavy oil cannot be directly refined by existing processes unless they are upgraded due to its complex composition and high concentration of heteroatoms (N, S, Ni, V, *etc.*). Of the variety of techniques for heavy oil upgrading, supercritical water (SCW) is gaining popularity because of its excellent ability to convert heavy oil into valued, clean light oil by the suppression of coke formation and the removal of heteroatoms. Based on the current status of this research around the world, heavy oil upgrading in SCW is summarized from three aspects: Transformation of hydrocarbons, suppression of coke, and removal of heteroatoms. In this work, the challenge and future development of the orientation of upgrading heavy oil in SCW are pointed out.

Keywords: heavy oil; upgrading; SCW; hydrocarbons transformation; coke suppression; heteroatoms removal

1. Introduction

Heavy oil is a collective term for unconventional crude oil with a gravity smaller than 20 API and a viscosity greater than 100 cP [1,2]. It includes heavy oil, high viscosity oil, bitumen, oil sand, oil shale, residue, *etc.* [3,4]. According to the statistical reports of the United States Geological Survey (USGS), in 2003, more than 70% of the remaining 10,000 billion barrels of petroleum in the world is from heavy oil resources [1,5]. Currently, with the rapid development of the economy and the dramatic growth of population, the demand for fuel oil is decreasing while the demand for light oil is increasing [6,7]. Unfortunately, the reserves of conventional crude oil suitable for the production of light oil is scarce and insufficient to meet the ever-growing energy demand [8,9]. To reduce the energy gap, taking the heavy oils as an oil substitute, and converting them into light fractions, may be an alternative choice [2,3,10,11]. However, heavy oil, usually characterized by its high viscosity, high density, small gravity, and low H/C ratio (1.2–1.4) cannot be directly refined by existing processes [2,10]. Additionally, high concentrations of heteroatoms (such as nitrogen, sulfur, nickel, and vanadium) accumulated in heavy oil will cause serious environmental concerns if not disposed [6,12,13]. Therefore, research on the technologies of upgrading heavy oil has, globally, received continuous attention.

The goal for upgrading heavy oil is to produce light oil suitable for further utilization, which can be realized through the cracking and removal of macromolecules, the elimination of the heteroatoms, the lowering of the viscosity, and the increasing of the H/C ratio [2,10]. In the past few years, numerous technologies for upgrading heavy oil had been developed, based on the carbon rejection and hydrogen addition route (see Table 1). Among the technologies for upgrading heavy oil, the technique of deasphalting is often used due to its effective removal of heteroatoms, along with the asphaltene, in the extraction processes [14]. Unfortunately, the extraction process usually consumes amounts of organic solvents and the mass loss of heavy oil reaches 30% [14,15]. Other techniques of carbon rejection, especially coking, are also preferred by refineries due to their lower investment [3,16]. However, with the decreasing demand for fuel oil, these processes will face a dilemma, as small amounts of liquid products but a great deal of coke are formed from these thermal processes [17,18]. Though the hydrogen addition processes can retard the formation of coke and convert heavy components into valuable light fraction, the cost of hydrogen is considerable [19]. Additionally, the deposition of coke and metals can easily deactivate the expensive catalysts for upgrading heavy oil [20]. Given the problems of the technologies, novel processes need to be developed in order to upgrade heavy oil.

Table 1. Classification of technologies for upgrading heavy oil [3,4].

Carbon Rejection	Hydrogen Addition
Deasphalting	Fixed bed hydrotreating
Visbreaking	Fixed bed hydrocracking
Thermal cracking	Ebullated bed hydrotreating
Coking	Ebullated bed hydrocracking
Catalytic cracking	-

Among the novel technologies, the technique of using supercritical water (SCW) may provide a way to upgrade heavy oil. SCW, defined as the thermodynamic state of water above critical temperature and pressure (374.3 °C and 22.1 MPa), has aroused a great deal of interest in researchers due to its

ubiquitous solvent properties and potential ability to donate hydrogen [19]. In contrast to deasphalting, upgrading heavy oil in SCW is a green process, without any auxiliary chemicals required. Moreover, the tunable dielectric constant (2 to 30) of SCW with temperature and pressure makes it as an ideal solvent [21]. Extensive applications of SCW techniques show that SCW can be miscible with most organic compounds and gases [21–25], which can greatly increase the recovery rate of heavy oil. In addition, the diminishing of hydrogen bonds and phase boundaries of SCW with an increase of temperature increases organic compound dissolution [21,23]. Compared with the techniques of coking, the timely and effective extraction of asphaltene nuclei can effectively retard the formation of coke [26]. Additionally, the SCW can act as an acid or base catalyst to take part in the reaction by manipulating the pressure [23,27]. Extensive research shows that upgrading heavy oil in SCW would produce cleaner light fractions and less coke than those in pyrolysis processes.

To date, a great deal of progress has been made in upgrading heavy oils (such as oil sand [28,29], oil shale [30,31], Bitumen [26,32,33], residues [34], and heavy oil [35]) in SCW. To understand the current status of upgrading heavy oil in SCW, a timely sorting and summary of the progress made for the processes of heavy oil upgrading in SCW are necessary. Camiaz *et al.* [4] reviewed the work of upgrading heavy oil in SCW from the aspect of process intensification. Timko *et al.* [36] mainly summarized the results of upgrading and desulfurization of heavy oil with SCW, achieved in Massachusetts Institute of Technology (MIT). As the upgrading of heavy oil in SCW is a comprehensive process, the systematic summary of previous work is essential for optimizing the reaction process. This paper is a systematic review from the following aspects: (1) transformation of hydrocarbons; (2) suppression of coke; and (3) removal of heteroatoms.

2. Transformations of Hydrocarbons

2.1. Extraction, Fractionation and Reaction of Hydrocarbons

Usually, heavy oil is comprised of saturates, aromatics, resins, and asphaltenes (SARA). Unfortunately, most of their components are of heavy fractions. To convert heavy oil into light oil, most of the previous research in upgrading heavy oil in SCW was concentrated on the transformation of hydrocarbons. Due to the ubiquitous physical and chemical properties of SCW, the transformation of hydrocarbons in SCW is a synergistic process of extraction, fraction, and reaction. With thermolysis, part of the hydrocarbons will be cracked into smaller molecules, while some hydrocarbons will form bigger molecules via the reactions of concentration and polymerization. Because of the superior miscibility of SCW with hydrocarbons, most of the hydrocarbons can be extracted and fractionated from the heavy oil using SCW.

Table 2. Summary of the effects of reaction parameters on the transformation of hydrocarbons from heavy oil source.

Heavy Oil	Reaction Parameters	Major Results	References
Maoming	<ul style="list-style-type: none"> Room temperature to 673 K at a rate of 8.5 K·min⁻¹, hold for 1 h: SCW and SCT. 	<ul style="list-style-type: none"> polar components were more easily decomposed in SCW. 	[37]
Bey pazari	<ul style="list-style-type: none"> Room temperature to 673 K at a rate of 5 K·min⁻¹: SCW and SCT. 	<ul style="list-style-type: none"> higher conversion but lower oil yield achieved in SCW; oil with higher asphaltic and polar compounds for SCT. 	[38]
Oil shale	<ul style="list-style-type: none"> Pyrolysis: Room temperature to 550 °C at a rate of 5 K·min⁻¹, hold for 2 h; Flash pyrolysis: 550 °C; SCW: Room temperature to 375 °C at a rate of 17 K·min⁻¹, hold for 60 min. 	<ul style="list-style-type: none"> highest oil yield achieved for SCW. 	[28]
	Timahdit	<ul style="list-style-type: none"> Room temperature to desired 380 °C at a rate of 4.5 K·min⁻¹, hold for 2.41 h, pressure at 23 MPa; Room temperature to desired 400 °C at a rate of 4.5 K·min⁻¹, hold for 1.48 h, pressure at 25 MPa; Room temperature to desired 400 °C at a rate of 4.5 K·min⁻¹, hold for 2.48 h, pressure at 25 Mpa. 	<ul style="list-style-type: none"> the oil yield and the fraction of aromatics increased with temperature ranging from 380 to 400 °C; asphaltenes and polars decreased when the residence time is increased.
Oil sand	<ul style="list-style-type: none"> Albert Athabaca 400 °C; Pressure: 14–24.5 MPa; Sweep rate: 2.3–10 mL·min⁻¹; Mole ratio of H₂O/CO: 1.7–12.2. 	<ul style="list-style-type: none"> insensitive effect on the bitumen extraction yield; extraction with water + CO greatly generated lower coke. 	[40]
	Tumuji	<ul style="list-style-type: none"> Extraction rates of bitumen, saturates, aromatics and resin; from 100 to 500 °C; from 20 to 30 Mpa. 	<ul style="list-style-type: none"> the extraction rates had a maximal values with the temperature increasing from 100 to 500 °C; the maximal extraction rates achieved at lower temperature with the pressure increasing.

Table 2. Cont.

Heavy Oil	Reaction Parameters	Major Results	References
From SAGD method	<ul style="list-style-type: none"> at 723 K, 30, 60, 90 min: Pyrolysis, SCW, SCW + HCOOH; at 723 K, 30 min, SCW + HCOOH: Water/oil = 0–3. 	<ul style="list-style-type: none"> highest asphaltene conversion and lowest coke yields achieved for SCW; higher asphaltene conversion and lower coke yields achieved at higher water/oil. 	[11]
Omsk Oil Refinery	<ul style="list-style-type: none"> 400 °C, 30 MPa; Zn; Al. 	<ul style="list-style-type: none"> the addition of <Zn> into SCW increased the volatile products, liquid products and resins up to 15.3%, 62.3% and 33.5%, respectively; the addition of <Al> into SCW increased the volatile products, and maltenes up to 38.2%, and 36.1% while decreased resins up to 7.5%. 	[41]
Bitumen	<ul style="list-style-type: none"> mole ratio of H₂O/CO = 1, air pressure = 2.1 MPa, 30 min: 653–723 K; 	<ul style="list-style-type: none"> higher temperature favored the asphaltene transformation, coke and gas formation; 	
From SAGD method	<ul style="list-style-type: none"> 673 K, air pressure = 2.1 MPa, 30 min: Ratio of H₂O/CO = 0–3; 673 K, 30 min, ratio of H₂O/CO = 1 (wt): Air pressure = 0–5 MPa. 	<ul style="list-style-type: none"> the ratio of CO/(CO + CO₂) increased about two times with the ratio of H₂O/CO ranging from 0 to 3; the increasing of air pressure would enhance the CO₂ yield whereas decreased the ratio of CO/(CO + CO₂). 	[42]
Canadian Athabasca	<ul style="list-style-type: none"> flow mode, ration of water/bitumen = 2, 3.5 h, temperature = 400 °C: 10, 25, 30 MPa. 	<ul style="list-style-type: none"> the optimal dispersion condition was obtained at 30 MPa; no coke found in the SCW flow. 	[43]
Shanghai Petroleum Co.	<ul style="list-style-type: none"> Temperature: 420–460 °C; mole ratio of H₂O/oil: 2–4; reaction time: 0–120 min. 	<ul style="list-style-type: none"> effects of reactions conditions on product quality could be ranked as: Temperature > H₂O/VR > reaction time > water density; Optimal condition: 420 °C, 1h, H₂O/oil = 2. 	[44]
Residues	<ul style="list-style-type: none"> Temperature: 380–460 °C; mole ratio of H₂O/oil: 0.78–4; reaction time: 5–120 min. 	<ul style="list-style-type: none"> a reduction of 30.9% in resins and asphaltenes; a reduction of 22.8% in aromatics; an increase of 98.6% in saturates; the viscosity of the product was reduced from 116 mPa s of the feedback to 6.2 mPa·s. 	[45]
Daqing	<ul style="list-style-type: none"> 415 °C: With or without SCW. 	<ul style="list-style-type: none"> less gases but more liquid products were generated from SCW. 	[46]
Gudao	<ul style="list-style-type: none"> 415 °C, 90 min, initial hydrogen pressure = 7 MPa: Molybdenum-dithiocarboxylate (MoDTC), FeNaphthenate, CoNaphthelate (Conaph), Ni(CH₃COO)₂, (Ni(Ac)₂), ((NH₄)₅MO₇O₂₄·4H₂O (AHM), (NH₄)₃PO₄·12MO₃·12H₂O (APM), PMA, (Fe(CO)₅), (NH₄)₂MOS₄ (ATTM)). 	<ul style="list-style-type: none"> the addition of catalysts effectively reduced the coke yield; the optimal catalyst was PMA. 	[47]

Table 2. Cont.

Heavy Oil	Reaction Parameters	Major Results	References
Gudao	<ul style="list-style-type: none"> 420 °C, PMA (500 µg/g), initial pressure = 7 MPa: H₂, H₂ + SCW, CO + H₂O and H₂ + CO + SCW. 	<ul style="list-style-type: none"> much lower coke yield achieved in these systems than that in pyrolysis; lowest coke yield and highest yield of 300–500 °C fraction were achieved for residue upgrading in H₂ + CO + SCW. 	[48]
Residues	<ul style="list-style-type: none"> Residual oil 693 K, 1 h, residual oil/PE = 40 (wt): Water densities = 0.10–0.30 g·cm⁻³. 	<ul style="list-style-type: none"> the yields of saturates, aromatics, resins increased from 21.0, 18.4, 10.8 wt % to 32.9, 19.4 13.9 wt % respectively. the phase structure evolved from a liquid/liquid/solid three-phase structure to a liquid/solid two-phase one 	[49]
	<ul style="list-style-type: none"> Residual oil 693 K, 30 min, water densities = 0.30 g·cm⁻³: Residual oil/PE = 40 (wt): The amounts of PE loading varied from 0.5 to 2.5 g. 	<ul style="list-style-type: none"> the yield of aromatic and maltene increased from 36.5, 65.2 to 42.9, 74.7 wt %, respectively; the yield of asphaltenes increased gradually to 9.4 wt % when the PE loadings higher than 2.0 g. 	[35]
	<ul style="list-style-type: none"> From heavy Tatar oil 380 °C, pressure 226 atm and stirring time 3 h. 	<ul style="list-style-type: none"> the formation of gas products, about 4.3%, the yield of products from the consecutive dissolution of hexane, benzene, chloroform were 30.0%, 10.6%, 5.7%, respectively. 	[50]
Asphaltene	<ul style="list-style-type: none"> Coal-tar 693 K, 713 K: SCW or N₂; 	<ul style="list-style-type: none"> asphaltene upgrading in SCW gave higher asphaltene conversion and higher maltene; the yield of maltene obtained at 713 K in SCW is 39.4 wt % and that is 1.5 times higher than that obtained in N₂. 	[51]
	<ul style="list-style-type: none"> From Canadian oilsand bitumen 400–450 °C and 20–35 MPa. 	<ul style="list-style-type: none"> the optimal condition was 440 °C and 29.8 MPa; the optimal miscibility parameters of SCW: Dielectric constant (DC) = 2.2, Hansen solubility parameter (HSP) δ_p = 6.4, and δ_h = 9.7. 	[52]
	<ul style="list-style-type: none"> Tahe 400 °C, 30 MPa, 0–120 min: SCW or SCW + NaOH. 	<ul style="list-style-type: none"> higher asphaltene conversion achieved in SCW + NaOH; asphaltene transformation in SCW + NaOH generated more maltene. 	[53]

To produce a more light oil, it is necessary to crack macromolecules into smaller molecules. Additionally, the timely separation of the light hydrocarbons from the reaction system, and restrict their secondary reaction to form gas and coke, is needed. However, in the SCW state, the cracking of macromolecules, the formation of coke, and the extraction of hydrocarbons are greatly influenced by certain reaction parameters (such as reaction conditions, reaction mode, catalysts, *etc.*). To transform a more heavy oil into light oil, it is necessary to optimize the reaction conditions, reaction mode, and choose the appropriate catalysts. In this section, the upgrading of heavy oil from different sources in SCW will be discussed from the aspects of extraction, fraction, and reaction of hydrocarbons. Additionally, the effects of the reaction conditions, reaction mode, catalysts, *etc.*, on the hydrocarbon transformation will be carefully elaborated (shown in Table 2).

2.1.1. Oil Shale

Oil shale, defined as the petroleum source rock, containing a high proportion of organic matter (kerogen), is a representative non-conventional oil resource. The potential reserve of shale oil is predicted to be more than four times that of the global petroleum resources [54]. Currently, the upgrading of oil shale in SCW may be an alternative way to recover oil (usually referred to as bitumen) and meet the increasing demand for transport fuels. The main objective of upgrading oil shale in SCW is to recover as much oil as possible through extraction, fraction, and reaction.

Funazukuri *et al.* [30,37] studied supercritical fluid extraction of Chinese oil shale and found that polar components were more easily decomposed in SCW than in supercritical toluene (SCT). Olukcu *et al.* [38] reported that upgrading Bey pazari oil shale in SCW gave a higher conversion but a lower oil yield than those in SCT. Oil obtained from SCT had more asphaltic and polar compounds than those from SCW.

Yanik *et al.* [28] performed experiments to investigate the effect of pyrolysis, flash pyrolysis, and SCW extraction on oil yield and the composition of the extract. The results showed that SCW extraction gave the highest oil yield, but this oil contained a high proportion of asphaltenes and polar compounds because of the extraction of SCW, and the reaction of SCW with the oil shale kerogens [39].

The effects of reaction conditions on the extract yield and the extract constituent of SCW have been reported by many researchers [30,37,39,55]. As expected, increasing temperature would transform more asphaltenes and polarities into paraffins and aromatics, and increase the oil yield. However, the yields of oil, paraffins, and aromatics had maximal values due to the polymerization, concentration, and decomposition of extracts with increasing temperature. Additionally, the increasing temperature would lower the ration of H/C of spent shale and reduce the amount of spent shale because of the interaction between SCW and minerals. With respect to reaction time, its extension would increase the yields of light hydrocarbons and aromatics, but would also reduce the fraction of asphaltenes and polarities because the solubility of SCW to hydrocarbons increased with pressure, which in turn slightly increased the yield of extract.

2.1.2. Oil Sand

Oil sand resources are one of the world's most abundant non-conventional energies. According to the exploration reports, the reserve of oil sands is estimated to be equal to the world's total reserve of conventional crude oil [56]. In recent years, with the decrease of conventional crude oil reserves and the increase of crude oil prices, oil sand has gradually been considered as an inexpensive substitute for crude oil [29]. As oil sand is primarily a mixture of quartz sand, clay, water, and bitumen, the main object of upgrading oil sand in SCW is to recover the bitumen through the extraction, fraction, and reaction of hydrocarbons [56].

For oil sand upgrading in SCW, the effects of reaction conditions on the yield of bitumen (expressed as percentage of bitumen removed from the oil sand sample) and its components cannot be neglected. Berkowitz *et al.* [40] reported that the pressure, sweep rate of SCW, and the mole ratio of H₂O/CO had an insensitive effect on the bitumen extraction yield for two Alberta Research Council's Sample Bank oil sand samples upgraded in SCW at 400 °C. Meng *et al.* [29] examined the effect of temperature and pressure on the extraction rates of bitumen, saturates, aromatics, and resin for Tumuji oil sand upgraded in subcritical water (Sub) and SCW with a semi-continuous apparatus. The results showed that the extraction rates of bitumen, saturates, aromatics, and resin all had a maximal values with the variation in temperature. In addition, the maximal extraction rate for bitumen, saturates, aromatics, and resin could be achieved at a lower temperature with an increase in pressure, from 20 to 30 MPa. As for gas, the increase in temperature would increase the volume percentages of H₂, CH₄, C₂H₆, and C₂H₄ but would decrease the volume percentages of CO and CO₂; while the effect of pressure on gas yields could be neglected.

2.1.3. Bitumen

Bitumen is an important part of heavy oil. It mainly comes from the extraction of oil sand and oil shale, and the petroleum refining process. In the past, bitumen was an underutilized resource because of its inherent poor quality. It is usually characterized by its high viscosity, high asphaltene, and heteroatom species. The goal of upgrading bitumen in SCW is to transform more bitumen into valuable light oil.

Hydrogenation through a water gas shift (WGS) reaction can be an effective method to upgrade bitumen as active hydrogen, formed from the WGS reaction, can rapidly react with the macromolecules and suppress coke formation. Formic acid (HCOOH) is reported to be an intermediate of the WGS reaction in SCW. To evaluate the effect of HCOOH on asphaltene decomposition and coke formation, experiments regarding the upgrading of bitumen were performed by Sato *et al.* [11]. The results showed that upgrading bitumen in SCW + HCOOH gave a higher conversions of asphaltene and lower coke yields than those of pyrolysis or with only SCW. This study also found that higher asphaltene conversion and lower coke yields were achieved at a higher water/oil.

Fedyeva *et al.* [41,57] reported the effect of zinc and aluminum on the upgrading of bitumen in SCW. In SCW, the reaction of zinc and aluminum with water ($mn\langle Zn \rangle + mn(H_2O) \rightarrow m(ZnO)_n + mnH_2$ and $mn\langle Al \rangle + 1.5mn(H_2O) \rightarrow 0.5m(Al_2O_3)_n + 1.5mnH_2$), both, would form amounts of active hydrogen and released a great deal of on-site heat simultaneously. As the active hydrogen could

prevent the recombination of hydrocarbon radicals while on-site heat could accelerate the cracking of long-chain hydrocarbons, the addition of zinc and aluminum, not only increased the bitumen conversion, but also greatly improved the product qualities. When adding <Zn> into bitumen, the yield of the volatile products, resins, and liquid product would increase. When adding <Al> into bitumen, the yield of the volatile products and maltenes would increase while the yield of resin would decrease.

Hydrogenation through the WGS reaction can also be accomplished via the formation of CO from partial oxidation of hydrocarbons as the reaction conditions have great influence on the degree of partial oxidation of hydrocarbons in SCW. Sato *et al.* [42] examined the effect of temperature (from 653 to 723 K), water/oil ratio (from 0 to 3), and air pressure (up to 5.1 MPa) on the partial oxidation of bitumen in SCW. The results showed that higher temperatures favored the asphaltene transformation, and coke and gas formation, while lower temperatures contributed to the selective partial oxidation of hydrocarbons, and the ratio of CO/(CO + CO₂) achieved a maximal value at 653 K. As for the water/oil ratio, its increase had a great influence on the ratio of CO/(CO + CO₂) but had little effect on asphaltene transformation and coke formation; with the water/oil ratio increasing from 0 to 3, the ratio of CO/(CO + CO₂) increased about two times, but the asphaltene and coke yields were almost constant. The increase of initial air pressure promoted gas formation, especially the formation of CO₂ whereas the ratio of CO/(CO + CO₂) decreased.

For bitumen upgrading in SCW, the reverse WGS reaction may be another way to offer active hydrogen. To evaluate the effect of the reverse WGS reaction on asphaltene decomposition and coke formation, experiments of upgrading bitumen in SCW, and its mixtures with hydrogen and carbon dioxide (SCW + H₂ + CO₂), were performed in semi-batch reactors by Sato *et al.* [58,59]. The results showed that the active hydrogen formed from the reverse WGS reaction might have some inhibiting effect on the polymerization of active fused-ring units. Thus, the upgrading of bitumen in SCW + H₂ + CO₂ gave a lower coke yield and a higher asphaltene yield than those in SCW.

Extensive studies show that the product yield for bitumen upgrading in SCW depends, not only on the nature of raw bitumen and reaction conditions, but also on the operation mode [60]. Currently, the commonly used operation modes for reactions in SCW include batch, semi-batch, or continuous reactors. Compared with the batch and semi-batch reactors, the advantage of continuous reactor is mainly reflected in the extraction and fraction of hydrocarbons. For bitumen upgrading in SCW, the recombination of the hydrocarbon radicals generated during hydrolysis can be prevented by SCW flow, due to its timely and effective extraction and separation, which greatly reduce the formation of coke and increase the liquid hydrocarbon yield [43,61].

2.1.4. Residues

Residues, referring to the heavy fraction remaining in crude oil after atmospheric (>343 °C) or vacuum distillation (>565 °C), is usually characterized by its extremely high density and rather high concentration of asphaltene and heteroatoms [3]. As the portion of residue in crude can reach 85 vol%, its effective transformation into light components is extremely important in view of the limited global oil storage and the increasing demand for light oil. This section mainly reviews the transformation of hydrocarbons in SCW.

Cheng *et al.* [44] studied the effect of reaction conditions on upgrading vacuum residue (VR) in SCW. In this study, the quality of the product was evaluated by simulated distillation expressed in terms of weight loss lower than 350 °C. The results of orthogonal experiments suggested that effects of reaction conditions on product quality could be ranked as: Temperature > H₂O/VR > reaction time > water density. The influence of temperature on upgrading vacuum residue in SCW could be reflected by the yields of saturates and coke. At conditions of 60 min, 0.15 g·cm⁻³ and H₂O/VR = 2, the saturate and coke yields increased from 75 wt % and 2.66 wt % to 85 wt % and 7.77 wt %, respectively, with the temperature ranging from 420 to 450 °C. As the increase of H₂O/VR ratio favored the dissolving of light oil (boiling point lower than 350 °C) and the reduction of transfer mass resistance between phase interfaces, the yield of light oil was increased from 77 wt % to 83 wt % with the ratio of H₂O/VR changing from 2 to 4. At the optimal conditions (420 °C, 0.15 g·cm⁻³, 4 g·g⁻¹, 1 h), the light yield for VR upgrading in SCW could reach 83.33 wt %. Zhao *et al.* [45] also reported the reaction condition on VR upgrading in SCW. Their work indicated that the increasing of pressure, VR/water, and temperature could effectively lower the molecular weight and viscosity of the liquid product (extracted by toluene) for VR upgrading in SCW.

Fan *et al.* [46] used a catalytic hydrocracking system to validate the effect of SCW on upgrading DaQing VR at 415 °C. The presentation of SCW considerably increased the liquid yield (boiling point less 320 °C) and reduced the gaseous yield. Cheng *et al.* [47] reported the effect of catalysts on upgrading Gudao residue with SCW-syngas. In these experiments, several oil soluble and water soluble metal catalysts were used to catalyze the hydrocracking of the residue. The results showed that the addition of catalysts could effectively enhance the reactivity of residue and lower the coke yield. Among the used catalysts, the activity of the water soluble catalyst H₃(P(MO₃O₁₀)₄)·xH₂O (PMA) was strongest from the aspect of the evaluation of parameter R (R = conversion (%)/yield of coke (%)), which achieved the maximal value of 26.23. Compared with residue hydrocracking in SCW, the addition of catalyst could suppress the over-cracking reaction of products. With respect to PMA, its addition could increase the yield of 300–500 °C fractions and lower the yield of <200 °C fractions. The optimum amount of PMA for residue hydrocracking was 500 µg·g⁻¹. Cheng *et al.* [48] also studied the effect of hydrogen sources on upgrading Gudao residue with SCW with optimum amounts of PMA. The alternative hydrogen sources were effective for the hydrocracking of residue in SCW. Because of the inhibition of the condensation reaction, upgrading residue in H₂, H₂ + SCW, CO + H₂O and H₂ + CO + SCW gave a much lower coke yield than that of pyrolysis. Due to the WGS reaction, the lowest coke yield and the highest yield of 300–500 °C fractions were achieved for residue upgrading in H₂ + CO + SCW.

Bai *et al.* [49] systematically studied the co-pyrolysis of residual oil and polyethylene (PE) in Sub or SCW at a temperature of 693 K and water densities from 0.10 to 0.30 g·cm⁻³. The co-pyrolysis of residual oil and PE can produce more aromatics, resins, and asphaltenes, but less saturates than the pyrolysis of residual oil alone. With the increase in water density, the phase structure of the co-pyrolysis system might evolve from a liquid/liquid/solid three-phase structure to a liquid/solid two-phase structure (Figure 1), which favored the contact of aromatic radicals from the pyrolysis of residual oil and paraffins to that of PE. Thus, more saturates, aromatics, and resins, but less asphaltene, were formed at a higher density. Tan *et al.* [35] reported that the extension of reaction time (from 30 to 60 min) had little effect on the yields of saturates, aromatics, resins, and asphaltenes at the ratio of heavy oil to PE of 10 (wt); whereas the changes of the PE loading amount had a significant effect on the

products yields. With the loading amounts of PE increasing from 0.5 to 2.5 g (corresponding to the ratio of heavy oil to PE being 40 to 8), the yield of aromatic and maltene increased from 36.5 wt %, 65.2 wt % to 42.9 wt %, 74.7 wt %, respectively. The yield of asphaltenes varied slightly around 6.6 wt % at PE loadings between 0.5 and 1.5 g but increased gradually to 9.4 wt % at PE loadings of 2.0 g or higher.

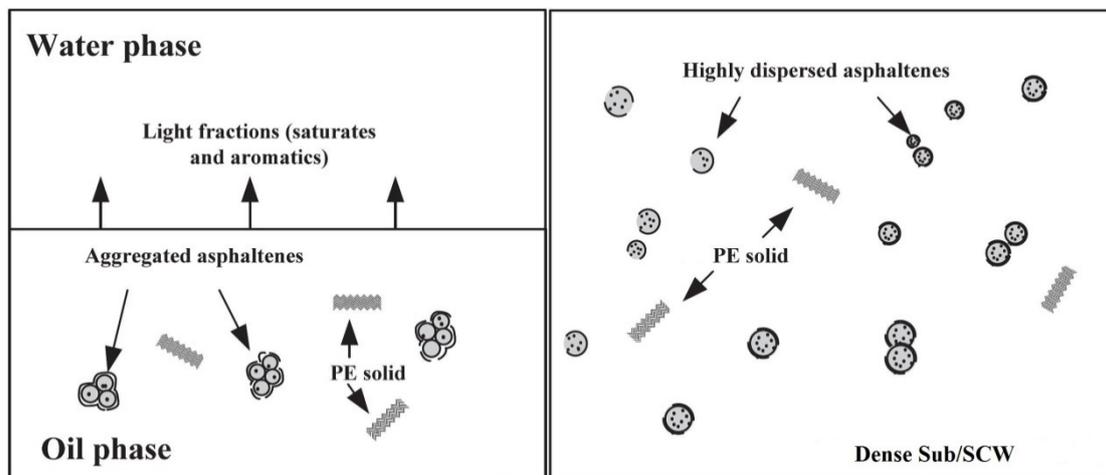


Figure 1. Initial phase structure of residual oil/PE/Sub or SCW; **(left)** liquid/liquid/solid three-phase structure; **(right)** liquid/solid two-phase structure. Reproduced with permission from [49], published by Elsevier Limited, 2013.

2.1.5. Asphaltene

Asphaltene, insoluble in light n-alkanes and soluble in aromatic solvents, is known as the most complex and heaviest fractions of heavy oil [62,63]. It usually consists of highly condensed polyaromatic macromolecules bearing long aliphatic chains and alicyclic substituents. Furthermore, asphaltene incorporates large amounts of heteroatoms (N, S, Ni, and V) [64]. In refining processes, asphaltene is prone to form coke and deactivate catalysts [65,66]. The goal of the upgrading of asphaltene in SCW is to convert asphaltene into light fraction, as much as possible, via the effective and timely extraction and fraction of asphaltene nucleus.

Kozhevnikov *et al.* [50] studied the transformation of asphaltene in SCW at a temperature of 380 °C, pressure 226 atm, and stirring time 3 h. They speculated that the formation of maltene, and gaseous and solid products (hexane-insoluble fraction) from the hydrothermal destruction of asphaltene is a process of dealkylation of substituents in the aromatic fragments of molecules and aromatization. Additionally, the yields of the products were 30%, 4.3%, and 64.9%, respectively.

Han *et al.* [51] reported on the effects of reaction systems (N₂ or SCW), origin of asphaltene, and reaction environment on coal-tar asphaltene upgrading in SCW. In contrast with pyrolysis in N₂ at 693 and 713 K, more maltene while less gas and coke could be produced from asphaltene upgrading in SCW at 26 ± 1 MPa. The results of three original asphaltene upgradings in SCW showed that product compositions were closely related to the ration of H/C of asphaltene. Usually, asphaltene with a higher H/C ration would give a higher maltene yield and less coke yield in SCW.

Morimoto *et al.* [52] used an extraction method to determine the optimal reaction condition for asphaltene upgrading in SCW at 400–450 °C and 20–35 MPa. Consequently, the maximum extraction

yield of degradative asphaltene was achieved at 440 °C and 29.8 MPa. Analysis of the dielectric constant and Hansen solubility parameter showed that the dispersion of SCW at 440 °C and 29.8 MPa was optimal. Li *et al.* [53] evaluated the effect of NaOH on asphaltene upgrading in SCW. Probably because the emulsion reaction between NaOH and asphaltene increased the solubility of asphaltene in SCW, asphaltene upgrading in SCW produced more maltene but less coke.

2.2. Mechanisms of Hydrocarbons Transformation

To convert more heavy oil into valued light fractions, it is essential to determine the transformation mechanism of hydrocarbons in SCW. However, the transformation mechanism of hydrocarbons in SCW has been a topic of controversy for a long time. The focus of the controversy is whether the SCW takes part in the transformation of hydrocarbons. A part of previous literature considered SCW as a reactant [59,61,67–70], which participated the transformation of hydrocarbons through the direct H-abstraction ($H\cdot$ and $HO\cdot$ donation, known as free radical mechanism) or hydrolysis (H^+ and HO^- donation, known as an ionic mechanism), while some just regarded SCW as a solvent [35], which only had some physical effects on the transformation of hydrocarbons [71].

To clarify the proposed roles of SCW in the process of hydrocarbon transformation, a few experiments were performed to support their views. Vostrikov *et al.* [72] reported the pyrolysis of eicosane in SCW and showed that water accelerated pyrolysis and reacted with a large amount of reaction intermediates. Dutta *et al.* [73] tested the hydrogen exchange from steam to thermally cracked bitumen molecules by doping water with D_2O in a temperature range of 623–803 K. They measured the exchanging degrees of three types hydrogen (α -, β -, γ -) in bitumen and found that the α -H were prone to be exchanged with the H of water. Gao *et al.* [74] used D_2O as a tracer to study the hydroconversion of Tahe residue in SCW. The results showed that water participated the hydrocarbon transformation through radicals and the proportion of water molecules involved in the hydrogen exchange was about 40% when the water content in the reaction mixture was 10 wt %. Olukcu *et al.* [38] suggested that the absence of *n*-alkenes-1 and the appearance of alcohols in the product might occur due to OH transferring from water to organic free radicals generated from an oil shale during SCW extraction. Fedyaeva *et al.* [61] implied that water took part in the upgrading of bitumen in an upflow reactor with the evidence of the appearance of oxygen and increasing the amount of hydrogen in the products and conversion residue. Kida *et al.* [75] demonstrated that water was a reactant in the desulfurization process of hexyl sulfide and generated the pentane and $CO + CO_2$ from its reaction with intermediates of hexyl sulfide decomposition.

Sato *et al.* [59] pointed out that the increase in maltene yield was a result of the reaction of $HO\cdot$ from water with the free radicals generated during the upgrading of asphalt in SCW. Liu *et al.* [34] reported that the residual oil upgrading in Sub and SCW with a batch reactor at temperatures of 653 to 713 K and water densities of 0.05 to 0.20 $g \cdot cm^{-3}$. They confirmed that the upgrading of residual oil in Sub and SCW was still dominated by the free radical mechanism based thermal cracking, whereas the ion mechanism based hydrolysis only had an extremely limited influence on the upgrading performance. Apart from the thermally induced $H\cdot$ and $HO\cdot$, the attack of H^+ and HO^- from the hydrolysis of water also leads to the decomposition of macromolecule hydrocarbons. Based on the study

of the VR upgrading in SCW, Zhao *et al.* [45] proposed a parallel mechanism of ions and radicals for VR upgrading in SCW.

Tucker *et al.* [76] proposed the solvating properties (such as cage effect) of supercritical fluids, which was supported later by other researchers. Cheng *et al.* [44] questioned the hydrogen donation ability of SCW, based on the absence of C=O compounds in the products generated from the upgrading of VR in SCW. They attributed the coke porous structure, higher light oil yield, and lower coke yield to the super dissolving capacity and unique dispersion ability of SCW. Morimoto *et al.* [77] also obtained similar conclusions. They ascribed the higher conversion, a greater amount of lighter products, and a lower yield of coke for oil sand bitumen upgrading in SCW than in nitrogen to the dispersion effect of SCW, which led to intramolecular dehydrogenation of heavy compounds and hindered intermolecular condensation. Vilcáez *et al.* [26] reported that the simultaneous enhancing of the bitumen conversion and the suppression of coke formation with a column flow reactor was closely related to the SCW property. Effective extraction of coke precursors and upgraded products from the oil phase at fast rates using column flow reactors, not only suppressed the coke formation, but also promoted the upgrading of bitumen. Xu *et al.* [78] confirmed that SCW could not donate H• and HO• radicals as no products formed from the reaction of HO• with three compounds, naphthalene, *p*-benzoquinone, and azobenzene, under SCW conditions. The different product distribution under the SCW conditions from the inert atmosphere was closely related to the increased solvent dispersion of radicals.

3. Suppression of Coke

The most difficult challenge encountered in the process of upgrading heavy oil is the suppression of coke formation. The formation of large amounts of coke, through the propagation reactions of radicals, the aggregation of asphaltene, and the addition between activated asphaltene precursors and low molecular radicals or olefins [50,79], not only affects the efficient exploitation of heavy oil, but also brings a series of problems, such as the deactivation of catalysts. Fortunately, the introduction of SCW into heavy oil can effectively reduce the yield of coke [11,73–75,80,81]. To further suppress the formation of coke, many novel SCW processes have been successfully developed. This section is to review the progress of suppressing coke in SCW.

3.1. Provision of Hydrogen

It is well known that the formation of coke is an H-deficient process [35]. The provision of hydrogen for heavy oil will strongly prevent the aggregation, concentration, and polymerization reaction of radicals or coke precursors to form coke. Although molecular hydrogen can effectively suppress the formation of coke, the cost of molecular hydrogen is considerable [5]. To suppress the formation of coke, numerous technologies, providing alternatives to hydrogen for the upgrading of heavy oil in SCW, were developed in the past few years.

3.1.1. Addition of Entrainers

Entrainers are usually referred to as chemical additives that can be added into SCW to improve the suppression performance of SCW to coke [4]. Currently, the synergistic effects of SCW and entrainers

on coke have been extensively studied by adding gases (H_2 , CO, CO_2 , etc.) or liquids (HCOOH) into SCW as entrainers.

Berkowitz *et al.* [40] conducted the extraction of oil sand bitumen in SCW at 673 K with a semi-batch type reactor and found that the introduction of CO into SCW significantly suppressed coke formation due to the formation of *in situ* hydrogen from the WGS reaction. Cheng *et al.* [48] examined the effect of H_2 , CO, and their mixture on coke yields and found that the addition of reducing gases into residual oil could significantly lower the coke yield. Probably because of the reaction of coke precursors with *in situ* hydrogen, the yield of coke was in the following order: $H_2 > (CO + H_2)/SCW > H_2/SCW > CO/SCW$.

Sato *et al.* [11] compared the performance of SCW, SCW + H_2 , SCW + CO and SCW + HCOOH on the suppression of coke for bitumen upgrading in SCW. Lower coke yields were achieved in these systems compared to those in pyrolysis due to the synergistic effects of SCW and entrainers. As the easy reaction of asphaltene and hydrogen atom formed through the decomposition of HCOOH capped the reactive fragments and restricted coke formation, the coke yield in SCW + HCOOH was lowest. Apart from this, they also found that the coke yield increased slightly with an increasing water/oil ratio from 1 to 3 in SCW, whereas it decreased and was almost constant in SCW + HCOOH. The suppression of coke in high water/oil ratio regions might be related to reactive species, such as H^+ and COO^- formed from the hydrolysis of HCOOH. Additionally, they proposed a possible kinetic model of coke formation for bitumen upgrading SCW + HCOOH by assuming the existence of a water-rich phase and oil-rich phase. In that model, coke formation mainly occurs in the oil-rich phase by polymerization of asphaltene cores. The provision of active hydrogen to the oil-rich phase could promote the cracking of the asphaltene core into maltene, which in turn would increase the solubility of the asphaltene core and prevent its transformation into coke for bitumen upgrading in SCW.

To evaluate the effect of the reverse WGS reaction on the formation of coke, experiments upgrading bitumen with a semi-batch reactor were performed in SCW and SCW + H_2 + CO_2 at temperatures from 633 to 693 K and a pressure of 30 MPa [58]. The results showed that more coke was generated from bitumen upgrading in SCW than in SCW + H_2 + CO_2 . This was mainly attributed to the reaction of the asphaltene core with *in situ* hydrogen, formed from reverse WGS reaction, which converted asphaltene into maltene and prevented the formation of coke.

3.1.2. Partial SCWO

SCW oxidation (SCWO) can be narrowly defined as the reaction of molecular oxygen and hydrocarbons occurring in SCW. The technique of SCWO is well known, not only because of the destruction of hazardous organic materials into CO_2 and H_2O [82,83], but also because hydrogenation can proceed without the supply of additional molecular hydrogen [84,85]. In SCW, CO, forming the partial oxidation of hydrocarbon, will undergo a WGS reaction to form *in situ* hydrogen [85].

The partial SCWO of some model hydrocarbon compounds [84–91] and asphalt [59] showed that the *in situ* hydrogen is more active than molecular hydrogen in the case of the hydrogenation of hydrocarbon. Sato *et al.* [42] reported the effects of reaction temperature, water/oil ratio, and air pressure as an oxygen source, on the formation of coke. These experiments were performed at

temperatures from 653 to 723 K, water/oil ratios from 0 to 3, and up to 5.1 MPa of air pressure. The results suggested that coke formation could be suppressed at lower temperatures and lower air pressures.

3.1.3. Addition of Hydrogen-Rich Materials

The formation of coke is also a re-distributed process of H sources. The H-abstraction from hydrogen-rich materials or their pyrolysis product may be an effective way to suppress coke formation. Currently, using castoff, such as light density PE, as hydrogen-rich materials can not only provide the hydrogen source for heavy oil upgrading and suppress coke formation but also can solve the environmental concerns caused by them.

Bai *et al.* [49] reported that the co-pyrolysis of residual oil and PE in Sub and SCW. As the H-rich paraffins formed from the pyrolysis of PE could provide the hydrogen source for aromatic radicals, the introduction of PE into residual oil significantly suppressed the formation of coke. At a water density of $0.30 \text{ g}\cdot\text{cm}^{-3}$, the yield of coke in co-pyrolysis is much lower than that in pyrolysis alone by 16.5 wt %. With the increasing of water density, the phase structure of the co-pyrolysis system would evolve from a liquid/liquid/solid three-phase structure to a liquid/solid two-phase, which enhanced the contacting possibility of aromatic radicals with paraffins. Thus, less coke was formed in co-pyrolysis in SCW at a higher water density. Tan *et al.* [35] found that the extension of time and the increasing of the PE loading amounts both favored the suppression of coke formation for the co-pyrolysis of PE and heavy oil in SCW at 693 K and a water density of $0.30 \text{ g}\cdot\text{cm}^{-3}$. Additionally, the suppression mechanism of coke for the co-pyrolysis of PE and heavy oil in SCW was discussed in detail. In their view, coke formation was closely related to two type hydrocarbon radicals, whose active sites are located on naphthenic (or aromatic) rings and the aliphatic side chains of aromatics, respectively. The former was mainly formed from the condensation of light oil fractions and its deep condensation would sequentially form heavy fractions, asphaltenes, and coke through dehydrogenation. The addition of the latter produced in the decomposition of asphaltenes and resins to light oil fractions with olefins would also form coke. Fortunately, these radicals were promptly saturated through the H-abstraction from the pyrolysis product of PE, which effectively prevented the condensation of asphaltene to form coke. The detailed mechanism of the suppression of coking is shown in Figure 2.

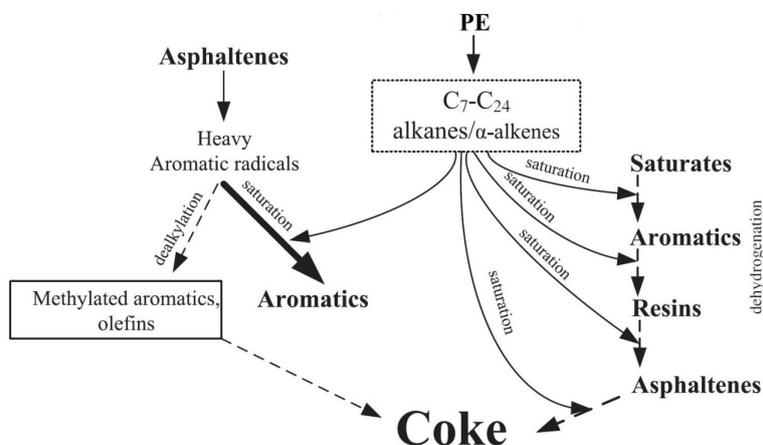


Figure 2. Proposed suppression mechanism of coke in co-pyrolysis of heavy oil and PE. Reproduced with permission from [34], published by Elsevier Limited, 2013.

3.1.4. Addition of Catalysts

The special qualities of catalysts, used for the upgrading of heavy oil in SCW, may be expressed in the induction of the splitting of H_2O to produce active oxygen or active hydrogen. Dejhosseini *et al.* [33] carried out experiments to classify the effect of CeO_2 nanoparticles on the cracking of Canadian oil sand bitumen in SCW at 723 K. The results showed that the addition of CeO_2 nanoparticles could significantly increase the conversion of asphaltene and lower the coke yield. These effects were further strengthened with the increase of the CeO_2 loading amounts. Compared with the octahedral CeO_2 , a lower coke yield was achieved with cubic CeO_2 due to its higher oxygen storage capacity and small particle size. They implied that the suppression of coke with the addition of CeO_2 nanoparticles was closely related to the active oxygen or active hydrogen formed from the redox reaction among the CeO_2 , H_2O , and bitumen. The presence of the active oxygen enabled the enhanced absorption and release of oxygen via the Ce^{4+}/Ce^{3+} redox cycle. In addition, the oxygen on the surface of the CeO_2 catalyst was unstable and would crack the heavy oil via oxidation.

Hosseinpour *et al.* [92] investigated the catalytic effect of silica-supported hematite iron oxide nanoparticles on the cracking of heavy petroleum residue in SCW. The results showed that the addition of silica-supported hematite iron oxide nanoparticles could effectively suppress coke formation. The active oxygen species generated from H_2O over magnetite particles spilled over the surface where the oxidized decomposition of heavy oil occurred. The remaining active hydrogen species were added to the lighter molecules. Consequently, SCW over iron oxide catalyst could suppress coke formation because of its physical (solvation and dispersion effects) and chemical effects as a solvent with hydrogen-donating capability. Figure 3 provides a schematic of the overall process, showing catalytic and pyrolytic cracking of heavy constituents.

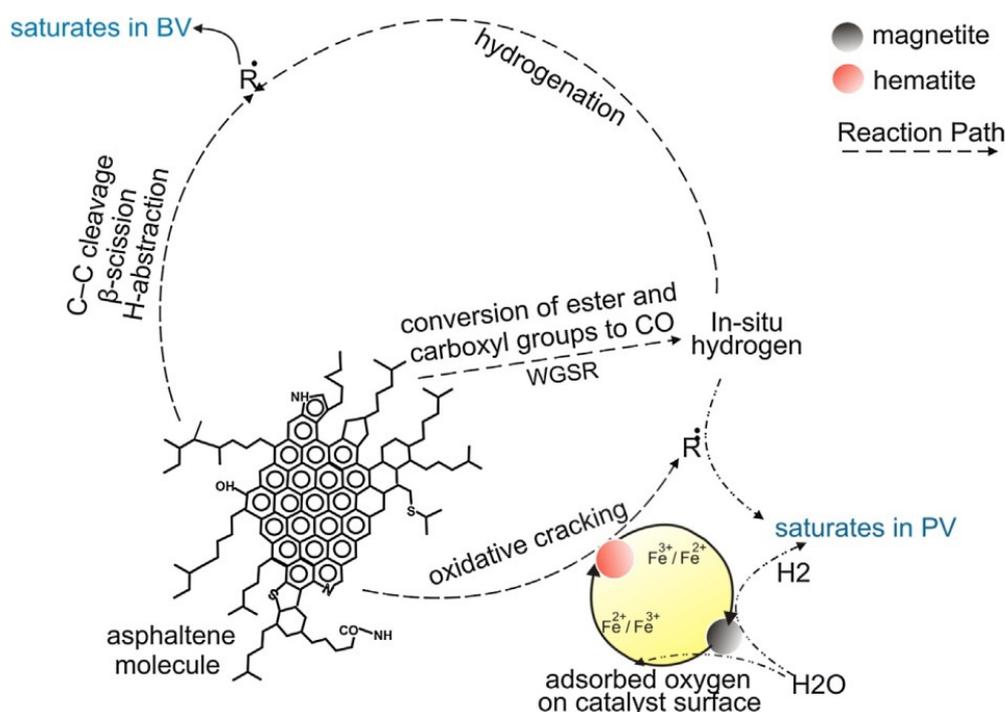


Figure 3. Schematic illustration of proposed pathway for the catalytic cracking of bitumen in SCW. Reproduced with permission from [92], published by Elsevier Limited, 2015.

3.2. Operation Mode

For heavy oil upgrading in SCW, the formation of coke is influenced, not only by the H/C ratio of raw and reaction conditions (temperature and density of SCW) [11,26,93], but also by the operation mode. In this paper, most of the results for the upgrading of heavy oil in SCW were obtained in batch autoclaves. Compared with the flow mode, the deficiency of the batch autoclave conversion may be its limited mass transfer. As the solubility of the SCW is finite, the high molecular radicals generated from pyrolysis will recombine in the bulk and subsequently form coke if not extracted and fractioned by the SCW in a timely and effective manner.

Vilcáez *et al.* [26] reported the continuous extraction of bitumen with near SCW in a column flow reactor at 340 °C, 3–6 MPa, and water flow of 3–10 g/mL and found that less coke was formed in a flow reactor than that in a batch autoclave. The results strongly demonstrated that the column flow reactor could simultaneously enhance the conversion of heavy oils and suppress the formation of coke. Additionally, they, in detail, analyzed the suppression mechanism of coke (sketched in Figure 4). In their view, the formation of coke was closely related to the extraction levels of asphaltene core in the oil phase. Low-level extraction of asphaltene core resulted in the formation of coke in the oil phase, whereas high-level extraction of asphaltene core would suppress coke formation.

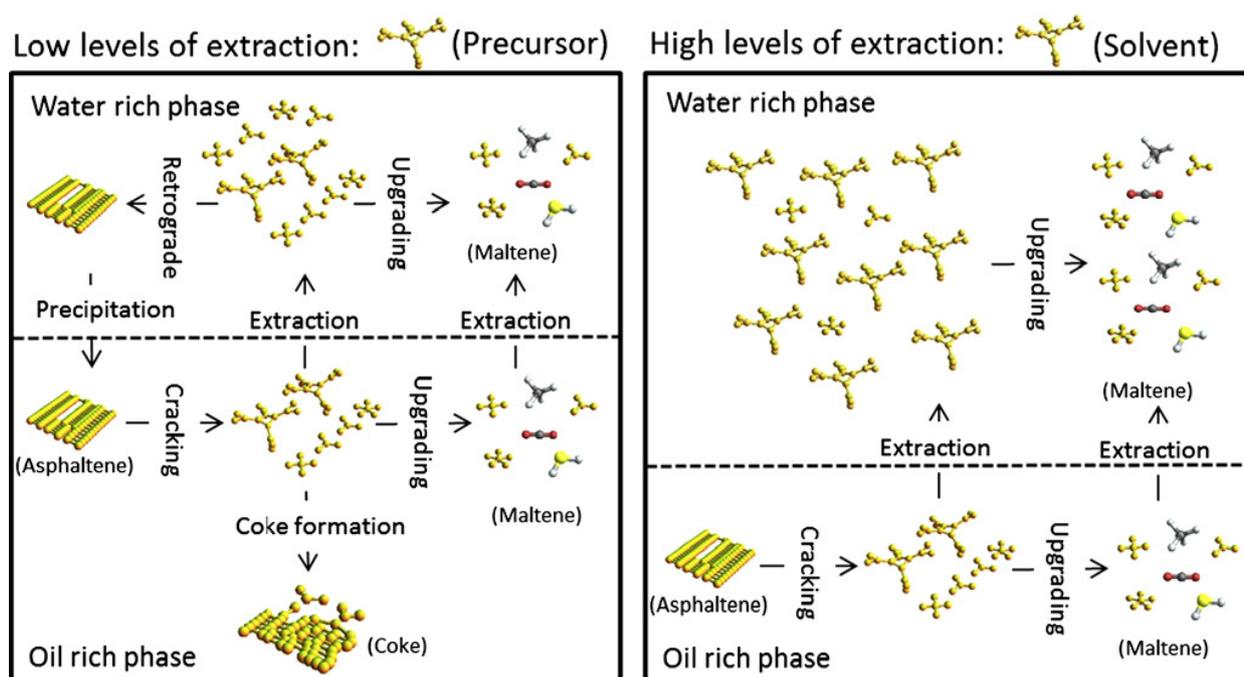


Figure 4. Schematic representation of the proposed mechanism of coke suppression. (Left) Low levels of extraction of asphaltene core; (Right) high levels of extraction of asphaltene core. Reproduced with permission from [26], published by Elsevier Limited, 2012.

Compared with the general SCW flow mode, the counter-current SCW flow mode may be more effective in the aspect of attenuating coke formation. Usually, the pre-heated heavy oil and SCW are simultaneously supplied into the vertically located tubular reactor, from the top and bottom of the reactor, respectively. After loading, the heavy oil will immediately be decomposed. The light hydrocarbons from the decomposition will be removed by the SCW flow. The heavy components from

the decomposition will accumulate at the bottom of the reactor and be converted into lighter hydrocarbons as the temperature increases. A related study showed almost no coke generated from heavy oil upgrading in a counter-current SCW flow reactor [61].

4. Removals of Heteroatoms

Usually, heavy oil enriches large amounts of heteroatoms, such as N, S, Ni, and V, whose contents are summarized in Table 3. It is well known that the combustion of hydrocarbon compounds containing N or S will release a great deal of air pollutants (NO_x , SO_x) [12,94], whereas the existence of Ni and V in heavy oil will enhance the viscosity of crude oil and deactivate the cracking catalyst. In addition, the Ni and V in refined oil will accelerate the wearing and corrosion of the turbo wall and the continuous emission of their oxidation have potential carcinogenic risk [95–97]. As environmental protection laws are becoming increasingly stringent, the removal of the heteroatoms is also an inevitable requirement of upgrading heavy oil. Fortunately, the upgrading of heavy oil in SCW is also the process of producing clean light oil. In this process, part of the heteroatoms (nitrogen, sulfur, nickel, and vanadium) is removed from light oil. To further improve the removal efficiency of heteroatoms with SCW techniques, some novel SCW technologies have been developed. This section mainly concentrates on the progress achieved for the removal of heteroatoms by SCW techniques.

Table 3. Concentration of heteroatoms in heavy oil [3,38,59,95].

Heavy Oil	S (wt %)	Ni + V (ppmw)
Alaska, north slope	1.8	71
Arabian, safaniya	4.3	125
Canada, Athabasca	5.4	374
Canada, Cold Lake	5.0	333
California, Hondo	5.8	489
Iranian	2.6	197
Kuwait, Export	4.1	75
Mexico, Maya	4.7	620
Venezuela Bachaqueo	3.0	509
Korea VR	5.3	142.6
Tahe Residual	2.1	236.9

4.1. Removal of Nitrogen and Sulfur

4.1.1. Removal of Nitrogen

Ogunsola *et al.* [70] reported that the removal of heterocyclic nitrogen from model compounds of quinoline and isoquinoline in SCW was more effective than by pyrolysis at 400 °C and 22 MPa for up to 48 h. Additionally, they presented the reaction pathway for the transformation of quinoline and isoquinoline in SCW and speculated that the rupture of $-\text{C}-\text{N}=\text{C}-$ was proceeded by hydrogenation and hydrocracking of the heterocycle. Yuan *et al.* [98] reported the catalytic denitrogenation of quinoline through partial SCWO in a bomb reactor at 623–723 K and 30–40 MPa over sulfided NiMo. Analysis showed that the denitrogenation of quinoline under catalytic SCWO environment is mainly composed the

in situ H₂ generation and hydrodenitrogenation (shown in Figure 5). Additionally, they also examined the effects of temperature, pressure, the amounts of O₂, and the amounts of catalysts on the denitrogenation of quinoline. The increase of temperature, the O₂ amounts and the catalysts amounts, except pressure, all favored the removal of nitrogen.

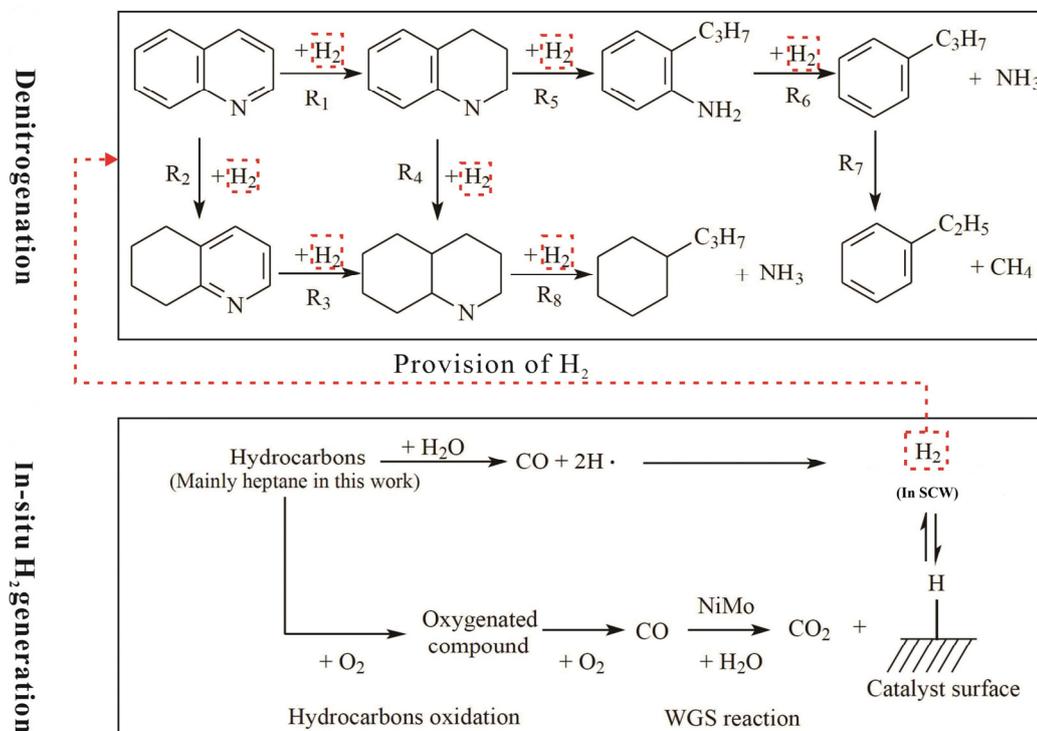


Figure 5. Mechanism of catalytic denitrogenation of quinoline in SCW. Reproduced with permission from [70], published by Elsevier Limited, 1995.

4.1.2. Removal of Sulfur

Sulfur exists as a bridge between core segments such as mercaptanes, sulfides or disulfides and in heterocycles, such as thiophene (shown in Table 4) [99]. In the SCW process, part of the sulfur was removed as H₂S or transferred to coke.

Table 4. Typical organosulfur compounds in heavy oil [98].

Type of Organic Sulfur Compounds	Chemical Structure
Mercaptanes	R-S-H
Sulfides	R ¹ -S-R ²
Disulfides	R ¹ -S-S-R ²
Thiophene	
Benzothiophene	
Dibenzothiophene	

Extensive studies showed that the introduction of SCW could effectively lower the sulfur content of heavy oil [12,59,75,100]. However, it is noteworthy that the removal of sulfur was closely related to the location of sulfur in compounds [12,94]. Usually, the aliphatic sulfur (in mercaptanes, sulfides and disulfides) cleaves easily in SCW, while the aromatic sulfur (in thiophene) is difficult to be reduced because of their steric hindrance [12,94,101].

Patwardhan *et al.* [94] reported that the reactivity of several model organosulfur compounds in SCW obeyed the following order: Dibenzyl sulfide \approx benzyl phenyl sulfide $>$ isopropyl phenyl sulfide \approx hexyl sulfide \approx tetrahydrothiophene \gg thiophene. Ates *et al.* [12] inferred that aliphatic sulfur could be effectively removed by SCW alone, while the efficient removal of sulfur from thiophene compounds was not possible without a suitable desulfurization catalyst. Olobunmi *et al.* [70] found that the breakout of heterocyclic sulfur from model compounds benzothiophene (BT), thianthrene, thiochroman-4-ol and 2 (methylthio) benzothiazole with SCW at 400 °C and 22 MPa could almost not proceed without the addition of the catalyst Fe_2O_3 . Vogelaar *et al.* [100] also reported that the desulfurization of gas oil using SCW at 673 K and 25 MPa was not possible without the presence of hydrogen and a suitable desulfurization catalyst, based on the analysis of products and the calculation of Gibb energy. The above analysis clearly indicated that a proper catalysts or hydrogen-source is needed in order to further improve the desulfurization efficiency of heavy oil in SCW.

Adschiri *et al.* [101] reported the study of catalytic hydrodesulfurization of dibenzothiophene (DBT) with $\text{NiMo}/\text{Al}_2\text{O}_3$ at 673 K and 30 MPa, in various atmospheres (H_2 -SCW, CO -SCW, CO_2 - H_2 -SCW, HCOOH -SCW, and O_2 -SCW). They found that the addition of $\text{NiMo}/\text{Al}_2\text{O}_3$ was the precondition for the formation of in-site hydrogen in various atmospheres. As the in-site hydrogen formed from WGS reaction, reverse WGS, or partial SCWO reaction was more active than H_2 , higher DBT conversion was achieved in CO -SCW, CO_2 - H_2 -SCW, HCOOH -SCW, and O_2 -SCW than that in H_2 -SCW.

Sato *et al.* [59] reported that the introduction of air into SCW could effectively lower the sulfur in maltene and asphaltene. Yuan *et al.* [102] reported the catalytic desulfurization of BT and VR through partial SCWO in a bomb reactor at 623–723 K and 30–40 MPa over sulfided $\text{CoMo}/\alpha\text{-Al}_2\text{O}_3$. They found that the desulfurization rate of BT and VR both had a threshold temperature ($T_R = 723$ K), which determined the desulfurization mechanism of VR (shown in Figure 6). When the temperature was above T_R , a significant desulfurization rate of BT and VR could be achieved. The increase of the O_2 amount had little influence on the desulfurization of BT while the desulfurization of VR would decrease slightly. Accordingly, a proper O_2 amount is needed to guarantee the catalytic desulfurization of VR at a minimum expense cost. Apart what is listed above, the effect of metals (Zn, Al) [41,103] and catalysts (ZnO , MoO_3 and MoS_2) [12] on the desulfurization of heavy oil and model compounds in SCW have also been reported. Kida *et al.* [75] proposed the reaction mechanism of hexyl sulfide (shown in Figure 7) in SCW, based on the analysis of experimental results and theory calculation.

In the SCW process, the reaction parameters have a great influence on the desulfurization of heavy oil and model compounds. Sato *et al.* [59] reported the effect of temperature and water density on the desulfurization of asphalt with SCW at 613–673 K, 0–0.5 $\text{g}\cdot\text{cm}^{-3}$ and 60 min. With the temperature increasing to 673 K, the sulfur in maltene decreased by 16 wt % at 60 min, while the sulfur in asphaltene showed little change. The desulfurization of asphalt increased slightly by increasing water density at 673 K for 60 min. Zhao *et al.* [45] studied the effect of temperature, pressure, and water/VR on

the desulfurization of VR with SCW at 420–460 °C, 23–27 MPa and water/VR ratio of 2–4. The results showed that higher temperature, higher pressure, and larger water/VR ratio all favored the removal of sulfur from VR.

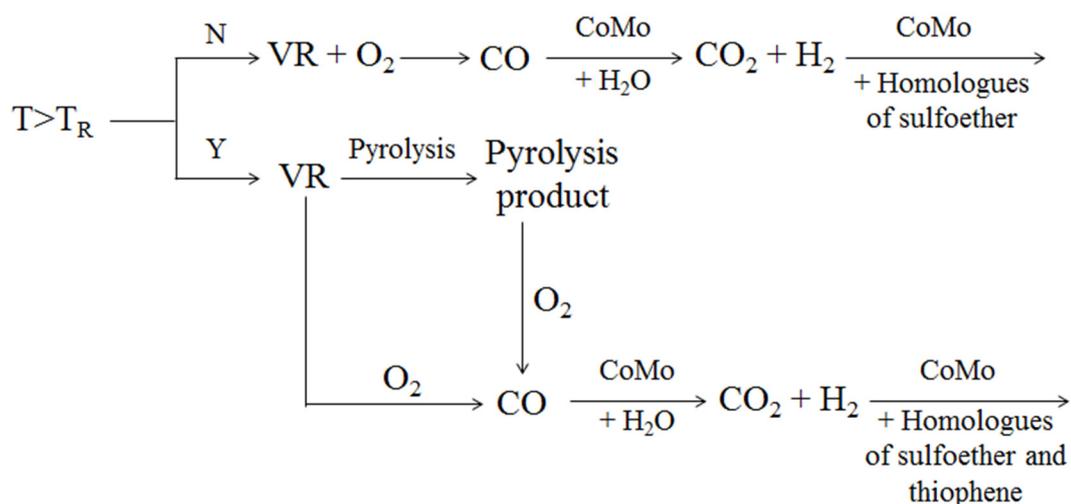


Figure 6. Sulfur reduction mechanism of VR through catalytic SCWO [101].

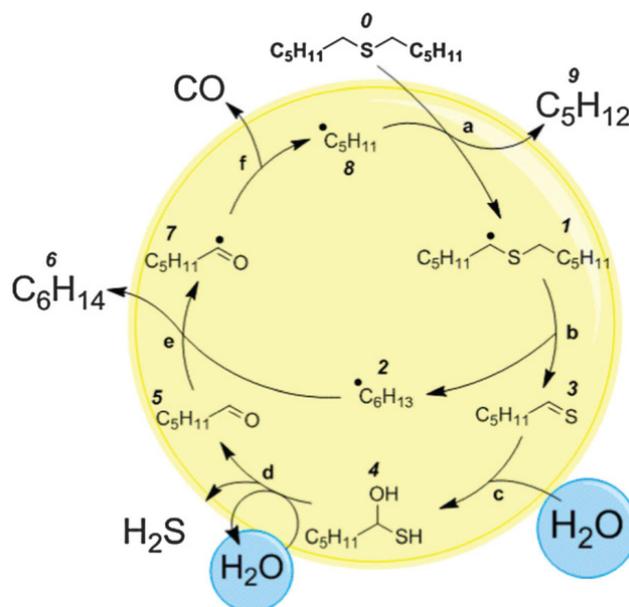


Figure 7. Reaction pathway of hexyl sulfide in SCW. Reproduced with permission from [75], published by The Royal Society of Chemistry, 2014.

4.2. Removal of Nickel and Vanadium

Heavy oil usually concentrates amounts of metal elements. Among these metals, the most abundant and undesirable ones are nickel and vanadium. Depending on the origin of crude oil, the concentration of vanadium varies, from as low as 0.1 ppm to as high as 1200 ppm, while that of nickel commonly varies from trace to 150 ppm [14]. Usually, vanadium and nickel exist in the form of porphyrin and nonporphyrin. Up to now, the study of vanadium and nickel has always focused on porphyrins because of their considerable role as geochemical markers and their deleterious effects. To reduce the deleterious effects of

Ni and V, some attempts have been made in SCW to remove Ni and V from heavy oil. Zhao *et al.* [44,45] reported that the upgrading of heavy oil in SCW could significantly lower the Ni and V content in the upgraded products. Mandal *et al.* [97,104–106] systematically studied the non-catalytic demetalization of three model porphyrinic compounds (nickel-5,10,15,20-tetraphenylporphine, nickel etioporphyrin, and vanadyl etioporphyrin) in SCW. In these experiments, they analyzed the effect of temperature and pressure on the demetalization of porphyrinic compounds. Additionally, they determined the reaction kinetic order of each porphyrin compound and proposed the possible demetalization mechanism of for each model compound.

5. Conclusions and Future Perspectives

With the growing heavier of the crude oil, upgrading heavy oil in SCW may be a promising alternative technique to meet the constantly increasing demand for clean light oil, due to its relatively superior performance in the transformation of hydrocarbons, the suppression of coke, and the removal of heteroatoms. Despite the fact that great progress has been made in the upgrading of heavy oil in SCW in recent years, this technique has never been attempted in an industrial scale application because the limited improvements to upgrading can hardly compensate for the expenditures on the high-pressure equipment and the rapidly growing operation costs. To realize the industrial scale application of SCW techniques, the emphasis of future research should be put on the following aspects: (1) Development of novel type catalysts with the ability to induce the splitting of H₂O to produce active hydrogen; In the process of upgrading heavy oil in SCW, the provision of sufficient hydrogen can, simultaneously, enhance the performance of the transformation of macromolecules to light fractions, the suppression of coke, and the removal of heteroatoms. As the expenditure of molecular hydrogen is costly and its activity is lower than that of *in situ* hydrogen, it is necessary to develop novel types of catalysts with the ability to induce the splitting of H₂O to produce active hydrogen in order to further improve the performance of SCW; (2) research on removal mechanism of Ni and V. Currently, there is little research on the removal of Ni and V from heavy oil with SCW. With the wide utilization of heavy oil resources, their hazardous effects will become increasingly prominent. Studies of their removal mechanisms are necessary to production of clean light oil; (3) design modernized SCW devices. Most of the existing SCW devices just have a few simple functions, this is not to speak of the automated control of experimental conditions and the automated collection and separation of the upgrading products. To provide more reliable data for industrialization, the design and development of advanced SCW devices must be accelerated.

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Author Contributions

Ning Li did the majority of the work on this paper. The work was supervised by Bo Yan and Xian-Ming Xiao. All authors contributed to editing and reviewing of the paper.

Conflicts of Interest

The authors declare no conflict of interest.

References

1. Santos, R.; Loh, W.; Bannwart, A.; Trevisan, O. An overview of heavy oil properties and its recovery and transportation methods. *Braz. J. Chem. Eng.* **2014**, *31*, 571–590.
2. Shah, A.; Fishwick, R.; Wood, J.; Leeke, G.; Rigby, S.; Greaves, M. A review of novel techniques for heavy oil and bitumen extraction and upgrading. *Energy Environ. Sci.* **2010**, *3*, 700–714.
3. Rana, M.S.; Sámano, V.; Ancheyta, J.; Diaz, J.A.I. A review of recent advances on process technologies for upgrading of heavy oils and residua. *Fuel* **2007**, *86*, 1216–1231.
4. Caniaz, R.O.; Erkey, C. Process intensification for heavy oil upgrading using supercritical water. *Chem. Eng. Res. Des.* **2014**, *92*, 1845–1863.
5. Kapadia, P.R.; Kallos, M.S.; Gates, I.D. A review of pyrolysis, aquathermolysis, and oxidation of athabasca bitumen. *Fuel Process. Technol.* **2015**, *131*, 270–289.
6. Upreti, S.R.; Lohi, A.; Kapadia, R.A.; El-Haj, R. Vapor extraction of heavy oil and bitumen: A review. *Energy Fuels* **2007**, *21*, 1562–1574.
7. Bridjanian, H.; Samimi, A.K. Bottom of the barrel, an important challenge of the petroleum refining industry. *Petrol. Coal* **2011**, *53*, 13–21.
8. Kiasari, H.; Nokandeh, N.; Khishvand, M.; Mansoori, A.; Firoozjaee, R. A review of SAGD-ISSLW. *Petrol. Sci. Technol.* **2014**, *32*, 753–760.
9. Wang, Z.J.; Deng, S.H.; Gu, Q.; Cui, X.J.; Zhang, Y.M.; Wang, H.Y. Subcritical water extraction of huadian oil shale under isothermal condition and pyrolysate analysis. *Energy Fuels* **2014**, *28*, 2305–2313.
10. Strausz, O.P.; Mojelsky, T.W.; Payzant, J.D.; Olah, G.A.; Prakash, G.K.S. Upgrading of alberta's heavy oils by superacid-catalyzed hydrocracking. *Energy Fuels* **1999**, *13*, 558–569.
11. Sato, T.; Mori, S.; Watanabe, M.; Sasaki, M.; Itoh, N. Upgrading of bitumen with formic acid in supercritical water. *J. Supercrit. Fluids* **2010**, *55*, 232–240.
12. Ates, A.; Azimi, G.; Choi, K.H.; Green, W.H.; Timko, M.T. The role of catalyst in supercritical water desulfurization. *Appl. Catal. B* **2014**, *147*, 144–155.
13. Rudyk, S.; Spirov, P. Upgrading and extraction of bitumen from nigerian tar sand by supercritical carbon dioxide. *Appl. Energy* **2014**, *113*, 1397–1404.
14. Ali, M.F.; Abbas, S. A review of methods for the demetallization of residual fuel oils. *Fuel Process. Technol.* **2006**, *87*, 573–584.
15. Brons, G.; Yu, J.M. Solvent deasphalting effects on whole cold lake bitumen. *Energy Fuels* **1995**, *9*, 641–647.

16. Castaneda, L.C.; Munoz, J.A.D.; Ancheyta, J. Current situation of emerging technologies for upgrading of heavy oils. *Catal. Today* **2014**, *220*, 248–273.
17. Siskin, M.; Kelemen, S.R.; Eppig, C.P.; Brown, L.D.; Afeworki, M. Asphaltene molecular structure and chemical influences on the morphology of coke produced in delayed coking. *Energy Fuels* **2006**, *20*, 1227–1234.
18. Xu, C.; Hamilton, S.; Mallik, A.; Ghosh, M. Upgrading of athabasca vacuum tower bottoms (VTB) in supercritical hydrocarbon solvents with activated carbon-supported metallic catalysts. *Energy Fuels* **2007**, *21*, 3490–3498.
19. Furimsky, E. Hydroprocessing in aqueous phase. *Ind. Eng. Chem. Res.* **2013**, *52*, 17695–17713.
20. Xu, Y.; Yuan, M.; Zhao, S.; Xu, C. Upgrading heavy oil using syngas as the hydrogen source with dispersed catalysts. *Petrol. Sci. Technol.* **2009**, *27*, 712–732.
21. Reddy, S.N.; Nanda, S.; Dalai, A.K.; Kozinski, J.A. Supercritical water gasification of biomass for hydrogen production. *Int. J. Hydrogen Energy* **2014**, *39*, 6912–6926.
22. Muthukumar, P.; Gupta, R.B. Sodium-carbonate-assisted supercritical water oxidation of chlorinated waste. *Ind. Eng. Chem. Res.* **2000**, *39*, 4555–4563.
23. Guo, Y.; Wang, S.Z.; Xu, D.H.; Gong, Y.M.; Ma, H.H.; Tang, X.Y. Review of catalytic supercritical water gasification for hydrogen production from biomass. *Renew. Sustain. Energy Rev.* **2010**, *14*, 334–343.
24. Azadi, P.; Farnood, R. Review of heterogeneous catalysts for sub- and supercritical water gasification of biomass and wastes. *Int. J. Hydrogen Energy* **2011**, *36*, 9529–9541.
25. Marrone, P.A. Supercritical water oxidation-current status of full-scale commercial activity for waste destruction. *J. Supercrit. Fluids* **2013**, *79*, 283–288.
26. Vilcaez, J.; Watanabe, M.; Watanabe, N.; Kishita, A.; Adschiri, T. Hydrothermal extractive upgrading of bitumen without coke formation. *Fuel* **2012**, *102*, 379–385.
27. Kruse, A.; Dinjus, E. Hot compressed water as reaction medium and reactant—Properties and synthesis reactions. *J. Supercrit. Fluids* **2007**, *39*, 362–380.
28. Yanik, J.; Yüksel, M.; Sağlam, M.; Olukçu, N.; Bartle, K.; Frere, B. Characterization of the oil fractions of shale oil obtained by pyrolysis and supercritical water extraction. *Fuel* **1995**, *74*, 46–50.
29. Meng, M.; Hu, H.Q.; Zhang, Q.M.; Ding, M. Extraction of tumuji oil sand with sub- and supercritical water. *Energy Fuels* **2006**, *20*, 1157–1160.
30. Hu, H.Q.; Zhang, J.; Guo, S.C.; Chen, G.H. Extraction of huadian oil shale with water in sub- and supercritical states. *Fuel* **1999**, *78*, 645–651.
31. Johannes, I.; Luik, H.; Palu, V.; Kruusement, K.; Gregor, A. Synergy in co-liquefaction of oil shale and willow in supercritical water. *Fuel* **2015**, *144*, 180–187.
32. Wahyudiono; Shiraishi, T.; Sasaki, M.; Goto, M. Non-catalytic liquefaction of bitumen with hydrothermal/solvothermal process. *J. Supercrit. Fluids* **2011**, *60*, 127–136.
33. Dejhosseini, M.; Aida, T.; Watanabe, M.; Takami, S.; Hojo, D.; Aoki, N.; Arita, T.; Kishita, A.; Adschiri, T. Catalytic cracking reaction of heavy oil in the presence of cerium oxide nanoparticles in supercritical water. *Energy Fuels* **2013**, *27*, 4624–4631.
34. Liu, Y.; Bai, F.; Zhu, C.C.; Yuan, P.Q.; Cheng, Z.M.; Yuan, W.K. Upgrading of residual oil in sub- and supercritical water: An experimental study. *Fuel Process. Technol.* **2013**, *106*, 281–288.

35. Tan, X.C.; Zhu, C.C.; Liu, Q.K.; Ma, T.Y.; Yuan, P.Q.; Cheng, Z.M.; Yuan, W.K. Co-pyrolysis of heavy oil and low density polyethylene in the presence of supercritical water: The suppression of coke formation. *Fuel Process. Technol.* **2014**, *118*, 49–54.
36. Timko, M.T.; Ghoniem, A.F.; Green, W.H. Upgrading and desulfurization of heavy oils by supercritical water. *J. Supercrit. Fluids* **2015**, *96*, 114–123.
37. Funazukuri, T.; Yokoi, S.; Wakao, N. Supercritical fluid extraction of chinese maoming oil shale with water and toluene. *Fuel* **1988**, *67*, 10–14.
38. Olukcu, N.; Yanik, J.; Saglam, M.; Yuksel, M.; Karaduman, M. Solvent effect on the extraction of beypazari oil shale. *Energy Fuels* **1999**, *13*, 895–902.
39. El harfi, K.; Bennouna, C.; Mokhlisse, A.; Ben chanaa, M.; Lemee, L.; Joffre, J.; Ambles, A. Supercritical fluid extraction of moroccan (timahdit) oil shale with water. *J. Anal. Appl. Pyrolysis* **1999**, *50*, 163–174.
40. Berkowitz, N.; Calderon, J. Extraction of oil sand bitumens with supercritical water. *Fuel Process. Technol.* **1990**, *25*, 33–44.
41. Fedyaeva, O.N.; Vostrikov, A.A. Hydrogenation of bitumen *in situ* in supercritical water flow with and without addition of zinc and aluminum. *J. Supercrit. Fluids* **2012**, *72*, 100–110.
42. Sato, T.; Trung, P.H.; Tomita, T.; Itoh, N. Effect of water density and air pressure on partial oxidation of bitumen in supercritical water. *Fuel* **2012**, *95*, 347–351.
43. Morimoto, M.; Sugimoto, Y.; Sato, S.; Takanohashi, T. Bitumen cracking in supercritical water upflow. *Energy Fuels* **2014**, *28*, 858–861.
44. Cheng, Z.M.; Ding, Y.; Zhao, L.Q.; Yuan, P.Q.; Yuan, W.K. Effects of supercritical water in vacuum residue upgrading. *Energy Fuels* **2009**, *23*, 3178–3183.
45. Zhao, L.Q.; Cheng, Z.M.; Ding, Y.; Yuan, P.Q.; Lu, S.X.; Yuan, W.K. Experimental study on vacuum residuum upgrading through pyrolysis in supercritical water. *Energy Fuels* **2006**, *20*, 2067–2071.
46. Fan, H.L.; Han, B.X.; Jiang, T.; Guo, J.; Wang, Q.; Cheng, Y.; Wu, S.X. Hydrocracking of anthracene to ethyl biphenyl promoted by coupling supercritical water and cracking catalysts. *ChemCatChem* **2011**, *3*, 1474–1479.
47. Cheng, J.; Liu, Y.H.; Lou, Y.H.; Que, G.H. Hydrocracking of Gudao residual oil with dispersed catalysts using supercritical water-syngas as a hydrogen source. *Pet. Sci. Technol.* **2005**, *23*, 1453–1462.
48. Cheng, J.; Liu, Y.; Luo, Y.; Quem, G. Hydrocracking of Gudao residual oil with dispersed catalysts using supercritical water-syngas as a hydrogen source. Part II: The comparison of residue hydrocracking in different hydrogen sources. *Petrol. Sci. Technol.* **2006**, *24*, 1339–1346.
49. Bai, F.; Zhu, C.C.; Liu, Y.; Yuan, P.Q.; Cheng, Z.M.; Yuan, W.K. Co-pyrolysis of residual oil and polyethylene in sub- and supercritical water. *Fuel Process. Technol.* **2013**, *106*, 267–274.
50. Kozhevnikov, I.V.; Nuzhdin, A.L.; Martyanov, O.N. Transformation of petroleum asphaltene in supercritical water. *J. Supercrit. Fluids* **2010**, *55*, 217–222.
51. Han, L.N.; Zhang, R.; Bi, J.C.; Cheng, L.M. Pyrolysis of coal-tar asphaltene in supercritical water. *J. Anal. Appl. Pyrolysis* **2011**, *91*, 281–287.
52. Morimoto, M.; Sato, S.; Takanohashi, T. Effect of water properties on the degradative extraction of asphaltene using supercritical water. *J. Supercrit. Fluids* **2012**, *68*, 113–116.

53. Li, N.; Yan, B.; Zhang, L.; Quan, S.X.; Hu, C.; Xiao, X.M. Effect of NaOH on asphaltene transformation in supercritical water. *J. Supercrit. Fluids* **2015**, *97*, 116–124.
54. Dyni, J.R. Geology and resources of some world oil-shale deposits. *Oil Shale* **2003**, *20*, 193–252.
55. Luik, H.; Luik, L. Extraction of fossil fuels with sub- and supercritical water. *Energy Sources* **2001**, *23*, 449–459.
56. Subramanian, M.; Hanson, F.V. Supercritical fluid extraction of bitumens from utah oil sands. *Fuel Process. Technol.* **1998**, *55*, 35–53.
57. Fedyaeva, O.N.; Vostrikov, A.A.; Sokol, M.Y.; Fedorova, N.I. Hydrogenation of bitumen in supercritical water flow and the effect of zinc addition. *Russ. J. Phys. Chem. B* **2013**, *7*, 820–828.
58. Sato, T.; Tomita, T.; Trung, P.H.; Itoh, N.; Sato, S.; Takanohashi, T. Upgrading of bitumen in the presence of hydrogen and carbon dioxide in supercritical water. *Energy Fuels* **2013**, *27*, 646–653.
59. Sato, T.; Adschiri, T.; Arai, K.; Rempel, G.L.; Ng, F.T.T. Upgrading of asphalt with and without partial oxidation in supercritical water. *Fuel* **2003**, *82*, 1231–1239.
60. Canter, D.A.; Bermejo, M.D.; Cocero, M.J. Reaction engineering for process intensification of supercritical water biomass refining. *J. Supercrit. Fluids* **2015**, *96*, 21–35.
61. Fedyaeva, O.N.; Shatrova, A.V.; Vostrikov, A.A. Effect of temperature on bitumen conversion in a supercritical water flow. *J. Supercrit. Fluids* **2014**, *95*, 437–443.
62. Sun, Y.D.; Yang, C.H.; Zhao, H.; Shan, H.H.; Shen, B.X. Influence of asphaltene on the residue hydrotreating reaction. *Energy Fuels* **2010**, *24*, 5008–5011.
63. Yasar, M.; Trauth, D.M.; Klein, M.T. Asphaltene and resid pyrolysis. 2. The effect of reaction environment on pathways and selectivities. *Energy Fuels* **2001**, *15*, 504–509.
64. Zhao, Y.X.; Wei, F.; Zhang, S.J.; Yu, Y. Kinetics and selectivity of asphaltene hydrocracking. *Fuel* **2011**, *90*, 1900–1906.
65. Ayala, M.; Hernandez-Lopez, E.L.; Perezgasga, L.; Vazquez-Duhalt, R. Reduced coke formation and aromaticity due to chloroperoxidase-catalyzed transformation of asphaltenes from maya crude oil. *Fuel* **2012**, *92*, 245–249.
66. Zhao, Y.X.; Yu, Y. Kinetics of asphaltene thermal cracking and catalytic hydrocracking. *Fuel Process. Technol.* **2011**, *92*, 977–982.
67. Cheng, Y.; Fan, H.F.; Wu, S.X.; Wang, Q.A.; Guo, J.; Gao, L.; Zong, B.N.; Han, B.X. Enhancing the selectivity of the hydrogenation of naphthalene to tetralin by high temperature water. *Green Chem.* **2009**, *11*, 1061–1065.
68. Akiya, N.; Savage, P.E. Roles of water for chemical reactions in high-temperature water. *Chem. Rev.* **2002**, *102*, 2725–2750.
69. Savage, P.E. Organic chemical reactions in supercritical water. *Chem. Rev.* **1999**, *99*, 603–621.
70. Ogunsola, O.M.; Berkowitz, N. Extraction of oil shales with sub-critical and near-critical water. *Fuel Process. Technol.* **1995**, *45*, 95–107.
71. Morimoto, M.; Sugimoto, Y.; Sato, S.; Takanohashi, T. Solvent effect of water on supercritical water treatment of heavy oil. *J. Jpn. Petrol. Inst.* **2014**, *57*, 11–17.
72. Vostrikov, A.A.; Dubov, D.Y.; Psarov, S.A. The effect of thermal explosion in a supercritical water. *Tech. Phys. Lett.* **2001**, *27*, 847–849.
73. Dutta, R.P.; McCaffrey, W.C.; Gray, M.R.; Muehlenbachs, K. Thermal cracking of athabasca bitumen: Influence of steam on reaction chemistry. *Energy Fuels* **2000**, *14*, 671–676.

74. Gao, L.A.; Liu, Y.D.; Wen, L.Y.; Huang, W.X.; Mu, X.H.; Zong, B.N.; Fan, H.L.; Han, B.X. The effect of supercritical water on the hydroconversion of Tahe Residue. *AICHE J.* **2010**, *56*, 3236–3242.
75. Kida, Y.; Class, C.A.; Concepcion, A.J.; Timko, M.T.; Green, W.H. Combining experiment and theory to elucidate the role of supercritical water in sulfide decomposition. *Phys. Chem. Chem. Phys.* **2014**, *16*, 9220–9228.
76. Tucker, S.C.; Maddox, M.W. The effect of solvent density inhomogeneities on solute dynamics in supercritical fluids: A theoretical perspective. *J. Phys. Chem. B* **1998**, *102*, 2437–2453.
77. Morimoto, M.; Sugimoto, Y.; Saotome, Y.; Sato, S.; Takanohashi, T. Effect of supercritical water on upgrading reaction of oil sand bitumen. *J. Supercrit. Fluids* **2010**, *55*, 223–231.
78. Xu, T.; Liu, Q.Y.; Liu, Z.Y.; Wu, J.F. The role of supercritical water in pyrolysis of carbonaceous compounds. *Energy Fuels* **2013**, *27*, 3148–3153.
79. Towfighi, J.; Sadrameli, M.; Niaei, A. Coke formation mechanisms and coke inhibiting methods in pyrolysis furnaces. *J. Chem. Eng. Jpn* **2002**, *35*, 923.
80. Kishita, A.; Takahashi, S.; Kamimura, H.; Miki, M.; Moriya, T.; Enomoto, H. Upgrading of bitumen by hydrothermal visbreaking in supercritical water with alkali. *J. Jpn. Petrol. Inst.* **2003**, *46*, 215–221.
81. Clark, P.D.; Kirk, M.J. Studies on the upgrading of bituminous oils with water and transition-metal catalysts. *Energy Fuels* **1994**, *8*, 380–387.
82. Guan, Q.Q.; Wei, C.H.; Shi, H.S.; Wu, C.F.; Chai, X.S. Partial oxidative gasification of phenol for hydrogen in supercritical water. *Appl. Energy* **2011**, *88*, 2612–2616.
83. Houser, T.J.; Zhou, Y.; Liu, X. The destruction of selected hazardous compounds using supercritical water. *J. Supercrit. Fluids* **1996**, *9*, 106–112.
84. Sato, T. Upgrading of heavy oil by hydrogenation through partial oxidation and water-gas shift reaction in supercritical water. *J. Jpn. Petrol. Inst.* **2014**, *57*, 1–10.
85. Arai, K.; Adschiri, T.; Watanabe, M. Hydrogenation of hydrocarbons through partial oxidation in supercritical water. *Ind. Eng. Chem. Res.* **2000**, *39*, 4697–4701.
86. Jin, F.M.; Zeng, X.; Cao, J.L.; Kawasaki, K.; Kishita, A.; Tohji, K.; Enomoto, H. Partial hydrothermal oxidation of unsaturated high molecular weight carboxylic acids for enhancing the cold flow properties of biodiesel fuel. *Fuel* **2010**, *89*, 2448–2454.
87. Sato, T.; Watanabe, M.; Smith, R.L.; Adschiri, T.; Arai, K. Analysis of the density effect on partial oxidation of methane in supercritical water. *J. Supercrit. Fluids* **2004**, *28*, 69–77.
88. Kim, Y.L.; Kim, J.D.; Lim, J.S.; Lee, Y.W.; Yi, S.C. Reaction pathway and kinetics for uncatalyzed partial oxidation of p-xylene in sub- and supercritical water. *Ind. Eng. Chem. Res.* **2002**, *41*, 5576–5583.
89. Watanabe, M.; Mochiduki, M.; Sawamoto, S.; Adschiri, T.; Arai, K. Partial oxidation of n-hexadecane and polyethylene in supercritical water. *J. Supercrit. Fluids* **2001**, *20*, 257–266.
90. Armbruster, U.; Martin, A.; Krepel, A. Partial oxidation of propane in sub- and supercritical water. *J. Supercrit. Fluids* **2001**, *21*, 233–243.
91. Lee, J.H.; Foster, N.R. Direct partial oxidation of methane to methanol in supercritical water. *J. Supercrit. Fluids* **1996**, *9*, 99–105.

92. Hosseinpour, M.; Ahmadi, S.J.; Fatemi, S. Successive co-operation of supercritical water and silica-supported iron oxide nanoparticles in upgrading of heavy petroleum residue: Suppression of coke deposition over catalyst. *J. Supercrit. Fluids* **2015**, *100*, 70–78.
93. Watanabe, M.; Kato, S.; Ishizeki, S.; Inomata, H.; Smith, R.L. Heavy oil upgrading in the presence of high density water: Basic study. *J. Supercrit. Fluids* **2010**, *53*, 48–52.
94. Patwardhan, P.R.; Timko, M.T.; Class, C.A.; Bonomi, R.E.; Kida, Y.; Hernandez, H.H.; Tester, J.W.; Green, W.H. Supercritical water desulfurization of organic sulfides is consistent with free-radical kinetics. *Energy Fuels* **2013**, *27*, 6108–6117.
95. Duong, A.; Chattopadhyaya, G.; Kwok, W.Y.; Smith, K.J. An experimental study of heavy oil ultrafiltration using ceramic membranes. *Fuel* **1997**, *76*, 821–828.
96. Dechaine, G.P.; Gray, M.R. Chemistry and association of vanadium compounds in heavy oil and bitumen, and implications for their selective removal. *Energy Fuels* **2010**, *24*, 2795–2808.
97. Mandal, P.C.; Wahyudiono; Sasaki, M.; Goto, M. Non-catalytic vanadium removal from vanadyl etioporphyrin (vo-ep) using a mixed solvent of supercritical water and toluene: A kinetic study. *Fuel* **2012**, *92*, 288–294.
98. Yuan, P.Q.; Cheng, Z.M.; Zhang, X.Y.; Yuan, W.K. Catalytic denitrogenation of hydrocarbons through partial oxidation in supercritical water. *Fuel* **2006**, *85*, 367–373.
99. Babich, I.V.; Moulijn, J.A. Science and technology of novel processes for deep desulfurization of oil refinery streams: A review. *Fuel* **2003**, *82*, 607–631.
100. Vogelaar, B.M.; Makkee, M.; Moulijn, J.A. Applicability of supercritical water as a reaction medium for desulfurisation and demetallisation of gasoil. *Fuel Process. Technol.* **1999**, *61*, 265–277.
101. Adschiri, T.; Shibata, R.; Sato, T.; Watanabe, M.; Arai, K. Catalytic hydrodesulfurization of dibenzothiophene through partial oxidation and a water-gas shift reaction in supercritical water. *Ind. Eng. Chem. Res.* **1998**, *37*, 2634–2638.
102. Yuan, P.Q.; Cheng, Z.M.; Jiang, W.L.; Zhang, R.; Yuan, W.K. Catalytic desulfurization of residual oil through partial oxidation in supercritical water. *J. Supercrit. Fluids* **2005**, *35*, 70–75.
103. Fedyaeva, O.N.; Antipenko, V.R.; Vostrikov, A.A. Conversion of sulfur-rich asphaltite in supercritical water and effect of metal additives. *J. Supercrit. Fluids* **2014**, *88*, 105–116.
104. Mandal, P.C.; Wahyudiono; Sasaki, M.; Goto, M. Nickel removal from nickel-5,10,15,20-tetraphenylporphine using supercritical water in absence of catalyst: A basic study. *J. Hazard. Mater.* **2011**, *187*, 600–603.
105. Mandal, P.C.; Sasaki, M.; Goto, M. Nickel removal from nickel etioporphyrin (Ni-EP) using supercritical water in the absence of catalyst. *Fuel Process. Technol.* **2012**, *104*, 67–72.
106. Mandal, P.C.; Goto, M.; Sasaki, M. Removal of nickel and vanadium from heavy oils using supercritical water. *J. Jpn. Petrol. Inst.* **2014**, *57*, 18–28.